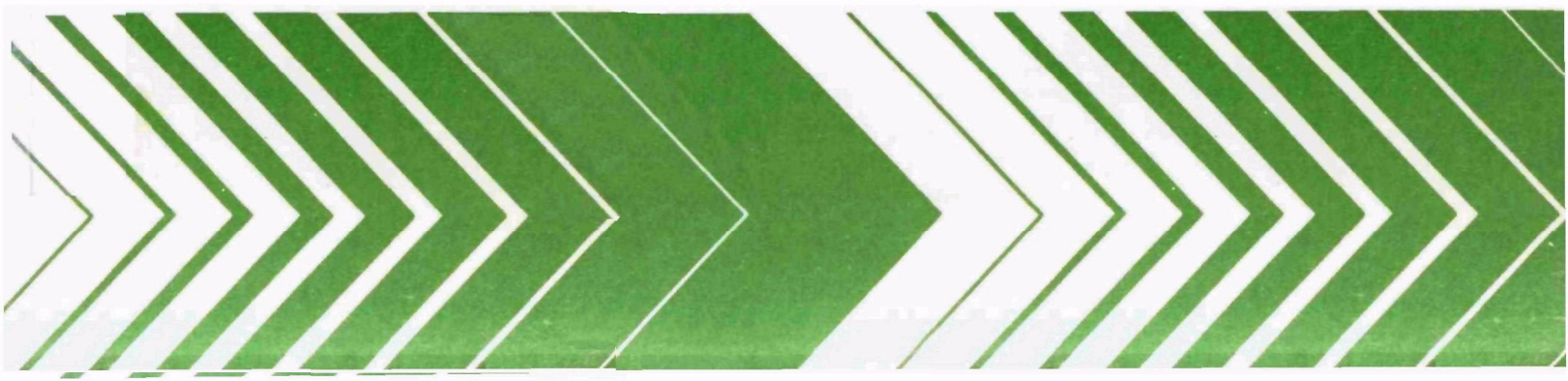

Research and Development



Removing Potential Organic Carcinogens and Precursors from Drinking Water

Volume I
and
Appendix A



RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

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EPA-600/2-80-130a
August 1980

REMOVING POTENTIAL ORGANIC CARCINOGENS AND
PRECURSORS FROM DRINKING WATER

Volume I and Appendix A

by

Paul R. Wood - Principal Investigator
Daniel F. Jackson
Drinking Water Quality Research Center
Florida International University
Miami, Florida 33199

James A. Gervers
Doris H. Waddell
Miami-Dade Water and Sewer Authority

Louis Kaplan
Dade County Department of Public Health
Miami, Florida 33125

Grant No. R804521-01

Project Officer

Jack DeMarco
Drinking Water Research Division
Municipal Environmental Research Laboratory
Cincinnati, Ohio 45268

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

To protect the consumer of public drinking water, this study was undertaken to develop feasible and economical methodology for reducing the amount of specific organic contaminants in drinking water.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

The principle objective of the two-year Research Project was to devise feasible and economical methodology for removing existing organic contaminants from and preventing development of potential carcinogens in the public water supplies in Dade County, Florida. Specifically, development of methodology to reduce the amount of four trihalomethanes (chloroform, bromodichloromethane, chlorodibromomethane, and bromoform) present in drinking water was the prime objective.

A four-phase study was designed to evaluate the efficiency of three adsorbents in removing 19 individual halogenated organics and trihalomethane precursors. These adsorbents were XE-340--a carbonized polymeric macroreticular resin; IRA-904--a strong base cationic resin designed to remove large molecular weight substances such as precursors from water; and granular activated carbon (GAC). Adsorbent columns were placed at various stages in the water processing system; i.e., the raw water stage, the lime softened stage at the up-flow Hydrotreator effluent and the finished water stage.

Four GAC Filtrasorb 400 columns, each 0.76 meters (2.5 feet) deep, arranged in series on the finished water line were most effective in reducing the level of the trihalomethanes present in the finished water that would be consumed by the public.

The Polanyi-Manes Theory of adsorption was applied and found helpful in interpreting results. Preliminary studies were made of the bacterial profile of the Preston Water Treatment Plant, raw and finished water, and effluent from four GAC columns. Distribution system samples were also analyzed.

This report was submitted in fulfillment of Grant No. R804521-01 by Dade County Department of Public Health under the Sponsorship of the U.S. Environmental Protection Agency. This report covers a period from June 1976 to June 1980, and work was completed as of May 1980.

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LIST OF ABBREVIATIONS

GAC	-- granular activated carbon
H.T.	-- Hydrotreator (up-flow lime softening unit)
NORS	-- National Organics Reconnaissance Survey
GC	-- gas chromatograph
GC/MS	-- gas chromatograph/mass spectrograph
TOC	-- total organic carbon
THM	-- trihalomethane(s)
HOC	-- halogenated organic compound(s)
THM FP	-- trihalomethane formation potential
Total THM	-- total trihalomethane(s)
Inst. THM	-- instantaneous trihalomethane(s)
Terminal THM	-- terminal trihalomethane(s)
BAC	-- biologically activated carbon
UV	-- ultraviolet
m ³ /s	-- cubic meters/second
mgd	-- million gallons per day
ED	-- experimental design
L/h	-- liters/hour
GPH	-- gallons per hour
MT _z	-- mass transfer zone
DOM	-- dissolved organic matter
EBCT	-- empty bed contact time

ACKNOWLEDGMENTS

Unquestionably, the most valuable help, leadership and guidance for the Project was provided by the Project Officer, Mr. Jack DeMarco. His unselfish and tireless effort in getting the study organized and keeping it moving in the proper direction was one of the major reasons for its success.

The support and cooperation of President Harold Crosby, Florida International University; Mr. Garrett Sloan, Director of the Miami-Dade Water and Sewer Authority, and Dr. Richard Morgan, Director of the Dade County Department of Public Health, are greatly appreciated.

The advice of the Technical Advisory Board was an important factor in evaluating accumulating results of the work. Their comments on projected goals are appreciated.

Advisory Board members were Mr. Anthony Clemente, Dade County Department of Environmental Resources Management; Mr. Glenn Dykes, State Department of Environmental Regulation; Mr. Sidney Berkowitz, Consultant; Dr. John Davies and Dr. Henry Enos from the University of Miami, as well as Dr. Morgan and Mr. Sloan.

The secretarial services of Ms. Phyllis Engles, Ms. Barbara Weil, Ms. Linda Rountree, Ms. Sarah Bostwick, Ms. Bess Simon, and Ms. Marlene Blosucci were well performed and appreciated.

The technical staff of Florida International University and the Metropolitan Dade County Water and Sewer Authority contributed much to the success of the program. These include Mr. Hunt Harween, Mr. Besteiro Palomeque, Mr. Kenneth Kirkman, Mr. Russell Lang, Mr. Cesar Ordaz, Mr. William Booth, and Ms. Laurie Miller.

Appreciation must be expressed also for the cooperation of the personnel in the business office and accounting department of the Dade County Department of Public Health, Florida International University, and the Metropolitan Dade County Water and Sewer Authority.

The technical assistance of Dr. Milton Manes, Chemistry Department, Kent State University, Kent, Ohio and Dr. Michael Rosene, Calgon Corporation, Calgon Center, Pittsburgh, Pennsylvania is also acknowledged.

SECTION I

INTRODUCTION

In 1975, the U.S. Environmental Protection Agency announced by their release of a report on "National Organics Reconnaissance Survey for Halogenated Organics in Drinking Water" (1) (NORS) that the drinking water of Dade County, Florida contained over 300 ppb chloroform and nearly 6 ppb vinyl chloride. Personnel at the Dade County Health Department, Miami-Dade Water and Sewer Authority, and the Drinking Water Quality Research Center of Florida International University in cooperation with the U.S. Environmental Protection Agency in Cincinnati, Ohio developed a research project to 1) develop an effective and economical method for removing, or substantially reducing, the chemicals of concern and 2) remove organic solutes (precursors) from the water to prevent regrowth of these chemicals in the distribution system where free chlorine is present. On June 22, 1976 a one-year study was approved by EPA and later extended to September 5, 1978.

The scope of the Project included 1) a study of the effectiveness of various adsorbents in removing potential carcinogens already present in raw water and those generated in the water treatment process, 2) removal of precursor substances which form halogenated organics upon reaction with chlorine in the treatment plant and distribution system, and 3) effect of the stage of treatment process on efficiency for removing contaminants.

Early in the Research Project the high levels of halogenated organics reported by the NORS (1) study were verified both in concentration and identification by GC/MS. These results were reported at once to local and state authorities.

This report describes the results of a study of two adsorbent resins and granular activated carbon for their effectiveness and efficiency in removing trihalomethane precursors, halogenated organic compounds and total organic carbon from three locations in the treatment plant, raw, lime softened and finished water. The resins were Ambersorb XE-340, a carbonized polymeric macroreticular resin, and IRA-904, a strong base cationic resin for anion exchange, both manufactured by Rohm and Haas Company, Philadelphia, Pa. The Granular Activated Carbon was Filtrasorb 400, 12 x 40 mesh, manufactured by Calgon Corporation, Pittsburgh, Pa.

The Miami-Dade Water and Sewer Authority furnishes water for over one million people through three major water plants. The John E. Preston Water Treatment Plant in Hialeah, Dade County, Florida, which operates at $2.63 \text{ m}^3/\text{s}$ (60 mgd), draws water from the Biscayne Aquifer from seven wells located on the plant site. The wells are approximately 27.4 meters (90 feet) deep. The raw ground water, which contains an average of 10 mg/L of Total Organic Carbon, is treated by lime softening in an up-flow Hydrotreator, breakpoint chlorination, and sand filtration. Before the water leaves the plant the free chlorine level is adjusted to 2.5 ppm.

The strata overlying the recharge area of the Biscayne Aquifer are predominately muck, which accounts for the relatively high color present in the source water. Thus organics of a natural origin comprise one problem that cannot be easily prevented by attempting to change sources of drinking water in this area. Other organic substances that are a result of man's activities are also present and pose another facet of the problem presented in using the ground water in the area. Thus initial studies of practical methods of removing organics were directed at attempting to find a broad based organic removal method.

The three adsorbents were studied in four experimental designs developed by Jack DeMarco, EPA Project Supervisor. Glass columns 2.54 cm (one inch) in diameter were connected directly to raw, lime softened (Hydrotreator effluent) and finished water lines from the Preston Plant. Adsorbent bed depths studied were 0.76, 1.52, 2.29 and 3.05 meters (2.5, 5, 7.5 and 10 feet) for Granular Activated Carbon, 0.76 and 1.52 meters (2.5 and 5 feet) for IRA-904 resin, and 0.76 meter (2.5 feet) for XE-340. A flow rate of $122 \text{ L}/\text{min.}/\text{m}^2$ ($3 \text{ gal.}/\text{min.}/\text{ft.}^2$) was maintained by rotometers through each column. Thus empty bed contact times were always 6.2 minutes whenever a 0.76 meter (2.5 feet) bed depth of adsorbent was used, 12.4 minutes for a 1.52 meter (5 feet) bed, 18.6 minutes for a 2.29 meter (7.5 feet) bed and 24.8 minutes for a 3.05 meter (10 feet) bed.

The 3.05 meter (10 feet) bed depth of Granular Activated Carbon (24.8 minutes Empty Bed Contact Time) showed the most promise for achieving broad based removal of organics. Water in the normal distribution system was evaluated as a comparison with experimental results obtained by using adsorbents.

SECTION II

CONCLUSIONS

Full Scale Plant Performance

1. Over the two-year study, the high levels of halogenated organic compounds reported by the national Organics Reconnaissance Survey (1) study were verified both in concentration and identification by Gas Chromatograph/Mass Spectrograph.
2. The average concentration of halogenated organic compounds present in raw water was approximately 15 percent less after lime softening (Hydrotreator effluent).
3. The average level of trihalomethanes in finished water leaving the plant over the two-year study was 67, 43, 28 and 2 $\mu\text{g/L}$ respectively for chloroform, bromodichloromethane, chlorodibromomethane and bromoform. The average total trihalomethane level leaving the plant was 140 $\mu\text{g/L}$. In the distribution system, this level can double in less than two days. The level would rise higher, but the free chlorine is exhausted in one to two days. When additional free chlorine is added at booster stations in the distribution system, trihalomethane levels reach their maximum.
4. The level of some non-trihalomethane halogenated organic compounds increased during the plant treatment process. A consistent increase was found for the summed concentration of 1,1,1-trichloroethane, 1,2-dichloroethane and carbon tetrachloride. Increases of this summed concentration ranged from 1.2 to 77 times the level in raw water. Since the three compounds were summed due to overlapping gas chromatograph peaks we do not know if the increase was due to one or more of the three substances. Some other non-trihalomethane halogenated organic compounds may have shown intermittent increases.
5. In general, non-trihalomethane halogenated organic substances were not consistently well removed by the existing full scale treatment plant.
6. Lime softening removed an average of 28 percent of the trihalomethane formation potential and little additional

actual removal was achieved by the sand filtration process. Calcium carbonate floc was believed to provide the mechanism for trihalomethane formation potential removal in the full scale plant.

7. In the Preston Plant, the amount of precursor removal by conversion to trihalomethanes by the combined chlorination-sand filtration process averaged 23 percent of the Hydrotreator effluent level.

Specific Organic Removal by Adsorbents

8. In both raw and finished water, XE-340 has more adsorptive capacity in weight of organic substance adsorbed per unit weight or volume of adsorbent, for individual halogenated organic compounds than granular activated carbon. While the values are different for each halogenated organic compound and different in raw and finished water, in general, XE-340 has approximately three times the adsorptive capacity of granular activated carbon.
9. The adsorptive capacity in weight of organic substances adsorbed per unit weight or volume of adsorbent of XE-340 for halogenated organic compounds is only slightly greater when treating raw water than when treating Hydrotreator water. The lower total organic compound concentration in the Hydrotreator water (approximately 30 percent lower) did not enhance the ability of the adsorbents for halogenated organic compound removal.
10. The adsorptive capacity of both XE-340 and granular activated carbon for cis 1,2-dichloroethene is less in finished water than raw water despite a reduction of 34 percent total organic carbon. The percent of cis 1,2-dichloroethene of total halogenated organic compounds in raw and finished water is 86.5 and 10 percent respectively. We attribute the 30 percent reduction in adsorptive capacity for cis 1,2-dichloroethene in finished water to increased competitive adsorption from the additional halogenated organics present in the finished water.
11. On raw and Hydrotreator water, IRA-904 resin showed no removal of any of the halogenated organic compounds present.
12. On finished water, IRA-904 resin appears to enhance the reaction of free chlorine with precursors to form halogenated organic compounds. The effluent of a 0.76 meter (2.5 feet) deep bed (empty bed contact time of 6.2 minutes) contained 1.75 and 1.13 times the influent concentration of

chloroform and bromodichloromethane respectively. Increases in concentration occurred in some of the non-trihalomethane halogenated organic compounds, but the majority showed no increase nor decrease in concentration as a result of the IRA-904 resin as observed in raw and Hydrotreator water.

13. A 3.05 meter (10 feet) deep bed of granular activated carbon with an empty bed contact time of 24.8 minutes was ineffective for vinyl chloride removal.

Total Organic Carbon and Trihalomethane Formation Potential Removal by Adsorbents

14. Total organic carbon data did not consistently correlate with trihalomethane formation potential data. Also, one cannot be converted into the other by a single conversion factor since total organic carbon analysis measures some substances that are not trihalomethane precursors. As expected, total organic carbon analysis is not a precise useful indicator of trihalomethane precursors. However, general trends might be noted at a given site.
15. In this report, the shape of the adsorption breakthrough curves for total organic carbon and trihalomethane formation potential removal by adsorbents are similar to specific halogenated organic compound removal curves.
16. A system was devised that could be used on total organic carbon and trihalomethane formation potential substances to allow a more complete understanding and comparison of adsorbent performance.
17. IRA-904 resin removed trihalomethane formation potential more efficiently from raw water than did the other two adsorbents tested based on percent removal and based on weight adsorbed per unit volume of adsorbent. However, granular activated carbon removed trihalomethane formation potential more efficiently than the other adsorbents based on the weight of trihalomethane formation potential adsorbed per unit weight of adsorbent.
18. Although IRA-904 resin was more effective for trihalomethane formation potential removal than granular activated carbon on a volume basis, and only 20 percent less effective on a weight basis, it is important to note that the resin allowed about 100 µg/L of trihalomethane formation potential to pass through the bed at start-up even with a 1.52 (5 feet) bed depth. The 0.76 meter (2.5 feet) granular activated carbon system was able to produce an effluent with about 12 µg/L of trihalomethane formation potential at start-up. Thus, a single measure of effectiveness cannot be applied without knowledge of performance required of the adsorbent. The breakthrough curve is important in determining the adsorbent

performance for a specific effluent criteria.

19. A direct comparison of 0.76 meter (2.5 feet) beds (6.2 minutes empty bed contact time) of granular activated carbon and XE-340 shows that carbon removed more trihalomethane formation potential on both an equal adsorbent weight and volume basis when receiving raw water. Furthermore, the breakthrough plot indicates that carbon maintained a lower effluent concentration than XE-340 for about 17 days. During this time period neither adsorbent was very effective for trihalomethane formation potential removal at the conditions tested.
20. Lime softening removed an average of 28 percent of trihalomethane formation potential precursors from raw water. This compares with 29 and 24 percent removal by 0.76 meter (2.5 feet), 6.2 minutes empty bed contact time, of granular activated carbon and XE-340 over a 119-day test and 46 percent removal by a bed of IRA-904 resin after 49 days of operation. If all three adsorbents are compared after 49 days of operation time, removals affected are 26, 24 and 46 percent for carbon, XE-340 and IRA-904 resin respectively. A bed of IRA-904 resin 1.52 meters (5 feet) deep, 12.4 minutes empty bed contact time, removed 55 percent after 49 days of operation.
21. On a weight basis, calcium carbonate floc removed one-third as much trihalomethane precursor from raw water as carbon.
22. The XE-340 bed removed an average of four percent trihalomethane formation potential from Hydrotreator water as compared with 24 percent removed from raw water.
23. The IRA-904 resin bed removed an average of 32 percent trihalomethane formation potential from Hydrotreator effluent as compared to 46 percent from raw water.
24. An XE-340 column 0.76 meter (2.5 feet) deep removed no trihalomethane formation potential from finished water.
25. A 0.76 meter (2.5 feet) deep bed of IRA-904 resin removed 13 percent trihalomethane formation potential from finished water. At no time during the test period was the effluent trihalomethane formation potential concentration from this column below 180 µg/L.
26. Granular activated carbon was more efficient in removing trihalomethane formation potential precursors from finished water than the other two adsorbents. For example, in two separate runs 0.76 meter (2.5 feet) of carbon removed 18 and 22 percent, and it was the only adsorbent tested that removed enough precursor to keep the trihalomethane form-

ation potential level below 100 $\mu\text{g/L}$.

Finished Water

27. Granular activated carbon was chosen for deep bed studies because it was the best broad based adsorbent for removal of organics in our system. The deep bed studies were carried out on finished water which had the lowest level of total organic carbon of any location in the plant, and did not suffer from excessive calcium carbonate precipitation. In our system, at a flow rate of 122L/min./m² (3 gpm/ft.²), an empty bed contact time of approximately 24.8 minutes in a 3.05 meter (10 feet) deep granular activated carbon bed was necessary to achieve a bed life of 81 days.
28. Free chlorine residuals were completely removed by 0.76 meter (2.5 feet) of granular activated carbon and IRA-904 resin throughout their respective test periods, whereas the XE-340 completely removed the free chlorine residual for about 17 days.
29. Combined chlorine residuals penetrated all adsorbents tested.
30. Laboratory bottle aging of finished water as a means of predicting trihalomethane growth in the distribution system produced comparable results.
31. An XE-340 adsorbent column, partially saturated with halogenated organics in finished water, was treated with halogenated organic-free water to test for halogenated organic leaching (desorption). Desorption of cis 1,2-dichloroethene, chloroform, bromodichloromethane, and chlorodibromomethane appeared to follow a curve that was the reverse of the adsorption curve.

General

32. The Polanyi-Manes Theory of adsorption was useful in interpreting and explaining our data.
33. A bacterial profile study was made on raw and finished water at the Preston Plant, and the effluent from the granular activated carbon columns. Two reports of this work are appended to this report. Clearly, we had a Biological Activated Carbon system. As no additional oxygen was added to the water (as in European practice), we call our system a partial biological activated carbon system. We cannot speculate on the results of the bacterial growth were not present. We do feel, however, that despite the massive bacterial growth that eventually prevented back washing of the columns, adsorptive capacity

of the granular activated carbon for halogenated organic carbon was not decreased. Initial breakthrough and saturation time for each halogenated organic compound through each column were too consistent to suggest blocking of active sites by the bacteria. Bacteria develop large populations in granular activated carbon columns which slough off into the column effluents in large numbers, necessitating disinfection before release into the distribution system.

SECTION III

RECOMMENDATIONS

1. As finished water leaves a 3.05 meter (10 foot) deep granular activated carbon bed, it has nil free chlorine and a high population of bacteria. It would have to be rechlorinated to again achieve disinfection and according to present practice in Florida it would have to contain approximately 2.5 ppm of free chlorine to provide residual disinfectant before it could enter the distribution system. As some precursors are still present, trihalomethane regrowth in the distribution system will occur. We therefore define granular activated carbon exhaustion or bed life as the point where trihalomethane regrowth in a sample of the 3.05 meter (10 foot) granular activated carbon bed effluent (after rechlorination to 2.5 ppm of free chlorine and aging for two days) reaches the proposed Minimum Concentration Level of trihalomethane or 0.1 mg/L (100 ppb). This level was reached in 81 days. Failure at 81 days, however, was not due solely to trihalomethane growth from precursors. The column had become saturated to chloroform. If the influent water had not contained such a high concentration of trihalomethanes (140 µg/L), the bed life would have been somewhat longer. We can only guess that bed life would have been extended another two weeks. If ozone replaced breakpoint chlorination after the Hydrotreator water, the high trihalomethane load would be eliminated, and, according to European reports, precursors would also be greatly reduced by subsequent granular activated carbon-biological activated carbon treatment. Bed life then would be greatly prolonged. This remains to be confirmed in our system. We therefore, recommend a pilot plant research project located at the Preston Water Treatment Plant to study the possibility of prolonging granular activated carbon bed life in our system by the use of ozone followed by biologically activated carbon.
2. Since a granular activated carbon column effluent contains a high population of bacteria and since such a column would probably be used at the end of a conventional treatment plant we recommend that a bacterial study be made before widespread use of such a system is adopted. Specifically, to determine if the disinfection with 2.5 ppm of free chlorine at the end of the treatment process is adequate

with the associated treatment plant contact time which will range widely from a few minutes to 24 hours or more before discharge into the distribution system. Our work indicates that the standard plate count method is apparently inadequate in assessing numbers and types of bacteria that are found in a granular activated carbon effluent. Conditions for an optimal bacterial method apparently are still being worked out. We recommend that a committee of bacteriologists should be formed to adopt interim bacteria test methods and set up research projects for further study to determine optimal methods.

3. Considerable work is being done in the field of adsorption kinetics. Perhaps more should be done with the Polanyi-Manes adsorption theory. This might include the individual adsorption of most of the specific halogenated organic compounds found in raw and treated water from purified water and water containing known amounts of total organic carbon and added amounts of other specific halogenated organic carbons to study competitive effects.
4. There are several questions about the source of halogenated organic carbon in raw water that should be answered, such as;
 - a. Source of our high level of cis 1,2-dichloroethene
 - b. Source of vinyl chloride
 - c. Lack of or very low level of trihalomethanes when other volatile halogenated organic carbons are present
 - d. Effect of ultraviolet and bacterial enzyme action on specific halogenated organic carbon.

SECTION IV

PLANT AND EQUIPMENT DESCRIPTION

PRESTON PLANT WATER SOURCE

The terrain in the vicinity of Miami and its neighboring municipalities consists of an outcropping of soft, porous, Oolite limestone rock. Water enters this porous rock from local rainfall, runoff, and from the extensive canal system in southern Florida. The approximate annual rainfall in the area is 152.4 cm (60 inches) per year. The porous water-bearing rock is the aquifer from which raw water is drawn by the water treatment plants in the area.

Seven wells have been drilled into the surface rock on or near the Preston Plant site. This groundwater has high color and contains dissolved iron. The color is attributed in large part to the organic matter leached from decaying vegetation through which the groundwater percolates. The water is slightly basic with an average pH of 7.2.

PRESTON PLANT SITE

The Miami-Dade Water and Sewer Authority, through its three major water plants, furnished water, either directly or indirectly for over one million people. One of these three major water plants is the John E. Preston Water Treatment Plant (Flow Diagram in Figure 1), located at 1100 West Second Avenue, Hialeah, Florida. The Preston Plant has been in operation approximately seven years.

At present the Preston Plant is rated at 2.63 m³/s (60 mgd), and in general is operated near or at maximum capacity. The wells supplying the Preston Plant are approximately 27.4 m (90 feet) deep. Each well can produce over 34065 m³ (nine million gallons) per day. Raw water from these seven wells is fed to a combination of three upflow Hydrotreator (H.T.) softeners, each rated at 0.88 m³/s (20 mgd). Silica, activated with chlorine, is added to the raw water just prior to its entrance into the upflow softener. The upflow softener effluent is channeled into a recarbonation flume. Sodium silica fluoride is added at this point. Chlorine is then added just before the water enters the chlorine contact basin. After an average retention time of 1.25 hours in the chlorine contact basin, the

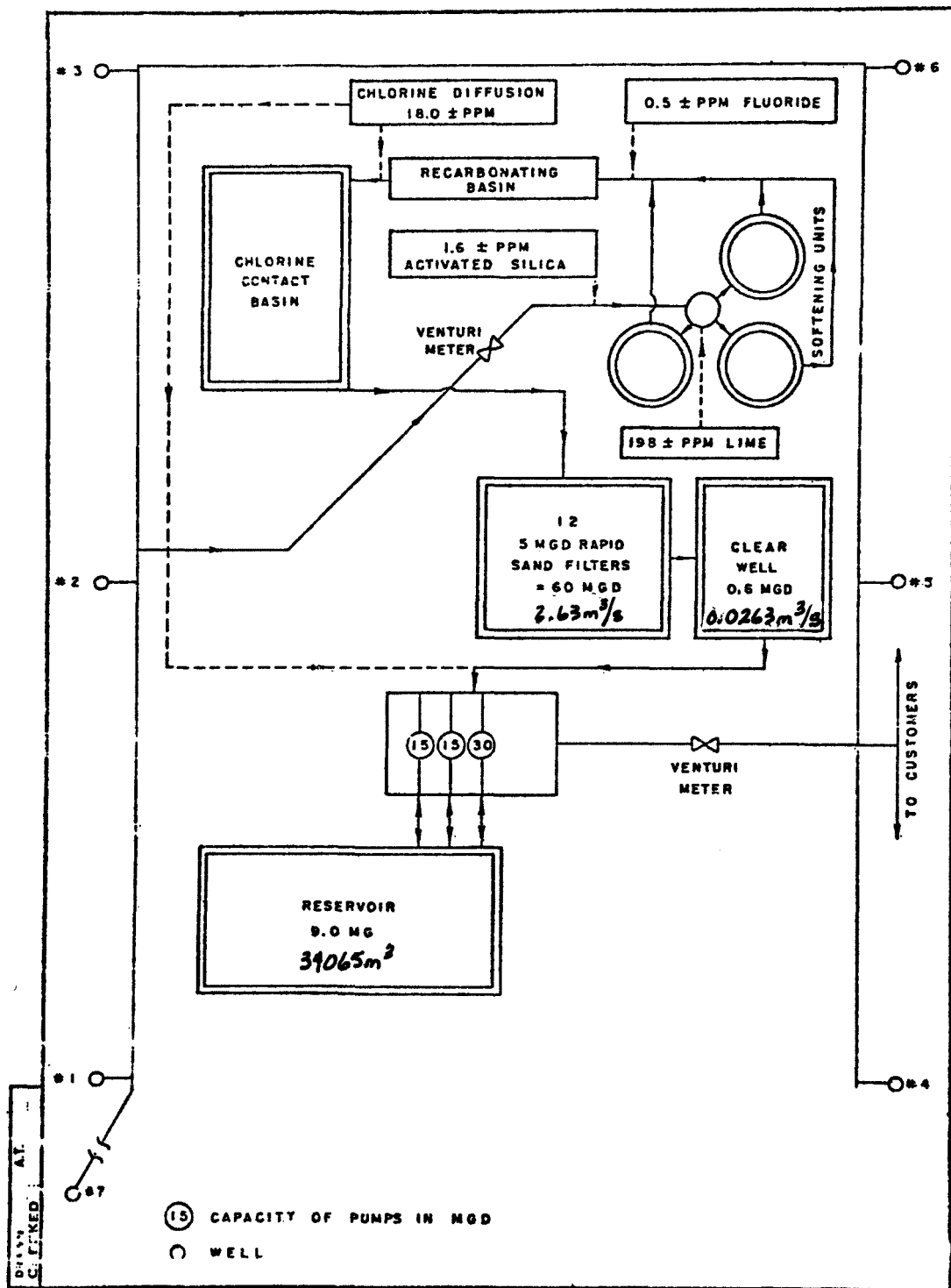


Figure 1. Flow diagram of John E. Preston Water Treatment Plant.

water flows into rapid sand filters $0.22 \text{ m}^3/\text{s}$ - $122\text{L}/\text{min.}/\text{m}^2$ (5 MGD - 3 GPM/ft.²), then to a 34065 m^3 (nine million gallon) reservoir. From the reservoir the water is diverted to the Hialeah Plant for pumping, or pumped directly to high pressure distribution lines. Tables 1 and 2 contain chemical data related to the Preston Water Treatment Plant.

BENCH SCALE ADSORPTION TEST UNIT

The Bench Scale Adsorption unit is located in the second-floor laboratory of the Preston Plant. Three sampling lines enter the laboratory from the plant raw water, Hydrotreator, and clear well composite lines. The water is constantly monitored by pH chart recorder, and samples are readily available at this one location. Routine testing is done hourly around-the-clock. A flow diagram of the Bench Scale Adsorption unit is shown in Figure 2. Each glass column is 1.52 meters (five feet) long by 2.54 cm (one inch) in diameter.

A flow rate of $122\text{L}/\text{min.}/\text{m}^2$ (3 gal./min./ft.²) was maintained by rotometers.

The pumps used on the three sample lines from the plant to the laboratory were three-quarter horsepower, water lubricated, with Teflon seals. All lines were copper pipe. Construction details of the Bench Scale Adsorption unit are shown in Figures 3 and 4.

TABLE 1. TYPICAL PARTIAL ANALYSES,
JOHN E. PRESTON WATER TREATMENT PLANT

	Well Water	After Softening, Before Chlorination	Treated Water Entering Distribution System
Alkalinity (CaCO ₃)			
Phenolphthalein	0.	16.	4.
Methyl Orange	230.	32.	40.
Hardness (CaCO ₃)			
Non-Carbonate	20.	21.	35.
Total	250.	53.	75.
Carbon Dioxide, Free (CO ₂)	25.	0.	0.
Chlorine Residual (Cl ₂) at plant	0.	0.05 (Combined)	2.0 (Free)
Chlorides (Cl)	40.	41.	55.
Fluorides (F)	0.2	0.1	0.7
Sulfates (SO ₄)	24.	----	24.
Calcium (Ca)	88.	----	23.
Iron (Fe)	0.8	0.1	0.0
Magnesium (Mg)	7.0	----	4.2
Sodium & Potassium (as Na)	29.	----	32.
Silica (SiO ₂)	8.0	----	9.0
Turbidity	Nil	Excess 50 units	Nil
Total Solids	350.	----	205.
Electrical Conductivity (EC x 10 ⁶ @ 25°C)	580.	----	305.
Color	50.	25.	6.
pH	7.3	10.0 - 10.3	8.8
(All units expressed as mg/L, (ppm), where applicable)			

TABLE 2. AVERAGE CHEMICAL APPLICATION TO
RAW WATER, JOHN E. PRESTON WATER TREATMENT PLANT

-
-
- Raw water influent to softening units:
 - 1.0 to 2.0 ppm chlorine-activated silica --
 - chlorine 0.3 to 0.7 ppm.
 - Softening units:
 - 160 to 180 ppm CaO as slaked Ca(OH)_2
 - Carbon dioxide addition after softening unit, as needed to achieve desired degree of stabilization.
 - Sodium silica fluoride addition, ± 0.5 ppm to bring fluoride level to 0.7 ppm in treated water.
 - Fifteen to 17 ppm chlorine dosage to achieve a chlorine residual in treated water leaving plant of 1.5 to 3.0 ppm free chlorine. Chlorine contact basin average retention time 1.25 hours. Average minimum free chlorine residual at far points in distribution system 0.5 ppm.
-
-

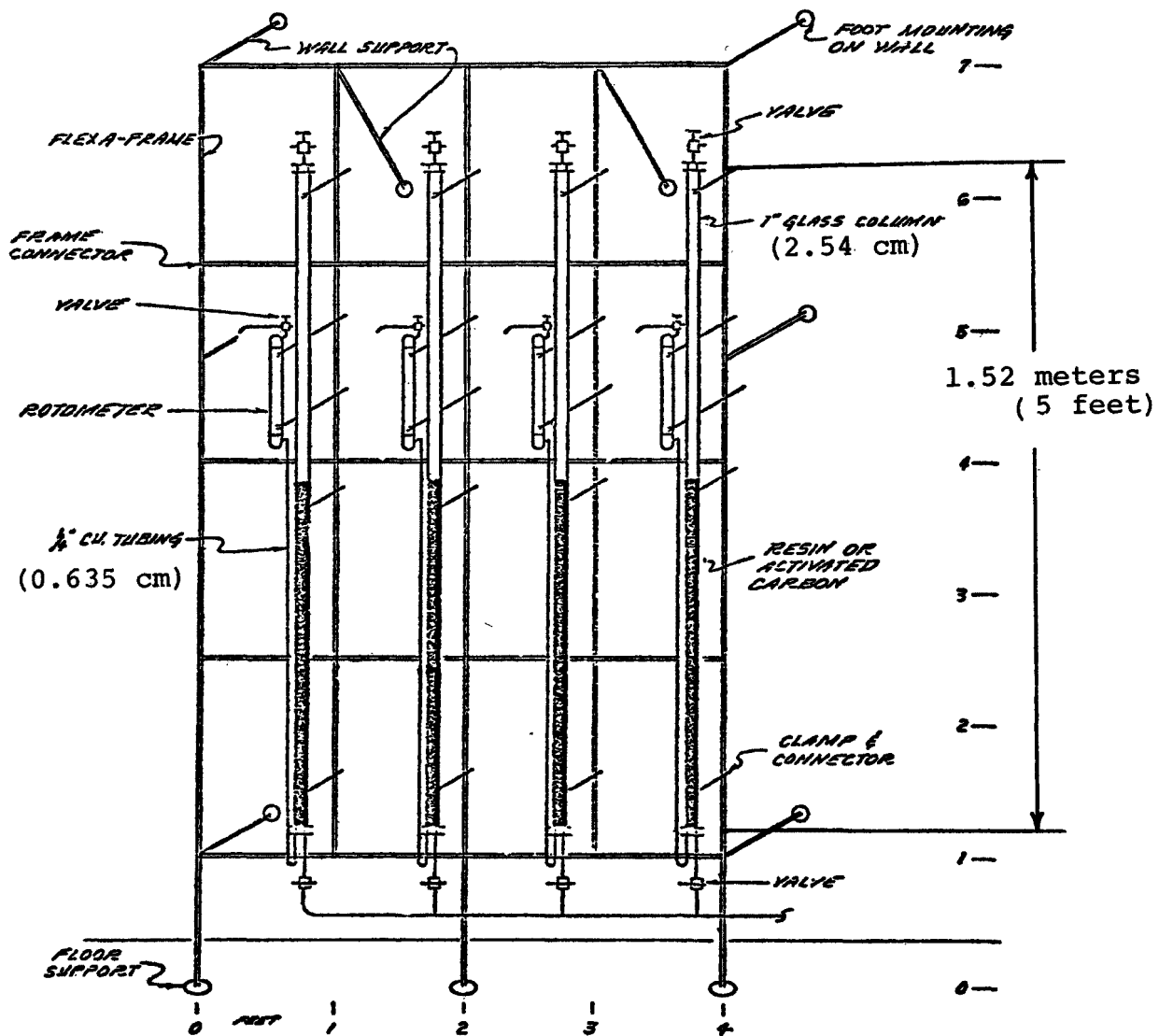


Figure 2. Bench Scale Column Adsorption Unit

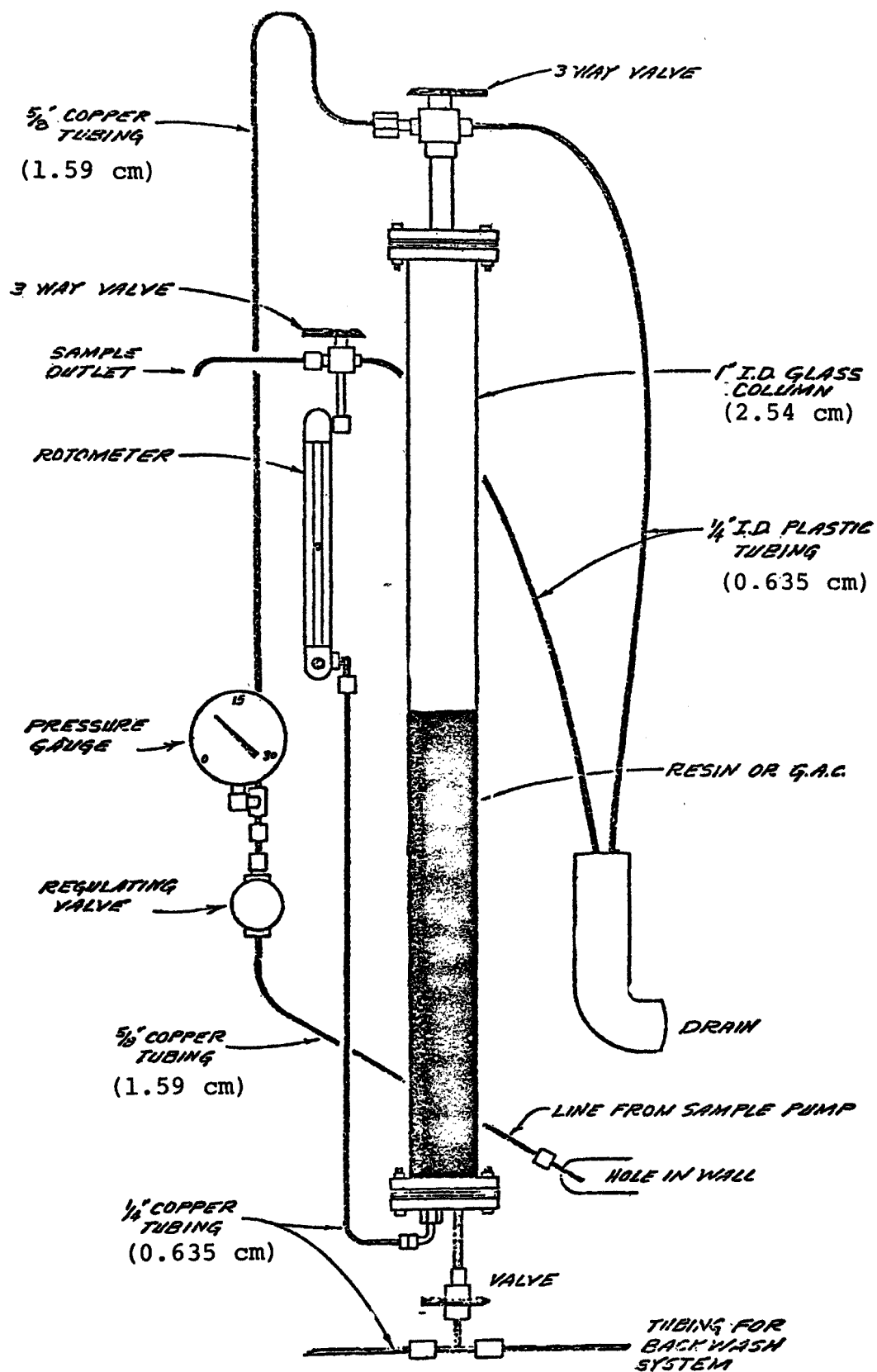


Figure 3. Plumbing for adsorption column.

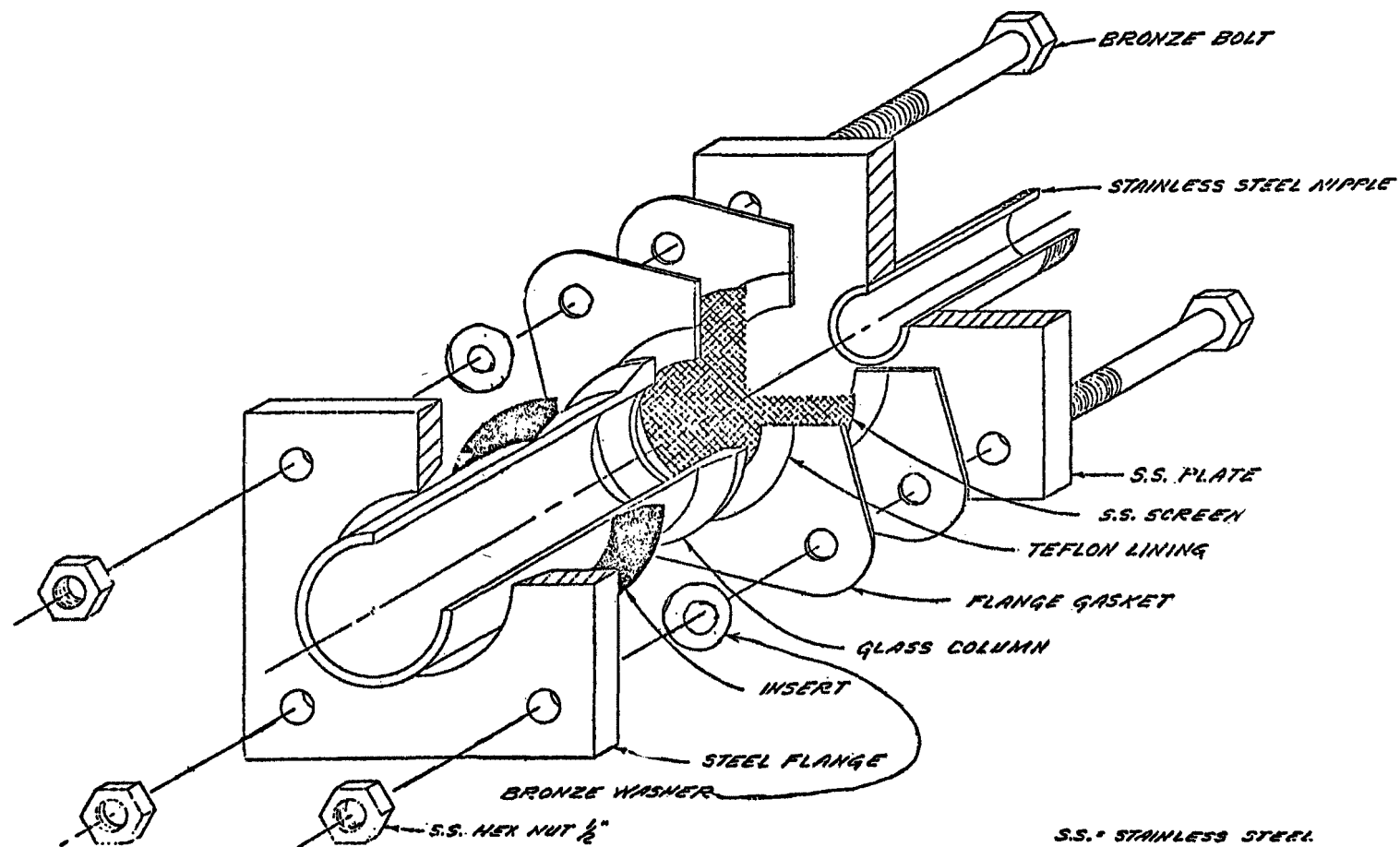


Figure 4. Detailed view of column fittings.

SECTION V

METHODS AND PROCEDURES

OPERATION OF BENCH SCALE ADSORPTION UNIT

A flow rate of 122L/min./m² (3 gal./min.ft.²) was maintained for this study and is equal to approximately 3.78L per hour (one gallon per hour), or 89.3 liters per day. Flow through the column was maintained at 3.78L/hr. (1.0 GPH) by adjusting the rotometer. This was checked periodically. The pressure was adjusted with the regulating valve in order to provide enough head to maintain the desired flow. Whenever the increase in pressure in the column was approximately 7 or 8 psi, the column was backwashed. The H.T. effluent pump, lines, and column were backwashed every day because of the rapid build-up of calcium carbonate. The backwash system for the columns is shown in Figure 5. Backwash water was prepared by passing tap water through a Barnstead Still, an ion-X-changer, and an activated carbon filter. This was followed by all glass redistillation. This water was then boiled and purged with zero-grade helium to remove volatile halogenated organics.

Specific data for each Experimental Design not specified below, such as backwash dates and time, pH, turbidity, color, and chlorine are presented in Appendix B of this report.

GC ANALYTICAL METHOD

Purgeable Halogenated Organic Compounds were analyzed according to the purge and trap method of Bellar and Lichtenberg (2) with modifications by Dressman and McFarren (3) for analysis of vinyl chloride.

Pure helium was bubbled through a water sample (0.5 to 7 mL) at a rate of 20 mL/min. for 11 minutes. Volatile halogenated organics were retained in a one-eighth inch O.D. by eight inch stainless still trap. The first two-thirds of the trap contained Tenax-GC and the upper one-third contained Silica Gel-15. Tenax-GC efficiently adsorbs most of the compounds, but Silica Gel-15 is more efficient in adsorbing the lower molecular weight highly volatile compounds such as vinyl chloride.

The trap was backflushed for six minutes at 220°C with helium (20 mL/min.) onto the GC column (1/8 in. x 7 ft. stain-

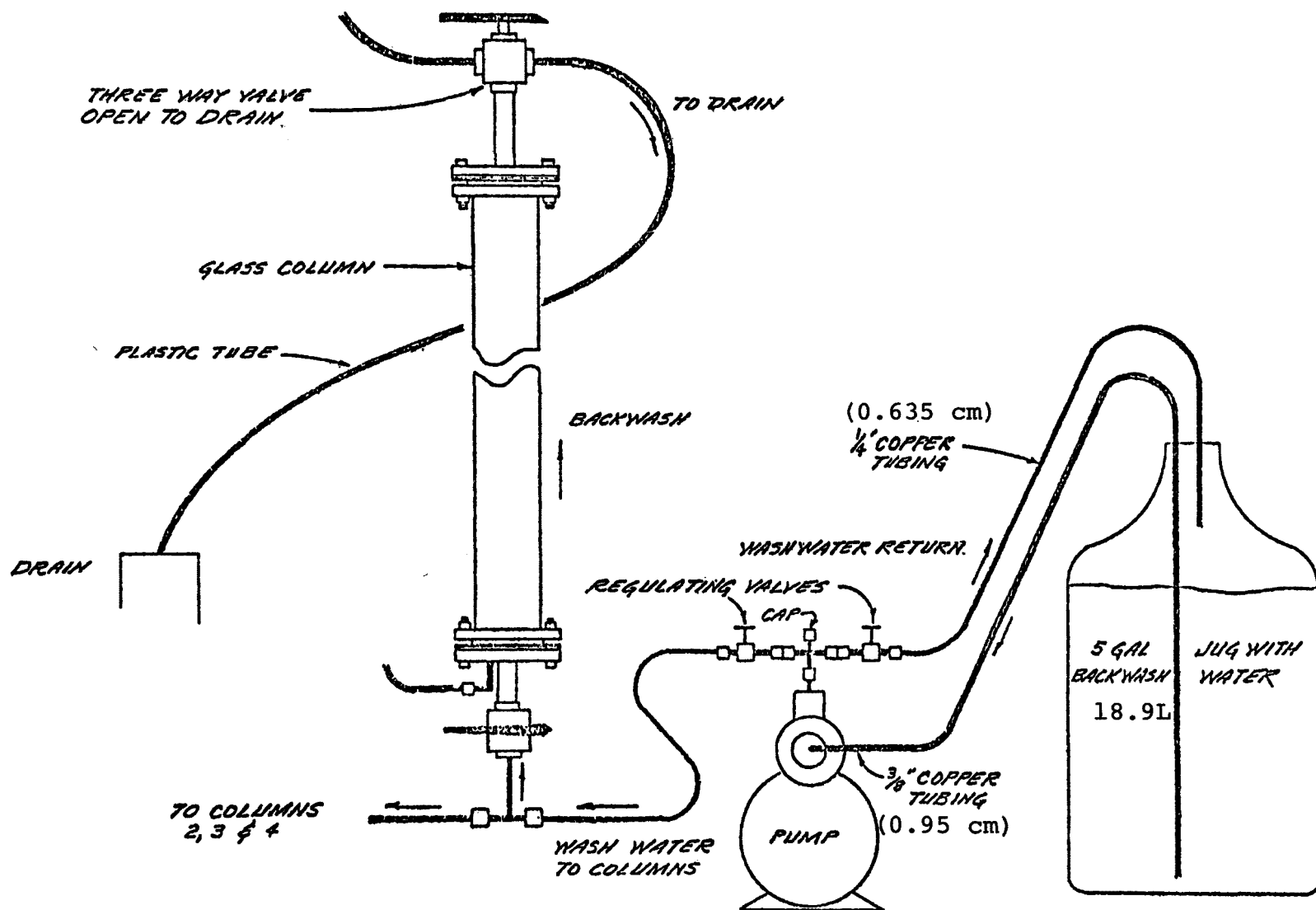


Figure 5. Backwash system for columns.

less steel packed with Tenax-GC). Helium carrier gas (40 mL/min.) was then turned on and the oven set for an 18-minute isothermal hold at 95°C. The balance of the full 52-minute run was programmed at 4°C/min. to 220°C. The Hall Electrolytic Conductivity Detector reduces all halogenated compounds to halogen acids, which are then detected.

A typical chromatogram of a standard sample is shown in Figure 6. These are the 19 specific halogenated organic compounds routinely monitored. Each peak is identified by the chemical name and number and concentration in micrograms in the standard. No significant amount of methyl iodide was found during this study. Values for compounds No. 7, 8, and 9 were summed because the three peaks overlapped and made separate analysis impractical. In most of this report values for the three isomers of dichlorobenzene were summed. In ED4 they were reported separately, because improved chromatographic technique separated the three isomers.

TOC ANALYSIS

TOC values were obtained by the EPA Laboratory in Cincinnati, Ohio on a Dohrmann-Envirotech Organic Analyzer with an Ultra Low Organics Module.

TRISHALOMETHANES, TERMINAL TRISHALOMETHANES AND TRISHALOMETHANE FORMATION POTENTIAL

Four general individual THM compounds were qualified and quantified in the study as a part of the HOC analytic program. They were chloroform, bromodichloromethane, dibromochloromethane, and bromoform. In order to facilitate the investigation of THM's and their control, other parameters were also utilized. These parameters are discussed elsewhere (4) in more detail and are defined here as they applied to this project.

1. Total trihalomethane (total THM) concentration is the summation of the concentrations of the individual THMs in a sample.
2. Instantaneous THM (inst. THM) is the concentration of TTHM in the water at the time the sample is collected.
3. Terminal THM (term. THM) is the sum of TTHM present in the water at the moment of sampling and TTHM subsequently formed during additional reaction time under defined conditions. This value may be used as a general estimate of THM concentrations that the consumer would receive if the water from the location sampled were subjected to the pH, temperature, free chlorine residual and storage time conditions that were used for the sample. During the project, the

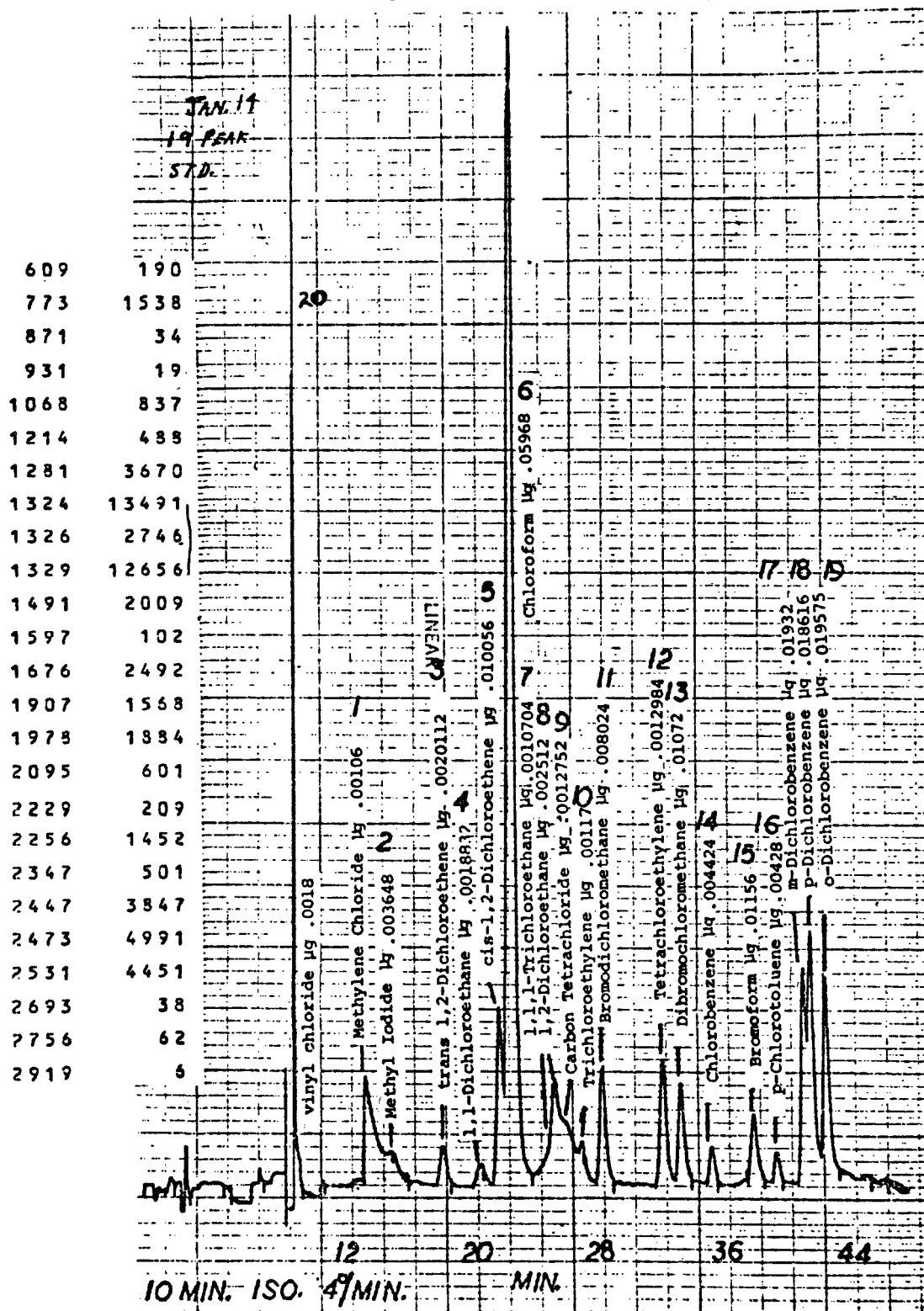


Figure 6. Typical chromatogram of halogenated organics.

reaction was driven toward completion by adding chlorine to exhaust the precursor. Samples were routinely stored at the finished water pH of 9.0 and a temperature of 22°C for six days, i.e., beyond the normal detention time in the distribution system of the utility, with sufficient free chlorine added to satisfy demand. After six days under storage conditions, a concentration was reached that was assumed to represent a maximum reaction for Preston plant distribution water. Modification of these conditions were made on additional samples in ED3 and ED4 as described later. This value may be used as a general estimate of THM concentrations that the consumer would receive if the water from the location sampled were subjected to the pH, temperature, free chlorine residual and storage time conditions that were used for the sample.

4. Trihalomethane formation potential (THM FP) is the difference between the terminal TTHM and the instantaneous TTHM (term. TTHM - inst. TTHM = THM FP), an indirect measure of the unreacted precursor in the water sampled. It is the increase in the TTHM concentration that occurred during the storage period for the determination of the terminal TTHM concentration. The unreacted precursor has the potential to further increase TTHM concentrations in the presence of free chlorine.
5. Handling procedures for HOC including Inst. THM's and Term. Trihalomethane Samples. All HOC samples for raw water and adsorbent column effluents on the raw water line were taken in septum bottles filled to the top and sealed with no air entrapment. No reagents were added. These are referred to as the odd number samples 1, 3 and 5. All HOC samples for the plant Hydrotreator and clear well effluent, as well as the adsorbent columns receiving these waters were sampled in the same way except the septum bottles contained one drop of 10 percent sodium thiosulfate. The sodium thiosulfate was added to quench the presence of any free chlorine residual in the sampled water. These samples are referred to as odd numbered samples 7, 9, 11, 13, 15, 17, 19, 21, 23 and 25.

All term. THM samples were taken at the same time as the HOC samples at each location. The septum bottles were filled to about the 3/4 level. An appropriate amount of buffer solution and free chlorine solution was added and the septum bottle then was quickly filled to the top with water sample. Care was taken to allow no overflow, but yet to avoid air entrapment in the sample bottle prior to sealing. The samples were delivered to FIU for six-day storage at 22°C. These samples are designated as even numbered samples 2 through 16, 20, 22, 24 and 26.

Additional samples were taken during ED3 and ED4 to compare the value of the laboratory stored samples for estimating the THM concentrations that occurred in the actual distribution system. Clear well effluent samples (designated as 11 + 2) were taken in empty septum bottles, filled to the top and sealed without the addition of any reducing agent or additional chlorine. These samples were stored for two days at 22°C and then delivered to FIU for analysis. Free chlorine residuals and pH were determined on these samples at the time of analysis. The samples were collected for comparison with inst. THM concentrations found at the Red Road distribution system sampling station which is two days water travel time from the plant. Thus, a clear well water sample was stored in a septum bottle for two days and compared to a sample taken in the distribution system two days later.

Additional samples from the Red Road distribution system location were also taken and buffer plus chlorine solution were added to these samples prior to bottle storage at pH 9 and 22°C for four days. These samples are designated as 17 + 4 and represent the THM concentration that was present in a water that was in the actual distribution system for two days with the pH and chlorine residuals normally present and four additional days in bottle storage with a pH of 9.0, temperature of 22°C and presence of free chlorine residual. The THM concentration of this six-day stored sample, two distribution days plus four bottle storage days (sample 17 + 4) was compared to the normally obtained six-day bottle stored term. THM concentration of the clear well water (sample 12).

Along with the sample of the clear well stored for two days in a bottle (sample 11 + 2), samples were taken from the effluent of the adsorbent columns. The column effluent samples were adjusted as required to assure that a free chlorine residual was present prior to sealing and two-day storage. The adsorbent effluent samples were used to estimate the THM concentration that might be received by a consumer two days from the plant, if a specific adsorbent were a part of the normal treatment system. The concentrations of these adsorbent effluent samples (i.e. samples designated 13 + 2, 15 + 2, 23 + 2 and 25 + 2) were compared with clear well water samples stored for two days in a bottle as well as the inst. THM samples collected at the Red Road sampling station two days water travel time from the plant.

DATA ANALYSIS

The format in this study was to plot all individual data points to form the adsorption or breakthrough curve. A typical plot of actual adsorption data for bromodichloromethane is shown

in Figure 66, page 125. Initial breakthrough times for each of the four columns in series is shown. Saturation times for the first two columns are shown. An extrapolated saturation time for the third column is shown and the saturation time for the fourth column cannot be extrapolated because of insufficient data to establish the slope. The average influent concentration in $\mu\text{g/L}$ is determined and each adsorption or breakthrough curve is integrated to determine the amount of substance entering, passing and adsorbed by the column at breakthrough, saturation and at the end of the test period or at some other time period in common with data in another ED. The breakthrough point was sometimes difficult to ascertain from the actual data and plotted curves. For each HOC, adsorbent type and bed depth studied there was sometimes intermittent low level leakage before the time we picked as the breakthrough point. In general, we define the breakthrough point as the time required to reach $2 \mu\text{g/L}$ on the breakthrough curve. Actual leakage values during the period before breakthrough are too low to plot on the $\mu\text{g/L}$ scale used for the complete breakthrough curves. In some cases the actual low level of breakthrough is shown above the plotted data point.

Throughout the study, 76.2 cm (30-inch) bed depths were used for each column. In all calculations an average weight value was used for GAC, XE-340 and IRA-904 resin per column. These values were, respectively, 176, 215, and 275 grams. The flow rate through each column was 122 L/min./m^2 ($3 \text{ gal./min./ft.}^2$), resulting in a flow of 89.3 L/day and approximately 3.785 L/hr. (1 gal./hr.).

Interpretation of results includes consideration of Mass Transfer Zone (MT_z). The Mass Transfer Zone for a specific substance is the minimum bed depth at a given flow rate necessary to prevent column breakthrough after initial flow. We used the following equation:

$$\text{MT}_z = \frac{T_s - T_b}{T_s} \times \text{Bed Depth}$$

T_s = saturation time

T_b = breakthrough time

The raw water feed for the Preston plant averaged 10 mg/L of TOC. However TOC is merely a representation of the carbon fraction present. The concentration of Dissolved Organic Matter (DOM) is some higher amount depending on the relative percent of carbon in the total molecular weights of organics present. We have estimated that the organics present contain an average of 60 percent carbon. We calculate approximate DOM values by dividing TOC values by 0.6. Our raw water feed thus contained approximately 17 mg/L of DOM. The DOM value is helpful when discussing competitive adsorption.

SECTION VI

EXPERIMENTAL PLAN

The two-year study contained four Experimental Designs (ED). These designs are listed below in Table 3 with their starting and ending dates. During the conduct of the experimental designs for the bench scale studies, the samples that were taken described the influent water to the bench scale experiments are also designed to describe the operation of the full scale Preston plant. Thus a long term comparison of the raw water, Hydrotreater effluent and finished water for the full scale treatment plant was a designed phase of the project and designated as Full Scale Plant Studies. The full scale plant study data can also be used with each bench scale study conducted. For example, during ED1 the samples on Figure 7 designated as 1, 2, 7, 8, 11 and 12 describe both the influent to the bench scale columns as well as the full scale treatment plant water at the locations noted.

TABLE 3. EXPERIMENTAL DESIGN NUMBER
AND STARTING AND ENDING DATES

ED	Dates
1	Aug. 13 - Dec. 7, 1976
1R	Jan. 18 - May 20, 1977
2	Jun. 3 - Aug. 5, 1977
3	Aug. 26 - Oct. 18, 1977
4	Nov. 1, 1977 - Mar. 3, 1978

The general purpose for each ED was as follows:

ED1

The flow diagram for ED1 is shown in Figure 7. Two

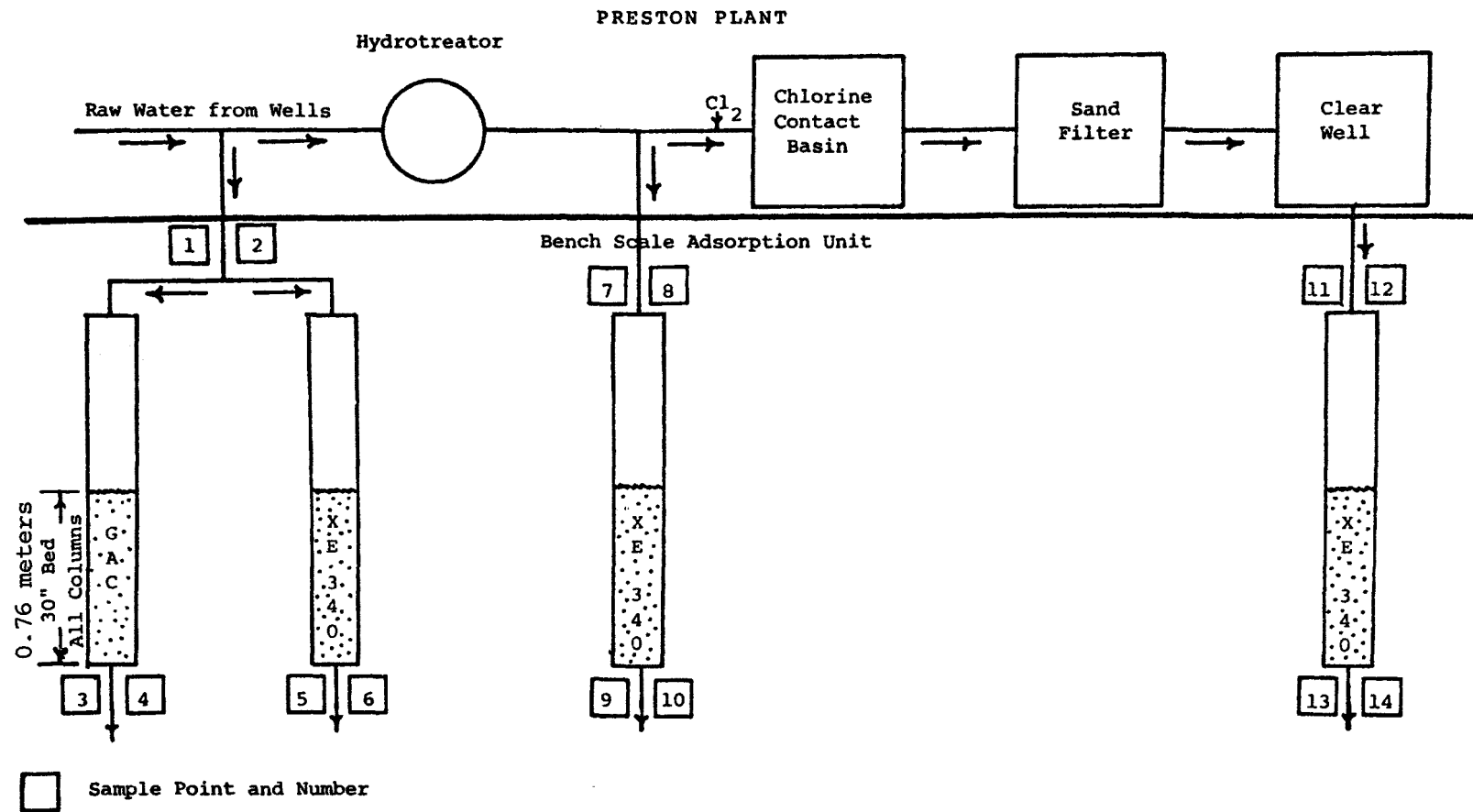


Figure 7. Flow diagram of Bench Scale Adsorption Unit for GAC and XE-340 study in ED1.

adsorbents were studied. Filtrasorb 400, 12 x 40 mesh obtained from Calgon Corporation, Pittsburgh, Pennsylvania, was chosen as the GAC adsorbent. The second adsorbent was Ambersorb XE-340 from Rohm and Haas Company, Philadelphia, Pennsylvania. Ambersorb XE-340 is a polymeric carbonaceous adsorbent tailored for removal of low molecular weight organics from water.

As shown in Figure 7, both adsorbents were placed in the raw water line. This enabled a comparison of their abilities to remove TOC, HOC and precursor substances from raw water. Precursor removal was measured by the THM FP method. Ambersorb XE-340 columns were also placed in H.T. and finished water lines to study HOC, TOC, and THM FP removal with the respective influent waters.

ED1R

As ED1 work progressed, changes in methodology were made and the desired complete data base from initial start-up was not obtained. This work was thus considered mainly as a shake-down phase and ED1 was repeated as originally planned.

ED2

The Flow Diagram for ED2 is shown in Figure 8. At the end of ED1R, the partially exhausted XE-340 column on the finished water line was selected for a leaching study because this type of data had not been previously collected. As shown in Figure 8, a fresh XE-340 column was placed on the finished water line ahead of the partially exhausted column. For a period of time, essentially all halogenated organics would be removed by the fresh column. The halogenated organic leaching rate for the second column was determined by analyzing the effluent sample 13A.

ED3

The Flow Diagram for ED3 is shown in Figure 9. Rohm and Haas indicated that IRA-904 resin, a strong base cationic adsorption resin, was one of the better polymeric adsorbents for precursor type substances. We did not select it for halogenated organic adsorption. To study the effect of bed depth, two IRA-904 resin columns in series were placed on the raw water line. One IRA-904 resin column was placed on the H.T. line. To compare the effectiveness of IRA-904 resin with GAC Filtrasorb 400, one column of each was placed on the finished water line.

ED4

The Flow Diagram for ED4 is shown in Figure 10. Four GAC Filtrasorb 400 columns in series were placed in the finished water line to study the effect of bed depth and contact time on halogenated organic and precursor removal.

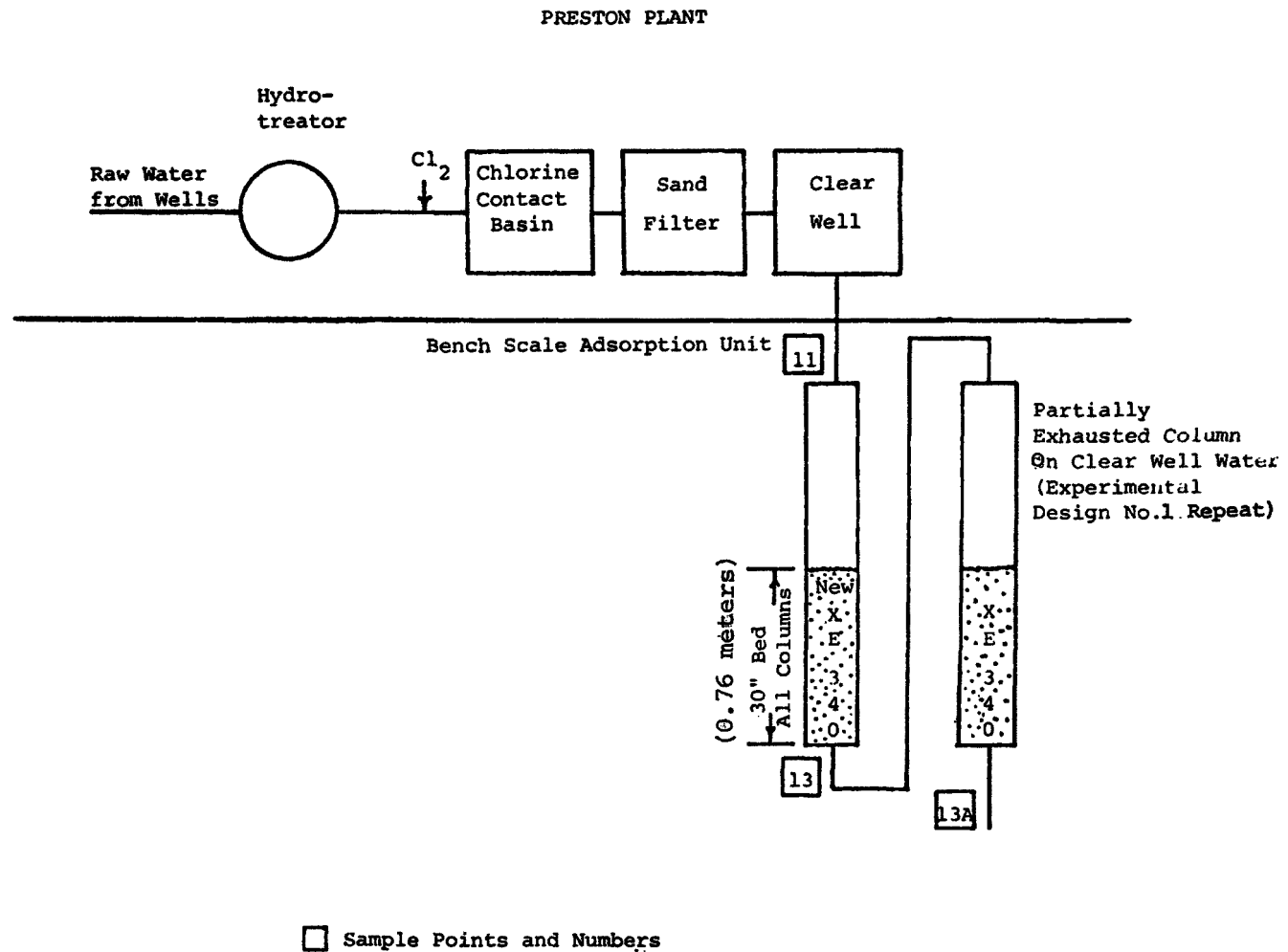


Figure 8. Flow diagram of Bench Scale Adsorption Unit for leaching study in ED2.

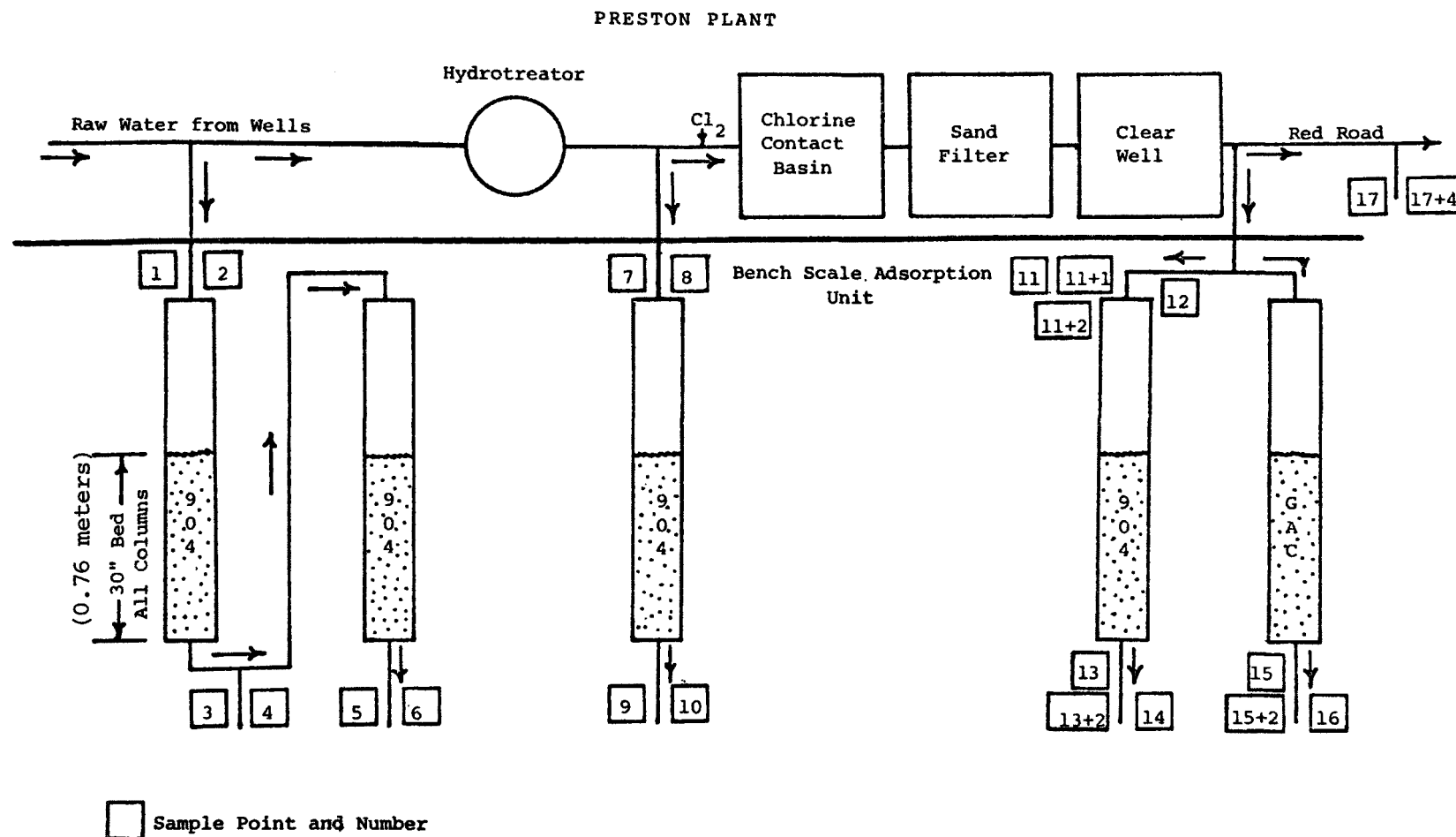


Figure 9. Flow diagram of Bench Scale Adsorption Unit for GAC and IRA-904 resin study in ED3.

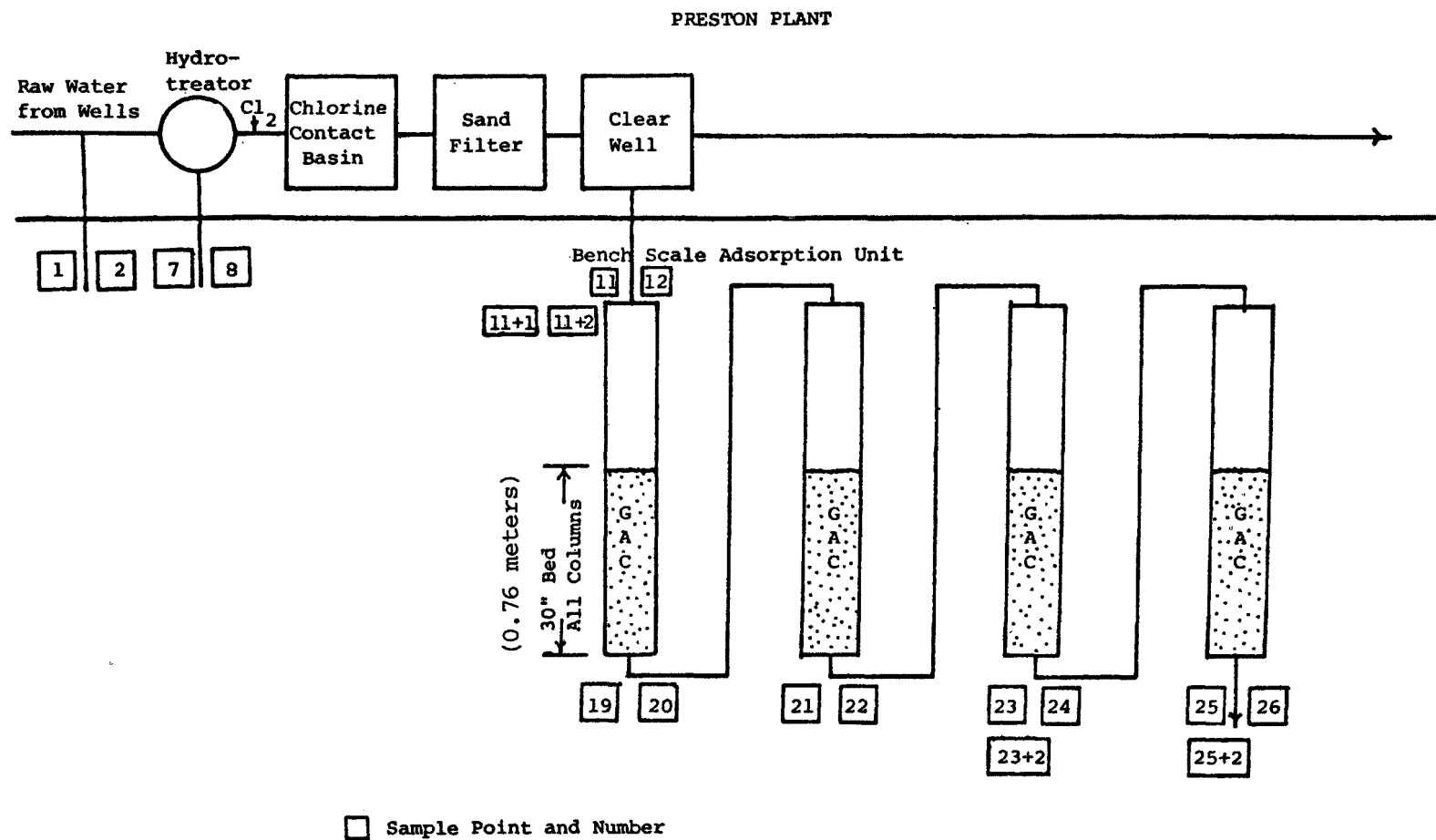


Figure 10. Flow diagram of Bench Scale Adsorption Unit for deep bed study in ED4.

SECTION VII

RESULTS AND DISCUSSION

Section VII, Results and Discussion, is divided into two parts; Full Scale Plant Studies and Bench Scale Studies. Full Scale Plant Studies refers to data obtained at sample points from the Preston Water Treatment Plant during the conduct of each bench scale experiment. These Full Scale Plant sample points include the raw water feed to the plant, effluent from the lime softening unit (H.T.), and finished water from the clear well. Bench Scale Studies refers to data obtained at sample points from the Bench Scale Column Adsorption Unit.

FULL SCALE PLANT STUDIES

Specific Halogenated Organics

Nineteen specific HOC were studied. The specific compounds with their chemical identification number for this report are given in Table 4. They are presented in their order of elution from the gas chromatograph using a Tenax GC column (Figure 6). The average concentration in the full scale raw, H.T. and finished water during the conduct of each bench scale ED are shown in Tables 5 and 6 respectively.

Raw Water Source--

Vinyl chloride levels were 0.8, 6.9, and 12.8 $\mu\text{g/L}$ respectively in ED1R, ED3, and ED4. This is an insufficient data base to indicate that vinyl chloride levels might be increasing, but the possibility should be studied further.

The level of methylene chloride also increased, 0.08, 0.1, and 0.45 $\mu\text{g/L}$. The level of trans 1,2-dichloroethene varied erratically from 1.3 to 2.0 $\mu\text{g/L}$. 1,1-Dichloroethane varied from 0.3 to 0.6 $\mu\text{g/L}$. The compound cis 1,2-dichloroethene was the highest level HOC in raw water and the four ED varied in no set pattern from 21.0 to 29.0 $\mu\text{g/L}$. The four THM present, chloroform, bromodichloromethane, chlorodibromoethane, and bromoform essentially averaged nil concentration in all ED except ED1R which showed levels of 0.16, 0.11, 0.04, and 0.02 $\mu\text{g/L}$ respectively. The summed value of 1,1,1-trichloroethane, 1,2-dichloroethane and carbon tetrachloride varied from 0.1 to 0.2 $\mu\text{g/L}$ in ED1R, ED3 and ED4. Trichloroethylene varied from 0.13 to 0.4 $\mu\text{g/L}$. Chlorobenzene varied from 0.19 to 1.3 $\mu\text{g/L}$.

TABLE 4. AVERAGE CONCENTRATION OF SPECIFIC HALOGENATED ORGANICS IN RAW WATER

Chem. I.D.#	Chemical Name	Average concentration in µg/L			
		Raw Water			
		ED1	ED1R	ED3	ED4
20	Vinyl Chloride		.8	6.9	12.8
1	Methylene Chloride		.08	.1	.45
3	Trans 1,2-Dichloroethene		1.3	2	1.5
4	1,1-Dichloroethane		.3	.6	.58
5	Cis 1,2-Dichloroethene	21	29	26.9	25.6
6	Chloroform	N	.16	N	.08
7	1,1,1-Trichloroethane				
8	1,2-Dichloroethane		.11	.2	.1
9	Carbon Tetrachloride				
10	Trichloroethylene		.13	.4	.34
11	Bromodichloromethane	N	.11	N	N
12	Tetrachloroethylene		.06	N	.003
13	Chlorodibromomethane	N	.04	N	N
14	Chlorobenzene		.19	1.3	1.1
15	Bromoform	N	.02	N	N
16	p-chlorotoluene		.11	.2	.02
17	m-dichlorobenzene				
18	p-dichlorobenzene		1.1	1.0	.51
19	o-dichlorobenzene				.17
Total			33.51	39.6	43.25

N = Nil

ND = Not Determined

TABLE 5. AVERAGE CONCENTRATION OF SPECIFIC HALOGENATED ORGANICS IN H.T. WATER

Chem. I.D.#	Chemical Name	Average concentration in µg/L			
		H.T. Water			
		ED1	ED1R	ED3	ED4
20	Vinyl Chloride		.7	6	9.7
1	Methylene Chloride		ND	ND	ND
3	Trans 1,2-Dichloroethene		.4	1.8	.95
4	1,1-Dichloroethane		.13	.89	.45
5	Cis 1,2-Dichloroethene	20	25.4	24.1	22.3
6	Chloroform	4	1.1	1.43	1.2
7	1,1,1-Trichloroethane				
8	1,2-Dichloroethane		.2	.09	.12
9	Carbon Tetrachloride				
10	Trichloroethylene		.07	.44	.33
11	Bromodichloromethane	1.7	.26	.6	.35
12	Tetrachloroethylene		.003	N	.004
13	Chlorodibromomethane	.62	.24	.46	.13
14	Chlorobenzene		.03	.84	.72
15	Bromoform	.09	N	.013	.007
16	p-chlorotoluene		.03	.16	.03
17	m-dichlorobenzene				N
18	p-dichlorobenzene		.39	.56	.28
19	o-dichlorobenzene				.16
Total		28.95	28.75	37.38	36.73

N = Nil

ND = Not Determined

TABLE 6 . AVERAGE CONCENTRATION OF SPECIFIC HALOGENATED ORGANICS IN FINISHED WATER

		Average concentration $\mu\text{g/L}$				
		Finished Water				
Chem. I.D.#	Chemical Name	ED1	ED1R	ED2	ED3	ED4
20	Vinyl Chloride		.6	.6	5.4	6.2
1	Methylene Chloride		ND	ND	ND	ND
3	Trans 1,2-Dichloroethene		.18	.86	1	.77
4	1,1-Dichloroethane		.2	.18	.3	.4
5	Cis 1,2-Dichloroethene	10.9	17.2	18.4	18.3	19.9
6	Chloroform	80.2	71.4	64	57	67.3
7	1,1,1-Trichloroethane					
8	1,2-Dichloroethane		.66	1.47	5.3	7.7
9	Carbon Tetrachloride					
10	Trichloroethylene		.2	.57	.1	.68
11	Bromodichloromethane	37.1	42.7	42.4	39	47
12	Tetrachloroethylene		.02	N	N	.003
13	Chlorodibromomethane	12	24.5	26.7	27	33.6
14	Chlorobenzene		.1	.08	.8	.86
15	Bromoform	.13	1.9	1.91	2.5	2.5
16	p-chlorotoluene		N	N	.2	.1
17	m-dichlorobenzene					N
18	p-dichlorobenzene		.63	2.1	.3	.21
19	o-dichlorobenzene					.14
Total			160.29	159.27	157.2	187.36

N = Nil

ND = Not Determined

p-Chlorotoluene varied from 0.02 to 0.2 $\mu\text{g/L}$. The summed value of m, p, and o-dichlorobenzene varied from 1.0 to 1.1 $\mu\text{g/L}$ in ED1R and ED3. In ED4, the three isomers of dichlorobenzene were reported separately with values of nil, 0.51 and 0.17 $\mu\text{g/L}$ respectively.

Thus, in general, the raw water contaminants were fairly consistent during the project.

Hydrotreator Effluent Source--

Three main factors in the lime softening stage of the plant probably contribute to changed levels of the specific HOC originally present in raw water. These factors are, volatile loss, adsorption on precipitated calcium carbonate (most of which is removed as sludge) and THM generation by a small amount of chlorine which is added before the lime to activate the sodium silicate used as a coagulating aid.

The percent removal or increase factor (the symbol "X" used as "times") based on raw water for the 19 specific HOC are shown in Table 7. Vinyl chloride was reduced by 12, 13, and 24 percent in ED1R, ED3, and ED4 respectively. Methylene chloride was not determined on H.T. or finished water since it was used as an internal standard for each GC determination. The average concentration of trans 1,2-dichloroethene was reduced by 69, 10, and 37 percent. The level of 1,1-dichloroethane was reduced by 57 and 22 percent in ED1R and ED4 respectively. In ED3, an increase factor of 1.5X was observed for 1,1-dichloroethane. This factor is determined by dividing the average concentration of the compound in the H.T. effluent water by the average concentration in raw water. There were 16 data points in ED3 and only 5 showed increase factors. Unless most of the data points show a consistent increase factor we should probably not put too much weight on the increase factor as determined.

The H.T. reduced levels of cis 1-2-dichloroethene by 5, 12, 10, and 13 percent in the four ED. The four THM, chloroform, bromodichloromethane, chlorodibromomethane and bromoform increased from almost nil levels in raw water to average values of 1.9, 0.7, 0.4, and 0.03 $\mu\text{g/L}$ in the H.T. effluent water. The summed value of 1,1,1-trichloroethane, 1,2-dichloroethane and carbon tetrachloride in ED1 and ED4 show increase factors of 1.8X and 1.2X respectively. The summed value was reduced 55 percent in ED3. Again, the actual data points do not show a consistent increase and partial removal is the usual case. Trichloroethylene, tetrachloroethylene and p-chlorotoluene exhibit a similar pattern. The H.T. reduced levels of chlorobenzene by 84, 35, and 34 percent in ED1R, ED3, and ED4 respectively. The isomers of dichlorobenzene are reduced by 65, 44, and 51 percent.

TABLE 7. PERCENT REMOVAL OR INCREASE FACTOR FOR
SPECIFIC HALOGENATED ORGANICS IN H.T. WATER
Percent removal or increased
factor based on raw water

Chem. I.D.#	Chemical Name	H.T. Water			
		ED1	ED1R	ED3	ED4
20	Vinyl Chloride		12	13	24
-1	Methylene Chloride				
3	Trans 1,2-Dichloroethene		69	10	37
4	1,1-Dichloroethane		57	1.5X	22
5	Cis 1,2-Dichloroethene	5	12	10	13
6	Chloroform				
7	1,1,1-Trichloroethane				
8	1,2-Dichloroethane		1.8X	55	1.2X
9	Carbon Tetrachloride				
10	Trichloroethylene		46	1.1X	3
11	Bromodichloromethane				
12	Tetrachloroethylene		95	N	1.3X
13	Chlorodibromomethane				
14	Chlorobenzene		84	35	34
15	Bromoform				
16	p-chlorotoluene		73	10	1.5X
17	m-dichlorobenzene				N
18	p-dichlorobenzene		65	44	45
19	o-dichlorobenzene				6

N = Nil

ND = Not Determined

X = Times Factor

Generally, the full scale plant H.T. process did not achieve significant reductions in the concentrations of the specific organics routinely monitored.

Finished Water Source--

Four main factors probably contribute to changed levels of HOC in the finished water of the full scale treatment plant. Volatile loss, removal of calcium carbonate (turbidity) by sand filtration which may contain adsorbed HOC, and oxidation of HOC by chlorine contribute to the overall HOC reduction. Breakpoint chlorination will greatly increase THM levels.

In Table 8 the reduction of vinyl chloride in finished water, based on raw water levels, is 25, 22, and 52 percent in ED1R, ED3, and ED4 respectively. The reduction in vinyl chloride is about the same in the H.T. portion of the plant and the breakpoint chlorination--chlorine contact basin--sand filtration stage of the plant. A pattern of further reduction in finished water compared to reduction in H.T. effluent was observed with trans 1,2-dichloroethene, 1,1-dichloroethane, cis 1,2-dichloroethene, tetrachloroethylene, chlorobenzene, p-chlorotoluene and the isomers of dichlorobenzene.

In Table 8 increase factors of 1.5X and 2X are shown for trichloroethylene in ED1R and ED4. The individual data points in both these ED show quite a consistent pattern of increase suggesting that this compound may indeed be increasing in finished water. The data in Table 8 for chlorobenzene suggest that in ED1R and ED4, less of the compound is removed on a percentage basis from finished water than H.T. water based on the original amount present in raw water. An explanation might be that chlorobenzene is actually increasing between the H.T. and finished water stages, but not enough to indicate an overall increase factor. Of the non-THM HOC compounds it appears that one or more of the summed group consisting of 1,1,1-trichloroethane, 1,2-dichloroethane and carbon tetrachloride increases in the finished water. The actual individual data points clearly show that the finished water concentrations were higher than raw and H.T. water in most of the samples in each design phase. Trichloroethylene and chlorobenzene may also show some increase. These increases may be formed by the reaction of chlorine with precursors or may be introduced with chlorine, or both.

The increase in inst. THM's through the treatment plant (raw water versus finished water) are clearly shown by comparing the chloroform data in Table 4 with the chloroform data in Table 6. The average summation of the concentrations of the four inst. THM species are shown for each ED in Table 9 (i.e. 129.4, etc.). Also the average percent of the total inst. THM's are shown for each species (i.e. chloroform was 62 percent of the 129.4 µg/L concentration for total inst. THM's for ED1).

TABLE 8. PERCENT REMOVAL OR INCREASE FACTOR FOR SPECIFIC HALOGENATED ORGANICS IN FINISHED WATER

Chem. I.D.#	Chemical Name	Percent removal or increase factor based on raw water			
		Finished Water			
		ED1	ED1R	ED3	ED4
20	Vinyl Chloride		25	22	52
1	Methylene Chloride				
3	Trans 1,2-Dichloroethene		86	50	49
4	1,1-Dichloroethane		33	50	31
5	Cis 1,2-Dichloroethene	48	41	29	6
6	Chloroform				
7	1,1,1-Trichloroethane				
8	1,2-Dichloroethane		6X	26.5X	77X
9	Carbon Tetrachloride				
10	Trichloroethylene		1.5X	75	2X
11	Bromodichloromethane				
12	Tetrachloroethylene		66	N	0
13	Chlorodibromomethane				
14	Chlorobenzene		47	38	22
15	Bromoform				
16	p-chlorotoluene		100	0	5X
17	m-dichlorobenzene				N
18	p-dichlorobenzene		43	33	59
19	o-dichlorobenzene				18

N = Nil

ND = Not Determined

X = Times Factor

TABLE 9. AVERAGE TOTAL INST. THM AND PERCENT OF INDIVIDUAL THM IN EACH EXPERIMENTAL DESIGN

	ED1	ED1R	ED2	ED3	ED4
Total Inst. THM ($\mu\text{g/L}$)	129.4	140.5	135.0	125.5	150.4
TOC (mg/L)		9.8		8.6	8.3
Percent of Individual Inst. THM					
chloroform	62	50.8	47.4	45	44.8
bromodichloromethane	28.6	30.4	31.4	31	31.2
chlorodibromomethane	9.3	17.4	19.8	22	22.3
bromoform	0.1	1.4	1.4	2	1.7

In Table 9 the data show that the average total inst. THM varied from 125.5 $\mu\text{g/L}$ to 150.4 $\mu\text{g/L}$. TOC values in mg/L for ED1R, ED3, and ED4 are also shown in Table 9 and they do not correlate with the average total inst. THM values. There appears to be a consistent trend in the data for the ratio of bromine compounds to increase from ED1 through ED4. The percent of individual inst. THM data indicates that there was a shift in the composition of the total inst. THM's, whereas chloroform comprised 62 percent of the total inst. THM's during ED1, it comprised only 44.8 percent during ED4. Other species increased accordingly. Although the reason is unknown, the possibility of slight salt water intrusion could exist.

TOC and THM FP Organics

Raw Water Source--

Average THM FP and TOC levels of raw water for ED1, ED1R, ED3 and ED4 are shown in Table 10. There appears to be no direct relationship between the concentrations of TOC and THM FP. Comparisons of data in Table 10 show that the highest average concentration of TOC was 9.8 mg/L in ED1R with a corresponding average THM FP concentration of 659 $\mu\text{g/L}$ and that the lower average TOC concentration of 8.3 mg/L in ED4 was not accompanied by a corresponding lower THM FP concentration.

H.T. Water Source--

Average THM FP levels of H.T. water for ED1, ED1R, ED3 and ED4 are shown in the upper half of Table 10. The percent of THM FP removed from raw water by lime softening is also shown.

TABLE 10. TOC AND THM FP REMOVAL BY
LIME SOFTENING IN FULL SCALE
PLANT

ED	Ave. THM FP in raw water µg/L	Ave. THM FP in H.T. water µg/L	Ave. Percent Removal %
1	816	573	30
1R	659	471	28
3	591	389	34
4	662	531	20
ED	Ave. TOC in raw water mg/L	Ave. TOC in H.T. water mg/L	Ave. Percent Removal %
1	-	-	-
1R	9.8	6.8	31
3	8.6	6.0	30
4	8.3	5.8	31

In 404 days of testing over the two-year study, the weighed average removed by lime softening was 27 percent.

Average TOC levels of H.T. water for ED1R, ED3 and ED4 appear in the lower half of Table 10 with percent removal data from raw water by lime softening. The weighed average removal was 31 percent. TOC and THM FP removals by lime softening appear to correlate quite well with values of 31 percent and 27 percent respectively.

Raw water entering the Preston Plant had an average total hardness of 245 ppm. Lime softening reduced the hardness to about 85 ppm. Non-carbonate hardness averaged 6 ppm. A decrease in carbonate hardness of 154 ppm is equal to 308 mg of calcium carbonate floc per liter. In all four ED the average THM FP removed from raw water by lime softening was 205 µg/L. This corresponds to 0.07 gram of THM FP adsorbed per 100 grams of calcium carbonate floc.

Finished water Source--

TOC and THM FP removal data resulting from the combined effects of breakpoint chlorination, residence in the chlorine contact basin and sand filtration are shown in Table 11. TOC in finished water (lower half of Table 11) is removed an average of 6 percent and the average THM FP removal is approximately 24 percent. However, the THM FP removal was in actuality simply a conversion of a part of the THM FP in the H.T. water to a combination of actual THM plus remaining THM FP (the sum of inst. THM and THM FP is terminal THM) in finished water. A comparison of the terminal THM values shown in parentheses in Table 11 shows this result. For example, in Table 11 the terminal THM concentration for the H.T. effluent during ED1 was 586 µg/L and the terminal THM concentration for the finished water was 580 µg/L. No practical difference exists between these two average values. Thus the H.T. water contained a THM FP concentration of 573 µg/L plus an inst. THM concentration of 13 µg/L while the finished water contained a THM FP concentration of 448 µg/L and an inst. THM concentration of 132 µg/L. Thus, whereas the combination of THM FP and inst. THM concentrations for the two locations were about equal, the THM's in the finished water increased by about 120 µg/L while the THM FP decreased by about the same amount. Thus the chlorination--contact basin--sand filtration step really achieved no removal of precursor but merely a conversion. The results are somewhat in line with the low TOC removal.

TOC data for raw, H.T. and finished water are plotted for ED1R, ED3 and ED4 in Figures 11, 12, and 13. THM FP data for raw and H.T. water for ED4 are plotted in Figure 14. These plots are presented at this point, mainly to show the variation in values of these parameters from sample date to sample date. Similar plots for the other ED appears later in the report with

TABLE 11. TOC, TERMINAL THM AND THM FP
REDUCTION BY CHLORINATION, CONTACT
BASIN AND/OR SAND FILTRATION

ED	Ave. THM FP in H.T. water µg/L	Ave. THM FP in finished water µg/L	Percent Removal %
1	573 (586)*	448 (580)*	22 (0)**
1R	471 (476)*	349 (495)*	26 (0)**
3	389 (397)*	274 (400)*	30 (0)**
4	531 (533)*	434 (584)*	18 (0)**
ED	Ave. TOC in H.T. water mg/L	Ave. TOC in finished water mg/L	Percent Removal %
1	-	-	-
1R	6.8	6.1	10
3	6.0	5.9	2
4	5.8	5.4	6

* Terminal THM figures in parentheses

** Percent removal based on Terminal THM values

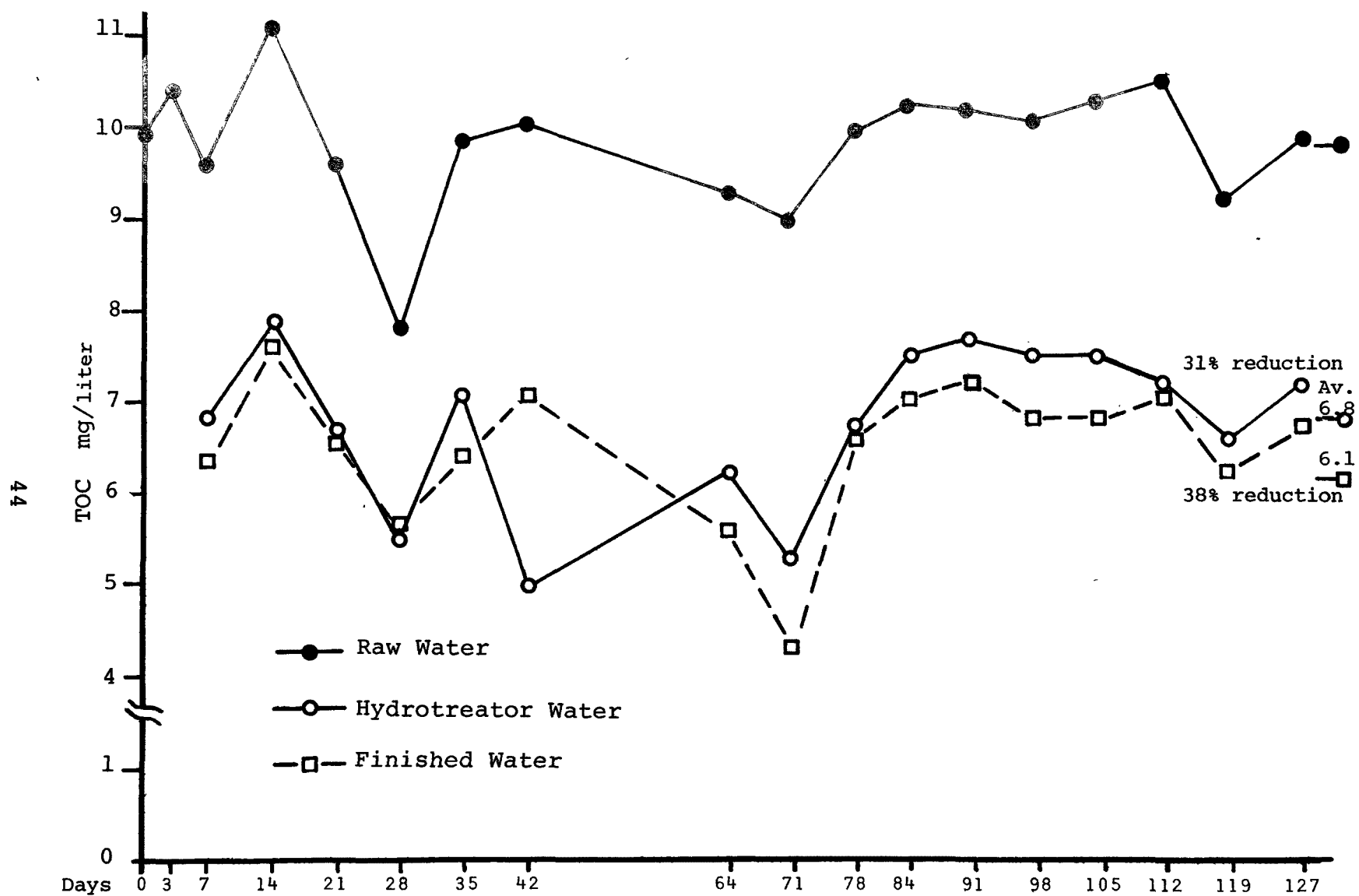


Figure 11. TOC in raw, Hydrotreator and finished water (ED1R).

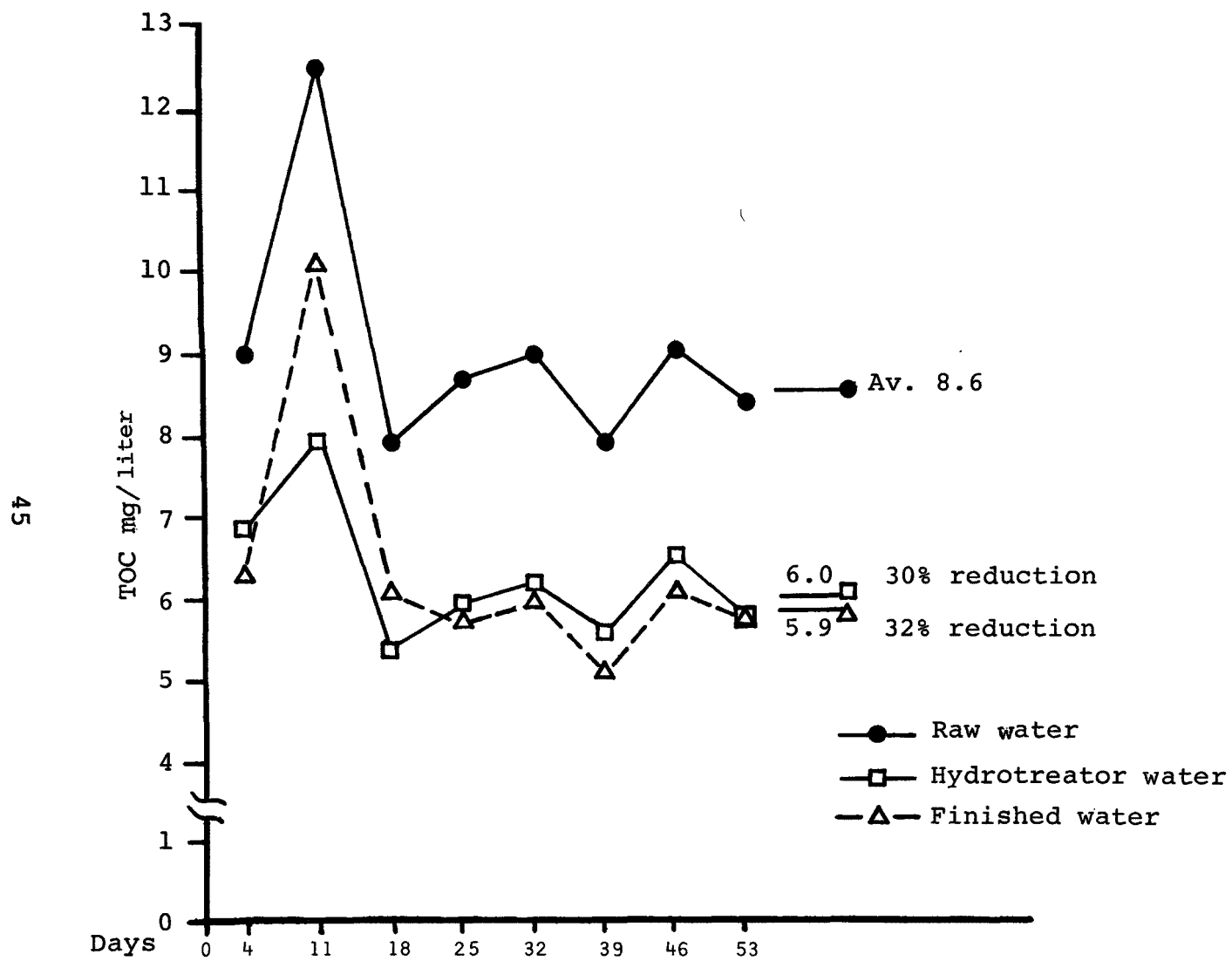


Figure 12. TOC in raw, Hydrotreator and finished water (ED3).

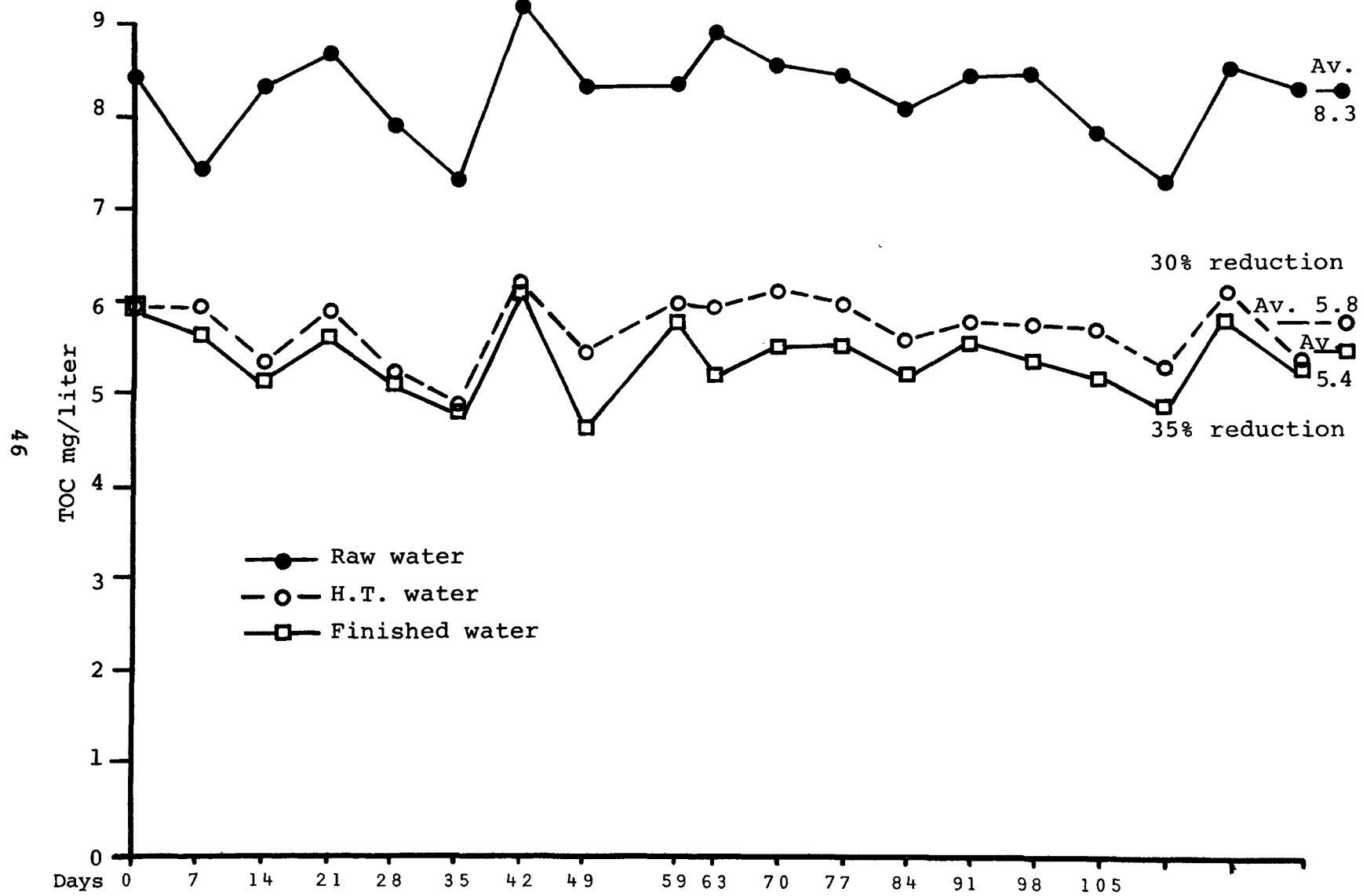


Figure 13. TOC in raw, Hydrotreator and finished water (ED4).

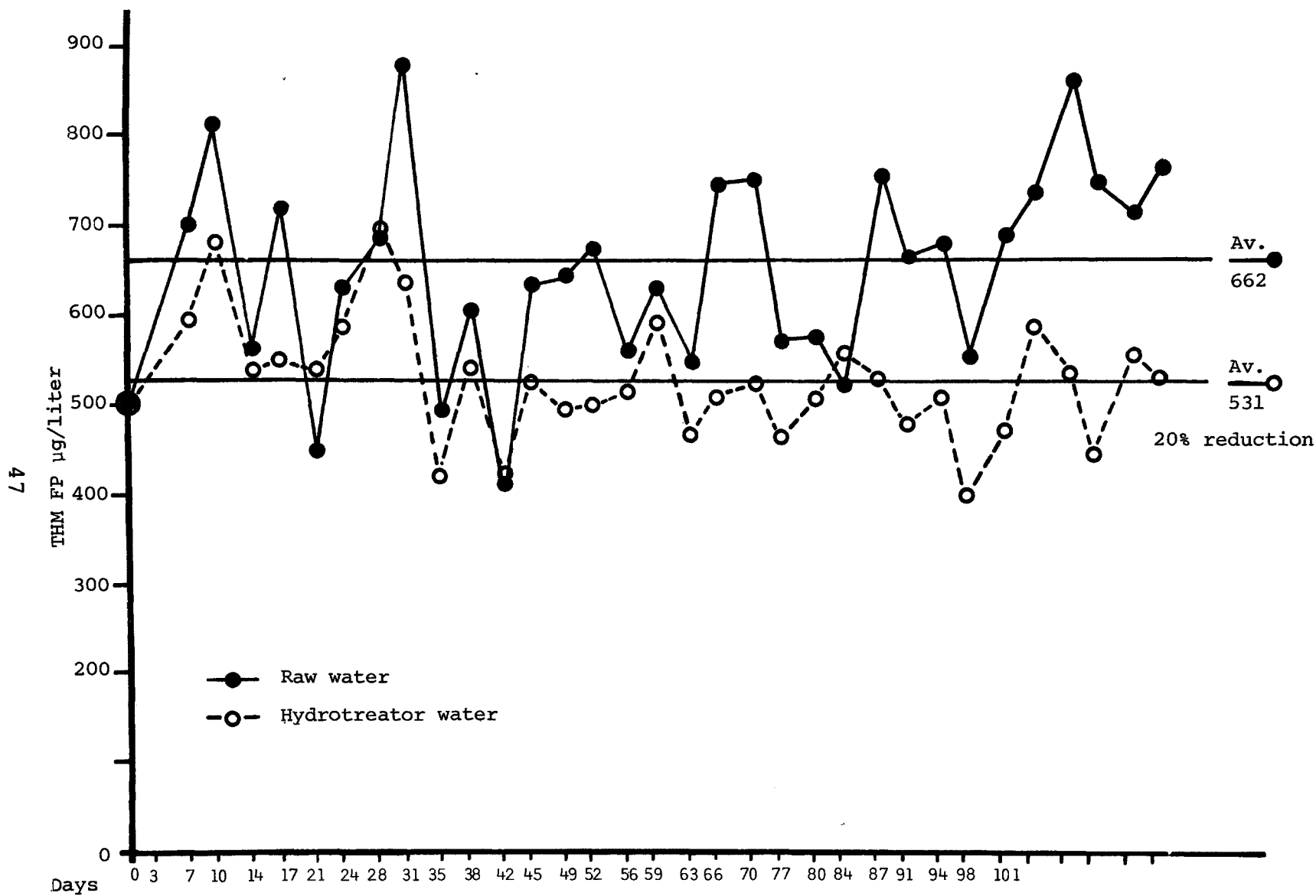


Figure 14. THM FP in raw water and removal by lime softening (ED4).

adsorbent plots.

Other Parameters

As an aid in interpreting data for each ED, plant profile information such as color, pH and turbidity of raw, H.T. effluent, and finished water, as well as free and combined chlorine for H.T. effluent and finished water were collected and the raw data is available in Appendix B. Rainfall data and chlorine levels of raw water are also available in Appendix B.

Rainfall and Chlorides--

The chloride concentration in raw water generally follows a cycle in response to the seasonal rainfall. Chloride levels rise when rainfall is low and decrease when rainfall is high. In southern Florida the wet season extends from May through October with the heaviest rains usually occurring in May. The dry season occurs between November and April. March and April are usually very dry. Chlorides reach a low concentration in September when rainfall is heavy and remain low until about February as the ground water level subsides, then gradually climb to a maximum in June.

Rainfall and TOC--

TOC levels in raw water may also be influenced by rainfall. TOC data were collected only in ED1R, ED3, and ED4. The longest period of least rainfall in the two-year study period occurred during most of ED1R which averaged the highest TOC level of 9.8 mg/L. ED3 and ED4 with more rainfall averaged 8.6 and 8.3 mg/L.

pH--

The pH of raw water remains constant at $7.2 \pm .01$ throughout the year. The average values of the pH in H.T. effluent and finished water, and the level of free chlorine in finished water is shown in Table 12.

TABLE 12 . AVERAGE pH AND FREE CHLORINE (PPM) VALUES IN EACH EXPERIMENTAL DESIGN

	ED1							
	H.T.	Fin.	H.T.	Fin.	H.T.	Fin.	H.T.	Fin.
pH	9.80	9.20	9.92	9.16	9.80	9.06	9.90	9.11
free chlorine (ppm)				2.49		1.91		2.06

There appears to be no apparent relationship between Total THM values in Table 9 with THM FP values in Table 10, nor with rainfall, chlorides, TOC, pH and chlorine data. Perhaps these two parameters which are controlled by the chemistry of the reaction of free chlorine with precursors is influenced by subtle changes in pH, time and temperature which are beyond the scope of our data.

Turbidity--

A record of H.T. effluent turbidity may be important because with higher levels, additional amounts of precursors may be carried over to the breakpoint chlorination step. However, questions about the turbidity data prevented assessing the relationship between the turbidity and THM FP. Tables of H.T. turbidity results are included in Appendix A. In ED1 and ED1R the turbidity of the H.T. effluent fluctuated widely from day to day. In ED3 and ED4 turbidity levels appear more uniform. The average turbidity during ED1 and ED1R was 10.2 NTU and 9.8 NTU respectively. In ED3 and ED4 it was 3.4 and 4.6 respectively. ED3 and ED4 data may be misleading because during these last two phases sampling was done only when the organic samples were taken, whereas it was done daily during ED1 and ED4. A check of the operators' daily turbidity records during ED4 showed a high of 25 NTUs, and an average of 9.3 NTUs. These values are more comparable to values reported for the first phases. Thus, it is possible that the H.T. effluent turbidity did not change substantially during the project.

Turbidity increased in the distribution system. Values increased from an average of 0.32 NTU in finished water to an average of 1.1 NTU in the distribution system sample.

Color--

Lime softening removed an average of 55 percent of the color from raw water. Another 10 PCU is removed by chlorination and sand filtration.

BENCH SCALE STUDIES

This portion of the report presents data on the effects of the three adsorbents evaluated on removal of specific HOC and other organics as measured by THM FP and TOC in raw, H.T. effluent and finished water. The pilot column configuration for each ED was previously presented in Section VI.

Specific Halogenated Organics

Raw Water Source--

The effect's of adsorbents on raw water were studied in ED1, ED1R, and ED3. Although the levels of the four THM were nil or too low to be evaluated, the adsorption results for the specific compounds discussed below show that the XE-340 was more efficient than GAC. IRA-904 resin removal, as expected, was poor and removal data for the raw source is only presented for cis 1,2-dichloroethene and vinyl chloride to show typical results with IRA-904 resin. Appendix A contains additional raw data tables for all substances if further data are required.

cis 1,2-Dichloroethene--The HOC occurring in highest concentration in raw water was cis 1,2-dichloroethene. It will be discussed first. Its general pattern will aid in interpreting the data from some of the substances present in low concentrations. Adsorption data appears in Table 13.

The adsorption data in Table 13 were obtained by integrating the actual breakthrough curves which appear in Figures 15, 16, 17, and 18. The breakthrough point (B) and saturation point (S) are shown on the curves. Using Table 13, a comparison of the effectiveness of GAC versus XE-340 can be made on an equal volume and equal weight basis at column saturation. At equal volumes of adsorbent, XE-340 had 3.8 times and 3.4 times the adsorptive capacity of GAC in ED1 and ED1R respectively. At equal weights of adsorbent, XE-340 had 3.2 times and 2.8 times the capacity of GAC. Column breakthrough on GAC occurred at 21 and 16 days and column saturation at 69 and 73 days respectively. Breakthrough occurred at 61 and 58 days for XE-340. Extrapolated column saturation values of 280 and 242 days were obtained for XE-340.

The MT_z for XE-340, 24 and 23 inches, is slightly more than for GAC, 21 and 23 inches. It is apparent that GAC (Figure 15) and XE-340 (Figure 17), both allow low level passage of cis 1,2-dichloroethene long before the value we have recorded as the breakthrough point. The actual value in $\mu\text{g/L}$, which are too low to plot on the "Y" axis scale, appear above the data point. No number above a data point means nil concentration. Consideration of this low level passage as breakthrough would, of course, greatly change the recorded MT_z values.

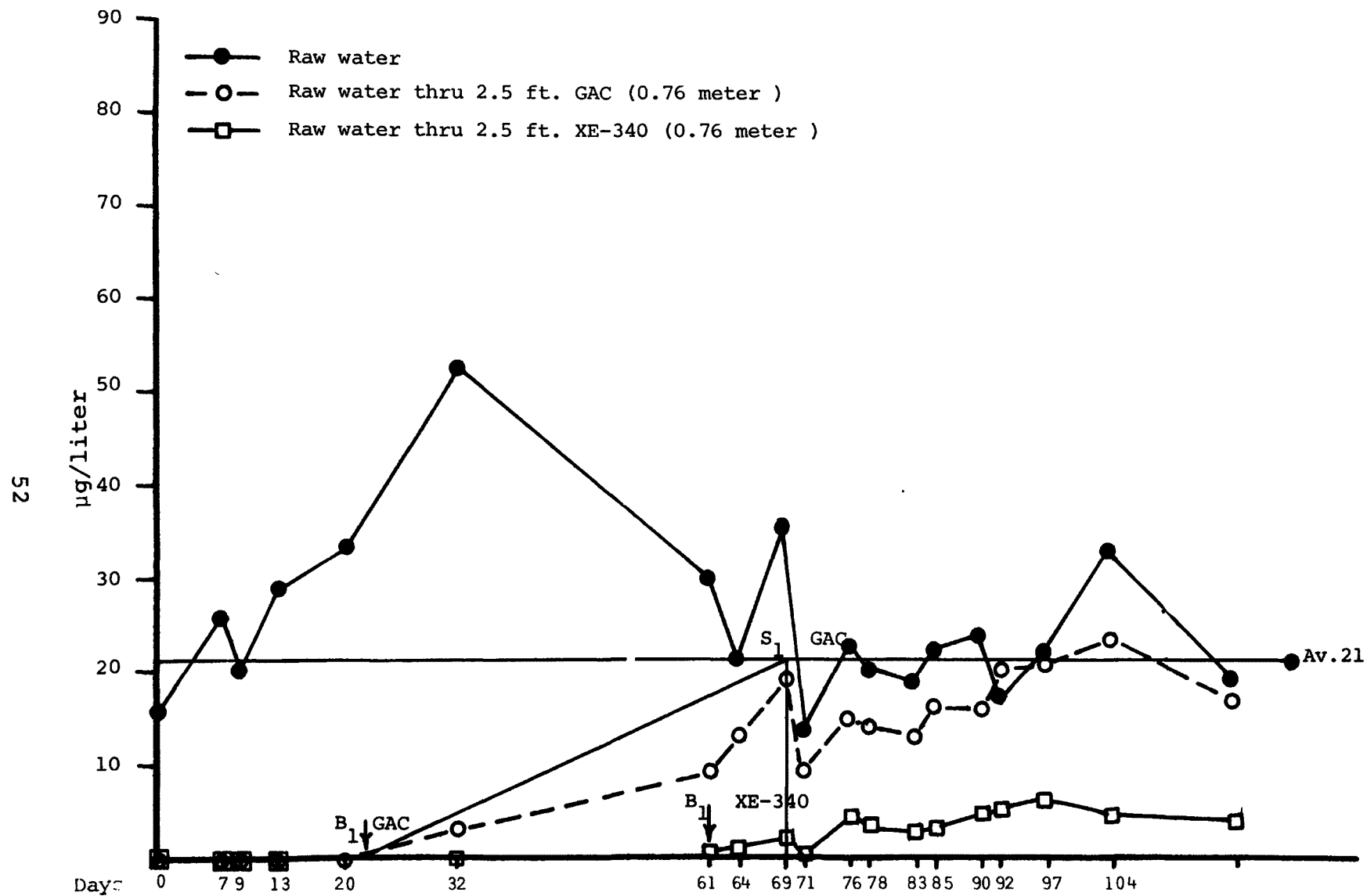


Figure 15. cis 1,2-Dichloroethene in raw water and removal by 0.76 meter (2.5 feet) of GAC and 0.76 meter (2.5 feet) of XE-340 (ED1).

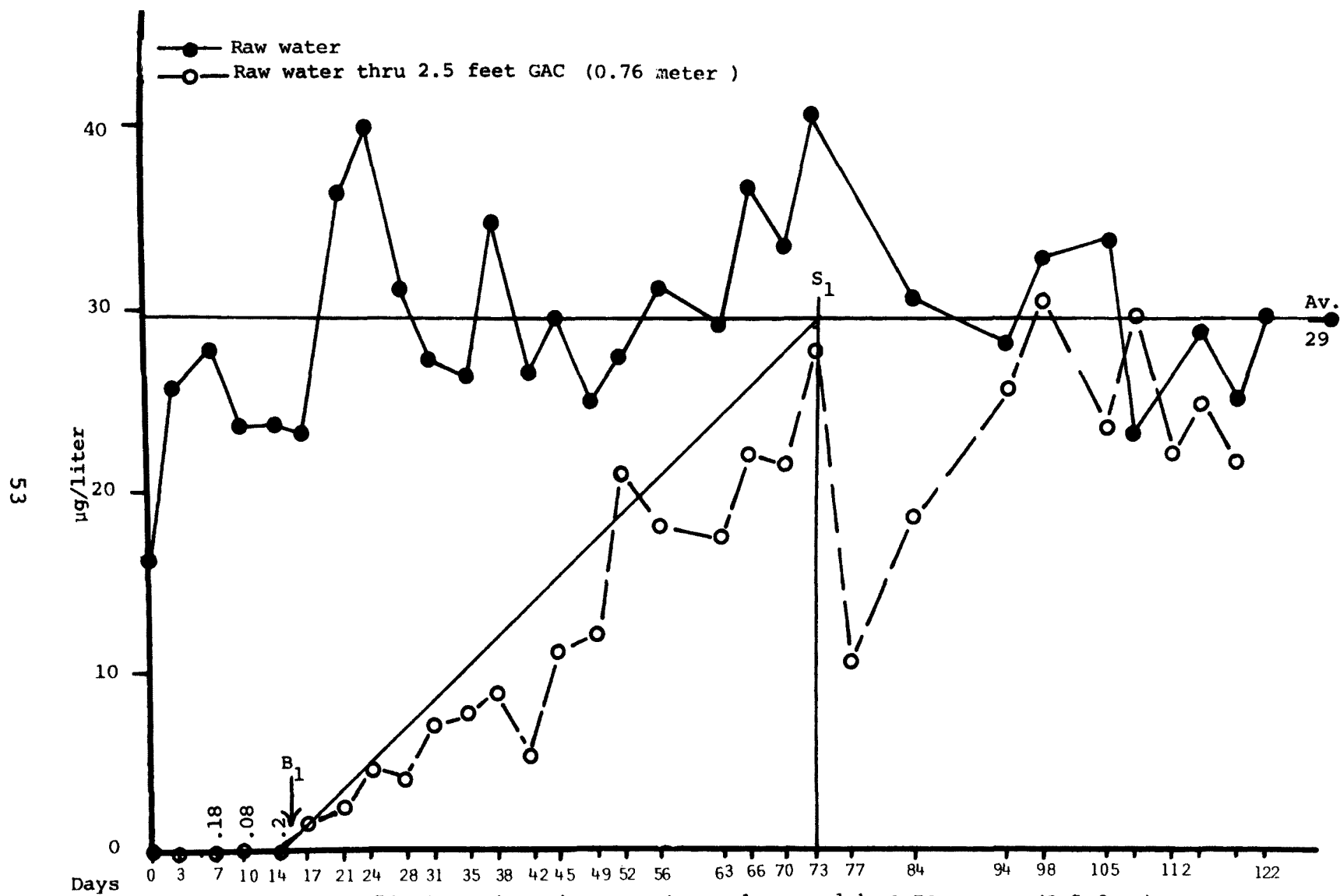


Figure 16 . cis 1,2-Dichloroethene in raw water and removal by 0.76 meter (2.5 feet) of GAC (ED1R).

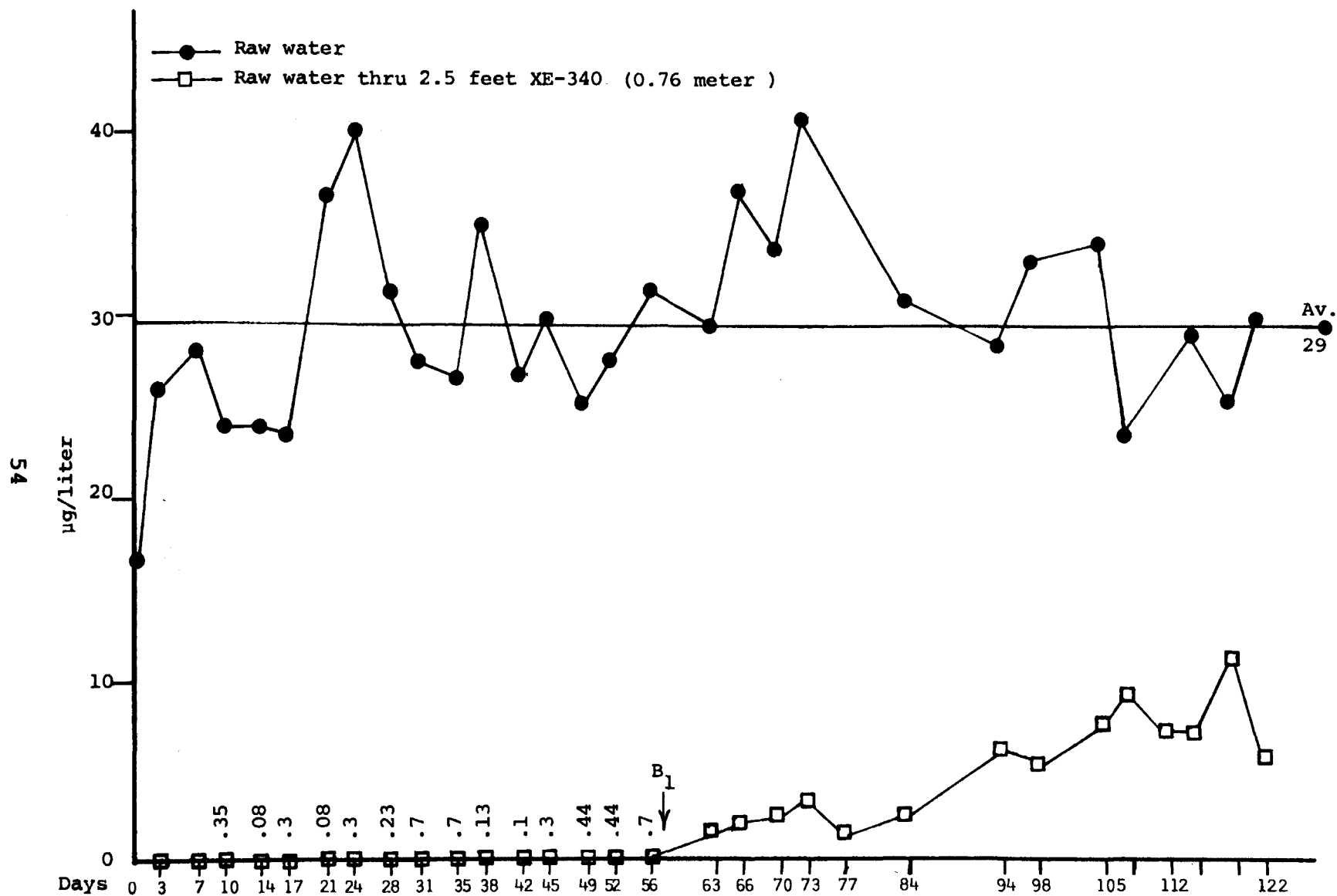


Figure 17. cis 1,2-Dichloroethene in raw water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

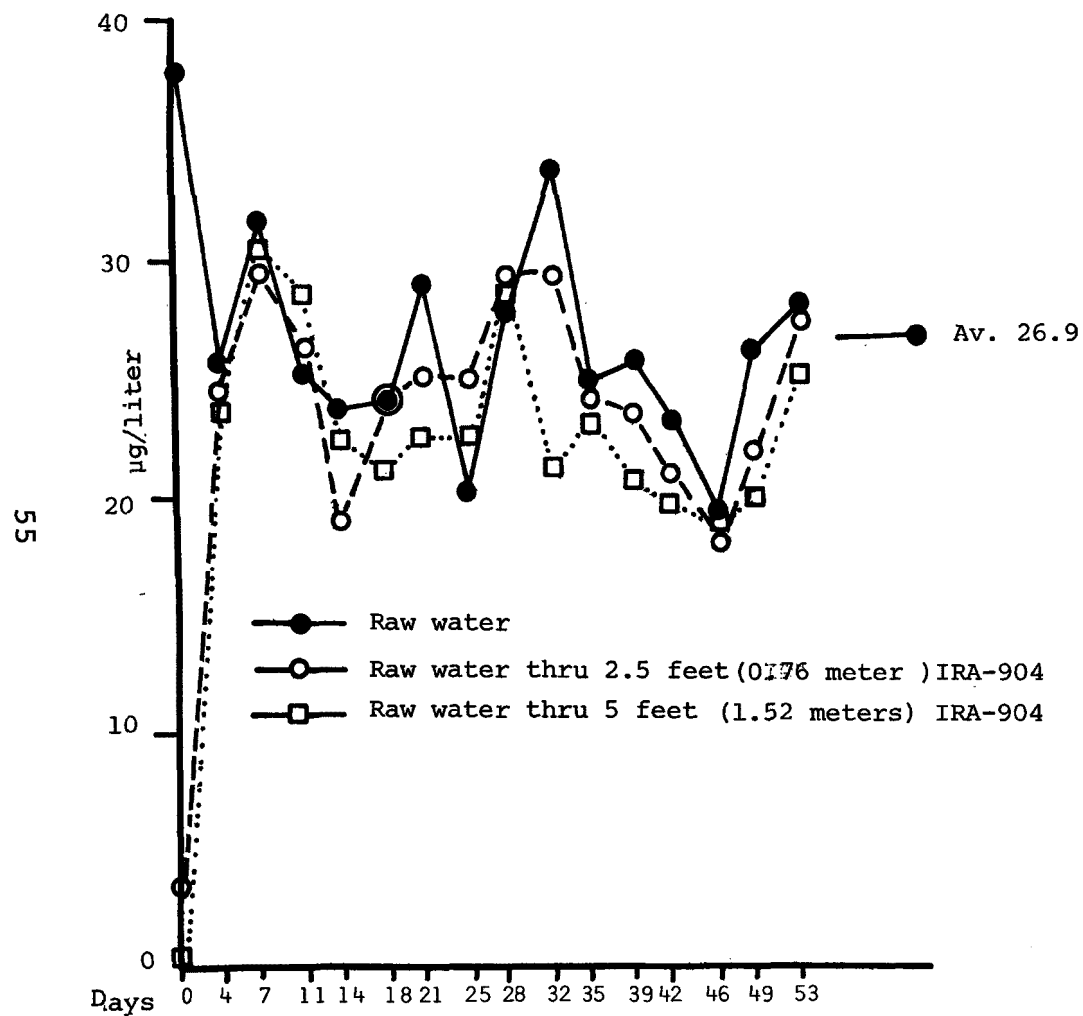


Figure 18. cis 1,2-Dichloroethene in raw water and removal by 0.76 meter (2.5 feet) and 1.52 meters (5 feet) of IRA-904 resin.

In ED3, 0.76 (2.5 feet) and 1.52 (5.0 feet) meters of the IRA-904 resin adsorbed no cis 1,2-dichloroethene. Discussion of the other HOC will follow their order of presentation in Table 8.

Vinyl chloride-- Analysis for vinyl chloride began on Test Day 94 of ED1R after modifications were made to the present equipment. Since vinyl chloride analysis did not begin until toward the end of the test period, we do not have breakthrough, saturation or MT_z information. The adsorption data obtained are plotted in Figure 19. From Test Day 94 to 122, the average level of vinyl chloride in the raw water was 0.80 $\mu\text{g/L}$ and the average level through GAC and XE-340 was 0.72 $\mu\text{g/L}$ and 0.77 $\mu\text{g/L}$ respectively. Therefore, if the differences in the average are considered significant, from day 94 to 122 there was 10 percent and 4 percent removal respectively.

Results on 0.76 (2.5 feet) and 1.52 (5.0 feet) meters of IRA-904 resin on raw water appear in Figure 20. Throughout the entire two-year study, IRA-904 resin did not adsorb other HOC from raw, H.T. or finished water. Therefore we read the individual curves and averages in Figure 20 as indicating no removal of vinyl chloride.

trans 1,2-Dichloroethene--The results of adsorbents for removal of trans 1,2-dichloroethene from raw water are shown in Table 14 and the breakthrough curves in Figures 21 and 22.

The HOC, trans 1,2-dichloroethene did not break through the XE-340 column (Figure 22) during the 122-day test period, therefore, we cannot compare GAC and XE-340 at column saturation. However, it is obvious that XE-340 has greater adsorptive capacity for trans 1,2-dichloroethene than GAC, both on an equal volume or equal weight basis. The GAC column allowed low level passage (Figure 21) long before the time designated as breakthrough. At the end of the test period, the GAC column had adsorbed 82 percent of the entering trans 1,2-dichloroethene and 73 percent at extrapolated saturation. XE-340 had adsorbed 100 percent at the end of the test period.

1,1-Dichloroethane--Removal results for 1,1-dichloroethane by adsorbents from raw water appear in Table 15 and Figure 23 respectively.

Table 15 data shows that breakthrough occurred at 21 days and 94 days for GAC and XE-340 respectively. Figure 23 shows that the GAC reached saturation at 94 days and that saturation did not occur in the XE-340 column. However, again from the Table 15 and Figure 23 data it is obvious that XE-340, both on an equal volume and equal weight basis has greater adsorptive capacity for 1,1-dichloroethane than GAC.

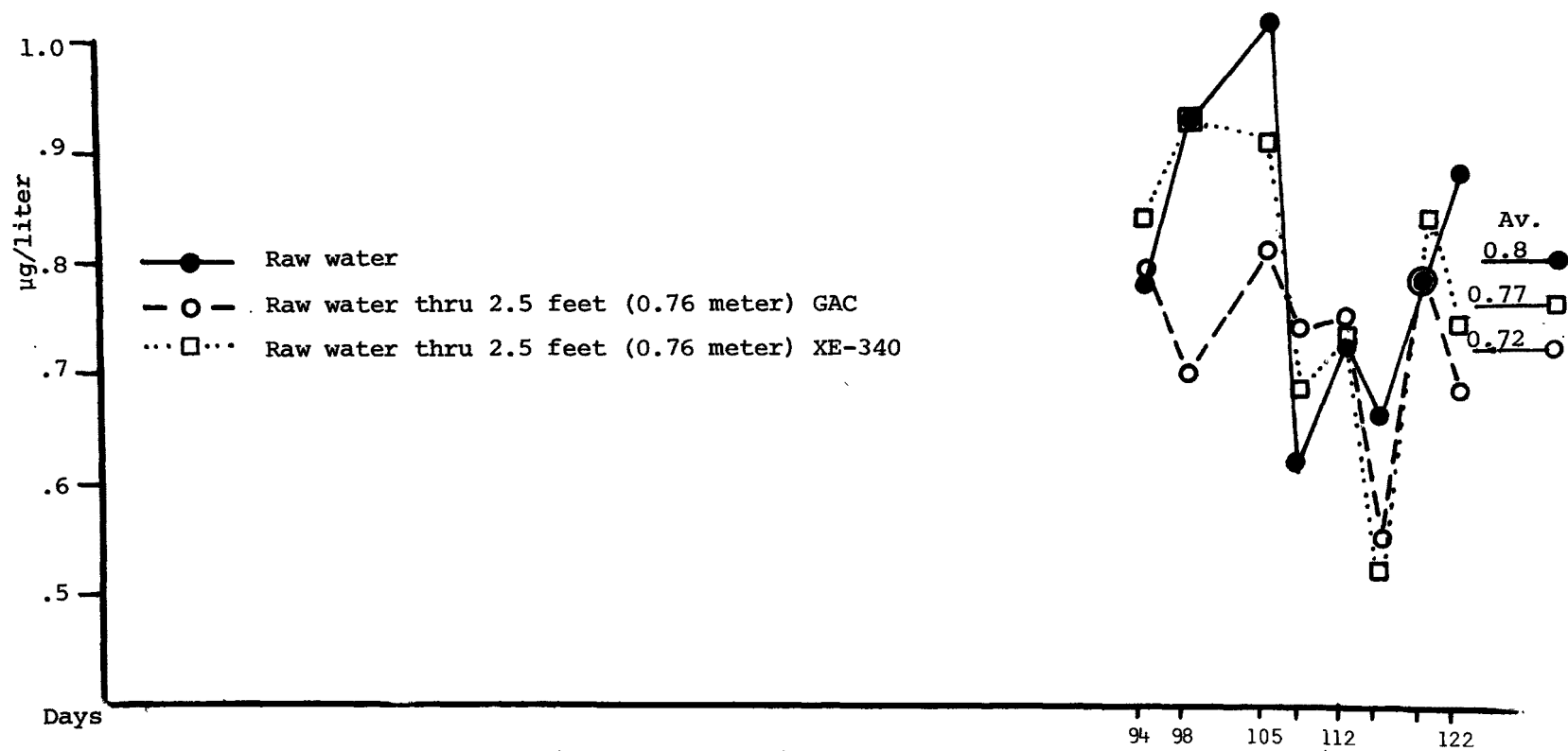


Figure 19. Vinyl chloride in raw water and removal by 0.76 meter (2.5 feet) GAC and 0.76 meter (2.5 feet) XE-340 (ED1R).

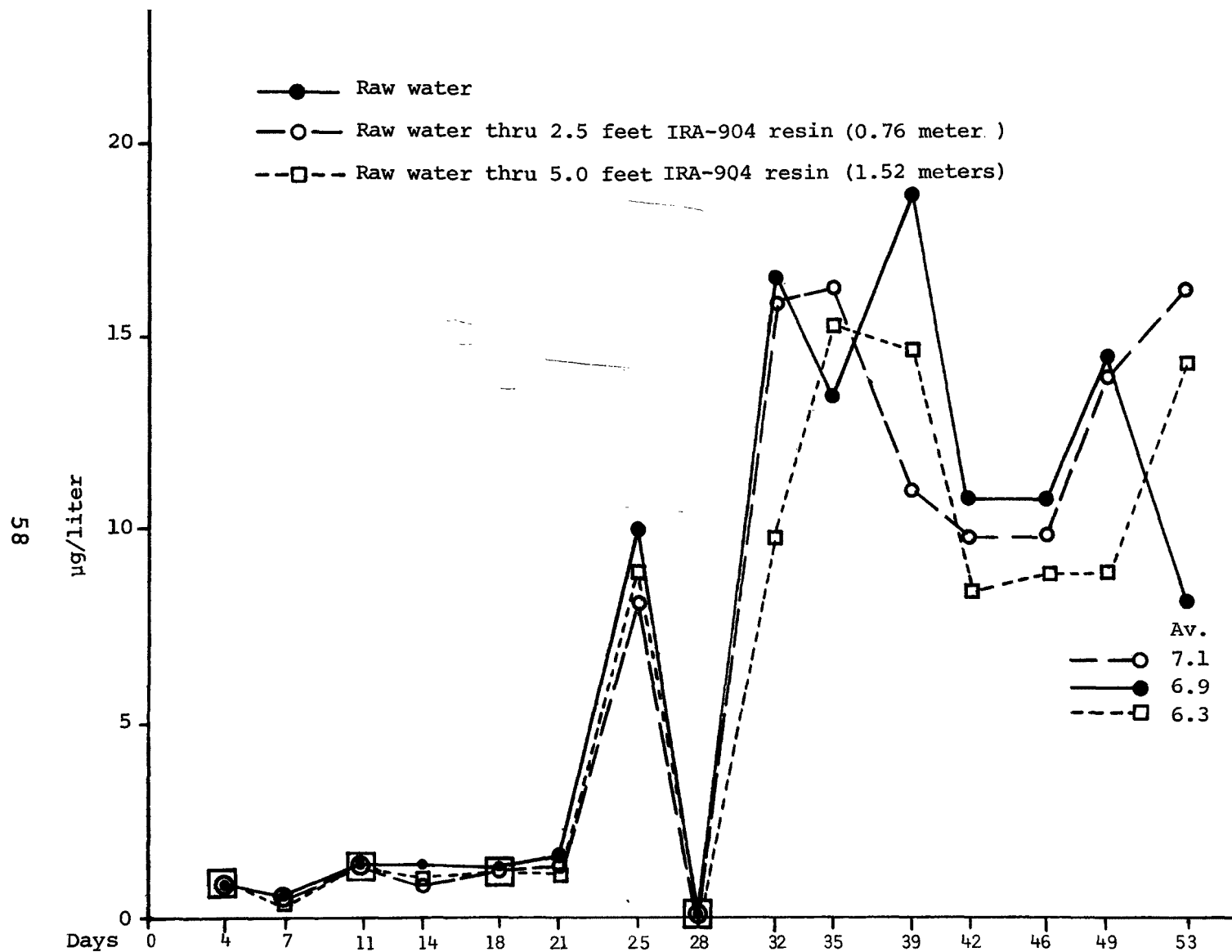


Figure 20. Vinyl chloride in raw water and removal by 0.76 and 1.52 meters (2.5 and 5 feet) of IRA-904 resin (ED3).

TABLE 14. trans 1,2-DICHLOROETHENE ADSORPTION DATA FROM RAW WATER

[illegible]

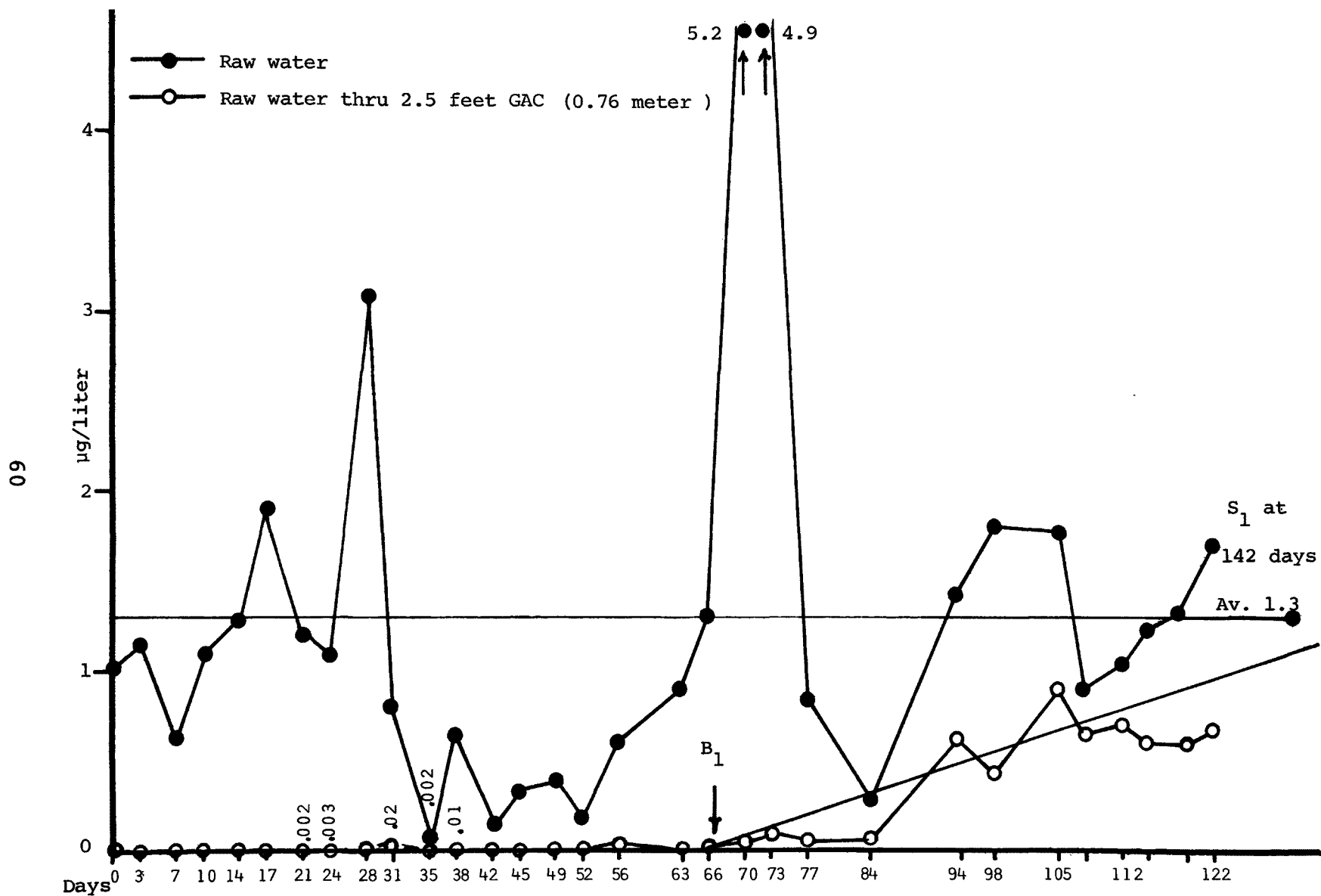


Figure 21. trans 1,2-Dichloroethene in raw water and removal by 0.76 meter (2.5 feet) of GAC (ED1R).

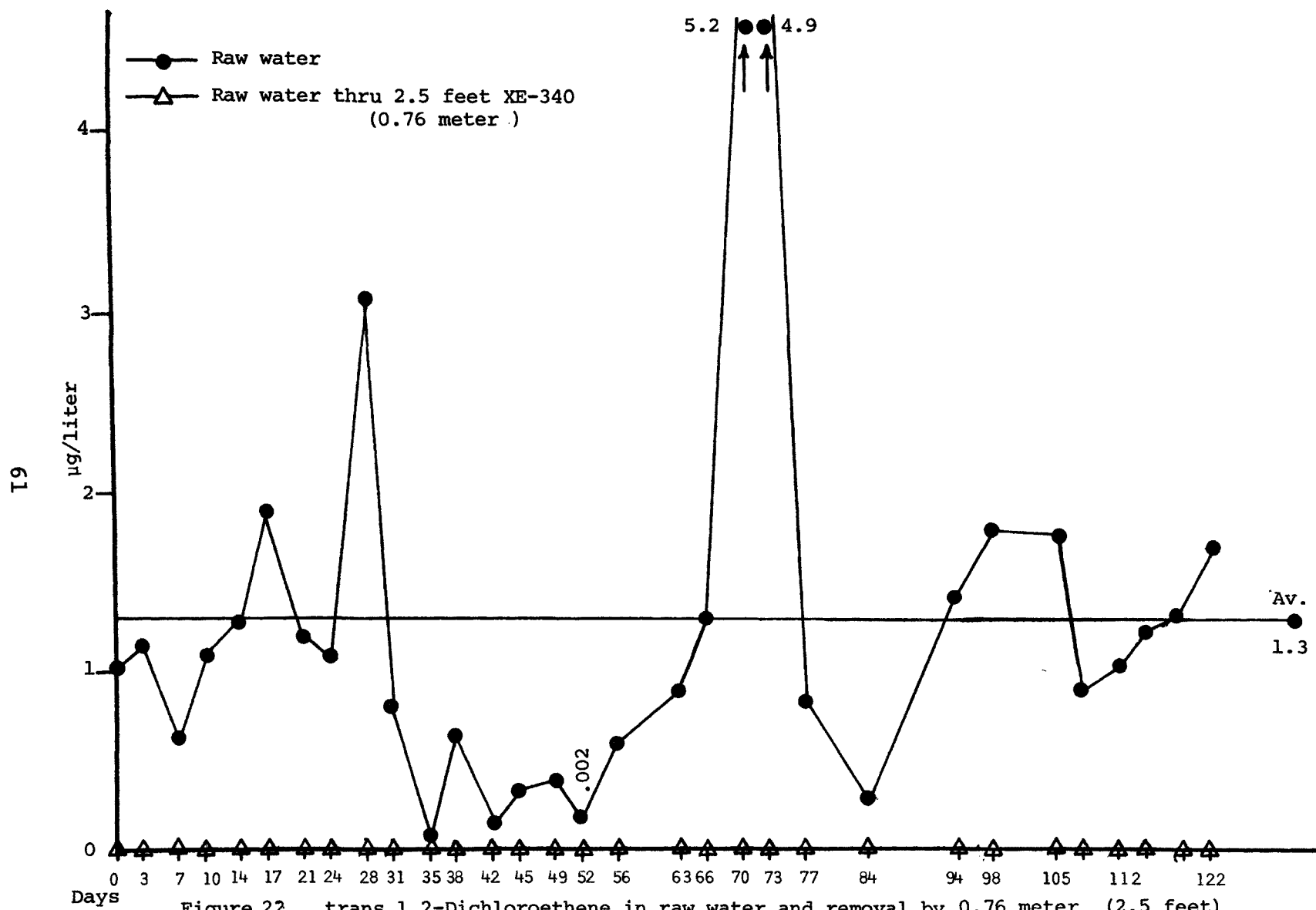


Figure 22. trans 1,2-Dichloroethene in raw water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

TABLE 15. 1,1-DICHLOROETHANE ADSORPTION DATA FROM RAW WATER

[illegible]

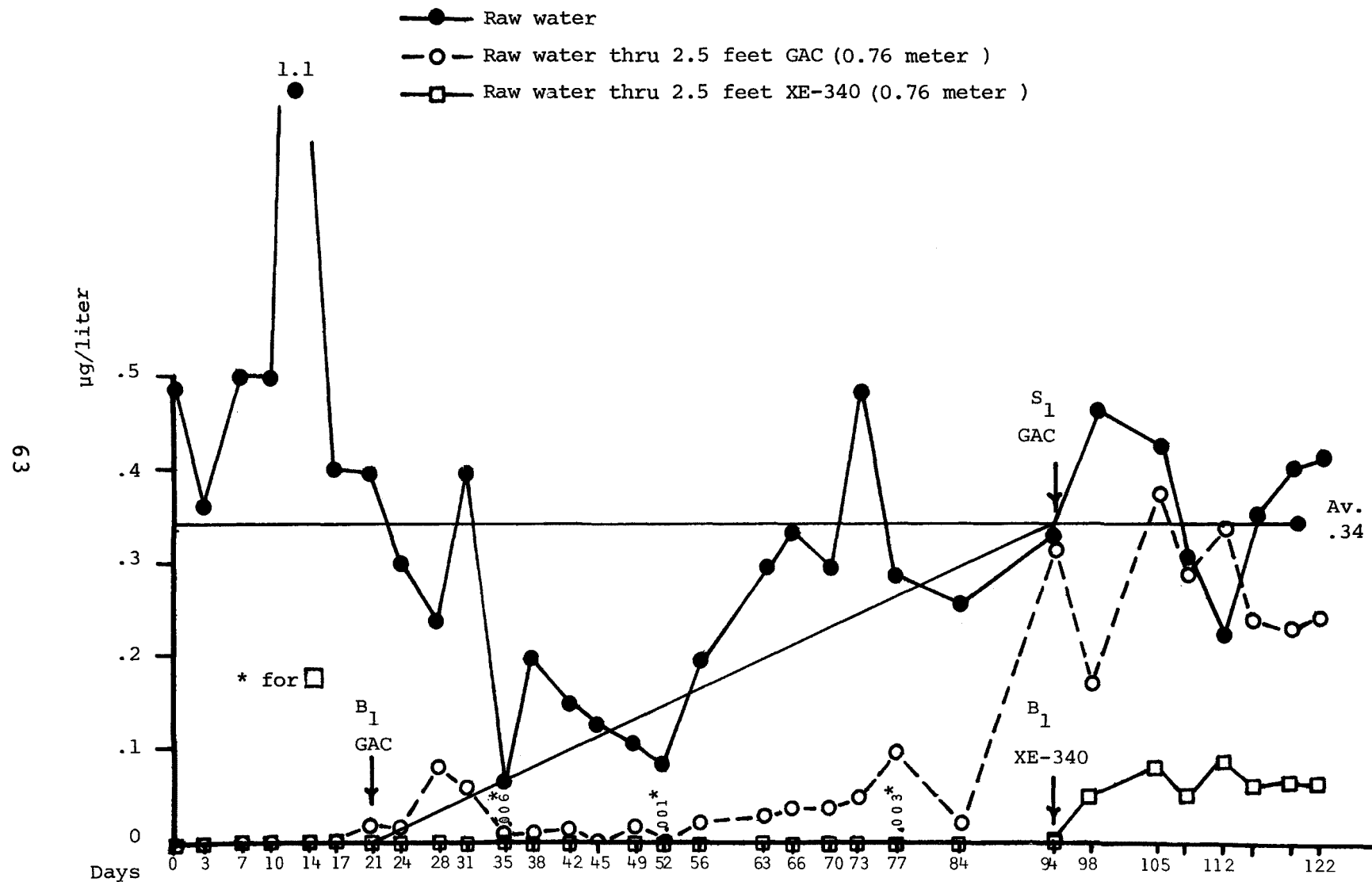


Figure 23. 1,1-Dichloroethane in raw water and removal by 0.76 meter (2.5 feet) of GAC and 0.76 meter (2.5 feet) of XE-340 (ED1R).

1,1,1-Trichloroethane, 1,2-dichloroethane, carbon tetrachloride--The removal results for the summed value of these three HOC by adsorbents from raw water appear in Table 16 and the breakthrough curves appear in Figures 24 and 25.

With the low average influent concentration of 0.104 µg/L, and the spread in individual data points, estimation of breakthrough and saturation times is difficult. Table 16, and Figures 24 and 25 show the estimated time of breakthrough for GAC and XE-340 to be about 21 and 77 days respectively. Reported saturation times are questionable. However, since the breakthrough times for XE-340 is greater than for GAC, we would expect XE-340 to again have a greater adsorptive capacity than GAC.

Trichloroethylene--Adsorption data appear in Table 17 and breakthrough curves in Figures 26 and 27.

Breakthrough occurred in 77 days and 96 days for the GAC and XE-340 respectively. The saturation times cannot be extrapolated because of insufficient data points after breakthrough to establish the slope of the curve. However, it is again apparent that since XE-340 breakthrough occurred after GAC breakthrough, XE-340 will have a higher adsorptive capacity than GAC.

Tetrachloroethylene--Adsorption of tetrachloroethylene by adsorbents from raw water was studied only in ED1R. The influent concentration to GAC and XE-340 columns was very low and erratic, 0.072 µg/L average for the first 31 days of the test and nil to traces for the balance of the 122-day test. Influent level and adsorption curves are shown in Figure 28. It is interesting to note that even at this low concentration, both adsorbents do adsorb a high percentage of the compound. No other conclusions are drawn.

Chlorobenzene--Adsorption data appear in Table 18 and adsorption curves in Figure 29. Influent concentration, plotted in Figure 29, was very erratic. XE-340 removed all of the compound for the entire test period. GAC removed essentially all of the compound except for the three test dates shown in Figure 29 when trace amounts passed.

p-Chlorotoluene--p-Chlorotoluene was studied in ED1R. The erratic level of influent concentration is shown in Figure 30. The average influent concentration was 0.38 µg/L. Both GAC and XE-340 removed all of the compound throughout the test period.

o, m and p-Dichlorobenzene--Adsorption from raw water by adsorbents of the summed value of the three isomers of dichlorobenzene was studied in ED1R. The influent concentration curve appears in Figure 31. The average concentration was 1.1 µg/L. Both GAC and XE-340 removed all of the compounds throughout the test period.

TABLE 16. 1,1,1-TRICHLOROETHANE, 1,2-DICHLOROETHANE, CARBON TETRACHLORIDE ADSORPTION DATA FROM RAW WATER

[illegible]

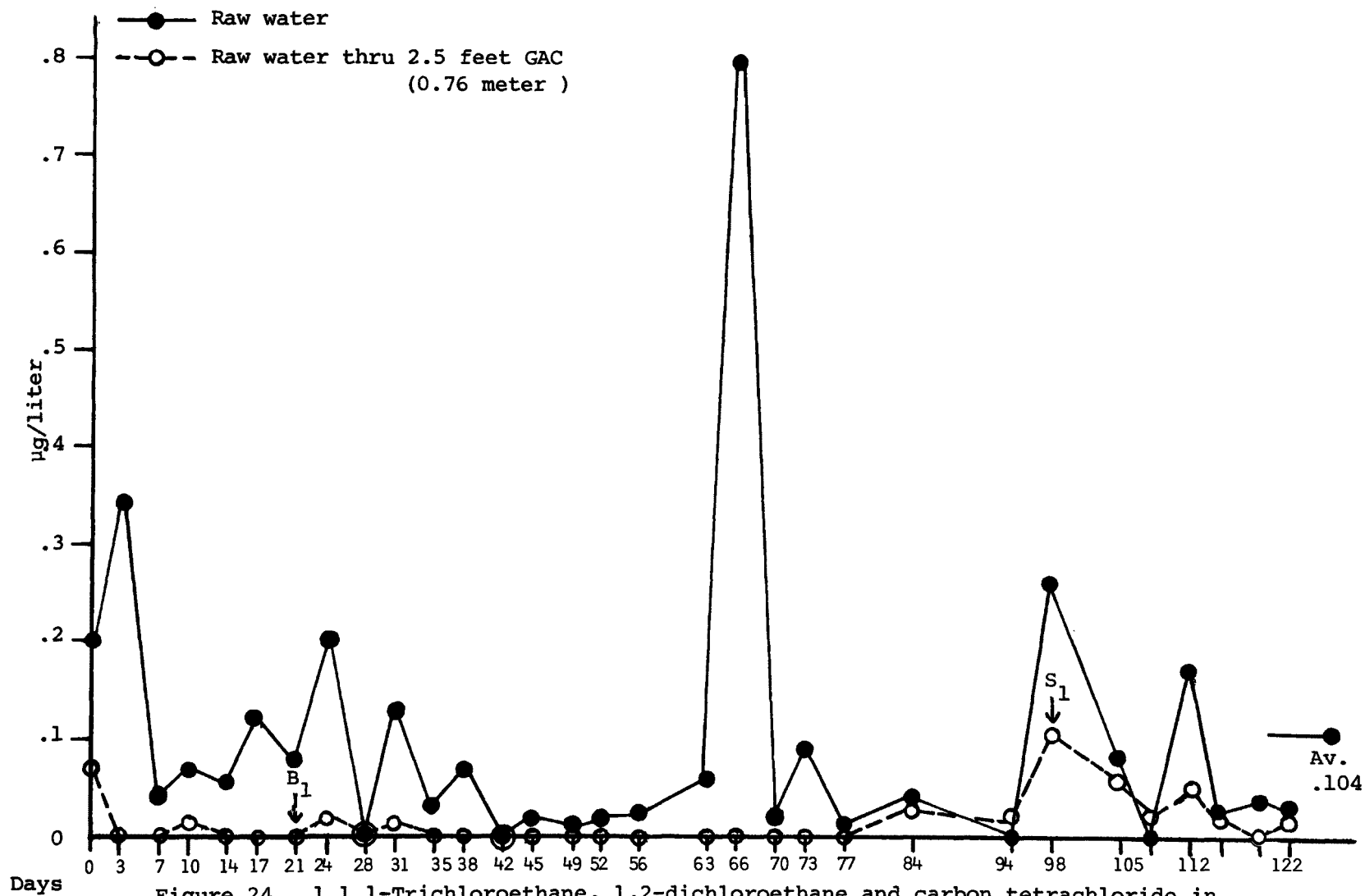


Figure 24. 1,1,1-Trichloroethane, 1,2-dichloroethane and carbon tetrachloride in raw water, and removal by 0.76 meter (2.5 feet) of GAC (ED1R).

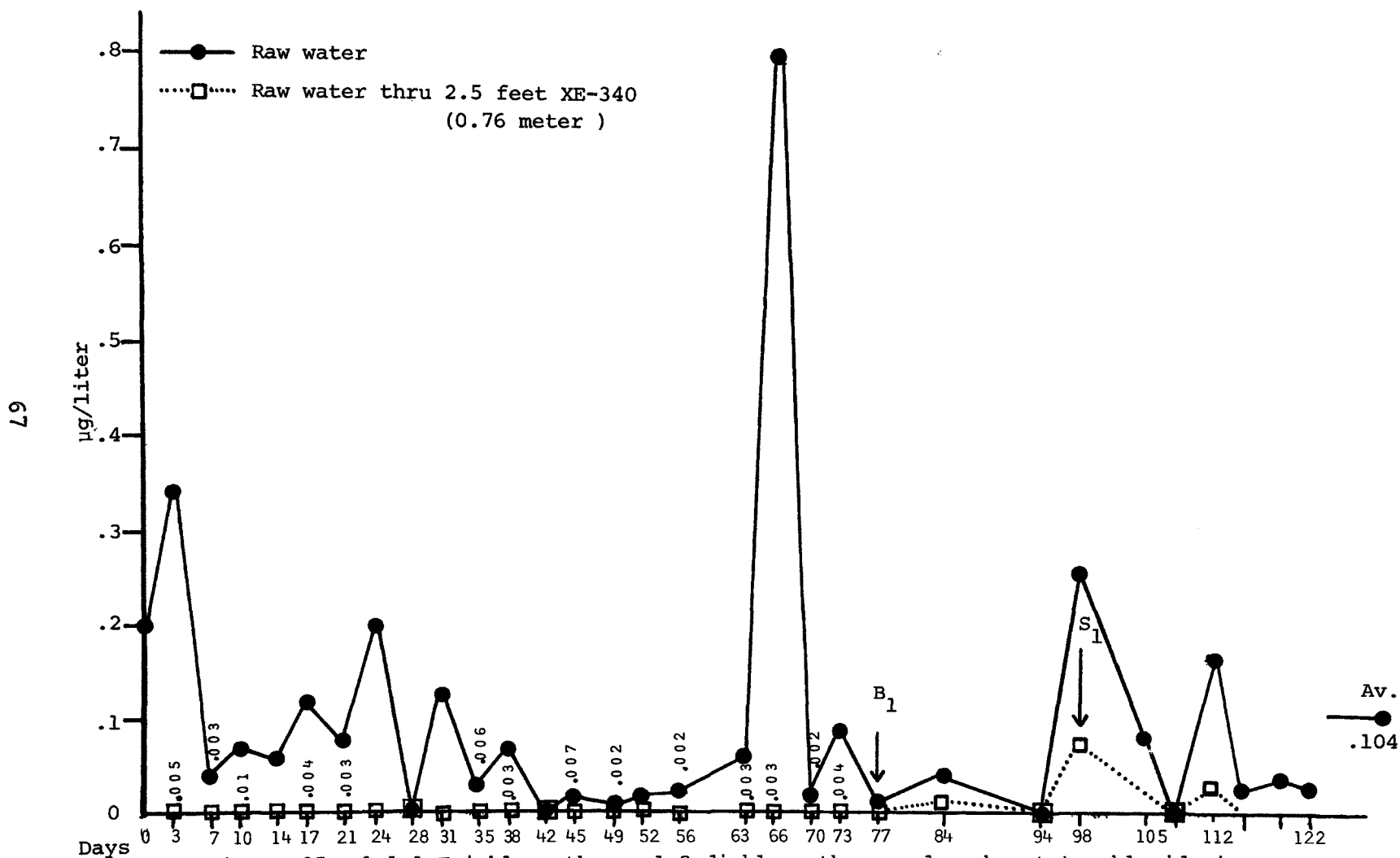


Figure 25. 1,1,1-Trichloroethane, 1,2-dichloroethane and carbon tetrachloride in raw water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

TABLE 17. TRICHLOROETHYLENE ADSORPTION DATA FROM RAW WATER

[illegible]

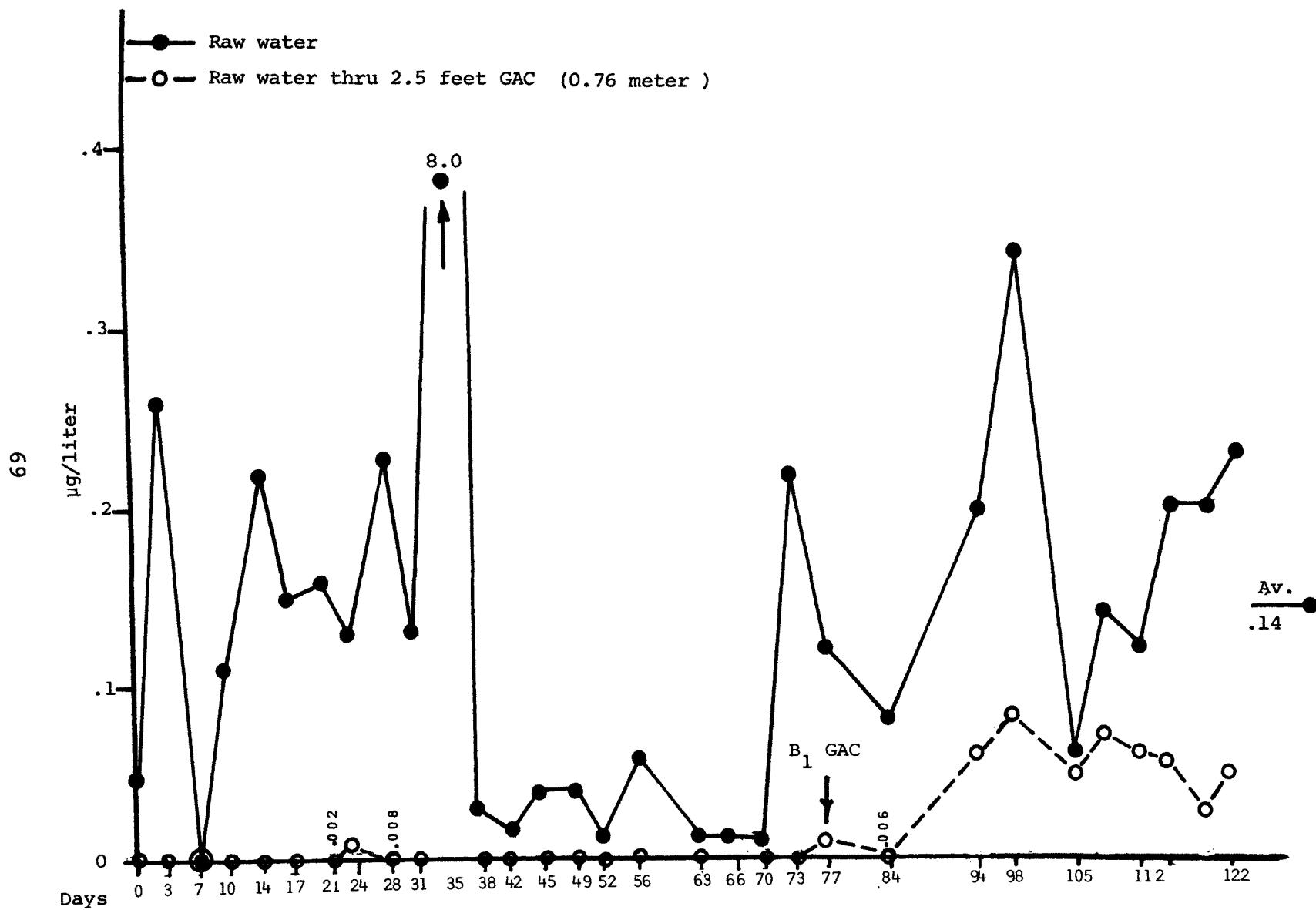
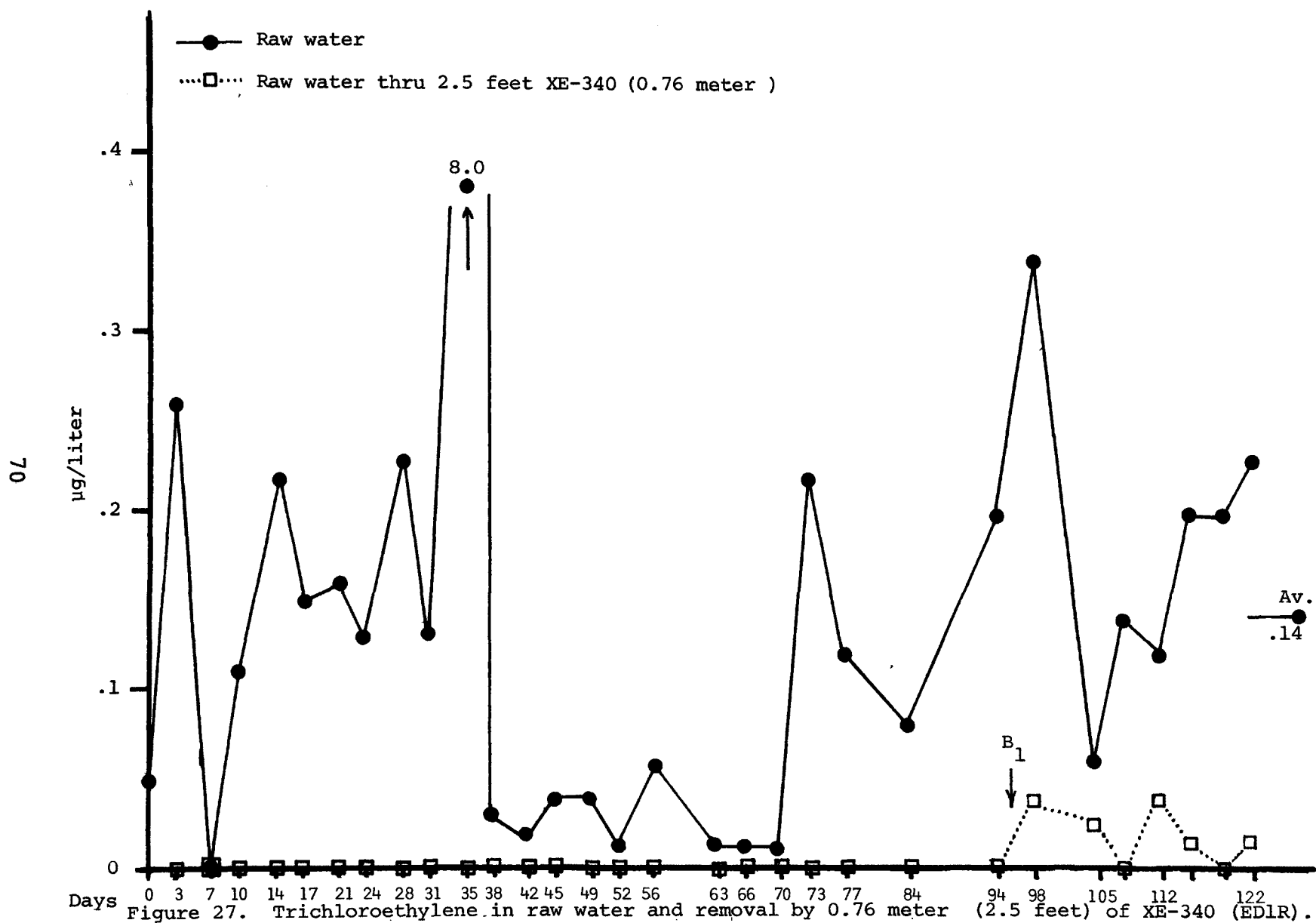


Figure 26. Trichloroethylene in raw water and removal by 0.76 meter (2.5 feet) of GAC (ED1R).



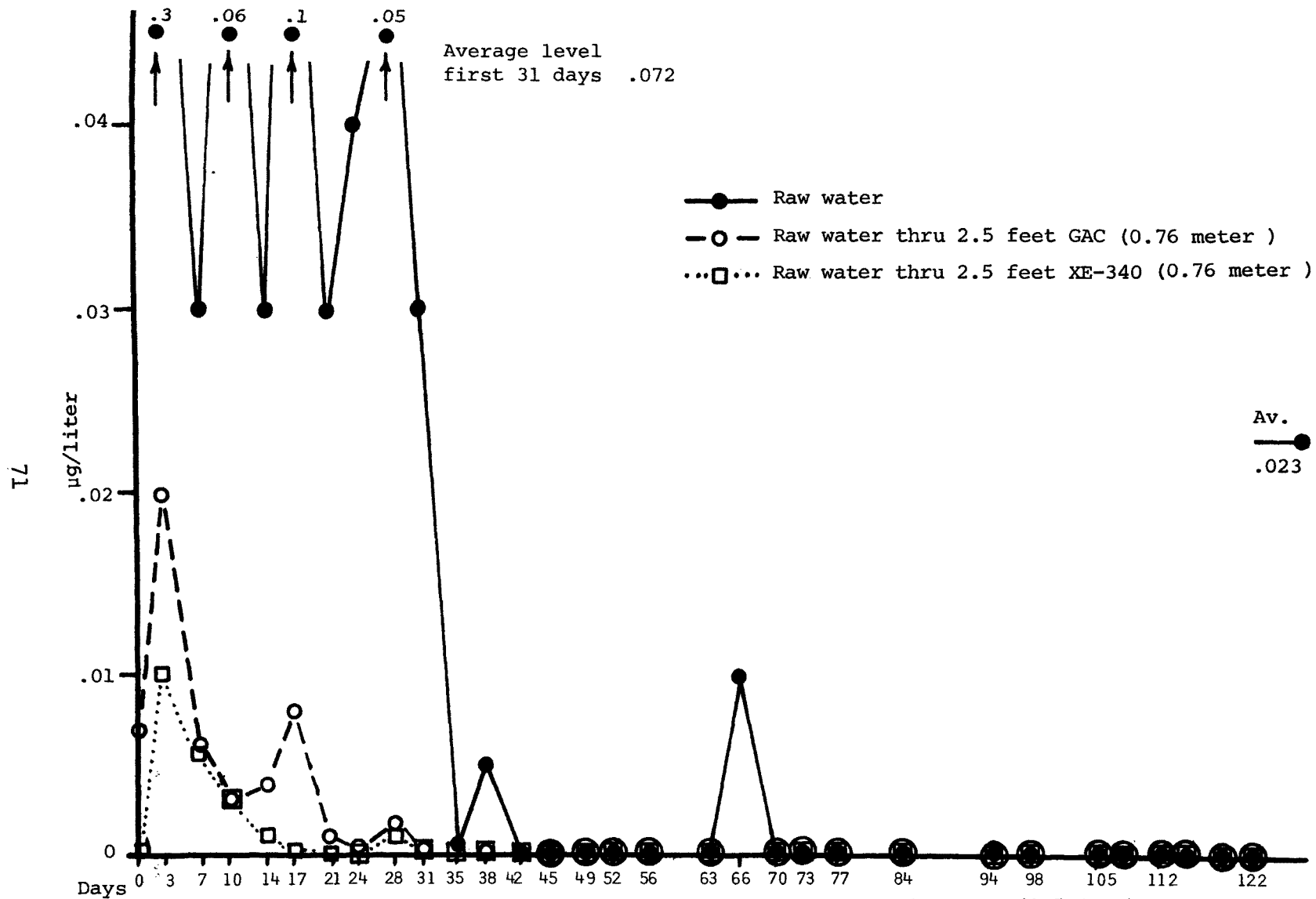


Figure 28. Tetrachloroethylene in raw water and removal by 0.76 meter (2.5 feet) of GAC and 0.76 meter (2.5 feet) of XE-340 (ED1R).

TABLE 18. CHLOROBENZENE ADSORPTION DATA FROM RAW WATER

ED	Bed Depth Feet	Adsorbent	Average Influent ug/L	Column Breakthrough Days	Column Saturation Days	M _T N Inch	Test Duration Days	Total Entering Each Column During Test Grams	Total Adsorbed by Each Column at End of Test Grams	Adsorbed by Each Column at Saturation Grams	% Adsorbed at End of Test %	% Adsorbed at Saturation %	Adsorption per 100 gms. Adsorbent at End of Test Grams	Adsorption per 100 gms. Adsorbent at Saturation Grams	CC
1R	2.5	GAC	.19	none			122	.0021	.0021		100		.001		
1R	2.5	XE- 340	.19	none			122	.0021	.0021		100		.001		
		2.5 feet = 0.76 meter													

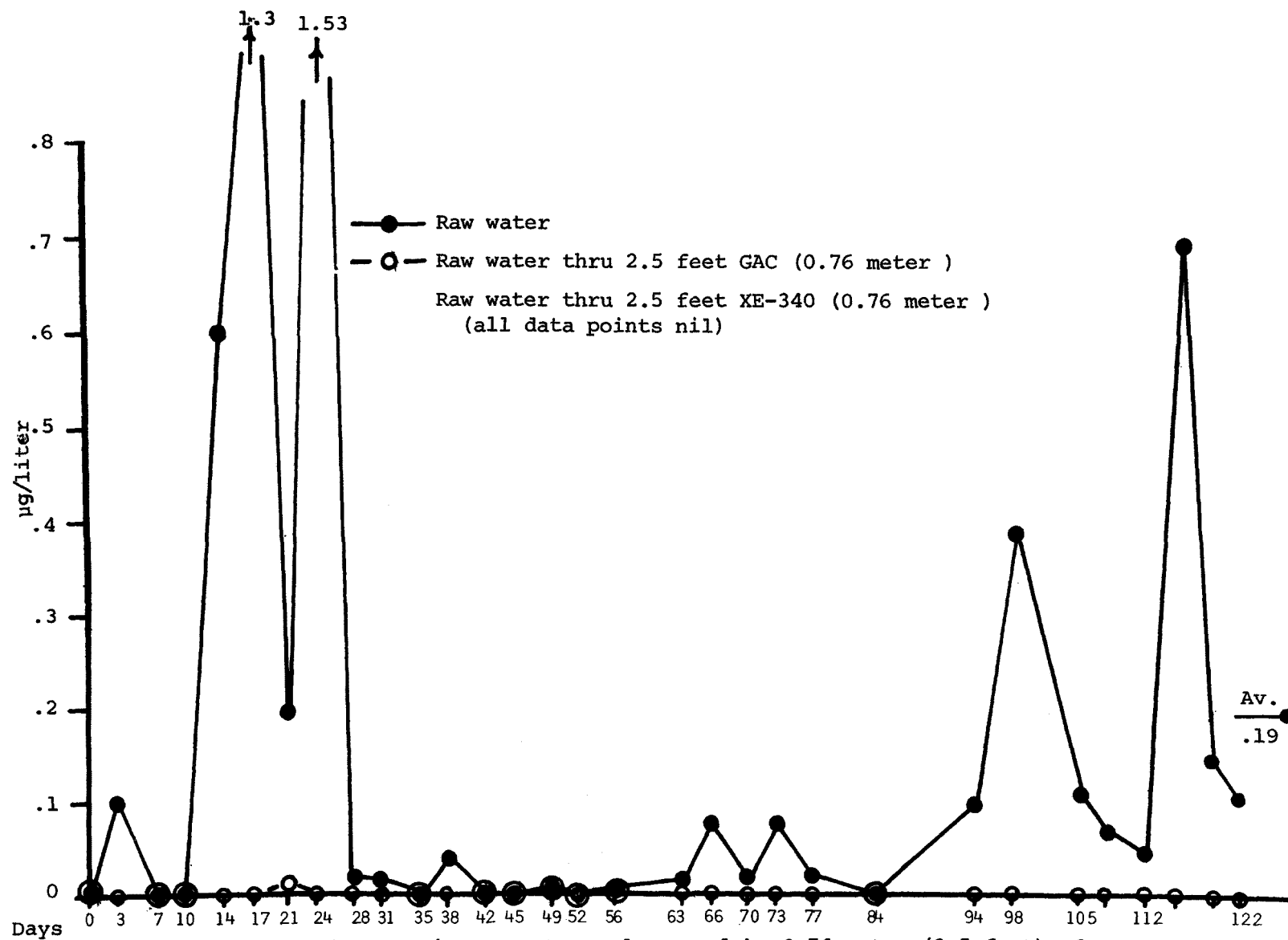


Figure 29. Chlorobenzene in raw water and removal by 0.76 meter (2.5 feet) of GAC and 0.76 meter (2.5 feet) of XE-340 (ED1R).

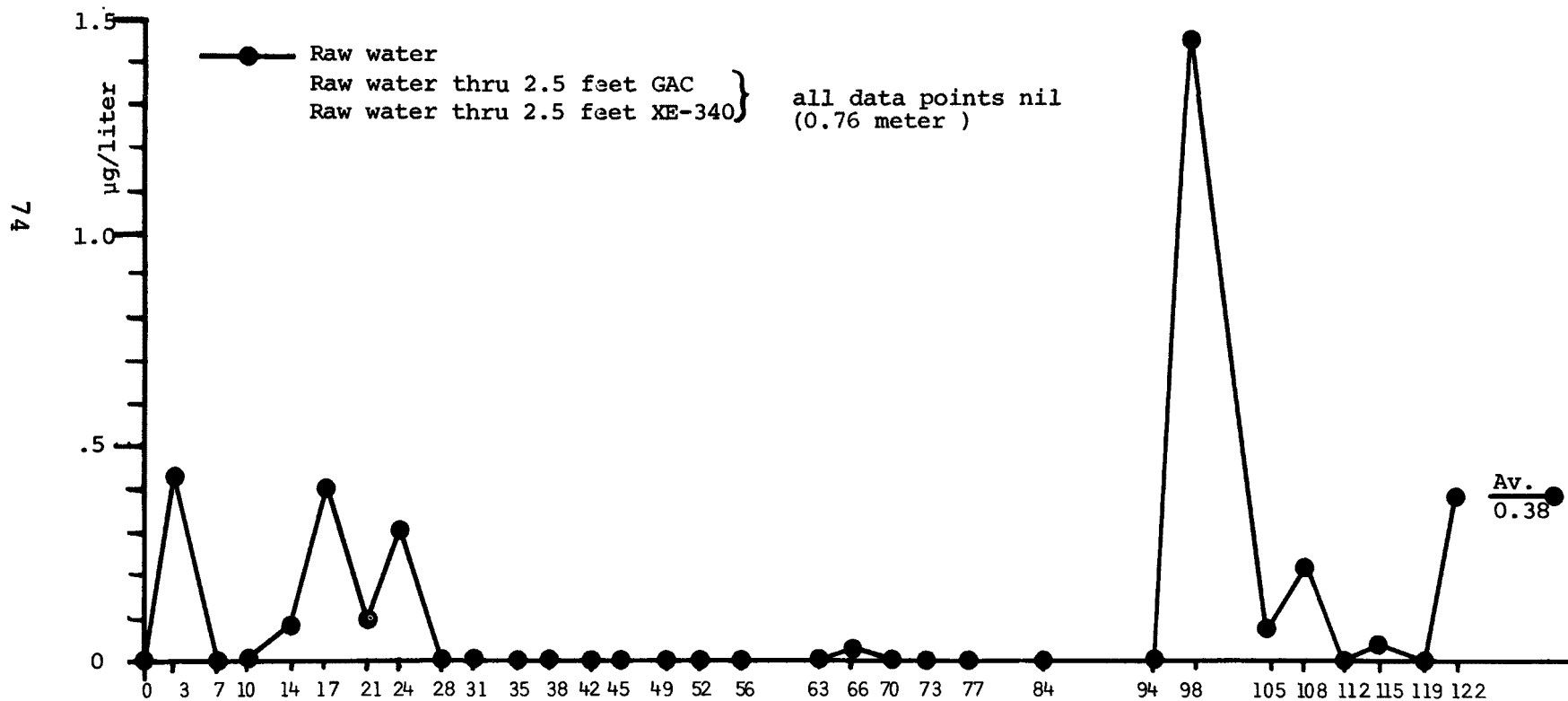
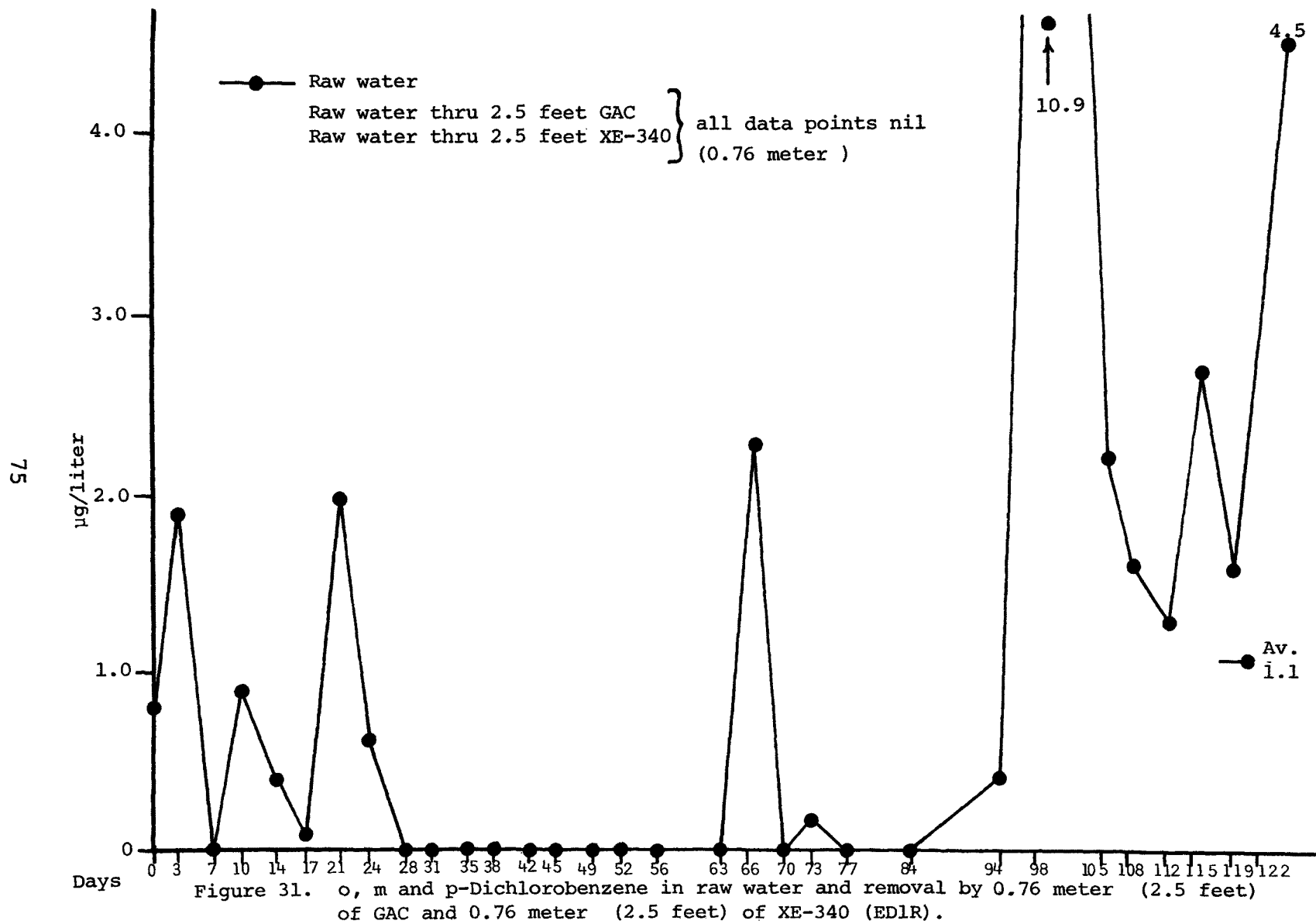


Figure 30. p-Chlorotoluene in raw water and removal by 0.76 meter (2.5 feet) of GAC and 0.76 meter (2.5 feet) of XE-340 (ED1R).



H.T. Water Source--

Low levels of the four THM, chloroform, bromodichloromethane, chlorodibromomethane and bromoform were present in H.T. effluent water and results on these compounds will be discussed first in this section. The synthetic organic removal results for IRA-904 resin again were poor, as expected, and only cis 1,2-dichloroethene data is presented to illustrate the poor adsorption. Additional synthetic organic data for the IRA-904 resin experiment (ED3) is available in Appendix B, Raw Data Tables.

THM

Tables 19 and 20 are presented for chloroform and chlorodibromomethane adsorption by XE-340 from H.T. water. Figures 32 through 39 are presented to show the influent and XE-340 effluent concentrations for the four THM substances measured. The variation in influent and effluent concentrations at these low concentrations makes conclusions relative to breakthrough times and saturation times difficult. In general the data show that these substances appear in lower concentrations after treatment of H.T. effluent water using XE-340 columns. Data for the THM removal by XE-340 and GAC are presented later based on a finished water influent.

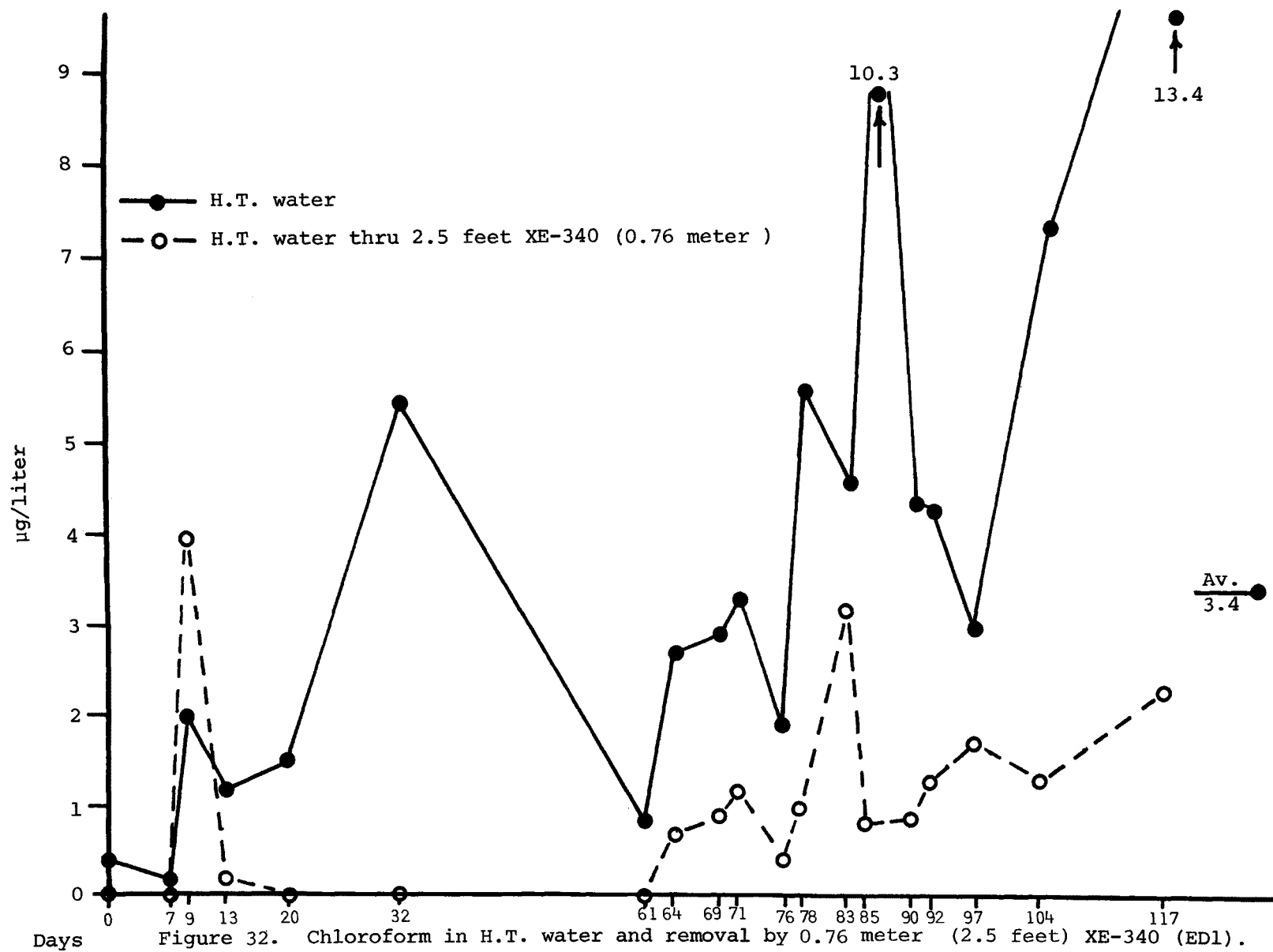
cis 1,2-Dichloroethene--Adsorption data appear in Table 21. Breakthrough curves appear in Figures 40, 41, and 42.

XE-340 was studied in ED1 and ED1R. The breakthrough and saturation performance of XE-340 on H.T. water in both ED follows the pattern on raw water (Table 13). The adsorptive capacity for XE-340 at 21 µg/L influent was calculated from the H.T. water tests by using a log-log plot to compare directly with raw water data at this influent concentration. Raw water and calculated H.T. water values were 0.32 and 0.3 gram per column and 0.117 and 0.108 cc per 100 grams respectively. From Table 4 and 5, the total HOC in ED1R for raw and H.T. water were 33.51 and 28.95 µg/L respectively. The percent of cis 1,2-dichloroethene of the total HOC were 86.5 percent and 87.7 percent respectively. Since the cis 1,2-dichloroethene to HOC ratio is quite similar, we would expect little change in adsorptive capacity due to competitive HOC. The closeness of the raw and H.T. water results calculated at a common influent level of 21 µg/L (0.32 and 0.3 gram per column) supports this assumption.

The effect of competitive adsorption by TOC on the adsorptive capacity for cis 1,2-dichloroethene can also be compared using TOC data from the raw water and H.T. locations. The average TOC concentration in the raw water was 9.8 mg/L and in the H.T. effluent the concentration was 6.8 mg/L. Since there was more TOC present in the raw water one might expect that the adsorptive capacity for cis 1,2-dichloroethene would be

TABLE 19. CHLOROFORM ADSORPTION DATA FROM H.T. WATER

[illegible]



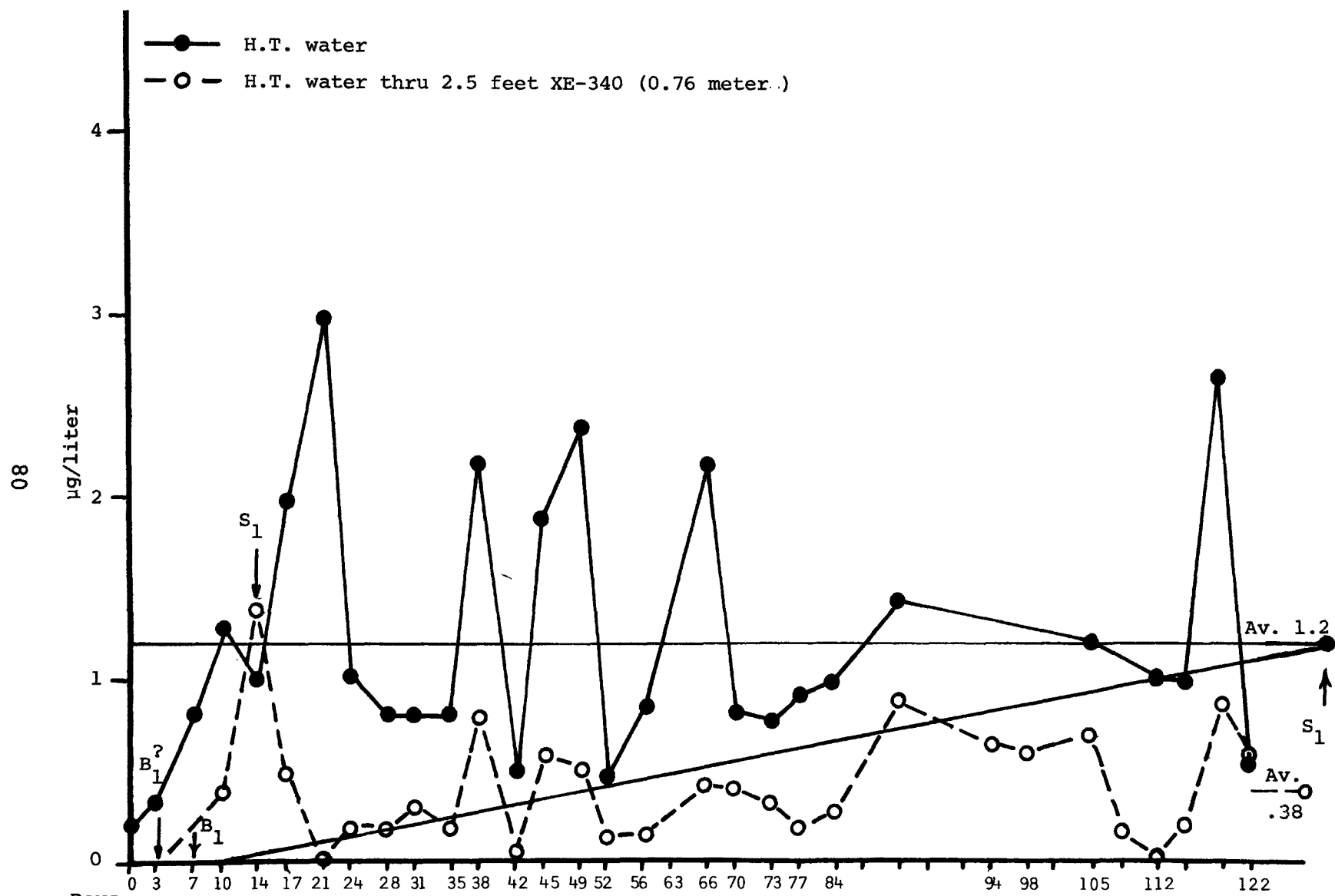


Figure 33. Chloroform in H.T. water and removal by 0.76 meter. (2.5 feet) XE-340 (ED1R).

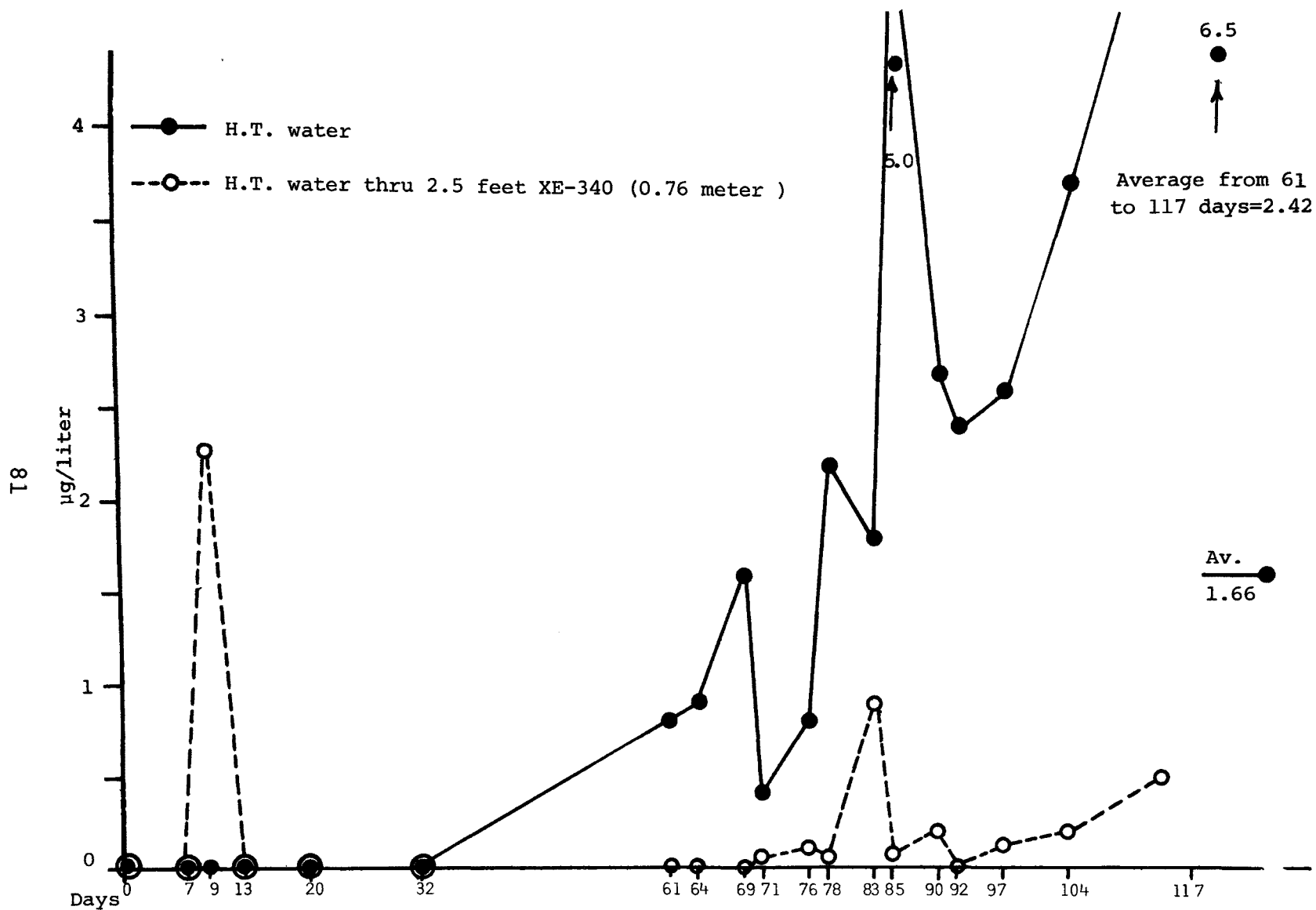


Figure 34. Bromodichloromethane in H.T. water and removal by 0.76 meter (2.5 feet) XE-340 (ED1).

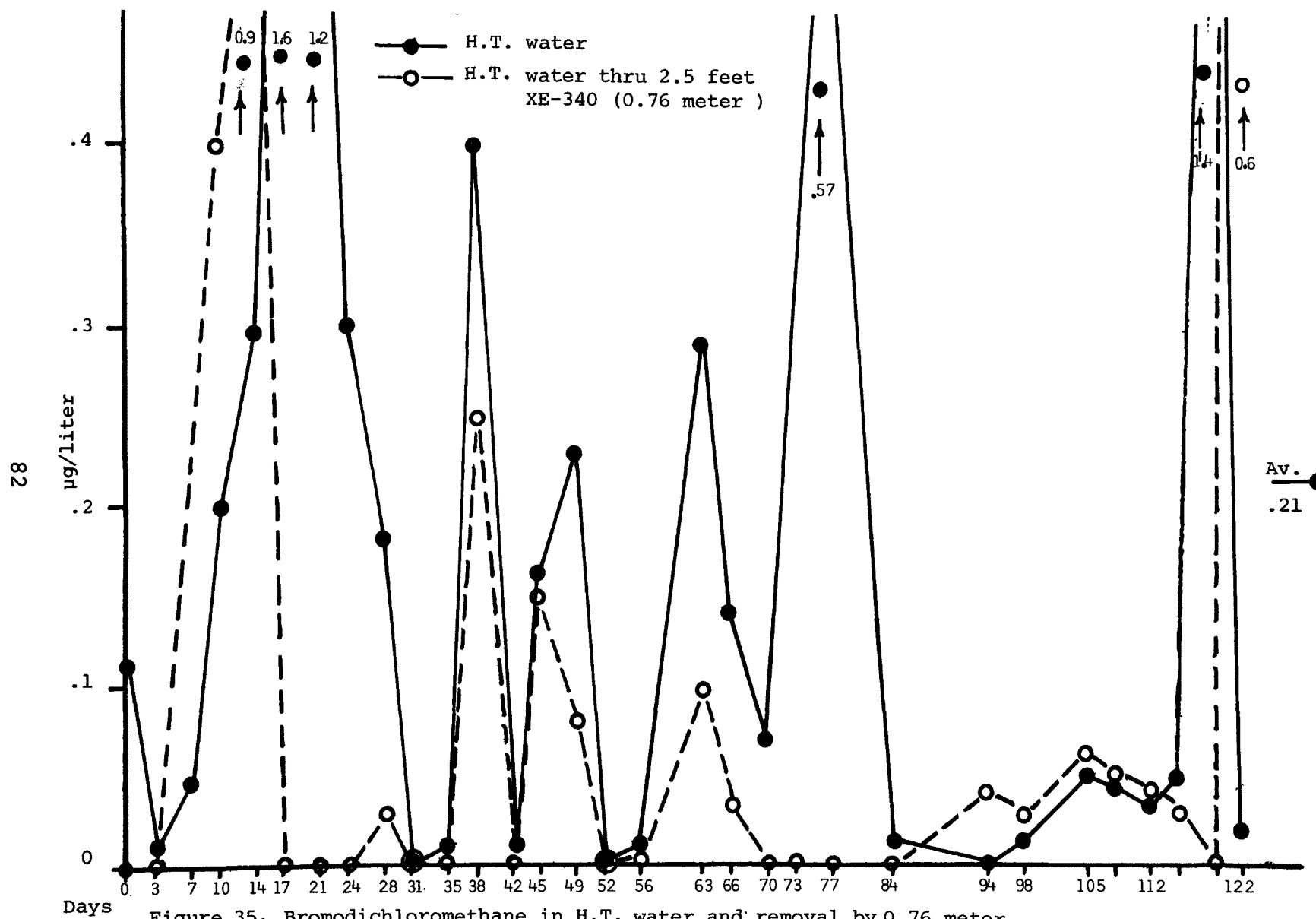


Figure 35. Bromodichloromethane in H.T. water and removal by 0.76 meter (2.5 feet) XE-340 (ED1R).

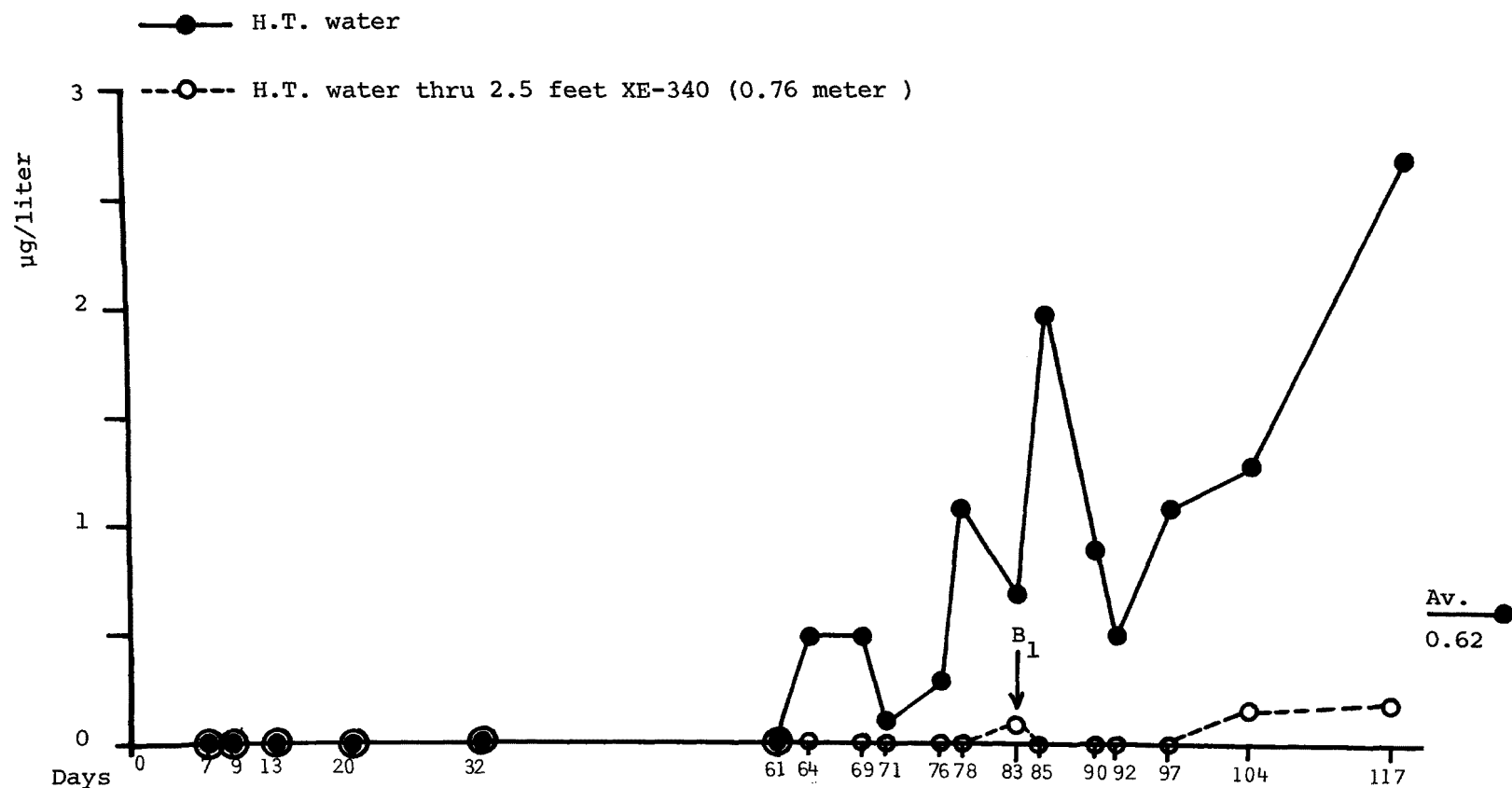


Figure 36. Chlorodibromomethane in H.T. water and removal by 0.76 meter (2.5 feet) XE-340 (ED1).

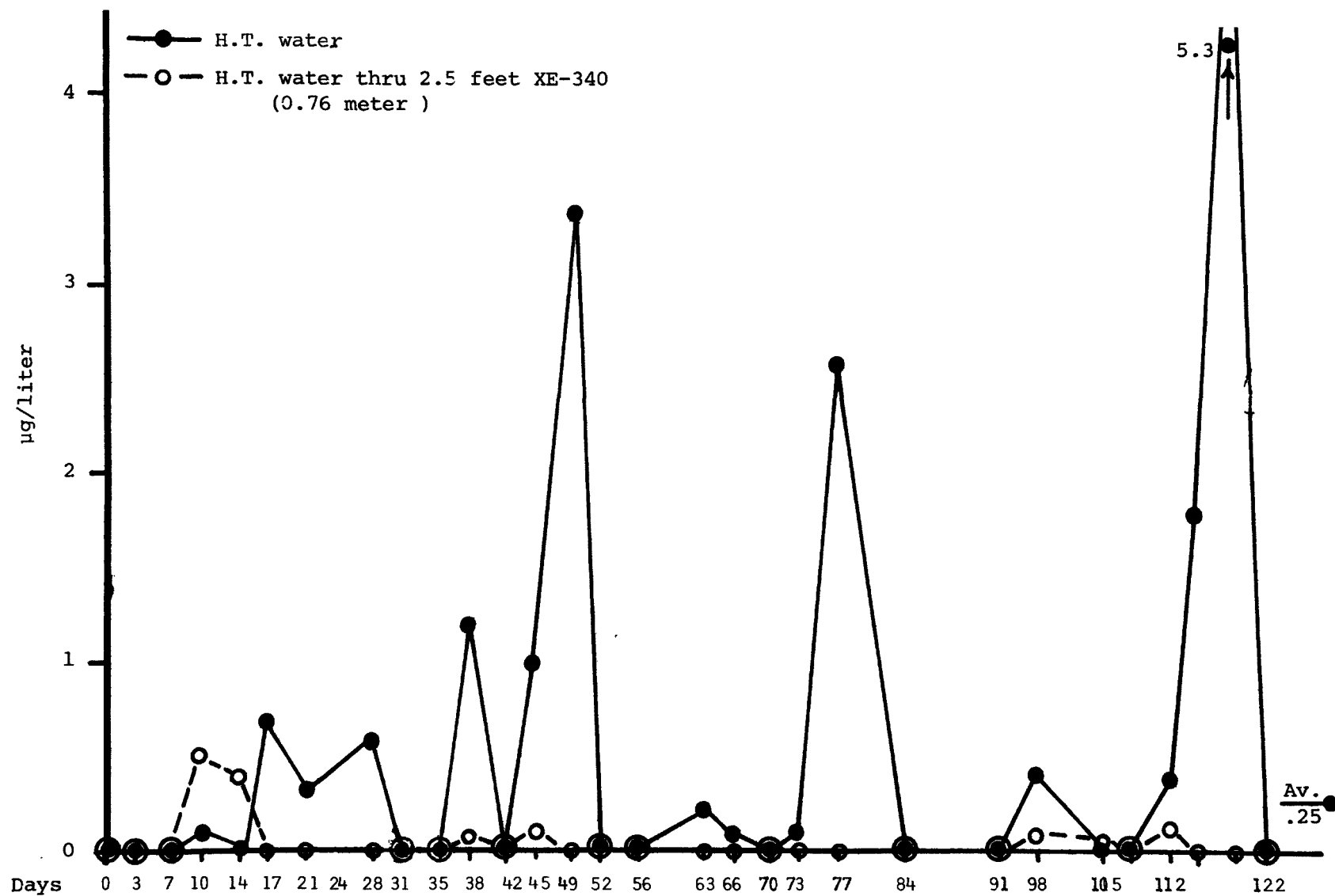
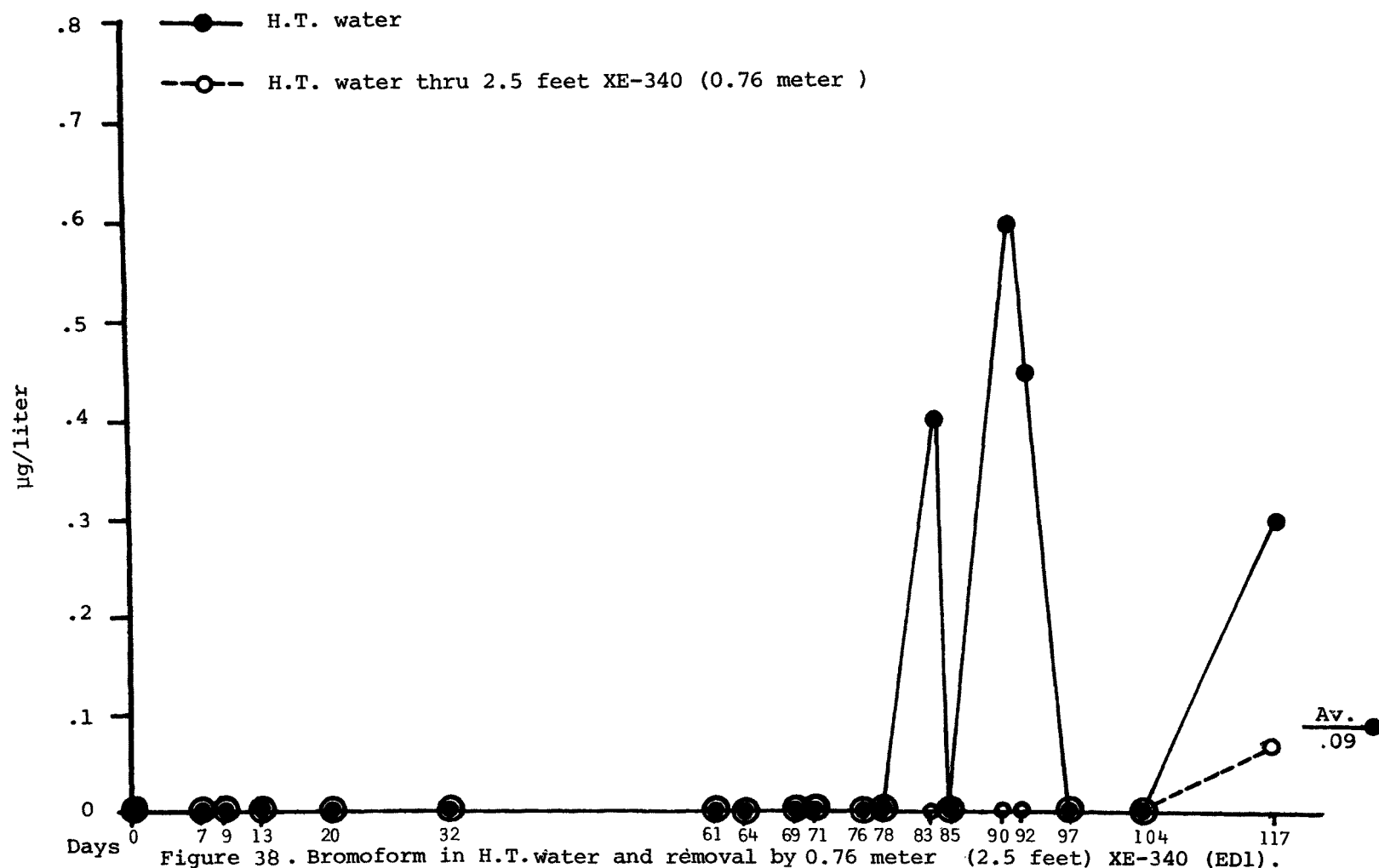


Figure 37. Chlorodibromomethane in H.T. water and removal by 0.76 meter (2.5 feet) XE-340 (ED1R).



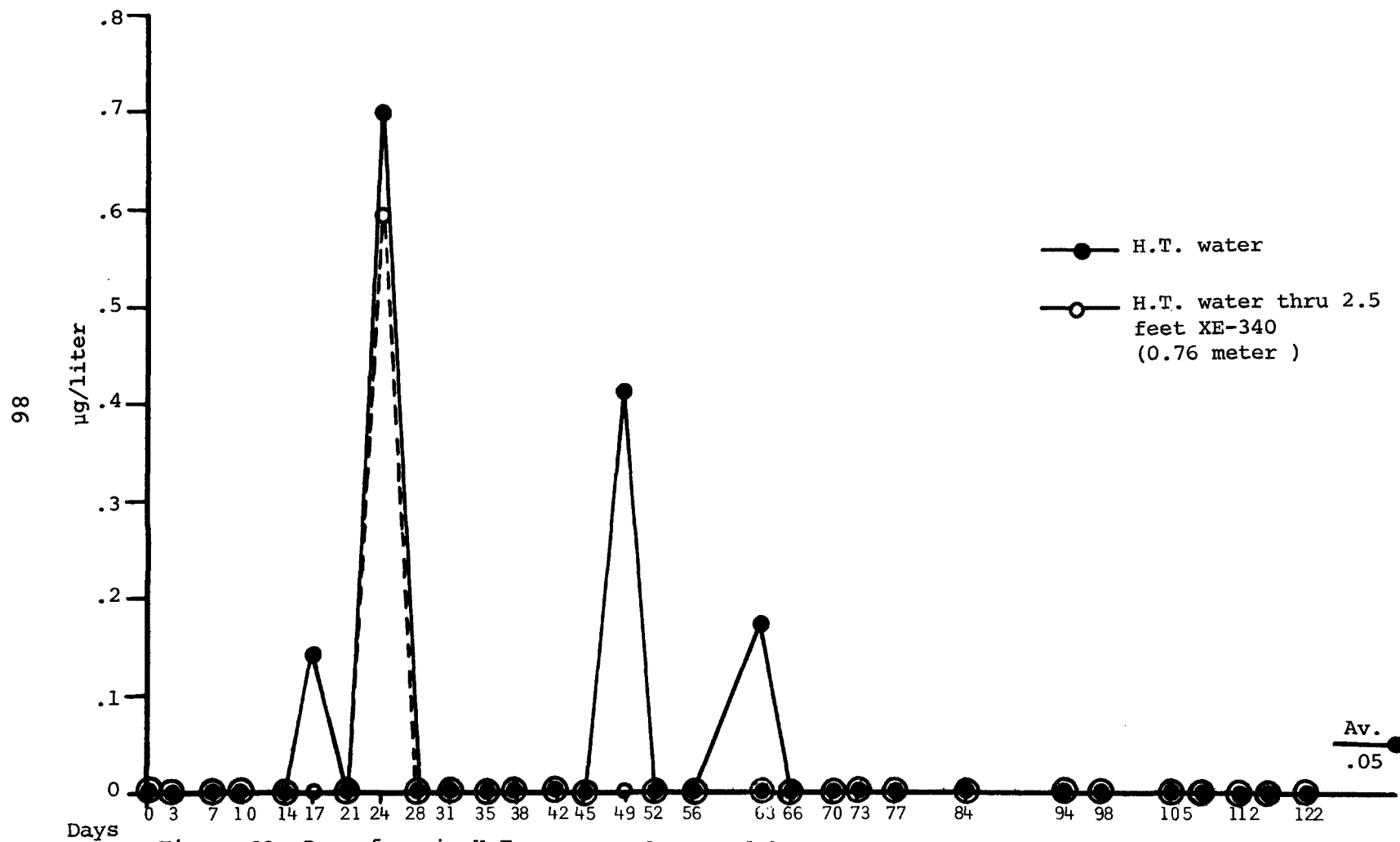


Figure 39. Bromoform in H.T. water and removal by 0.76 meter (2.5 feet) XE-340 (ED1R).

TABLE 21. cis 1,2-DICHLOROETHENE ADSORPTION DATA FROM H.T. WATER

ED	Bed Depth Feet	Adsorbent	Average Influent µg/L	Column Breakthrough Days	Column Saturation Days	MT N Inch	Test Duration Days	Total Entering Each Column During Test Grams	Total Adsorbed by Each Column at End of Test Grams	Adsorbed by Each Column at Saturation Grams	% Adsorbed at End of Test %	% Adsorbed at Saturation %	Adsorption per 100 gms. Adsorbent at End of Test Grams	Adsorption per 100 gms. Adsorbent at Saturation Grams	CC
1	2.5	XE-340	20	32	274	27	117	.209	.196	.287	90	56	.09	.134	.104
1R	2.5	XE-340	25.4	28	270	27	122	.277	.235	.337	85	55	.109	.157	.122
3	2.5	904	24.1	no adsorption			53	.114	0		0		0		
		2.5 feet = 0.76 meter													

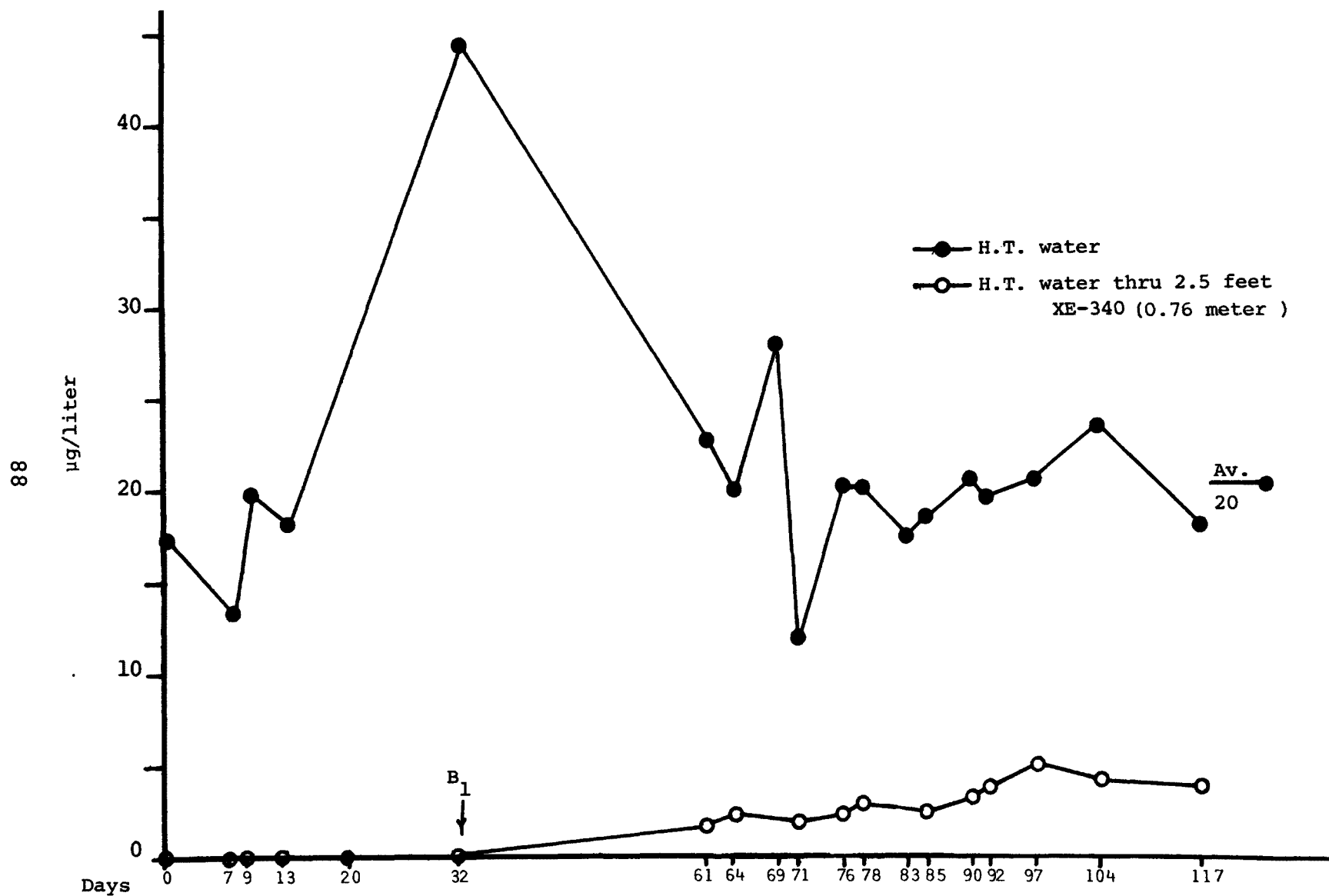


Figure 40. cis 1,2-Dichloroethene in H.T. water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1).

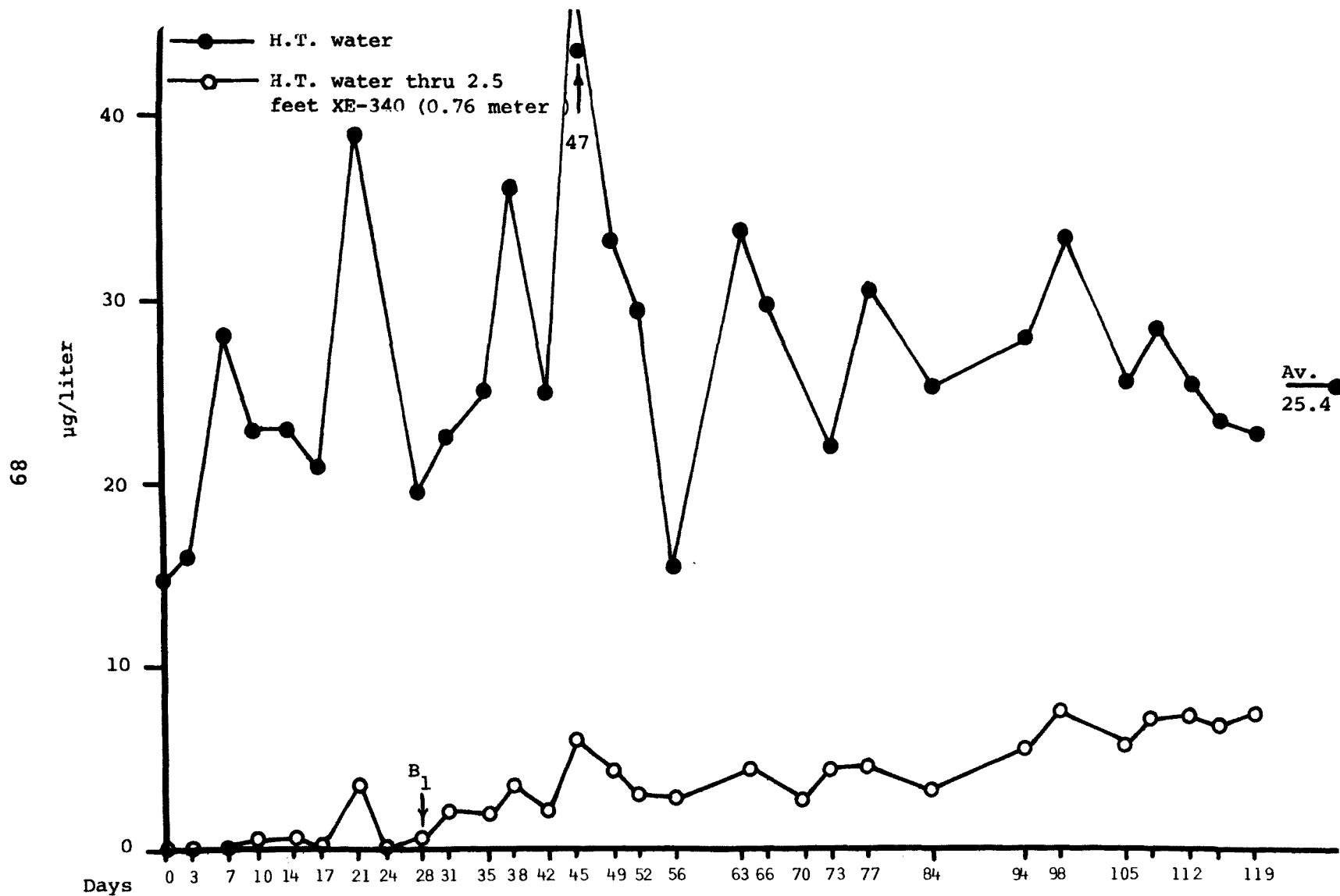


Figure 41. cis 1,2-Dichloroethene in H.T. water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

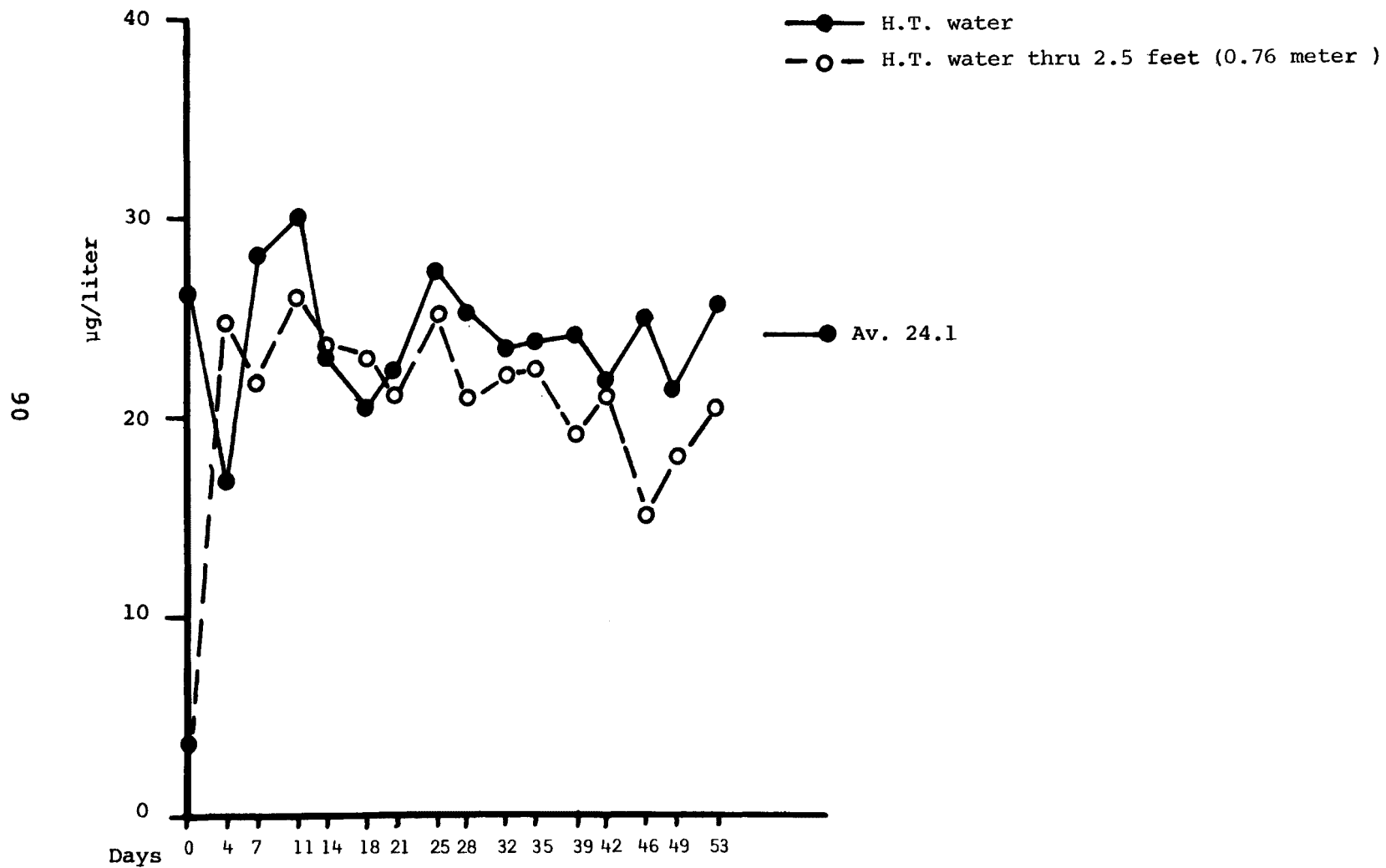


Figure 42. cis 1,2-Dichloroethene in H.T. water and removal by 0.76 meter (2.5 feet) of IRA-904 resin (ED3).

decreased in the raw water if TOC competes with the cis 1,2-dichloroethene and HOC's adsorption sites. Since the adsorptive capacity for cis 1,2-dichloroethene by XE-340 receiving the raw water (0.32 gram per column) was not appreciably different from the adsorptive capacity for cis 1,2-dichloroethene by XE-340 receiving H.T. water (0.30 gram per column) one might tentatively conclude that TOC does not compete with cis 1,2-dichloroethene for the XE-340. The general lack of removal of TOC by the XE-340 also may support this observation.

Vinyl chloride--Influent and effluent curves appear in Figure 43. The average influent was 0.69 $\mu\text{g/L}$ and the average effluent was 0.5 $\mu\text{g/L}$. Since there was essentially no adsorption of vinyl chloride by XE-340 from raw water in the same time period of 94 to 122 days, these values may not indicate adsorption. If they do represent adsorption, 27 percent was removed.

trans 1,2-Dichloroethene--Breakthrough curves appear in Figure 44.

The influent concentration curves in Figure 44 illustrates a condition which makes data interpretation difficult. For the first 84 days of the test, the influent concentration averaged 0.11 $\mu\text{g/L}$. From day 84 to 112 the average was 1.2 $\mu\text{g/L}$. Breakthrough occurred at the same time the influent concentration increased approximately tenfold. Research needs to be done on adsorption of a single substance from pure water as well as a mixture of many substances from pure and actual plant water. Such research may indicate that breakthrough under a given condition may occur at approximately the same time for a wide range of concentrations for a specific substance. If such is the case, breakthrough might occur at approximately the same time, but the level of breakthrough would be much less if the influent concentration remained at the 0.11 $\mu\text{g/L}$ level throughout the test. In Figure 22, when the average raw water influent concentration of trans 1,2-dichloroethene was 1.3 $\mu\text{g/L}$, the same bed depth of XE-340 exhibited no breakthrough throughout the 122-day test. Without the additional research mentioned above, it is probably best not to attempt to explain such differences obtained on such a complex system. We can conclude that XE-340 removes all compound from H.T. water for a period of 84 days even when the concentration averaged only 0.11 $\mu\text{g/L}$.

1,1-Dichloroethane--Adsorption data appear in Table 22. The breakthrough curve appears in Figure 45.

The influent concentration, plotted in Figure 45, appears quite erratic, averaging 0.13 $\mu\text{g/L}$. Estimation of the breakthrough point from this curve is not too difficult, but the extrapolated saturation point is questionable and was based on adsorption data of this compound through the whole two-year

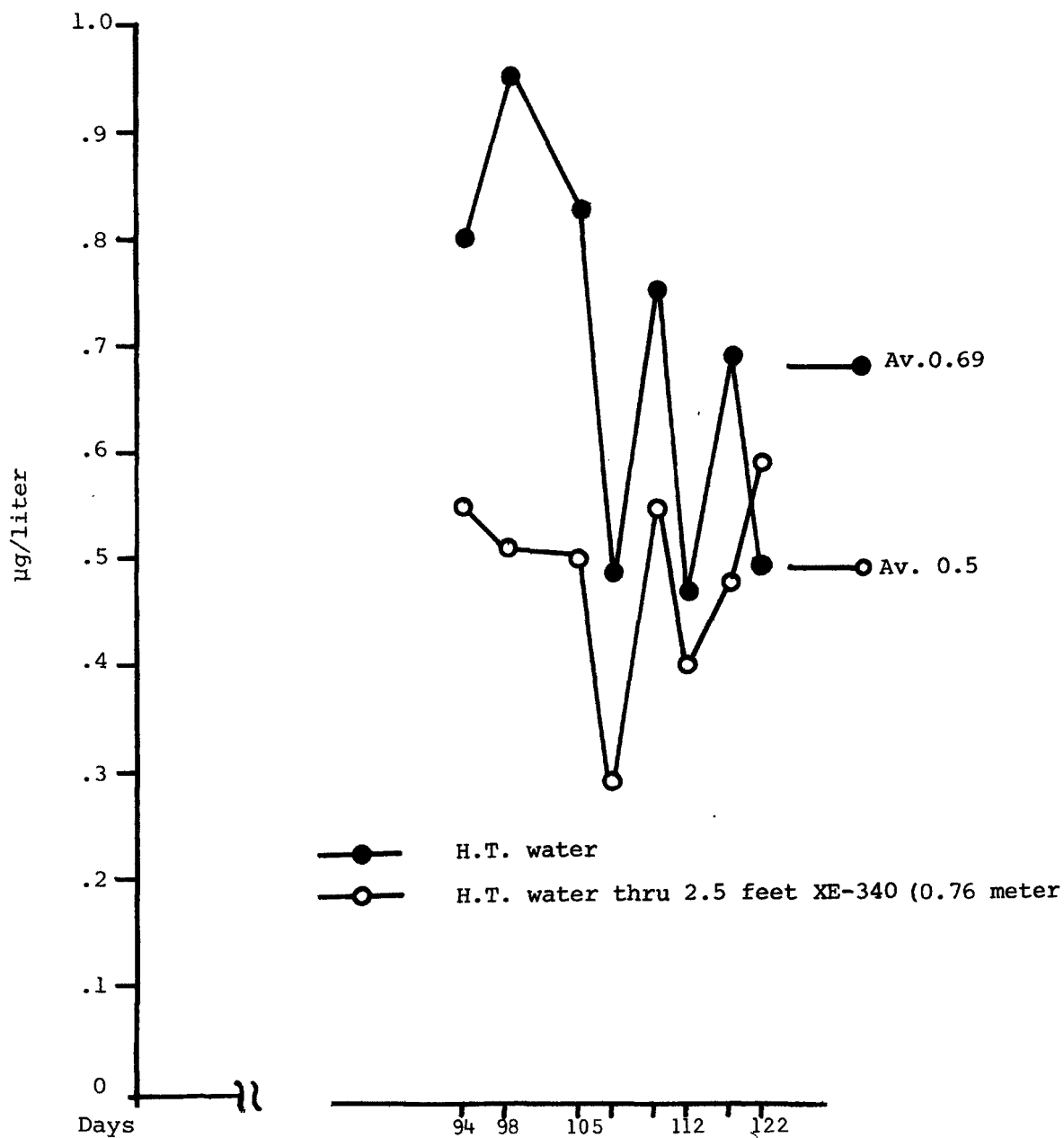


Figure 43. Vinyl chloride in H.T. water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

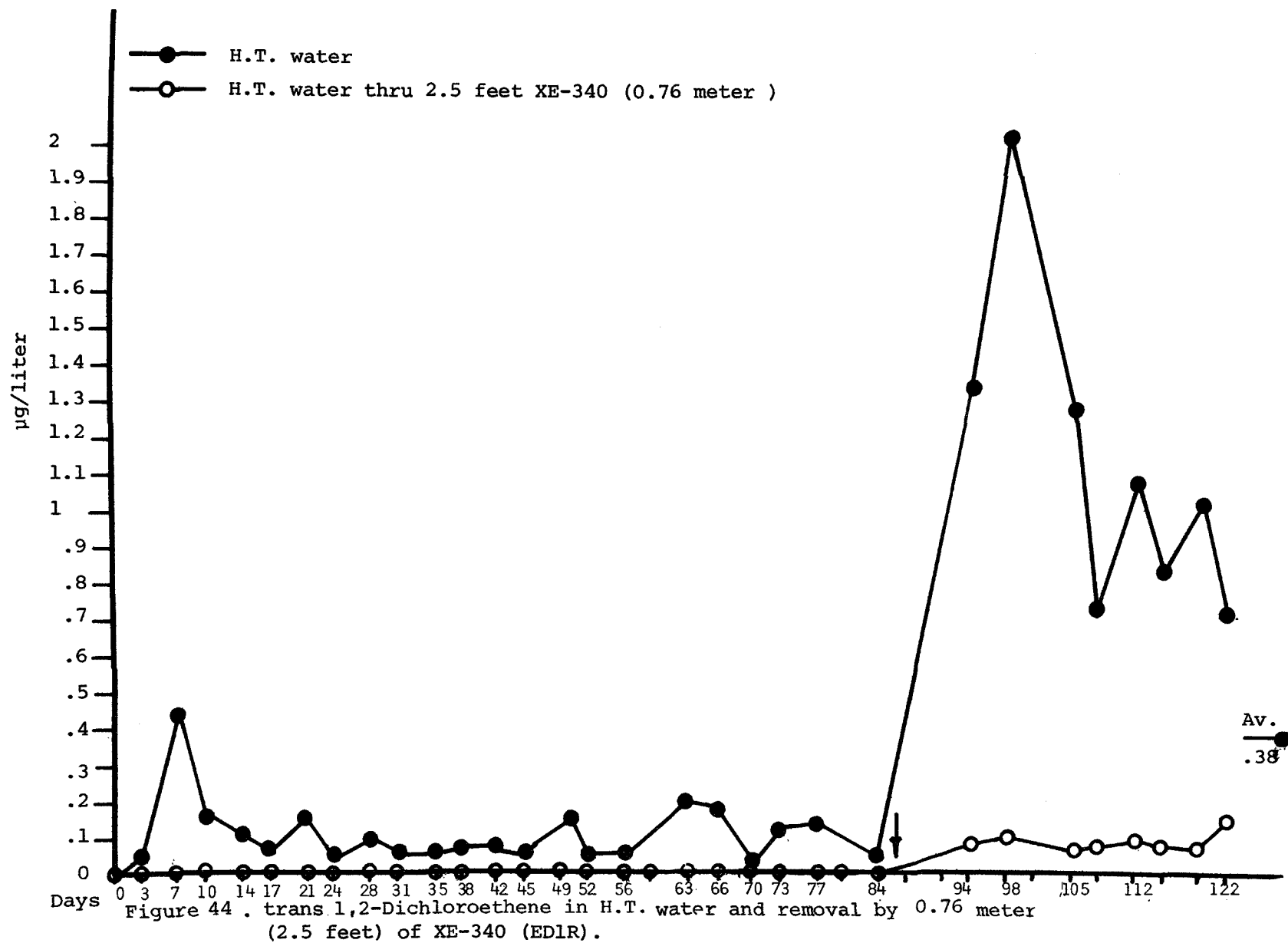


TABLE 22 . 1,1-DICHLOROETHANE ADSORPTION DATA FROM H.T. WATER

ED	Bed Depth Feet	Adsorbent	Average Influent µg/L	Column Breakthrough Days	Column Saturation Days	MT N Inch	Test Duration Days	Total Entering Each Column During Test Grams	Total Adsorbed by Each Column at End of Test Grams	Adsorbed by Each Column at Saturation Grams	% Adsorbed at End of Test %	% Adsorbed at Saturation %	Adsorption per 100 gms. Adsorbent at End of Test Grams	Adsorption per 100 gms. Adsorbent at Saturation Grams	CC
1R	2.5	XE- 340	.13	94	131	9	122	.00142	.00129	.00131	91	92	.0006	.0006	.00052
	2.5 feet = 0.76 meter														

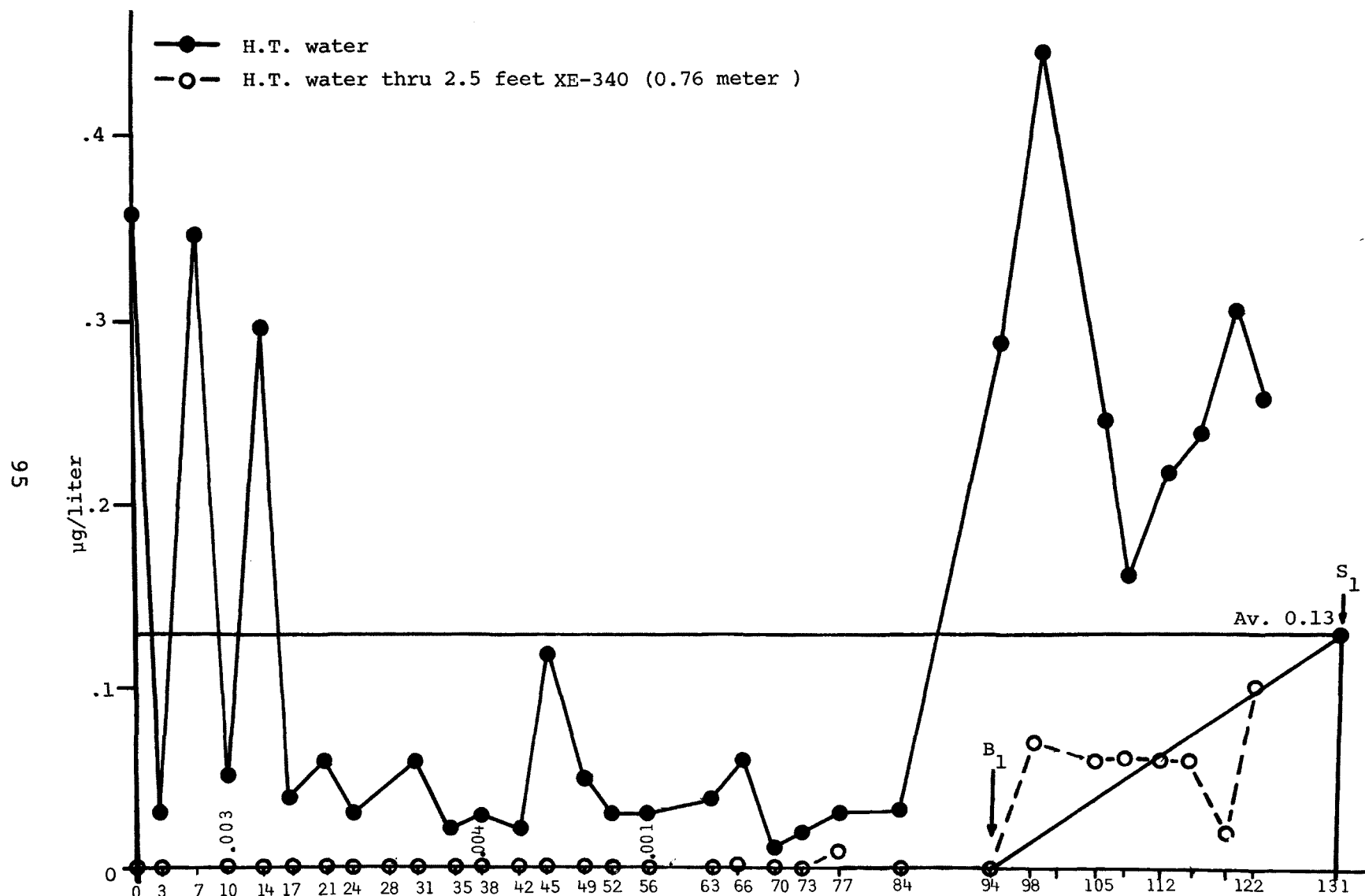


Figure 45. 1,1-Dichloroethane in H.T. water and removal by 0.76 meter (2.5 feet) XE-340 (ED1R).

study. Such estimations are intended to aid overall data interpretation and are not intended to be considered factual. We can conclude that XE-340 on H.T. water as on raw water removes all the compound even when present at the average low level of 0.13 $\mu\text{g/L}$ for a period of time up to approximately 94 days.

1,1,1-Trichloroethane, 1,2-dichloroethane, carbon tetrachloride (summed concentration)--The average influent concentration, plotted in Figure 46, was only 0.022 $\mu\text{g/L}$, which is probably too low to attempt conclusions. Periodically throughout the test, the XE-340 column appears to allow some of the material to pass while most is adsorbed.

Trichloroethylene--Adsorption data appear in Table 23. The breakthrough curve appears in Figure 47.

Along with a very low influent concentration averaging 0.066 $\mu\text{g/L}$, we again have a much lower average of only 0.020 $\mu\text{g/L}$ entering for the first 84 days with the remaining number of days averaging 0.240 $\mu\text{g/L}$. XE-340 removed all the compound for the first 84 days except for trace amounts on two sample dates.

Tetrachloroethylene--The average influent concentration was only 0.0025 $\mu\text{g/L}$. The influent and adsorption curves are shown in Figure 48. The average concentration was higher during the first part of the test and the XE-340 column allowed some passage even on initial start-up.

Chlorobenzene--The average influent concentration in ED1R was 0.048 $\mu\text{g/L}$ and individual data points are plotted in Figure 49. For the first 84 days of the test the average was 0.007 $\mu\text{g/L}$ which was all removed by the XE-340 column. From day 94 to the end of the test, the average entering was 0.08 $\mu\text{g/L}$, of which a high percentage was removed.

p-Chlorotoluene--Seven samples of the 30 sampled during the test period had low levels of p-chlorotoluene ranging from .008 $\mu\text{g/L}$ to .540 $\mu\text{g/L}$. The influent data point curve appears in Figure 50. All data points for samples through the XE-340 column showed nil concentration except for the sample on day 108, at 1.2 $\mu\text{g/L}$. No conclusions are made.

o, m and p-Dichlorobenzene--Adsorption data appear in Table 24. Influent and adsorption curves appear in Figure 51.

Except for three sample points showing low levels of the summed values of the compounds, XE-340 removed all the compounds from H.T. water. Removal was essentially complete.

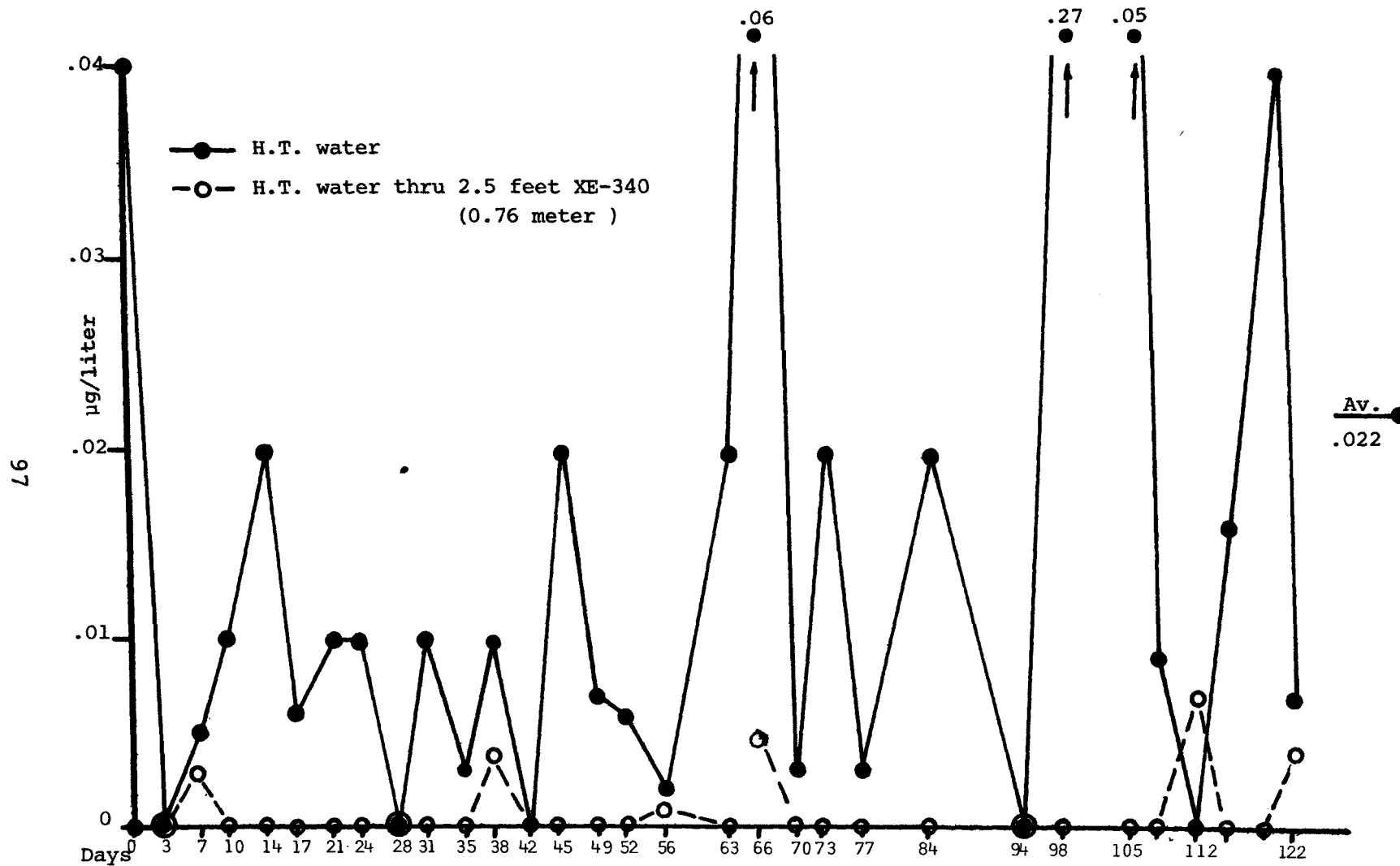
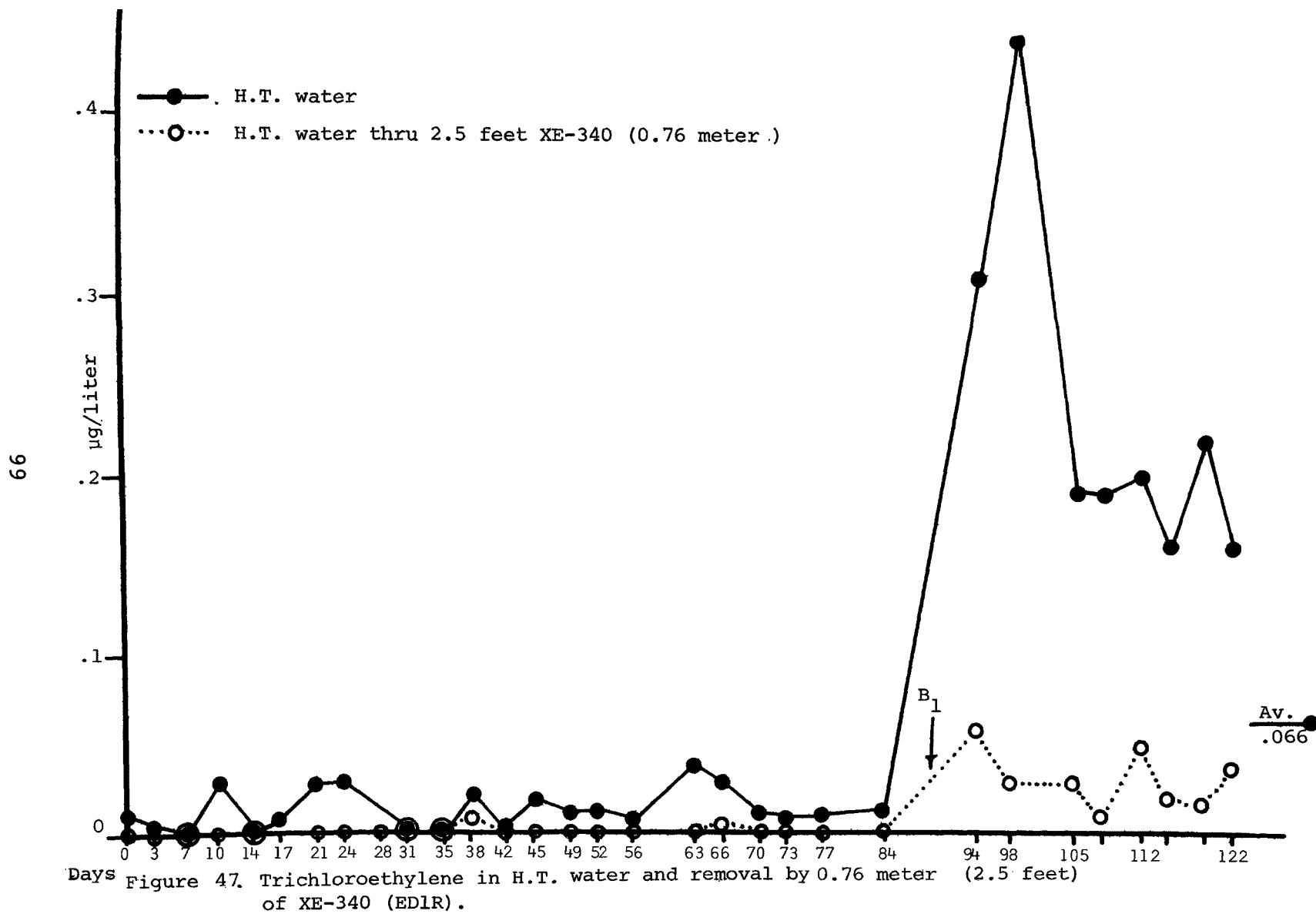


Figure 46. 1,1,1-Trichloroethane, 1,2-dichloroethane and carbon tetrachloride in H.T. water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

TABLE 23. TRICHLOROETHYLENE ADSORPTION DATA FROM H.T. WATER

[illegible]



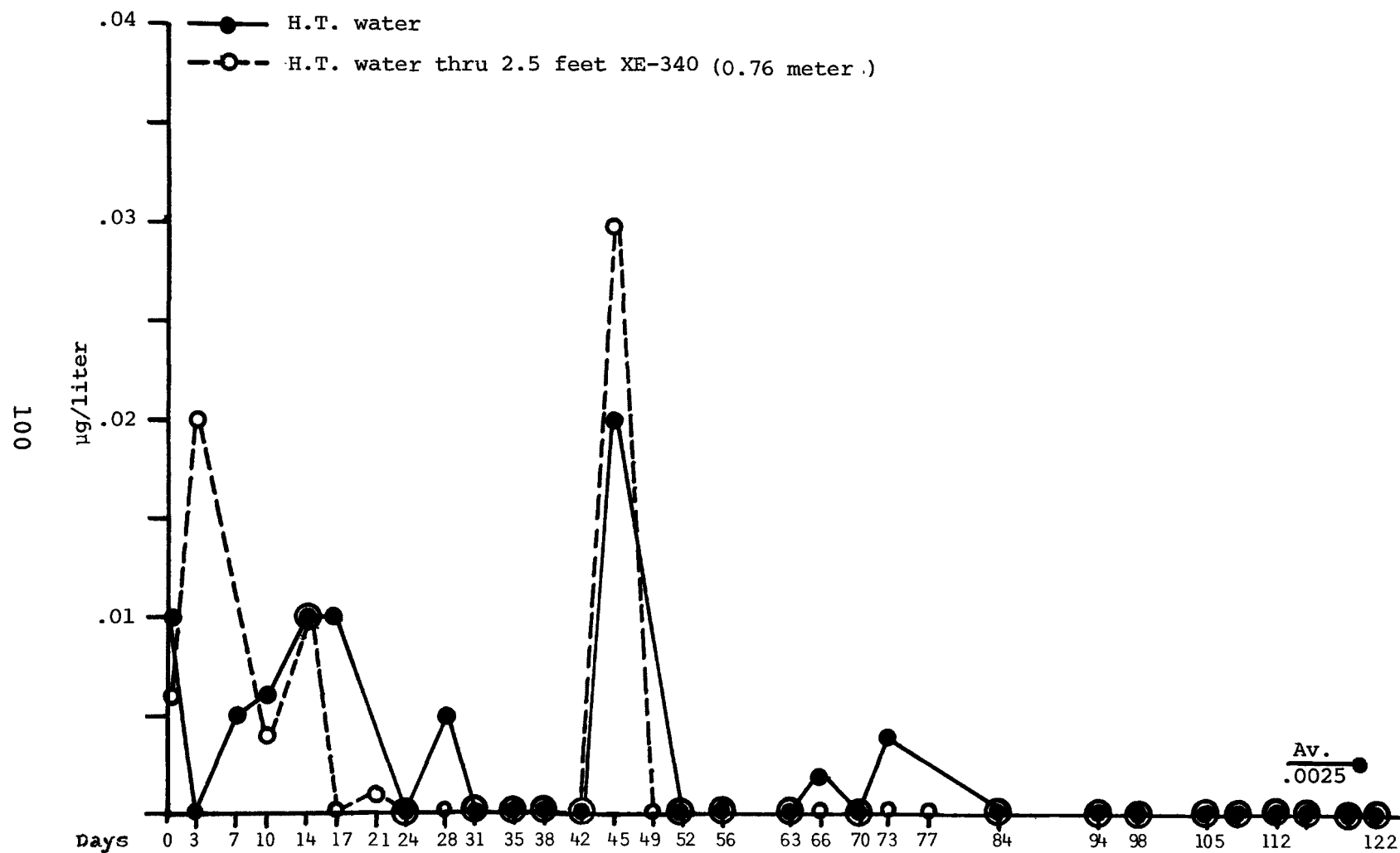


Figure 48. Tetrachloroethylene in H.T. water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

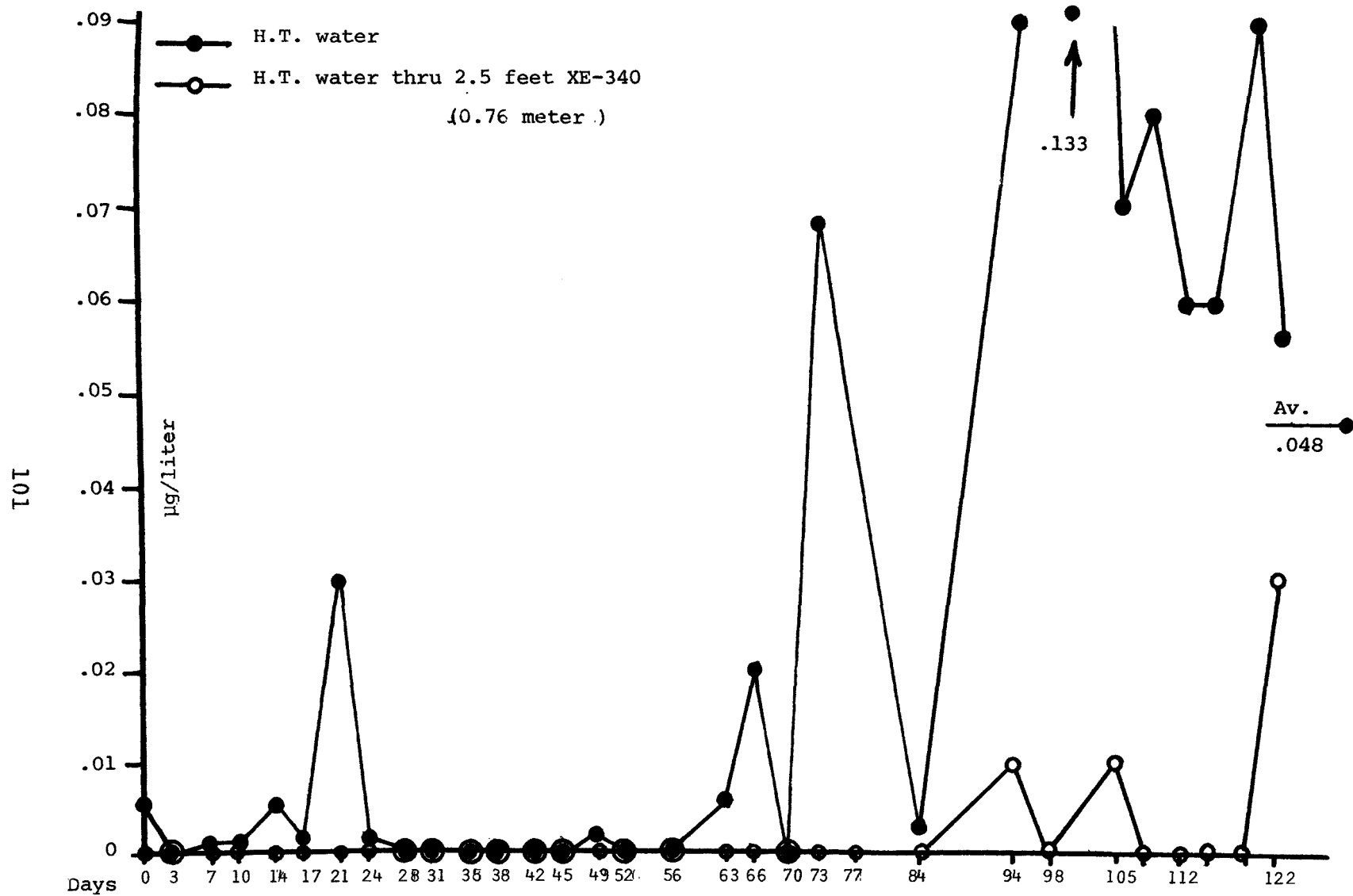


Figure 49. Chlorobenzene in H.T. water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1).

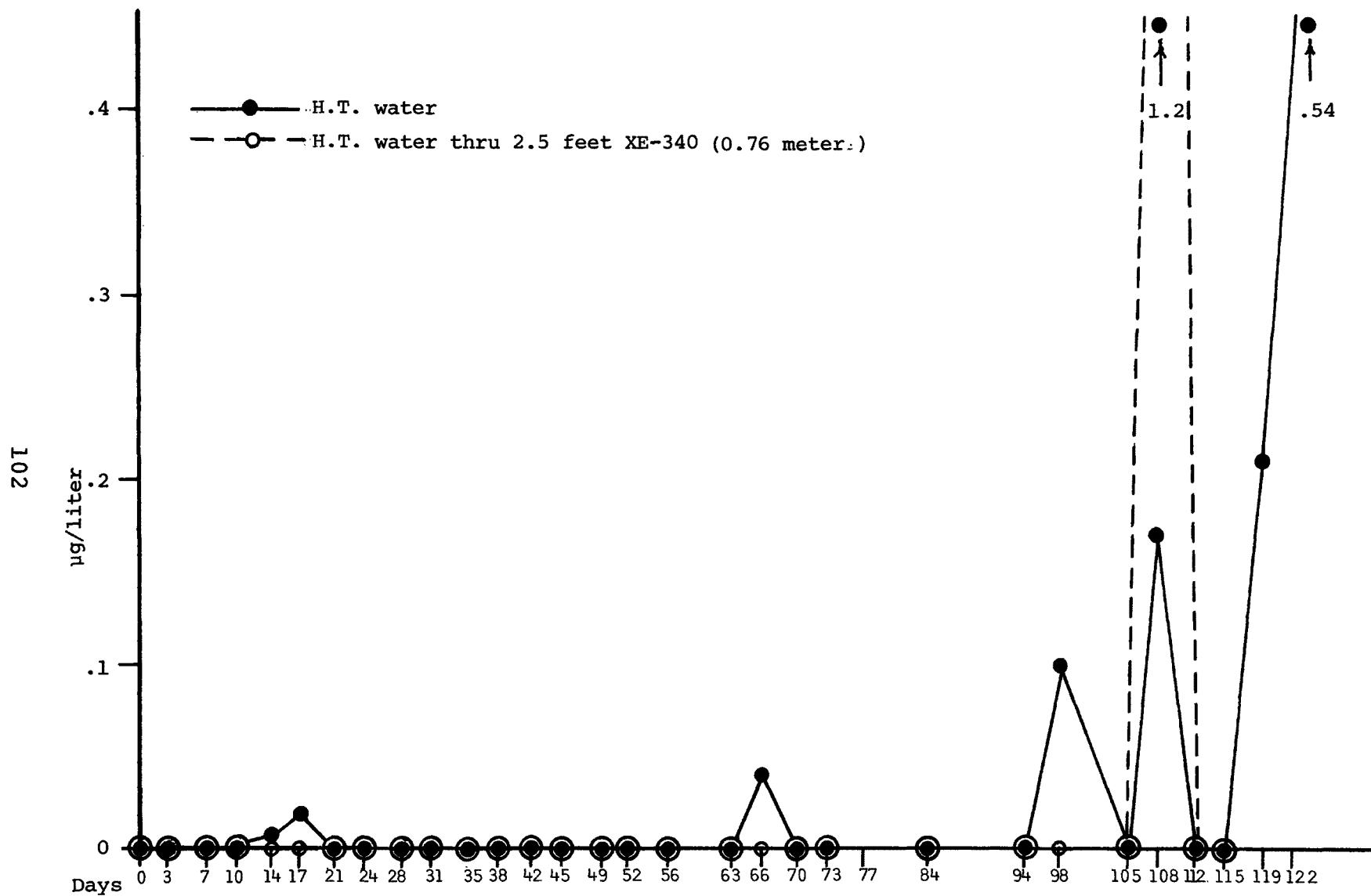


Figure 50. p-Chlorotoluene in H.T. water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

TABLE 24. o, m, AND p-DICHLOROBENZENE ADSORPTION DATA FROM H.T. WATER

[illegible]

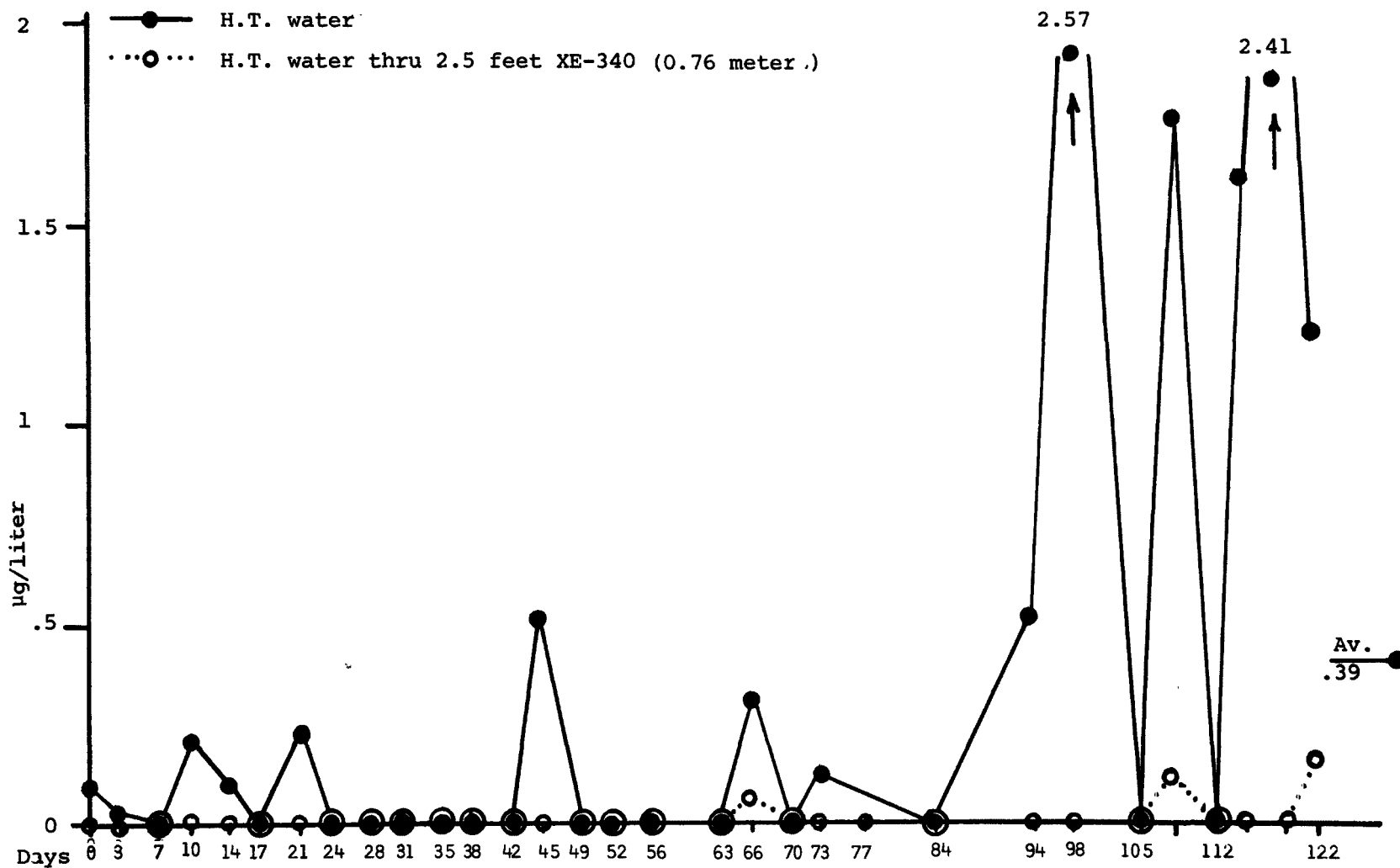


Figure 51. o, m and p-Dichlorobenzene in H.T. water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

Finished Water Source--

Chlorination in the plant process between the H.T. effluent sample point and the finished water sample point resulted in large increases of the THM. Chloroform data will be discussed first in this section. A discussion of cis 1,2-dichloroethane follows chloroform so the two compounds occurring most frequently and at the highest concentrations can be compared.

Chloroform--Adsorption data appear in Table 25. Influent and adsorption curves appear in Figure 52, 53, 54, 55, and 56. ED4, is shown in Table 25. Although the average influent level varied from 57 for ED3 to 67.3 $\mu\text{g/L}$ for ED4, initial breakthrough and saturation times were quite uniform at approximately 7 and 22 days and 8 and 23.5 days respectively. The MT_z also were quite uniform at 21 and 20 inches respectively. Thus, The variation in influent water conditions were such that they did not greatly affect these parameters. This is more likely to occur in ground water sources which are generally subject to lesser variations in quality than river water sources. Also maintenance of consistent contact times are more easily accomplished in pilot systems as compared to full scale plants.

For these two study periods, a comparison of the grams of chloroform adsorbed per 100 grams of adsorbent at saturation (last column of figures in Table 25) with their respective average influent level, shows that the adsorptive capacity of GAC for chloroform increased (0.028 cc and 0.0358 cc) as the influent concentration increased (57 to 67.3 $\mu\text{g/L}$), as predicted by the Polanyi-Manes Theory, which is discussed beginning on page 283. In ED4, the adsorptive capacity in cc's per 100 grams of GAC at saturation appears to have increased slightly with increasing bed depth, 0.0449, 0.048, and 0.049 cc for 1.52 (5.0 feet), 2.29 (7.5 feet), and 3.05 (10 feet) meters of bed depth respectively. This is to be expected because more strongly adsorbed substances, both HOC and non-HOC, are removed in the shallower bed depths thus reducing competitive adsorptive effects. This point will be discussed later in more detail.

Chloroform adsorption from finished water by 0.76 meter (2.5 feet) of XE-340 was studied during ED1, ED1R and ED2 (Table 25). Although the average influent concentration varied from 80.2, 69.3, and 64 $\mu\text{g/L}$, initial breakthrough and saturation times for each ED were quite uniform at approximately 3 and 150 days respectively. The MT_z also were quite uniform at nearly the entire column length of 76.2 cm (30 inches) which was greater than that found for GAC. A comparison of the grams of chloroform adsorbed per 100 grams of adsorbent at saturation with their respective average influent level shows that the adsorptive capacity of XE-340 for chloroform decreased (0.177, 0.148, and 0.134 cc) as the influent concentration decreased.

TABLE 25. CHLOROFORM ADSORPTION DATA FROM FINISHED WATER

ED	Bed Depth Feet	Adsorbent	Average Influent µg/L	Column Breakthrough Days	Column Saturation Days	MT N Inch	Test Duration Days	Total Entering Each Column During Test Grams	Total Adsorbed by Each Column at End of Test Grams	Adsorbed by Each Column at Saturation Grams	% Adsorbed at End of Test %	% Adsorbed at Saturation %	Adsorption per 100 gms. Adsorbent at End of Test Grams	Adsorption per 100 gms. Adsorbent at Saturation Grams	CC
1	2.5	XE-340	80.2	3	156	29	117	.838	.497	.569	59	51	.231	.265	.177
1R	2.5	XE-340	69.3	3	150	29	122	.736	.456	.473	62	52	.212	.22	.148
2	2.5	XE-340	64	0	150	30	63	.36	.247	.429	69	50	.115	.2	.134
3	2.5	GAC	57	7	22	21	53	.27	.074	.074	27	66	.042	.042	.028
3	2.5	904	57				53	average increase of 1.75X							
4	2.5	GAC	67.3	8	23.5	20	122	.733	.094	.094	13	67	.0534	.0534	.0358
4	5	GAC	67.3	29	49	24.5	122	.733	.235	.235	32	80	.067	.067	.0449
4	7.5	GAC	67.3	49	76	32	122	.733	.376	.376	51	82	.071	.071	.048
4	10	GAC	67.3	72	98	31.8	122	.733	.511	.511	70	87	.073	.073	.049
2.5 feet = 0.76 meter				5 feet = 1.52 meters			7.5 feet = 2.29 meters			10 feet = 3.05 meters					

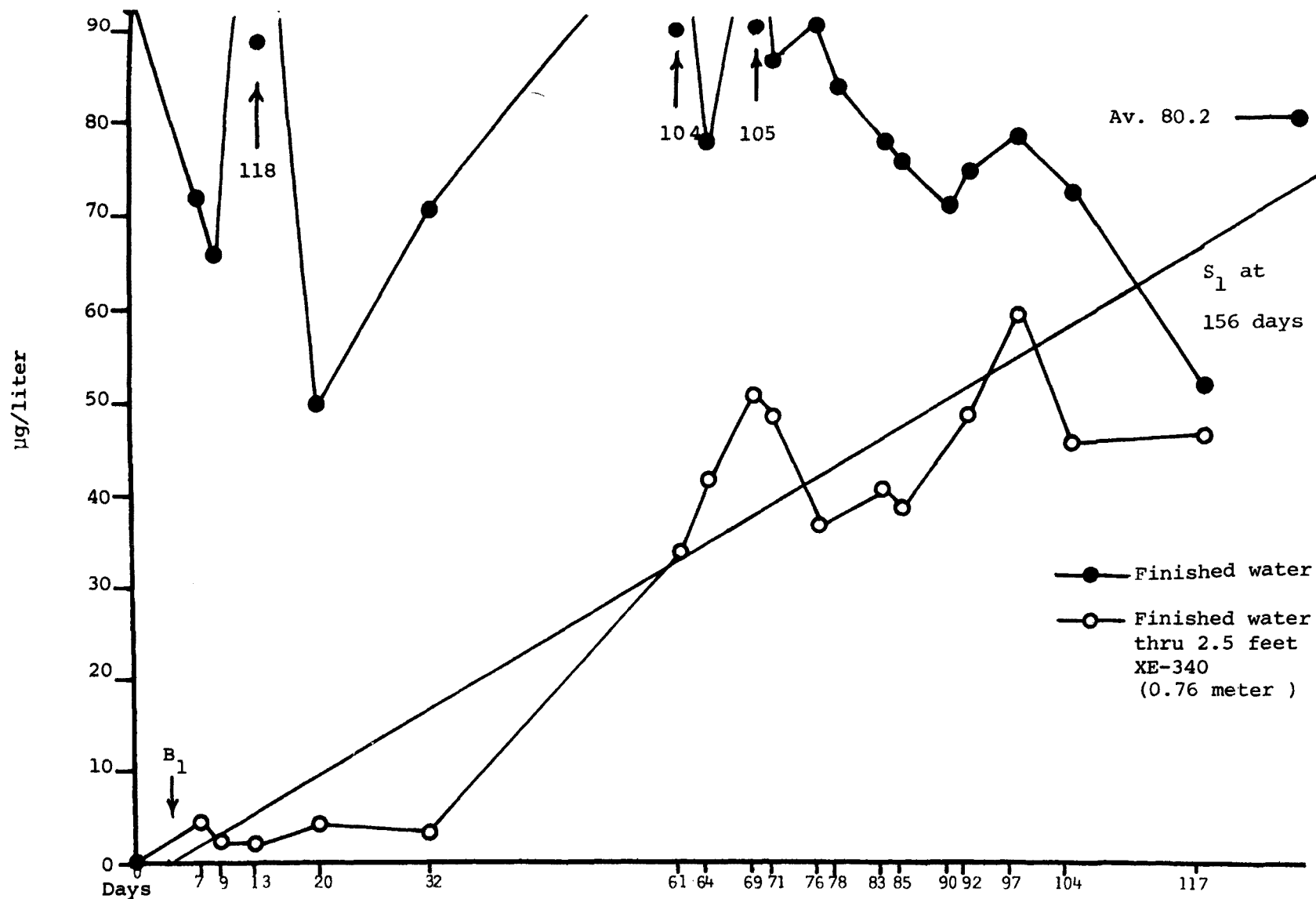


Figure 52. Chloroform in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1).

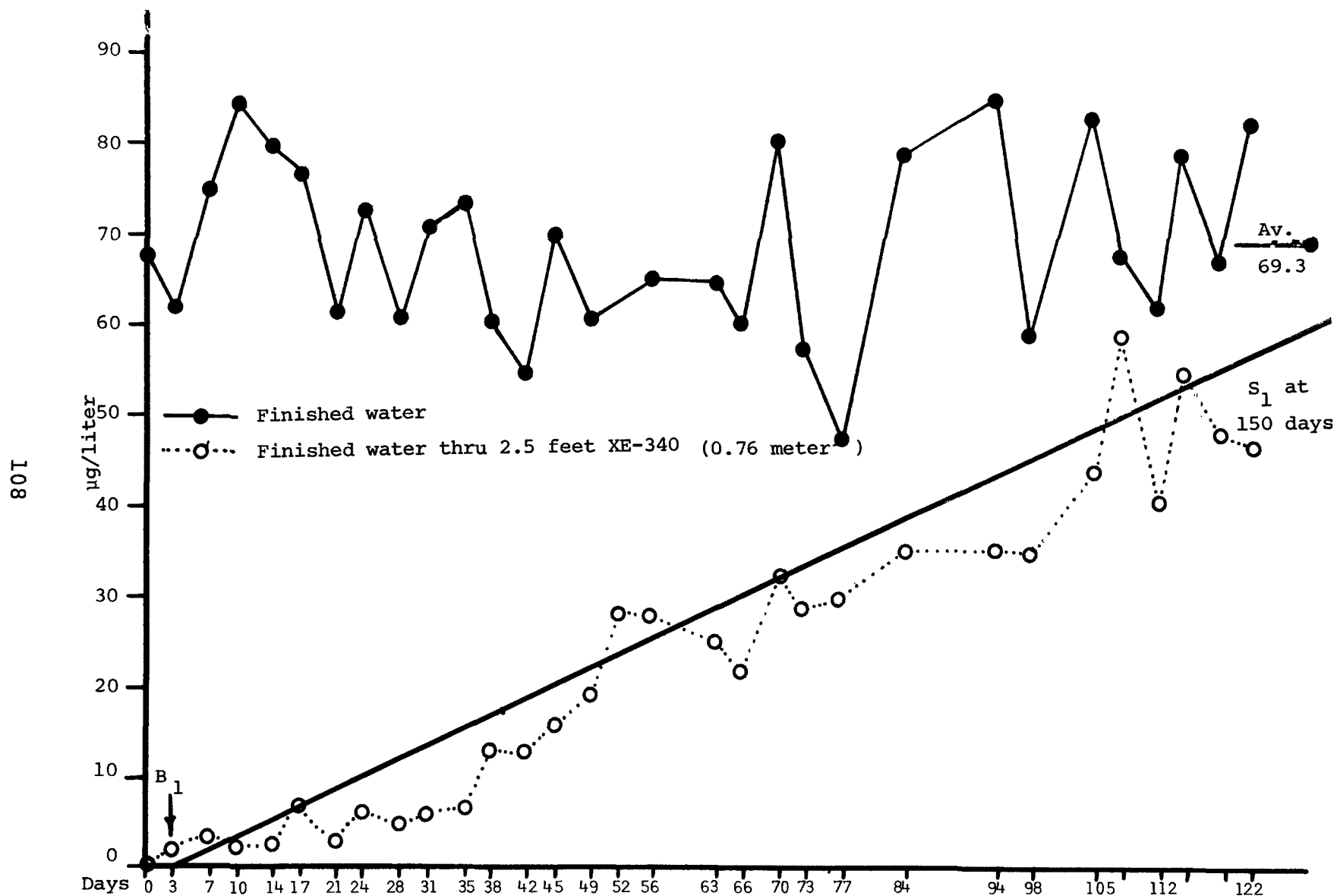


Figure 53. Chloroform in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

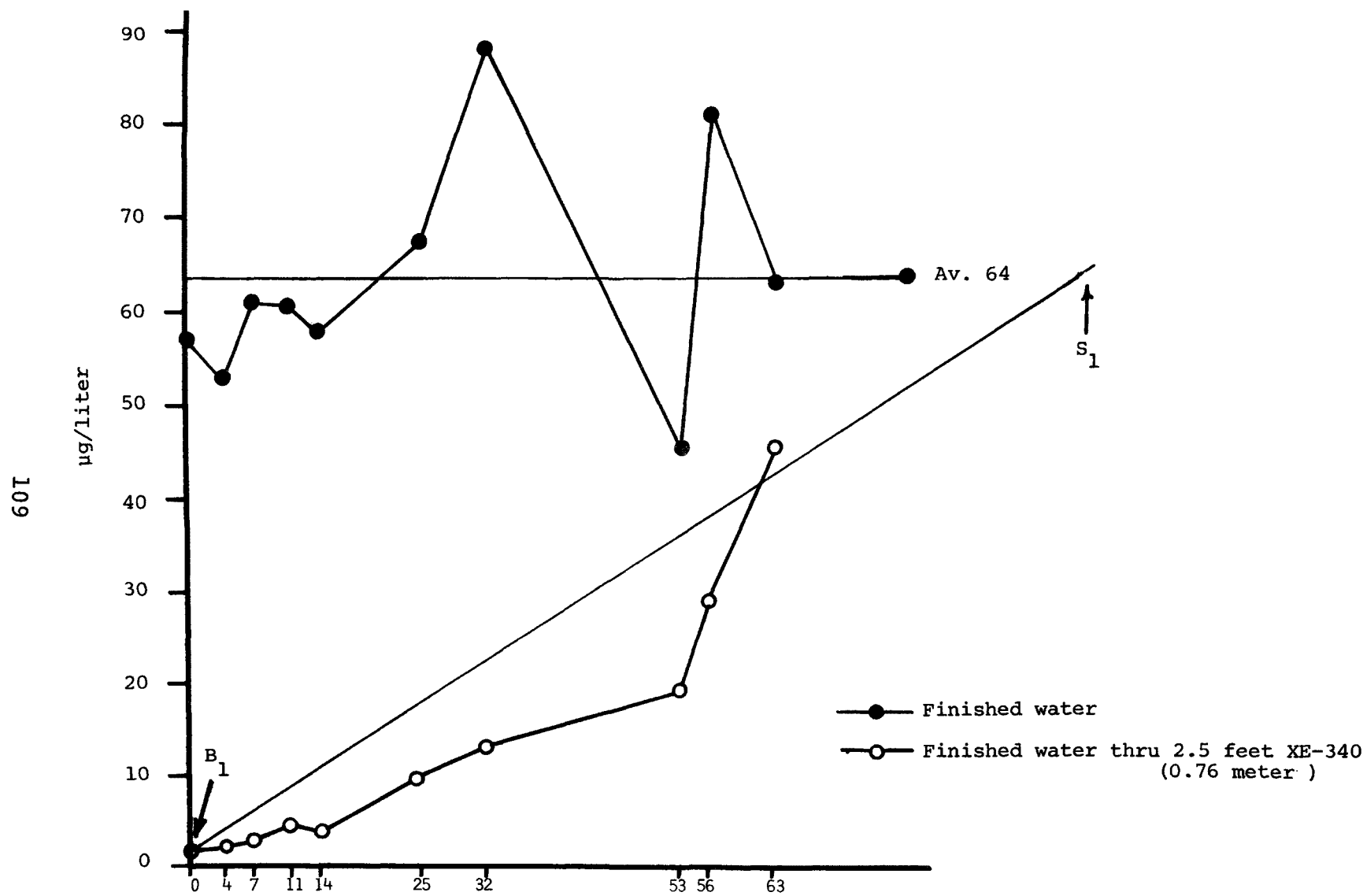
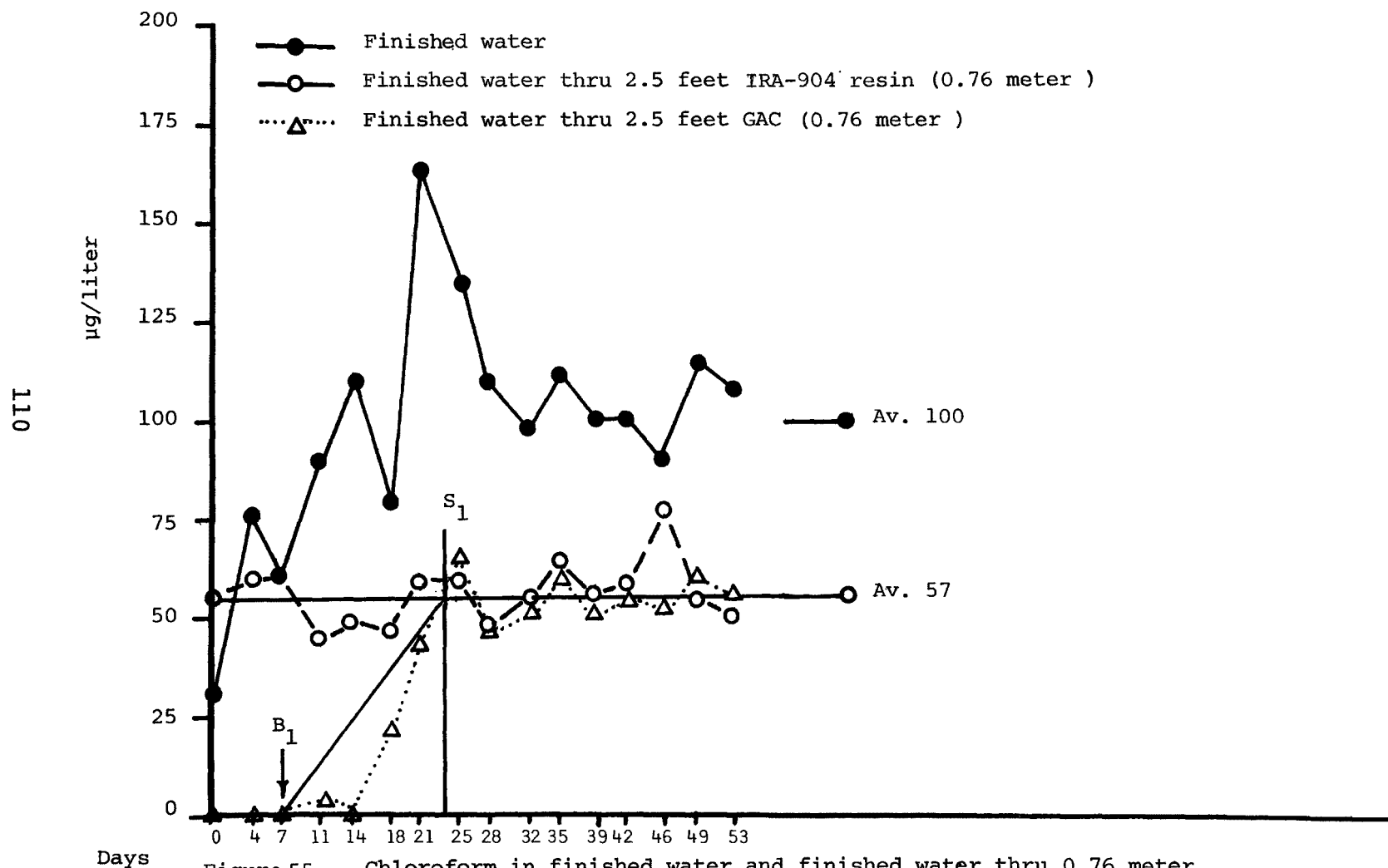


Figure 54. Chloroform in finished water and removal by 0.76 meter (2.5feet) of XE-340 (ED2).



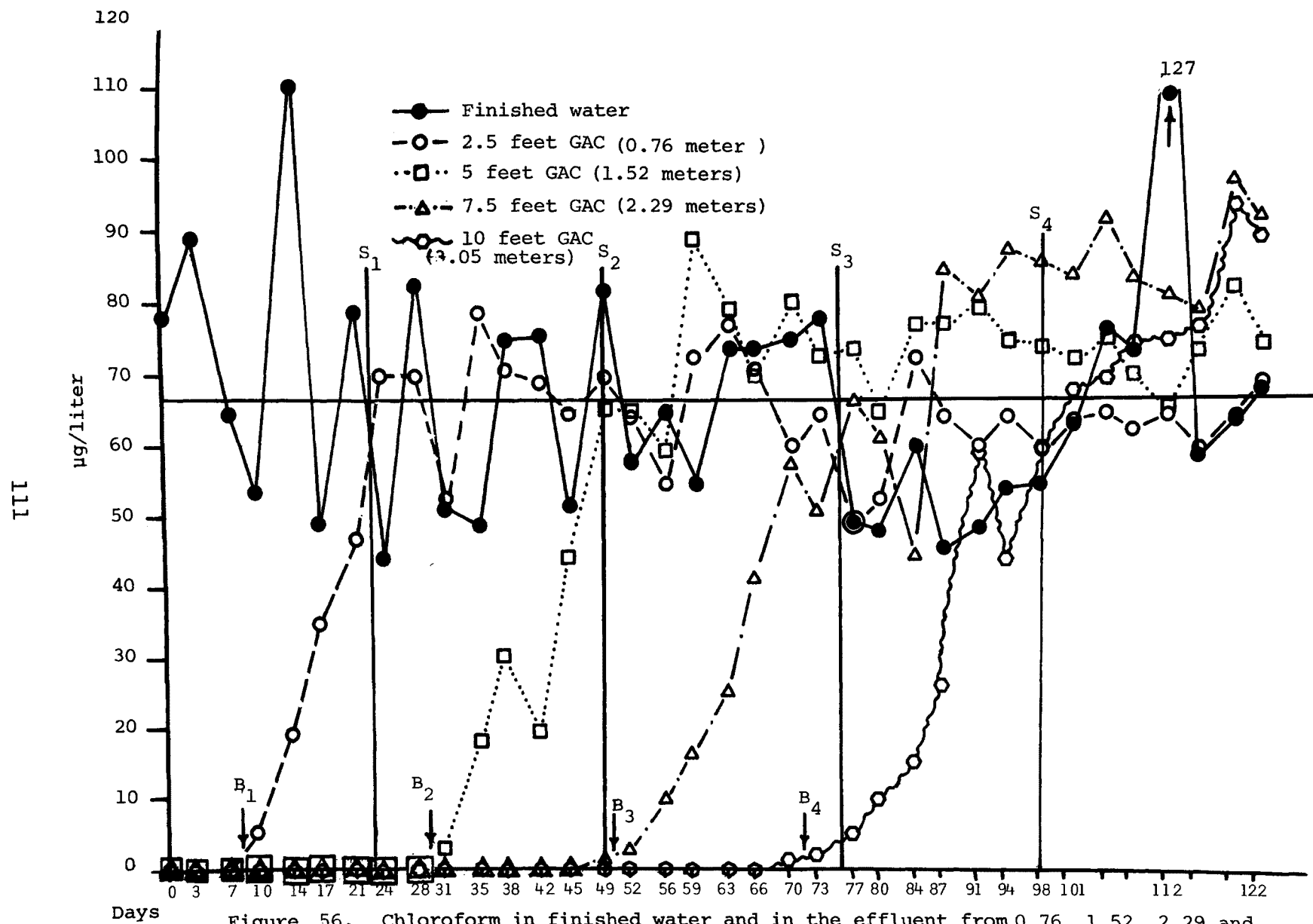


Figure 56. Chloroform in finished water and in the effluent from 0.76, 1.52, 2.29 and 3.05 meters (2.5, 5, 7.5 and 10 feet) of GAC (ED4).

Because the adsorptive capacity for GAC and XE-340 is dependent on influent concentration, the influent concentrations should be equal to compare the two adsorbents. If the three XE-340 data points for adsorptive capacity and influent concentration are plotted on a log-log scale, the resulting plot is a straight line. This also applies to our GAC data and to other HOC on both adsorbents. This straight line applies to the concentration range of interest in the particular water tested, and only when the total HOC profile varies in intensity, but not when there is a large change in the ratio of specific HOC. It appears that the raw, H.T. effluent, and finished water individually meet these requirements. However, the finished water location could not be compared to the H.T. or raw because the HOC ratios are not the same. Therefore, we can predict the adsorptive capacity at saturation for a specific HOC from the straight line plot for a given water. In this way, two adsorbents, or the same adsorbent run at times of different influent concentrations can be compared at the same concentration. An explanation of why these data points form a straight line on a log-log scale plot and why predictions can be made is presented in the section on the Polanyi Theory and Manes modifications, page 283.

Using the log-log straight line plot for XE-340, we can calculate the capacity at $67.3 \mu\text{g/L}$ and compare it directly with the value for GAC at $67.3 \mu\text{g/L}$ in ED4. For XE-340 at $67.3 \mu\text{g/L}$, the grams adsorbed per column is 0.458 and the cc's adsorbed per 100 grams is 0.144. The GAC data (ED4) in Table 25 shows that for 0.76 meter (2.5 feet) of GAC that the grams adsorbed per column is 0.094 and the cc's adsorbed per 100 grams is 0.0358. Therefore, XE-340 has 4.9 times (0.458 divided by 0.094) the adsorptive capacity for chloroform in our finished water as GAC per column where the volume of the two adsorbents are the same. XE-340 had 4 times (0.144 divided by 0.0358) the capacity of GAC, calculated on an equal weight basis of 100 grams of adsorbent. This information, the data in Table 25, and the individual breakthrough curves give a comprehensive view of chloroform adsorption in our system.

As shown in Table 25, the effect of IRA-904 resin on finished water was studied in ED3. The level of chloroform leaving the 0.76 meter (2.5 feet) deep column was 1.75 times the level entering. A possible explanation is that the resin was acting as a phase-transfer catalyst, accelerating the reaction of free chlorine with precursors to form HOC in the empty bed contact time of only 6.2 minutes. A review of phase-transfer catalysts is available from Aldrich Chemical Company (5).

During ED1R on H.T. water, the influent concentration to the XE-340 column for chloroform was $1.2 \mu\text{g/L}$ and the adsorptive capacity at saturation of XE-340 was 0.0027 cc per 100 grams (Table 19). The log-log straight line plot of XE-340 influent

concentration and adsorptive capacity for finished water predicts 0.004 cc per 100 grams for finished water. When extrapolated to 1.2 $\mu\text{g/L}$ using the log-log plot of finished water data. Based on the data in Table 5, during ED1R, chloroform was 3.8 percent of the total HOC in H.T. water and 45 percent of the total in finished water, (Table 6). Because of the higher ratio of competing HOC in H.T. water we would expect less chloroform adsorptive capacity in H.T. water. Thus, the observed 0.0027 cc value obtained on H.T. water is, as expected, less than the finished water predicted value of 0.004 cc. As previously mentioned, the ratio of specific HOC is an important factor in predicting performance under various conditions.

cis 1,2-Dichloroethene--Adsorption data appear in Table 26. Influent and adsorption from finished water curves appear in Figures 57, 58, 59, 60 and 61.

XE-340, 0.76 meter (2.5 feet) deep, was studied in ED1, ED1R and ED2. Column breakthrough and saturation time in ED1R and ED2 are almost identical. The column breakthrough reported in ED1 is questionable since no data points were taken between day 32 and 61 (Figure 57).

GAC, 0.76 meter (2.5 feet) deep, was studied in ED3 and ED4. Breakthrough and saturation times are very close in both ED, as shown in Table 26 and Figures 60 and 61. Using the log-log plot to compare GAC and XE-340 at the same influent concentration, at column saturation, XE-340 has an average of 3.1 times the capacity of GAC at equal volumes of adsorbent and an average of 2.5 times per 100 grams. Calculated at the same influent level of 21 $\mu\text{g/L}$, the adsorptive capacity of both GAC and XE-340 is approximately 30 percent less in finished water than it is in raw water. The TOC values for raw and finished water average approximately 8.5 and 5.7 mg/L respectively (Table 4). Again, one might expect somewhat increased capacity as the TOC values decrease. During ED1R the total HOC level in finished water was 159.6 $\mu\text{g/L}$ and cis 1,2-dichloroethene was only 10 percent of the total (Table 6) as compared to the previously stated 86.5 percent of the total HOC in the raw water for ED1R. The 30 percent reduction in capacity in finished water probably was due to the competitive adsorption of other HOC.

As was seen with chloroform, the adsorptive capacity of GAC for cis 1,2-dichloroethene appeared to increase slightly per 100 grams of GAC as the bed depth increased. The IRA-904 resin removed no cis 1,2-dichloroethene from H.T. or finished water and none was generated.

Bromodichloromethane--Finished water adsorption data appear in Table 27. Curves appear in Figures 62, 63, 64, 65 and 66.

TABLE 26 . cis 1,2-DICHLOROETHENE ADSORPTION DATA FROM FINISHED WATER

ED	Bed Depth Feet	Adsorbent	Average Influent µg/L	Column Breakthrough Days	Column Saturation Days	M _T N Inch	Test Duration Days	Total Entering Each Column During Test Grams	Total Adsorbed by Each Column at End of Test Grams	Adsorbed by Each Column at Saturation Grams	Adsorbed at End of Test %	Adsorbed at Saturation %	Adsorption per 100 gms. Adsorbent at End of Test Grams	Adsorption per 100 gms. Adsorbent at Saturation Grams	CC
1	2.5	XE-340	10.9	617	128	16	117	.114	.091	.092	80	74	.042	.043	.003
1R	2.5	XE-340	19.4	38	191	24	122	.206	.166	.2	81	60	.077	.093	.0724
2	2.5	XE-340	18.4	38	190	24	63	.1035	.099	.187	96	60	.046	.087	.068
3	2.5	GAC	18.3	18	53	20	53	.0867	.058	.058	67	66	.033	.033	.0257
3	2.5	904	18.3	no adsorption			53	.09	0		0		0		
4	2.5	GAC	19.9	17	66	22	122	.217	.073	.073	34	63	.039	.039	.03
4	5	GAC	19.9	59	119	30	122	.217	.159	.159	73	75	.045	.045	.035
4	7.5	GAC	19.9	101	171	37	122	.217	.212	.242	98	79	.0458	.0458	.0357
4	10	GAC	19.9	none			122	.217	.217		100		.031		
2.5	feet=0.76 meter			5	feet=1.52 meters		7.5	feet=2.29 meters		10	feet=3.05 meters				

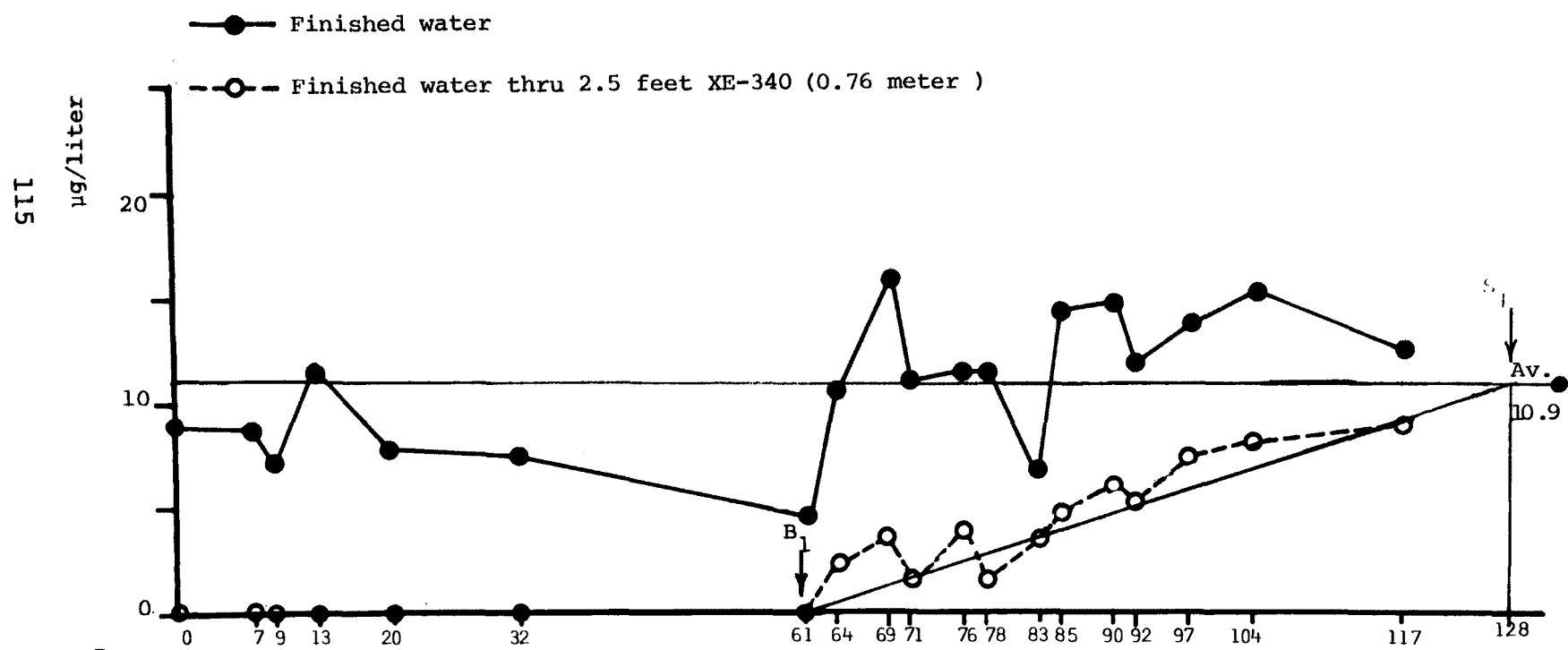


Figure 57. cis 1,2-Dichloroethene in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1).

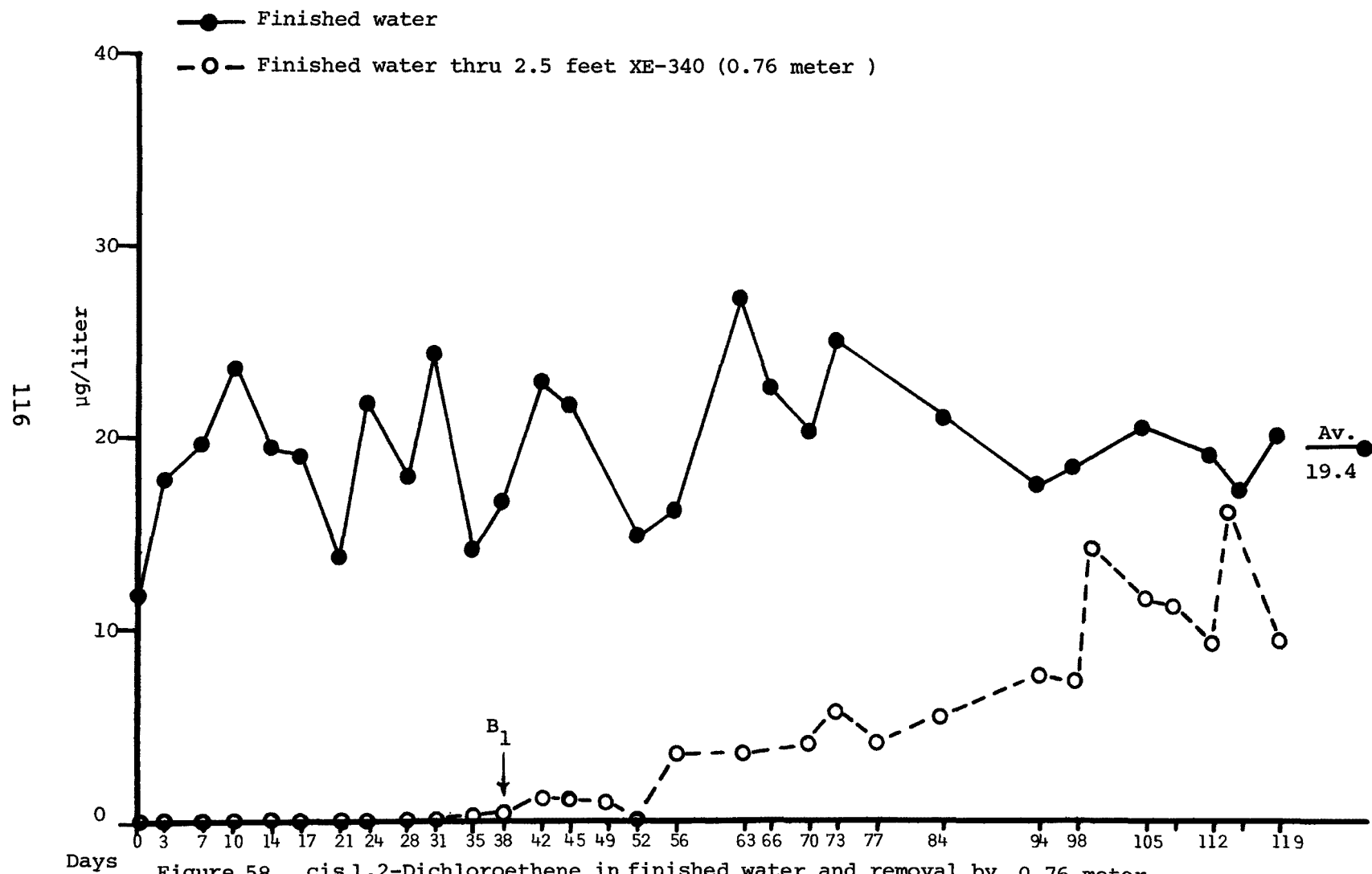


Figure 58. cis 1,2-Dichloroethene in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

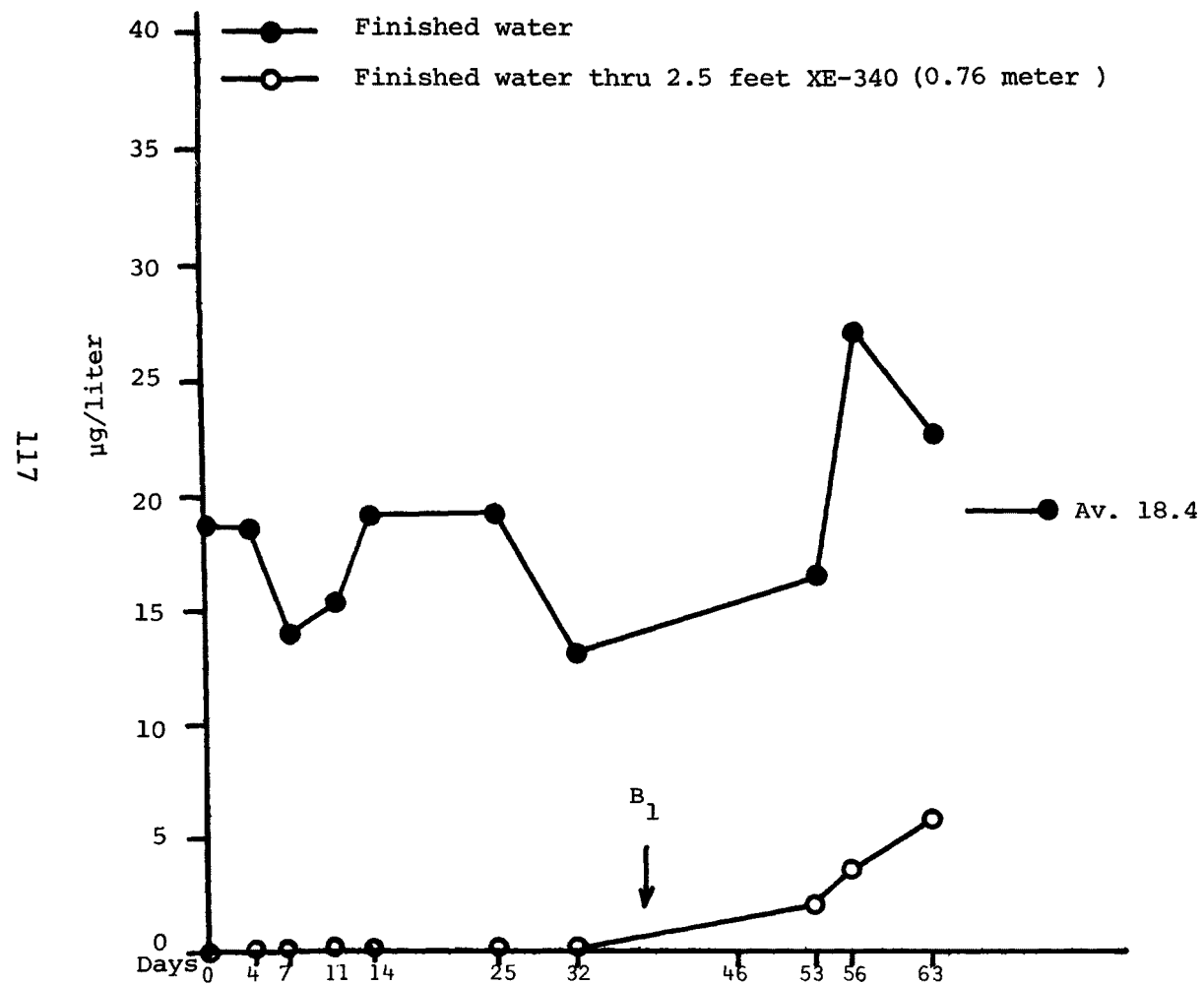


Figure 59. cis 1,2- Dichloroethene in finished water and removal by 0.76 meter (2.5 feet) XE-340 (ED2).

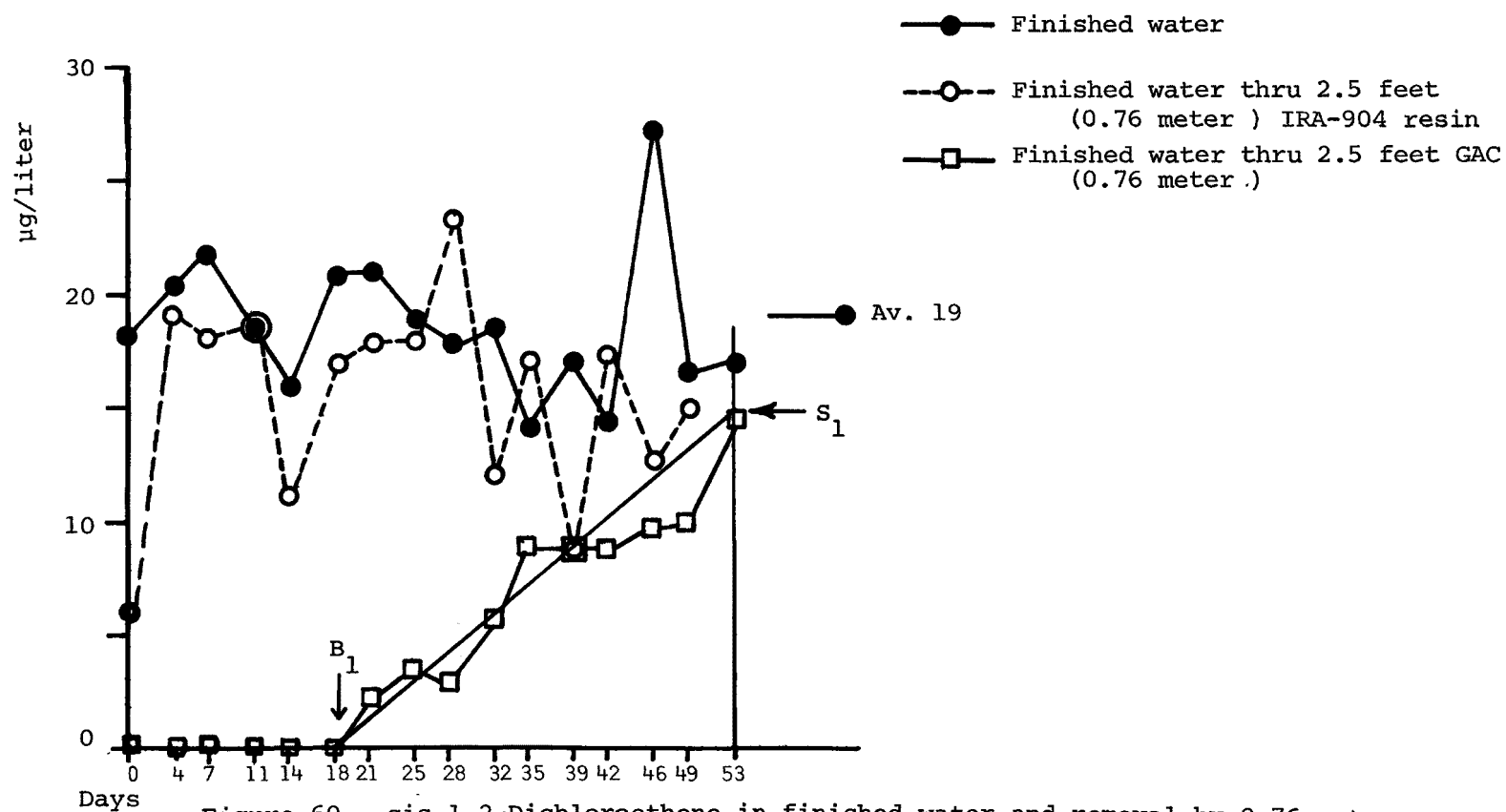


Figure 60. cis 1,2-Dichloroethene in finished water and removal by 0.76 meter (2.5 feet) of GAC and 0.76 (2.5 feet) of IRA-904 resin (ED3).

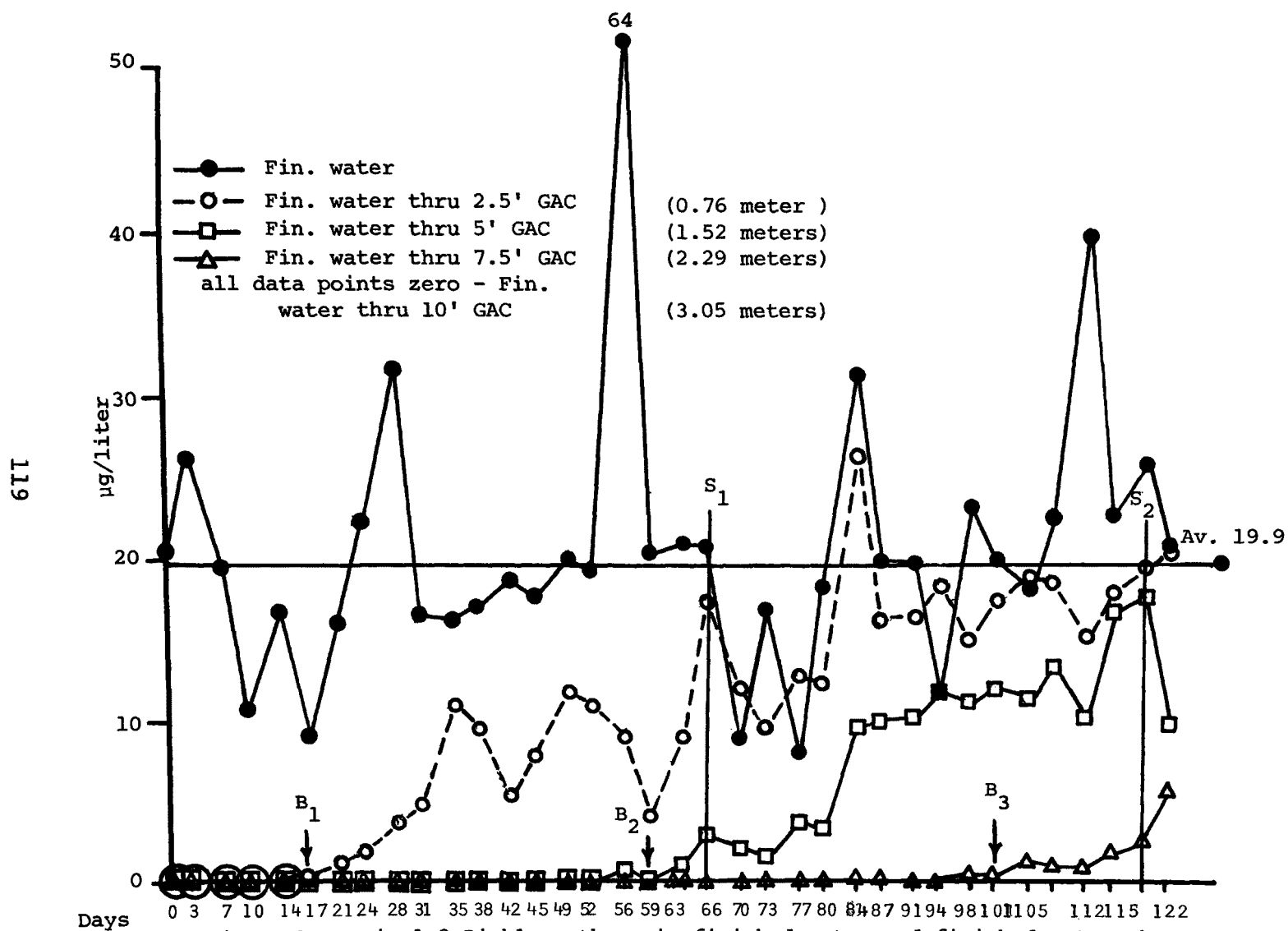


Figure 61. cis 1,2-Dichloroethene in finished water and finished water thru 0.76, 1.52, 2.29 and 3.05 meters (2.5, 5, 7.5 and 10 feet) of GAC (ED4).

TABLE 27. BROMODICHLOROMETHANE ADSORPTION DATA FROM FINISHED WATER

ED	Bed Depth Feet	Adsorbent	Average Influent µg/L	Column Breakthrough Days	Column Saturation Days	MT N Inch	Test Duration Days	Total Entering Each Column During Test Grams	Total Adsorbed by Each Column at End of Test Grams	Adsorbed by Each Column at Saturation Grams	% Adsorbed at End of Test %	% Adsorbed at Saturation %	Adsorption per 100 gms. Adsorbent at End of Test Grams	Adsorption per 100 gms. Adsorbent at Saturation Grams	CC
1	2.5	XE-340	37.1	20	216	27	117	.388	.301	.391	78	55	.14	.182	.0907
1R	2.5	XE-340	42.7	20	210	27	122	.465	.36	.439	77	54	.167	.204	.1017
2	2.5	XE-340	42.4	22	can't extrap.		63	.239	.225		94		.105		
3	2.5	GAC	39	16	53	21	53	.185	.121	.121	65	65	.069	.069	.0344
3	2.5	904	39				53	average increase of 1.13X							
4	2.5	GAC	47	14	56	22.5	122	.512	.147	.147	29	63	.084	.084	.0419
4	5	GAC	47	42	98	34.3	122	.512	.293	.293	57	71	.083	.083	.0414
4	7.5	GAC	47	73	139	42.7	122	.512	.444	.444	87	76	.084	.084	.0419
4	10	GAC	47	105	can't extrap.		122	.512	.51		99		.072		
2.5	feet=0.76 meter			5	feet=1.52 meters		7.5	feet=2.29 meters		10	feet=3.05 meters				

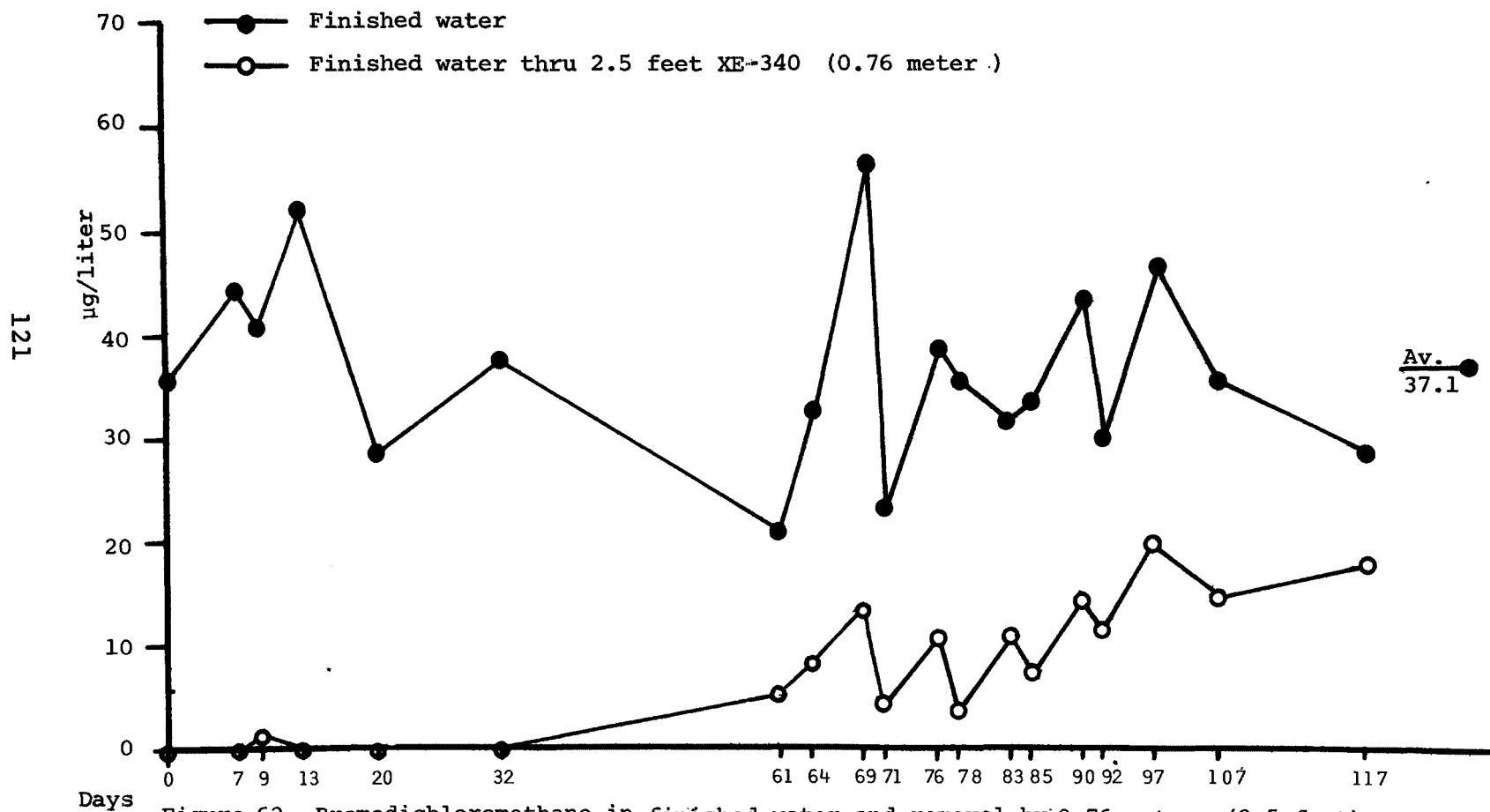


Figure 62. Bromodichloromethane in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1).

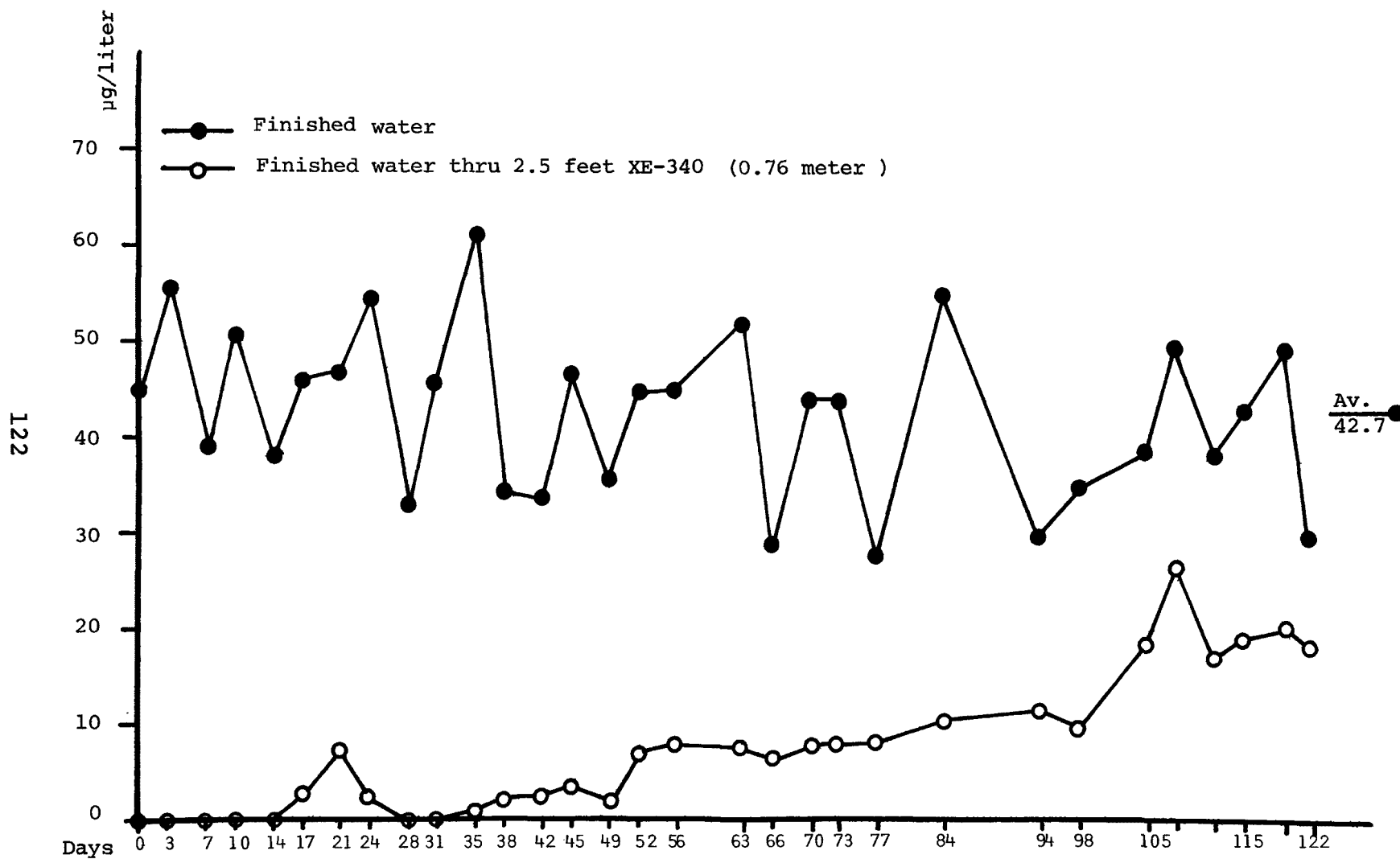


Figure 63. Bromodichloromethane in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

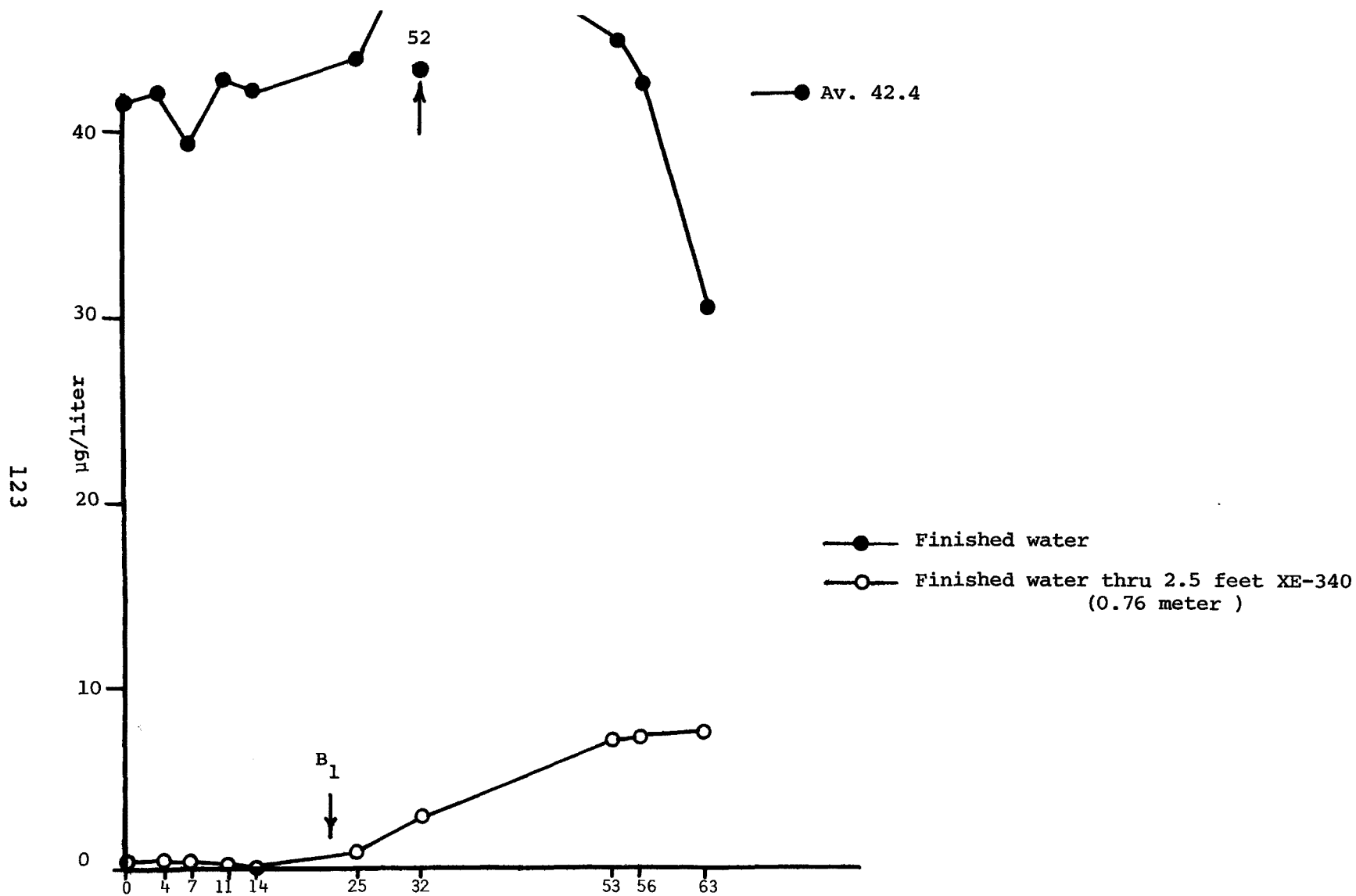


Figure 64. Bromodichloromethane in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED2).

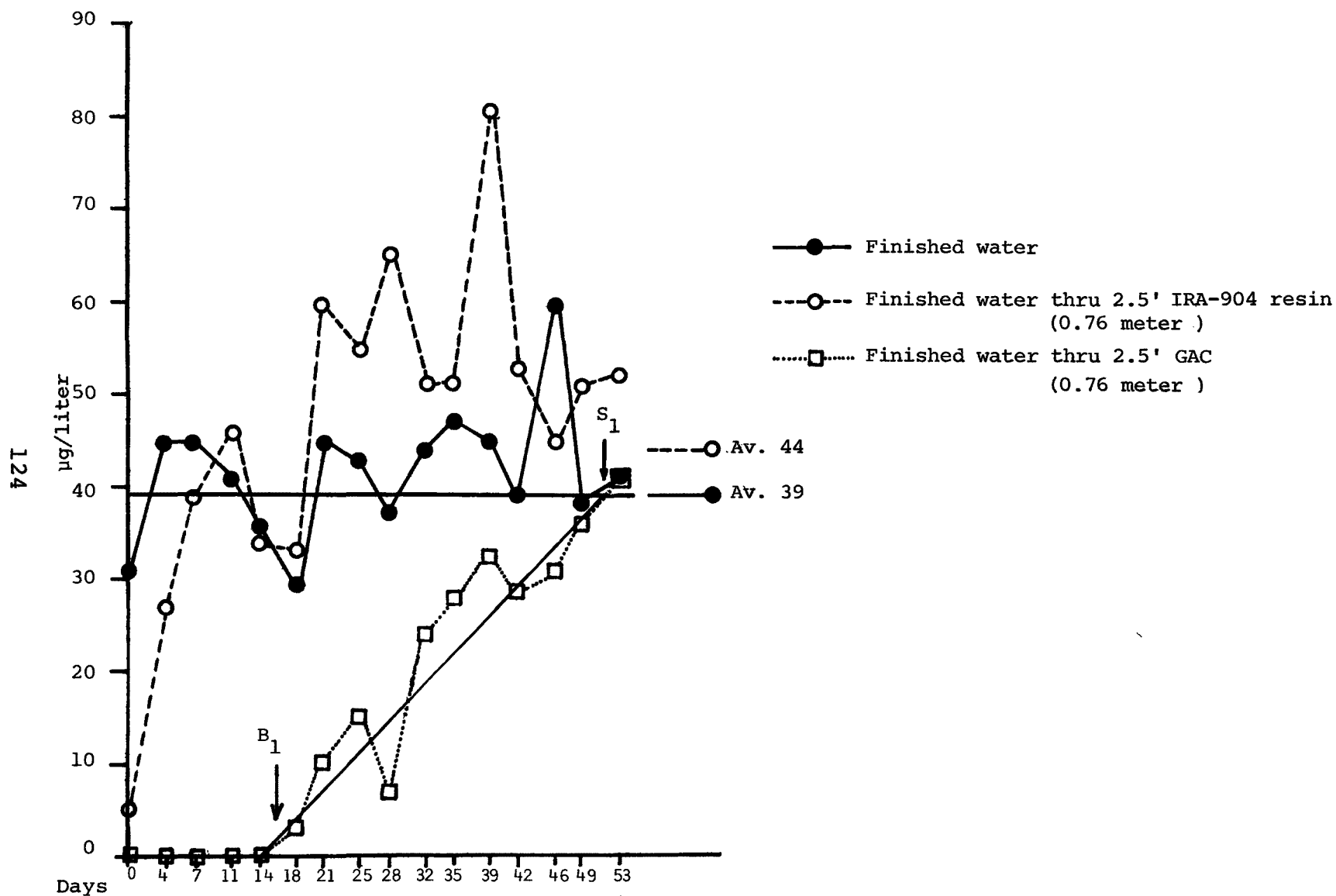


Figure 65. Bromodichloromethane in finished water and removal by 0.76 meter (2.5 feet) of GAC and 0.76 meter (2.5 feet) of IRA-904 resin (ED3).

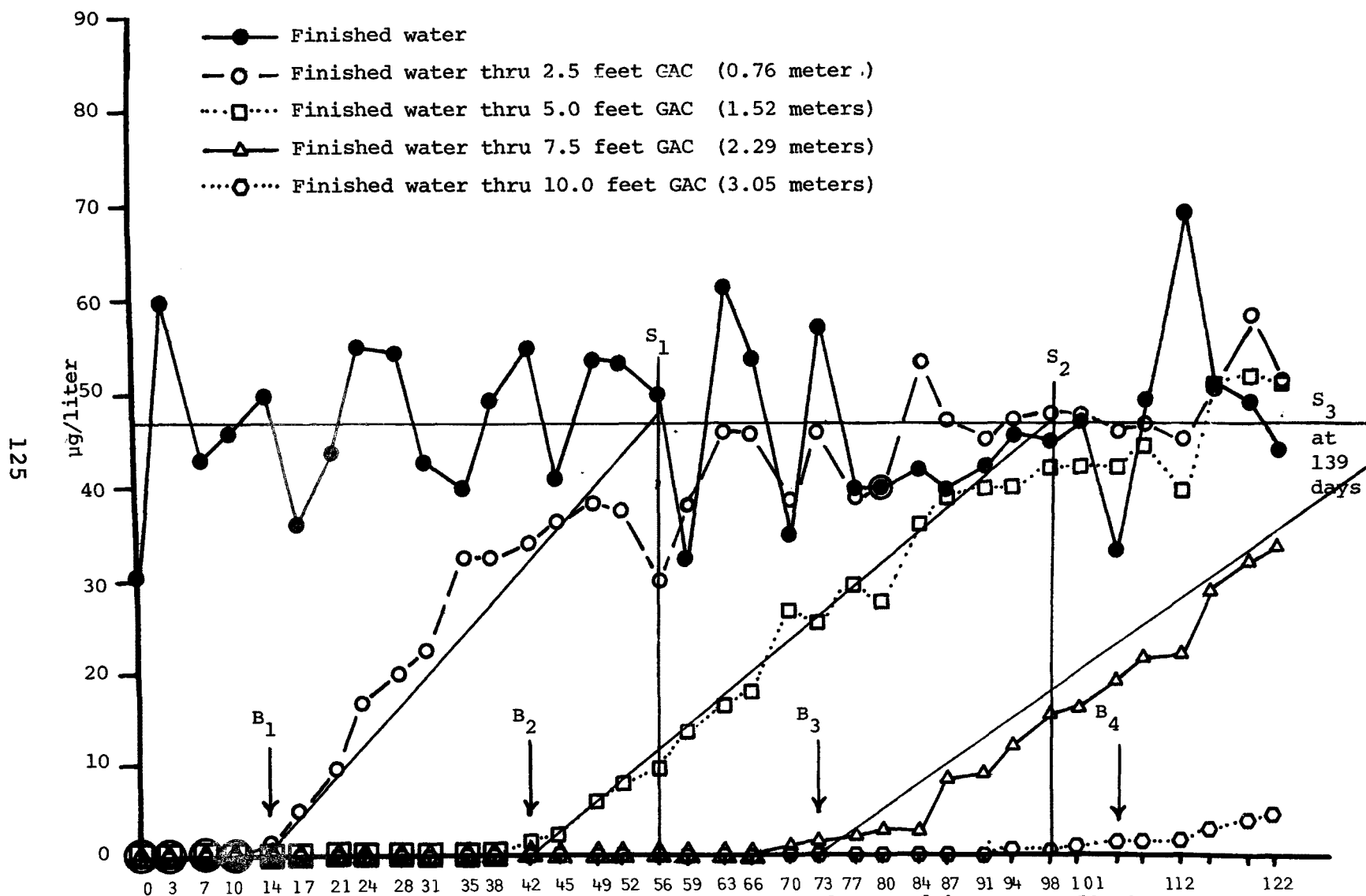


Figure 66. Bromodichloromethane in finished water and removal by 0.76, 1.52, 2.29 and 3.05 meters (2.5, 5, 7.5 and 10 feet) of GAC (ED4).

On finished water, calculated at the same influent concentration of 39 $\mu\text{g/L}$, XE-340 had 3.4 times the capacity of GAC per column and 2.8 times per 100 grams. It appears that for both GAC and XE-340 the tests with higher influent concentrations yielded higher amounts of bromodichloromethane adsorbed than the tests with lower influent concentrations as expected and demonstrated throughout for all substances. The adsorptive capacity per 100 grams of GAC did not appear to change as the GAC bed depth increased. Initial breakthrough of bromodichloromethane occurred in all runs on GAC and XE-340, but saturation was not always reached. The IRA-904 resin caused an increase of 1.13 times the influent level.

Chlorodibromomethane--Adsorption data appear in Table 28. Curves appear in Figures 67, 68, 69, 70, and 71.

On finished water at calculated equal influent concentrations, XE-340 had 3.0 times the capacity of GAC per column and 2.5 times per 100 grams. There appeared to be no change in capacity of GAC at 0.76 meter (2.5 feet) and 1.52 meters (5.0 feet) of depth. The IRA-904 resin did not reduce or increase the level of chlorodibromomethane in finished water.

Bromoform--Adsorption data appear in Table 29. Curves appear in Figures 72, 73, 74, 75, and 76.

Saturation by bromoform from finished water was not reached consistently on XE-340. Saturation was reached in 0.76 meters (2.5 feet) of GAC, but not in deeper GAC beds. There was no removal and no increase of bromoform by the IRA-904 resin in finished water.

Vinyl chloride--Adsorption data appear in Table 30. Curves appear in Figures 77, 78, 79, 80, and 81.

The curves for ED1R appear in Figure 77. The influent average from day 94 to day 122 was 0.55 $\mu\text{g/L}$. The average effluent from the 0.76 meter (2.5 feet) deep XE-340 column was 0.4 $\mu\text{g/L}$. As discussed on H.T. water, it is questionable whether these figures represent adsorption. If adsorption did occur, 27 percent was removed.

In ED2, the curves in Figure 78 show that column breakthrough occurred very early. Since samples were taken at 0 days and 4 days, we show a figure of 2 days for breakthrough.

In ED3, the curves in Figure 79 show that the vinyl chloride effluent from a 0.76 meter (2.5 feet) deep IRA-904 resin column averaged 3.9 $\mu\text{g/L}$ over the test period. The influent average was 5.4 $\mu\text{g/L}$. Based on our other IRA-904 resin data with other HOC, we do not believe that this represents any adsorption. In Figure 79, the average level of effluent from a 0.76 meter

TABLE 28. CHLORODIBROMOMETHANE ADSORPTION DATA FROM FINISHED WATER

ED	Bed Depth Feet	Adsorbent	Average Influent µg/L	Column Breakthrough Days	Column Saturation Days	MT N Inch	Test Duration Days	Total Entering Each Column During Test Grams	Total Adsorbed by Each Column at End of Test Grams	Adsorbed by Each Column at Saturation Grams	% Adsorbed at End of Test %	% Adsorbed at Saturation %	Adsorption per 100 gms. Adsorbent at End of Test Grams	Adsorption per 100 gms. Adsorbent at Saturation Grams	CC
1	2.5	XE-340	12	47	260	25	117	.125	.109	.165	87	59	.053	.077	.031
1R	2.5	XE-340	24.5	45	260	25	122	.267	.239	.334	89	59	.111	.155	.063
2	2.5	XE-340	26.7	25	can't extrap		63	.15	.149		99		.07		
3	2.5	GAC	27	21	76	21.7	53	.128	.105	.117	82	64	.06	.067	.027
3	2.5	904	27	no adsorption			53	no increase			0				
4	2.5	GAC	33.6	21	101	23.8	122	.366	.183	.183	50	60	.104	.104	.042
4	5	GAC	33.6	59	174	39.7	122	.366	.349	.349	95	67	.1	.1	.041
4	7.5	GAC	33.6	98	can't extrap		122	.366	.364	can't extrap	99		.069		
4	10	GAC	33.6	none			122	.366	.366		100		.038		
2.5	feet=0.76	meter		5	feet=1.52	meters	7.5	feet=2.29	meters	10	feet=3.05	meters			

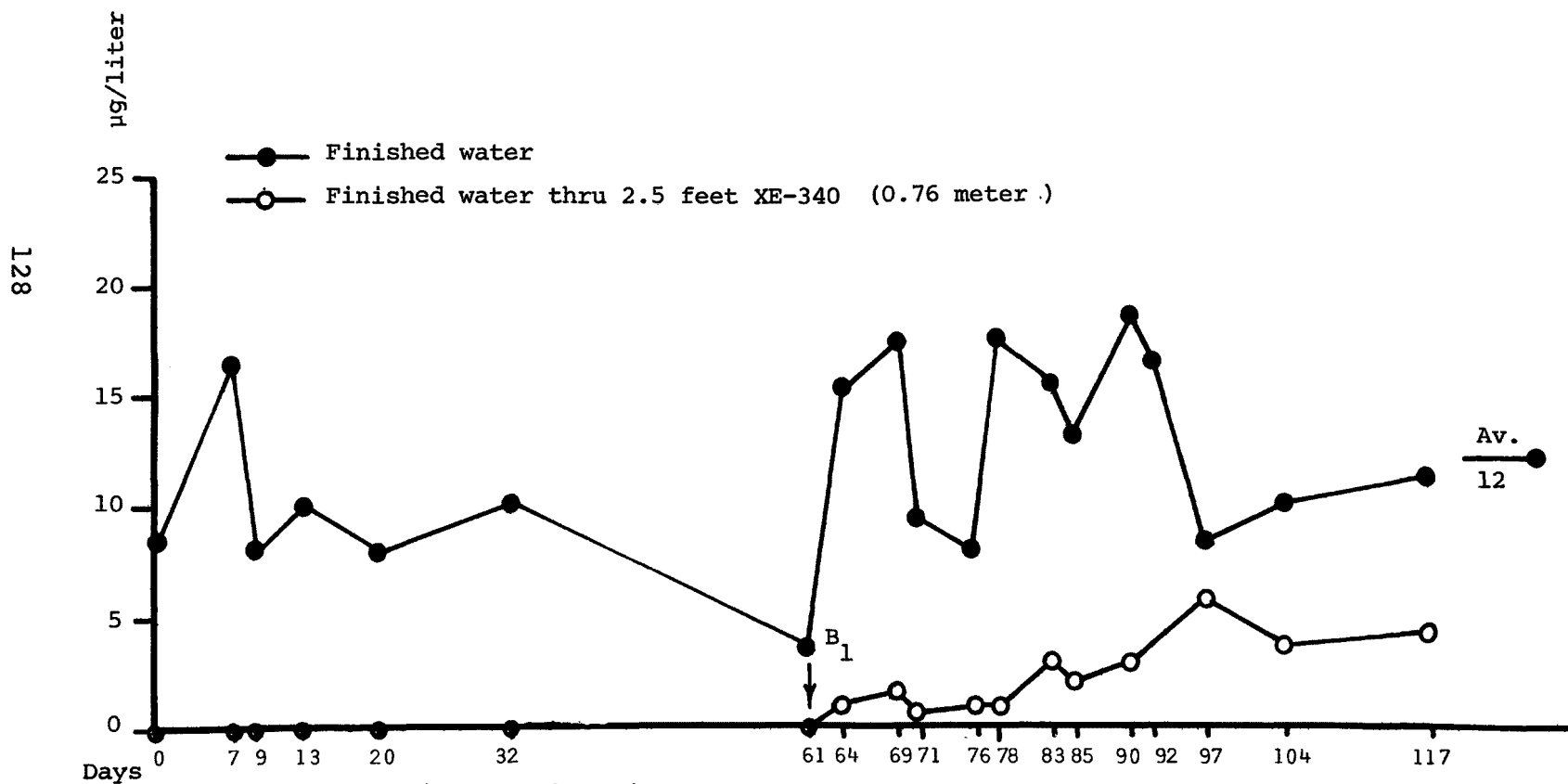


Figure 67. Chlorodibromomethane in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1).

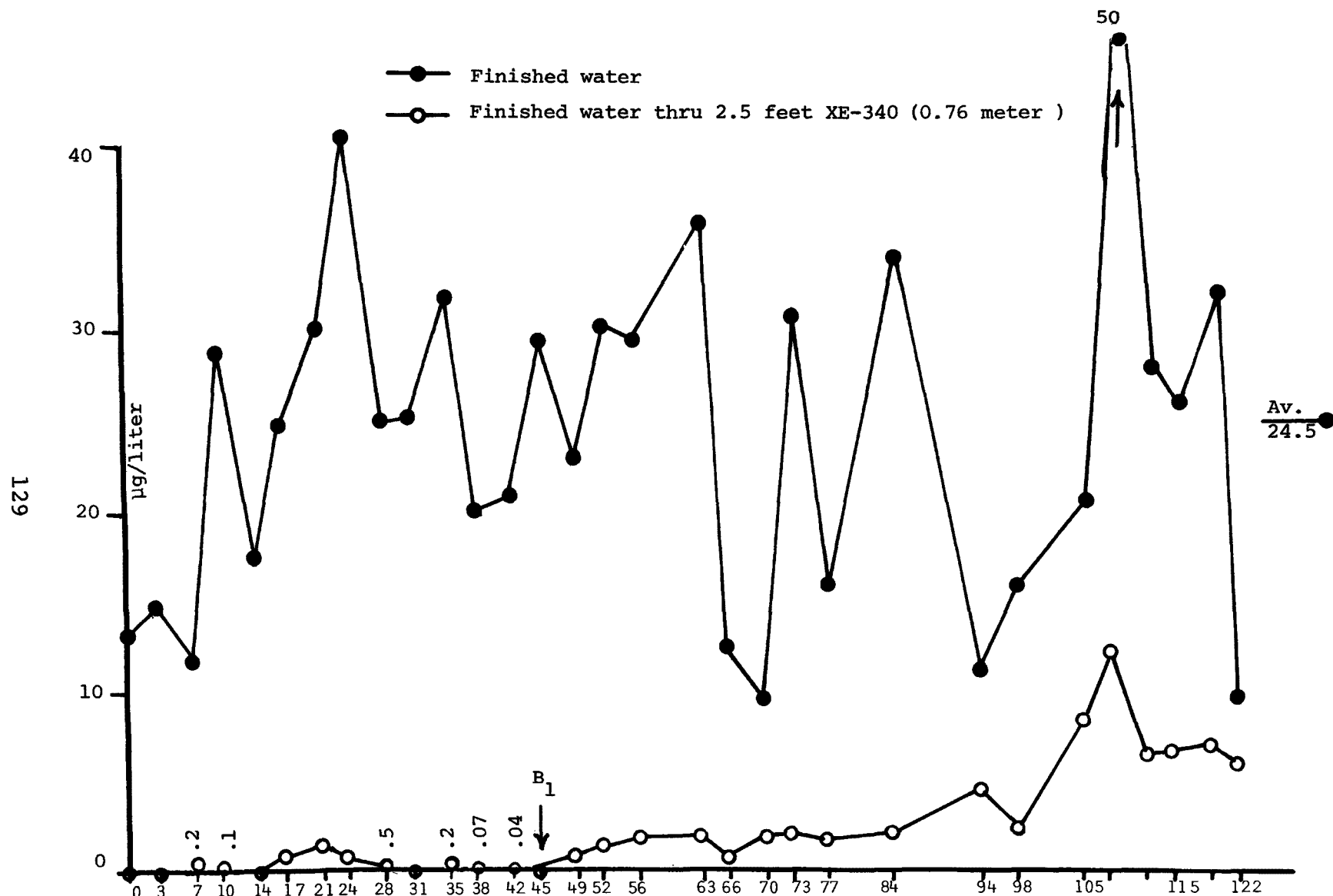


Figure 68. Chlorodibromomethane in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

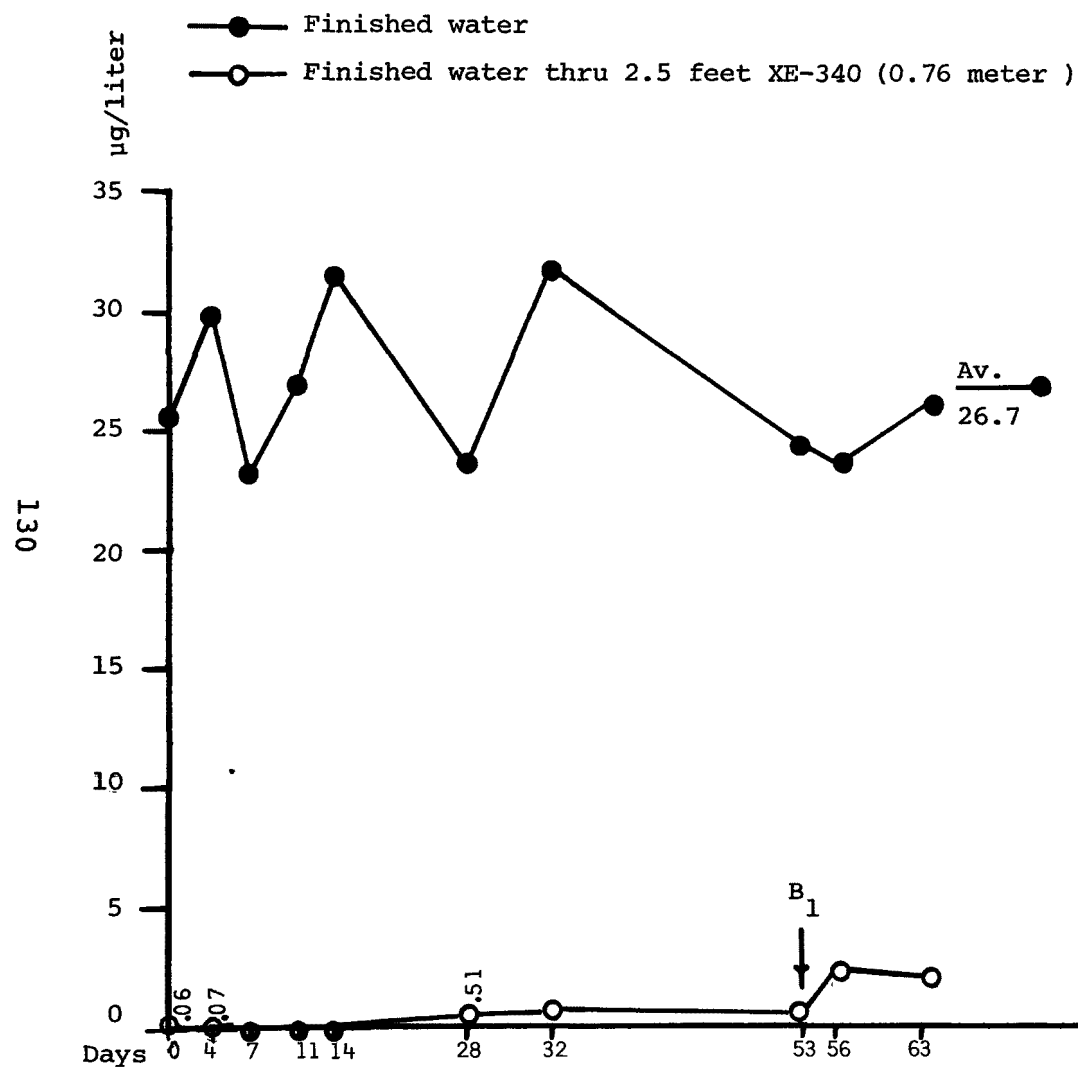


Figure 69. Chlorodibromomethane in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED2).

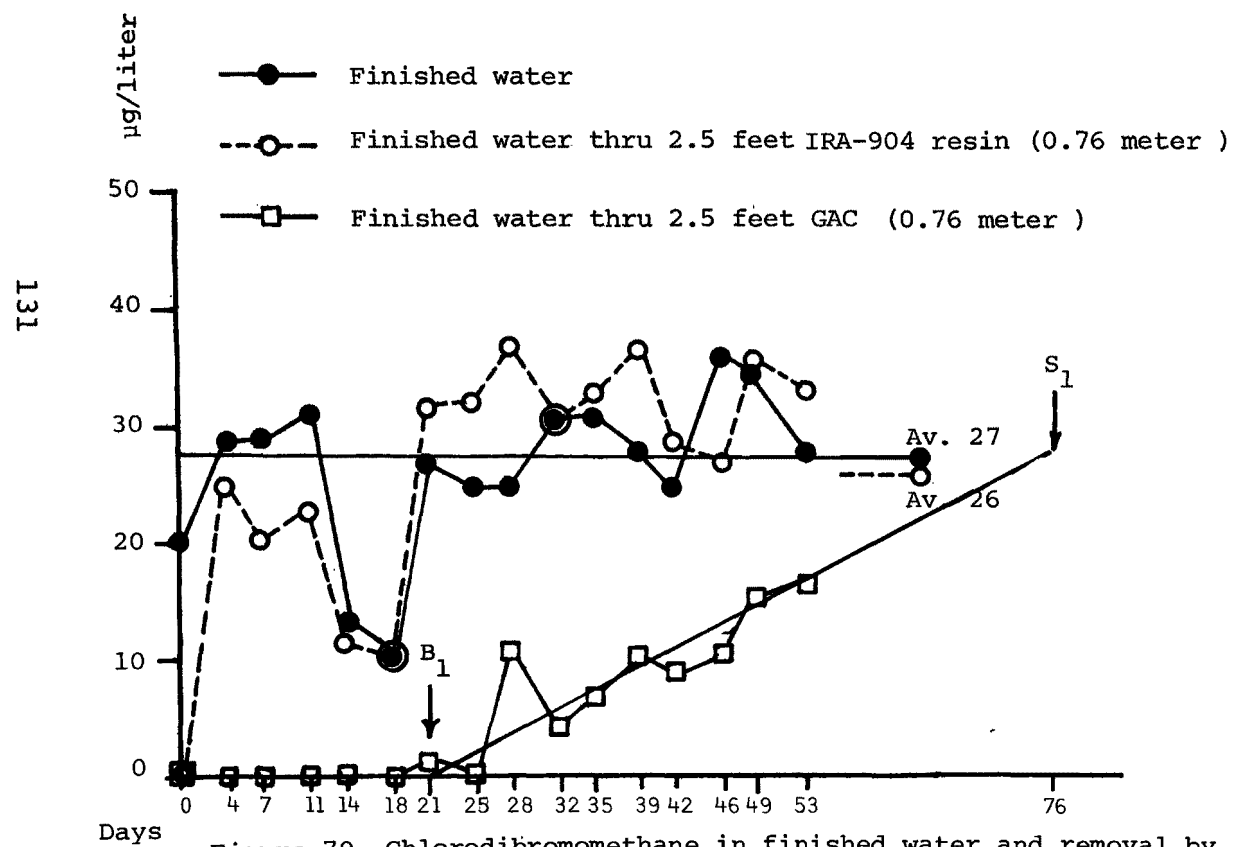


Figure 70. Chlorodibromomethane in finished water and removal by 0.76 meter (2.5 feet) of IRA-904 resin and 0.76 meter (2.5 feet) of GAC (ED3).

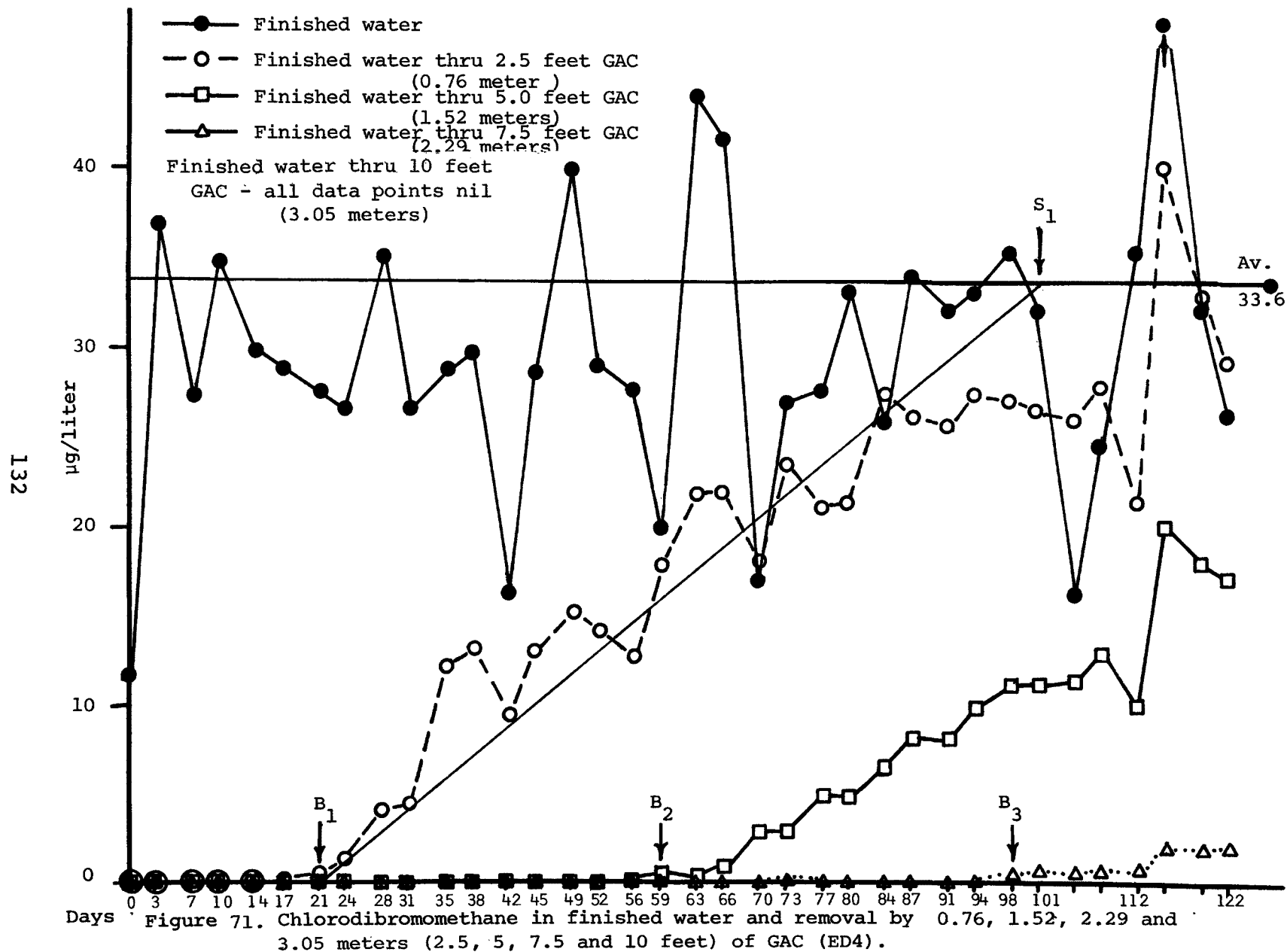


TABLE 29. BROMOFORM ADSORPTION DATA FROM FINISHED WATER

ED	Bed Depth Feet	Adsorbent	Average Influent ug/L	Column Breakthrough Days	Column Saturation Days	MT N Inch	Test Duration Days	Total Entering Each Column During Test Grams	Total Adsorbed by Each Column at End of Test Grams	Adsorbed by Each Column at Saturation Grams	% Adsorbed at End of Test %	% Adsorbed at Saturation %	Adsorption per 100 gms. Adsorbent at End of Test Grams	Adsorption per 100 gms. Adsorbent at Saturation Grams	CC
1	2.5	XE-340	.1?				117								
1R	2.5	XE-340	1.9	?			122								
2	2.5	XE-340	1.91	63	can't extrap		63	.0108	.0108		100		.005		
3	2.5	GAC	2.5	none			53	.012	.012		100		.007		
3	2.5	904	2.5				53	no increase - no removal			0				
4	2.5	GAC	2.5	42	94	16.6	122	.027	.0152	.013	56	72	.0071	.00605	.0021
4	5	GAC	2.5	91	can't extrap		122	.027	.0265		98		.0075		
4	7.5	GAC	2.5	none			122	.027	.027		100		.005		
4	10	GAC	2.5	none			122	.027	.027		100		.004		
2.5 feet=0.76 meter		5 feet= 1.52 meters		7.5 feet=2.29 meters		10 feet=3.05 meters									

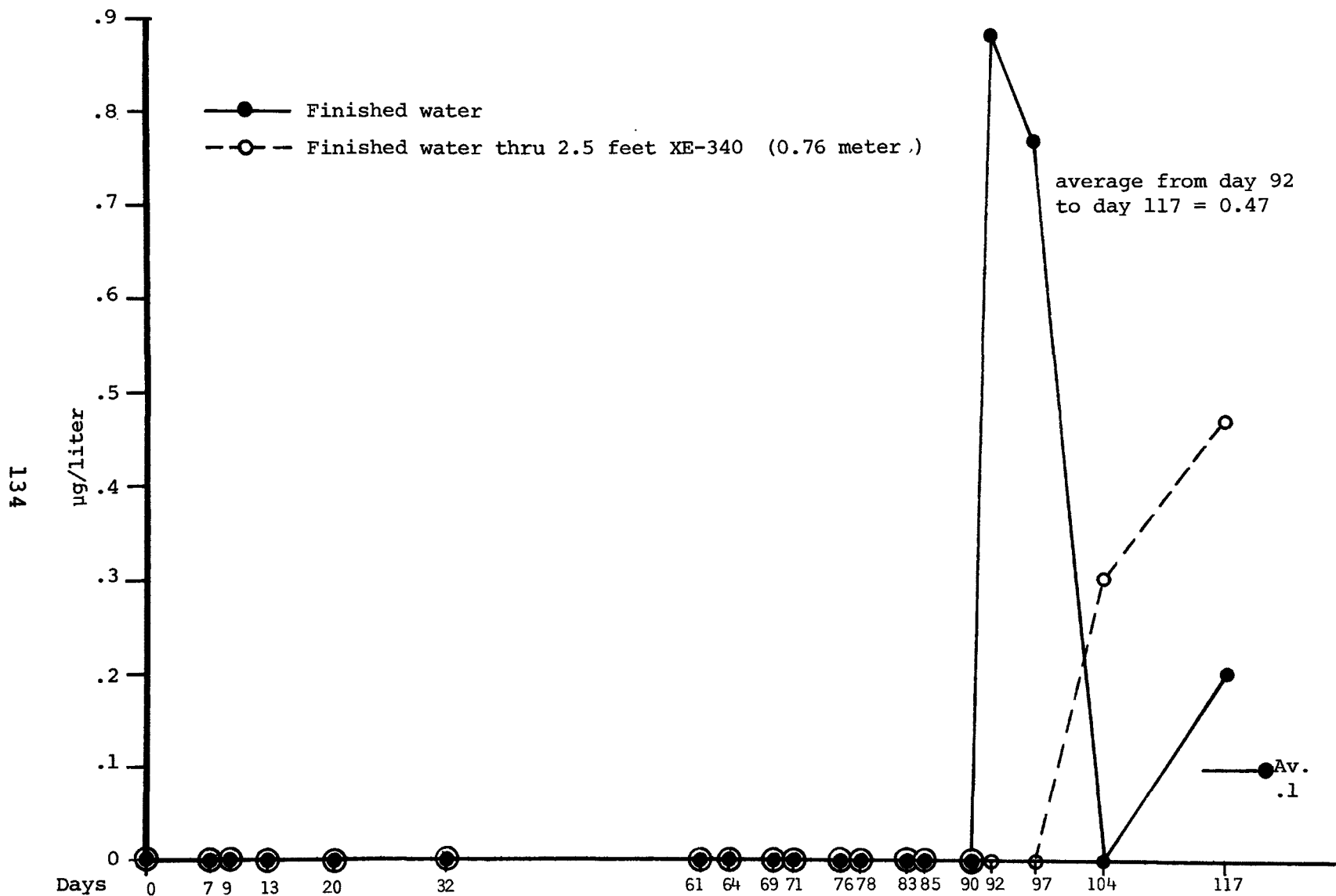


Figure 72. Bromoform in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1).

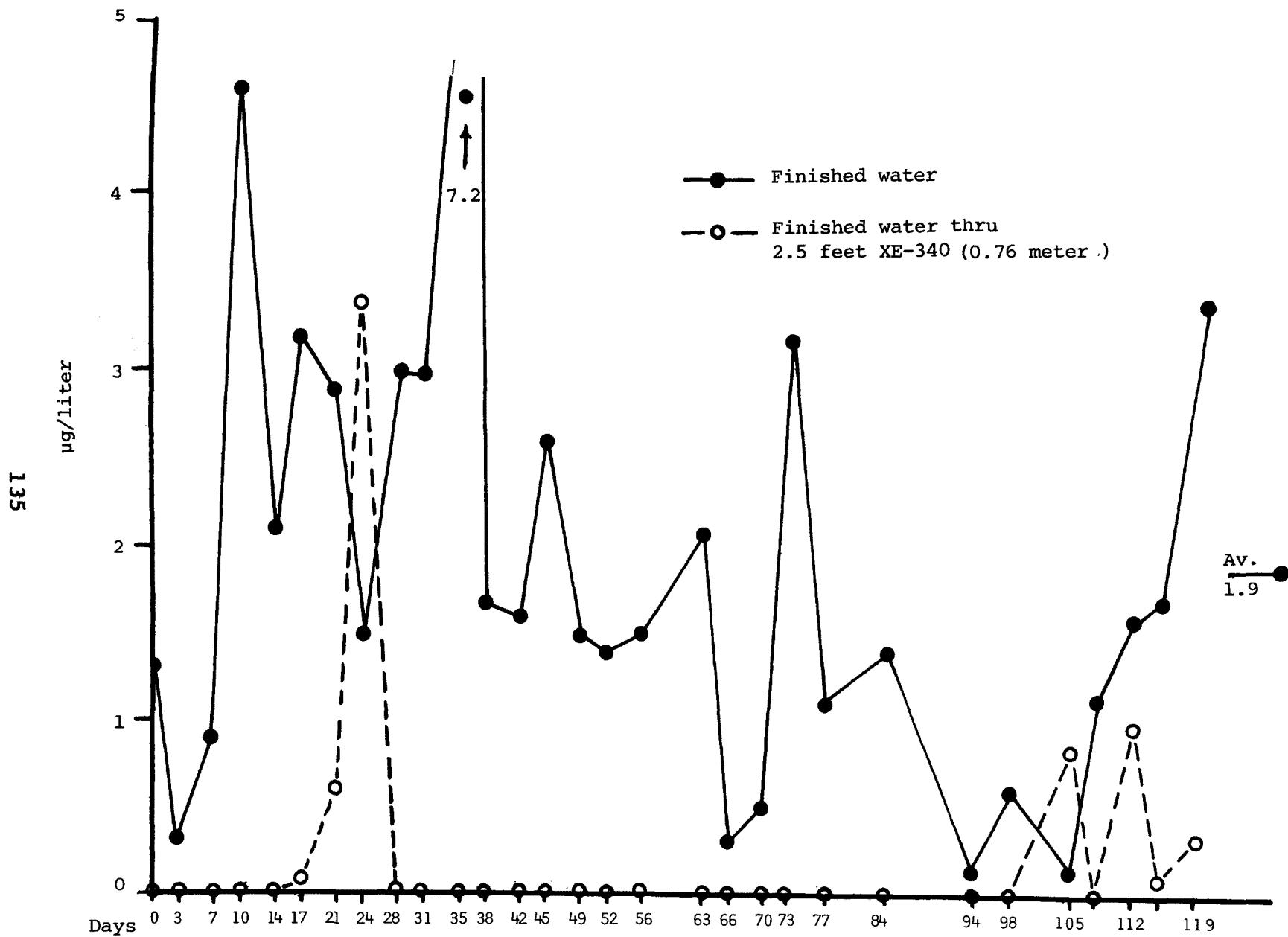


Figure 73. Bromoform in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

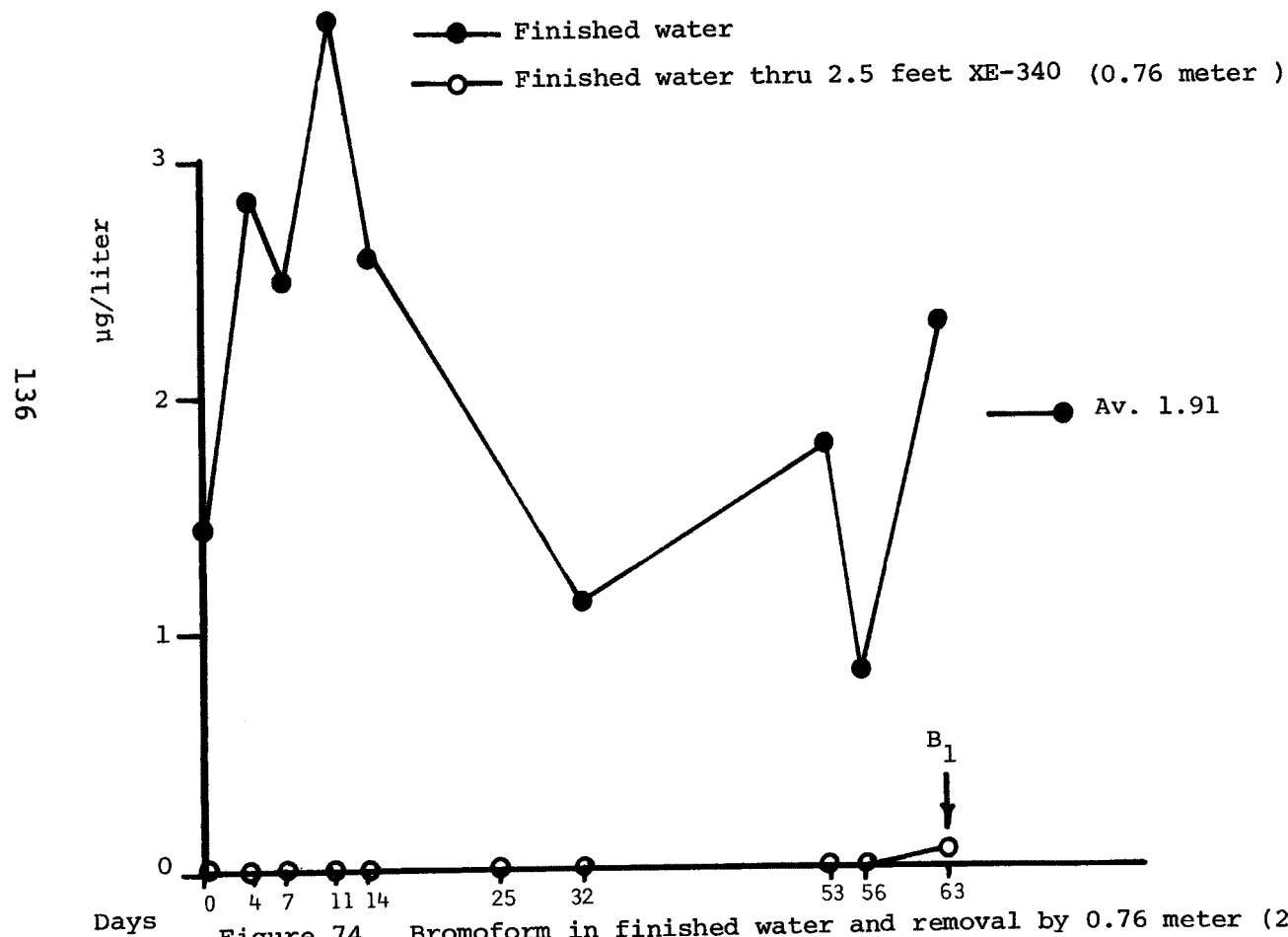


Figure 74. Bromoform in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED2).

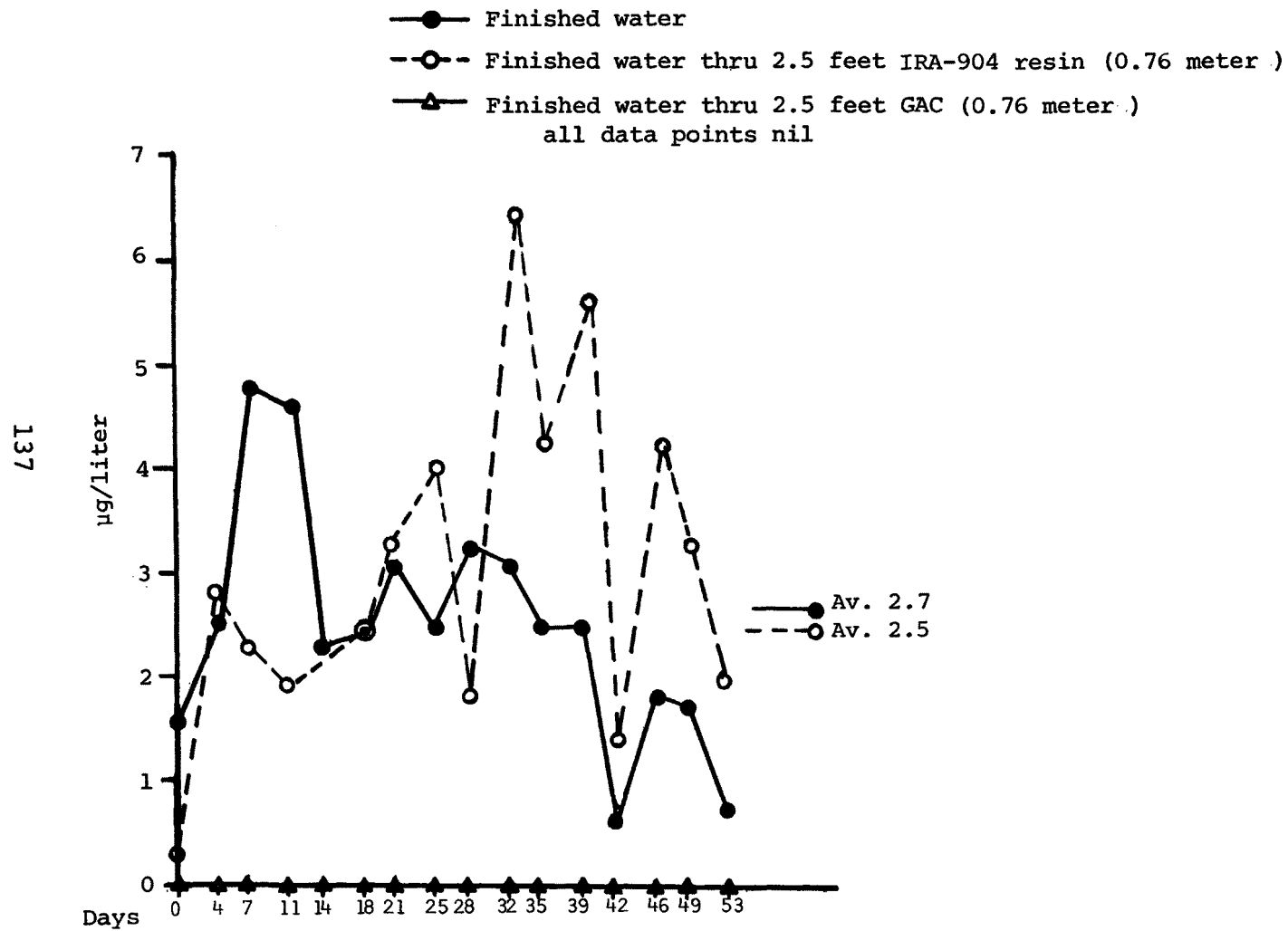


Figure 75. Bromoform in finished water and removal by 0.76 meter (2.5 feet) of GAC and 0.76 meter (2.5 feet) of IRA-904 resin (ED3).

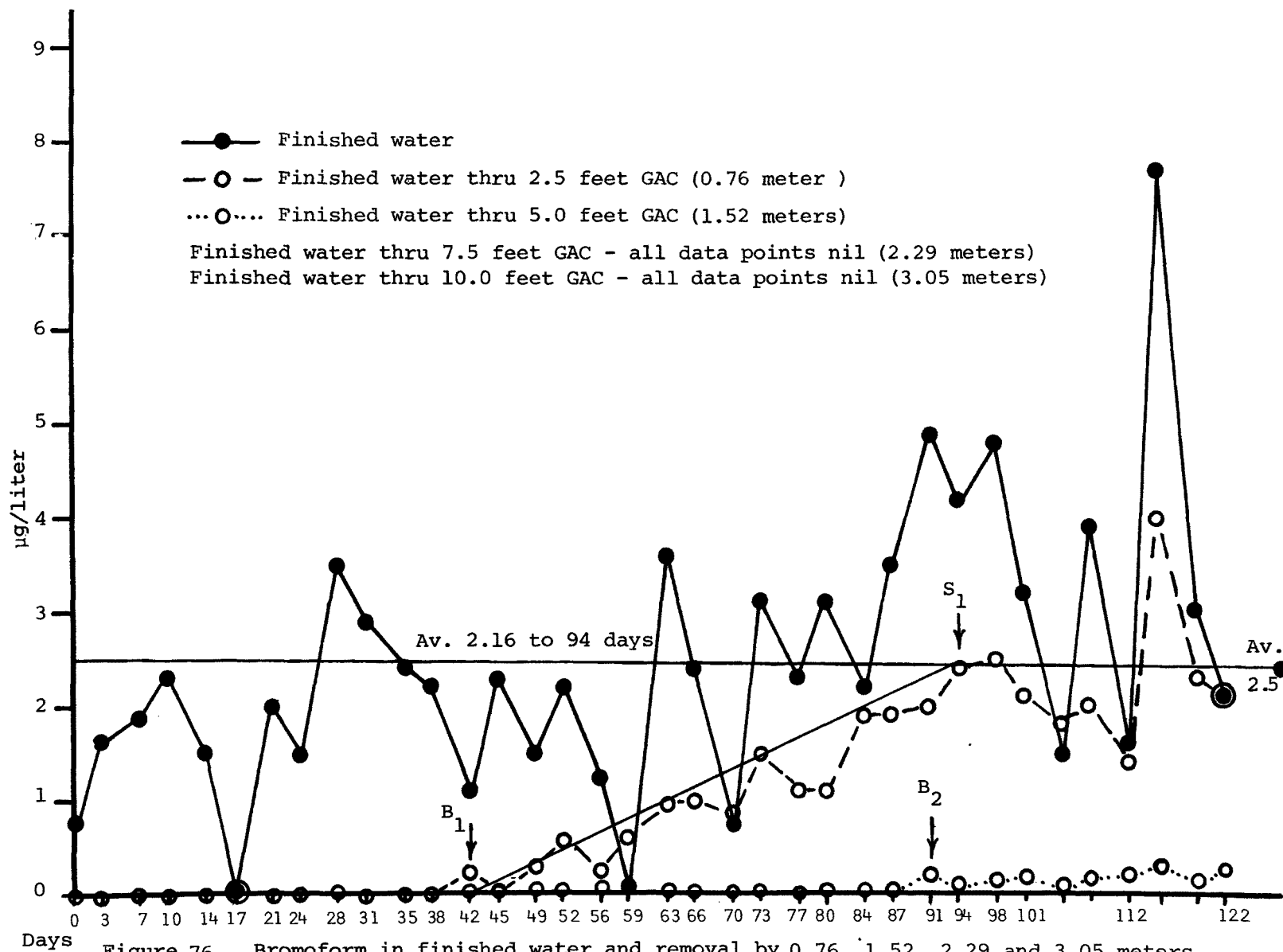


Figure 76. Bromoform in finished water and removal by 0.76, 1.52, 2.29 and 3.05 meters (2.5, 5, 7.5 and 10 feet) of GAC (ED4).

TABLE 30 . VINYL CHLORIDE ADSORPTION DATA FROM FINISHED WATER

ED	Bed Depth Feet	Adsorbent	Average Influent µg/L	Column Breakthrough Days	Column Saturation Days	MT N Inch	Test Duration Days	Total Entering Each Column During Test Grams	Total Adsorbed by Each Column at End of Test Grams	Adsorbed by Each Column at Saturation Grams	% Adsorbed at End of Test %	% Adsorbed at Saturation %	Adsorption per 100 gms. Adsorbent at End of Test Grams	Adsorption per 100 gms. Adsorbent at Saturation Grams	CC
1R	2.5	XE-340	.55				122	.0014							
2	2.5	XE-340	.6	2	7	21	63	.0034		.00025		34		.00012	
3	2.5	GAC	5.7				53	.027							
3	2.5	904	5.7	no removal			53	.027	0		0		0		
4	2.5	GAC	8.4	3	10	21	122	.092	.0049	.0049	5	65	.0028	.0028	
4	5	GAC	8.4	10	21	31	122	.092	.0117	.0117	13	74	.0033	.0033	
4	7.5	GAC	8.4	17	45	56	122	.092	.019	.019	21	56	.0036	.0036	
4	10	GAC	8.4	35	87	72	122	.092	.045	.045	49	69	.006	.006	
2.5	feet=0.76 meter			5	feet=1.52 meters		7.5	feet=2.29 meters		10	feet=3.05 meters				

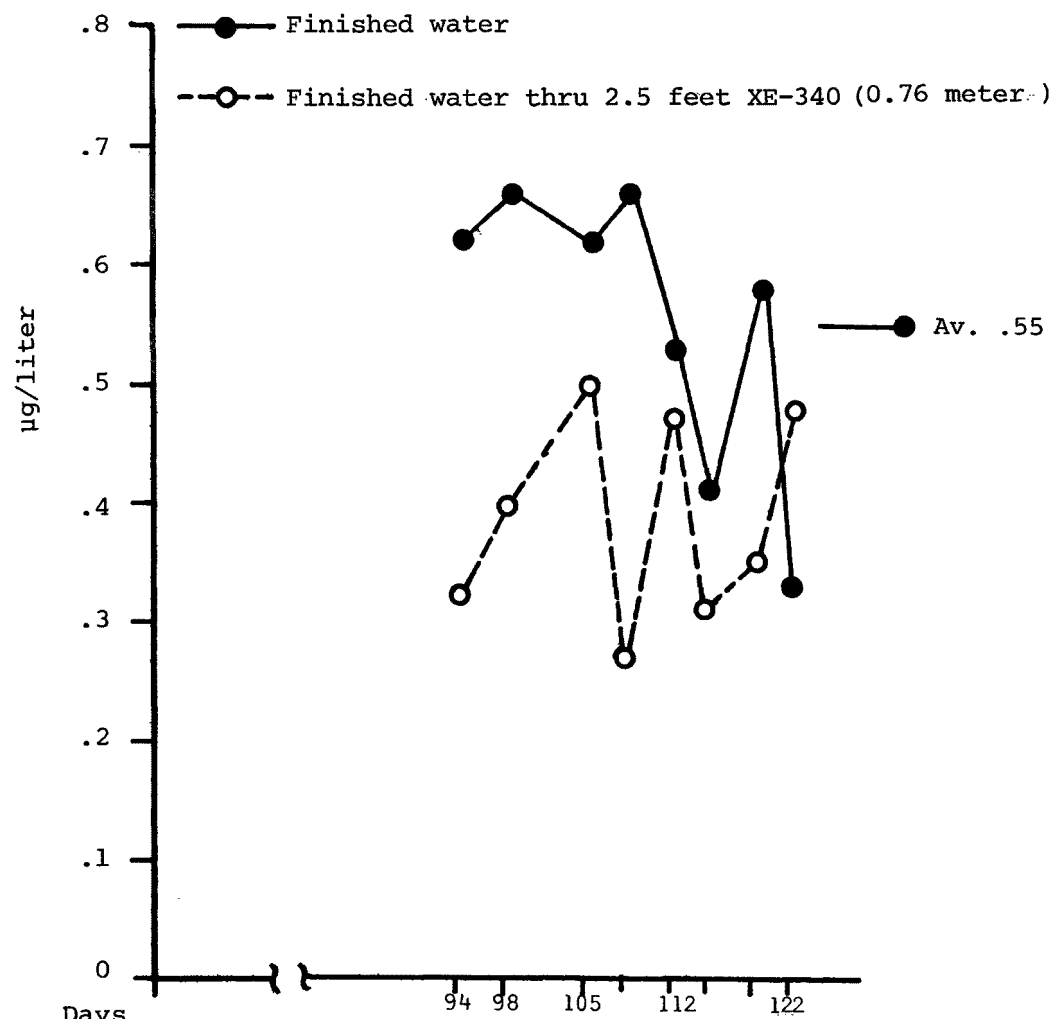


Figure 77. Vinyl chloride in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

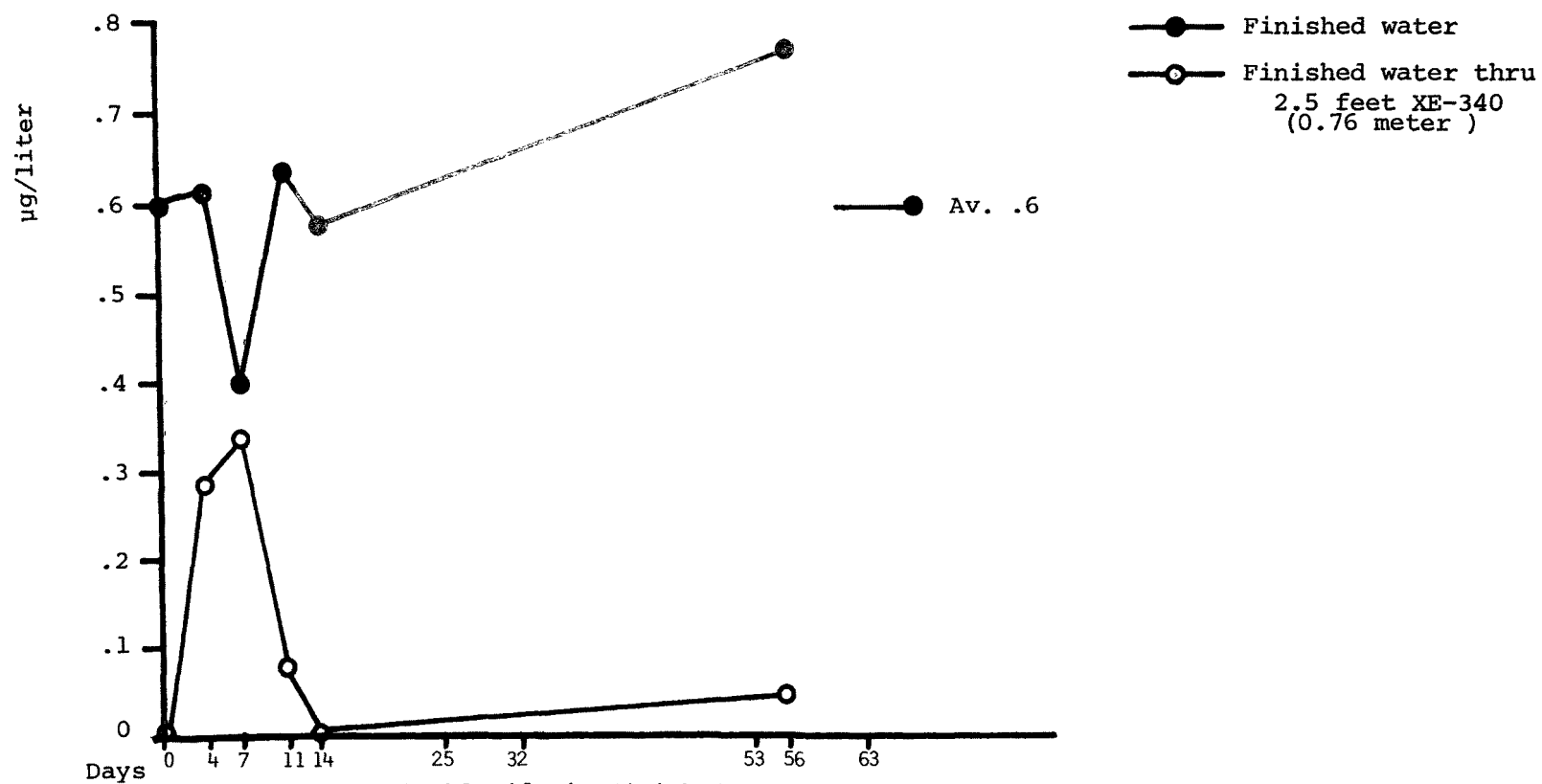
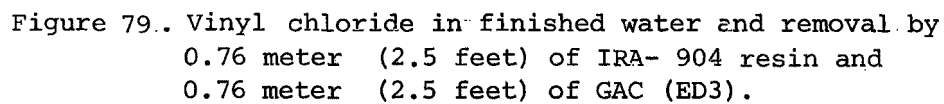


Figure 78. Vinyl Chloride in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED2).



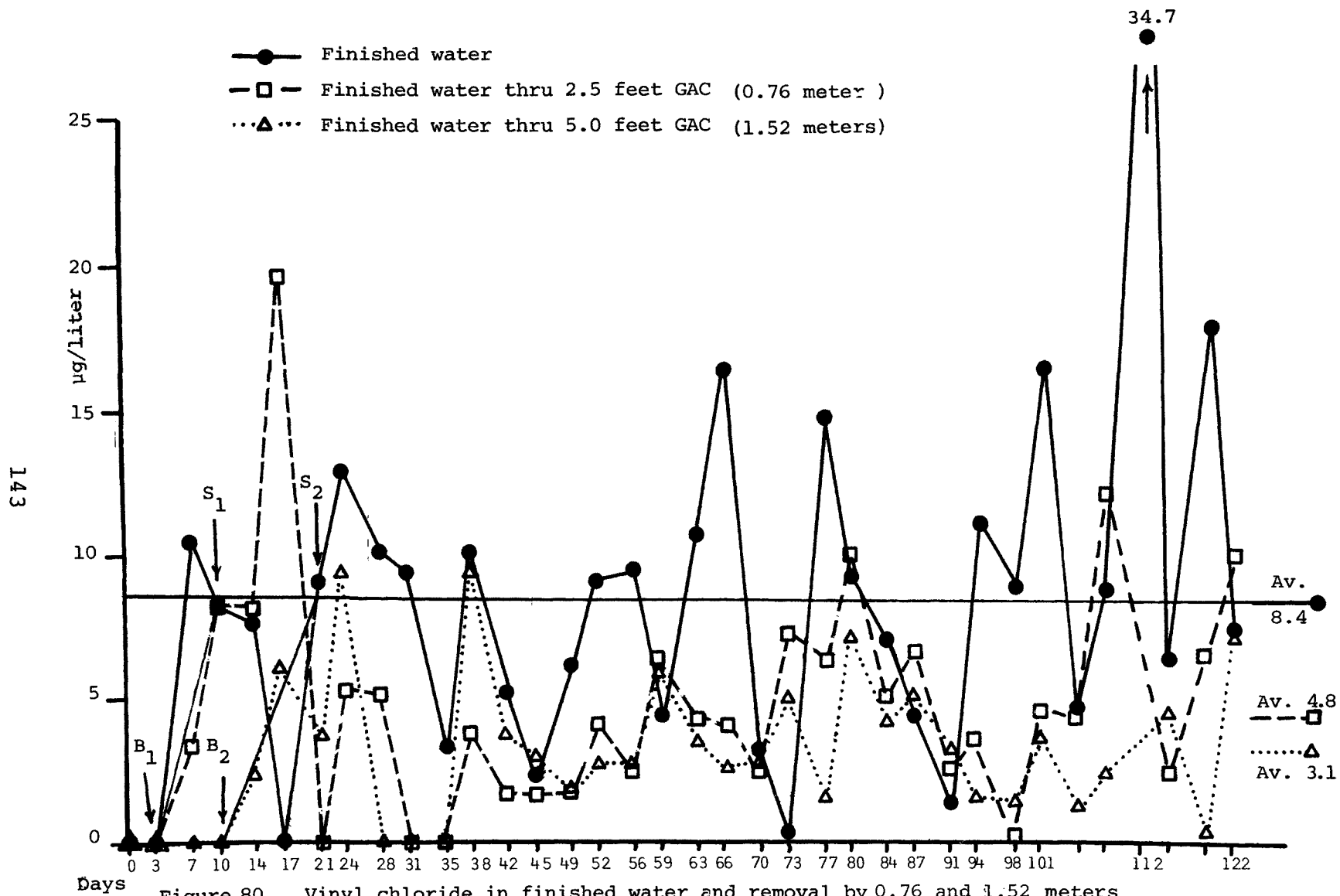


Figure 80. Vinyl chloride in finished water and removal by 0.76 and 1.52 meters (2.5 and 5 feet) of GAC (ED4).

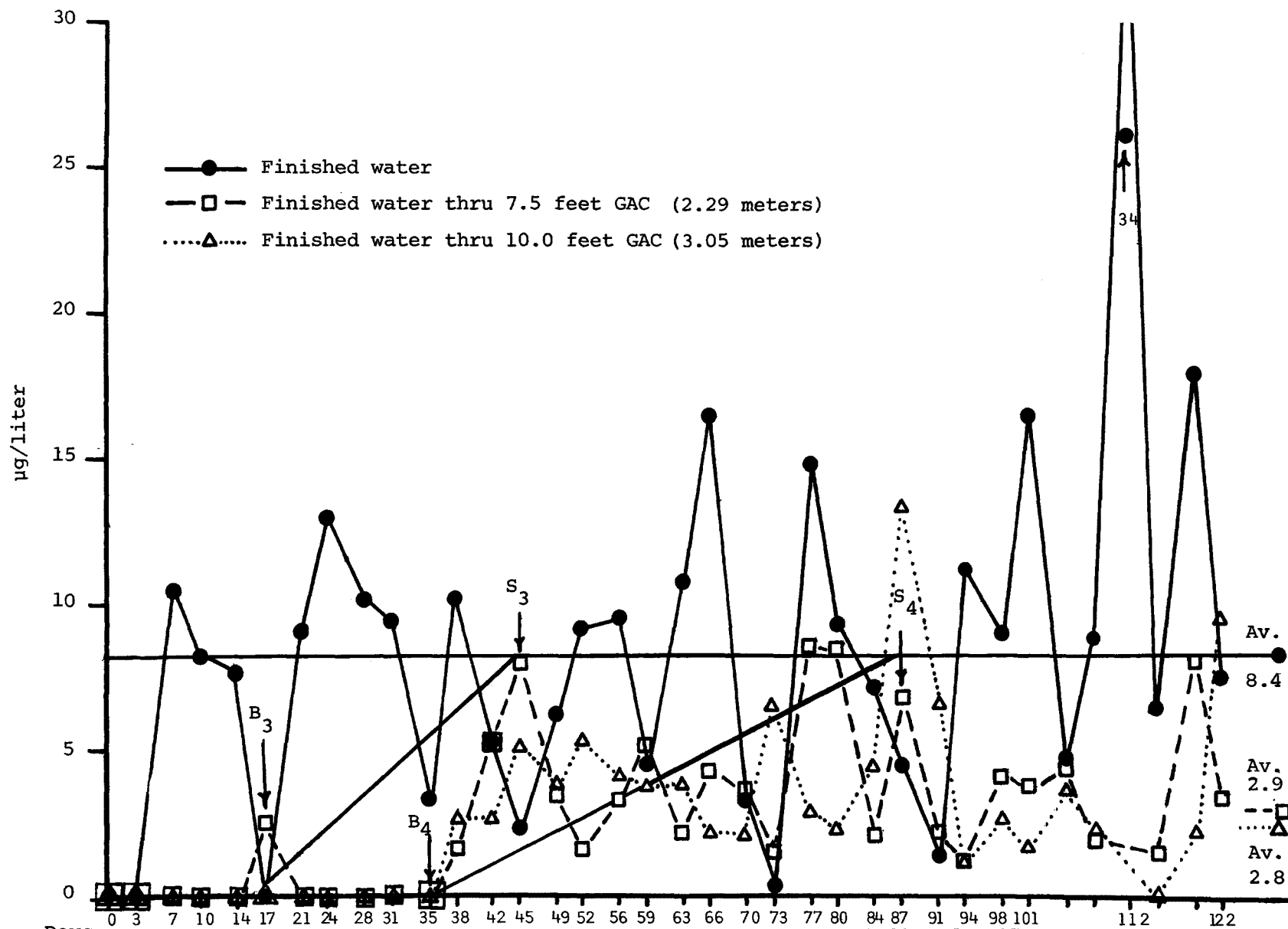


Figure 81. Vinyl chloride in finished water and removal by 2.29 and 3.05 meters (7.5 and 10 feet) of GAC (ED4).

(2.5 feet) deep GAC column was 2.2 $\mu\text{g/L}$. Based on our other work with GAC, with other HOC, this probably represents some adsorption, but it is probably incorrect to divide the GAC effluent by the influent to get a percentage figure of 59 percent removal. With vinyl chloride data, many more data points over the test period would have to be taken to determine the exact nature of adsorption and possible desorption (roll-over) that may be occurring with this substance.

The curves in Figures 80 and 81 show the influent and effluent concentration for four bed depths of GAC for ED4. Breakthrough and saturation times for the four bed depths (as seen from the curves and reported in Table 30) show a steady increase with bed depth indicating that adsorption does appear to be taking place. It is possible that after initial saturation is reached on each column that roll-over occurs. That is, some of the previously adsorbed vinyl chloride is desorbed. After roll-over it appears that another period of adsorption may occur. Considering the average influent and effluent from each bed depth over the 122 day test period has questionable merit but may show a trend. The average influent was 8.4 $\mu\text{g/L}$ while the effluent was 4.8 $\mu\text{g/L}$, 3.1 $\mu\text{g/L}$, 2.9 $\mu\text{g/L}$, and 2.8 $\mu\text{g/L}$ respectively for 0.76 (2.5 feet), 1.52 (5.0 feet), 2.29 (7.5 feet), and 3.05 (10 feet) meters of GAC bed. This represents removal of 43 percent, 63 percent, 64 percent and 67 percent.

trans 1,2-Dichloroethene--Adsorption data appear in Table 31. Curves appear in Figures 82, 83, 84, and 85.

Columns 0.76 meter (2.5 feet) deep of XE-340 were studied in ED1R and ED2. In Figure 82, breakthrough was reported at 84 days and extrapolated saturation at 134 days. The same bed depth of XE-340 was studied in ED2. In Figure 83, no breakthrough occurred, which is as expected since the test duration for ED2 was only 63 days, which was considerably less than the breakthrough time of 84 days in ED1R.

In ED3, the 0.76 meter (2.5 feet) deep IRA-904 resin column removed none of the compound (Figure 82). GAC columns, 0.76 meter (2.5 feet) deep, were studied in ED3 and ED4 (curves in Figures 84 and 85). The adsorption curve for GAC in Figure 84 except for two data points, indicates essentially complete removal for the 53-day test period. No breakthrough is recorded for ED3. We are probably justified in ignoring the two low level passages at days 14 and 35 in Figure 84 since the adsorption curve for 0.76 meter (2.5 feet) of GAC in ED4 (Figure 85) shows no breakthrough at all (all sample points nil) up to day 56.

Comparing XE-340 and GAC, both in 0.76 meter (2.5 feet) deep columns, at the same influent concentration (using log-log method) XE-340 had 2.0 times the adsorptive capacity of GAC at equal volumes of adsorbent, and 1.3 times at equal weights.

TABLE 31. trans 1,2-DICHLOROETHENE ADSORPTION DATA FROM FINISHED WATER

ED	Bed Depth Feet	Adsorbent	Average Influent µg/L	Column Breakthrough Days	Column Saturation Days	MH N Inch	Test Duration Days	Total Entering Each Column During Test Grams	Total Adsorbed by Each Column at End of Test Grams	Adsorbed by Each Column at Saturation Grams	% Adsorbed at End of Test %	% Adsorbed at Saturation %	Adsorption per 100 gms. Adsorbent at End of Test Grams	Adsorption per 100 gms. Adsorbent at Saturation Grams	CC
1R	2.5	XE-340	.54	84	134	11	122	.0059	.0052	.0053	88	90	.003	.003	.00238
2	2.5	XE-340	.86	none			63	.00484	.00484		100		.0023		
3	2.5	GAC	1.04	none			53	.0049	.0049		100		.0028		
3	2.5	904	1.04	no adsorption			53	.0049	0		0		0		
4	2.5	GAC	.77	52	63?	5	122	.0084	.004	.004	48	93	.0023	.0023	.00183
4	5	GAC	.77	none			122	.0084	.0084		100		.0034		
4	7.5	GAC	.77	none			122	.0084	.0084		100		.0016		
4	10	GAC	.77	none			122	.0084	.0084		100		.0012		
2.5	feet=0.76	meter		5	feet=1.52	meters	7.5	feet=2.29	meters	10	feet=3.05	meters			

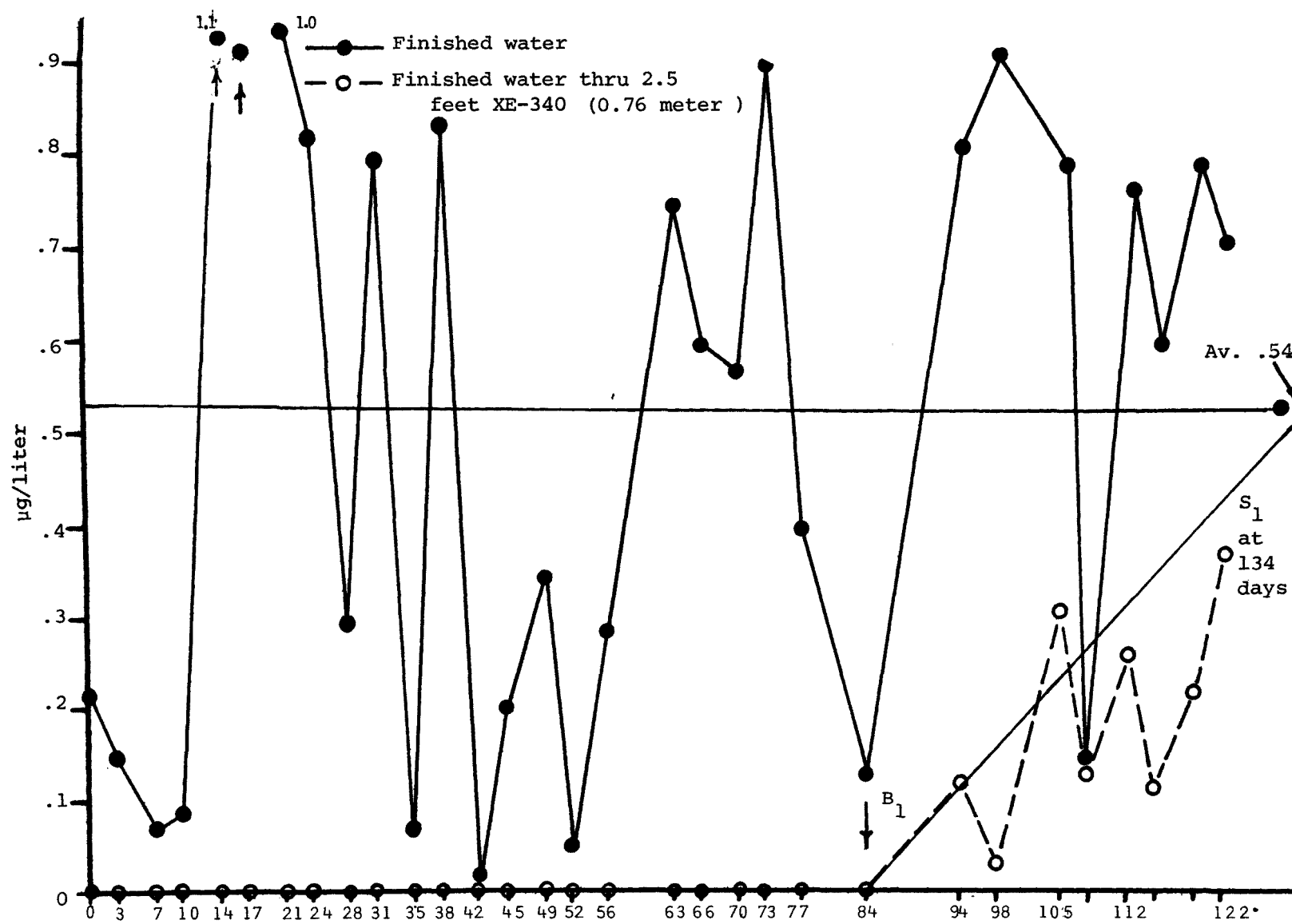


Figure 82 . trans 1,2-Dichloroethene in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

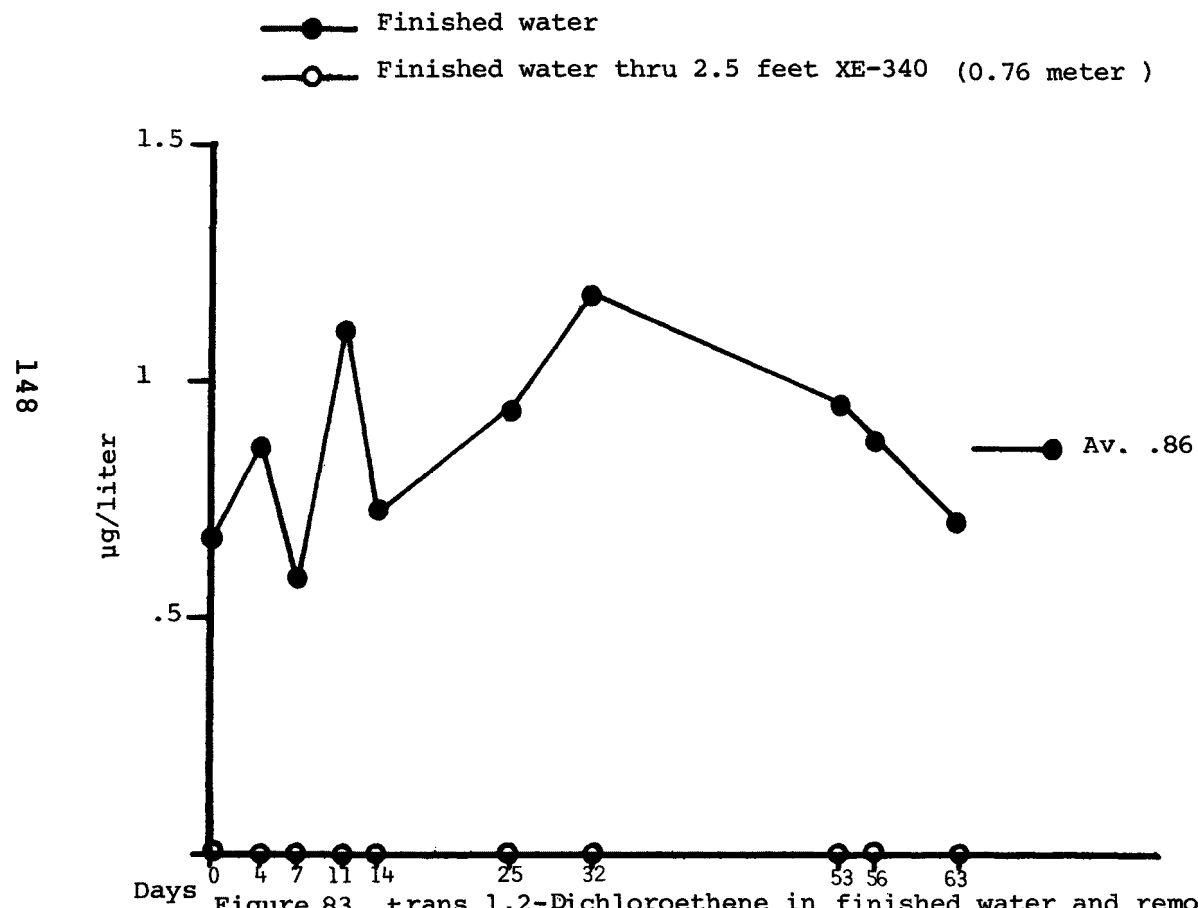


Figure 83. trans 1,2-Dichloroethene in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED2).

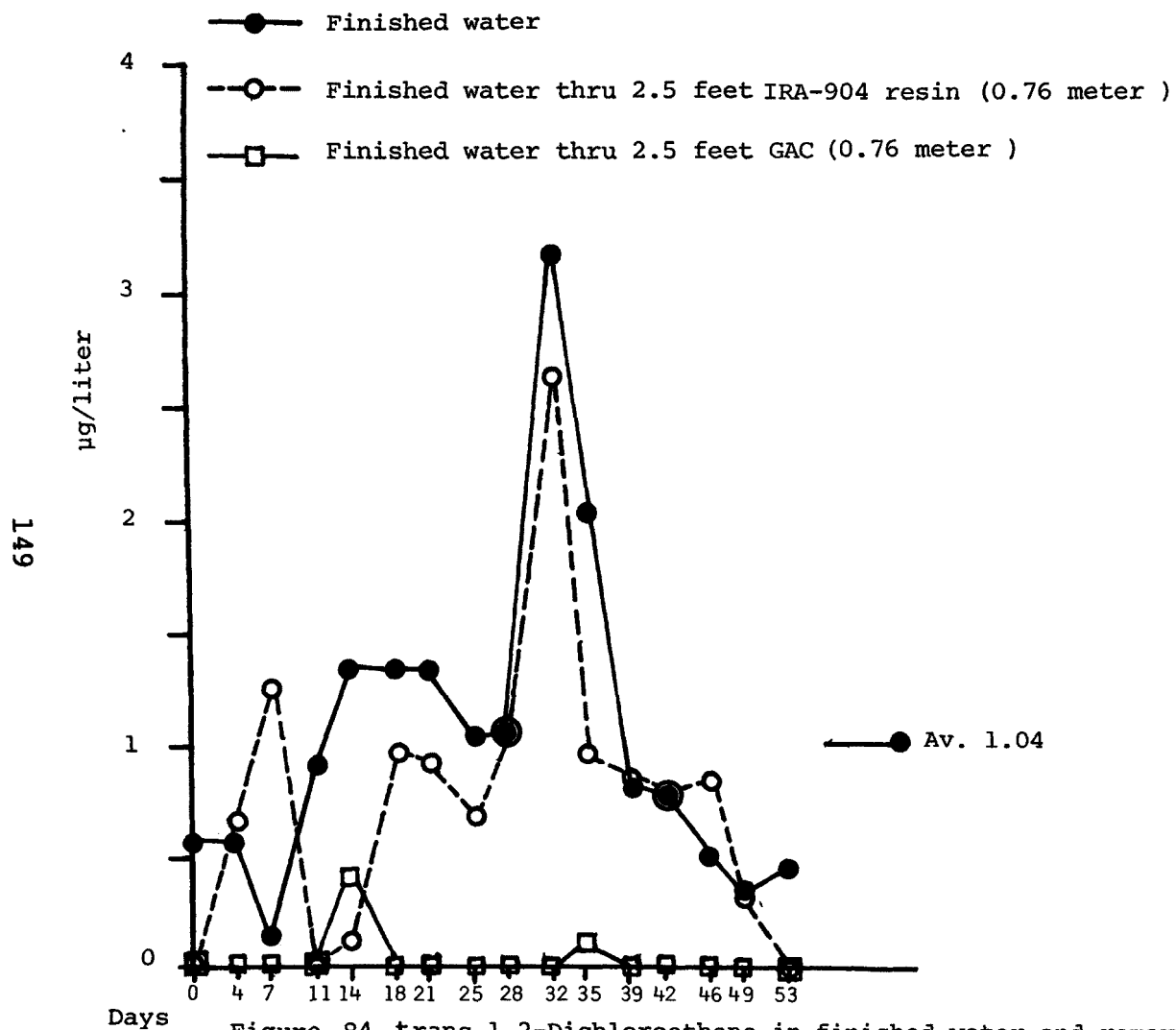


Figure 84. trans 1,2-Dichloroethene in finished water and removal by 0.76 meter (2.5 feet) of GAC and 0.76 meter (2.5 feet) of IRA-904 resin (ED3).

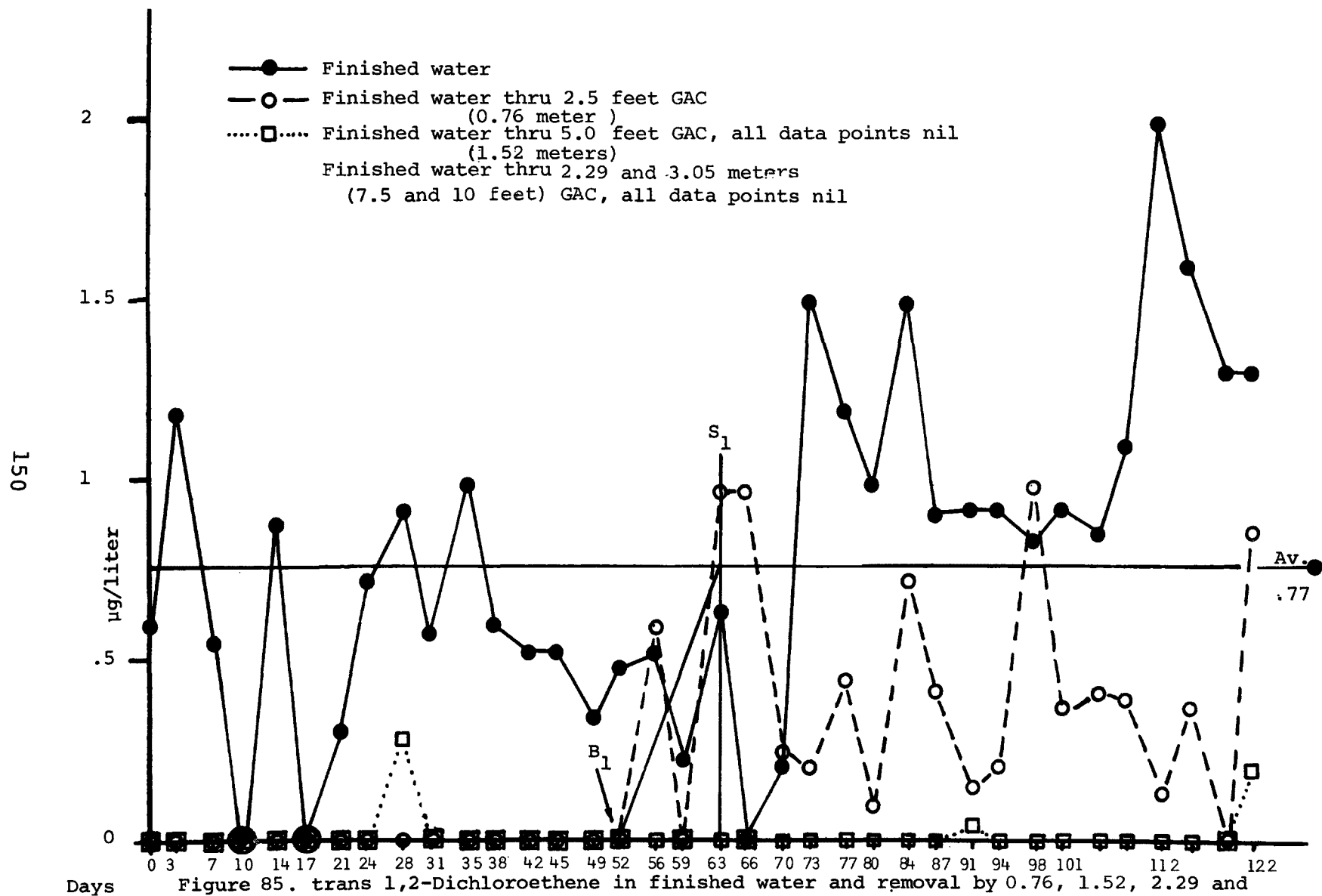


Figure 85. trans 1,2-Dichloroethene in finished water and removal by 0.76, 1.52, 2.29 and 3.05 meters (2.5, 5, 7.5 and 10 feet) of GAC (ED4).

The adsorption curve for the 1.52 meters (5.0 feet) deep GAC column in ED4, Figure 85, shows three low level passages of the compound at three widely separated sample dates (days 28, 91, and 122). Since all the other data points showed nil concentration, these three points are not considered as breakthrough. All data points for the 2.29 (7.5 feet) and 3.05 (10 feet) meters deep GAC columns were nil. Adsorption was complete over the full test range for these two bed depths.

1,1-Dichloroethane--Adsorption data appear in Table 32. Curves appear in Figures 86, 87, 88, 89, and 90.

XE-340, 0.76 meter (2.5 feet) deep, was studied in ED1R and ED2. Taking both adsorption curves into account, Figures 86 and 87, we record breakthrough at 84 days in ED1R and 63 days in ED2. In Figure 86 we also could consider the extremely low level passage (.002 $\mu\text{g/L}$) on days 49, 63, and 66 as part of the breakthrough curve, thus setting the breakthrough point at 49 days which is still in fair agreement with the 63 days in ED2. The adsorption curve in Figure 88 for the IRA-904 resin, 0.76 meter (2.5 feet) deep indicates no removal of the compound in ED3. GAC, 0.76 meter (2.5 feet) deep, was studied in ED3 and ED4. Considering the data as a whole, the breakthrough and saturation times recorded in Table 32 are fairly close for ED3 and ED4. In ED4, Table 32, we observe a steady increase in breakthrough and saturation time as GAC bed depth increases despite the spread of data points in the adsorption curves in Figures 89 and 90.

1,1,1-Trichloroethane, 1,2-dichloroethane, carbon tetrachloride (summed value)--Adsorption data appear in Table 33. Curves appear in Figures 91, 92, 93, and 94.

XE-340, 0.76 meter (2.5 feet) deep, was studied in ED1R and ED2. In Table 33, breakthrough at 98 days was reported for ED1R. The adsorption curve in Figure 91 indicates complete removal up to day 49, at which time a very low passage occurred up to day 98 when passage increased sharply. On raw water, Figure 25, a similar low level passage occurred from day 3 to day 84, at which time the passage increased sharply. On H.T. water, Figure 46, the low level passage started on day 7. It appears that the trend for XE-340 is to allow some low level passage of this summed group of substances from very early after initial flow has begun, then to reach a period of increased breakthrough varying from 98 days, 84 days and 66 days respectively for ED1R, ED2 and ED4.

IRA-904 resin, 0.76 meter (2.5 feet) deep, was studied in ED3, and the adsorption curve in Figure 93 indicates no removal. GAC, 0.76 meter (2.5 feet) deep, was studied in ED3 and ED4. If the data point at day 3 (Figure 94) for the 0.76 meter (2.5 feet) deep GAC column is not considered, both 0.76 meter

TABLE 32. 1,1-DICHLOROETHANE ADSORPTION DATA FROM FINISHED WATER

ED	Bed Depth Feet	Adsorbent	Average Influent µg/L	Column Breakthrough Days	Column Saturation Days	MT N Inch	Test Duration Days	Total Entering Each Column During Test Grams	Total Adsorbed by Each Column at End of Test Grams	Adsorbed by Each Column at Saturation Grams	% Adsorbed at End of Test %	% Adsorbed at Saturation %	Adsorption per 100 gms. Adsorbent at End of Test Grams	Adsorption per 100 gms. Adsorbent at Saturation Grams	CC
1R	2.5	XE-340	.18	84	105	6	122	.002	.00153	.00153	75	90	.0009	.0009	.00077
2	2.5	XE-340	.8	none			63	.001	.001		100		.00047		
3	2.5	GAC	.32	16	21	7	53	.0015	.00053	.00053	35	88	.00025	.00025	.00021
2	2.5	904	.32	no adsorption			53	.0015	0		0		0		
4	2.5	GAC	.4	28	49	13	122	.0044	.0014	.0014	32	79	.0008	.0008	.00068
4	5	GAC	.4	42	56	15	122	.0044	.0018	.0018	41	88	.0005	.0005	.00042
4	7.5	GAC	.4	52	59	11	122	.0044	.002	.002	46	94	.0004	.0004	.00034
4	10	GAC	.4	77	87	14	122	.0044	.003	.003	68	94	.0004	.0004	.00034
2.5	feet=0.76	meter		5	feet=1.52	meters	7.5	feet=2.29	meters	10	feet=3.05	meters			

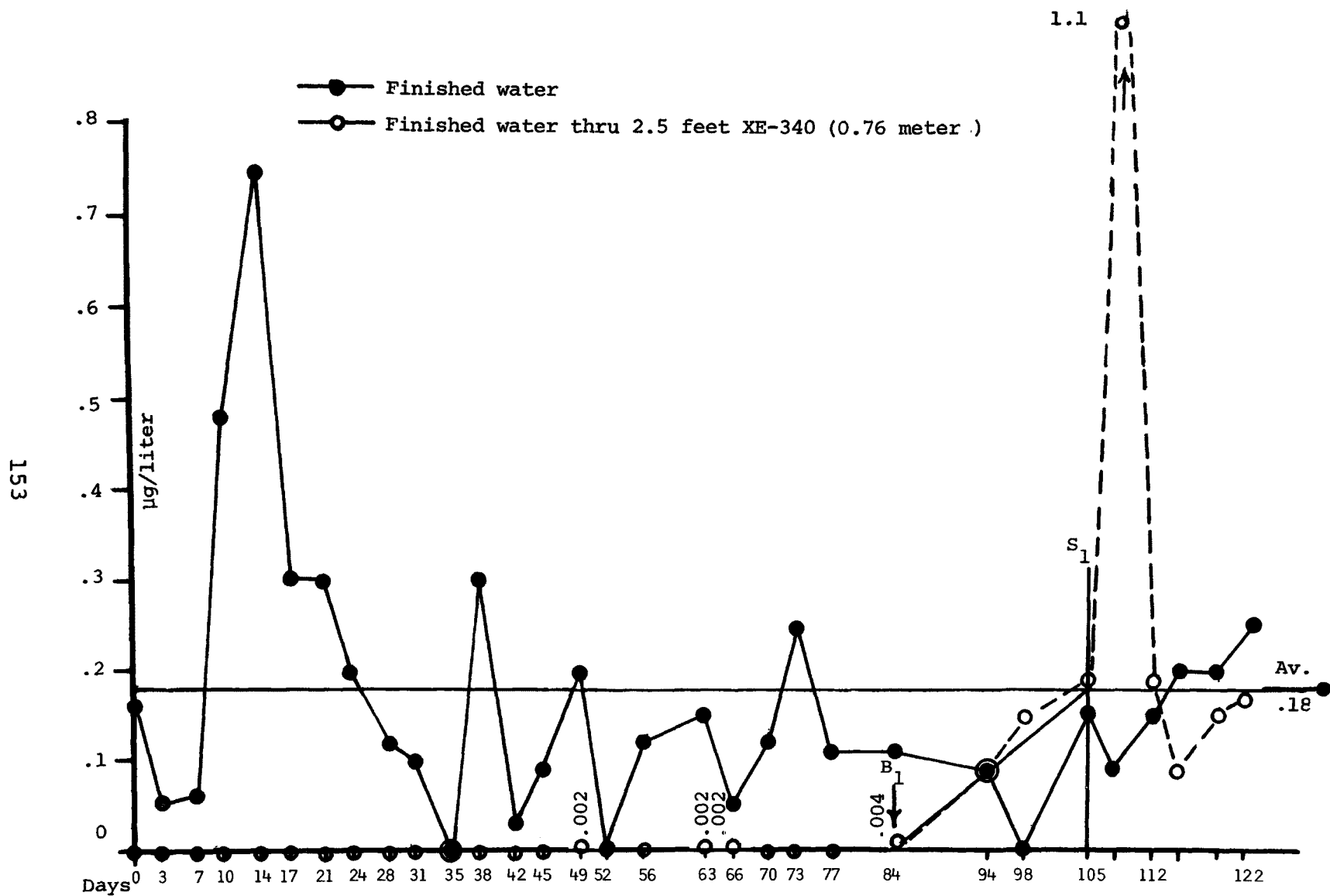


Figure 86. 1,1-Dichloroethane in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

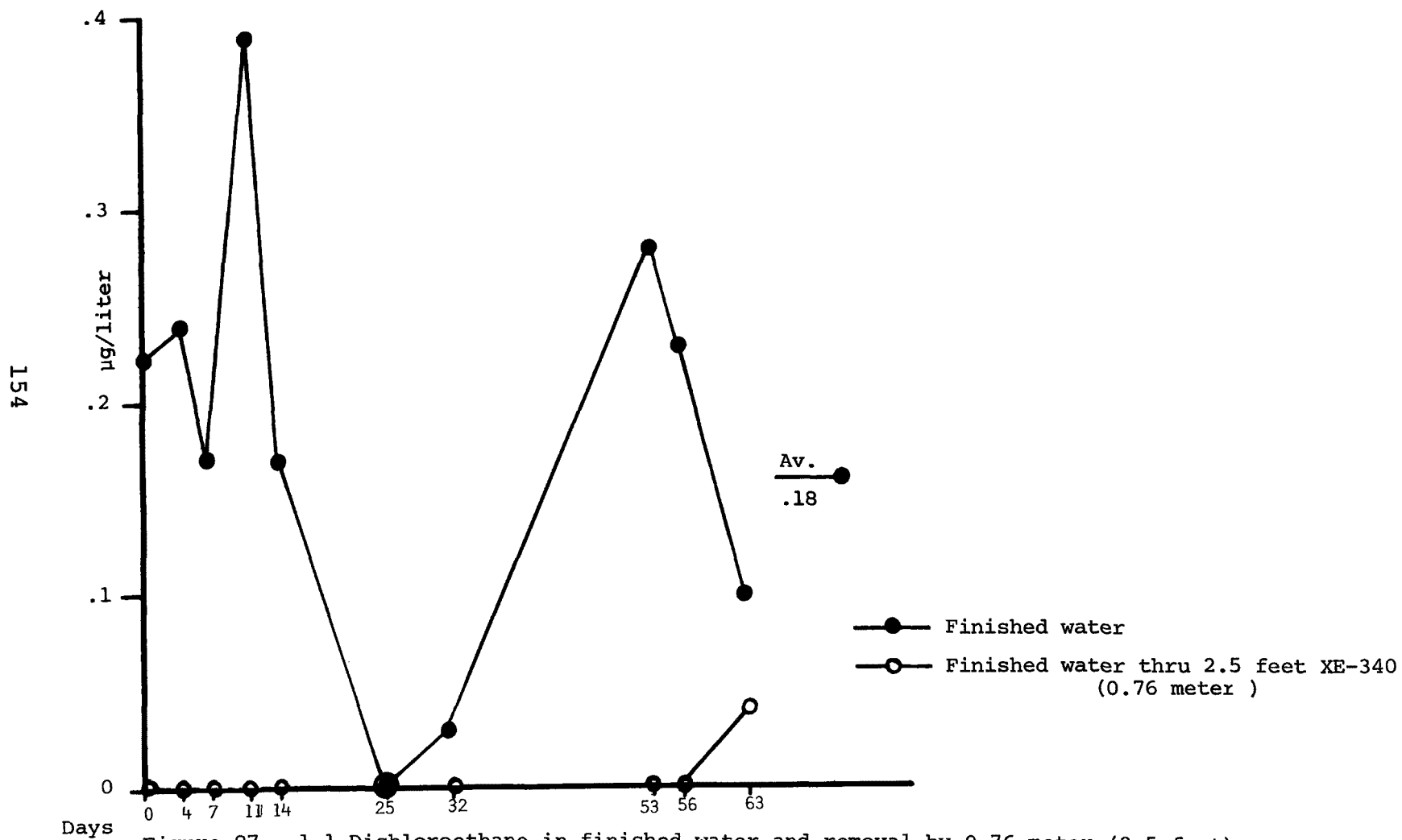


Figure 87. 1,1-Dichloroethane in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED2).

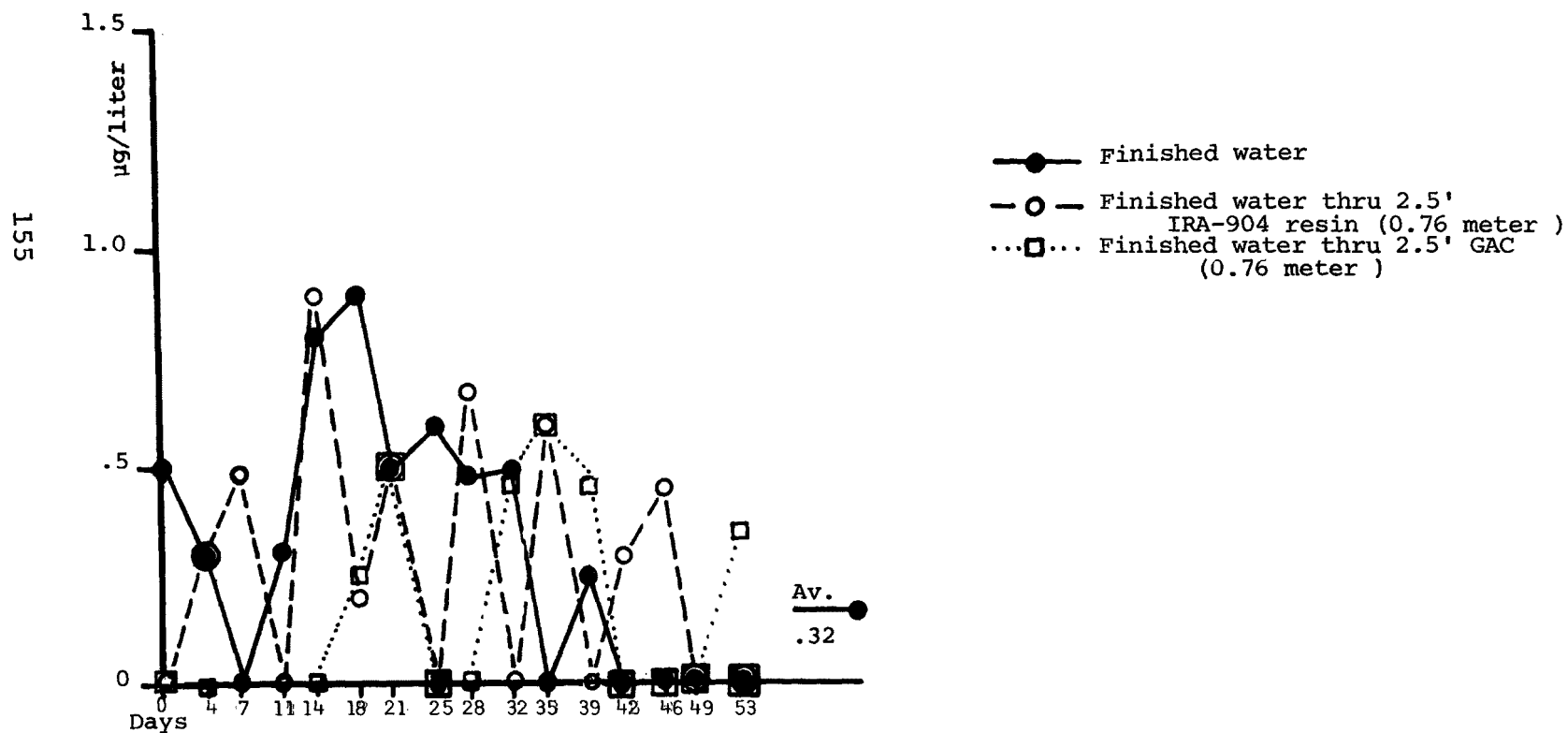
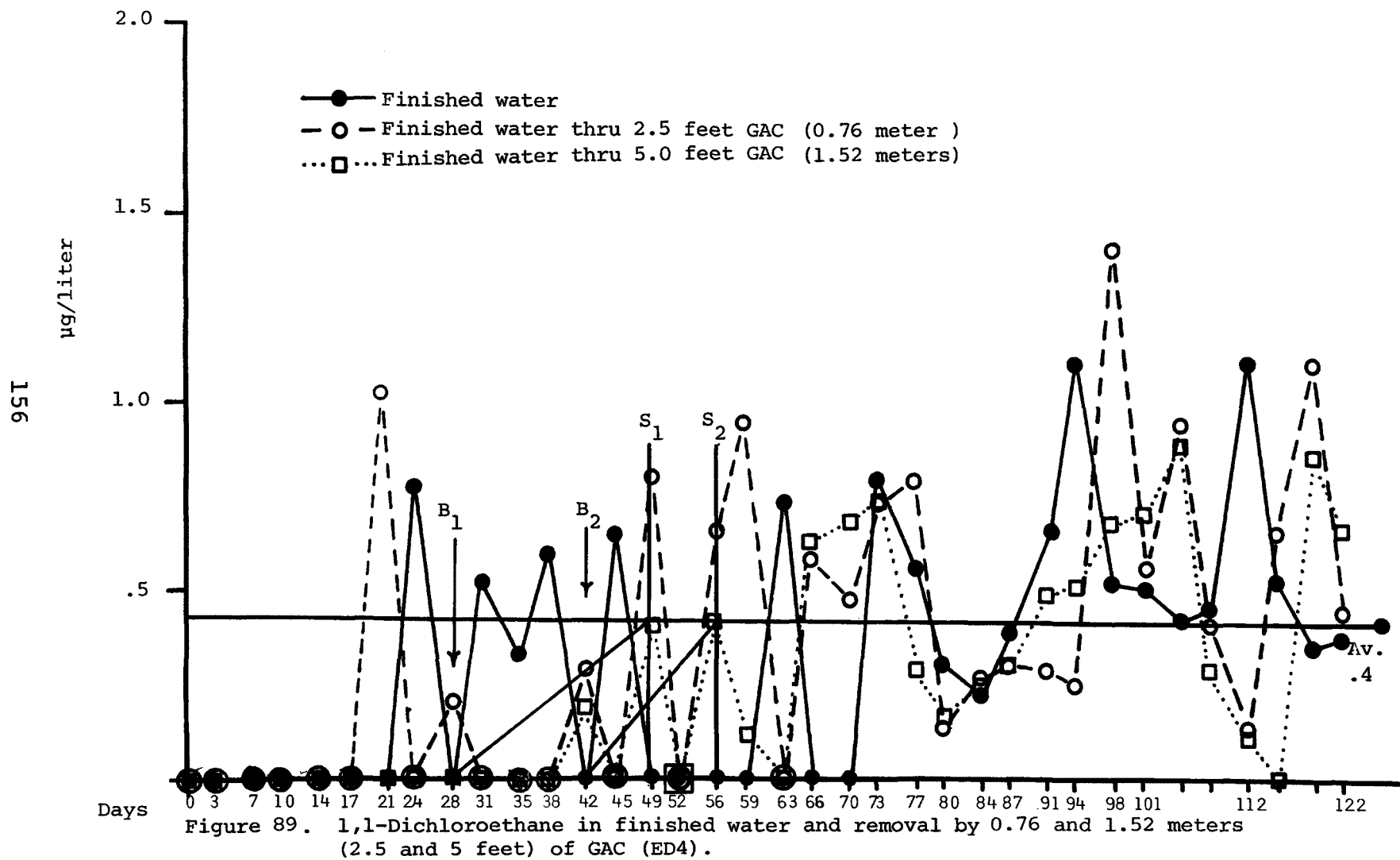


Figure 88. 1,1-Dichloroethane in finished water and removal by 0.76 meter (2.5 feet) of GAC and 0.76 meter (2.5 feet) IRA-904 resin (ED3).



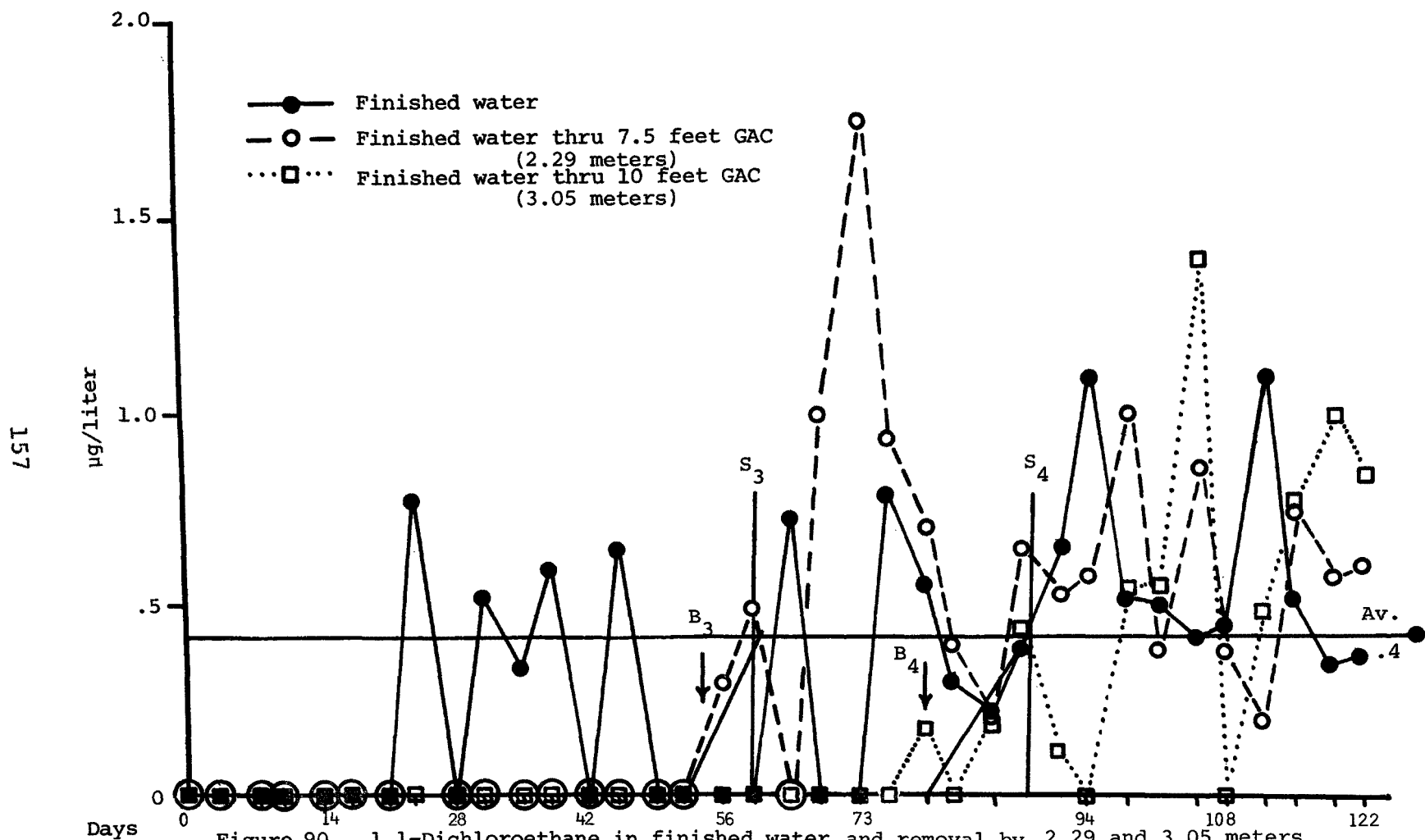


TABLE 33. 1,1,1-TRICHLOROETHANE, 1,2-DICHLOROETHANE AND CARBON TETRACHLORIDE ADSORPTION DATA FROM FINISHED WATER

ED	Bed Depth Feet	Adsorbent	Average Influent µg/L	Column Breakthrough Days	Column Saturation Days	MF _N Inch	Test Duration Days	Total Entering Each Column During Test Grams	Total Adsorbed by Each Column at End of Test Grams	Adsorbed by Each Column at Saturation Grams	% Adsorbed at End of Test %	% Adsorbed at Saturation %	Adsorption per 100 gms. Adsorbent at End of Test Grams	Adsorption per 100 gms. Adsorbent at Saturation Grams	CC
1R	2.5	XE-340	.66	98			122	.0072	.0067		93		.0038		
2	2.5	XE-340	1.47	none			63	.0083	.0083		100		.0039		
3	2.5	GAC	5.3	28	58	16	53	.025	.02	.0204	80	74	.0114	.0116	
3	2.5	904	5.3				53	average increase of 1.5X							
4	2.5	GAC	7.7	38	73	14	122	.084	.038	.038	45	76	.0148	.022	
4	5	GAC	7.7	87	199	34	122	.084	.078	.098	93	72	.022	.0278	
4	7.5	GAC	7.7	none			122	.084	.084		100		.0159		
4	10	GAC	7.7	none			122	.084	.084		100		.0119		
2.5	feet=0.76 meter				5 feet=1.52 meters		7.5	feet=2.29 meters					10 feet=3.05 meters		

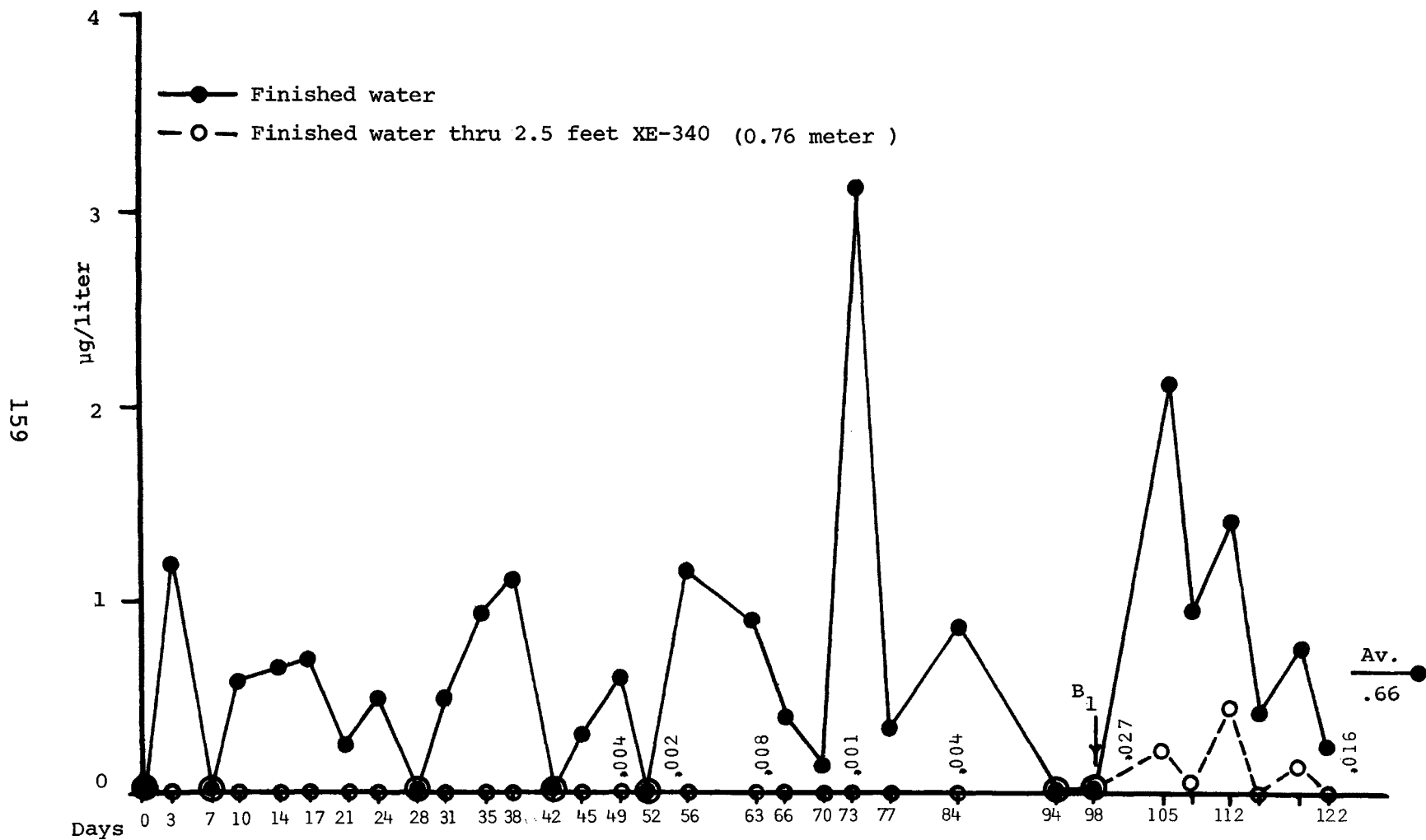


Figure 91. 1,1,1-Trichloroethane, 1,2-dichloroethane and carbon tetrachloride in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

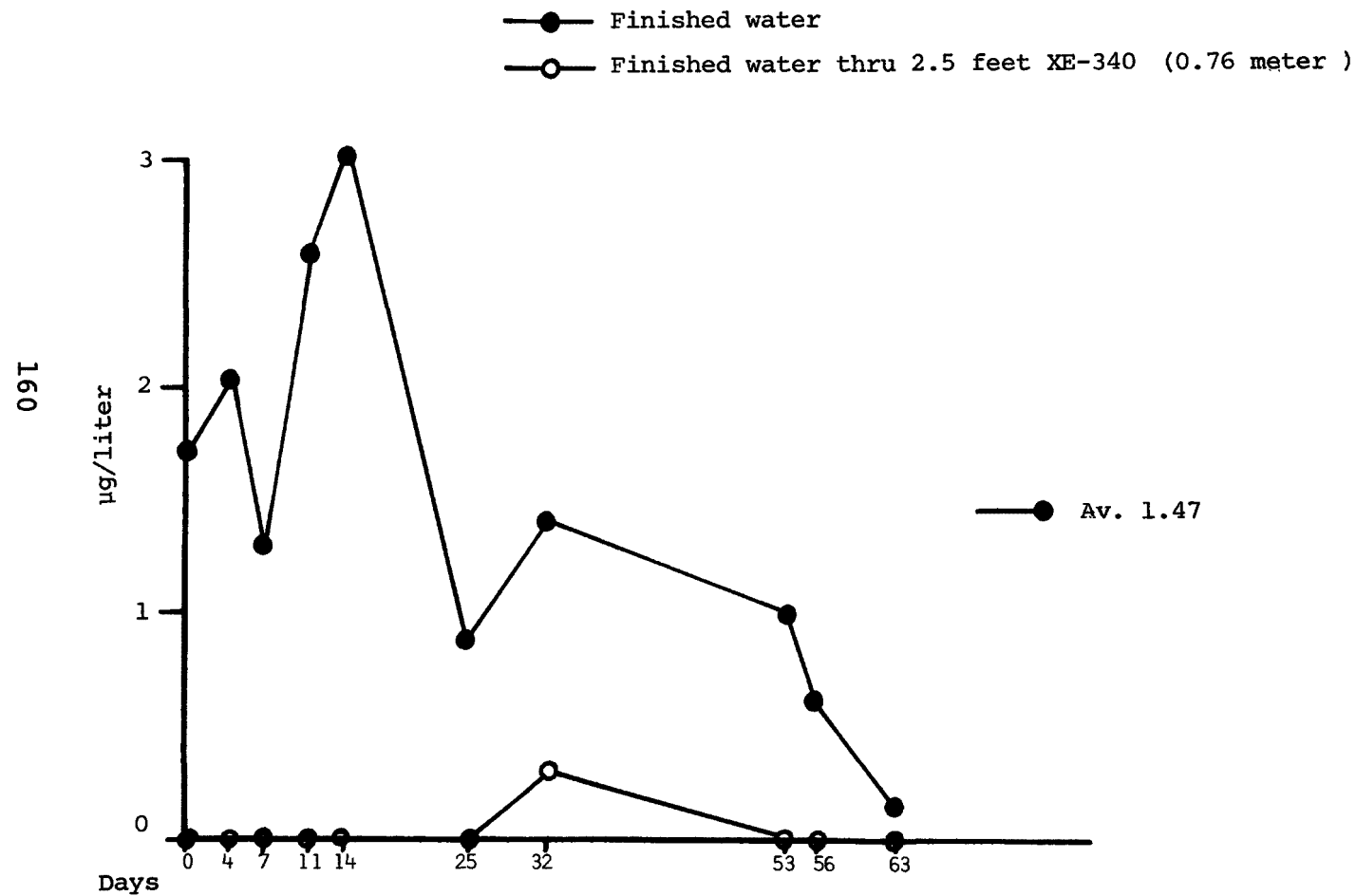


Figure 92. 1,1,1-Trichloroethane, 1,2-dichloroethane and carbon tetrachloride in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED2).

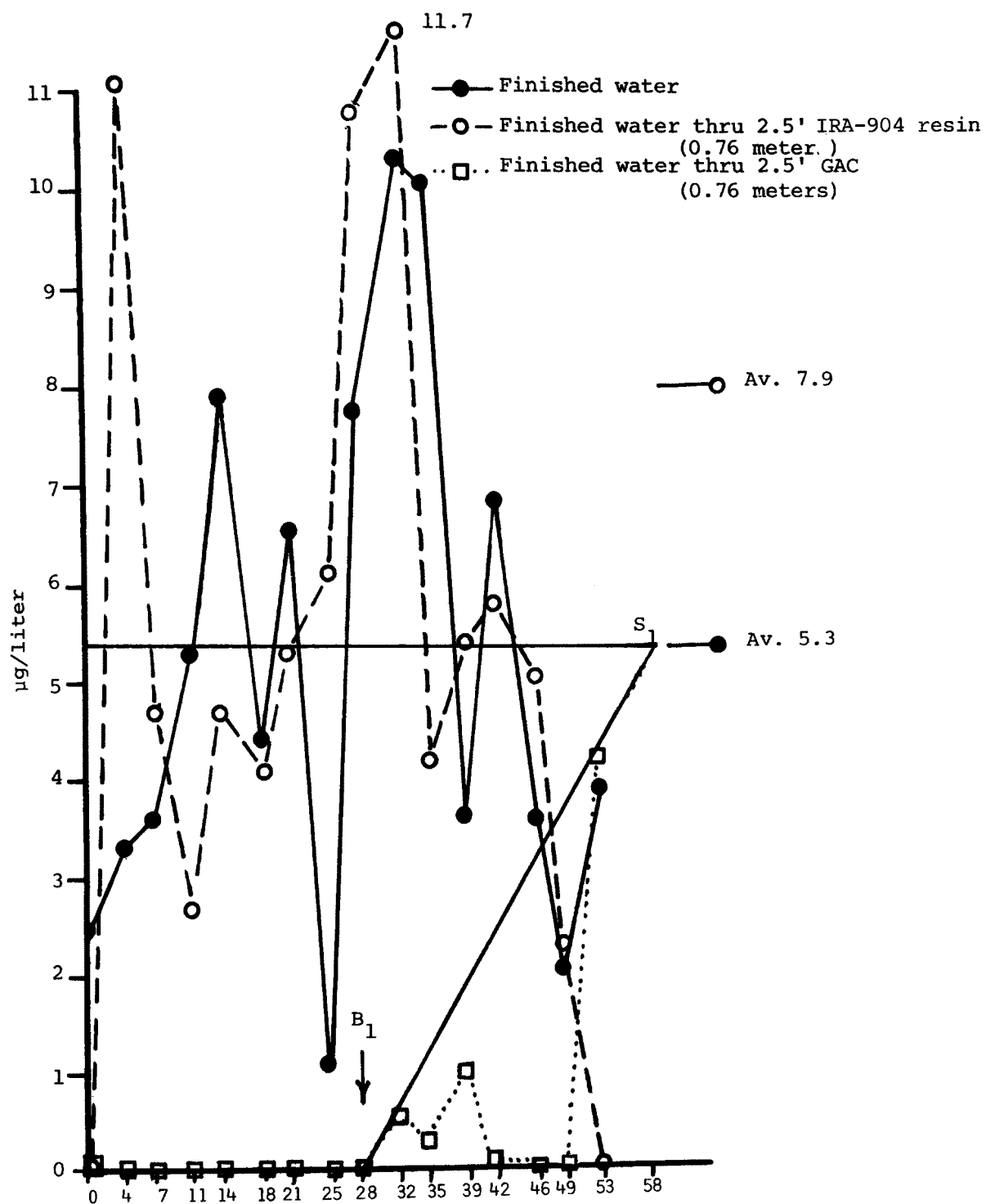


Figure 93. 1,1,1-Trichloroethane, 1,2-dichloroethane and carbon tetrachloride in finished water and removal by 0.76 meter (2.5 feet) of GAC and 0.76 meter (2.5 feet) of IRA-904 resin (ED3).

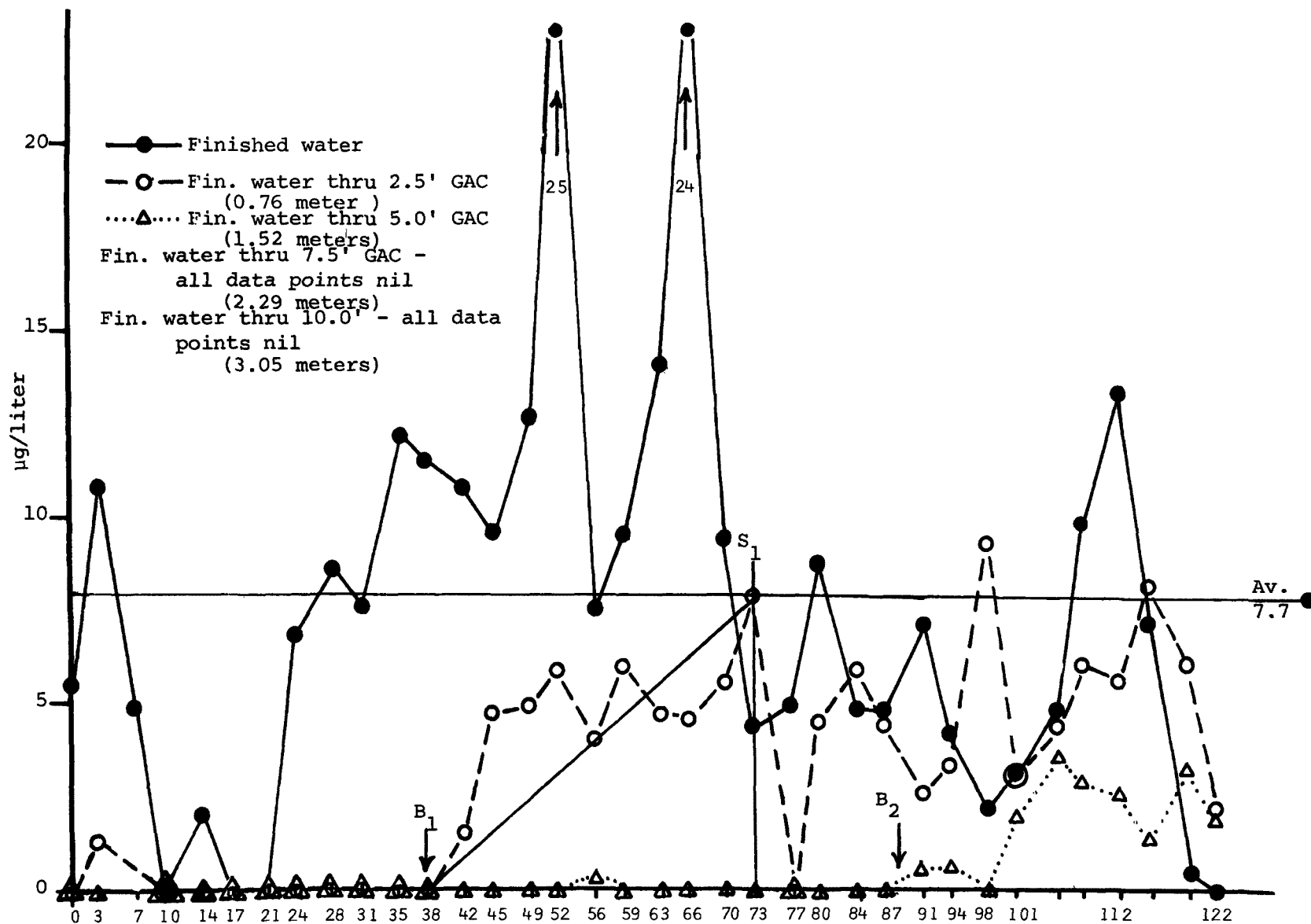


Figure 94. 1,1,1-Trichloroethane, 1,2-dichloroethane and carbon tetrachloride in finished water and removal by 0.76, 1.52, 2.29 and 3.05 meters (2.5, 5, 7.5 and 10 feet) of GAC (ED4).

(2.5 feet) deep GAC curves (Figures 93 and 94) are similar because breakthrough times are 28 days and 38 days and saturation times are 58 days and 73 days respectively. As expected, as the GAC bed depth increases, the time to breakthrough increases (Figure 94).

Trichloroethylene--Adsorption data appear in Table 34. Curves appear in Figures 95, 96, 97, 98, 99, 100, 101 and 102.

XE-340, 0.76 meter (2.5 feet) deep, was studied in ED1R and ED2. A breakthrough time of 94 days was determined from the adsorption curve in Figure 95. This compares closely with a reported breakthrough on raw water of 96 days and 88 days for H.T. water. Saturation was not reached and at the end of the test, 122 days, the adsorbent removed 96 percent of the compound entering. The adsorption curve in Figure 96 for ED2 appears to be the first contradictory data of the whole project. Trichloroethylene breakthrough occurred on initial start-up and XE-340 effluent from test day 14 to day 32 was higher than the influent. All other results on trichloroethylene adsorption from raw, H.T. and finished water in the two-year study were in line and as expected with related substances and concentrations.

Results with a 0.76 meter (2.5 feet) deep column of IRA-904 resin in ED3 are shown in Figure 97. The IRA-904 resin effluent average concentration over the test period was 10 times the influent concentration. It appears that trichloroethylene is being generated by the column. The adsorption curve for 0.76 meter (2.5 feet) deep of GAC in ED3 is shown in Figure 98. The average influent concentration was very low, 0.075 $\mu\text{g/L}$. The GAC column effluent contained trichloroethylene on two sample dates. From test day 28 to the end of the test at 53 days, the influent and effluent concentration was nil. Because of the very low average influent, establishment of a breakthrough or saturation time was not considered.

In ED4, the average influent concentration was 0.68 $\mu\text{g/L}$ and adsorption curves for 0.76 (2.5 feet), 1.52 (5.0 feet), 2.29 (7.5 feet) and 3.05 (10 feet) meters of GAC are shown in Figures 99, 100, 101 and 102 respectively. The reported breakthrough and saturation times are open to question, but when considering all four bed depths, overall removals were 39 percent, 80 percent, essentially 100 percent, and essentially 100 percent respectively in the 0.76 (2.5 feet), 1.52 (5.0 feet), 2.29 (7.5 feet) and 3.05 (10 feet) meters deep columns. The respective adsorption curves clearly show increased adsorption with increasing bed depth. The effluent concentration for all data points for the 2.29 (7.5 feet) and 3.05 (10 feet) meters deep columns was nil except for trace passage for two points and points and three points respectively.

TABLE 34 . TRICHLOROETHYLENE ADSORPTION DATA FROM FINISHED WATER

ED	Bed Depth	Adsorbent	Average Influent $\mu\text{g/L}$	Column Breakthrough	Column Saturation	MT ²	Test Duration	Total Entering Each Column	Total Adsorbed by Each Column at End of Test	Adsorbed by Each Column at Saturation	% Adsorbed at End of Test	% Adsorbed at Saturation	Grams Adsorption per 100 gms. Adsorbent at End of Test	Grams Adsorption per 100 gms. Adsorbent at Saturation	CC
1R	2.5	XE-340	.21	94	can't extrapolate		122	.0023	.0022		96		.0013		
2	2.5	XE-340	.57	0	can't calculate		63	.0032							
3	2.5	GAC	.075				53	concentration too low to evaluate							
3	2.5	904	.075				53	average increase of 10x							
4	2.5	GAC	.68	38	56	9.6	122	.0074	.0029	.0029	39	84	.0017	.0017	.00116
4	5	GAC	.68	84	108	13.3	122	.0074	.0059	.0059	80	89	.0017	.0017	.00116
4	7.5	GAC	.68	none			122	.0074	.0074		100		.0014		
4	10	GAC	.68	none			122	.0074	.0074		100		.0011		
2.5	feet=0.76 meter			5	feet=1.52 meters		7.5 meters		feet=2.29 meters		10	feet=3.05 meters			

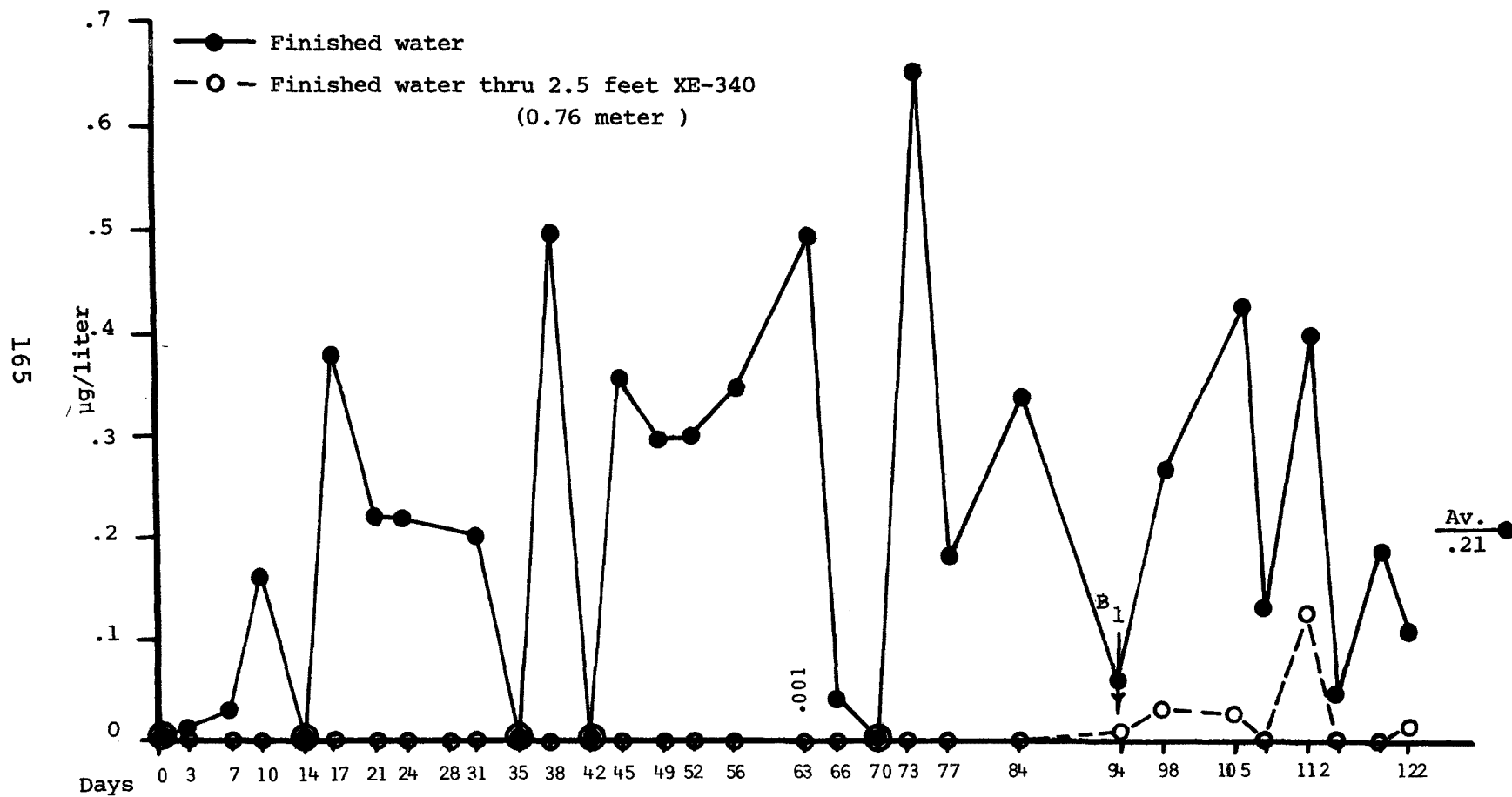


Figure 95. Trichloroethylene in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

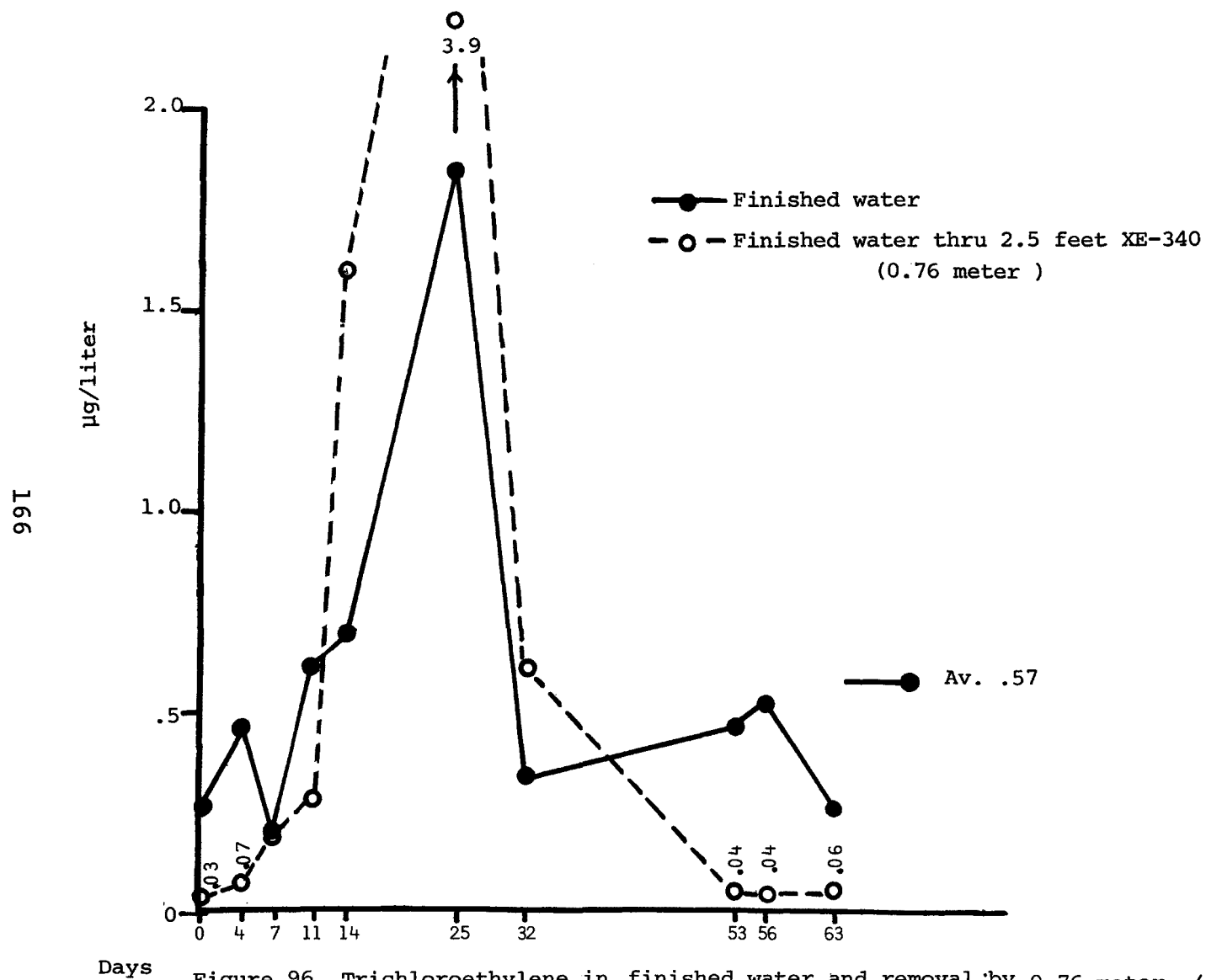


Figure 96. Trichloroethylene in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED2).

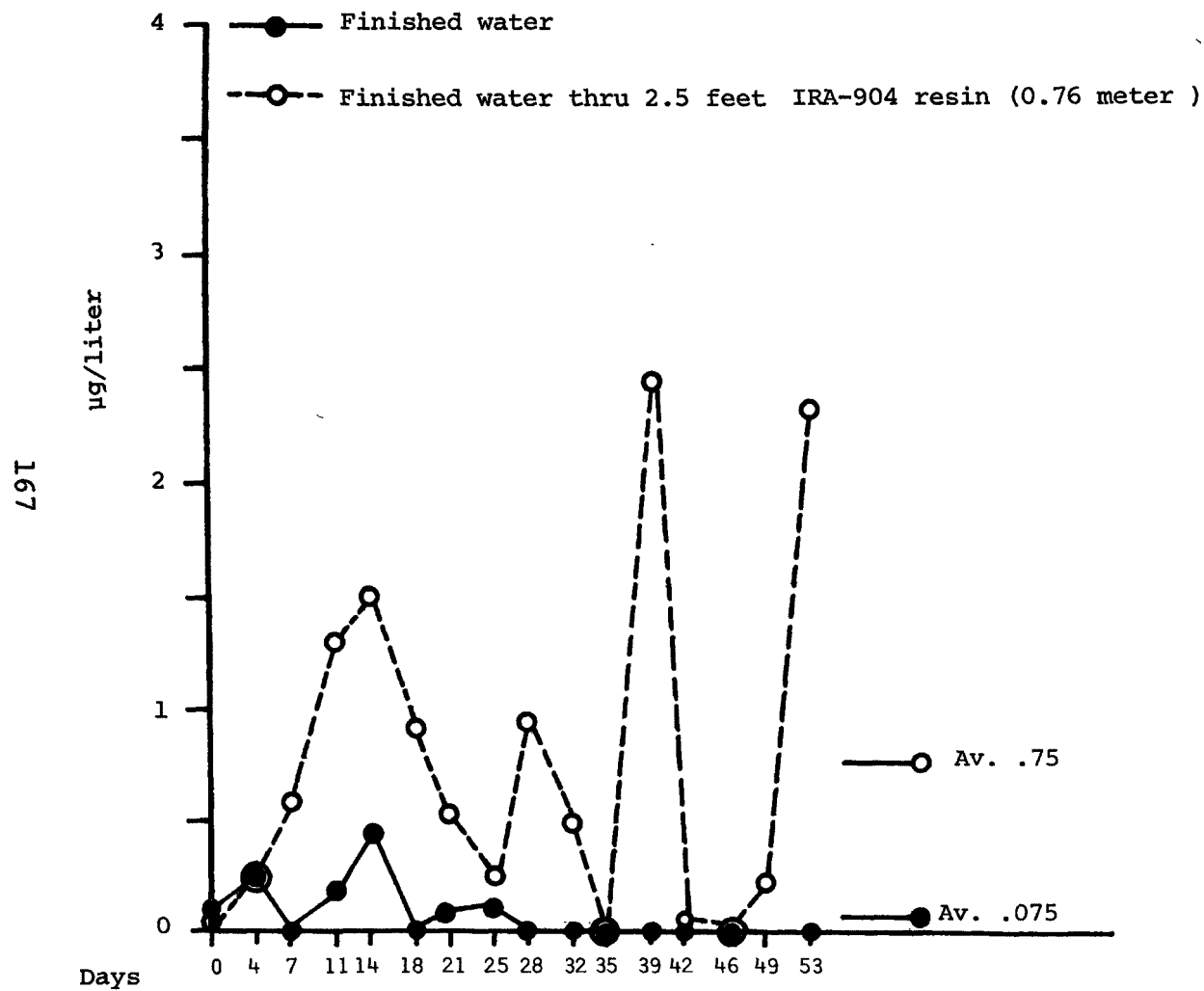


Figure 97. Trichloroethylene in finished water and removal by 0.76 meter (2.5 feet) of IRA-904 resin (ED3).

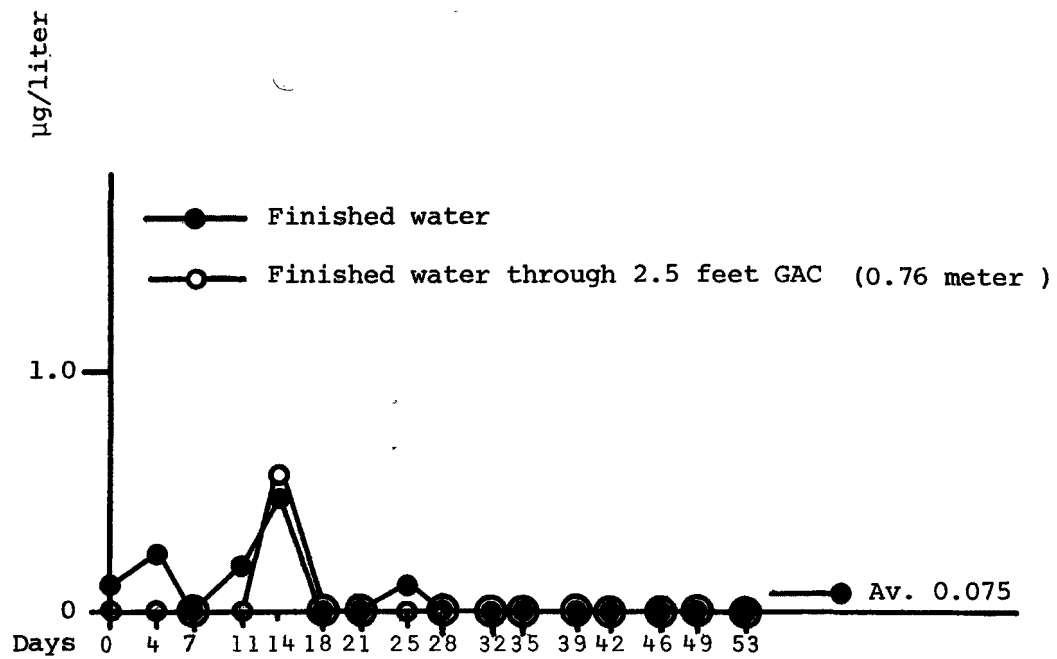


Figure 98. Trichloroethylene in finished water and removal by 0.76 meter (2.5 feet) of GAC (ED3).

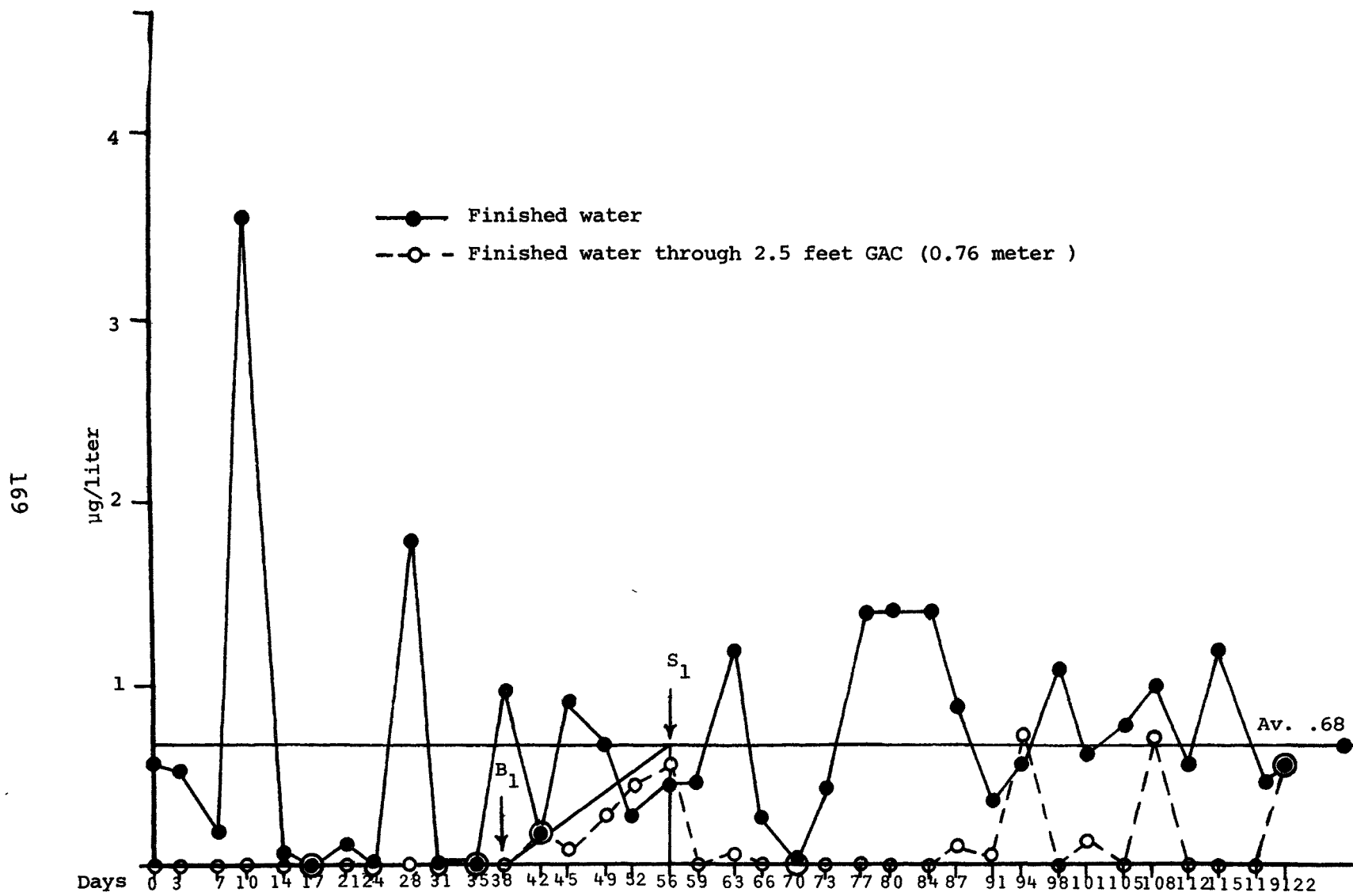


Figure 99. Trichloroethylene in finished water and removal by 0.76 meter (2.5 feet) of GAC (ED4).

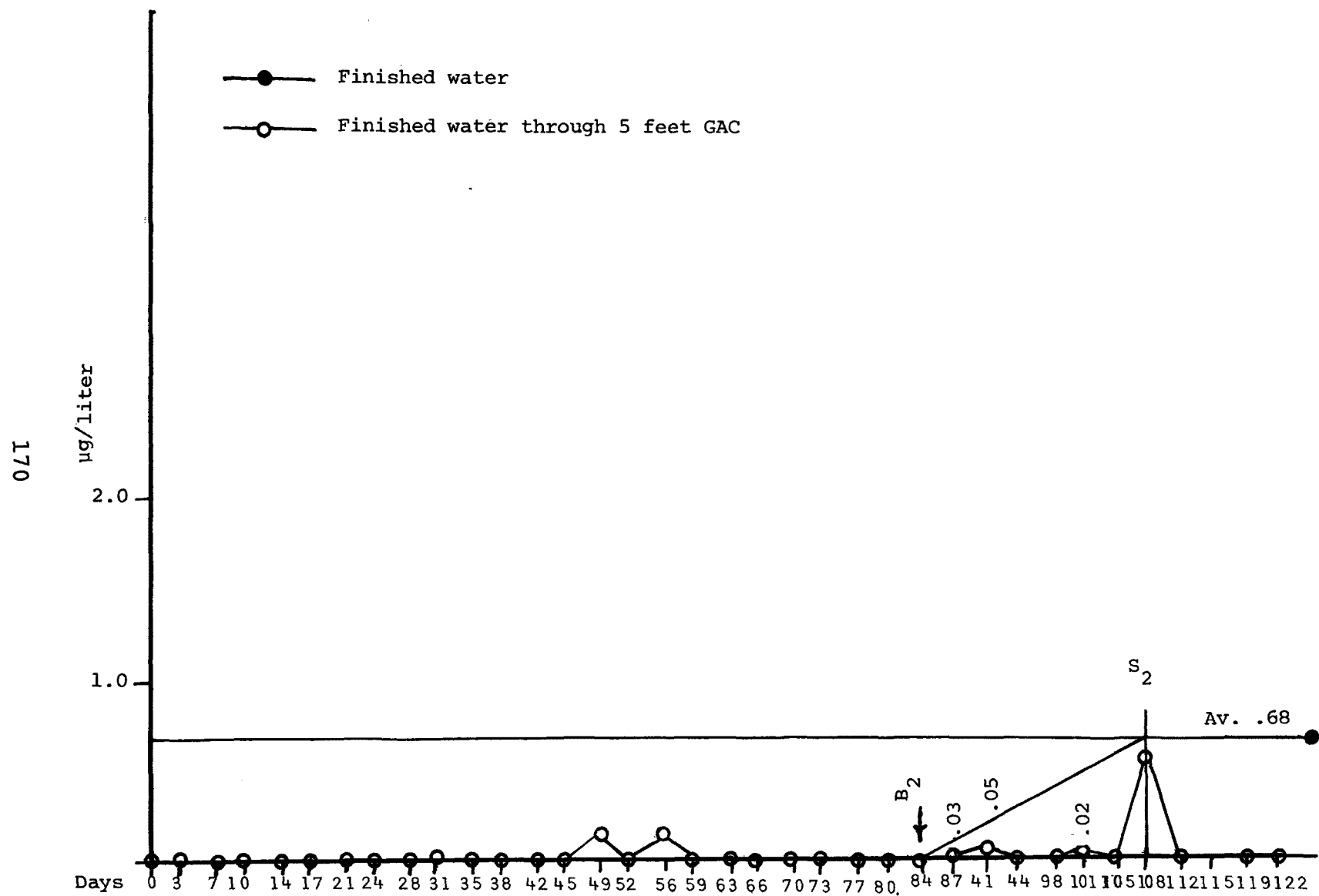


Figure 100. Trichloroethylene in finished water and removal by 1.52 meters (5 feet) of GAC (ED4).

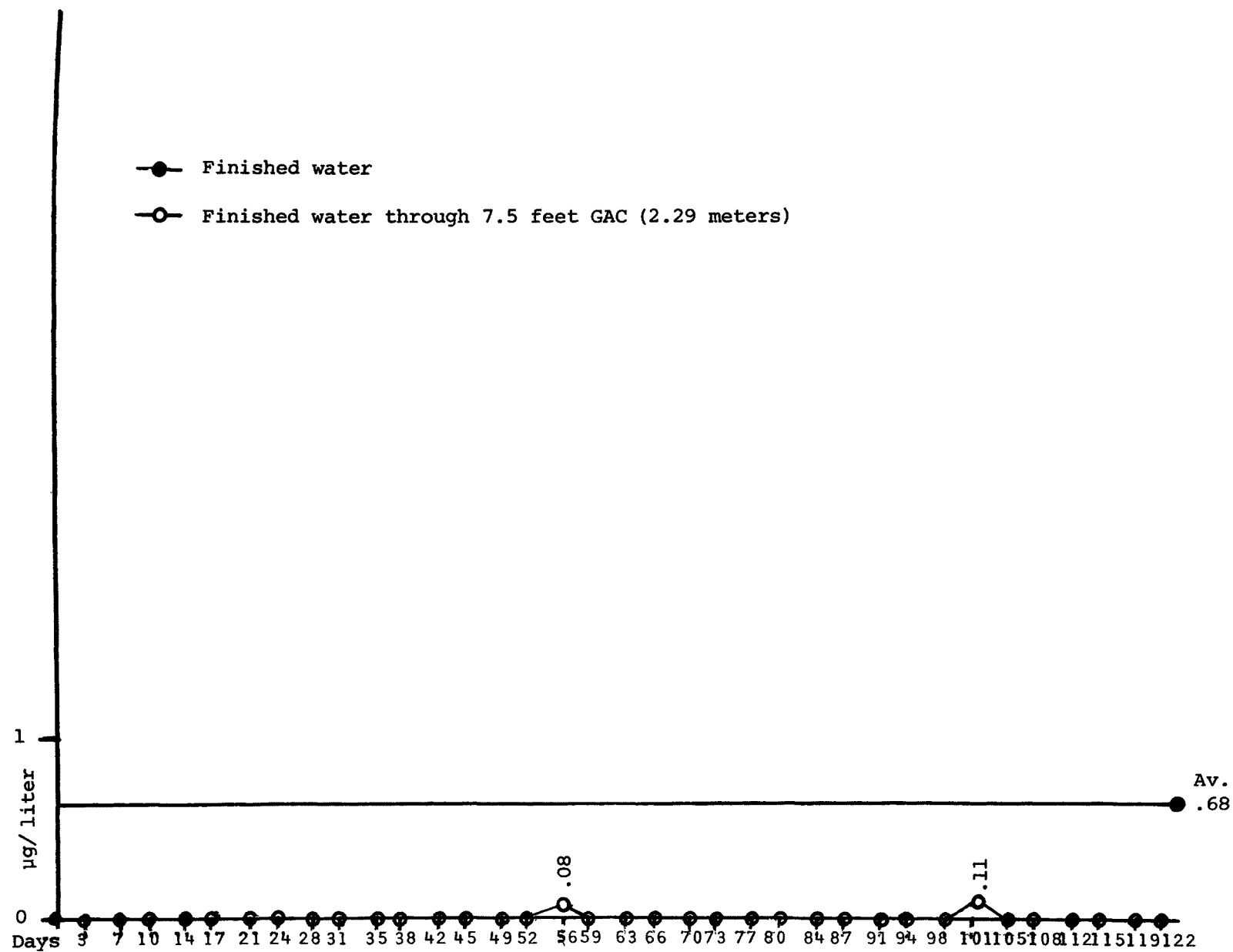
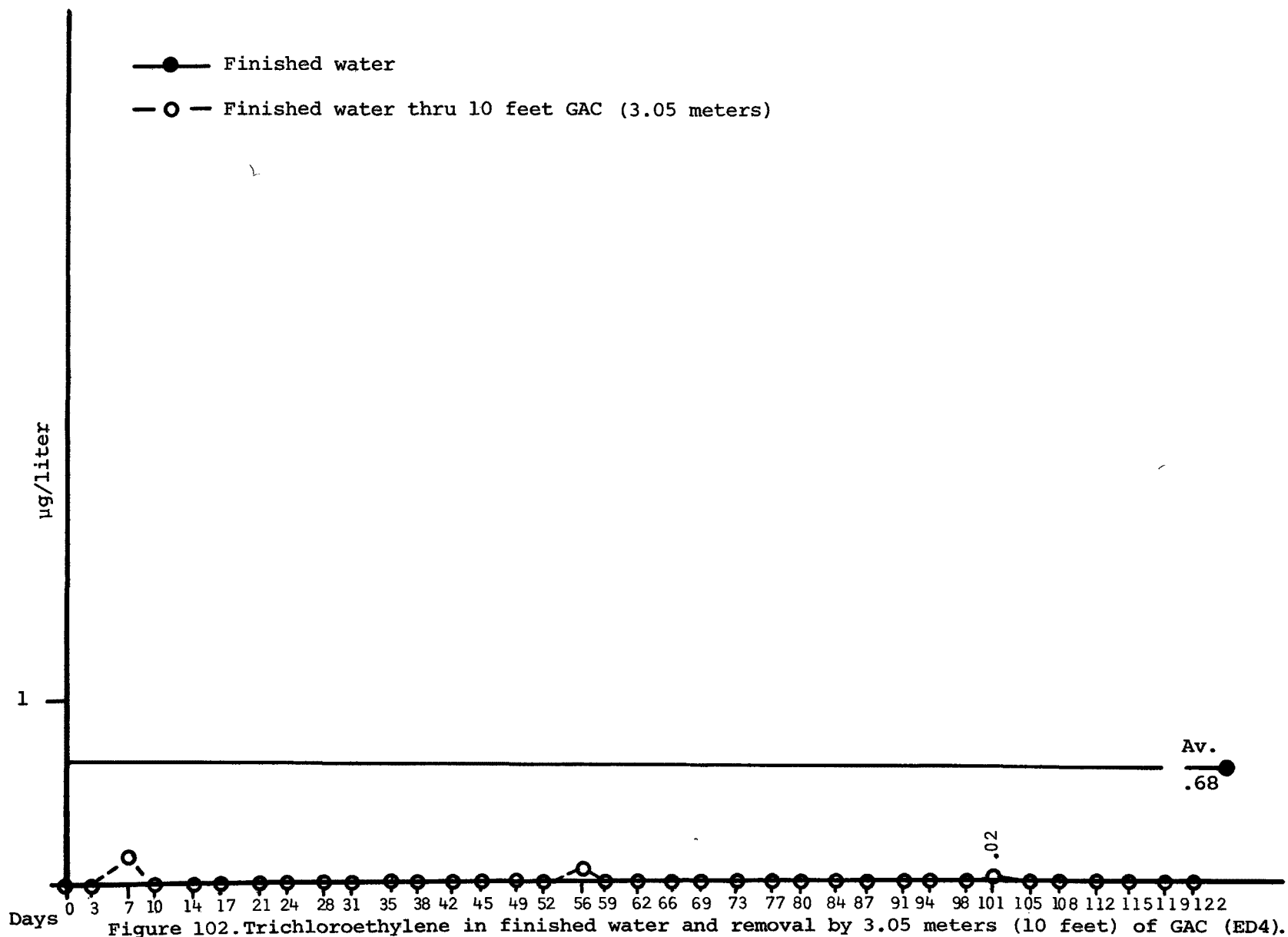


Figure 101. Trichloroethylene in finished water and removal by 2.29 meters (7.5 feet) of GAC (ED4).

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Tetrachloroethylene--The influent concentration in all ED was very low. The average in ED1R was 0.016 µg/L. The concentration in ED2 and ED3 was nil for all test points. In ED4, all points were nil to test day 108 and from day 108 to the end of the test at 122 days, the average concentration was only 0.02 µg/L. The influent concentration and adsorption curves for XE-340, 0.76 meter (2.5 feet) deep, in ED1R are plotted in Figure 103. The column allowed trace passage at test day 10, 14, 17 and 98. In ED3, while the influent concentration was nil for all test points, the effluent from the IRA-904 resin column, 0.76 meter (2.5 feet) deep, had low levels on six of the sixteen test points. In ED3, all effluent test points showed nil concentration through a parallel GAC column 0.76 meter (2.5 feet) deep. In ED4, all effluent test points showed nil concentration through all four bed depths of GAC.

Chlorobenzene--Finished water adsorption data appear in Table 35. Curves appear in Figures 104, 105, 106, and 107.

The influent concentration to the 0.76 meter (2.5 feet) deep XE-340 column in ED1R was erratic as shown by the curve in Figure 104. The influent concentration was nil on more than half of the test days. The column effluent contained no chlorobenzene during any of the test dates. In ED2, the average influent concentration was lower, Figure 105. The XE-340 column removed all chlorobenzene up to day 56, when a trace level was noted in the effluent occurring after a peak in the influent concentration. On test day 63, the column again had no chlorobenzene in the effluent. In ED3, Figure 106, the IRA-904 resin column had more chlorobenzene in the effluent than in the influent, the average increase being 1.4 times. GAC, 0.76 meter (2.5 feet) deep, was studied in ED3 and ED4. In ED3, Figure 106, except for one data point, test day 4, all the chlorobenzene was removed for the entire test period of 53 days. When repeated in ED4, Figure 107, all the chlorobenzene was removed to the breakthrough time of 84 days. It is questionable whether saturation occurred as indicated in Figure 107, or if the data point at day 115 was merely a spike in the effluent. In deeper GAC columns, 1.52 (5.0 feet), 2.29 (7.5 feet), and 3.05 (10 feet) meters, no trace of chlorobenzene was found in the column effluents throughout the test period of 122 days.

p-Chlorotoluene--The influent concentration in ED1R, ED2, ED3, and ED4 was essentially nil and the effluent from all adsorbent columns was essentially nil.

o, m and p-Dichlorobenzene--Adsorption data appear in Table 36. Curves appear in Figures 108, 109, 110, 111 and 112.

The influent and adsorption curves for the summed value of the three isomers in ED1R are shown in Figure 108. The XE-340 column, 0.76 meter (2.5 feet) deep, removed the isomers to

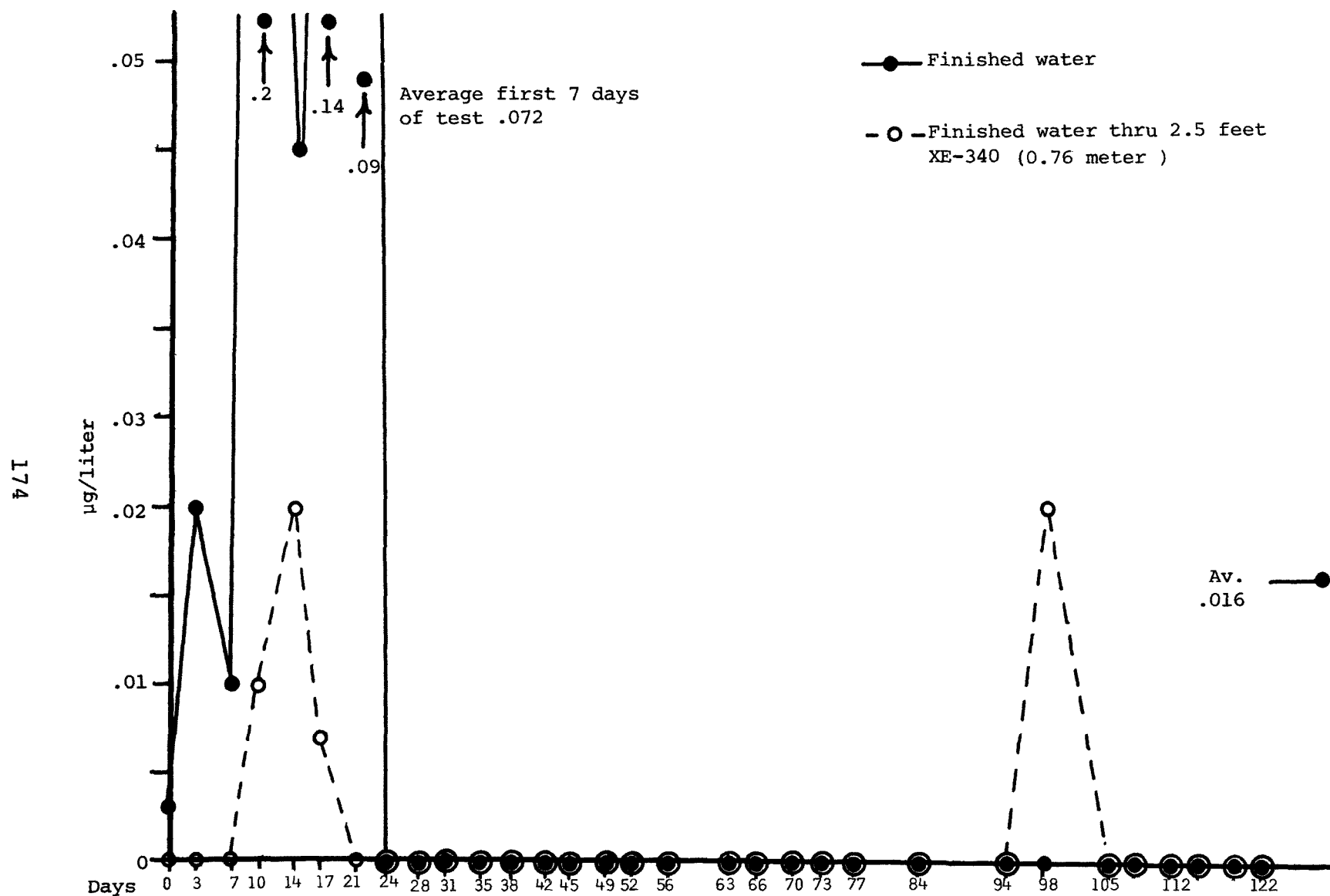
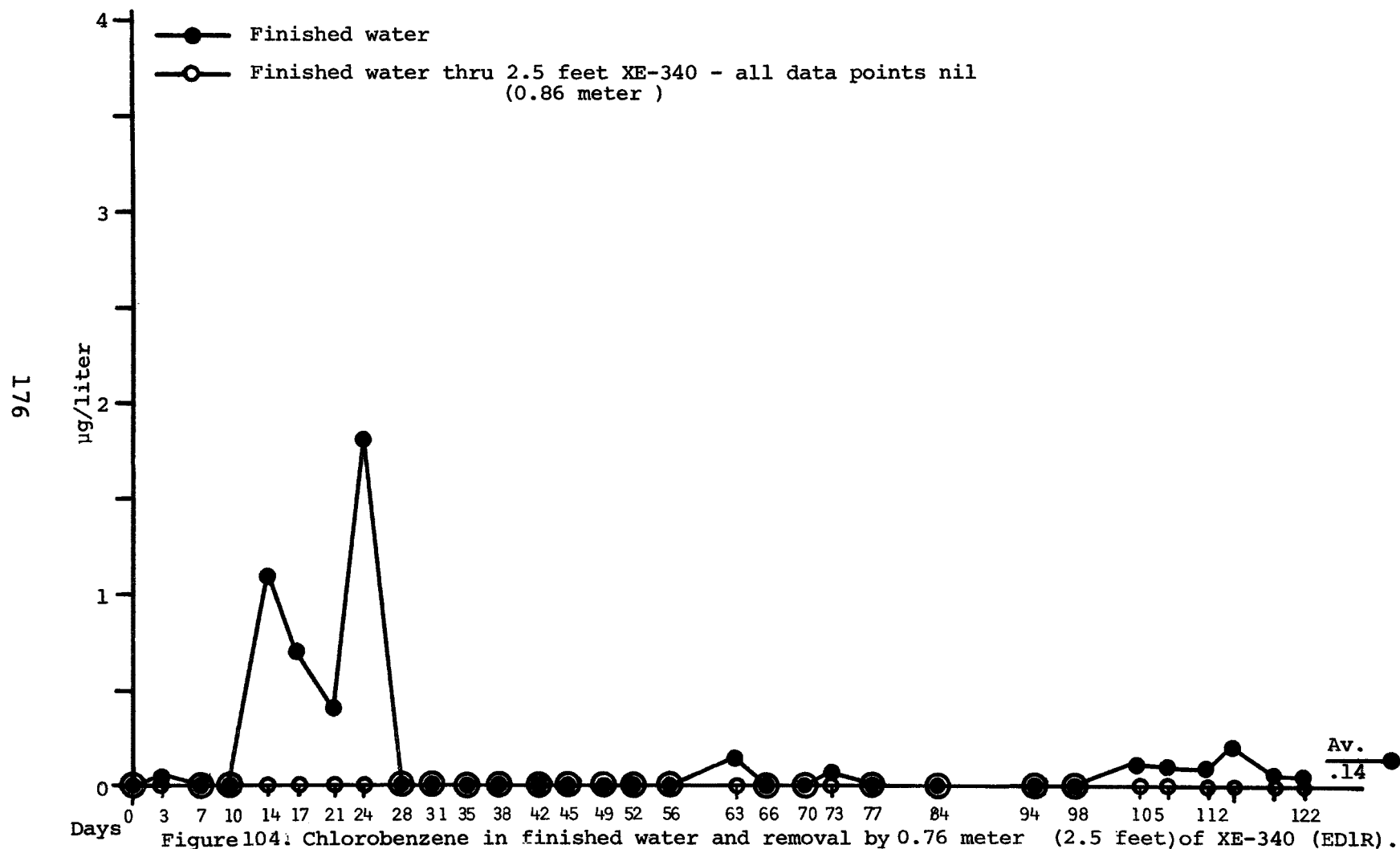


Figure 103. Tetrachloroethylene in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R)

TABLE 35. CHLOROBENZENE ADSORPTION DATA FROM FINISHED WATER

ED	Bed Depth Feet	Adsorbent	Average Influent µg/L	Column Breakthrough Days	Column Saturation Days	MT Inch	Test Duration Days	Total Entering Each Column During Test Grams	Total Adsorbed by Each Column at End of Test Grams	Adsorbed by Each Column at Saturation Grams	% Adsorbed at End of Test %	% Adsorbed at Saturation %	Adsorption per 100 gms. Adsorbent at End of Test Grams	Adsorption per 100 gms. Adsorbent at Saturation Grams	CC
1R	2.5	XE-340	.14	none			122	.0015	.0015		100		.0007		
2	2.5	XE-340	.08	none			63	.00045	.00045		100		.00021		
3	2.5	GAC	.8	none			53	.0038	.0038		100		.0022		
3	2.5	904	.8				53	Average increase of 1.4X							
4	2.5	GAC	.86	84	115?	8	122	.0094	.0076	.0076	81	86	.0043	.0043	.0039
4	5	GAC	.86	none			122	.0094	.0094		100		.0027		
4	7.5	GAC	.86	none			122	.0094	.0094		100		.0018		
4	10	GAC	.86	none			122	.0094	.0094		100		.0013		
2.5	feet=0.76 meter			5	feet=1.52 meters			7.5	feet=2.29 meters			10	feet=3.05 meters		



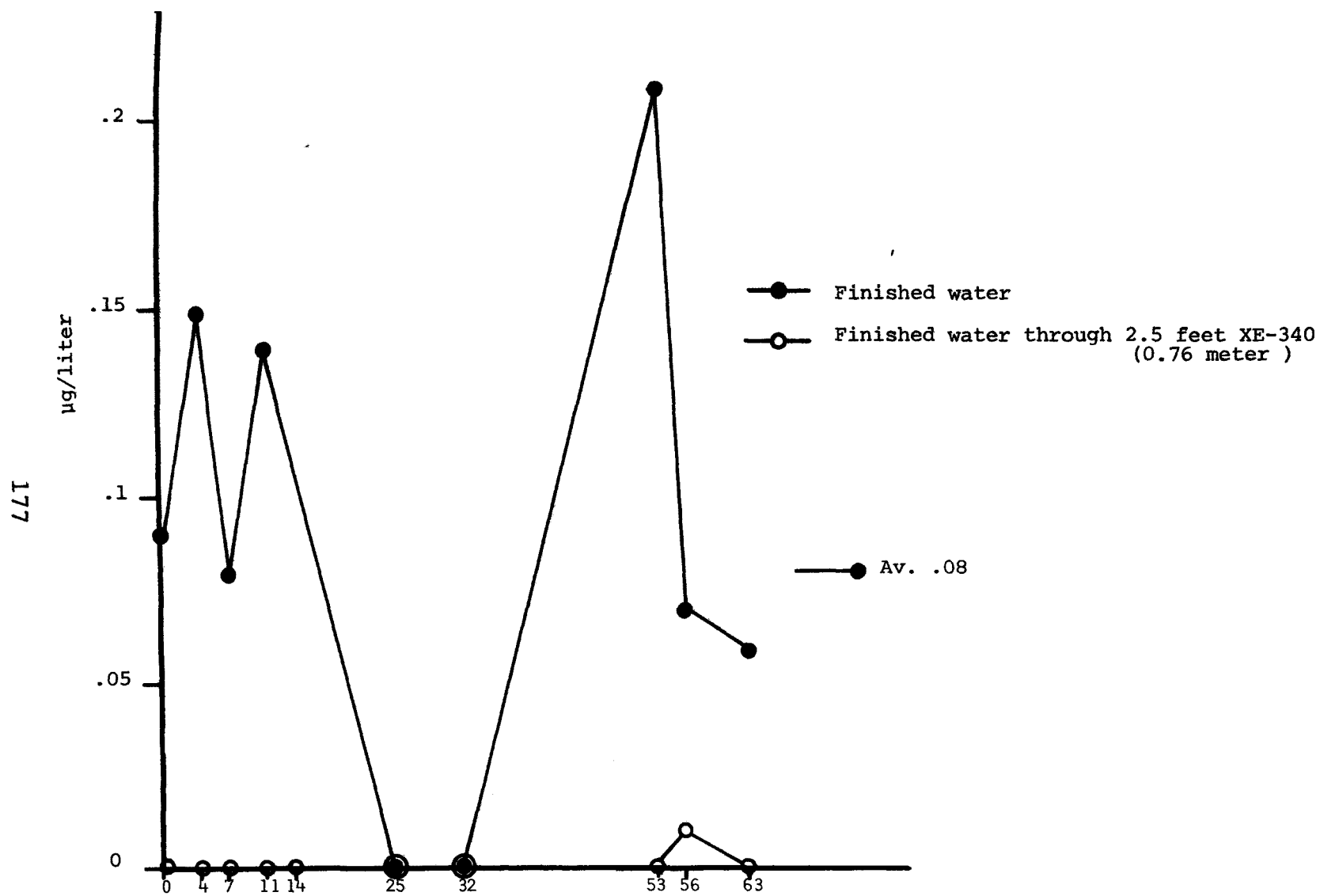


Figure 105. Chlorobenzene in finished water and removal by 0.76 meter (2.5 feet) XE-340 (ED2).

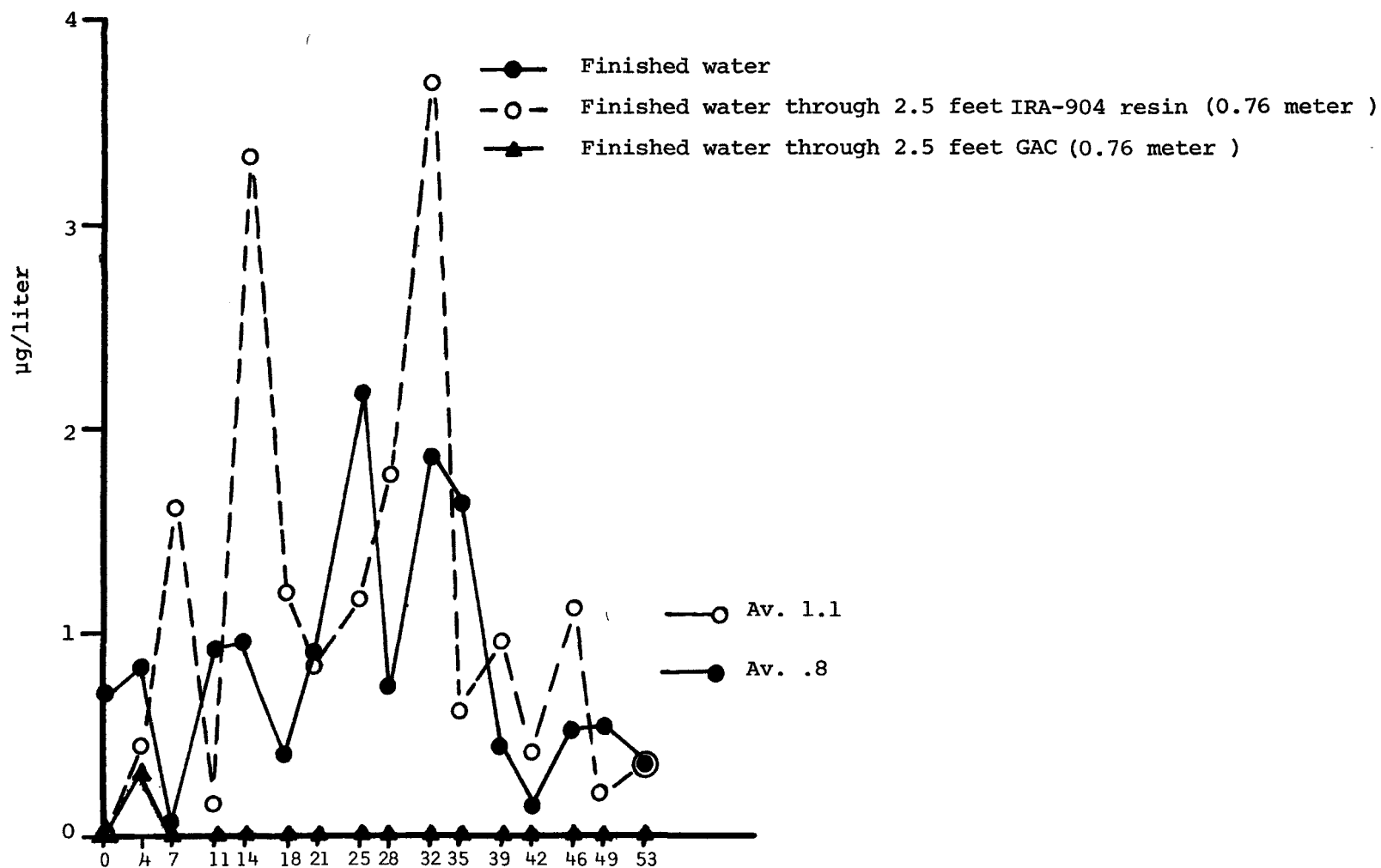


Figure 106. Chlorobenzene in finished water and removal by 0.76 meter (2.5 feet) of GAC and 0.76 meter (2.5 feet) of IRA-904 resin (ED3).

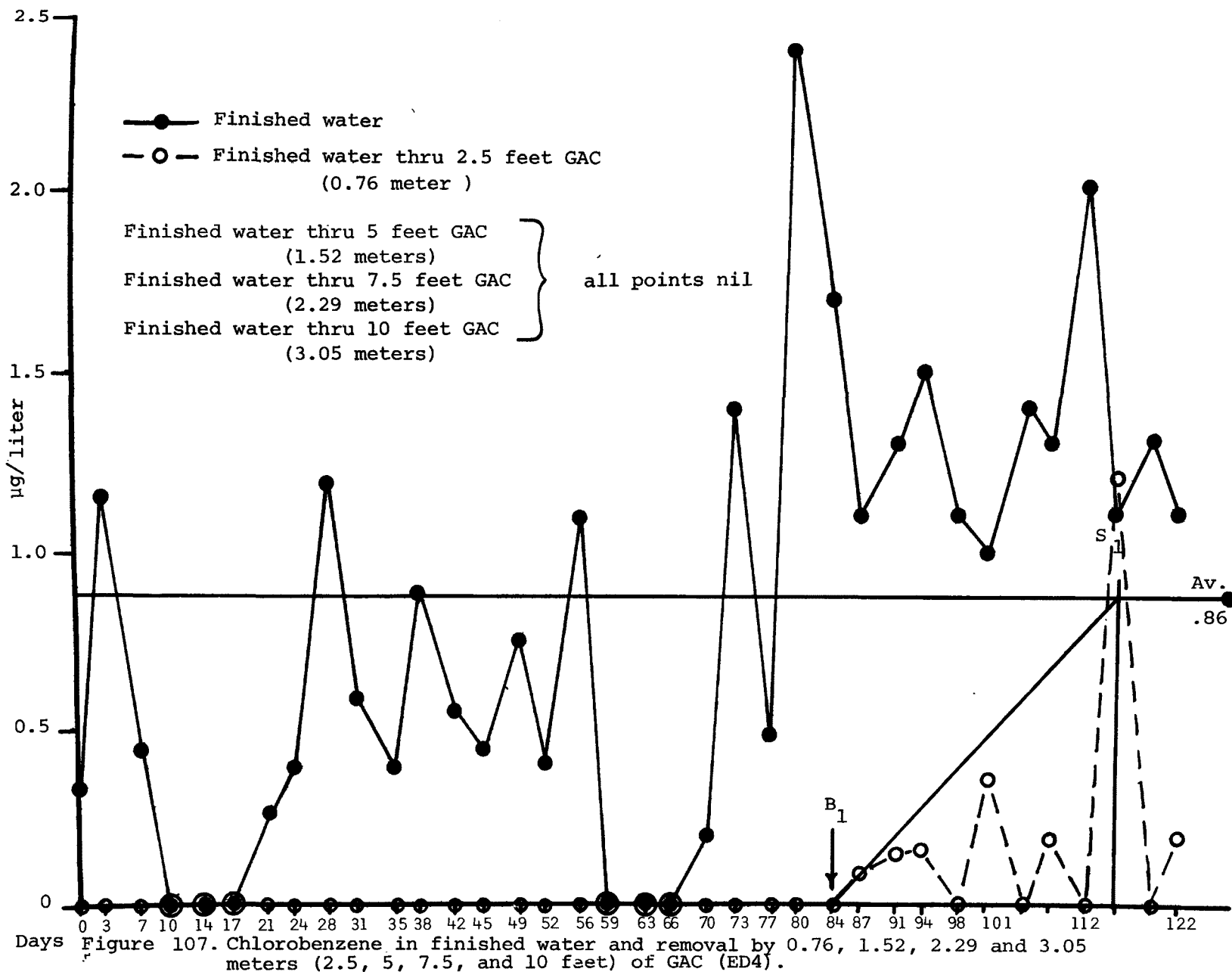


TABLE 36. o, m, AND p-DICHLOROBENZENE ADSORPTION
DATA FROM FINISHED WATER

ED	Bed Depth Feet	Adsorbent	Average Influent µg/L	Column Breakthrough Days	Column Saturation Days	MT _N Inch	Test Duration Days	Total Entering Each Column During Test Grams	Total Adsorbed by Each Column at End of Test Grams	Adsorbed by Each Column at Saturation Grams	% Adsorbed at End of Test %	% Adsorbed at Saturation %	Adsorption per 100 gms. Adsorbent at End of Test Grams	Adsorption per 100 gms. Adsorbent at Saturation Grams	CC
	THREE ISOMERS SUMMED														
1R	2.5	XE-340	.63	none			122	.0069	.0069		100		.0032		
2	2.5	XE-340	2.1	none			63	.0068	.0068		100		.0032		
3	2.5	904	.3	increased	2.7X										
	m-DICHLOROBENZENE														
4	2.5	GAC	nil concentration during entire test				122								
4	5	GAC	nil concentration during entire test				122								
4	7.5	GAC	nil concentration during entire test				122								
4	10	GAC	nil concentration during entire test				122								
													(continued)		

2.5 feet=0.76 meter 5 feet=1.52 meters 7.5 feet=2.29 meters 10 feet=3.05 meters

TABLE 36. (CONT.)

ED	Bed Depth Feet	Adsorbent	Average Influent µg/L	Column Breakthrough Days	Column Saturation Days	MT N Inch	Test Duration Days	Total Entering Each Column During Test Grams	Total Adsorbed by Each Column at End of Test Grams	Adsorbed by Each Column at Saturation Grams	% Adsorbed at End of Test %	% Adsorbed at Saturation %	Adsorption per 100 gms. Adsorbent at End of Test Grams	Adsorption per 100 gms. Adsorbent at Saturation Grams	CC
	P-DICHLOROBENZENE														
4	2.5	GAC	.24	none			122	.0026	.0026		100		.0015		.0012
4	5	GAC	.24	none			122	.0026	.0026		100		.00074		
4	7.5	GAC	.24	none			122	.0026	.0026		100		.00049		
4	10	GAC	.24	none			122	.0026	.0026		100		.00037		
	O-DICHLOROBENZENE														
4	2.5	GAC	.14	none			122	.0015	.0015		100		.00085		.00065
4	5	GAC	.14	none			122	.0015	.0015		100		.00043		
4	7.5	GAC	.14	none			122	.0015	.0015		100		.00028		
4	10	GAC	.14	none			122	.0015	.0015		100		.00021		

2.5 feet=0.76 meter 5 feet=1.52 meters 7.5 feet=2.29 meters 10 feet=3.05 meters

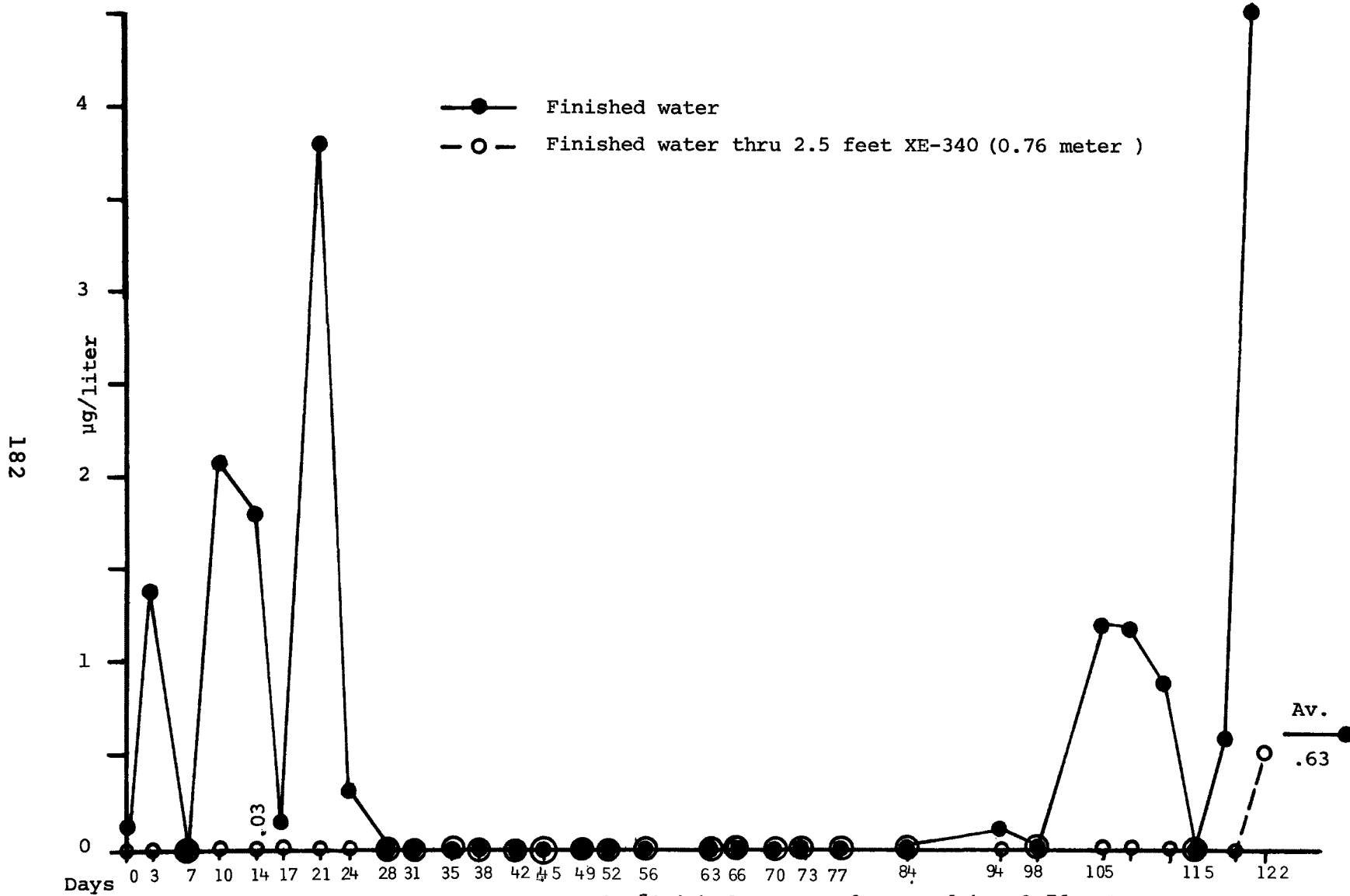
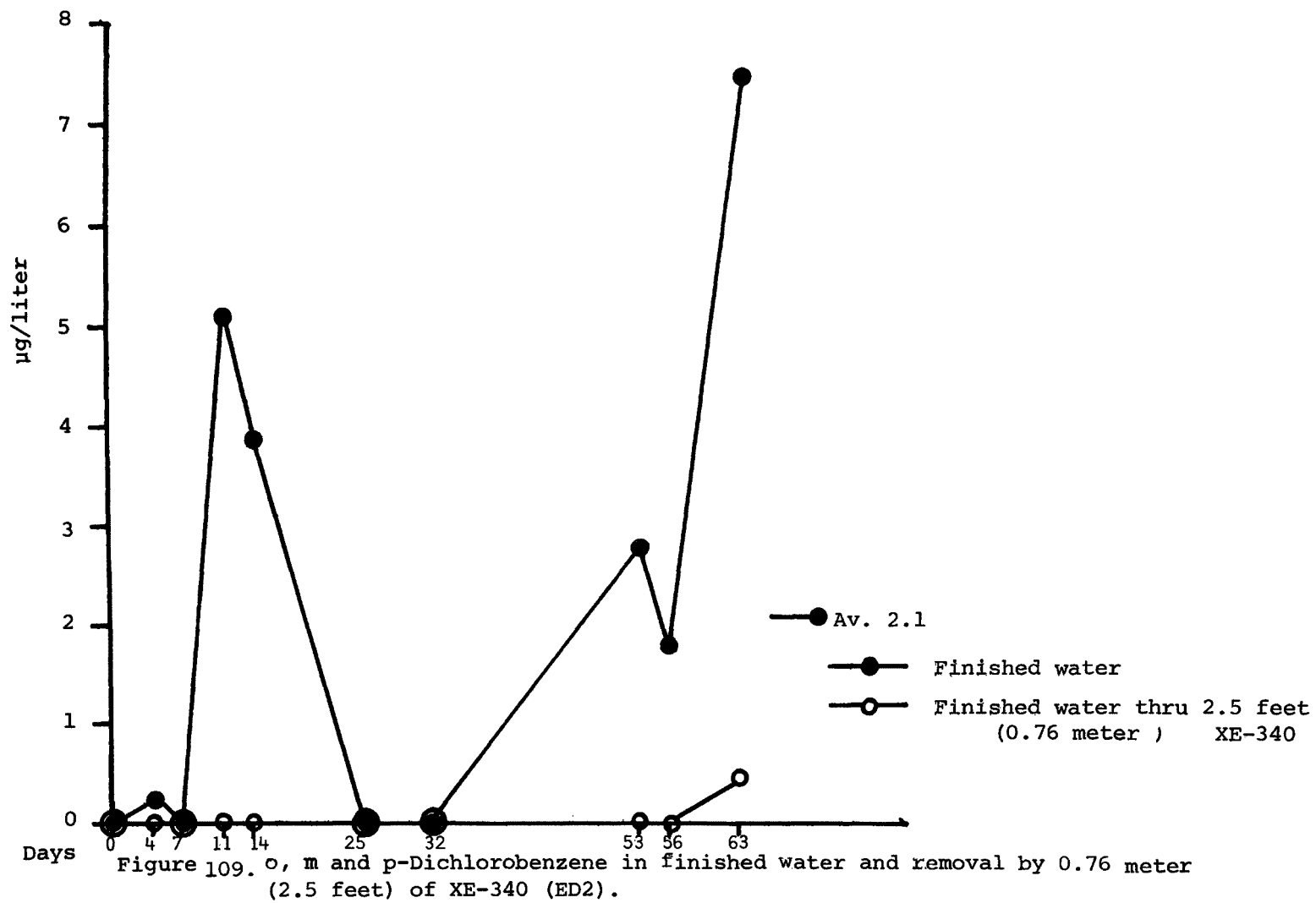


Figure 108. o, m and p-Dichlorobenzene in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).



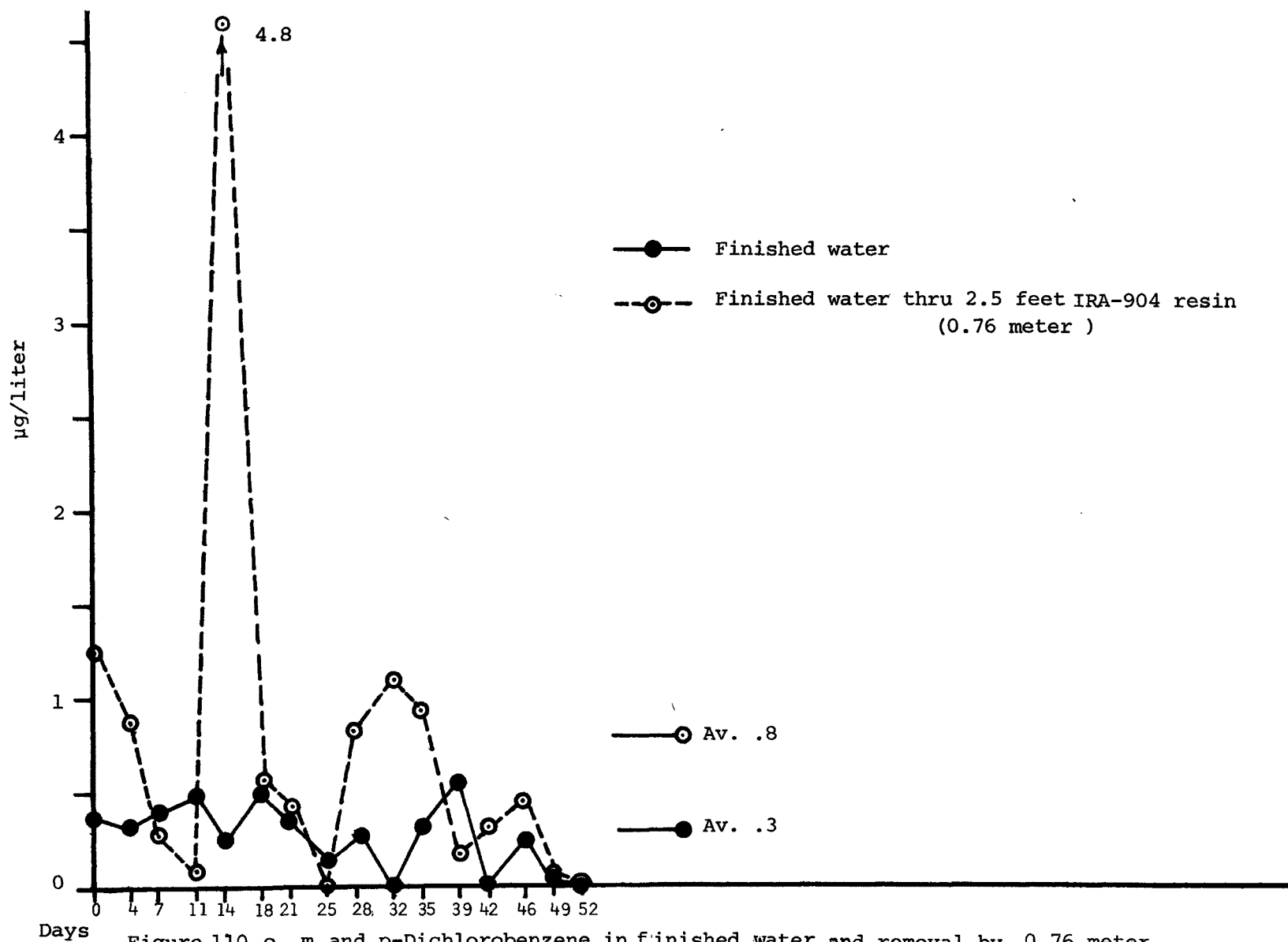


Figure 110. o, m and p-Dichlorobenzene in finished water and removal by 0.76 meter (2.5 feet) of IRA-904 resin (ED3).

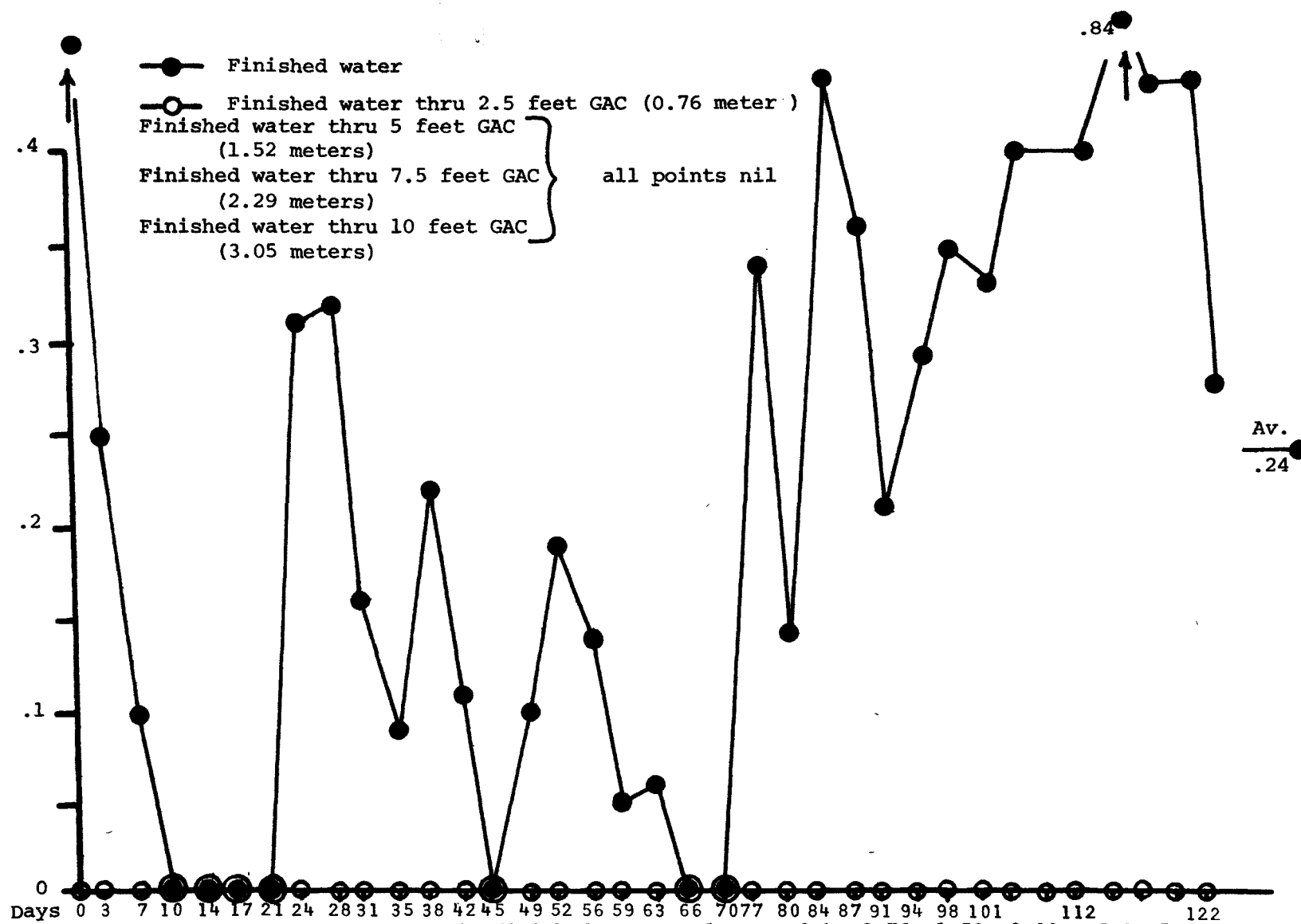


Figure 111. p-Dichlorobenzene in finished water and removal by 0.76, 1.52, 2.29 and 3.05 meters (2.5, 5, 7.5 and 10 feet) of GAC (ED4).

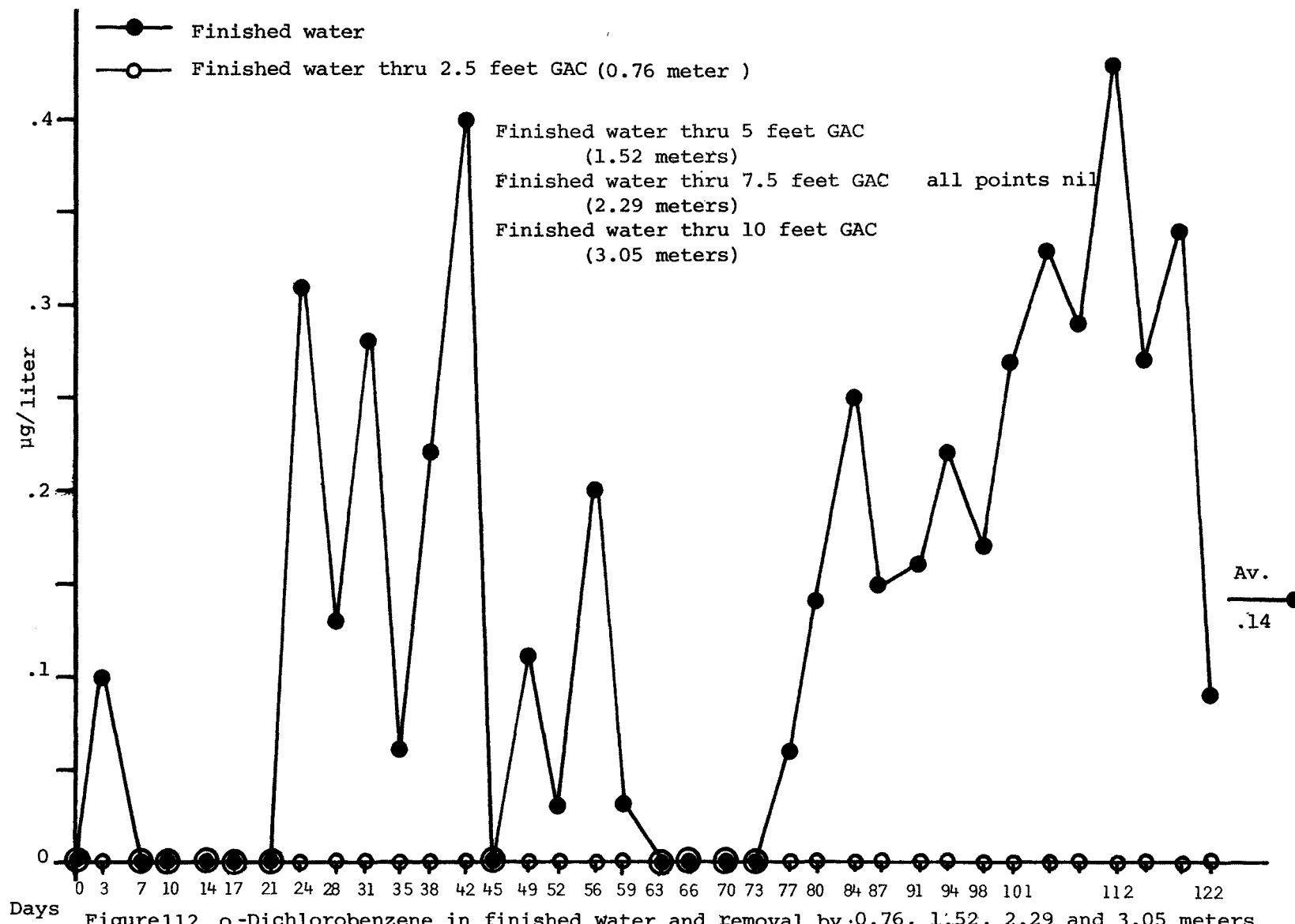


Figure 11. 1,2-Dichlorobenzene in finished water and removal by 0.76, 1.52, 2.29 and 3.05 meters (2.5, 5, 7.5 and 10 feet) of GAC (ED4).

test day 122 when a low level of passage occurred. A large spike in the influent concentration on test day 122 was noted. XE-340, 0.76 meter (2.5 feet) deep, gave similar results in ED2, as indicated by the curves in Figure 109. In ED3, Figure 110, the IRA-904 resin, 0.76 meter (2.5 feet) deep, appears to have a higher level of isomers in the column effluent (2.7 times) than in the influent.

In ED4, each isomer was reported separately. The influent concentration and effluent concentration of m-dichlorobenzene was nil for all GAC bed depths. The average influent concentration, Figure 111, for p-dichlorobenzene was 0.24 $\mu\text{g/L}$. The effluent concentration for all bed depths was nil for all test points. The average influent concentration, Figure 112, for o-dichlorobenzene was 0.14 $\mu\text{g/L}$. The effluent concentration for all bed depths was nil for all test points.

Adsorption by XE-340--

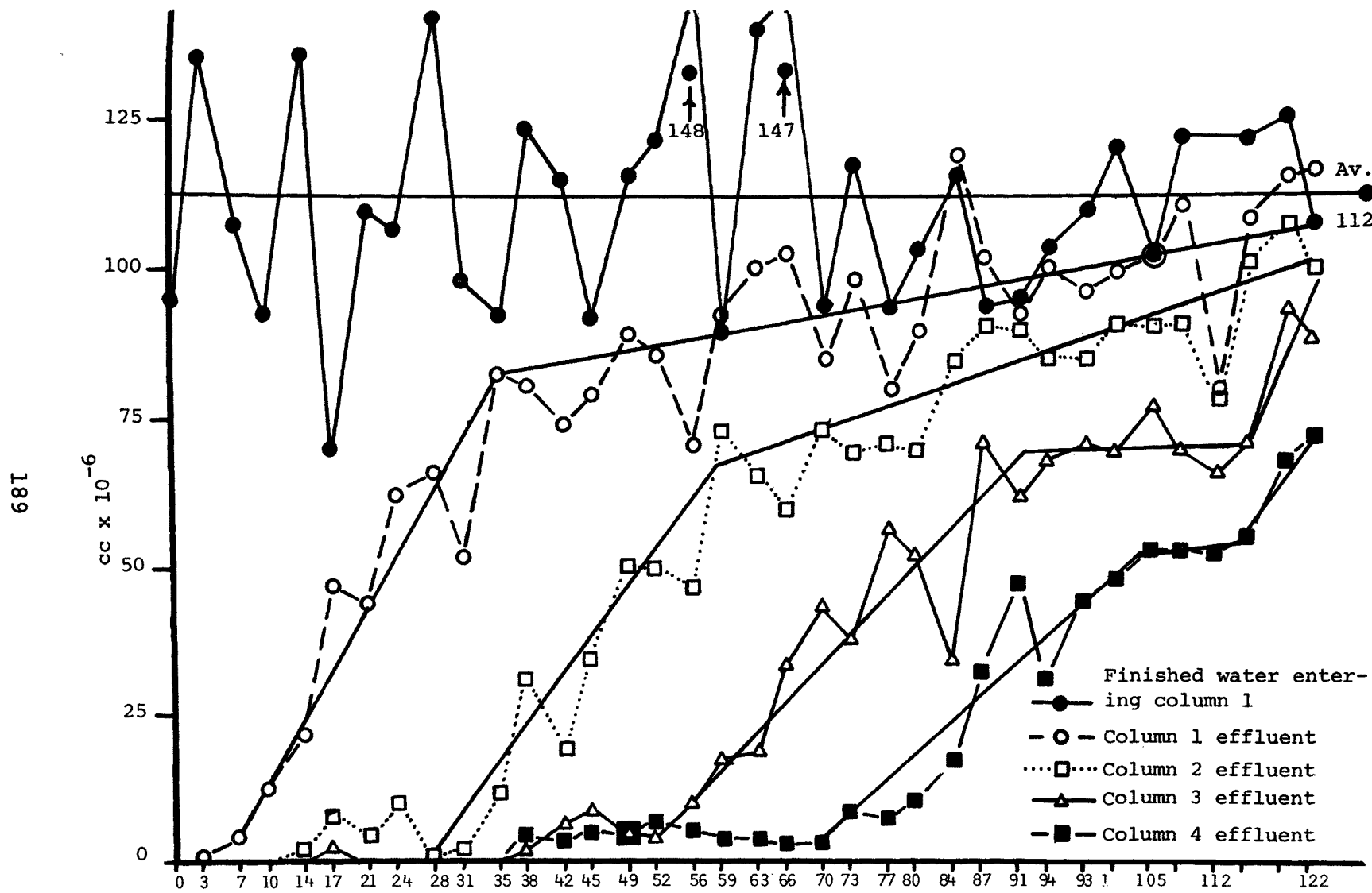
We have presented much data showing that XE-340 resin has approximately three times the adsorptive capacity for individual HOC as GAC. The adsorptive capacity of adsorbents is usually compared by measuring their capacity to adsorb butane gas. The adsorbent which adsorbs the most butane is usually considered to have more adsorptive capacity for substances like HOC than an adsorbent which adsorbs less butane. Butane gas phase adsorption data for the GAC and XE-340 used in this study appear in Figure 170. The method of obtaining these curves and their interpretations are discussed in the section of the report in which they appear. For the moment we will say only that the curves show that based on butane adsorption data GAC should have about seven times the adsorptive capacity of XE-340. This figure is arrived at by projecting a vertical line, from 20 for example on the "X" axis to the Butane Gas Phase (XE-340) and Butane Gas Phase (GAC) curves, and then at the intersect points, reading the corresponding cc adsorbed per 100 grams of adsorbent on the "Y" axis. Values of 0.7 cc and 0.1 cc are obtained for GAC and XE-340 respectively. Thus GAC adsorbs seven times as much butane as an equal weight of XE-340. It has been shown by Neely (6) that XE-340 adsorption does not follow the usual pattern of physical adsorption on GAC because in addition to adsorption in micropores, substances like HOC are taken into the polymer matrix of the resin. The resin matrix swells as a result of this incorporation. Thus, in our tests, XE-340 exhibits approximately three times the adsorptive capacity for HOC as GAC because of adsorption into the polymer matrix. We will show later in the report, that for substances which are not so readily taken up by the polymer matrix, GAC has more adsorptive capacity than XE-340, as predicted by the order of butane adsorption data. These are the fulvic acid degradation substances which make up the bulk of substances measured by TOC and THM FP analysis, generally known as precursors.

Adsorptive Capacity and Competitive Adsorption--

Figure 113 is a plot of the total volume in cc's of all the purgeable HOC in the finished water entering and leaving each of the four GAC beds in the 122-day test, ED4. Integration of these curves produces the three curves in Figure 114. Curve I indicates the total volume in cc's of HOC entering each column. Curve II indicates the total volume in cc's of HOC adsorbed by each column and the cc's adsorbed per 100 grams of GAC. Curve III indicates the total cc's adsorbed by 0.76 (2.5 feet), 1.52 (5.0 feet), 2.29 (7.5 feet) and 3.05 (10 feet) meters of GAC. In 122 days, the finished water entering column 1 contained 1.235 cc of HOC, the entire first column adsorbed 0.382 cc or 0.217 cc per 100 grams of GAC. The next three columns each received less and adsorbed less HOC than the preceding column. When Curve II is projected to the "Y" axis the total adsorptive capacity in cc's of HOC, 0.27 cc per 100 grams of GAC, for our particular system is indicated. Adsorption per column decreased as the concentration of adsorbate decreased. Therefore, for maximum adsorbent use, the greatest amount of adsorbent possible should be in contact with the highest possible concentration of adsorbate. These data support the generally accepted view on carbon use. The most efficient adsorbent usage would be a continuous in-out GAC system. According to our data such a system would have approximately 43 percent greater adsorptive capacity than a single 3.05 meters (10 feet) deep bed. Multiple beds in series also offer advantages in better carbon usage. General practice is to operate the series system until the last bed in series reaches the effluent criteria. The first bed is then replaced with regenerated carbon and becomes the last bed in the series arrangement. The new lead bed is the one that was previously second in the series. In this way, four columns, each 0.76 meter (2.5 feet) deep, arranged in series would have about 31 percent more adsorptive capacity than one single column 3.05 meters (10 feet) deep. However, the actual design configuration must take into consideration the higher capital costs of these systems, as well as, the reduced operating costs. The lowest total cost system is the one desired. Data described in this study are important in achieving the most practical design (7).

The curves in Figure 115 were obtained by integrating the curves in Figure 113 at various sampling dates and more clearly show the rates of saturation. It is evident from the top curve in Figure 115 that column 1 will probably reach saturation at the 0.27 cc value discussed above.

We have already presented data suggesting that the adsorptive capacity of GAC and XE-340 for cis 1,2-dichloroethene is 30 percent less in finished water than in raw water, probably due to competitive HOC adsorption. To aid the discussion of competitive HOC adsorption, Figure 116 shows the adsorption wave



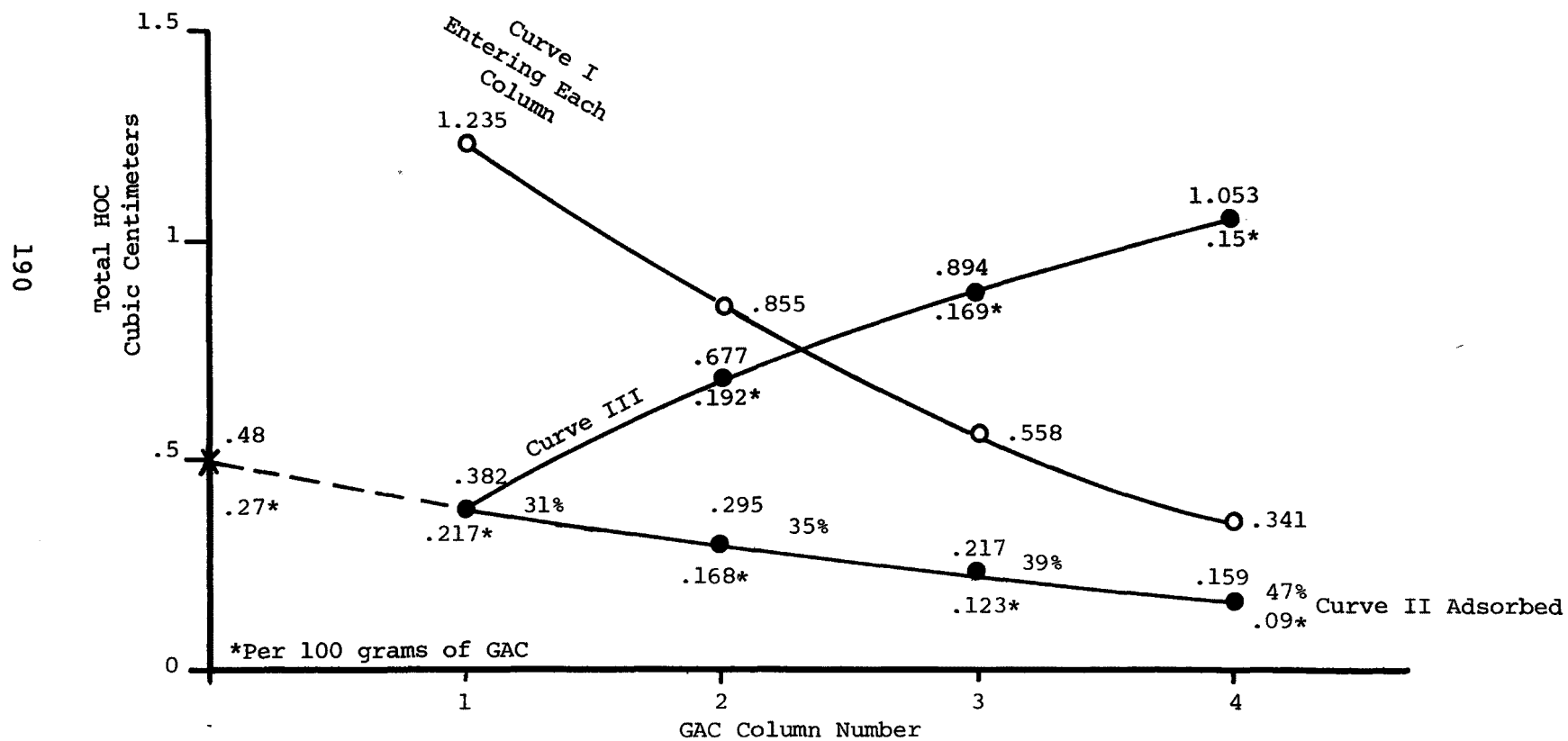


Figure 114. Cubic centimeters of total HOC entering and adsorbed by GAC column #1, 2, 3 and 4 in 122 days (ED4).

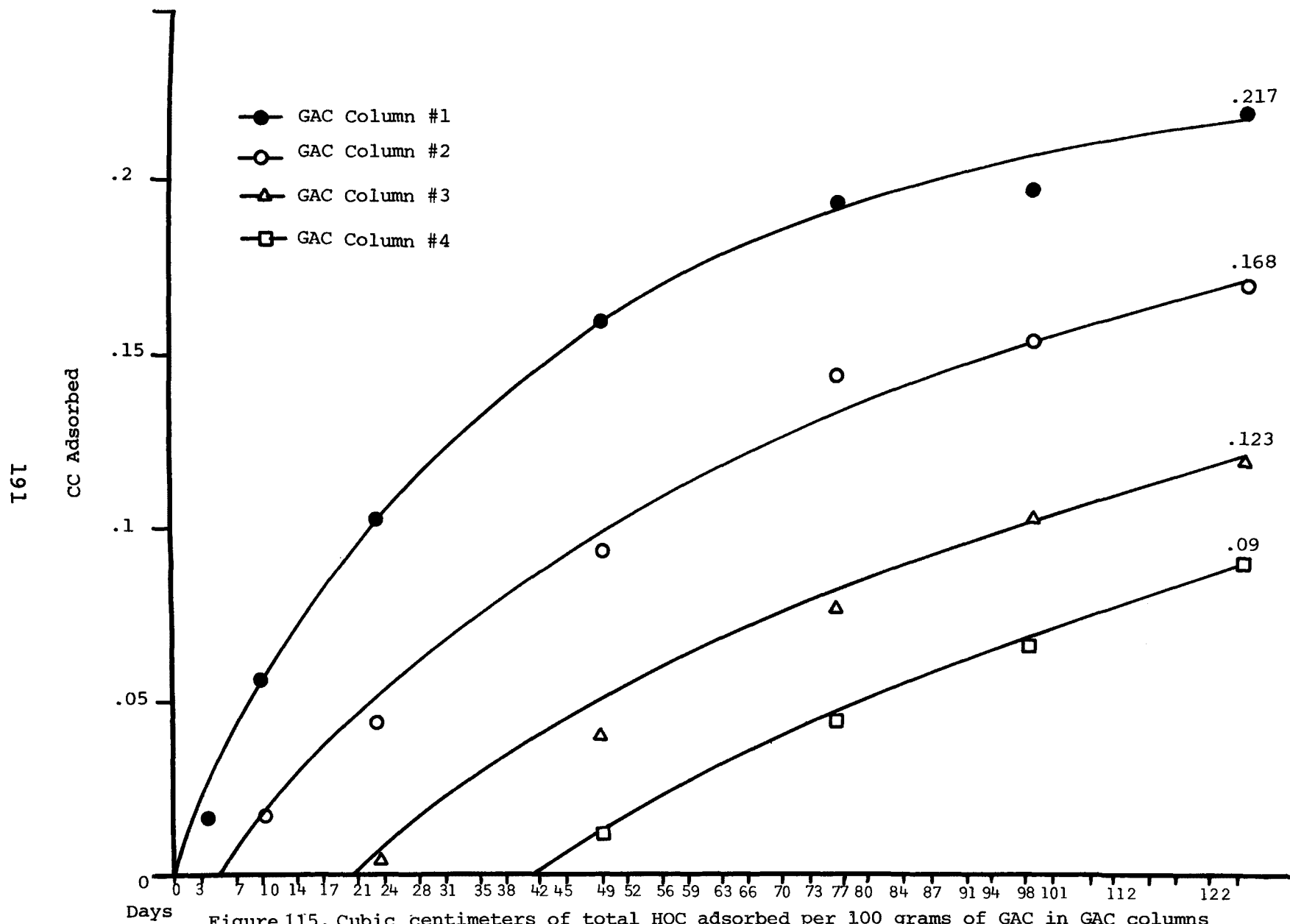


Figure 115. Cubic centimeters of total HOC adsorbed per 100 grams of GAC in GAC columns #1, 2, 3 and 4 in 122 days (ED4).

fronts defined by breakthrough and saturation time for several HOC and Type II and III substances on a 0.76 meter (2.5 feet) deep bed of GAC. The vertical height at the end of each HOC curve represents the concentration in $\mu\text{g/L}$ of each HOC. The concentration is read on the "Y" axis scale. The "X" intercept for each curve is the days until breakthrough occurs and the vertical projection of the end of each line to the "X" axis is the time until saturation for that substance. The first number in the parenthesis also gives the breakthrough time in days and the second number gives the time to saturation. The Type II and III substances shown in Figure 116 are defined in the discussion of precursor removal that follows on page 192. Finished water entering the first GAC column contains 7.8 mg/L Dissolved Organic Matter (DOM) of Type II substances and 0.58 mg/L of Type III, which corresponds to 4.69 and 0.36 mg/L respectively of TOC. The curve for the Type II substances in Figure 116 merely represents the initial breakthrough and saturation time of 0 and 16 days respectively. The arrow at the end of the curve indicates that the mg/L concentration cannot be shown on the $\mu\text{g/L}$ scale on the "Y" axis. The dash-line curve representing the Type III substances in Figure 116 merely indicates that these strongly adsorbed substances have an initial breakthrough and saturation time of unknown values which are much beyond the breakthrough and saturation time for all the HOC studied in this work. We have calculated an average MT_{10} for Type III substances of about three inches. Type III substances, which are adsorbed by the top portion of the GAC column, do not offer competition to adsorption of all the HOC throughout most of the column. On the other hand, Type II substances compete with HOC throughout the column.

Of the five HOC shown in Figure 116, chloroform encounters the least competitive HOC adsorption and bromoform encounters the most competition. The results of this competitive adsorption are shown in Table 37. These values show the predicted adsorptive capacity of each of five HOC from pure water at saturation for the GAC used in this study. These values are based on calculations using the Polanyi Theory and modifications by Manes and Hofer which are described beginning on page 283.

Chloroform at the concentration in our finished water is adsorbed 5 percent of its predicted capacity from pure water. Bromodichloromethane, chlorodibromomethane and bromoform which are present in progressively decreasing concentration, nevertheless, have higher predicted capacities than chloroform. However, the percent of predicted values steadily decreases (3.6, 1.8 and 0.12 percent) because of increasing competitive HOC adsorption as indicated by the order of their wave front curves in Figure 116. Cis 1,2-dichloroethene is present at a lower concentration than chloroform and has a predicted adsorptive capacity, as shown in Table 37, less than chloroform (0.46 compared to 0.68). The observed adsorptive capacity is 6.5 percent

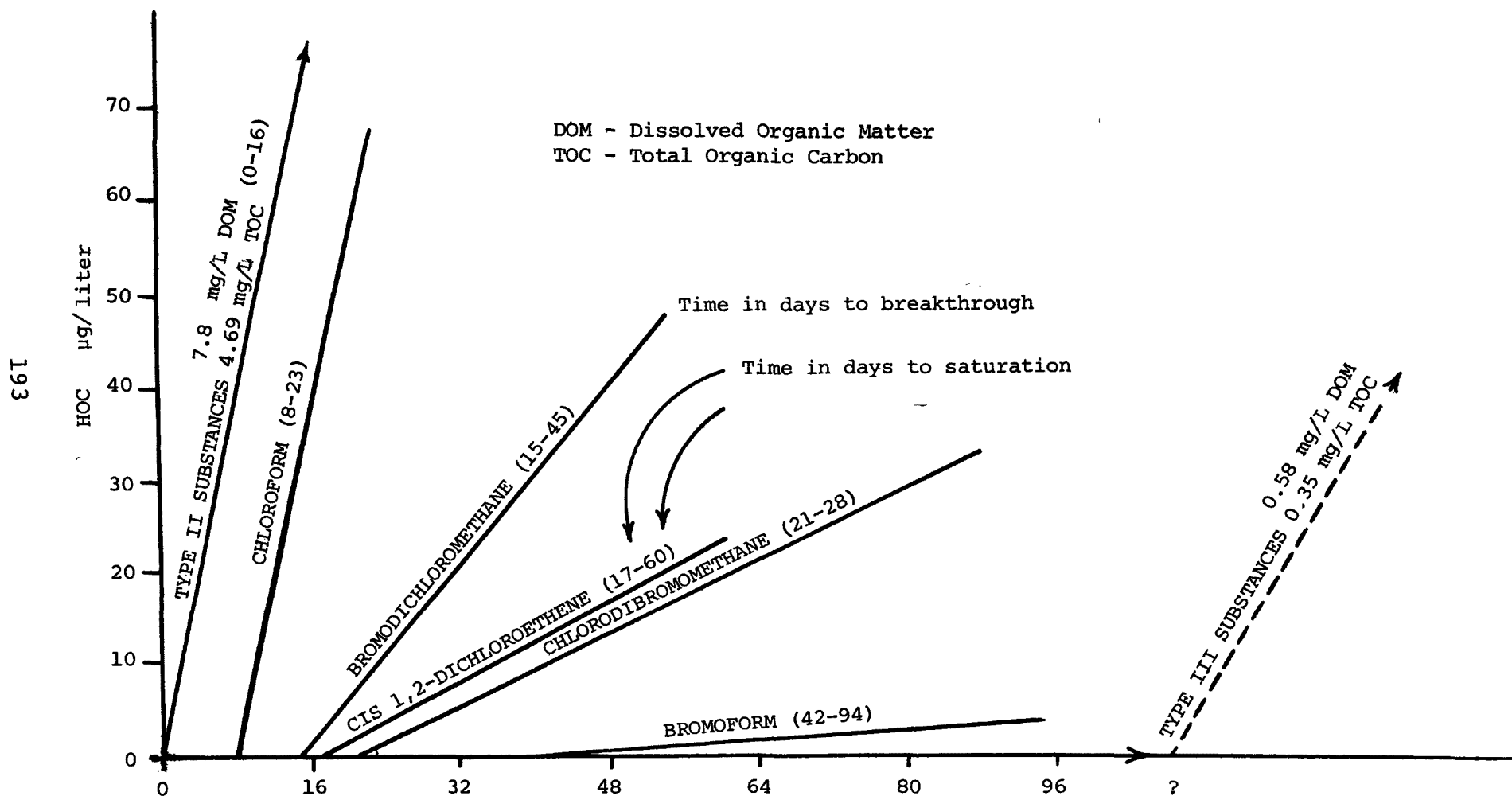


Figure 116. Adsorption wave front defined by breakthrough and saturation time for HOC and Type II and Type III substances thru 0.76 meter (2.5 feet) of GAC (ED4).

of the predicted value. These data appear to present no problem until the wave front curve for cis 1,2-dichloroethene is considered. The Manes-Hofer scale factor calculated from the refractive index of a compound (described on page 284) in general predicts the order of elution of the HOC compounds in our water both from the GC Tenax column used for their analysis and from the bench scale GAC columns on the water lines. On the GC Tenax analysis column, cis 1,2-dichloroethene elutes before chloroform. On the GAC columns on the water lines, cis 1,2-dichloroethene elutes after bromodichloromethane (Figure 116). Because of its wave front position in Figure 116, cis 1,2-dichloroethene encounters more competitive HOC adsorption than chloroform, yet in Table 37 the percent of predicted adsorption is higher than for chloroform. Apparently the refractive index scale factor does not predict the stronger than predicted adsorption shown by this compound. Manes (private communication) has indicated that carbon tetrachloride exhibits less adsorption than predicted by its scale factor. Molecular geometry and other physical chemical properties such as dipole moment can result in divergence from the scale factor predicted value. Carbon tetrachloride has a dipole moment of zero and due to its molecular structure presents a small surface area to the carbon surface compared to its molar volume. This results in less adsorption than predicted by the Manes scale factor based on refractive index. Perhaps the double bond in cis 1,2-dichloroethene has greater affinity for the carbon surface than a single bond resulting in greater adsorption than predicted. Our data also indicate that trans 1,2-dichloroethene and trichloroethylene exhibit more adsorption than predicted and a shift in the wave front as found with cis 1,2-dichloroethene.

TABLE 37. OBSERVED ADSORPTIVE CAPACITY OF 100 GRAMS OF GAC FOR FIVE HOC FROM FINISHED WATER COMPARED TO THE POLANYI-MANES PREDICTED VALUE FOR EACH COMPOUND FROM PURE WATER (adsorbed by 0.76 meter [2.5 feet] of GAC)

	Polanyi-Manes Predicted Capacity from Pure Water cc	Observed Capacity from Finished Water cc	Percent of Predicted
cis 1,2-Dichloroethene	0.46	0.029	6.5
Chloroform	0.68	0.032	5.0
Bromodichloromethane	1.14	0.04	3.6
Chlorodibromomethane	2.2	0.04	1.8
Bromoform	1.7	0.002	0.12

The percent of predicted values in Table 37 and their relationship to the wave fronts shown in Figure 116 apply only for our finished water as it appeared during this study. Any treatment plant modification that changed the ratios of the component HOC would change all values in Table 37. We have indicated that the maximum adsorption capacity of 0.76 meter (2.5 feet) of Filtrasorb 400 GAC for total HOC in our finished water was approximately 0.27 cc per 100 grams (Figure 114). We expect that if the concentration of the four THM were reversed, the maximum adsorptive capacity would rise considerably above the present 0.27 cc capacity. All observed capacities and percent of predicted values would change in Table 37.

In Table 37, the observed adsorptive capacity of chloroform per 100 grams of GAC is 0.032 cc, only 5 percent of the predicted value for pure water. It would be interesting to know how much of this reduction is due to the competitive adsorption of DOM (or TOC) and how much is due to other HOC. We can probably determine this from our existing data. Chloroform made up approximately 98 percent of the entire volume of all the HOC entering GAC column 4 during ED4 for up to 98 days. We therefore can conclude that this column was receiving only chloroform from finished water. Integration of the 3rd and 4th GAC column curves in Figure 56 shows that the 4th GAC column adsorbed 0.093 cc of chloroform at saturation (98 days), which corresponds to 0.053 cc per 100 grams of GAC. This value is 8 percent of the value that the Polanyi-Manes Theory predicts should be adsorbed from pure water. Therefore, DOM (or TOC) substances accounted for 92 percent of the reduction in adsorptive capacity of chloroform from finished water compared with its capacity from pure water. The competitive effect of other HOC in finished water further reduces the capacity to 95.3 percent of the capacity for pure water (Table 37). GAC column 1, had an adsorptive capacity for chloroform of 0.0358 cc/100 grams of GAC. Column 4 had a capacity of 0.053 cc/100 grams of GAC, which is 32 percent higher than column 1. This percentage value is very close to the 30 percent increased capacity found for cis 1,2-dichloroethene in raw water compared with finished water, which we feel is due to the absence of competitive adsorption of HOC.

As shown in Table 25, the four bed depths of GAC in ED4 show increasing values of adsorptive capacity for chloroform per 100 grams of GAC; 0.0358, 0.0449, 0.048, and 0.049 cc respectively for each column. This was because the adsorptive capacity for chloroform increased in each consecutive column as the HOC competitive adsorption decreased.

The percent of predicted adsorptive capacity decreased as the number of bromine atoms in the adsorbed molecular increased (Table 37). The adsorptive capacity of these bromine-containing THM on GAC from pure water has not been determined experimentally. The Polanyi-Manes predicted values given in Table 37 for these

three compounds are thus not confirmed values. Therefore, we do not know if the decrease in percent of predicted value for these three compounds as shown in Table 37 is caused by only increasing competitive HOC adsorption or if part is due to an error in the predicted value itself. For example, it is possible that the predicted values are too high because of steric exclusion resulting from the greater bulk of bromine atoms compared to chlorine atoms. Further work is needed to determine the adsorptive capacity of these molecules from pure water.

The amount of total cubic centimeters of HOC adsorbed in a given column was always less than in a preceding column (Figure 114). It might first appear that the explanation for this is simply that, as expected with a single HOC in water, the adsorptive capacity decreases as the concentration in the column influent decreases. It is not that simple. We have already shown that if a single HOC in our system reached saturation in all four columns (as chloroform did), the adsorptive capacity actually increased from column 1 to column 4. To explain the results shown in Figure 114, one must consider the contribution of each individual HOC. Column 1 adsorbed more HOC than the other columns because it was receiving more of certain individual HOC that had higher adsorptive capacities (Table 37).

Throughout this study, we did not observe much roll-over (displacement of an adsorbed substance by a more strongly adsorbed substance). There are several possible explanations that may apply either alone or collectively. Unknowns such as this make prediction of adsorptive capacity difficult if the ratios of HOC in our system were to change greatly. We are not without predictive capabilities, but we also recognize the limitations of present methods and the direction further research should take to improve this capability.

TOC and THM FP Organics

Precursors in this study were measured by TOC and THM FP analysis. Both methods measure a complex family of compounds instead of a specific substance as is the case for analysis of individual HOC. TOC includes some substances that are not THM precursors at all. It is likely that only a small portion of the TOC represents precursors for THM. If a single test method measured the whole family of organics present, the resulting adsorption breakthrough curve would look quite different from that of an individual organic breakthrough curve. This effect is shown in Figure 113 where the total cubic centimeters of the HOC mixture entering and adsorbed by 0.76 (2.5 feet), 1.52 (5.0 feet), 2.29 (7.5 feet) and 3.05 (10 feet) meters of GAC bed are plotted. After initial breakthrough the frontal adsorption zone has a steep slope, similar to that observed by a specific HOC. However, the total HOC curve then changes to a gradual

slope that approaches a plateau in some cases. During the 122-day test period, none of the total HOC curves reached the influent level curve. As the GAC bed depth increased, the difference between effluent and influent curves increased. This was because the more strongly adsorbed compounds were adsorbed in various degrees up to complete adsorption. The total HOC curves in Figure 113 representing 19 specific compounds are similar to those obtained when TOC and THM FP data, which measure a larger number of substances, are plotted except that the plateaus of the TOC and THM FP curves are more pronounced. Examples of such breakthrough are shown in Figures 117 and 118. It is possible that the plateaus exhibited on TOC and THM FP breakthrough curves are the result of biological degradation occurring along with adsorption. Thus the apparent plateaus on the curves for the TOC and THM FP may have partially different explanations than those for the total HOC.

Figure 117 shows the THM FP in $\mu\text{g/L}$ entering the first GAC column and in the effluent from each of the four 0.76 meter (2.5 feet) deep columns connected in series. Figure 118 shows TOC data in mg/L of effluent from the same four GAC columns. In Figure 118, the TOC breakthrough curves show three distinct areas. There is some TOC breakthrough from all four columns right from the beginning of initial flow. This breakthrough appears to be about equal through all four columns. It is possible that this represents a nonadsorbable fraction of TOC. It appears that after this base line breakthrough we observe a rapid rise in the curves. This rapid rise begins further from time zero as the bed depth increases. These rapid rise or steep slope regions then change into apparent plateaus for each column depth.

The curves in Figure 117 are replotted individually for each column in Figures 119, 120, 121 and 122. These individually plotted THM FP curves more clearly show the same patterns shown by the TOC data in Figure 118. In Figures 119, 120, 121 and 122 we again have three distinct zones of the breakthrough curves. Starting from a base line of a consistent low level THM FP passing through all four columns, there is an initial breakthrough period from start of flow that increases in time as the bed depth increases. The breakthrough then expands into a rapid rise or steep slope zone to a plateau. The plateau can be seen to occur at lower concentrations with increase in column bed depth. These differences will be discussed later.

The adsorption curve for THM FP adsorbed from raw water by 0.76 (2.5 feet) and 1.52 (5.0 feet) meters of IRA-904 resin is shown in Figure 123. The level of THM FP passing through the 1.52 meter (5.0 feet) deep bed of IRA-904 resin from start of initial flow is about equal to the value from the 0.76 meter (2.5 feet) deep bed. However, in the 1.52 meter (5.0 feet) deep bed, the steep slope portion of the curve begins four days

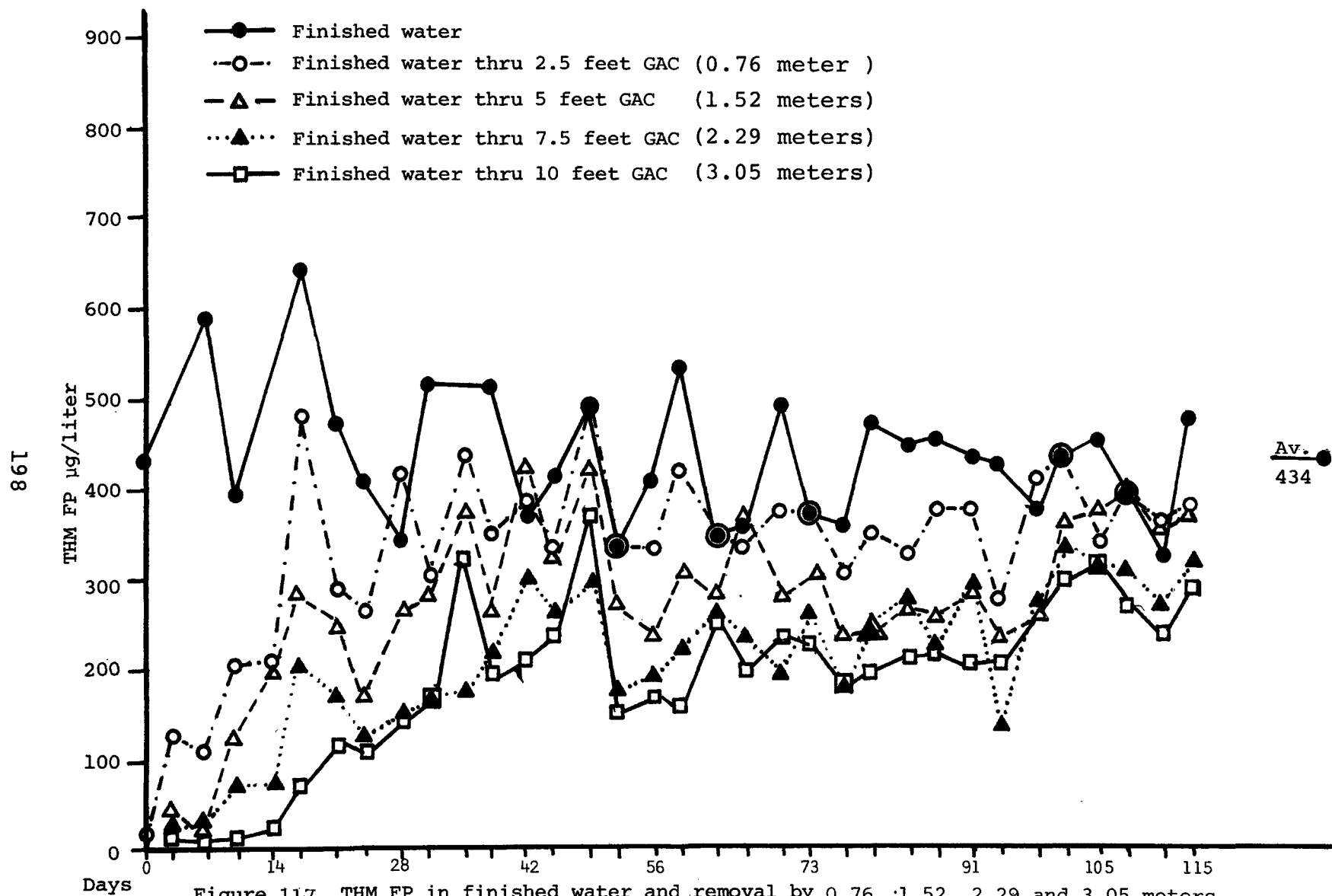


Figure 117. THM FP in finished water and removal by 0.76, 1.52, 2.29 and 3.05 meters (2.5, 5, 7.5, and 10 feet) of GAC (ED4).

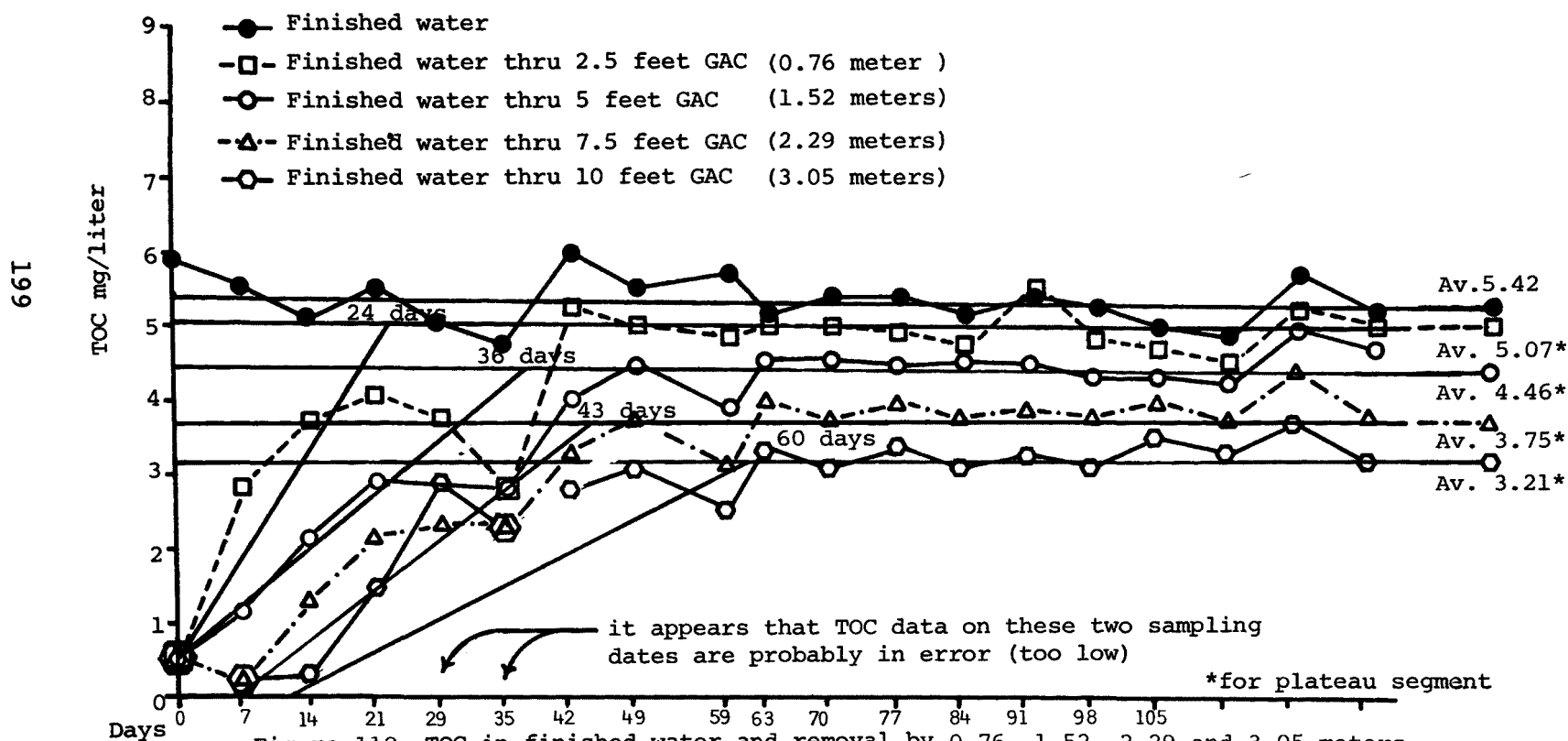
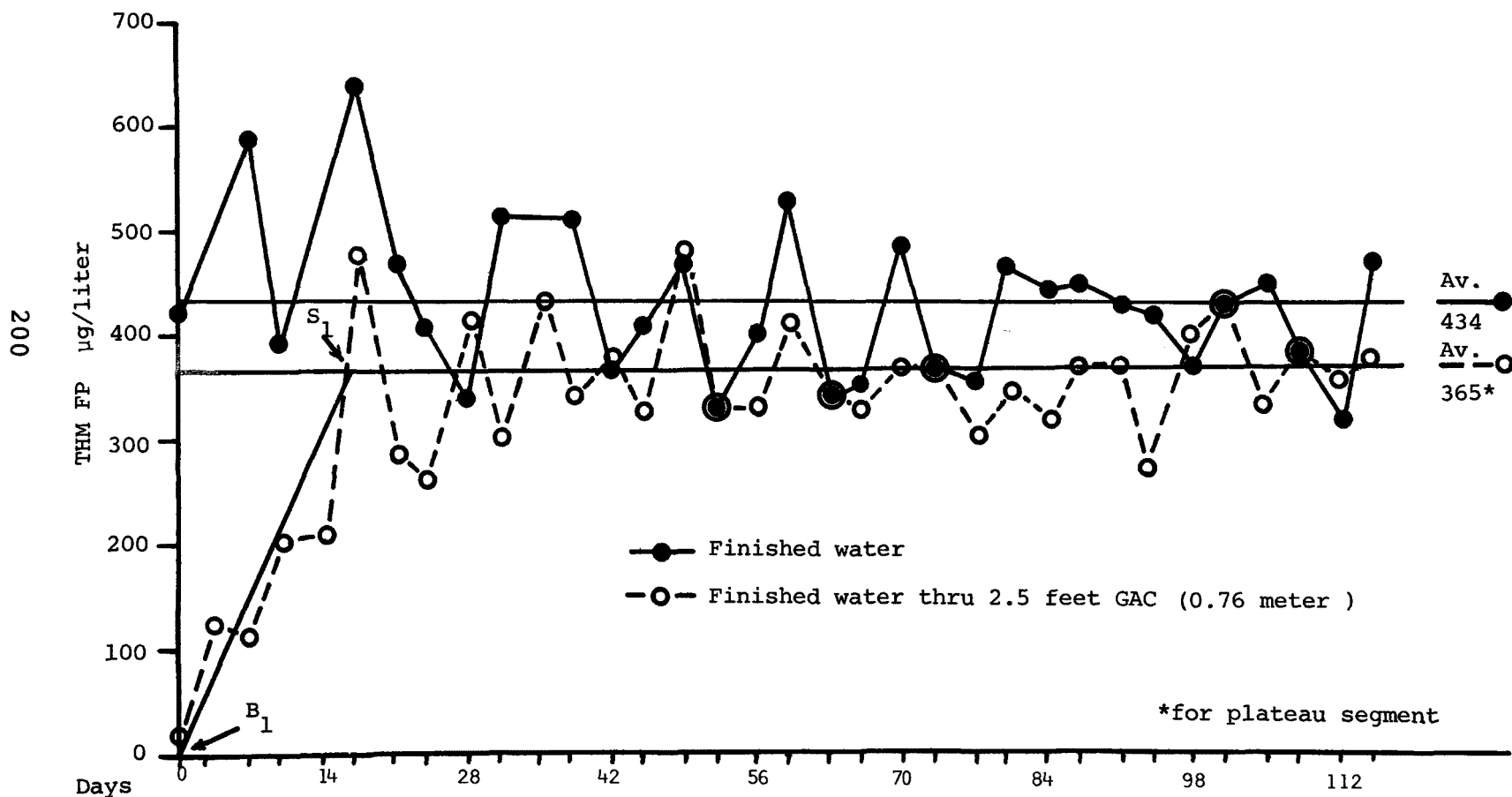
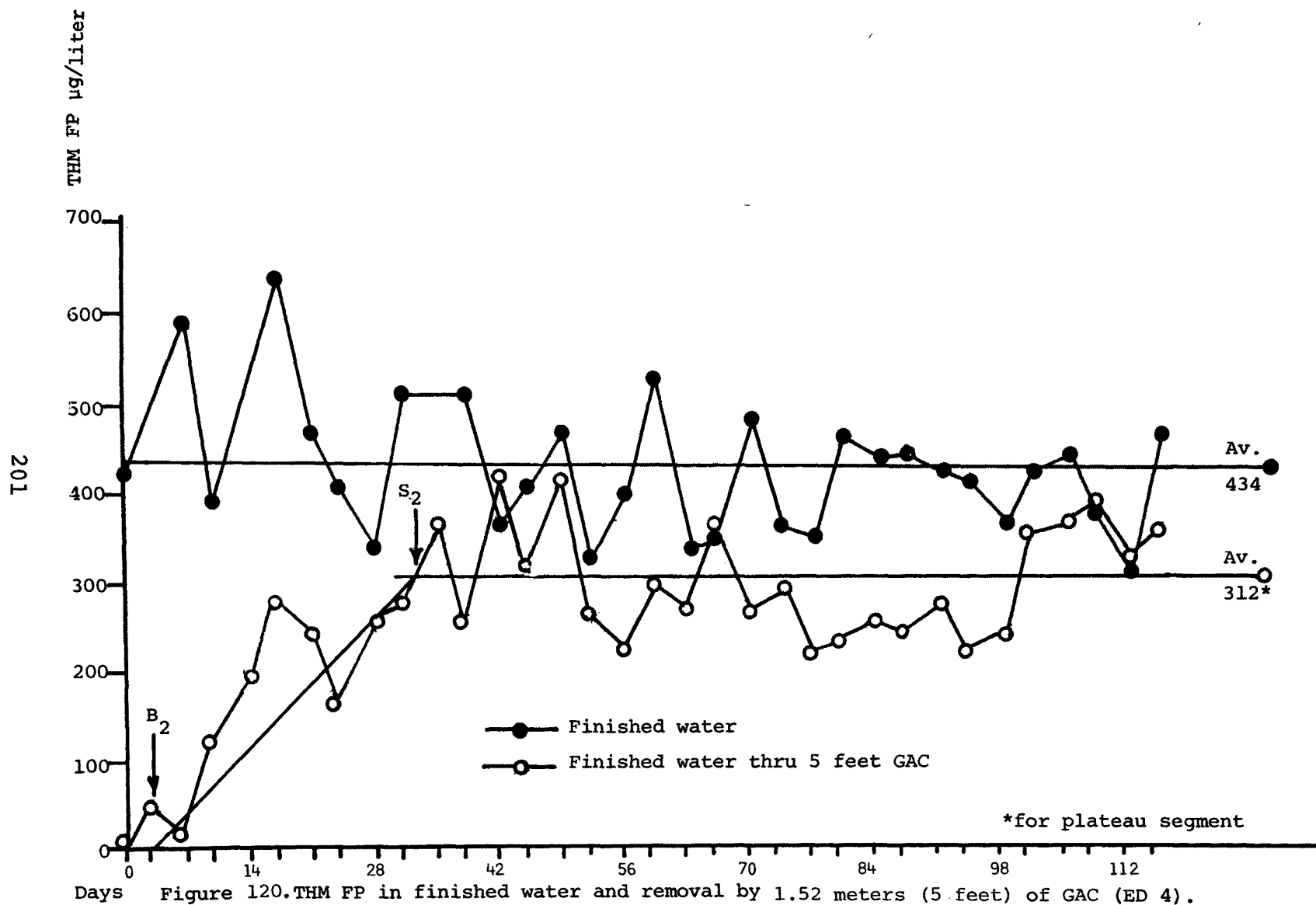


Figure 118. TOC in finished water and removal by 0.76, 1.52, 2.29 and 3.05 meters (2.5, 5, 7.5, and 10 feet) of GAC (ED4).





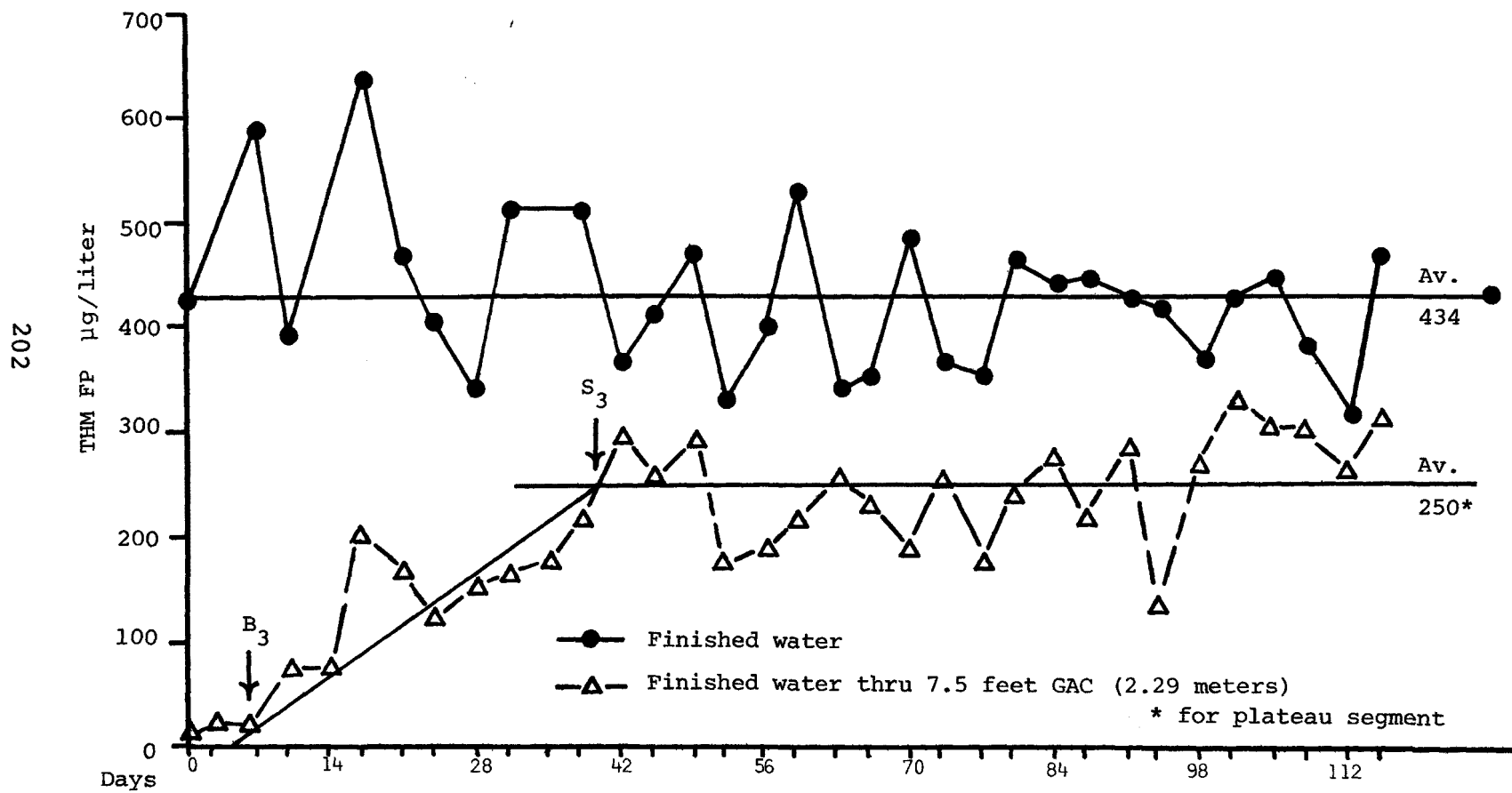


Figure 121. THM FP in finished water and removal by 2.29 meters (7.5 feet of GAC (ED4)).

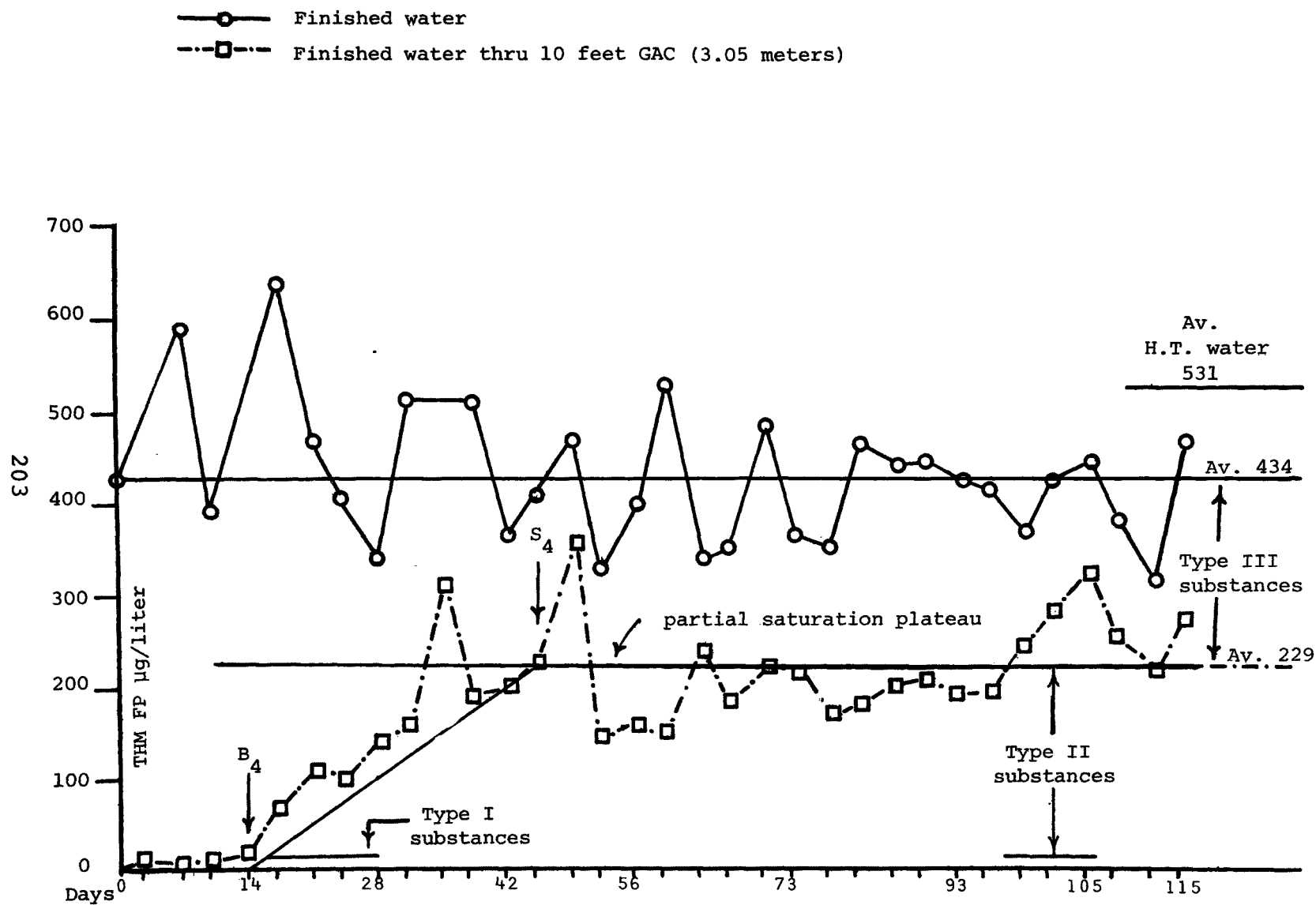


Figure 122. THM FP in finished water and removal by 3.05 meters (10 feet) of GAC (ED4).

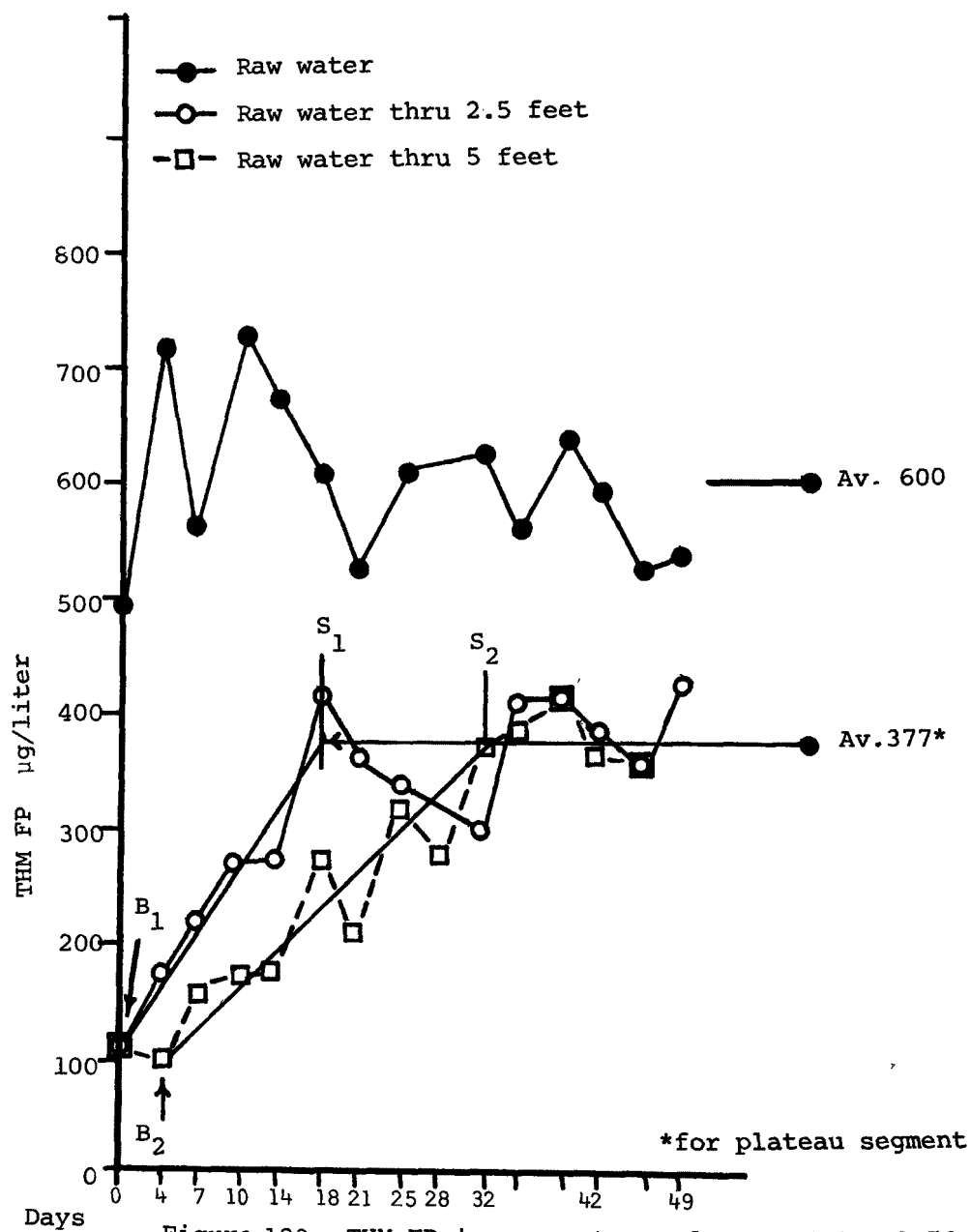


Figure 123. THM FP in raw water and removal by 0.76 and 1.52 meters (2.5 and 5 feet) of IRA-904 resin (ED3).

after a period of initial breakthrough. Again, partial saturation plateaus are reached and in this case they appear to be equal for both bed depths, but the plateau for the 1.52 meter (5.0 feet) deep bed occurs 14 days later than for the 0.76 meter (2.5 feet) deep bed.

Adsorption data tables were prepared for HOC adsorption curves. A problem arises when this is attempted with TOC and THM FP curves. The three zones of the curves and perhaps some idea of what produces these three zones should be taken into account. Although the predominant substance that acts as precursors for THM formation have been cited as being humic acid or fulvic acid, it is reasonable to assume that such complex substances may adsorb like a family of different compounds possessing various adsorption affinities with a given adsorbent. Likewise, TOC can more easily be seen to comprise a family of different substances with varying adsorption affinities.

THM FP data will be discussed by assuming that three types of substances comprise the precursors for THM in the Florida water tested. The broad definitions for each type of substance is as follows:

- TYPE I - Substances that are not initially adsorbed under the conditions tested.
- TYPE II - Substances that are initially adsorbed and/or biodegraded within the adsorbent column, but that eventually breaks through in increasing concentrations under the conditions tested.
- TYPE III - Substances that are completely adsorbed and/or biodegraded within the adsorbent column under the conditions tested.

Figure 122 shows the relationship of the three types of substances to the three zones of adsorption. In this figure, the Type I substances are shown as the fraction that passes through 3.05 meters (10 feet) of GAC, with a contact time of 24.8 minutes from the start of initial flow of water through the column. This could be a nonadsorbable fraction or a fraction nonadsorbable at that concentration with the contact time, type of GAC used and other conditions of the test.

Type II are substances that show a rather classic pattern of complete adsorption initially, followed by breakthrough and increasing effluent concentrations up to an apparent plateau value below equilibrium with the influent concentration. This could be either a substance with a given adsorption affinity or a family of substances that have various adsorption affinities that yield the effluent curve as shown.

Type III substances might be those that have a very strong adsorption affinity such that they are completely adsorbed within the adsorbent column for the duration that the study was conducted, a biodegradable fraction of the THM FP, or a combination of both. Either assumption could be used to provide a possible explanation of the plateau shown on the curve. We have limited data to suggest that in our system as studied, that strong adsorption of the Type III substances accounts for more of the plateau level than could be accounted by biodegradation. These data are shown in Figure 124. The average values for the plateau levels in Figures 119, 120, 121 and 122 which extend to the end of the test period of 115 days, are presented again in Figure 124. At the end of the test period in ED4, the columns were allowed to operate further and two additional samples were taken on days 176 and 177. These two data points are plotted in Figure 124 and their average value is shown. For each carbon bed depth, it is seen that the plateau level rises. For example, for 0.76 meter (2.5 feet) of GAC, at 115 days, the plateau level was 84 percent of the influent level and at 177 days it was 94 percent of the influent level. This suggests that the Type III substances from test day 115 to test day 177 are showing a typical breakthrough pattern. From these limited data we cannot determine how closely the breakthrough curve at Type III saturation will approach the influent level. However, even at test day 177, it is apparent that biodegradation can only account for a maximum of 6 percent of the influent level if the Type III breakthrough curve levels off at the 177 day level. We suspect that the breakthrough will continue further. Since the test was primarily designed for a four month period, the frequency of testing beyond that time does not allow more than speculation that the apparent plateau may be caused more by adsorption than biodegradation. It is obvious that we do not know the true reason for the apparent plateau at this time. It is likely that both factors play a role. Future studies will collect data relative to factors influencing the apparent plateau and ways to enhance it.

In evaluating data in Figures 119, 120, 121 and 122, using the assumptions regarding the three types of substances, it is apparent that the difference between the influent THM FP concentration and apparent plateau, which defines Type III, becomes greater as the bed depth and contact time are increased from 0.76 (2.5 feet) to 3.05 (10 feet) meters (6.2 minutes EBCT to 24.8 minutes EBCT). Concurrently the Type II substances defined by the difference between the plateau concentration and breakthrough concentration decreases with increased bed depth and contact time. The general definitions state that each class of substance is defined at a given set of conditions and each figure present a different condition. However, the changes in the amounts of Type II and III substances with different contact times may be explained as the effect of increased carbon volume and contact times that provide more

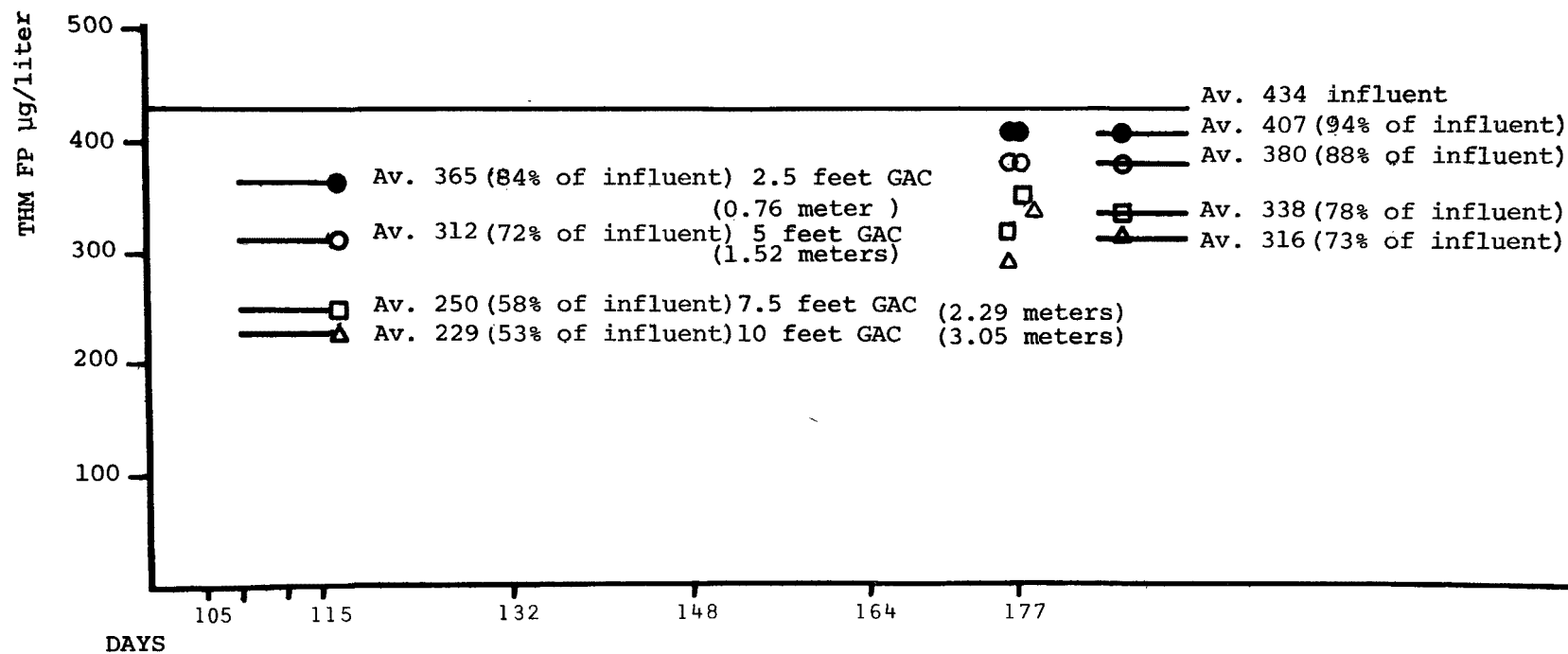


Figure 124. Test extension data for THM FP removal by 0.76, 1.52, 2.29 and 3.05 meters (2.5, 5, 7.5 and 10 feet) of GAC (ED4).

effective adsorption of Type II substances with adsorption affinities closer to Type III substances while also more effectively removing substances of weaker adsorption affinities. One cannot dismiss the possibility that biodegradation is the cause for the different plateaus. As previously stated, it is likely a combined effect that causes the plateau and we cannot as yet discern a primary factor.

Using this devised system of data presentation we have assumed that Type I substances continuously break through at constant levels and the Type III substances are completely adsorbed by a specific bed depth and contact time at the same level during the test period under the conditions of the study.

This assumption allows analysis of the TOC and THM FP data and presentation in tabular form such as presented for the halogenated organic compounds.

Raw Water Source--

THM FP adsorption data appear in Table 38. Adsorption curves appear in Figures 125, 126 and 127.

ED1 data are plotted in Figure 125. Since collection of data began on test day 61, complete analysis cannot be made on this ED. Comparison of the average values from day 61 to the end of the test period can be made from Figure 125. The average influent THM FP was 816 $\mu\text{g/L}$. The average effluent from the 0.76 meter (2.5 feet) deep GAC column was 757 $\mu\text{g/L}$, a reduction of seven percent. The effluent from the 0.76 meters (2.5 feet) deep XE-340 column was 833 $\mu\text{g/L}$, about two percent higher than the influent.

Column 0.76 meter (2.5 feet) deep of GAC and XE-340 were studied in ED1R. Adsorption curves appear in Figure 126. In Figure 126, average values are shown for the influent and for the column effluents from a point after Type II saturation on the plateau portion of the adsorption curves. Considering these average values, from test day 17 to the end of the test period, GAC and XE-340 removed 24 percent and 20 percent respectively of the influent THM FP. Integration of the curves for the whole test period produced the results in Table 38 (ED1R). During ED1R 0.76 meter (2.5 feet) of GAC adsorbed 29 percent of the THM FP precursors from entering raw water over the entire test period. Type I substances represented two percent; Type II, 72 percent; and Type III, 26 percent of the total precursors entering. Also during ED1R, 0.76 meter (2.5 feet) of XE-340 adsorbed 24 percent of the precursors from entering raw water over the entire test period as compared with 29 percent adsorbed by the same bed-depth of GAC. One hundred grams of GAC adsorbed 1.5 times as much precursor substances as 100 grams of XE-340 during the 119-day test period. When equal volumes of the two adsorbents are compared, at 119 days, GAC

TABLE 38. THM FP ADSORPTION DATA FROM RAW WATER

ED	Bed Depth Feet	Adsorbent	Average Influent THM FP µg/L	Type II Substances			Test Duration Days	Total THM FP Entering Each Column During Test Grams	Total THM FP Adsorbed By Each Column At End of Test Grams	% of Total THM FP Entering	Total THM FP Adsorbed By Each Column At Type II Saturation Grams	% of Total THM FP Entering	Type III Substances	
				Column Breakthrough Days	Column Saturation Days	MT N Inch							Adsorbed per Column Grams	% of Total THM FP Entering
1	2.5	GAC	816	?	116	Partial run	only	-	cannot calculate					
1	2.5	XE-340	816	?	90	"	"	"	"		"			
1R	2.5	GAC	659	0	10	30	119	7.1	2.07	29	.37	5	1.85	26
1R	2.5	XE-340	659	<3	<3	30+	119	7.1	1.71	24	No Sat		1.71	24
3	2.5	904	600	0	18	30	49	(2.96) 2.63	(.98) 1.2	(34) 46	.59	22	(.76) .98	(26) 37
3	5	904	600	4	34	27	49	2.63	1.44	55	1.14	43	.99	37
												(continued)		

2.5 feet=0.76 meter 5 feet=1.52 meters

TABLE 38. (continued)

ED	Bed Depth Feet	Adsorbent	Average Influent THM FP µg/L	Type II Substances					Type I Substances		THM FP Adsorbed			
				Adsorbed per Column Grams	Passed Each Column Grams	Total Entering Each Column Grams	% of Type II Adsorbed %	% of Total THM FP Entering %	Total Passed Grams	% of Total THM FP Entering %	Per 100 grams of Adsorbent			Per Col.
											At end of Test Grams	At Type II Saturation Grams	At 49 days Grams	At 49 days Grams
1	2.5	GAC	816											
1	2.5	XE-340	816											
1R	2.5	GAC	659	.22	4.93	5.15	4	72	.11	2	1.18	.21	.56	.99
1R	2.5	XE-340	659	0	5.28	5.28	0	74	.11	2	.8	No Sat	.33	.71
3	2.5	904	600	(.22) .22	(1.9) .95	(2.21) 1.17	45	(72) 45	(.04) .48	(2) 18	(.56) .44	.22	.44	1.21
3	5	904	600	.45	.7	1.15	44	45	.48	18	.26	.21	.26	1.43

2.5 feet=0.76 meter 5 feet=1.52 meters

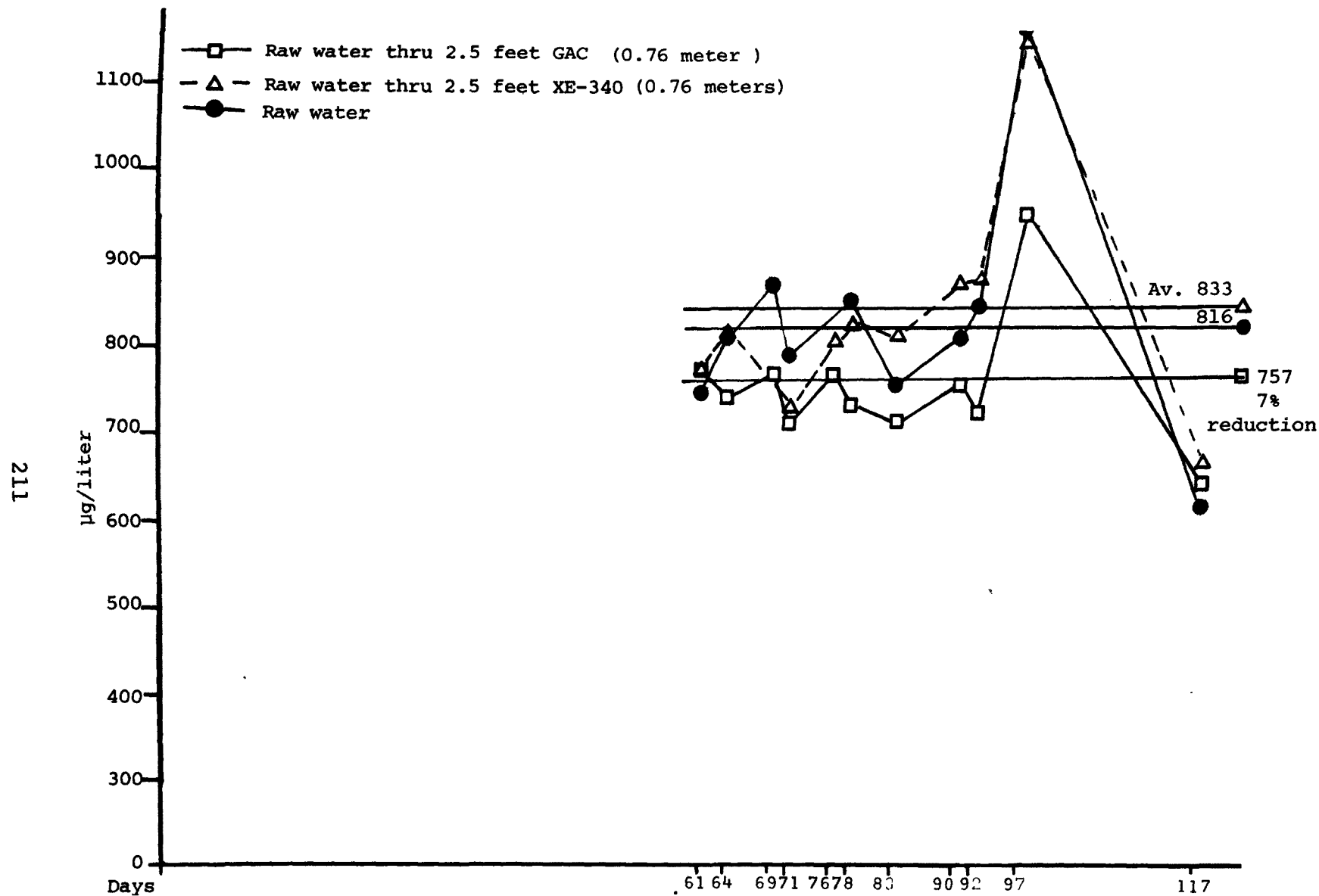


Figure 125. THM FP in raw water and removal by 0.76 meter (2.5 feet) of GAC and 0.76 meters (2.5 feet) of XE-340 (ED1).

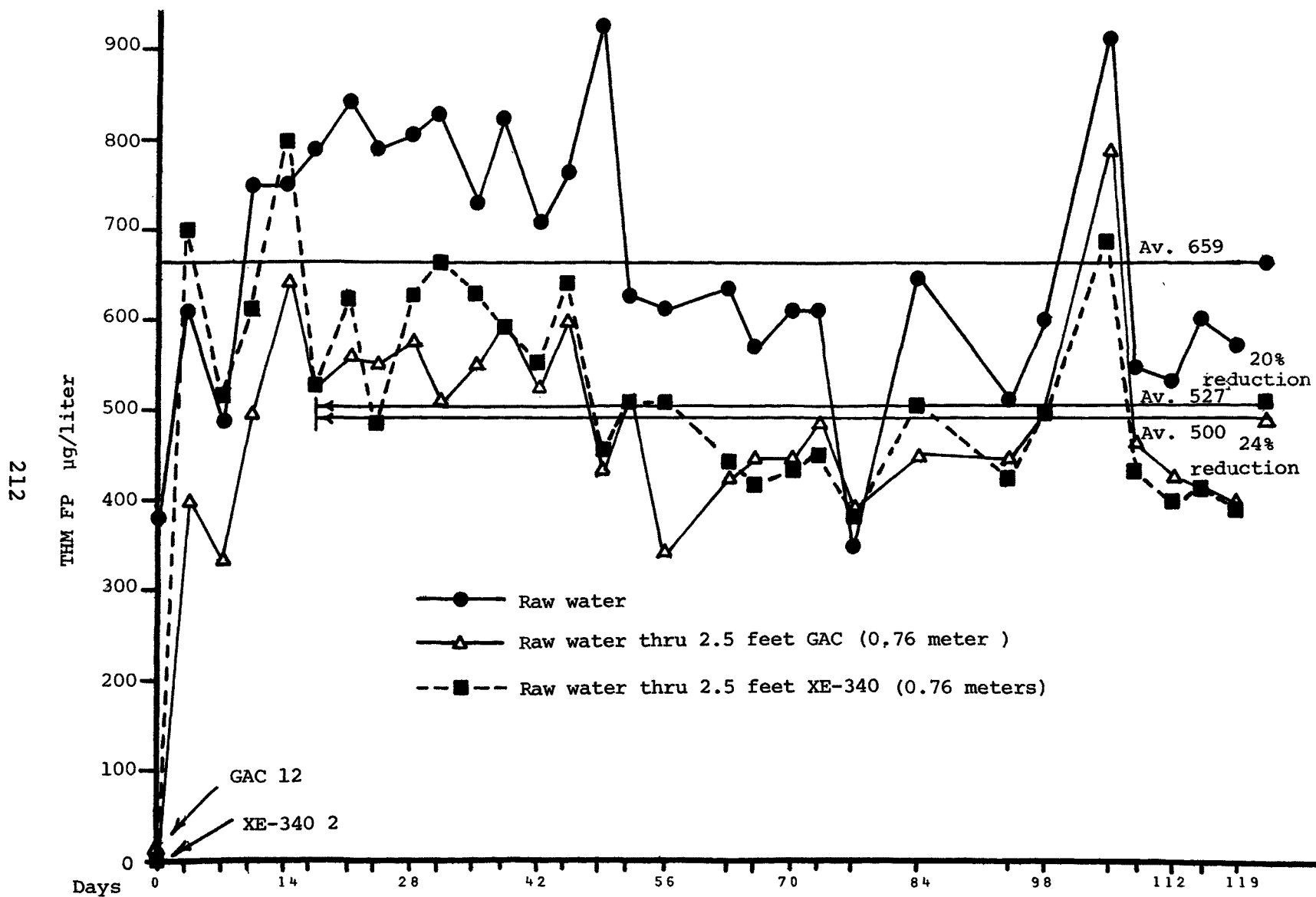
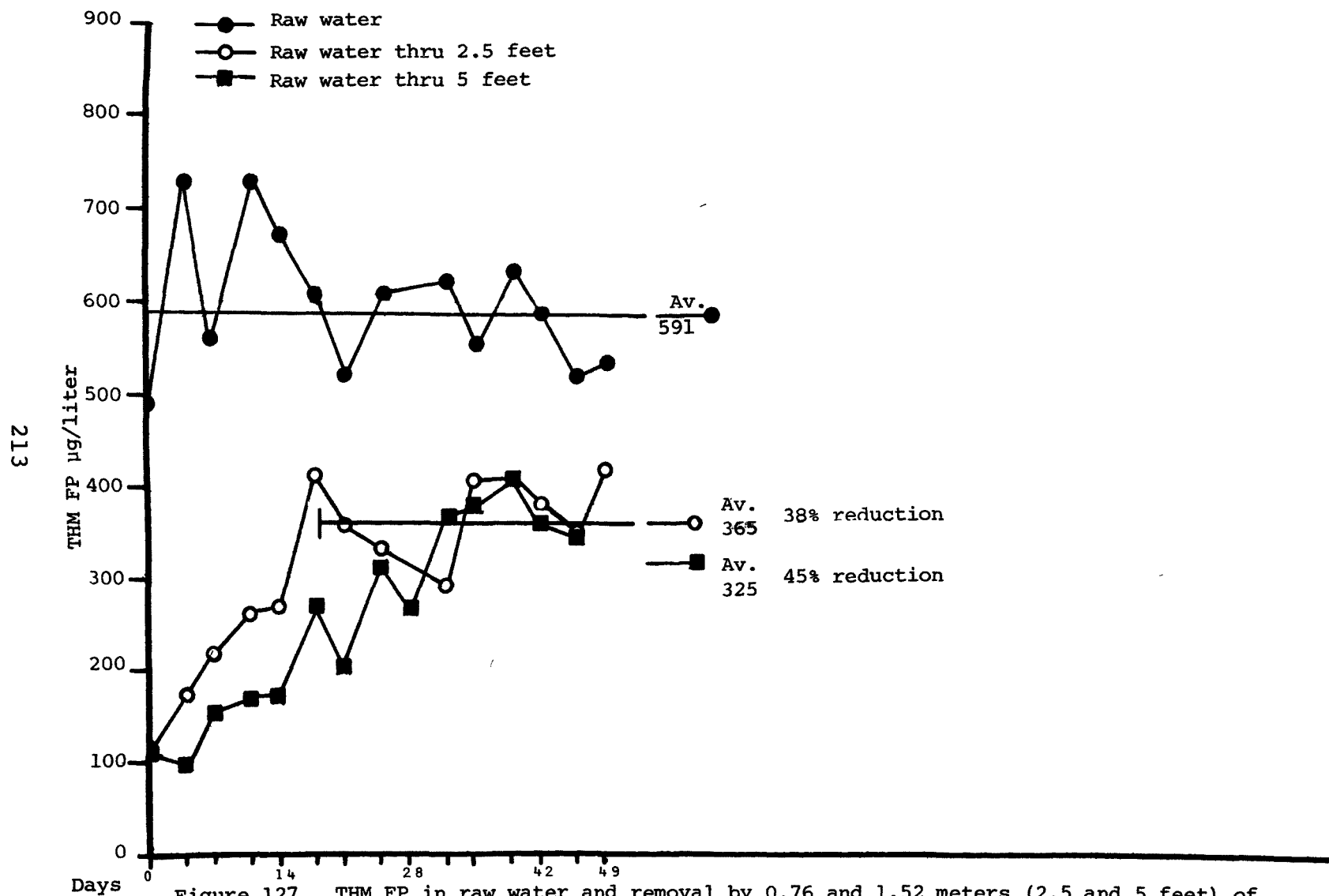


Figure 126. THM FP in raw water and removal by 0.76 meter (2.5 feet) of GAC and 0.76 meter (2.5 feet) of XE-340 (ED1R).



adsorbed 1.2 times as much precursor substance as XE-340. XE-340 had about three times the capacity of GAC for HOC adsorption. If Type II substances have an initial breakthrough and saturation time through XE-340, the values are less than three days when the first datum point after initial flow was obtained.

In ED3, 0.76 meter (2.5 feet) of IRA-904 resin was evaluated for 49 days on raw water compared with a test period of 119 days for adsorbents used in ED1R. Since the THM FP influent levels of the ED1R and ED3 are quite close, 659 $\mu\text{g/L}$ and 600 $\mu\text{g/L}$ respectively, the two sets of data can be compared. For purposes of comparison, integration values for 0.76 meters (2.5 feet) of GAC at 49 days in ED1R are shown in parentheses in Table 38. At 49 days 0.76 meter (2.5 feet) of GAC adsorbed 34 percent and 0.76 meters (2.5 feet) of IRA-904 resin adsorbed 46 percent of the precursors entering each column. A bed of 1.52 meters (5.0 feet) of IRA-904 resin adsorbed 55 percent of precursors from raw water during ED3. The adsorption curves for both IRA-904 resin bed depths are shown in Figure 127.

We have no way of knowing the status of the IRA-904 resin plateau after the end of the 49-day test period. If it remained at the same level for the same number (119) of test days as in ED1R, 41 percent would have been adsorbed compared with 29 percent for GAC. In Figure 127 the plateau levels are equal for both bed depths of IRA-904 resin. We can speculate, but have no explanation for the two levels being equal.

Initial breakthrough and saturation times for the Type II substances were longer in the 1.52 meter (5.0 feet) deep IRA-904 resin bed than in the 0.76 meter (2.5 feet) deep bed. The level of Type I substances was the same through both bed depths of IRA-904 resin.

The last four columns of data in Table 38 present the adsorption of total precursors per 100 grams of adsorbent at the end of the test period, at Type II saturation, at a common point in time of 49 days, and adsorption per column at 49 days which was the shortest test duration. If 0.76 meter (2.5 feet) of GAC, 0.76 meter (2.5 feet) of IRA-904 resin, and 1.52 meters (5.0 feet) meters of IRA-904 resin columns were all regenerated at their respective Type II saturation times of 10, 18, and 34 days, adsorption per 100 grams of adsorbent would be similar; i.e., 0.21, 0.22, and 0.21 grams respectively per 100 grams of adsorbent. If all adsorbents tested (0.76 meter [2.5 feet] of GAC, XE-340, and IRA-904 resin, and 1.52 meters (5.0 feet) of IRA-904 resin) were generated at the same time, 49 days, adsorption in grams per 100 grams of adsorbent would be 0.56, 0.33, 0.44, and 0.26 respectively. GAC removed the most total precursor per 100 grams of adsorbent. The last column of values in Table 38 are amounts of precursors adsorbed by the entire column of each adsorbent containing equal volumes of the adsorbents.

When equal volumes of the three adsorbents (0.76 meter [2.5 feet] of GAC, XE-340 and IRA-904 resin) are considered, the adsorption from raw water at 49 days is 0.99, 0.71, and 1.21 grams respectively. When compared on a volume basis, IRA-904 resin adsorbes more precursors than GAC. However, the initial breakthrough concentration of precursors was the highest for the IRA-904 resin at about 100 µg/L at start-up, and the lowest at start-up was obtained by GAC. At this point, no meaningful conclusions can be made regarding the total merits of the three adsorbents applied to raw water without a specific objective in mind and research on regeneration of each adsorbent and the accompanying cost.

In 404 days of testing, we found that lime softening of raw water removed an average of 27 percent of the THM FP. This compares favorably with THM FP removal of 29 percent by GAC and 24 percent by XE-340 for 119 days by 0.76 meter (2.5 feet) deep beds. A 0.76 meters (2.5 feet) deep bed of IRA-904 resin removed 46 percent of the precursor from raw water for 49 days when the test ended. If all three adsorbents were assessed at the end of 49 days, the expected results would be removal of 34 percent by GAC, 24 percent by XE-340 and 46 percent by IRA-904 resin. As is the case with HOC results, the shape of the adsorption curves affect data interpretation. Choosing a reference point for comparison of adsorbent capacity is important.

The flocculated calcium carbonate in the H.T. can be considered as still another adsorbent and compared with our column adsorbents. Earlier in the report, it was shown that adsorption occurring on calcium carbonate floc in the H.T., under normal operating conditions of the Preston Plant, removed 0.07 grams of THM FP per 100 grams of floc. The 0.76 meter (2.5 feet) deep GAC column in ED1R, Table 38, at Type II saturation removed 0.21 grams of THM FP per 100 grams of GAC. It is interesting to note that the type of adsorption occurring on calcium carbonate floc removed about 33 percent of the precursors, as measured by THM FP as was removed by GAC on a weight basis.

TOC adsorption data from raw water appears in Table 39. Adsorption curves appear in Figures 128 and 129.

In Figure 128, from the start of initial flow through the XE-340 column, essentially no TOC was removed. Over the entire test period an average of all test data indicates that the XE-340 column removed only two percent of the influent TOC. The GAC column removed 8 percent of the influent TOC, calculated after Type II saturation. In Table 39, the results obtained by integration of the entire adsorption curves are presented, GAC and XE-340 removed 12 percent and two percent of the influent TOC respectively. The same columns removed 29 percent and 24 percent respectively of THM FP. The GAC column removed 10.2 times and 8.4 times as much TOC as the XE-340 column on an equal

TABLE 39. TOC ADSORPTION DATA FROM RAW WATER

ED	Bed Depth Feet	Adsorbent	Average Influent TOC mg/L	Type II Substances			Test Duration Days	Total TOC Entering Each Column During Test Grams	Total TOC Adsorbed By Each Column At End of Test Grams	% of Total TOC Entering %	Total TOC Adsorbed By Each Column At Type II Saturation Grams	% of Total TOC Entering %	Type III Substances	
				Column Breakthrough Days	Column Saturation Days	M _T N Inch							Adsorbed per Column Grams	% of Total TOC Entering %
1R	2.5	GAC	9.8	0	14	30	127	111.1	13.2	12	5.1	5	9.1	8
1R	2.5	XE-340	9.8	0	0		127	111.1	2.3	2	No Sat.		2.3	2
3	2.5	904	8.6	0	25	30	53	40.7	10.5	26	9.2	23	2.4	6
3	5	904	8.6	0	39	30	53	40.7	15.4	38	14.6	36	2.8	7

(continued)

2.5 feet=0.76 meter 5 feet=1.52 meters

TABLE 39. (continued)

ED	Bed Depth Feet	Adsorbent	Average Influent TOC mg/L	Type II Substances					Type I Substances		TOC Adsorbed			
				Adsorbed per Column Grams	Passed Each Column Grams	Total Entering Each Column Grams	% of Type II Adsorbed %	% of Total TOC Entering %	Total Passed Grams	% of Total TOC Entering %	Per 100 grams of Adsorbent		Per Col.	
											At end of Test Grams	At Type II Saturation Grams	At 49 days Grams	At 49 days Grams
1R	2.5	GAC	9.8	4.1	61.6	65.7	7	59	37.4	33	7.5	2.9	4.3	7.6
1R	2.5	XE- 340	9.8	0	0	0	0	0	108.8	98	1.1	No Sat.	.42	.9
3	2.5	904	8.6	8.1	26.4	34.5	24	20	3.8	9	3.8	3.3	3.8	10.5
3	5	904	8.6	12.5	21.5	34	27	84	3.8	9	2.8	2.7	2.8	15.4

2.5 feet=0.76 meter 5 feet=1.52 meters

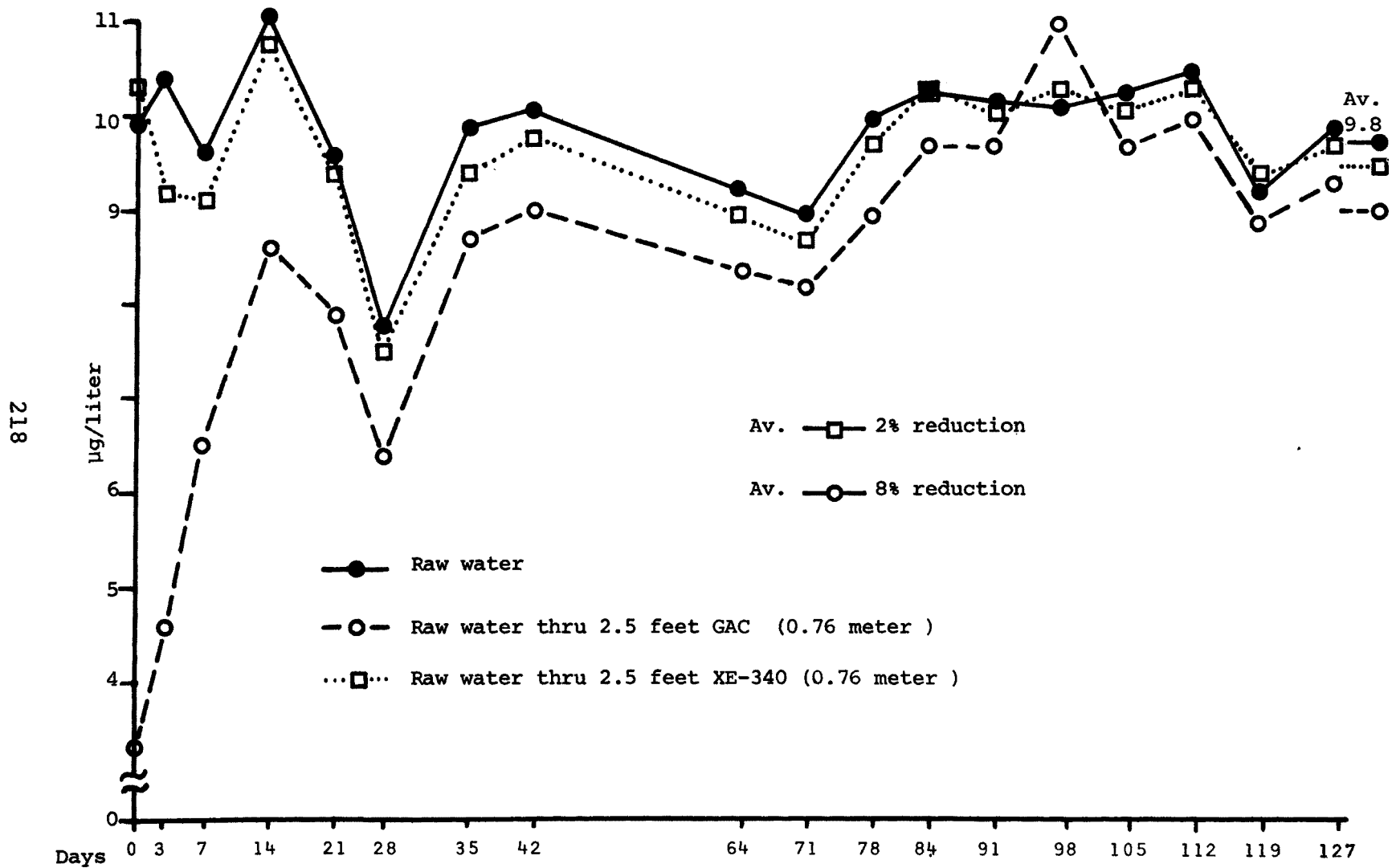


Figure 128. TOC in raw water and removal by 0.76 meter (2.5 feet) of GAC and 0.76 meter (2.5 feet) of XE-340 (ED1R).

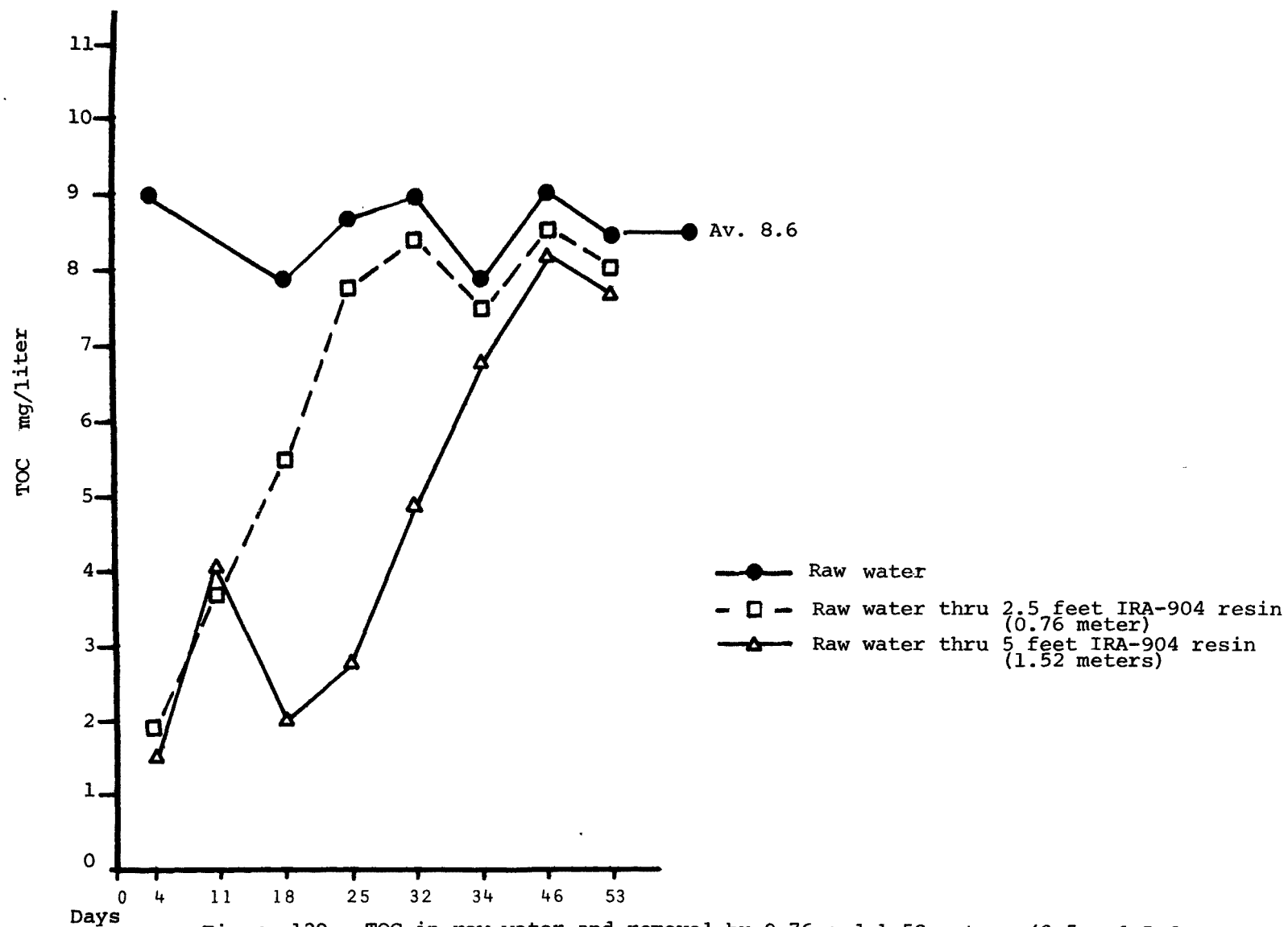


Figure 129. TOC in raw water and removal by 0.76 and 1.52 meters (2.5 and 5 feet) of IRA-904 resin (ED3).

volume and equal weight basis respectively.

In ED3, Table 39 and Figure 129, 0.76 (2.5 feet) and 1.52 (5.0 feet) meters of IRA-904 resin removed 26 percent and 38 percent of the influent TOC respectively. Comparing 0.76 meter (2.5 feet) of IRA-904 resin with 0.76 meter (2.5 feet) of GAC at an equal time of 49 days, the resin removed 0.9 times and 1.4 times as much TOC as GAC on an equal weight and equal volume basis.

H.T. Water Source--

THM FP adsorption data appear in Table 40. Adsorption curves appear in Figures 130, 131, and 132.

XE-340, 0.76 meter (2.5 feet) deep, was studied in ED1 and adsorption data shown in Figure 130. Since collection of data began on day 61, complete analysis is not possible. From day 61 to the end of the test period, the XE-340 column removed four percent of the influent THM FP. On raw water, the XE-340 column removed seven percent during the same time period. However, while we will continue to compare THM FP and TOC adsorption across water sources, raw, H.T. and finished, it really is not a valid way to interpret these data. We will show in the discussion on Finished Water Source, which follows later, that one cannot compare directly across water sources when the influent levels of THM FP and TOC change.

In ED1R, Figure 131, 0.76 meter (2.5 feet) of XE-340 was studied from initial column start-up. The XE-340 column removed two percent of the influent THM FP compared to 24 percent removal (Table 38) from raw water.

In ED3, 0.76 meter (2.5 feet) of IRA-904 resin was studied, Figure 132 and Table 40. The IRA-904 resin removed 32 percent of the influent THM FP compared to 46 percent from raw water. In Figure 132, the adsorption curve suggest that additional Type II substances are being removed from H.T. water but no Type III (at Type II saturation the influent and effluent curves coincide).

TOC adsorption data appear in Table 41. Adsorption curves appear in Figures 133 and 134.

In ED1R, 0.76 meter (2.5 feet) of XE-340 removed six percent of the influent TOC compared to 24 percent from raw water. In ED3, 0.76 meter (2.5 feet) of IRA-904 resin removed 41 percent of the influent TOC compared to 46 percent from raw water.

Finished Water Source--

THM FP adsorption data appear in Table 42. Adsorption curves appear in Figures 135, 136, 137, 138, 139, 140, 141, and 142.

TABLE 40. THM FP ADSORPTION DATA FROM H.T. WATER

ED	Bed Depth Feet	Adsorbent	Average Influent THM FP µg/L	Type II Substances			Test Duration Days	Total THM FP Entering Each Column During Test Grams	Total THM FP Adsorbed By Each Column At End of Test Grams	% of Total THM FP Entering %	Total THM FP Adsorbed By Each Column At Type II Saturation %	% of Total THM FP Entering %	Type III Substances	
				Column Breakthrough Days	Column Saturation Days	MP N Inch							Adsorbed per Column Grams	% of Total THM FP Entering %
1	2.5	XE-340	580		Partial run only			- cannot calculate						
1R	2.5	XE-340	474	<3	<3	30+	119	5.0	.12	2	No Sat		.12	2
3	2.5	904	394	0	39	30	49	1.72	.55	32	.55	32	0	0
												(continued)		

$$2.5 \text{ feet} = 0.76 \text{ meter}$$

TABLE 40. (continued)

ED	Bed Depth Feet	Adsorbent	Average Influent THM FP µg/L	Type II Substances					Type I Substances		THM FP Adsorbed			
				Adsorbed per Column Grams	Passed Each Column Grams	Total Entering Each Column Grams	% of Type II Adsorbed %	% of Total THM FP Entering %	Total Passed Grams	% of Total THM FP Entering %	Per 100 grams of Adsorbent		Per Col.	
											At end of Test Grams	At Type II Saturation Grams	At 49 days Grams	At 49 days Grams
1	2.5	XE-340	580											
1R	2.5	XE-340	474	0	4.88	4.88	0	98	can't measure		.068	No Sat	.03	.053
3	2.5	904	394	.55	.83	1.38	40	80	.34	20	.2	.2	.2	.55

2.5 feet=0.76 meter

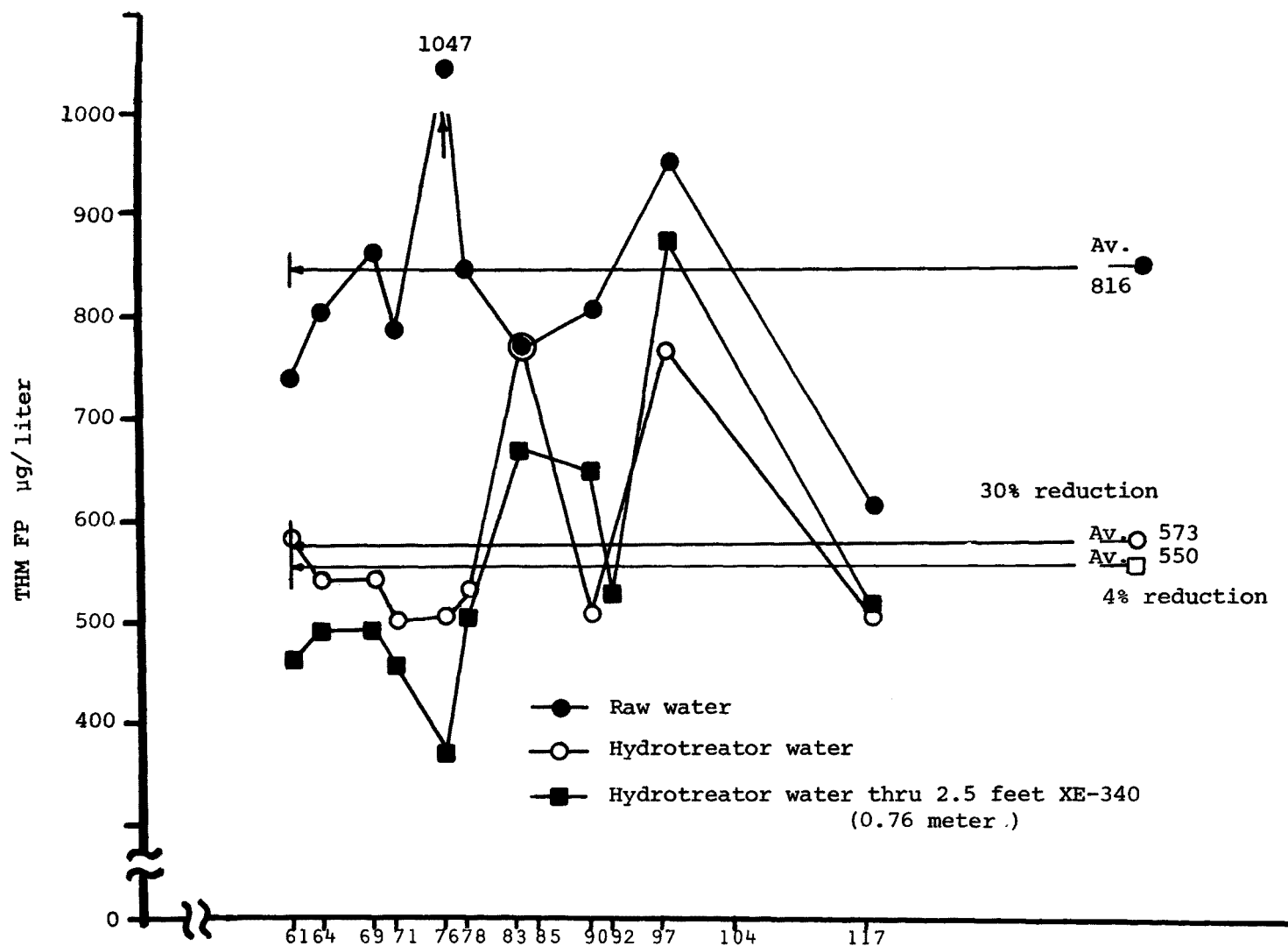


Figure 130. THM FP in raw water, and removal by lime softening and by 0.76 meter (2.5 feet) of XE-340 on H.T. water (ED1).

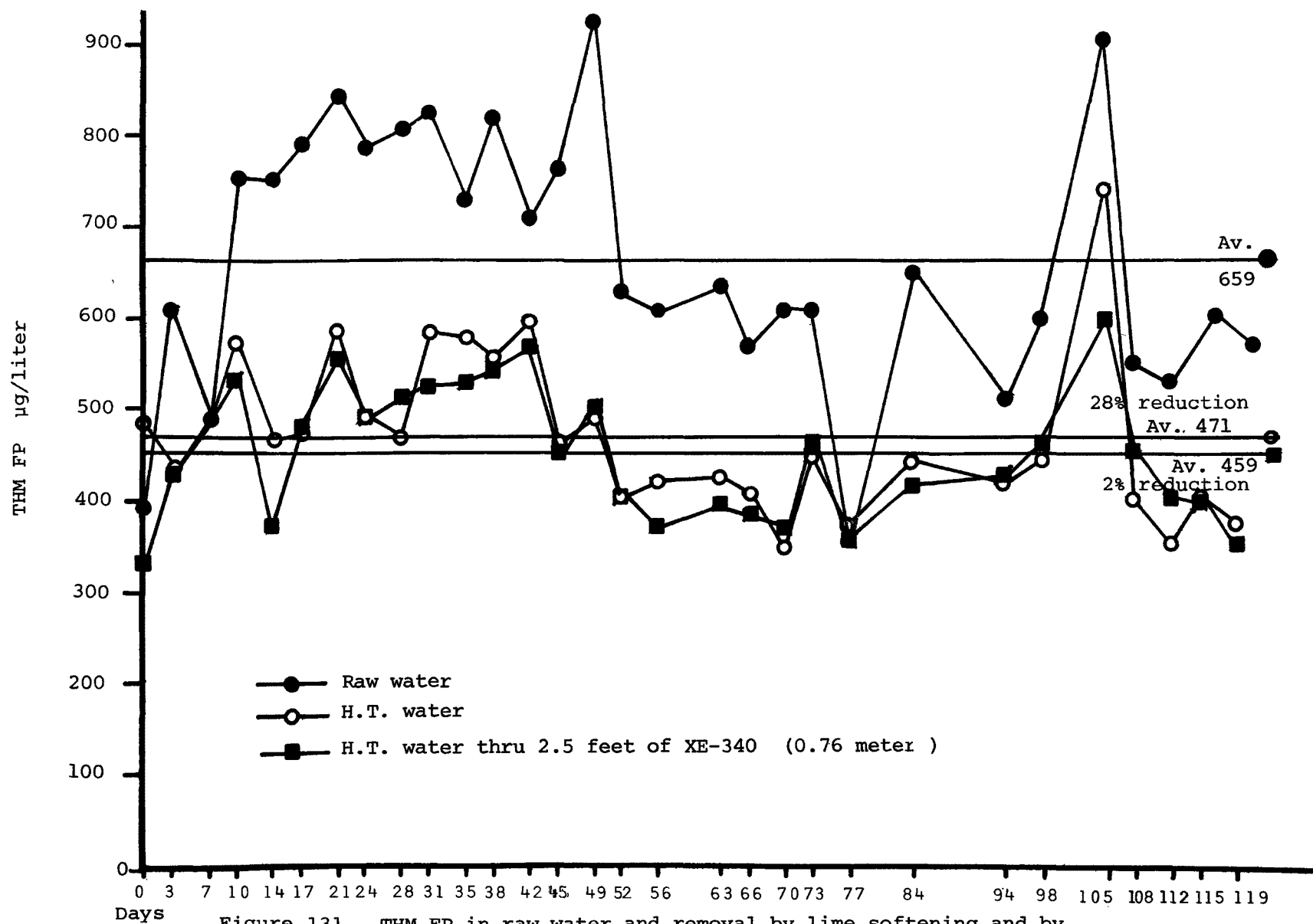


Figure 131. THM FP in raw water and removal by lime softening and by 0.76 meter (2.5 feet) of XE-340 on H.T. water (ED1).

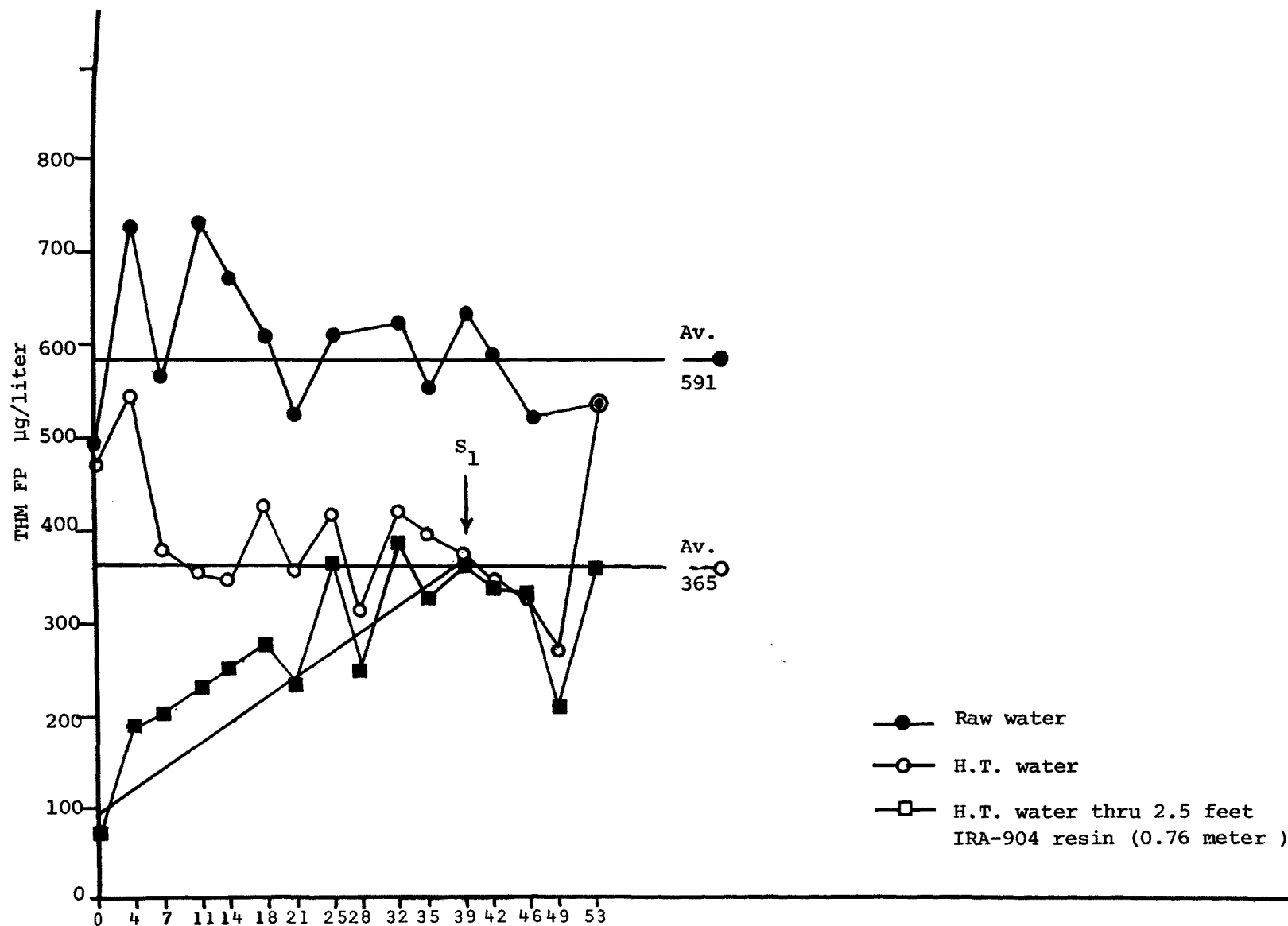


Figure 132. THM FP in raw water and removal by lime softening and by 0.76 meter (2.5 feet) of IRA-904 resin on H.T. water (ED3).

TABLE 41. TOC ADSORPTION DATA FROM H.T. WATER

ED	Bed Depth Feet	Adsorbent	Average Influent TOC mg/L	Type II Substances			Test Duration Days	Total TOC Entering Each Column During Test Grams	Total TOC Adsorbed By Each Column At End of Test Grams	% of Total TOC Entering %	Total TOC Adsorbed By Each Column At Type II Saturation Grams	% of Total TOC Entering %	Type III Substances	
				Column Breakthrough Days	Column Saturation Days	MT N Inch							Adsorbed per Column Grams	% of Total TOC Entering %
1R	2.5	XE-340	6.8	?	?	?	127	77.1	3.1	4	No Sat.		3.1	4
3	2.5	904	6.0	0	46	30	53	28.4	11.3	40	10.9	38	3.1	11
(continued)														

2.5 feet=0.76 meter

TABLE 41. (continued)

ED	Bed Depth Feet	Adsorbent	Average Influent TOC mg/L	Type II Substances					Type I Substances		TOC Adsorbed Per 100 grams of Adsorbent			Per Col..
				Adsorbed per Column Grams	Passed Each Column Grams	Total Entering Each Column Grams	% of Type II Adsorbed %	% of Total TOC Entering %	Total Passed Grams	% of Total TOC Entering %	At end of Test Grams	At Type II Saturation Grams	At 49 days Grams	At 49 days Grams
1R	2.5	XE-340	6.8	0							1.4		.6	1.2
3	2.5	904	6.0	8	10.5	18.5	43	65	6.6	14	4.1	2.9	4	11.1

2.5 feet=0.76 meter

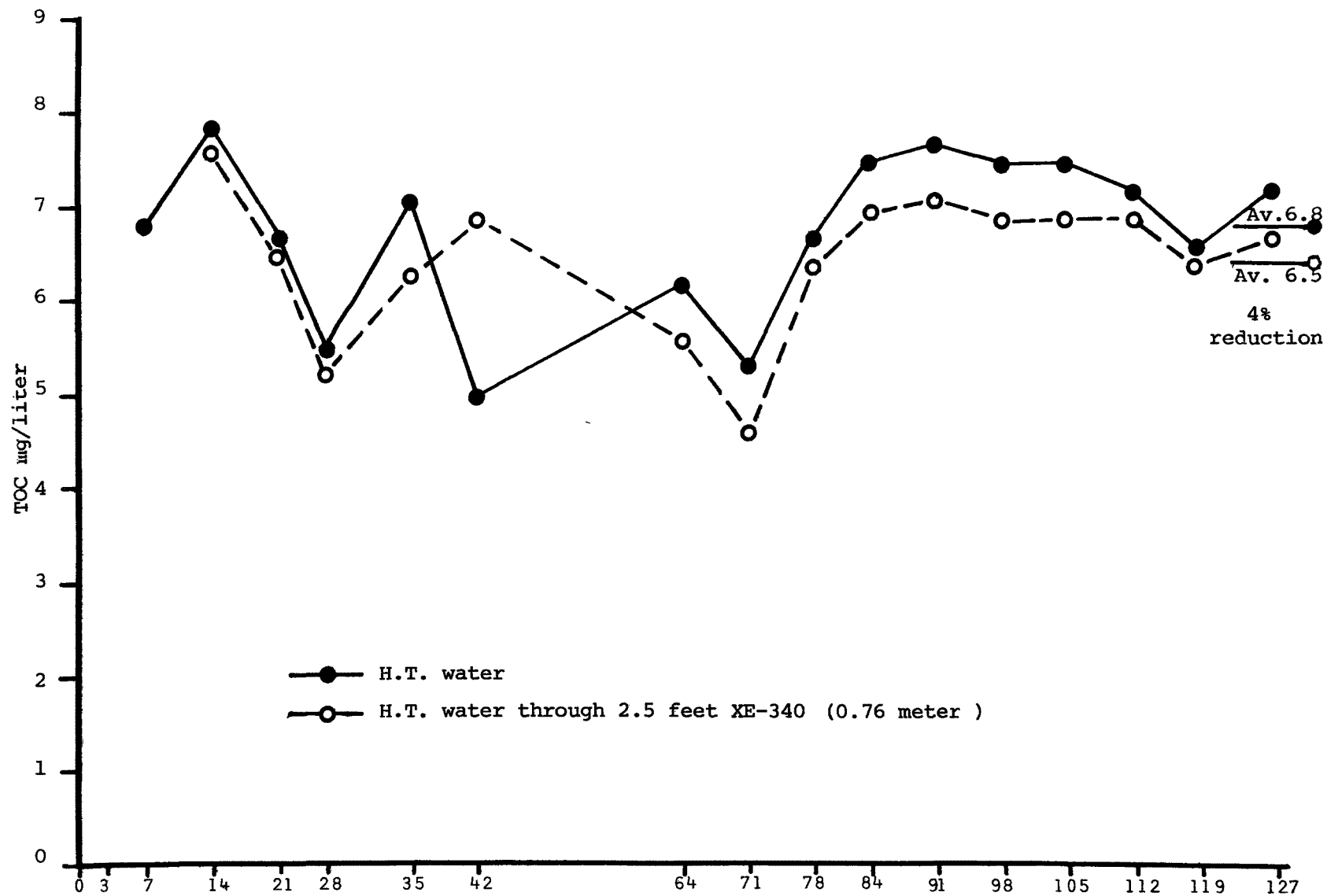


Figure 133. TOC in H.T. water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

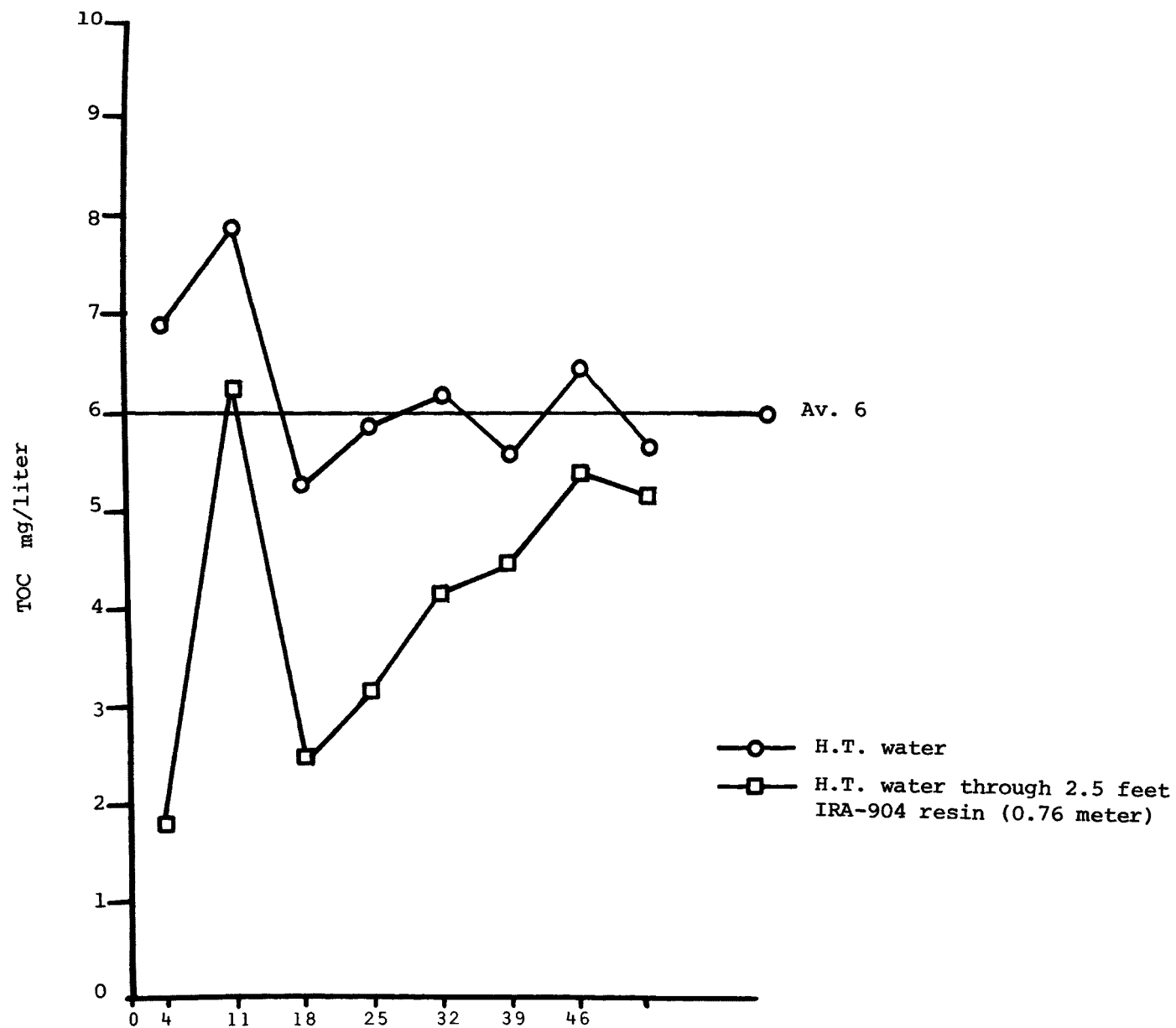


Figure 134. TOC in H.T. water and removal by 0.76 meter (2.5 feet) of IRA-904 resin (ED3).

TABLE 42. THM FP ADSORPTION DATA FROM FINISHED WATER

ED	Bed Depth Feet	Adsorbent	Average Influent THM FP µg/L	Type II Substances			Test Duration Days	Total THM FP Entering Each Column During Test Grams	Total THM FP Adsorbed By Each Column At End of Test Grams	% of Total THM FP Entering %	Total THM FP Adsorbed By Each Column At Type II Saturation Grams	% of Total THM FP Entering %	Type III Substances	
				Column Breakthrough Days	Column Saturation Days	MT N Inch							Adsorbed per Column Grams	% of Total THM FP Entering %
1	2.5	XE-340	451	Partial run only - cannot					calculate					
1R	2.5	XE-340	355	0	0	30+	119	3.85	.138	3			.138	3
3	2.5	GAC	274	0	11	30	49	1.2	.22	18	.14	12	.11	9
3	2.5	904	274	0	0	30+	49	1.2	.15	13	No Sat		.15	13
4	2.5	GAC	434	0	16	30	115	4.46	.96	22	.36	8	.71	16
4	5	GAC	434	3	33	55	115	4.46	1.74	39	.84	19	1.25	28
4	7.5	GAC	434	6	40	77	115	4.46	2.38	53	1.15	26	1.89	43
4	10	GAC	434	14	46	84	115	4.46	2.68	60	1.41	32	2.11	48
												(continued)		

2.5 feet=0.76 meter 5 feet=1.52 meters 7.5 feet=2.29 meters 10 feet=3.05 meters

TABLE 42. (continued)

ED	Bed Depth Feet	Adsorbent	Average Influent THM FP µg/L	Type II Substances					Type I Substances		THM FP Adsorbed Per 100 grams of Adsorbent			Per Col.
				Adsorbed per Column Grams	Passed Each Column Grams	Total Entering Each Column Grams	% of Type II Adsorbed %	% of Total THM FP Entering %	Total Passed Grams	% of Total THM FP Entering %	At end of Test Grams	At Type II Saturation Grams	At 49 days Grams	At 49 days Grams
1	2.5	XE-340	451											
1R	2.5	XE-340	355								.078		.032	.057
3	2.5	GAC	274	.11	.89	1.0	11	83	.09	8	.13	.08	.13	.23
3	2.5	904	274	?	?	?	?	?	?	?	.07	No Sat	.07	.19
4	2.5	GAC	434	.25	3.39	3.64	7	82	.11	2	.55	.2	.3	.53
4	5	GAC	434	.49	2.61	3.1	16	70	.11	2	.49	.24	.29	1.02
4	7.5	GAC	434	.49	1.97	2.46	20	55	.11	2	.45	.22	.25	1.32
4	10	GAC	434	.57	1.67	2.24	26	50	.11	2	.38	.2	.21	1.48

2.5 feet=0.76 meter 5 feet=1.52 meters 7.5 feet=2.29 meters 10 feet=3.05 meters

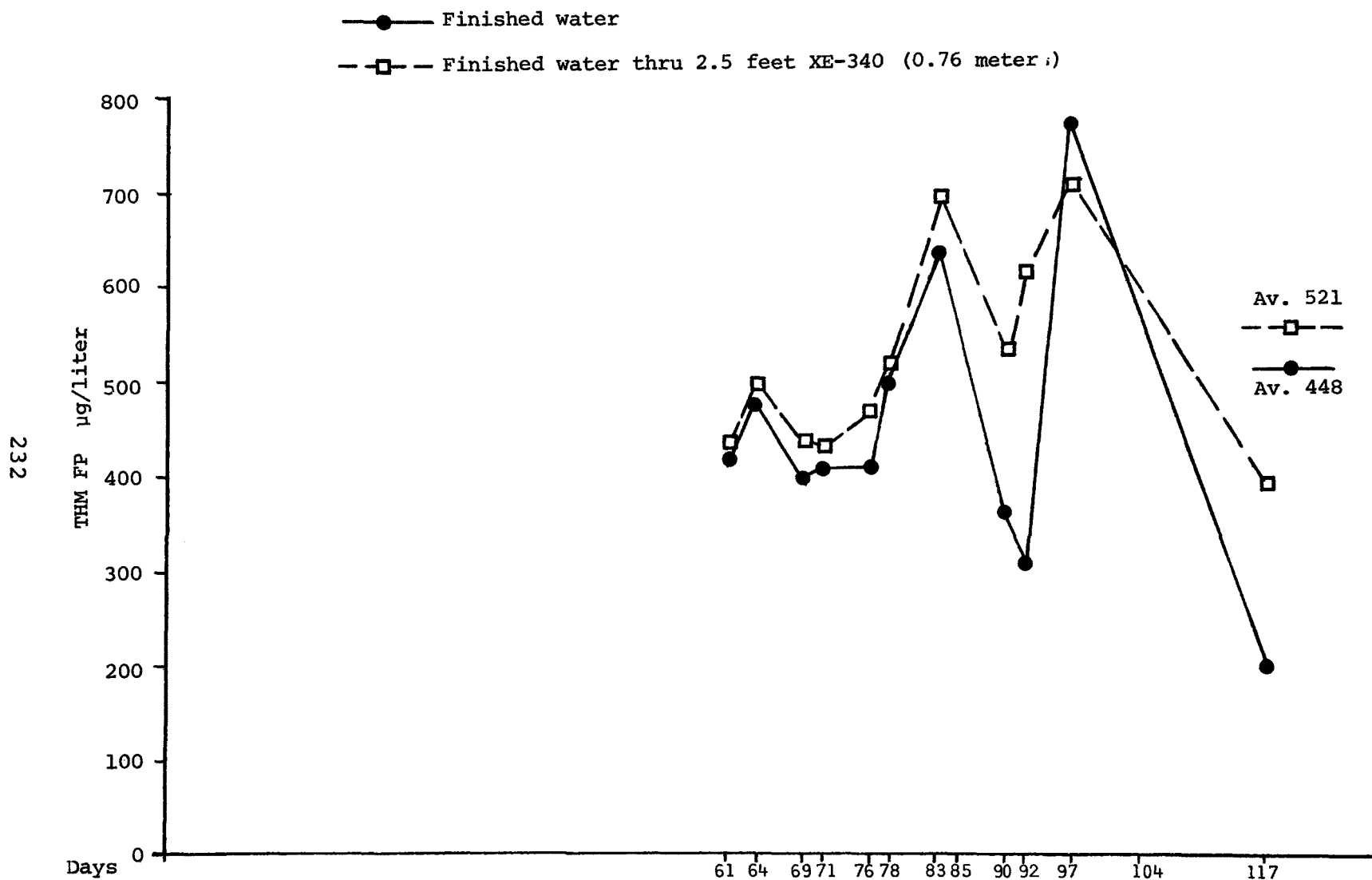


Figure 135. THM FP in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1).

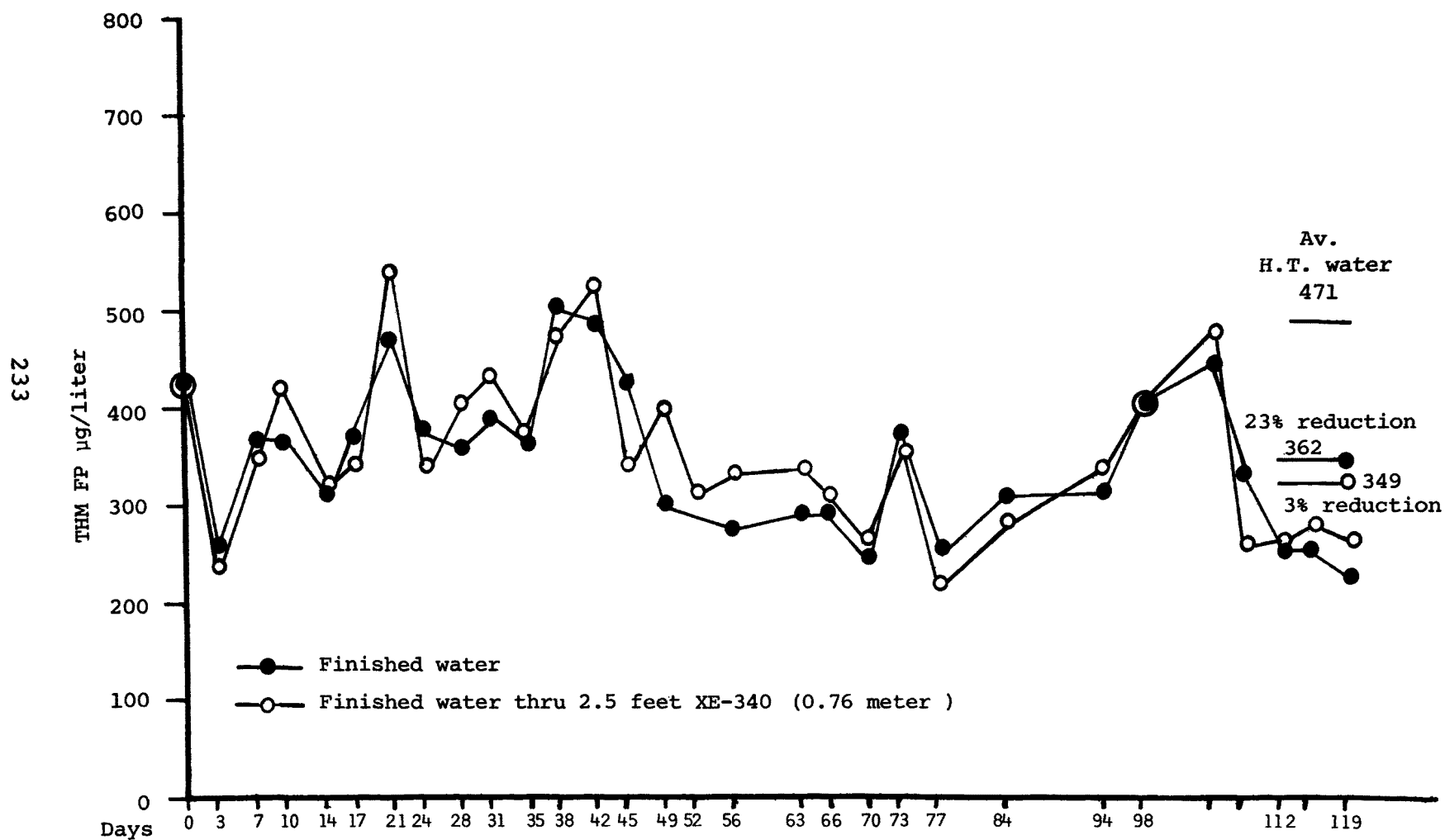


Figure 136. THM FP in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

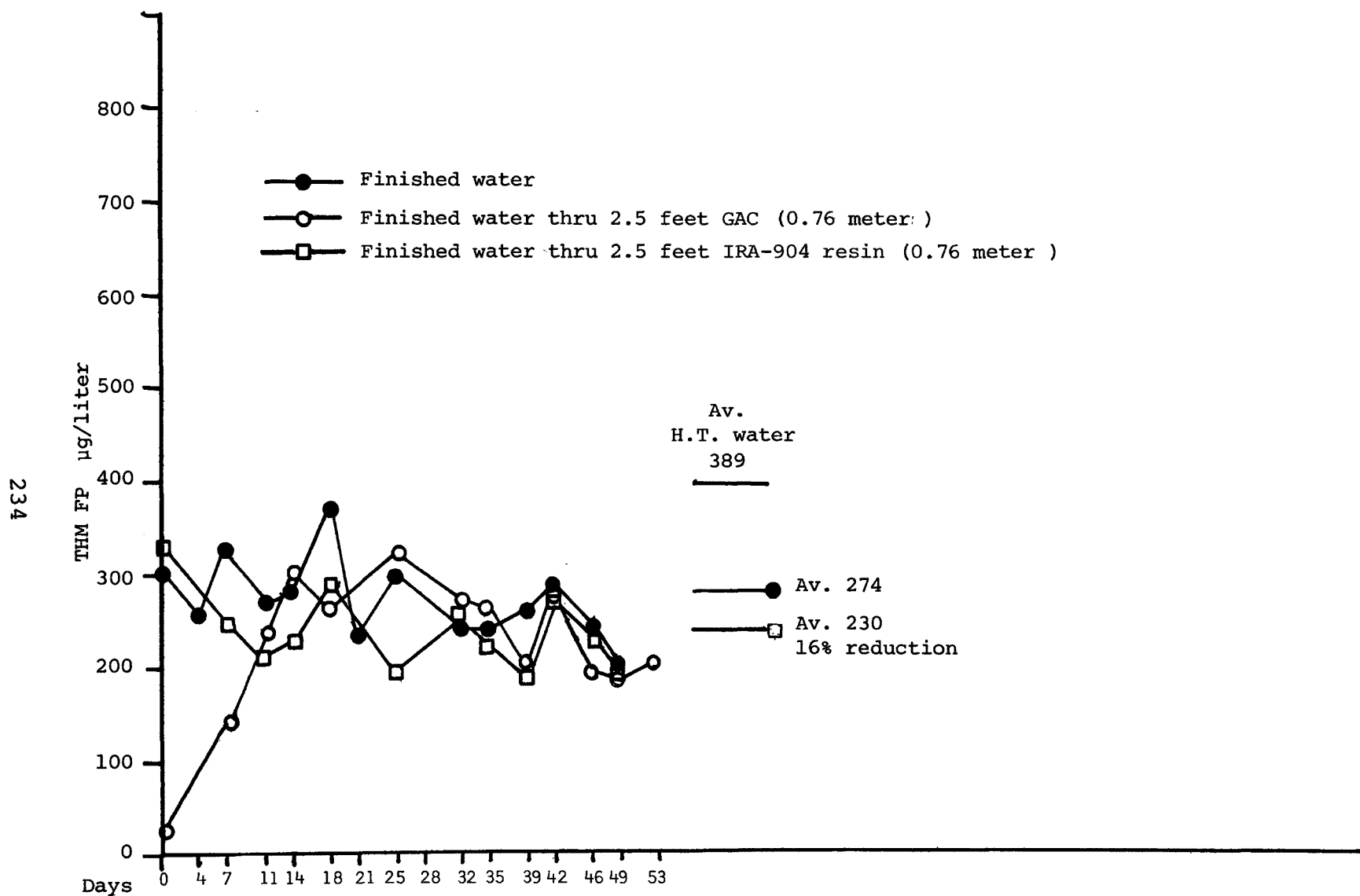
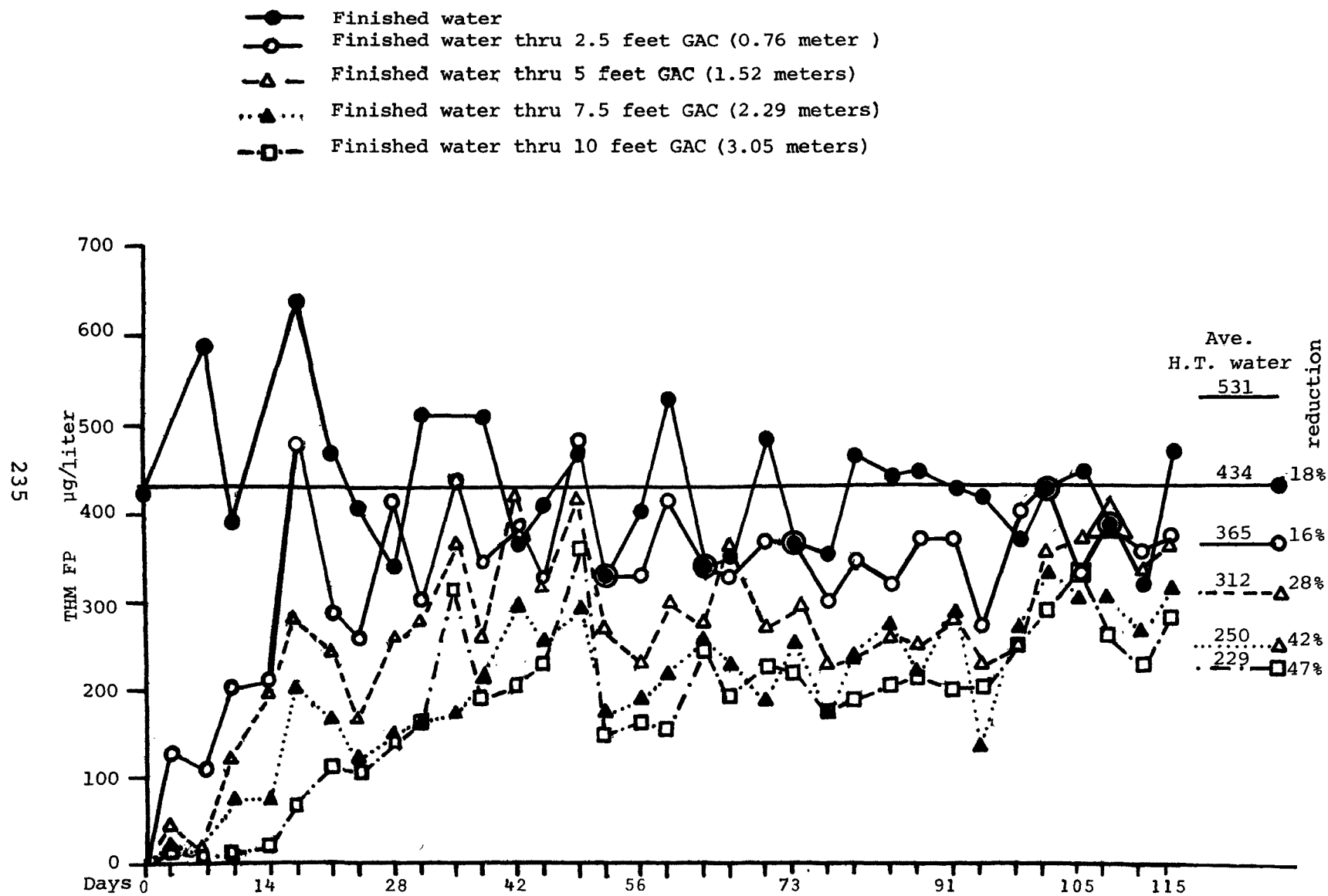


Figure 137. THM FP in finished water and removal by 0.76 meter (2.5 feet) of GAC and 0.76 meter (2.5 feet) of IRA-904 resin (ED3).



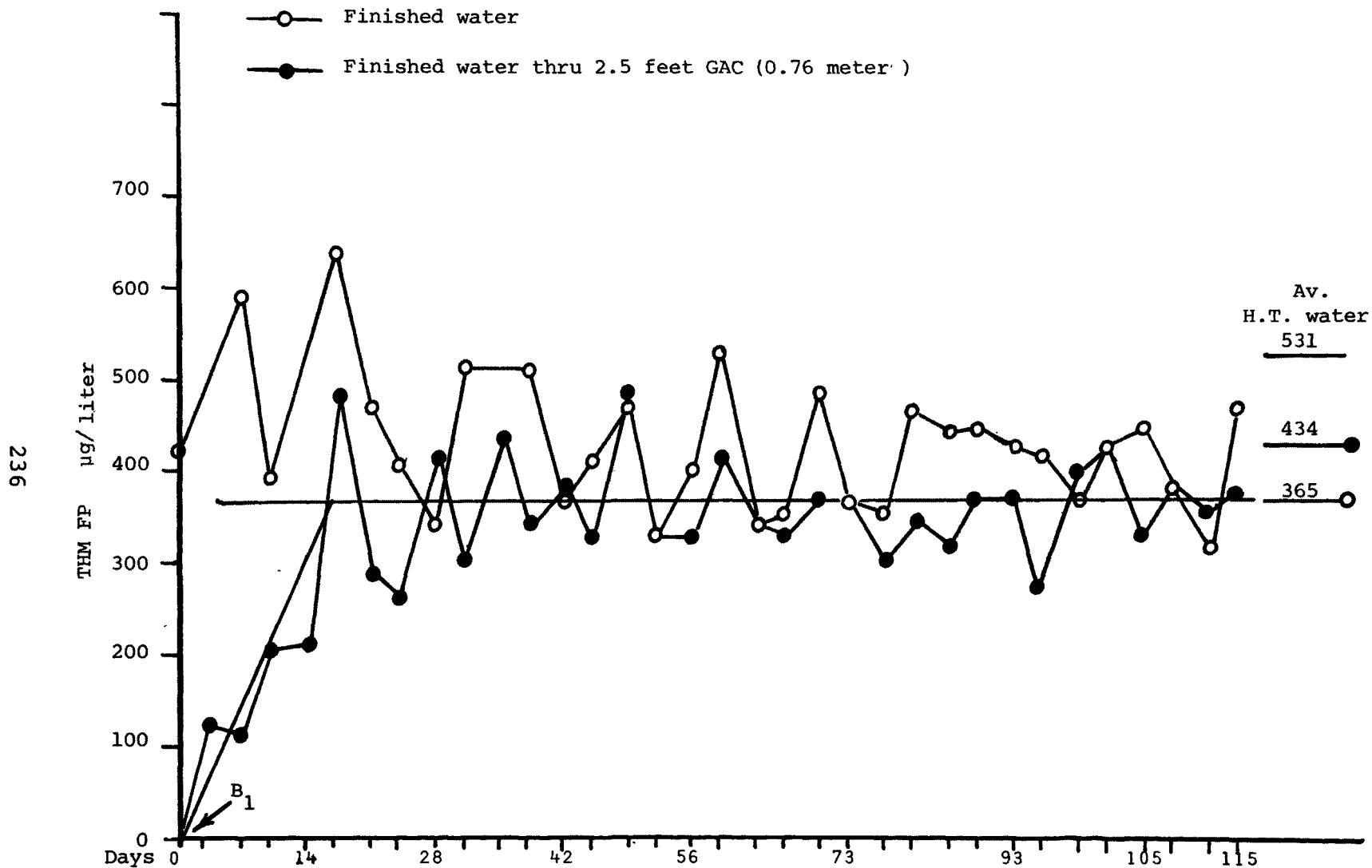


Figure 139. THM FP in finished water and removal by 0.76 meter (2.5 feet) of GAC (ED4).

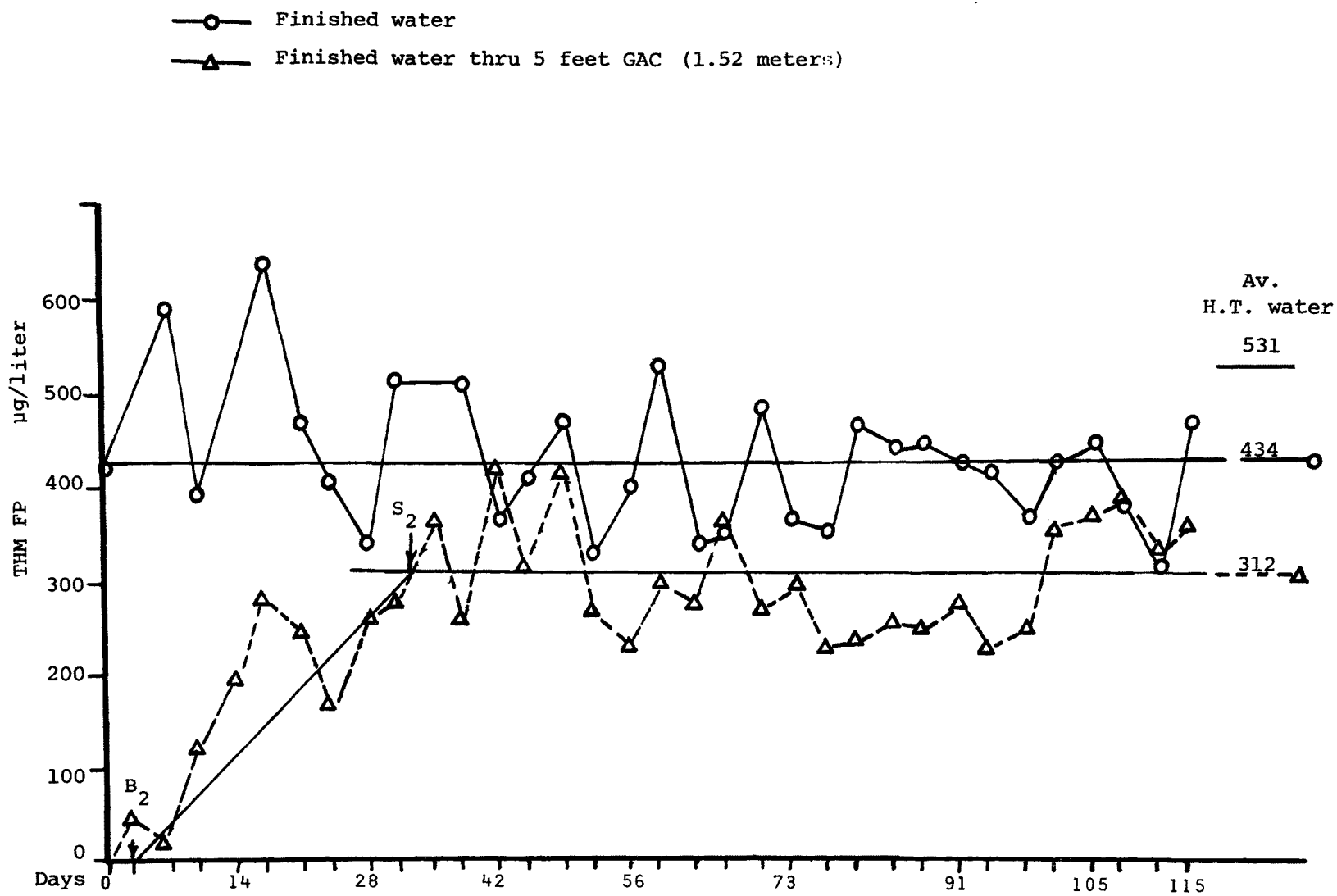


Figure 140. THM FP in finished water and removal by 1.52 meters (5 feet) of GAC (ED4).

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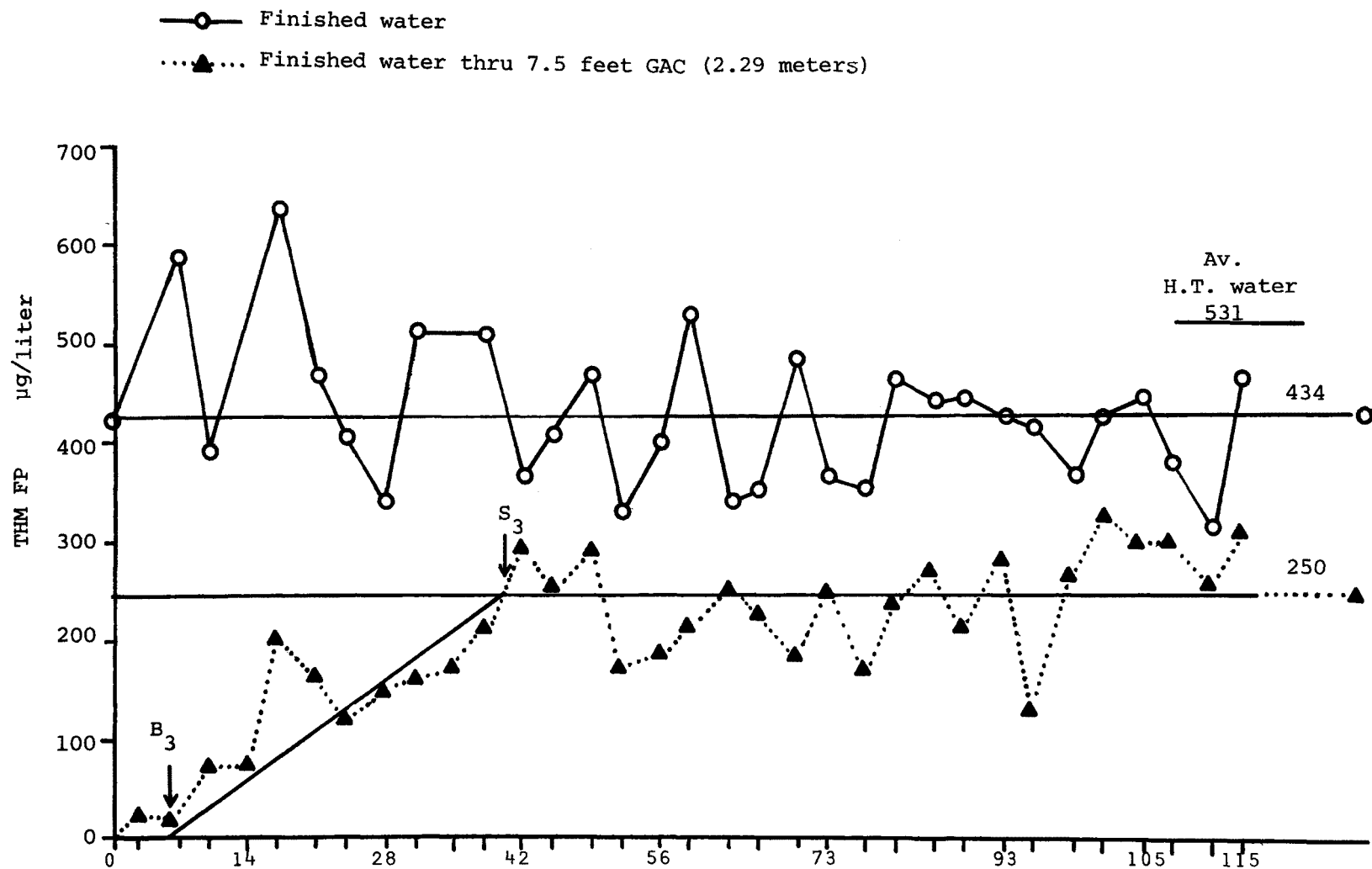


Figure 141. THM FP in finished water and removal by 2.29 meters (7.5 feet) of GAC (ED4).

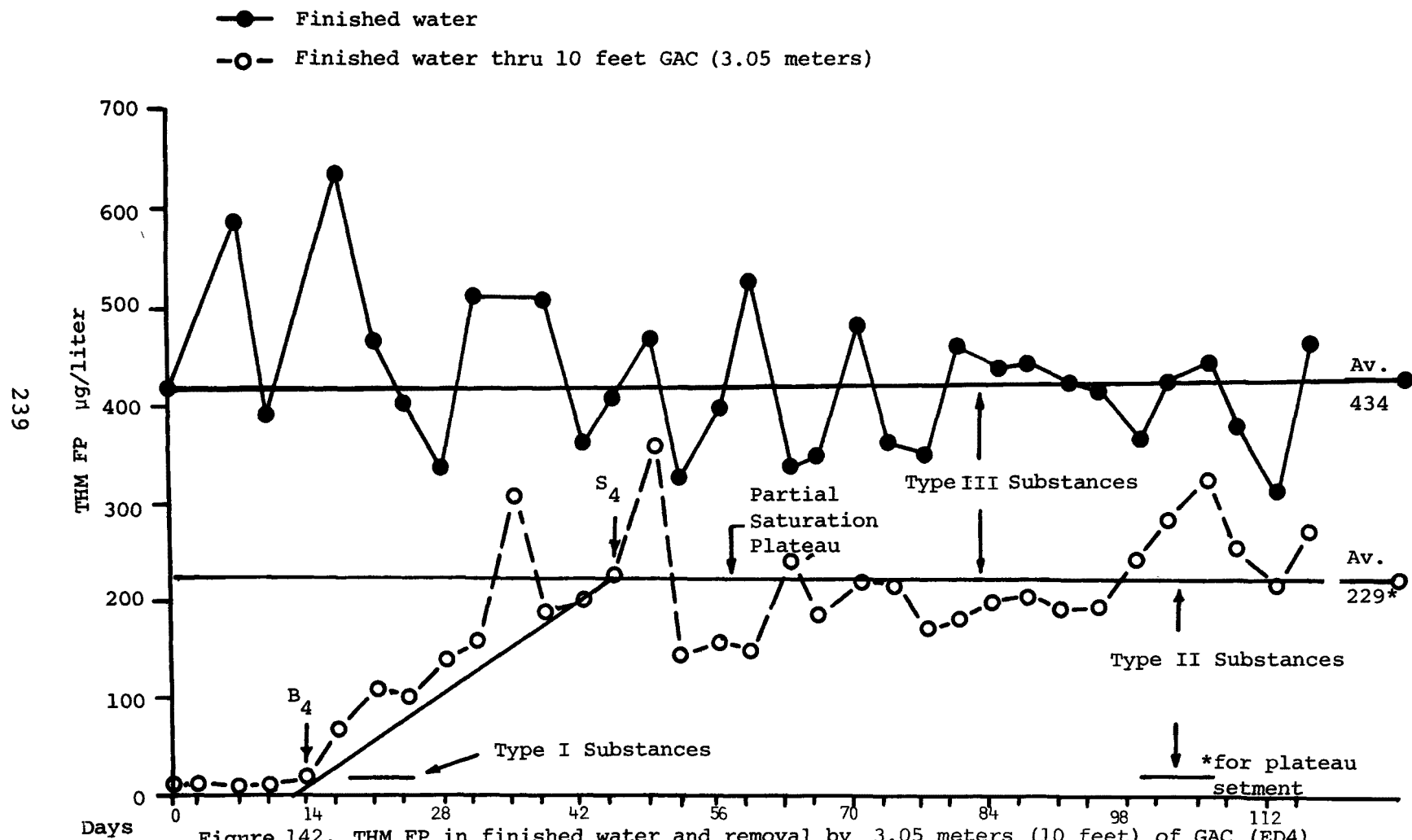


Figure 142. THM FP in finished water and removal by 3.05 meters (10 feet) of GAC (ED4).

In ED1, Figure 135, from day 61 to the end of the test period, the average THM FP effluent from the 0.76 meter (2.5 feet) deep XE-340 column was greater than the influent. In ED1R, Figure 136, the average THM FP effluent from the 0.76 meters (2.5 feet) deep XE-340 column was three percent below the influent, indicating essentially nil removal from finished water. Adsorption curves from ED3 for 0.76 meter (2.5 feet) of GAC and IRA-904 resin appear in Figure 137. It is interesting to note that the GAC column is removing additional Type II substances, as evidenced by the 0 and 7 day test point portion of the adsorption curve. From time 0, this portion of the adsorption curve is absent from the IRA-904 resin column. After Type II saturation, the average THM FP reduction was 10 percent for GAC and 16 percent for IRA-904 resin (calculated from time 0). Because of the Type II portion of the adsorption curve, the GAC column at the end of the test period removed 18 percent of the influent THM FP compared to 13 percent for IRA-904 resin (Table 42). At a common point in time of 49 days, GAC removed 1.9 times and 1.2 times as much THM FP as IRA-904 resin on an equal weight and equal volume basis respectively.

Unlike the 0.76 meter (2.5 feet) deep bed of IRA-904 resin evaluated in ED3 on finished water, the carbon bed showed a typical Type II substance removal zone. The time of Type II saturation was only 11 days. However, of the three adsorbents tested on finished water, GAC was the only one to exhibit low Type I bleed, some Type II adsorption and greater total precursor removal. Because of this, GAC was selected for study in ED4. Four 0.76 meter (2.5 feet) deep columns were connected in series providing carbon bed depths of 0.76 (2.5 feet), 1.52 (5.0 feet), 2.29 (7.5 feet) and 3.05 (10 feet) meters. THM FP adsorption curves for all four bed depths for ED4 appear in Figure 138. The curves for individual bed depths appear in Figures 139, 140, 141 and 142. The data from the 0.76 meter (2.5 feet) deep bed in ED4 can be compared with the data from the same bed depth in ED3. The average influent level of THM FP was 274 $\mu\text{g/L}$ in ED3 and 434 $\mu\text{g/L}$ in ED4. Total precursor adsorption at Type II saturation was 0.08 grams per 100 grams of carbon in ED3 and 0.2 grams per 100 grams of carbon in ED4. This indicates that adsorptive capacity for precursor substances increases as adsorbate concentration increases, as was found with HOC adsorption. GAC beds, deeper than 0.76 meter (2.5 feet), ED4 showed increased Type II breakthrough and saturation time; i.e., 14 and 46 days respectively in the 3.05 meters (10 feet) deep bed. Total THM FP adsorption data for the four columns are summarized in Figure 143. Column 1 received 4.46 grams of THM FP substances and adsorbed 0.97 grams. The other columns received and adsorbed less. However, about 20 percent of the influent THM FP to each column was uniformly removed. The THM FP adsorbed per 100 grams of carbon is also shown in Figure 143 for each 0.76 meter (2.5 feet) column on Curve II and the 0.76 (2.5 feet), 1.52 meters (5 feet), 2.29 meters (7.5 feet) and 3.05 meters (10 feet)

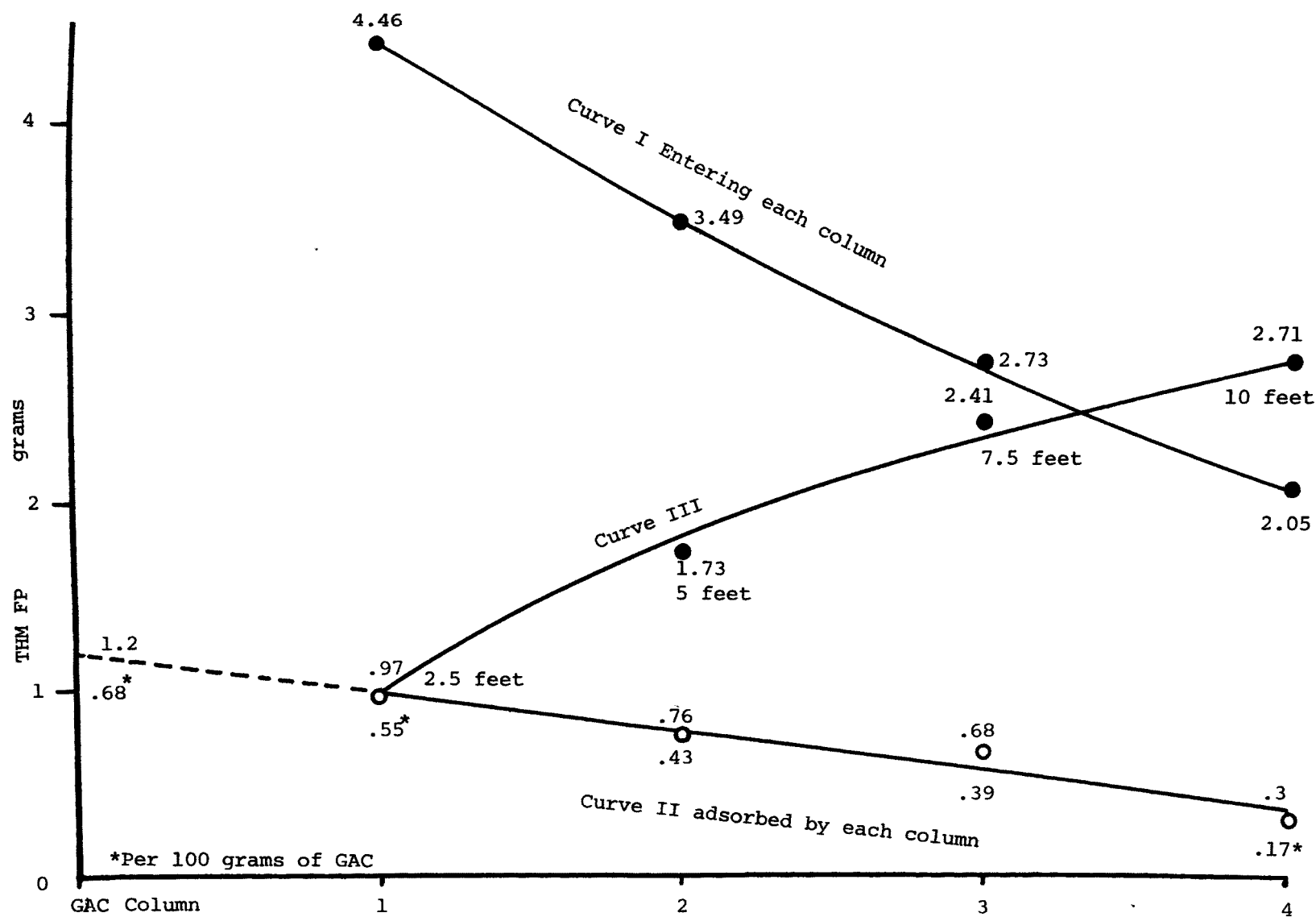


Figure I43. THM FP substances in grams entering and adsorbed by each GAC column in 115 days (ED4).

columns on Curve III. Extension of the bottom curve to the "Y" axis may provide a rough estimate of the maximum adsorptive capacity of GAC at 1.2 grams per column and 0.68 grams per 100 grams. Further work is needed to verify the usefulness of such an approach.

It was mentioned earlier that comparing THM FP adsorption by adsorbents across water sources was not really a valid method of interpreting these data because of the change of THM FP influent across water sources. Some of the THM FP adsorption data from Tables 38, 40 and 42 appear plotted in Figures 144 and 145 for further consideration. Figure 144 presents THM FP adsorption per column (0.76 meter [2.5 feet] deep) by GAC, XE-340 and IRA-904 resin at a common point in time of 49 days. The three data points from raw, H.T. and finished water for GAC and IRA-904 resin fall on a straight line. The three data points for XE-340 do not fall on a straight line. The XE-340, H.T. and finished water data points are small numbers, 0.053 grams and 0.057 grams respectively. These values were obtained by integrating the adsorption curves, and it is possible that the minor adsorption over the test period of only two percent and three percent respectively is itself not a very accurate base. In Figure 144, it is probably not very important which XE-340 line is accepted, A-B through the H.T. water point, A-D through the finished water point, or an average line A-C. For our first discussion, we can eliminate the XE-340 curve. The GAC and IRA-904 resin curves, both containing three data points, appear to be a straight line. This might indicate that the change in THM FP influent across water sources, decreasing from raw to H.T. to finished water, is the predominant cause of decreased adsorption per column. To compare the effectiveness of different adsorbents across water sources, the curves in Figure 144 may lead to a more accurate interpretation of data. Raw water adsorption data for the three adsorbents is compared in Table 43, with varying THM FP influent levels and at a constant THM FP level.

In Figure 144, the horizontal line of 600 $\mu\text{g/L}$ may indicate what the adsorption would be at that uniform THM FP level. Line A-C was chosen for the XE-340 curve for this discussion. The data in Table 43 show that the effectiveness of IRA-904 resin compared to GAC and XE-340 varies when influent concentration is considered. The slopes of the GAC and IRA-904 resin curves are different, and as the influent THM FP level decreases the curves cross. At low influent levels, GAC becomes more effective than IRA-904 resin. Comparison of adsorbents would be different if a different common time point was chosen. The results are also different at 49 days when compared at an equal adsorbent weight basis, Figure 145. In Figure 145, GAC is more effective than IRA-904 resin in all three water sources. In both Figures 144 and 145, XE-340 has considerably less adsorptive capacity than GAC or IRA-904 resin.

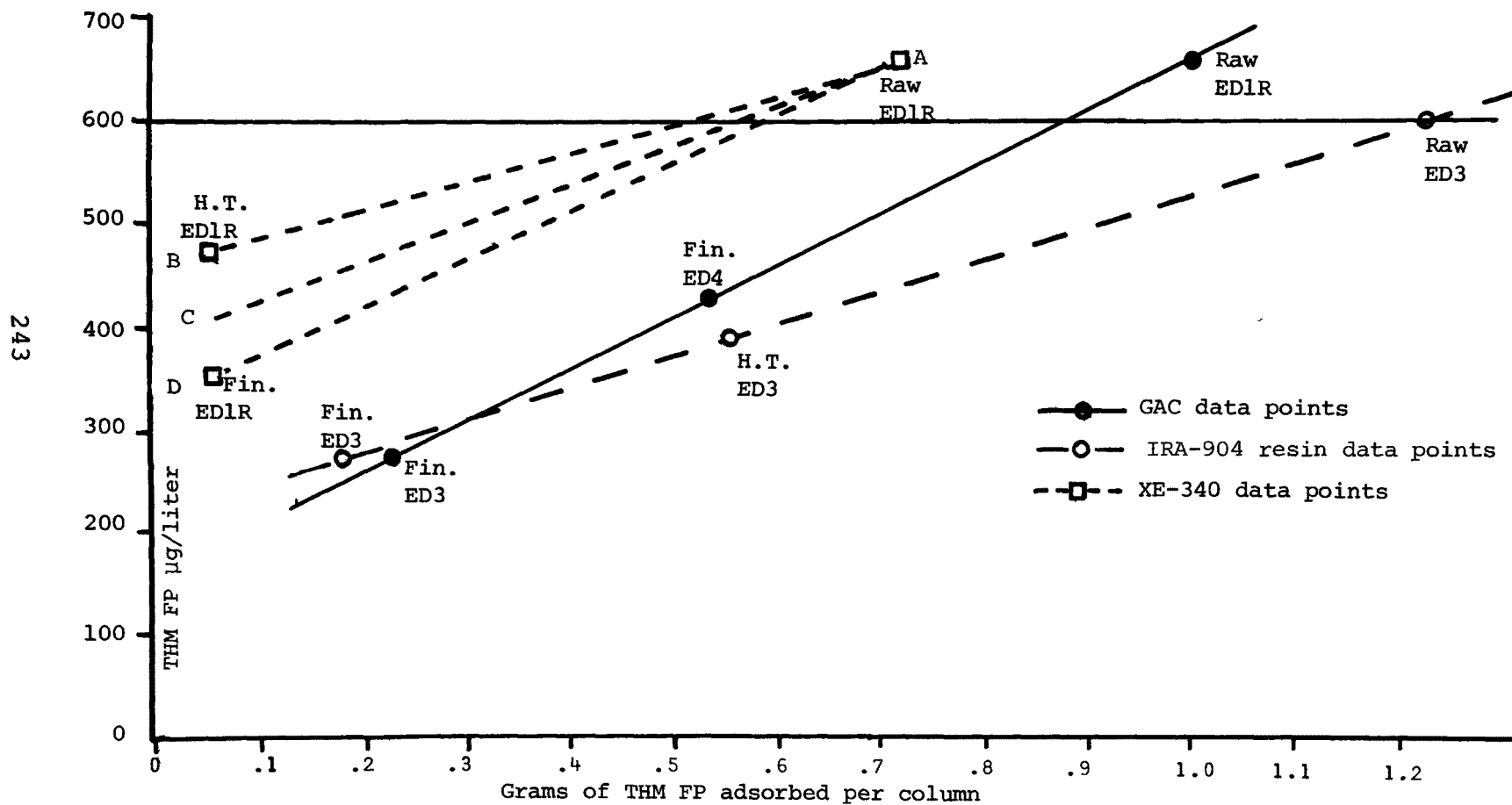


Figure 144. THM FP adsorption by GAC, XE-340 and IRA-904 resin per column 0.76 meter deep (2.5 feet) at 49 days.

	Adsorption per column at 49 days at varying THM FP influent levels (from Table 38)	Adsorptive capacity of 904 resin compared to GAC and XE-340	Adsorption per column at 49 days at 600 µg/ of THM FP influent level (from Figure 144)	Adsorptive capacity of 904 resin compared to GAC and XE-340
adsorbent	grams of THM FP		grams of THM FP	
2.5 feet 904 resin	1.21		1.21	
2.5 feet GAC	.99	1.22 times	.88	1.38 times
2.5 feet XE-340	.71	1.70 times	.57	2.12 times
2.5 feet=0.76 meter				

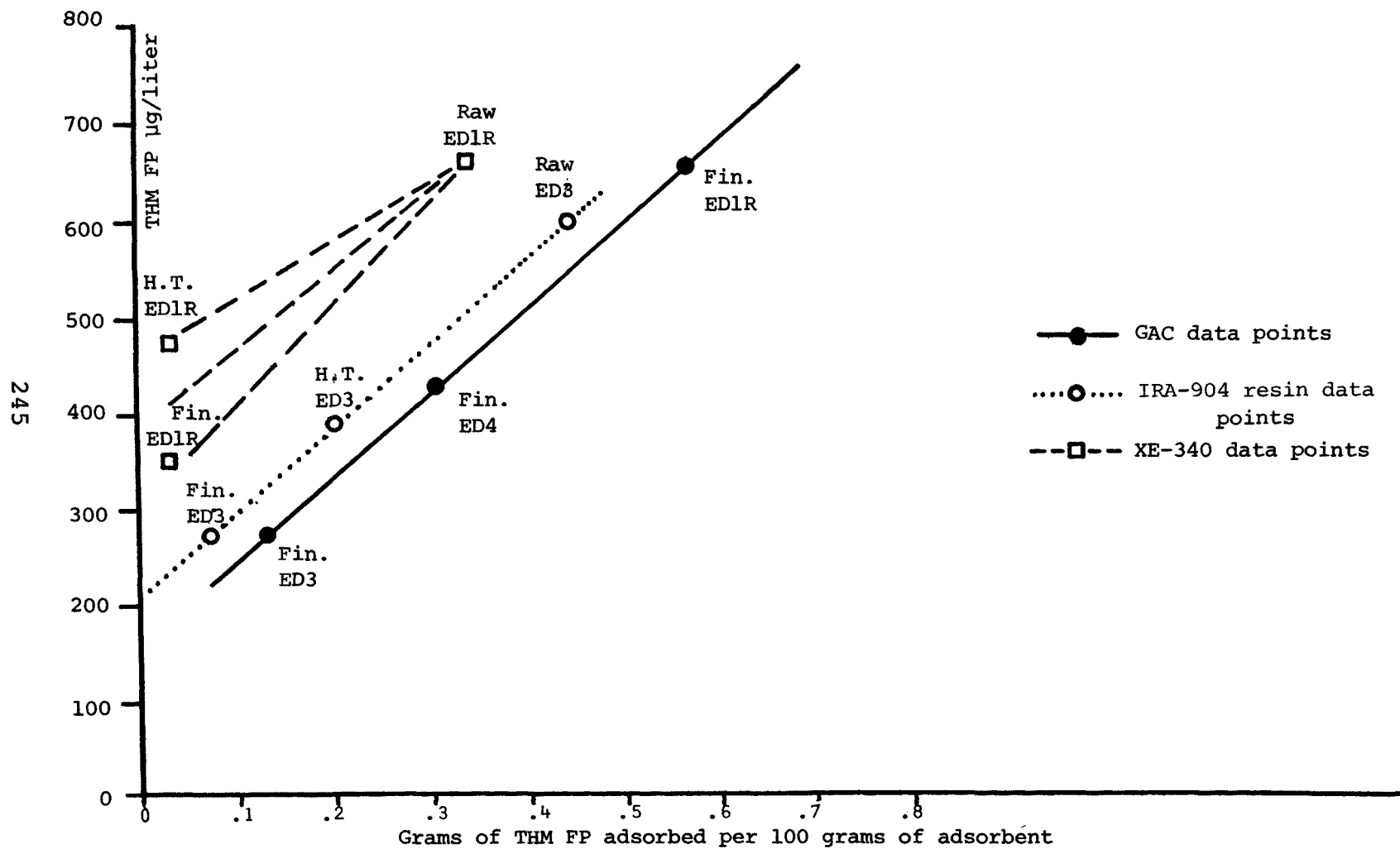


Figure 145. THM FP adsorption by GAC, XE-340 and IRA-904 resin per 100 grams of adsorbent at 49 days.

TOC adsorption data from finished water appear in Table 44. Adsorption curves appear in Figures 146, 147 and 118.

XE-340, 0.76 meter (2.5 feet) deep, was studied in ED1R, Table 44 and Figure 146. TOC removal averaged three percent of the influent. Removal was also very low in raw and H.T. water, five percent and four percent respectively.

GAC and IRA-904 resin, 0.76 meter (2.5 feet), were studied in ED3. In Figure 147, both GAC and IRA-904 resin appear to remove some Type II TOC substances. In Figure 137, the IRA-904 resin did not appear to remove Type II THM FP substances. In ED3, the IRA-904 resin removed 1.3 times as much TOC from finished water as GAC on an equal volume basis. On an equal weight basis, GAC removed 1.2 times as much as IRA-904 resin. GAC, 0.76 meter (2.5 feet) deep, was studied in both ED3 and ED4. As the influent TOC level decreased, the adsorptive capacity decreased. In Figure 118, it is clear that increased GAC bed depth resulted in larger periods of time to breakthrough and saturation. In Figure 118, it appears that the TOC data collected on test days 29 and 35 are too low and should probably be discarded. When adsorptive data for the three adsorbents are compared across water sources some problems arise. TOC adsorption data from Tables 44, 46 (see page 257), and 49 (see page 300) are plotted in Figures 148 and 149. Straight lines were not obtained with the three data points for each adsorbent. In both Figures 148 and 149, there appears to be a trend to increased adsorption for each adsorbent as the influent TOC level decreases, which does not appear reasonable. Perhaps additional work with TOC data in future research is necessary before conclusions can be reached. In Figure 148, the adsorptive capacity (equal volume basis) of IRA-904 resin was always better than GAC and GAC always better than XE-340. In Figure 149, on an equal weight basis, GAC was generally better than IRA-904 resin and IRA-904 resin was always better than XE-340.

Other Parameters

Chlorine--

The effect of free and combined chlorine in finished water as it passes through adsorbent columns is included in this section with the chlorine data on finished water. XE-340 removes essentially all free chlorine for 17 days. Free chlorine in the effluent then steadily rose and by the end of the test (122 days) was about one-third the influent level. Throughout the test period the level of combined chlorine in XE-340 effluent remained about one-half of the influent. IRA-904 resin removed all free chlorine and 93 percent of the combined chlorine throughout the 53-day test. In the same test period, GAC removed all free chlorine and initially 90 percent of the combined chlorine. Combined chlorine gradually increased in the effluent, reaching 72 percent removal at the end of the test. Increased amounts of

TABLE 44. TOC ADSORPTION DATA FROM FINISHED WATER

ED	Bed Depth Feet	Adsorbent	Average Influent TOC mg/L	Type II Substances			Test Duration Days	Total TOC Entering Each Column During Test Grams	Total TOC Adsorbed By Each Column At End of Test Grams	% of Total TOC Entering	Total TOC Adsorbed By Each Column At Type II Saturation Grams	% of Total TOC Entering	Type III Substances	
				Column Breakthrough Days	Column Saturation Days	M _H N Inch							Adsorbed per Column Grams	% of Total TOC Entering
1R	2.5	XE-340	6.5	can't calc.			127	73.7	2.2	3			2.2	3
3	2.5	GAC	5.9	0	32	30	53	27.9	9.7	35	8.6	31	2.8	10
3	2.5	904	5.9	0	39	30	53	27.9	12.7	46	11.3	41	4.7	17
4	2.5	GAC	5.4	0	24	30	127	61.5	9.1	15	5.9	10	4	7
4	5	GAC	5.4	0	32	30	127	61.5	17.5	28	9.7	16	10.9	18
4	7.5	GAC	5.4	7	43	25	127	61.5	26.5	43	14	23	18.9	31
4	10	GAC	5.4	14	60	23	127	61.5	34.5	56	21.2	35	25.1	41
												(continued)		

2.5 feet=0.76 meter 5 feet=1.52 meters 7.5 feet=2.29 meters 10 feet=3.05 meters

TABLE 44. (continued)

ED	Bed Depth Feet	Adsorbent	Average Influent TOC mg/L	Type II Substances					Type I Substances		TOC Adsorbed Per 100 grams of Adsorbent			Per Col.
				Adsorbed per Column Grams	Passed Each Column Grams	Total Entering Each Column Grams	% of Type II Adsorbed %	% of Total Entering %	Total Passed Grams	% of Total TOC Entering %	At end of Test Grams	At Type II Saturation Grams	At 49 days Grams	At 49 days Grams
1R	2.5	XE-340	6.5								1.02		.8	1.7
3	2.5	GAC	5.9	6.9	15.8	22.7	44	81	2.4	9	5.5	4.9	5.4	9.5
3	2.5	904	5.9	7.8	13.4	21.2	37	76	2	7	4.6	4.1	4.6	12.7
4	2.5	GAC	5.4	5.1	48.4	53.5	10	87	4	6	5.2	3.4	3.9	6.9
4	5	GAC	5.4	6.6	40	46.6	14	76	4	6	5.0	2.8	3.2	5.6
4	7.5	GAC	5.4	7.6	31	38.6	20	63	4	6	5.0	2.7	2.9	5.1
4	10	GAC	5.4	9.4	23	32.4	29	53	4	6	4.9	3.0	2.8	4.9

2.5 feet=0.76 meter 5 feet=1.52 meters 7.5 feet=2.29 meters 10 feet=3.05 meters

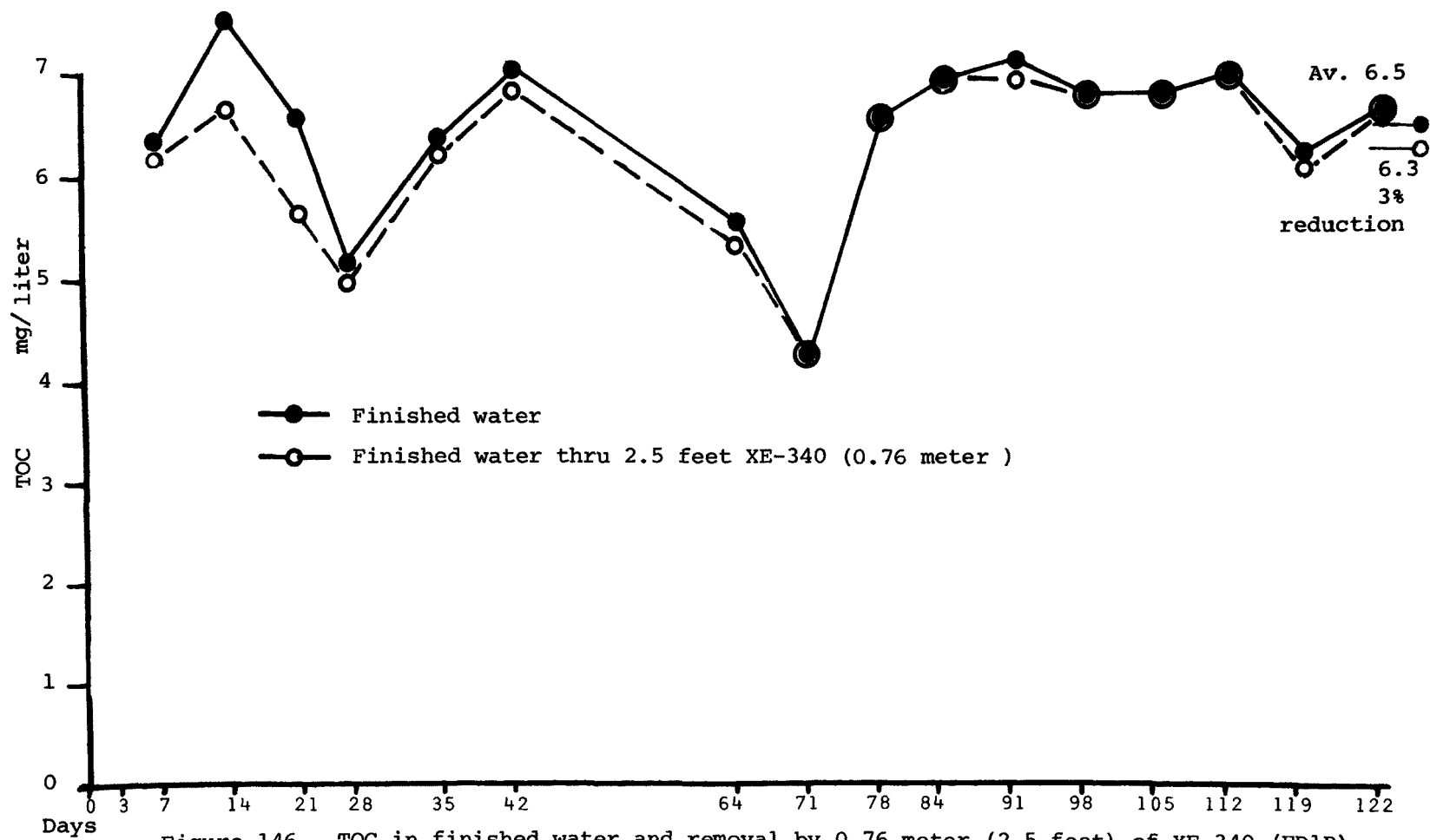


Figure 146. TOC in finished water and removal by 0.76 meter (2.5 feet) of XE-340 (ED1R).

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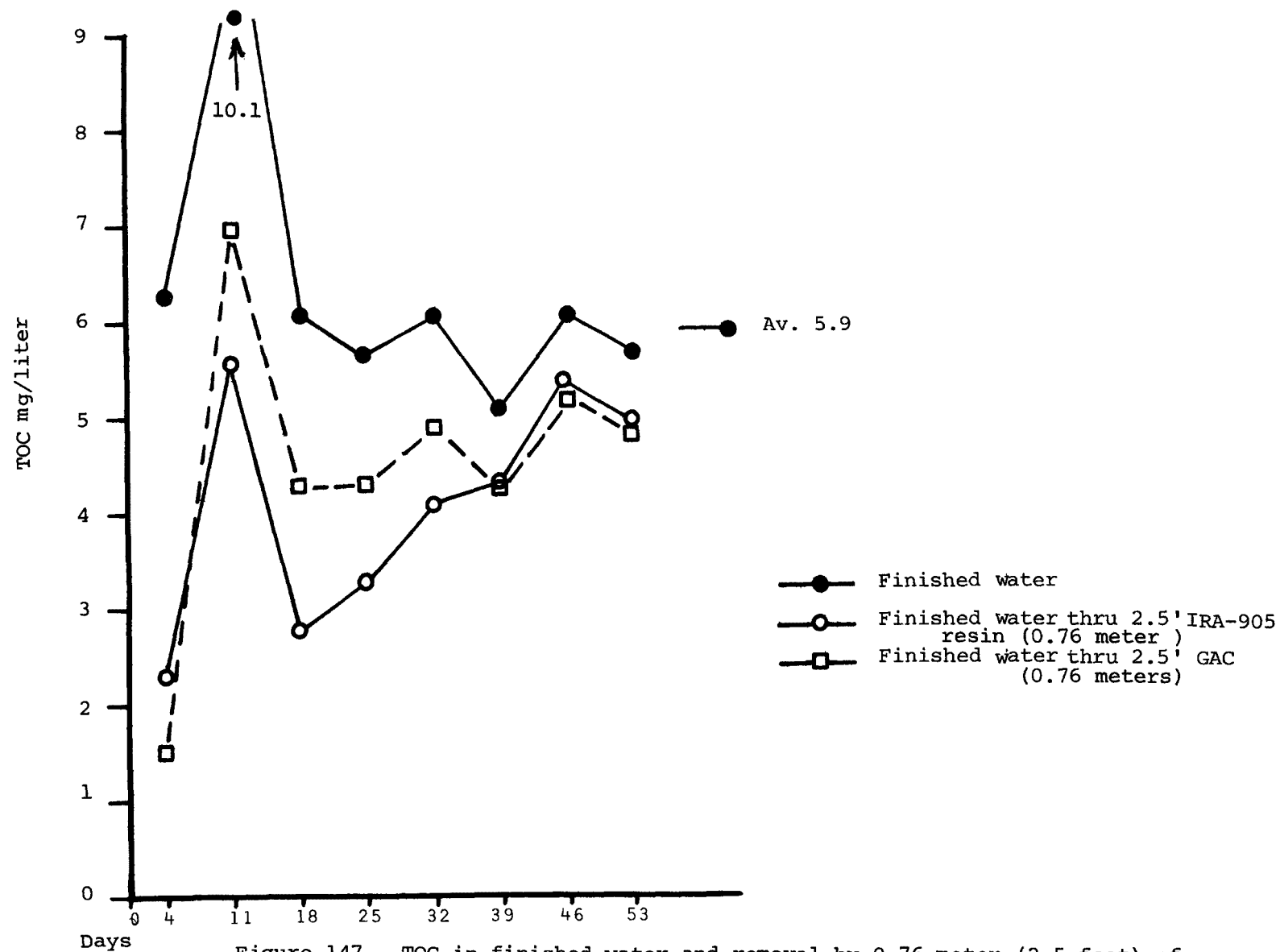


Figure 147. TOC in finished water and removal by 0.76 meter (2.5 feet) of IRA-904 resin and by 0.76 meter (2.5 feet) of GAC (ED3).

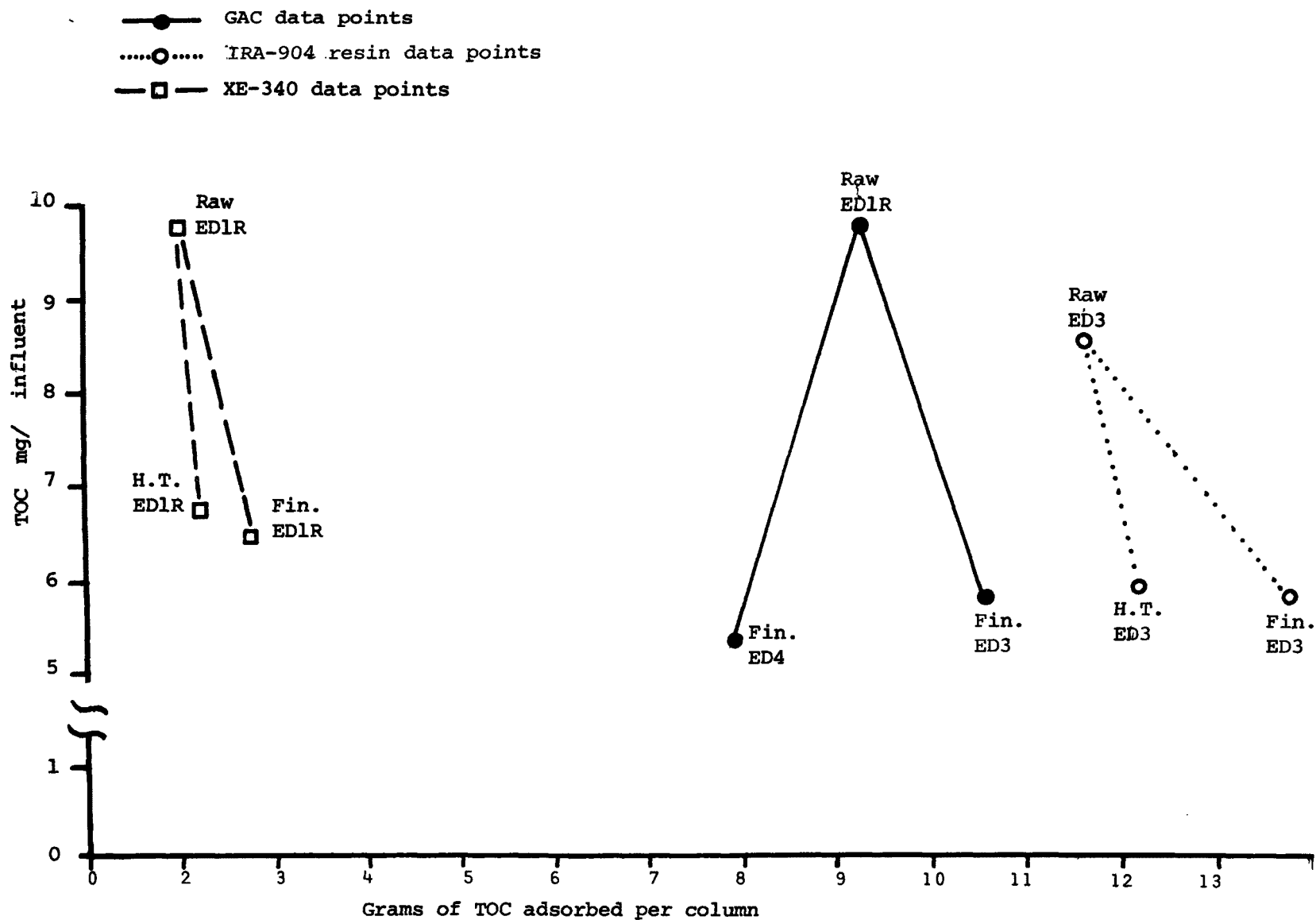
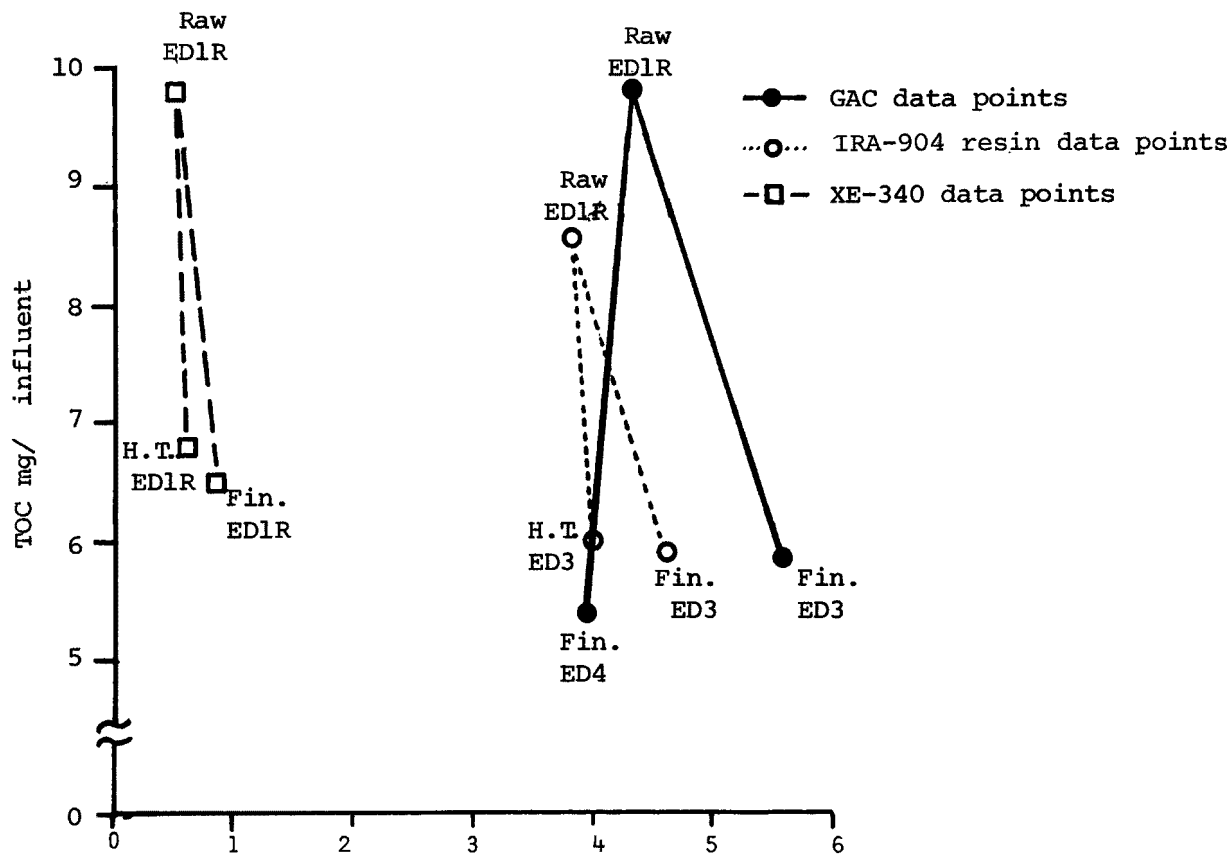


Figure 148. TOC adsorption by GAC, XE-340 and IRA-904 resin per column 0.76 meter (2.5 feet) deep at 49 days.



Grams of TOC adsorbed per 100 grams of adsorbent
 Figure 149. TOC adsorption by GAC, XE-340 and IRA-904 resin per 100 grams of adsorbent at 49 days.

combined chlorine were removed with increased GAC bed depth.

Turbidity--

The effect on turbidity when raw, H.T. and finished water pass through adsorbents and turbidity in the distribution system are included in Appendix A.

Adsorbents removed turbidity from H.T. effluent but turbidity of the raw water increased considerably after passing through XE-340. Turbidity also increased as raw water passed through IRA-904 resin. This same resin removed turbidity from finished water and H.T. effluent.

Color--

No color was removed from raw water by XE-340 or GAC.

pH--

The effect on pH of raw, H.T. and finished water as they pass through adsorbent columns is included in this section with other pH data. The average pH of raw water through GAC, XE-340 and IRA-904 resin increased by approximately 0.1. The average pH through XE-340 was one-tenth lower than H.T. water; through IRA-904 resin it was three-tenths lower. There was no change through GAC. The average pH of finished water decreased 0.1 when passed through XE-340, and 0.2 through GAC and IRA-904 resin.

Comparison of Laboratory and Distribution System Aging

It is important to know if bottle aging in the laboratory to determine total THM, terminal THM or THM FP correlates with actual distribution system formation of these parameters. To avoid confusion, we will refer to the THM growth of two-day aged samples as total THM growth. The parameter, terminal THM will be reserved for THM growth occurring in six-day aged samples which is the time factor used throughout this study in determining THM FP (THM FP = term. THM - inst THM). Based on measurements of the length of time it took for abrupt changes in fluoride concentrations made at the plant to reach certain points in the distribution system, we estimated that it takes two days for finished water leaving the Preston Plant to reach the Red Road sampling point. A sampling procedure to determine THM growth was established as part of ED3 to compare laboratory bottle aged samples with samples taken directly from the distribution system sampling point at Red Road. The sampling procedure appears in Table 45.

The data obtained are presented in Figure 150. During the 53-day test period of ED3, the Inst. THM levels of finished water at the Preston Plant are shown by the lower curve in Figure 150. Finished water leaving the Preston Plant had an average Inst. THM level of 128 $\mu\text{g/L}$. Total THM levels of finished

TABLE 45. SAMPLING PROCEDURE TO COMPARE LABORATORY AND DISTRIBUTION
SYSTEM AGING

WATER SAMPLE	TREATMENT
Finished water at Preston Plant	aged 2 days in bottle with no additional chlorine
Finished water at Preston Plant	pH 9 buffered and excess free chlorine added then aged 6 days in bottle
Red Road distribution system sample	has been aged approximately 2 days in distribution system
Red Road distribution system sample	sample taken and treated after approximately 2 days in distribution system with pH 9 buffer and excess free chlorine and then stored in bottle in laboratory for 4 days before analysis (represents a total of 6 days aging)

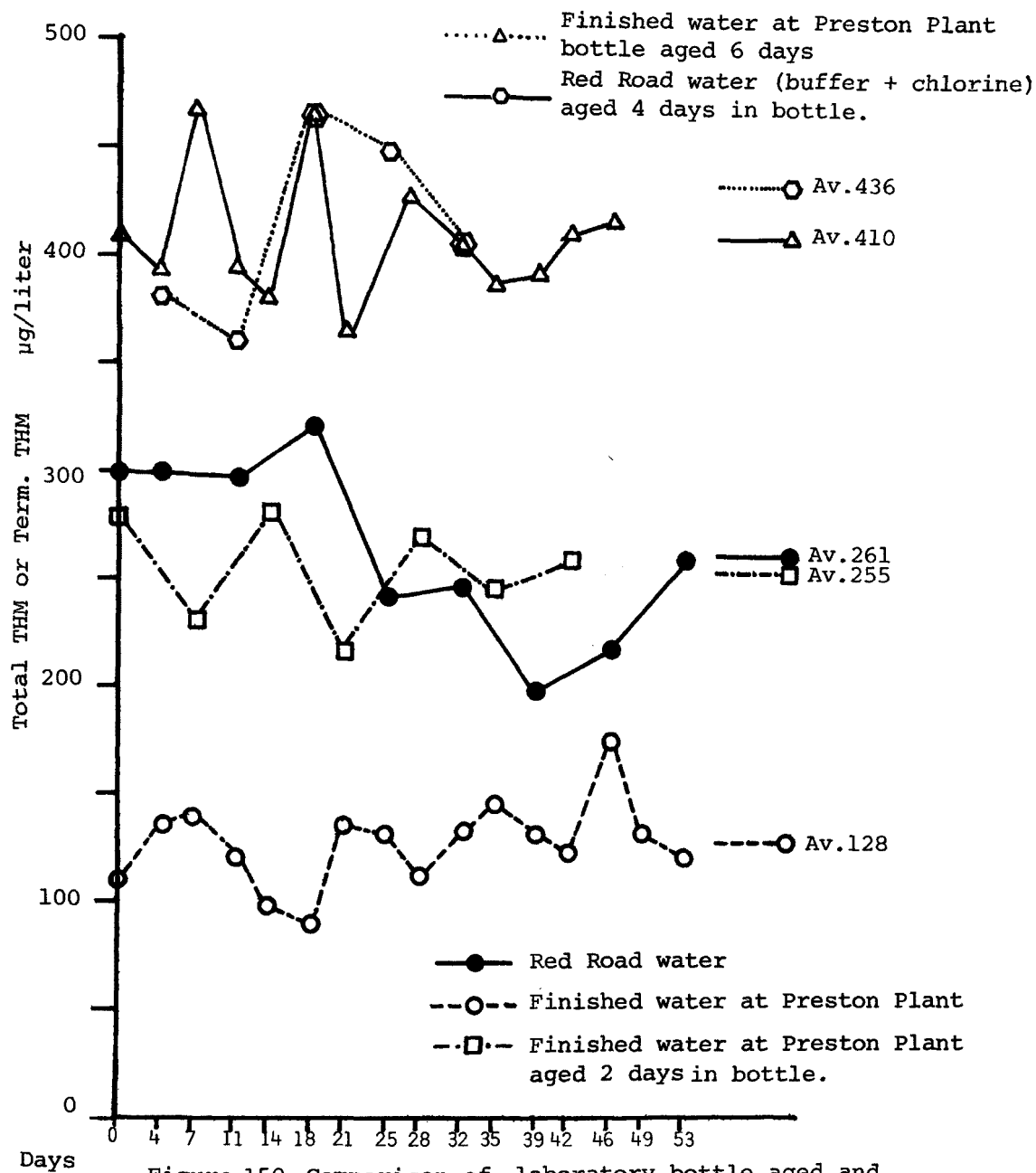


Figure 150. Comparison of laboratory bottle aged and distribution system THM growth (ED3).

water at the Preston Plant aged two days in a bottle also are plotted in Figure 150, indicating an average total THM level of 255 $\mu\text{g/L}$, a growth of 1.99 times. The Red Road distribution system sample had an average total THM level of 261 $\mu\text{g/L}$, a growth of 2.04 times, which is very close to the average value of the bottle aged growth. Although the specific two-day bottle and actual distribution sample values vary more widely than the average values, the general magnitude of the distribution water values can be roughly estimated by laboratory aged samples. Curves II and III in Figure 155, show additional data on the comparison of bottle aged and distribution system samples.

Finished water from the Preston Plant aged six days in a bottle with a pH 9 buffer and excess free chlorine (data plotted in Figure 150) had an average terminal THM level of 410 $\mu\text{g/L}$, a growth of 3.2 times. The Red Road sample, aged in a bottle for four days with a pH 9 buffer and excess free chlorine (a total of six days from leaving the Preston Plant when including the two days travel in the distribution system plus four days bottle storage) had an average terminal THM level of 436 $\mu\text{g/L}$ (data plotted in Figure 150), a growth of 3.4 times, which again is very close to the six-day bottle aged sample. Therefore, laboratory bottle aging compares fairly closely with actual distribution system aging. It should be noted that the finished water sample from the Preston Plant that was aged two days and the Red Road sample that had been in the actual distribution system for two days, had no free chlorine left at the end of two days, and would have had higher total THM values if free chlorine had been maintained.

Total THM Growth in Adsorbent Column Effluents

As finished water passes through an adsorbent column, it loses all of its free chlorine and various amounts of its combined chlorine. The column effluent would have to be rechlorinated to a free chlorine level of approximately 2.5 ppm before entering the distribution system. To study the effect of total THM growth with two days of chlorine contact on such effluent samples from 0.76 meter (2.5 feet) deep columns of GAC and IRA-904 resin, a sampling procedure was established as part of ED3. The sampling procedure appears in Table 46.

TABLE 46. TOTAL THM GROWTH IN ADSORBENT COLUMN EFFLUENTS

WATER SAMPLE	TREATMENT
Finished water through 0.76 (2.5 feet) meter of IRA-904 resin	buffered at pH 9 and free chlorine added to 2.5 ppm, bottle aged 2 days
Finished water through 0.76 (2.5 feet) meter of GAC	buffered at pH 9 and free chlorine added to 2.5 ppm, bottle aged 2 days

The data obtained are presented in Figures 151, 152, 153 and 154. In Figure 151, as a reference base, curves are presented showing the inst. THM in finished water at the Preston Plant and the total THM growth occurring after two days of bottle aging. The average inst. THM level in finished water was 128 $\mu\text{g/L}$ and the total THM after two days of bottle aging averaged 255 $\mu\text{g/L}$. The inst. THM levels in the 0.76 meters (2.5 feet) deep IRA-904 resin column effluent is also presented in Figure 151. The average level was 176 $\mu\text{g/L}$. This level is higher than in the finished water entering the IRA-904 resin column due to the catalytic generation of THM in the column as previously discussed. The average THM growth in the column was 48 $\mu\text{g/L}$ (176 $\mu\text{g/L}$ - 128 $\mu\text{g/L}$). Total THM levels in the IRA-904 resin column effluent, buffered to pH 9, rechlorinated to 2.5 ppm of free chlorine and bottle aged two days are presented in Figure 151. The average value of THM growth resulting from catalytic generation, 48 $\mu\text{g/L}$, is subtracted from the 309 $\mu\text{g/L}$ average above, an average value of 261 $\mu\text{g/L}$ is obtained. This average value is very close to the 255 $\mu\text{g/L}$ average value (Figure 151) for the Total THM growth obtained by aging finished water for two days. These data indicate that the IRA-904 resin column did not remove much THM FP from finished water in ED3. This separate information confirms the information reported in Table 42, that the IRA-904 resin column in ED3 0.76 meter (2.5 feet) deep removed only 13 percent of the influent THM FP.

The curve shown in Figure 152 was obtained by subtracting Curve III from Curve IV in Figure 151. It represents the total THM growth in the IRA-904 resin column effluent due only to THM FP conversion. It clearly shows that throughout the test period even from initial startup, the IRA-904 resin never removed enough THM FP to keep THM regrowth below 100 $\mu\text{g/L}$.

In Figure 153, the total THM growth in a 0.76 meter (2.5 feet) deep GAC column effluent which had been buffered, rechlor-

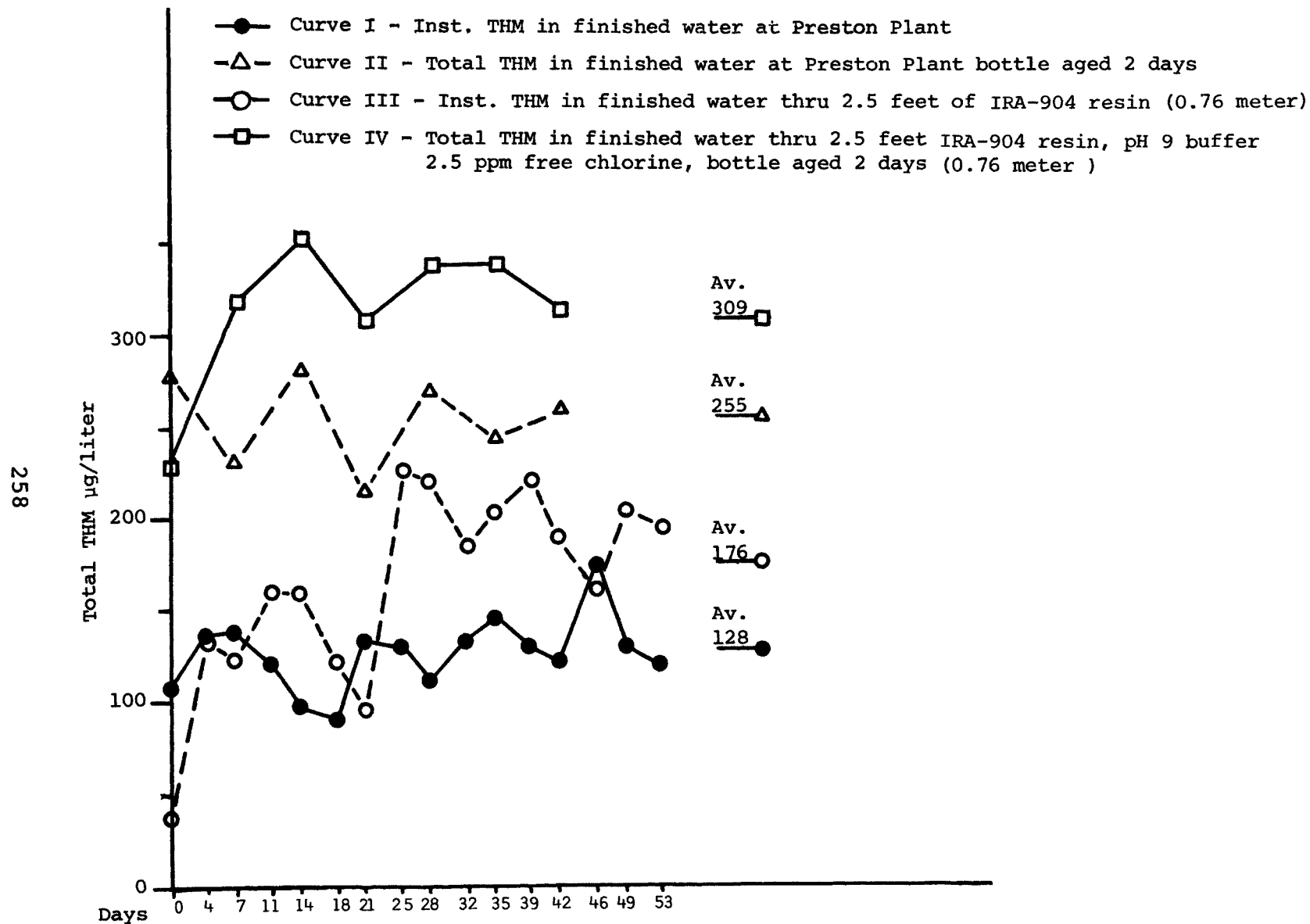
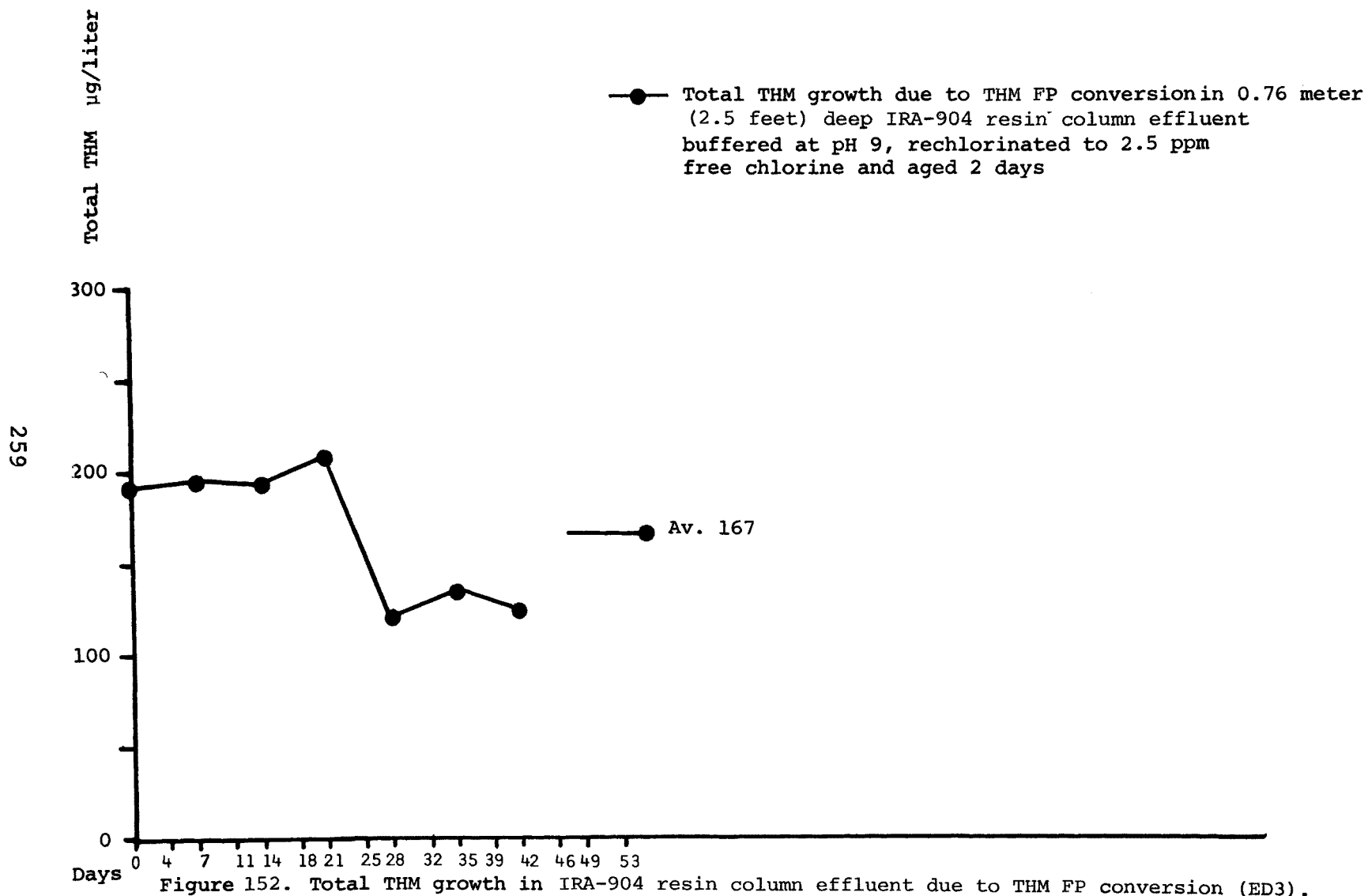


Figure 151. Total THM growth in rechlorinated - 2 day aged IRA-904 resin column effluent(ED3).



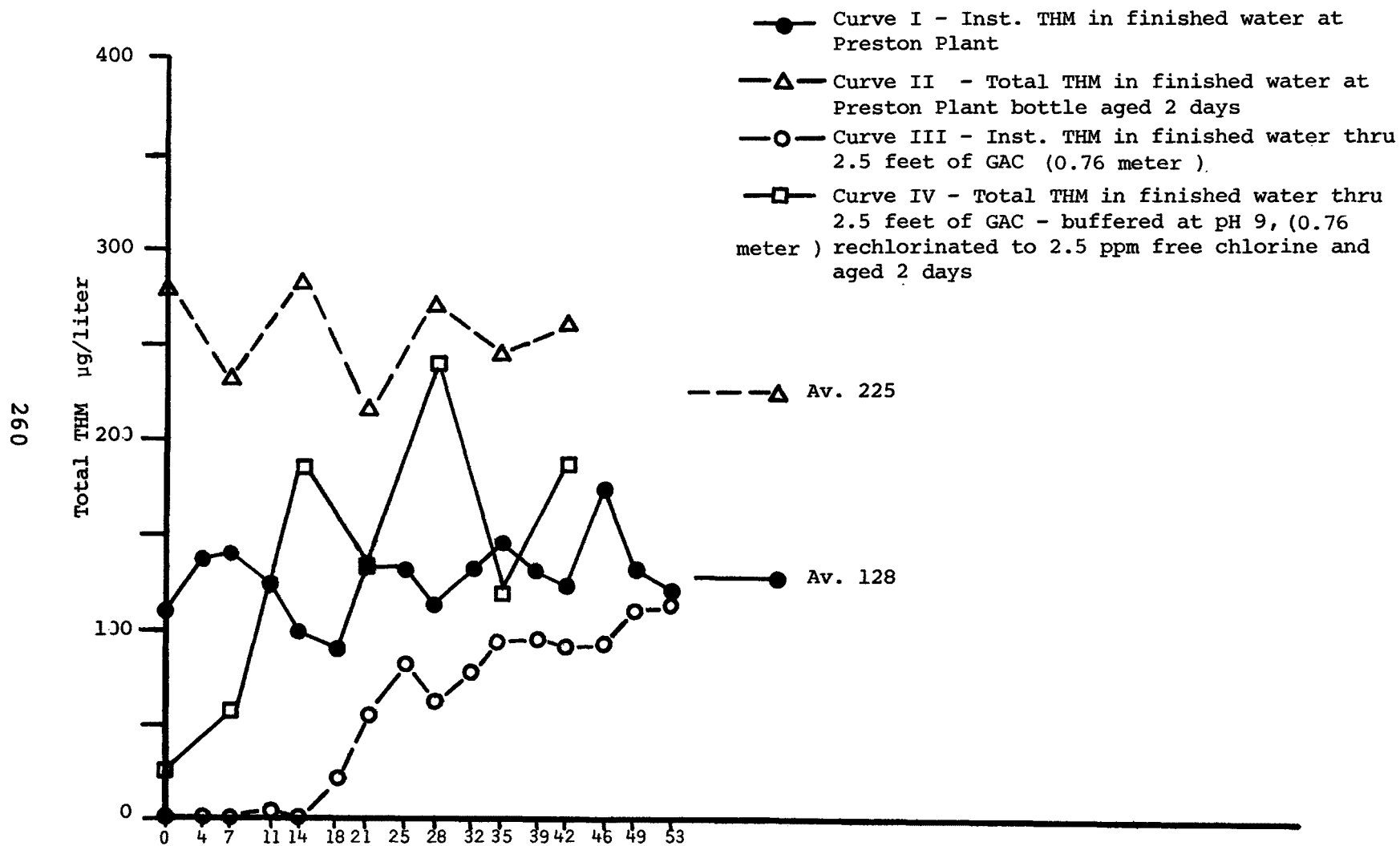


Figure 153. Total THM growth in rechlorinated - 2 day aged GAC column effluent (ED3).

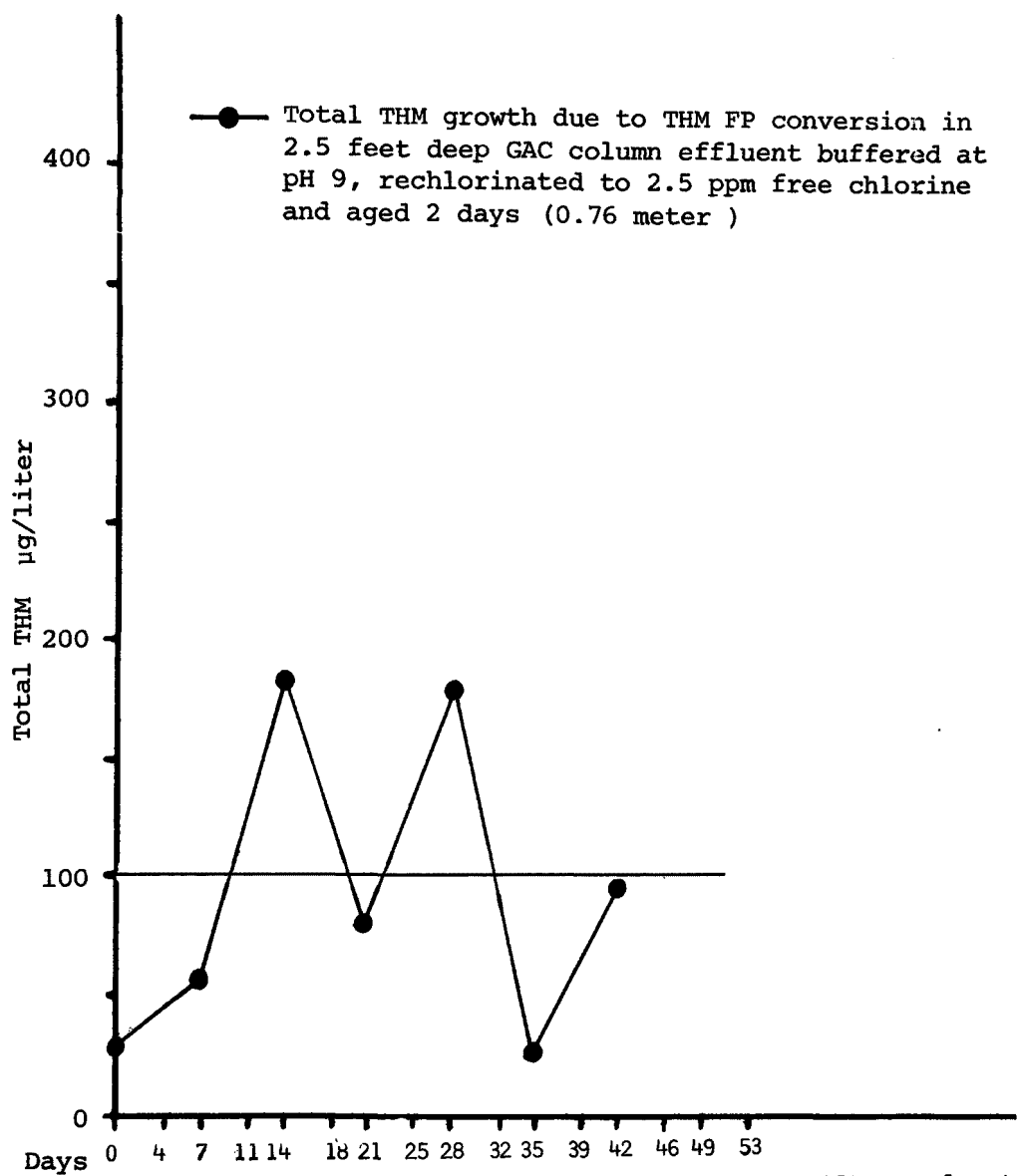


Figure 154. Total THM growth in GAC column effluent due to THM FP conversion (ED3).

inated and aged two days is shown. Curve IV represents the total THM present after two days aging. Unlike the similarly treated IRA-904 resin column effluent, Curve IV in Figure 151, the GAC curve indicates that for a period of time after initial column flow, the GAC removed sufficient THM FP precursors to keep the total THM below 100 $\mu\text{g/L}$. The curve shown in Figure 154 was obtained by subtracting Curve III from Curve IV in Figure 153. It represents the total THM growth in the GAC column effluent due only to THM FP conversion. It indicates that up to some point between 7 and 14 days, the GAC column removes sufficient THM FP precursor to keep the total THM growth below 100 $\mu\text{g/L}$. Of the three adsorbents tested, GAC, XE-340 and IRA-904 resin, GAC was the only adsorbent to show this characteristic. This was the basic reason for studying deeper GAC columns in ED4.

Bed Life Criteria in Deep GAC Columns

In ED4, the effluents from the 2.29 meters (7.5 feet) and 3.05 meters (10 feet) deep GAC columns were buffered to pH 9, rechlorinated to 2.5 ppm of free chlorine and aged two days to study total THM growth. The results should give some idea of the bed life one could expect from such columns. GAC exhaustion criteria at this point can be expressed in various ways. The EPA tentatively has proposed basing exhaustion time of GAC to assure maximum protection for the consumer (8).

In this report we are determining GAC exhaustion based only on the proposed MCL regulations that the total THM should not exceed 100 $\mu\text{g/L}$. As mentioned previously, finished water passing through a GAC column will have nil free chlorine. It would therefore have to be rechlorinated to approximately 2.5 ppm of free chlorine before it could enter the distribution system. Since precursors are still present, the addition of free chlorine would cause THM regrowth. We therefore define GAC exhaustion or bed life at the point where THM regrowth in a sample of GAC column effluent after rechlorination to 2.5 ppm of free chlorine and aging for two days, reaches the THM MCL level of 0.1 mg/L (100 ppb). The results obtained in ED4 on the 2.29 meters (7.5 feet) and 3.05 meters (10 feet) deep GAC columns are shown in Figure 155. Instantaneous THM level variations in Preston Plant finished water (carbon column influent) are shown in Curve I. The average value was 147 $\mu\text{g/L}$. When Preston Plant finished water was bottle aged two days, additional THM growth occurred and the Total THM present is shown by Curve II. The average was 243 $\mu\text{g/L}$, an increase of 1.7 times. Bottle aging and distribution system aging was compared in ED4. Samples were again taken at the Red Road sampling point in the distribution system. Total THM levels are represented by Curve III. The average value was 218 $\mu\text{g/L}$, an increase of 1.5 times. This demonstrates again that the laboratory bottle aging approximates Total THM growth in the distribution system.

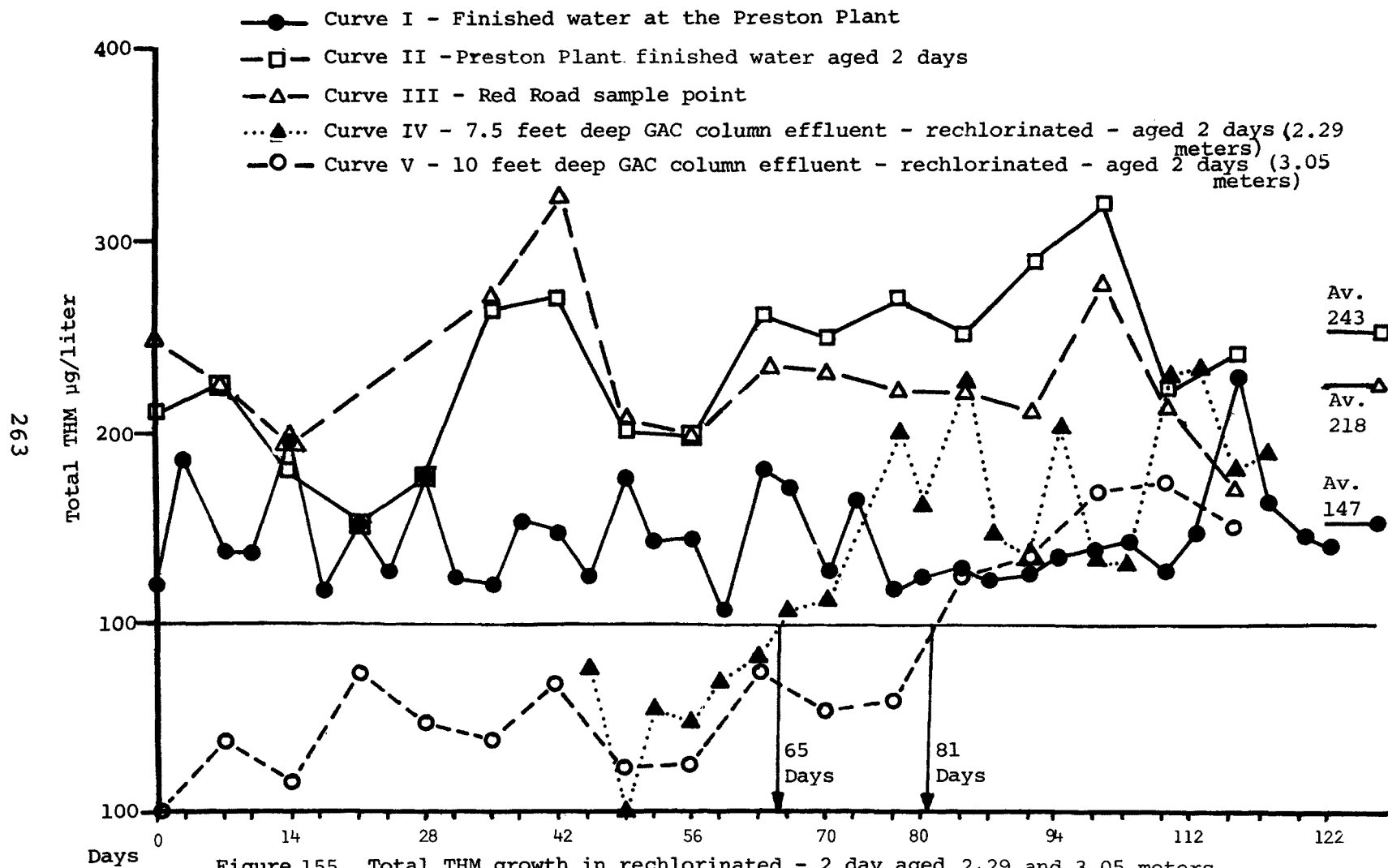


Figure 155. Total THM growth in rechlorinated - 2 day aged 2.29 and 3.05 meters (7.5 and 10 feet) GAC.

In Figure 155, data points prior to day 42 were not determined for the 2.29 meters (7.5 feet) deep GAC column. In Figure 155, GAC bed life (based on when the rechlorinated GAC effluent reaches 100 $\mu\text{g/L}$) is shown to be 65 days for 2.29 meters (7.5 feet) and 81 days for 3.05 meters (10 feet). The total THM in the two-day aged 2.29 meters (7.5 feet) and 3.05 meters (10 feet) deep GAC column effluents are the result of two conditions, 1) increasing amounts of inst. THM in the effluent due to column breakthrough and 2) increasing amounts of THM growth due to the THM FP breakthrough and conversion. Curve I in Figure 156, shown the total THM in the rechlorinated two-day aged 2.29 meters (7.5 feet) deep GAC column effluent and Curve II, is obtained by subtracting the inst. THM levels in the column effluent, breakthrough and indicates the contribution of total THM resulting from THM FP breakthrough and conversion. On test day 56, inst. THM began to breakthrough the column. It is seen that at day 65 when Curve I reached the 100 $\mu\text{g/L}$ level, approximately 63 percent of the THM was due to THM FP and 37 percent due to inst. THM breakthrough. From test day 65 to the end of the test period the average of the data points for Curve II is 93 $\mu\text{g/L}$, which is below the 100 $\mu\text{g/L}$ limit. It would appear that the 2.29 meters (7.5 feet) deep GAC column removes sufficient THM FP precursor to keep the average THM regrowth below 100 $\mu\text{g/L}$ at least up to the 115 day test period. Thus, one might attribute column failure at 65 days to inst. THM breakthrough, since if the THM did not break through, the column might last over 115 days. In Figure 158, it is apparent that THM breakthrough alone would cause bed life failure (reaching 100 $\mu\text{g/L}$) in 94 days.

Curve I in Figure 157, shows the total THM in the rechlorinated two-day aged 3.05 meters (10 feet) deep GAC column effluent. Curve II, obtained by subtracting the inst. THM levels in the column effluent, indicates the contribution of total THM resulting from THM FP breakthrough and conversion. On test day 70, inst. THM began to break through the column. It is seen that at day 81, when Curve I reached the 100 $\mu\text{g/L}$ level, only a very small amount of the total THM was due to THM breakthrough, approximately 8 percent. Thus one might attribute bed failure at 81 days to THM FP breakthrough. However, from test day 81 to the end of the test period the average of the data points for Curve II is 95 $\mu\text{g/L}$, which is below the 100 $\mu\text{g/L}$ limit. As with the 2.29 meters (7.5 feet) deep GAC column, it appears that the 3.05 meters (10 feet) deep column removes sufficient THM FP precursor to keep the average THM growth below 100 $\mu\text{g/L}$ at least up to the 115 day test period. Again, one might attribute column failure at 81 days and beyond for the 3.05 meters (10 feet) deep GAC bed to inst. THM breakthrough. In Figure 158, it is apparent that THM breakthrough alone would cause bed life failure in 119 days. GAC bed failure is thus caused by a combination of THM and THM FP breakthrough and the ratio of the two components at bed failure probably varies with bed depth and

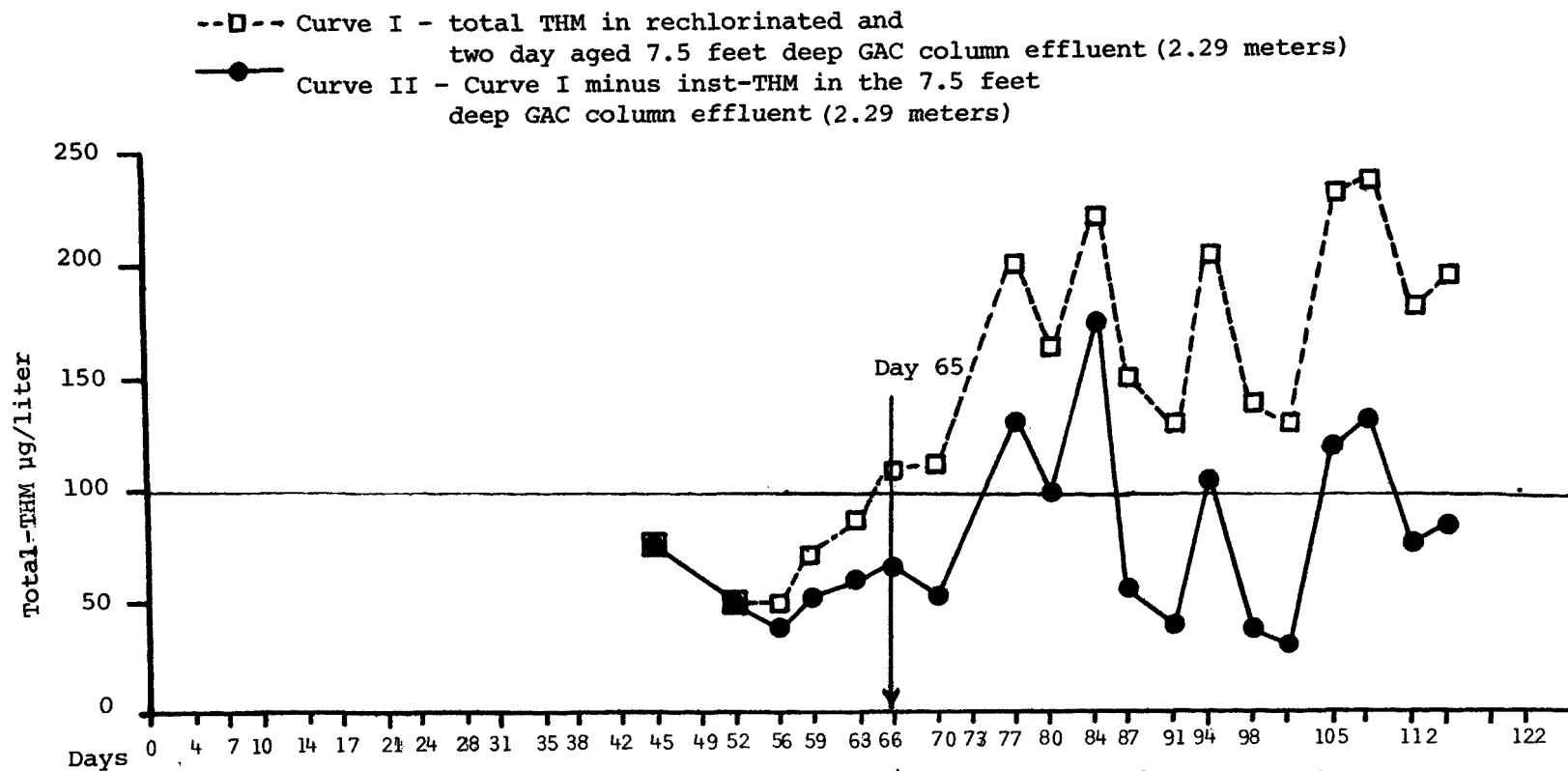


Figure 156. THM breakthrough and THM FP conversion components of Total-THM in two day aged effluent from 2.29 meters (7.5 feet) deep GAC column (ED4).

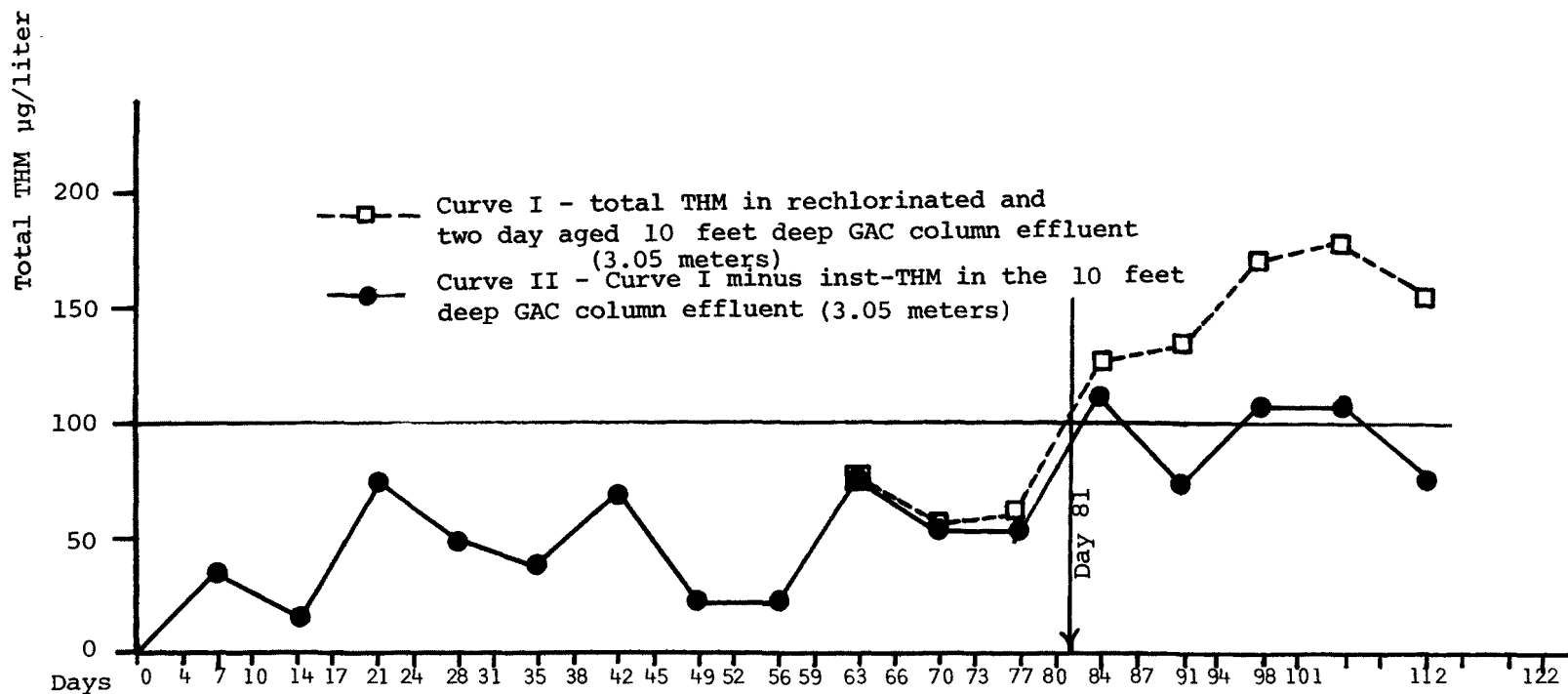


Figure 157. THM breakthrough and THM FP conversion components of total-THM in 2 day aged effluent from 3.05 meters (10 feet) deep GAC column (ED4).

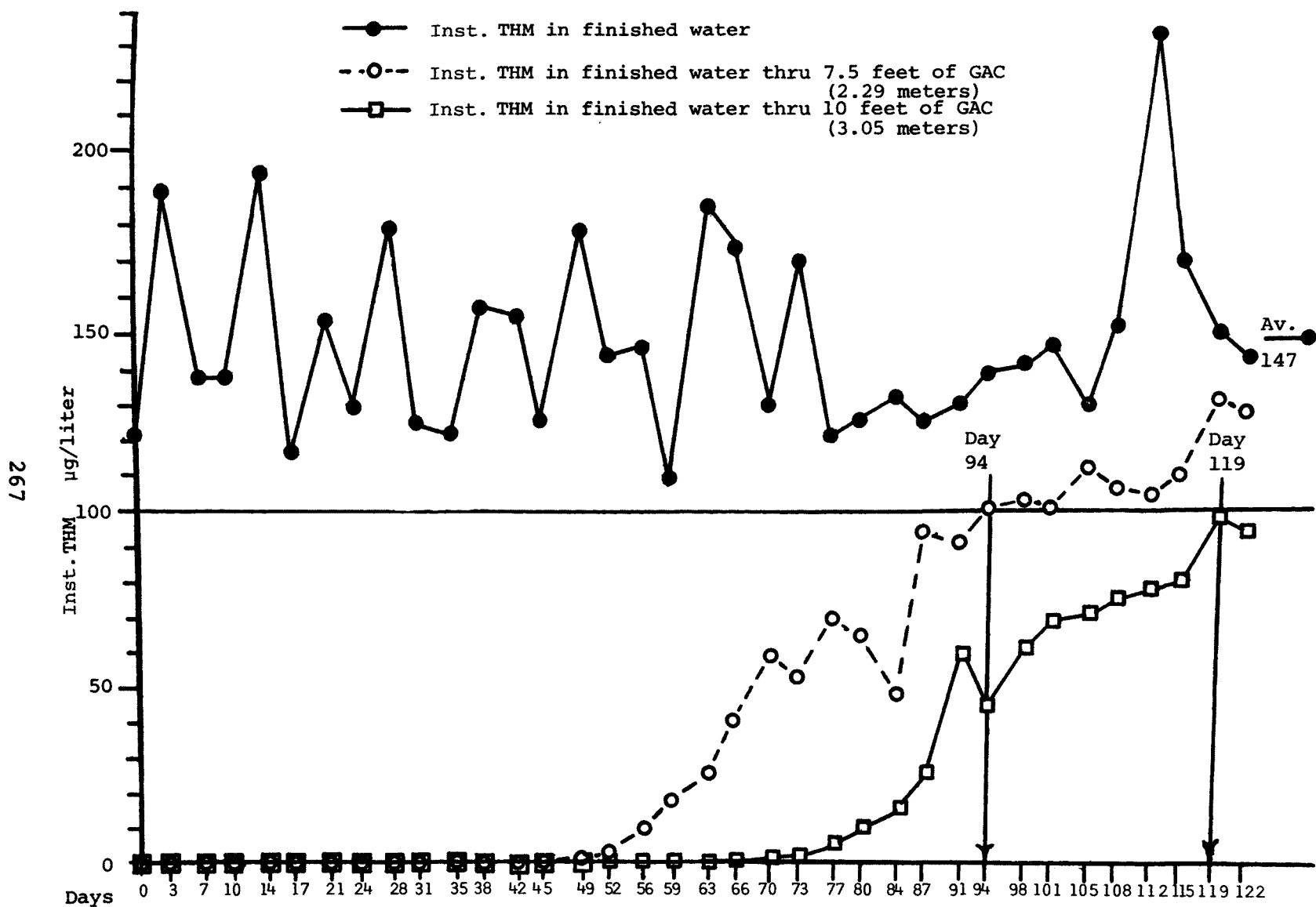


Figure 158. Inst. THM in finished water and finished water through 2.29 and 3.05 meters (7.5 and 10 feet) of GAC (ED4).

influent concentrations of both.

The curves in Figure 143, show that the first column, which received the highest concentration of adsorbate, adsorbed the greatest amount over the test period. Therefore, for greatest GAC efficiency, as much of the carbon in a bed as possible should at some time be exposed to the highest possible concentration of adsorbate. If 3.05 meters (10 feet) of bed is necessary, by using four beds 0.76 meter (2.5 feet) deep in series, and removing the first bed at saturation while placing a new bed at the end of the series, we expect 31 percent increased adsorptive capacity. This would increase the bed life from 81 days to 106 days. A continuous in-out bed would increase bed life by 43 percent to 116 days.

In Figure 155, it is apparent that if a MCL below 100 $\mu\text{g/L}$ were chosen, bed life would seriously be reduced. At 50 $\mu\text{g/L}$ and 25 $\mu\text{g/L}$, bed life for a 3.05 meters (10 feet) deep GAC bed would be approximately 18 days and 4 days respectively.

Relationship of TOC and THM FP Data

Determination of the THM FP of water is a new analytical method. When a new method is introduced the question of its relationship or correlation with an existing method or methods usually arises. In this case, the relationship to the determination of TOC arises. From our research work, we can divide a discussion on this subject into two parts, 1) relationship in the treatment plant and 2) relationship in GAC column effluents. TOC and THM FP data were simultaneously collected in ED1R, ED3 and ED4. TOC and THM FP data from Tables 10 and 11 are plotted in Figure 159. ED1R data points for raw, H.T. and finished water are connected by line segments A-B and B-C. As one might expect, the slope of these two segments are different. A-B is the result of adsorption on precipitated calcium carbonate, and B-C is the result of conversion by chlorination, oxidation and sand filtration. The two segments in ED3, A'-B' and B'-C', are quite similar to those in ED1R. The length of the segments differ in proportion to the percent removal data in Tables 14 and 15. If only these two sets of data were available, ED1R and ED3, one might conclude that correlation between TOC and THM FP results are quite close. However, the ED4 data points show a considerable shift to the right. The two segments, in ED4, A"-B" and B"-C", are relatively parallel to the segments in ED1R and ED3. If an unknown point "X" were chosen within the triangle formed by the three raw water data points and parallels were drawn to all segments in the three ED, the shaded area represents the predicted zone of results from data point "X". While there may be some degree of confidence in this prediction, the value of it is unknown. If point "X" were chosen outside the triangle, the degree of confidence might be less. In our treatment plant data, one could say that there is

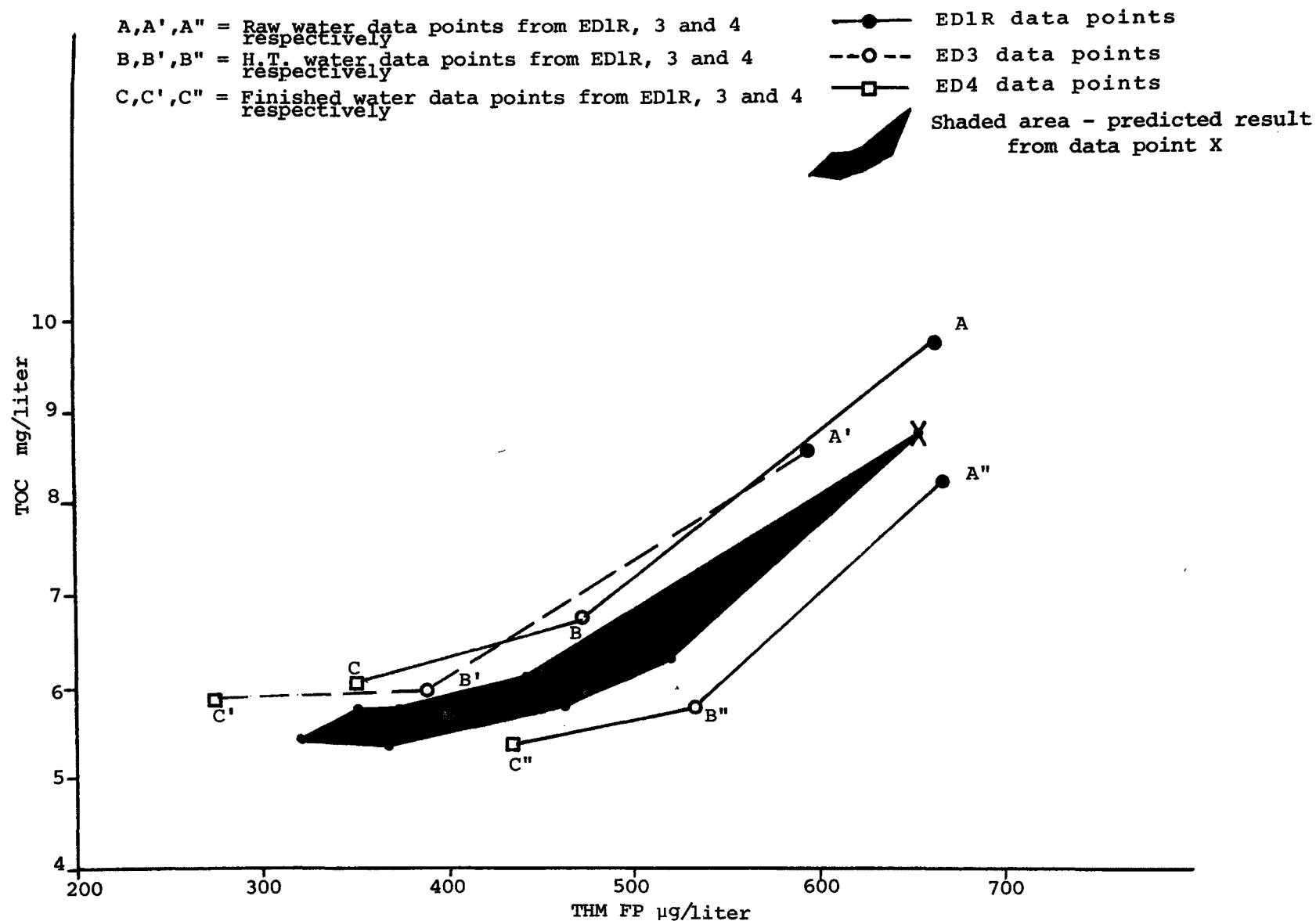


Figure 159. Relationship of TOC and THM FP data in raw, H.T. and finished water.

a relationship between TOC and THM FP data, but one cannot be converted into the other by a single or simple conversion factor.

TOC and THM FP data from the 3.05 meters (10 feet) GAC effluent in ED4 are plotted in Figure 160. The average level of TOC for the first 14 days was 0.37 mg/L. The average THM FP for this same period was 17 µg/L. From day 14 to day 49, both curves show a steady rise. The THM FP curve has a steeper slope. From day 49 to the end of the test period, when the plateau portion of both curves was attained, the TOC level averaged 3.0 mg/L and the THM FP level averaged 240 µg/L. The TOC concentration increased 8.1 fold, from 0.37 to 3.0 mg/L. The THM FP concentration increased 14.1 fold from 17 µg/L to 240 µg/L. There is a relationship in the segments of the two curves, but, again, no single or simple conversion factor for converting one to the other. As GAC bed depth changes, a segment relationship exists, but is different for each bed depth.

We can probably conclude that while there is some degree of predictable relationship between TOC and THM FP data in both our treatment plant and a separate degree of predictable relationship in our GAC effluent waters, both tests yield separate and valuable information which are not convertible one into the other by a single or simple conversion factor. It is unlikely that this situation will change as more data are collected, especially when different geographical relationships are considered.

Leaching Study on XE-340 Resin Column

The experimental design of the leaching study on a 0.76 meter (2.5 feet) deep XE-340 column is discussed under ED2. In ED2, a fresh XE-340 column was installed, preceding the partially exhausted XE-340 column on the finished water line of ED1R, to supply halogenated organic free water for the leaching study on the partially exhausted column. In this discussion we will first present data on chlorodibromomethane. The level of chlorodibromomethane entering and leaving the leaching study column in the 63-day test period is plotted in Figure 161. A weakness in the experimental design is apparent. The lower curve indicates the chlorodibromomethane in the fresh XE-340 column effluent and entering the leaching study column. Ideally, to obtain a mass balance of leached substances, we should have replaced the fresh XE-340 column with a new fresh XE-340 column before breakthrough of HOC occurred. Actually, it also would have been better to use a deeper XE-340 column, because as seen on the chloroform data to follow, the MT_z for chloroform is greater than 0.76 meter (2.5 feet). Nevertheless, despite the breakthrough of chlorodibromomethane we can still draw some conclusion on leaching from Figure 161. If we consider the data up to test day 53, the level of chlorodibromomethane entering

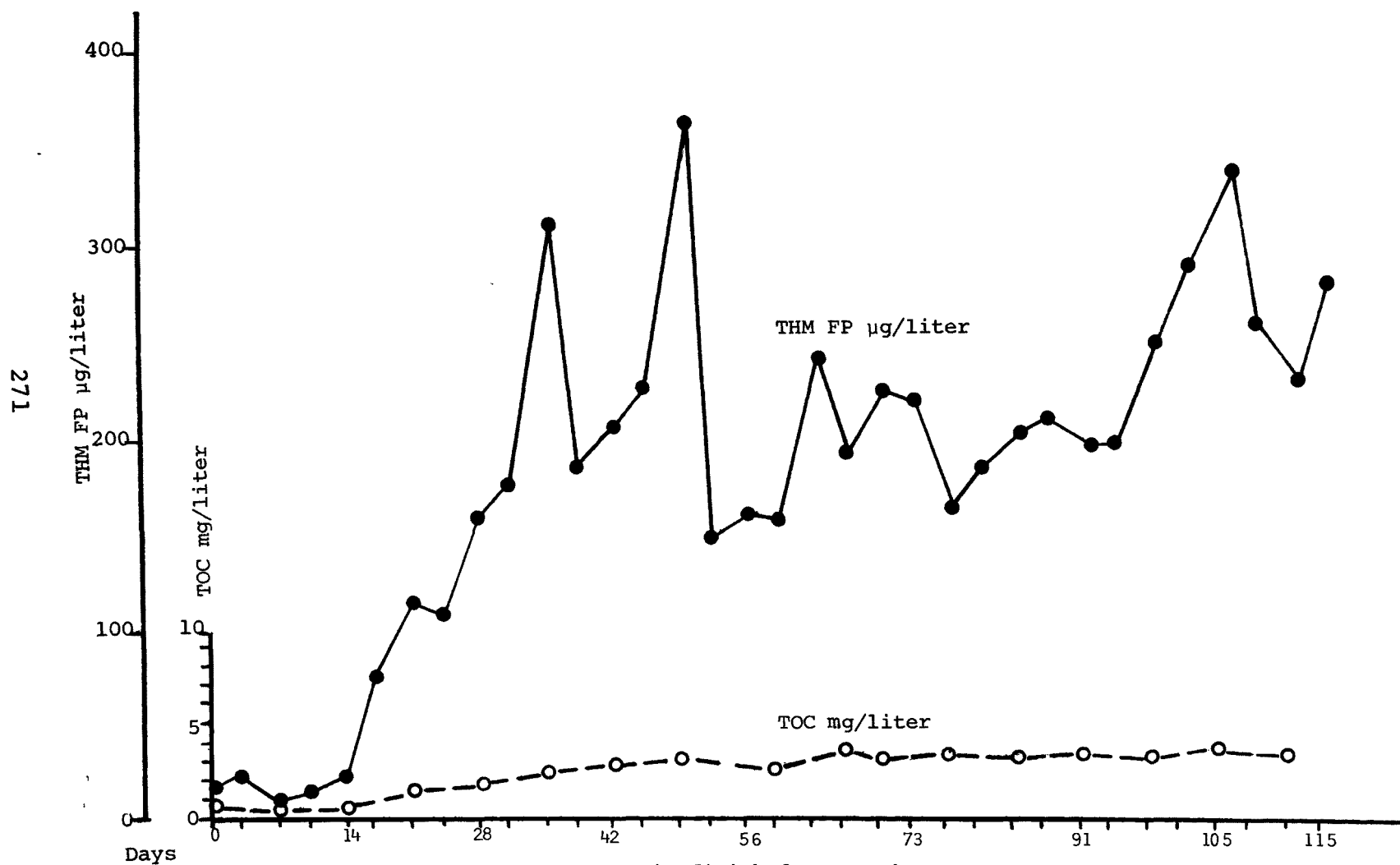


Figure 160. TOC and THM FP in finished water thru 3.05 meters (10 feet) of GAC (ED4).

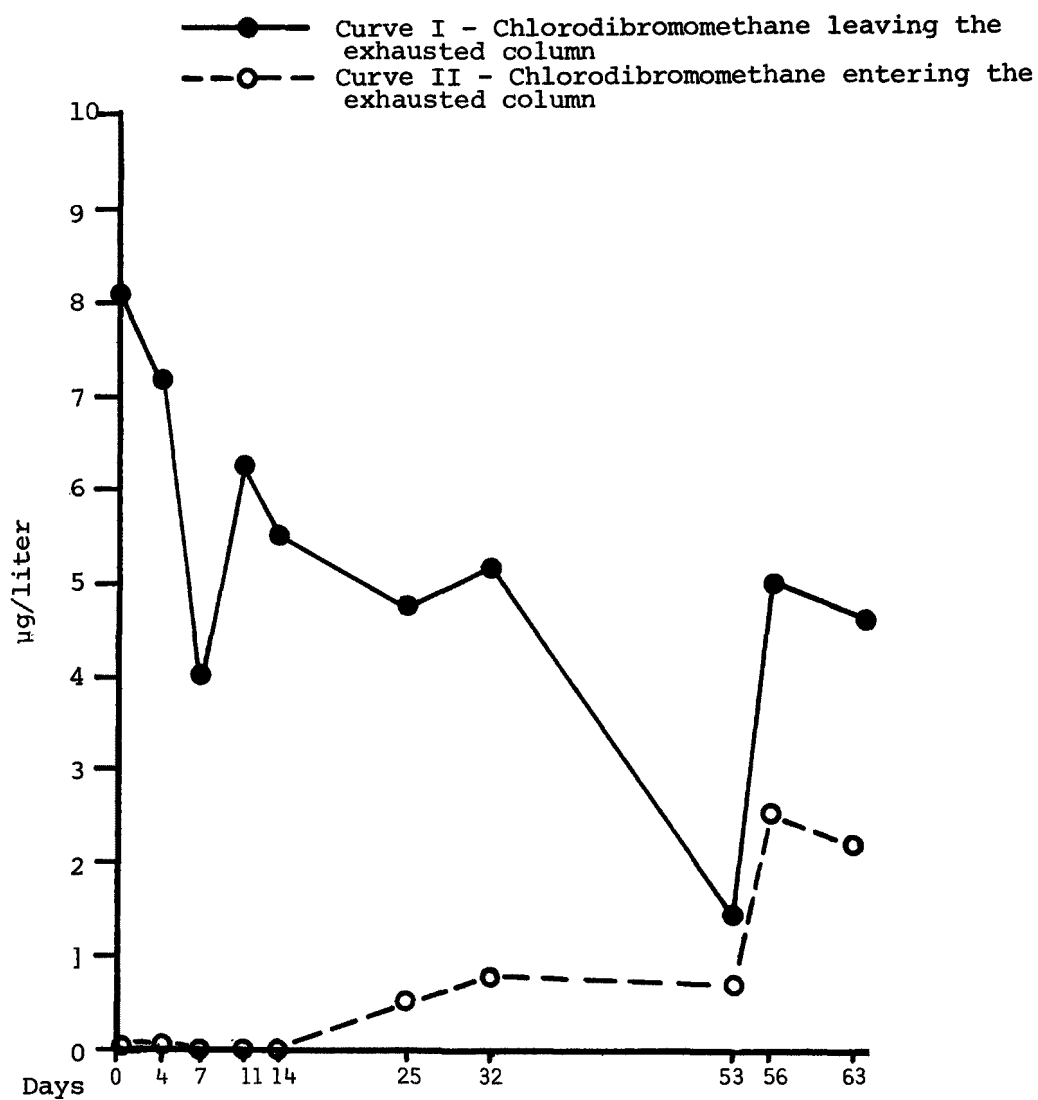


Figure 161. Level of chlorodibromomethane entering and leaving the partially exhausted 0.76 meter (2.5 feet) deep XE-340 column (ED2).

the leaching study column for most of the period was below 1 $\mu\text{g/L}$. Of this 53 day period, the data point at day 53 on Curve I is in greatest error. It would not be scientifically correct merely to subtract Curve II from Curve I to obtain the true leaching curve without the interference of entering chlorodibromomethane. We can at this point only be aware that the test point on Curve I at test day 53 is considerably lower than plotted. Curve I is replotted in Figure 162, with the full chlorodibromomethane adsorption curve indicating the level of breakthrough leaving the XE-340 column at the end of the ED1R study. In Figure 162, it is seen that the breakthrough level of the column on test day 122 of ED1R and the leaching from the column on test day 0 in ED2 are approximately equal at about 8 $\mu\text{g/L}$. As the leaching study continued (Curve II) it is apparent that the leaching curve is just the reverse of the adsorption curve (Curve I).

The level of bromodichloromethane entering and leaving the leaching study column is plotted in Figure 163. Leaching data points to test day 32 are plotted in Figure 164. Again, it is apparent that the breakthrough level of the column on test day 122 of ED1R is approximately equal to the leaching level on test day 0 of ED2 (20 $\mu\text{g/L}$). Again, the leaching curve appears to be the reverse of the adsorption curve. Similar results are shown for chloroform in Figures 165 and 166 and for cis 1,2-dichloroethane in Figures 167 and 168. It is not surprising to find that on XE-340, desorption of the four HOC discussed above appears to be the reverse curve of adsorption. It is well known that adsorption and desorption on GAC follows this pattern with some substances while other substances may exhibit some hysteresis on desorption.

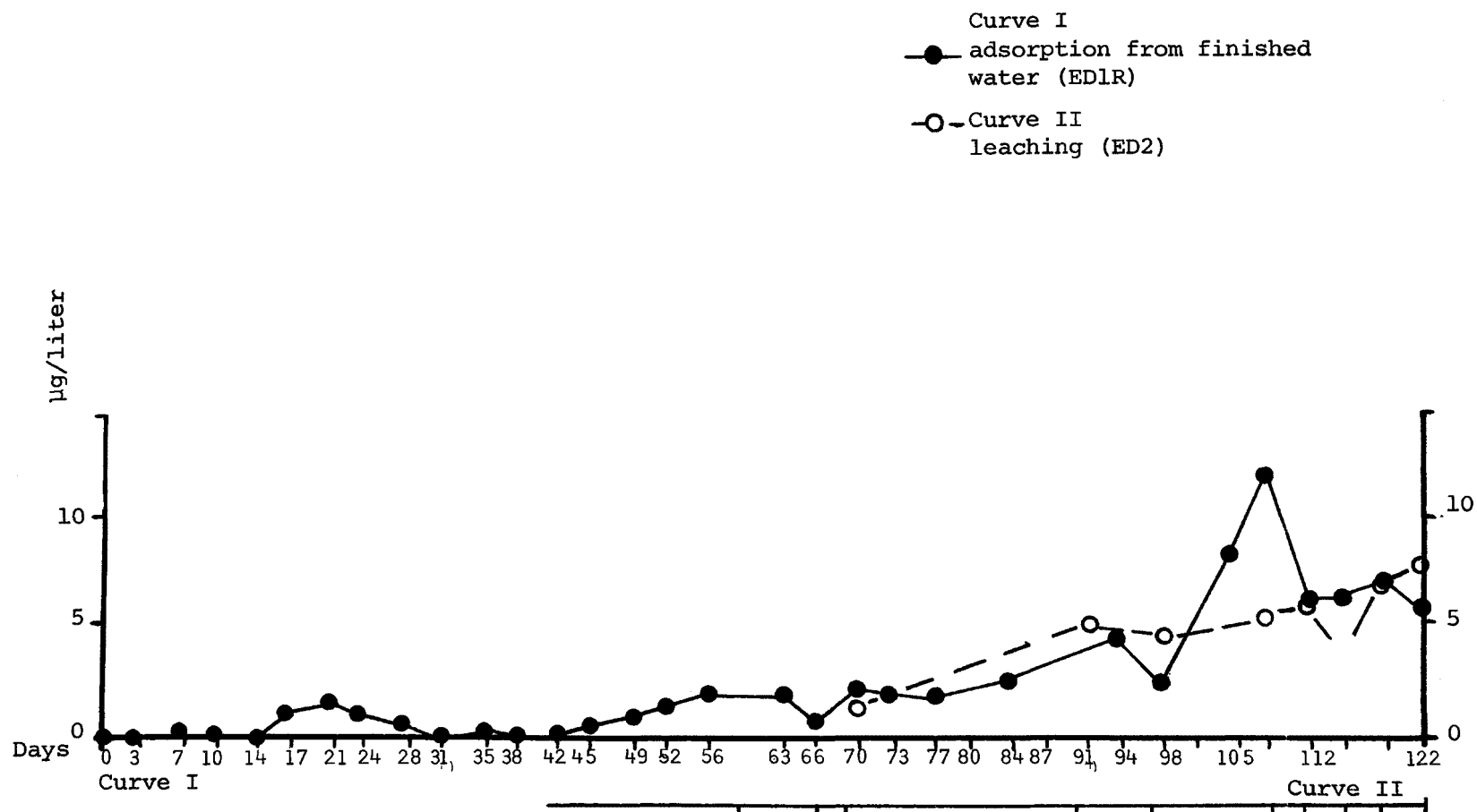


Figure 162. Adsorption and leaching of chlorodibromomethane on a 0.76 meter (2.5 feet) deep XE-340 column (ED1R and ED2).

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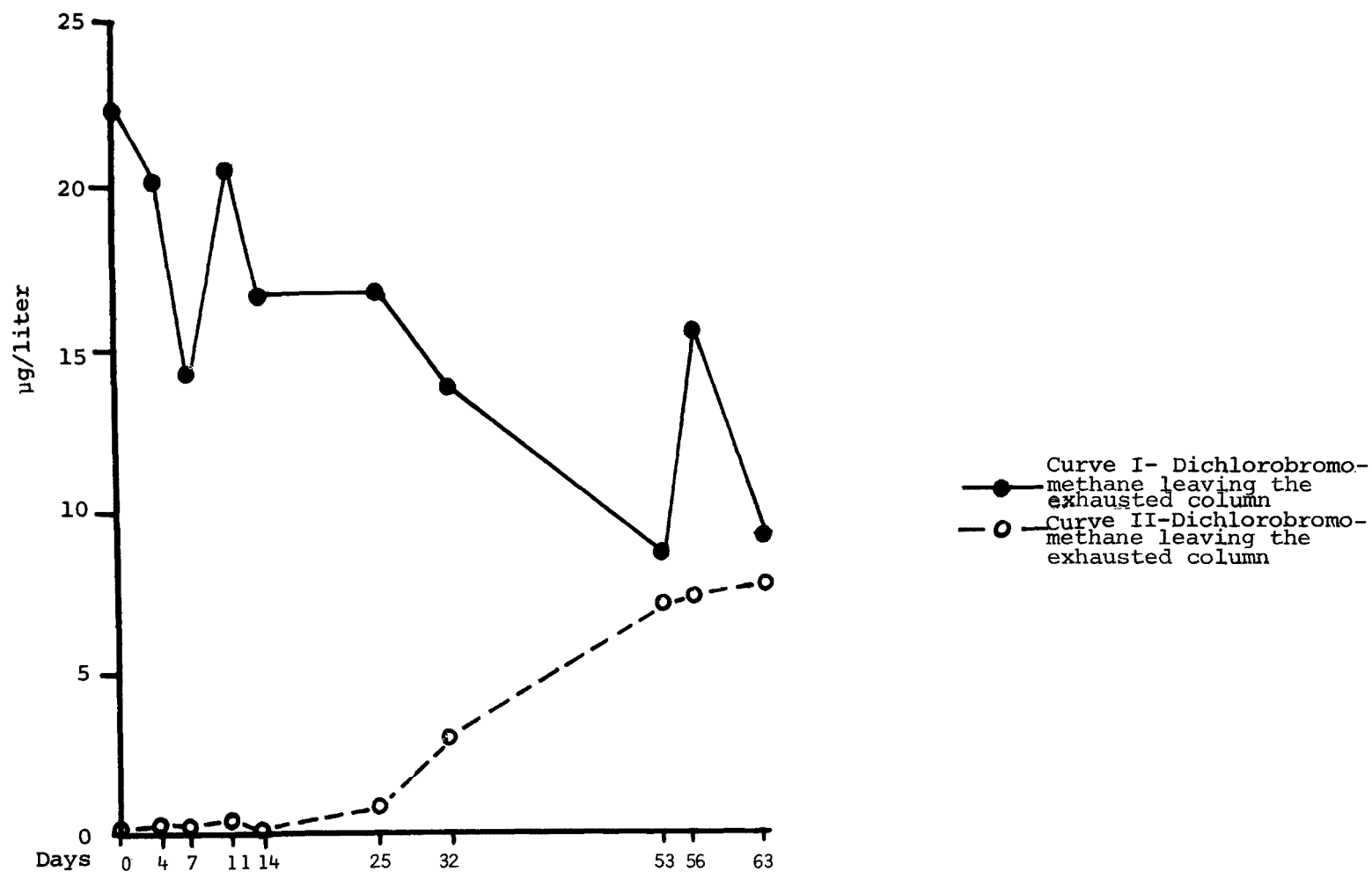


Figure 163. Level of Bromodichloromethane entering and leaving the partially exhausted 0.76 meter (2.5 feet) deep XE-340 column (ED2).

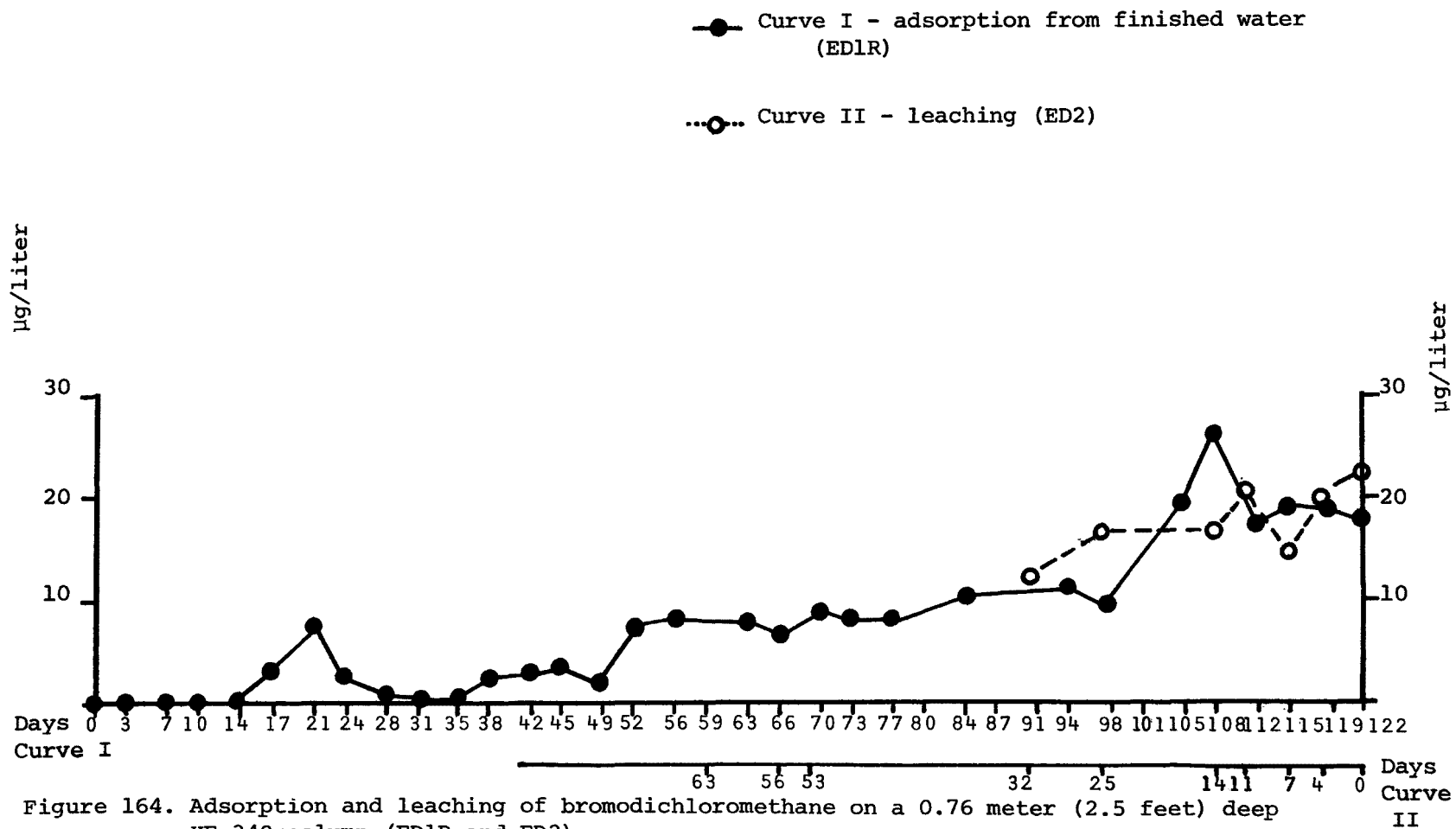


Figure 164. Adsorption and leaching of bromodichloromethane on a 0.76 meter (2.5 feet) deep XE-340 column (ED1R and ED2).

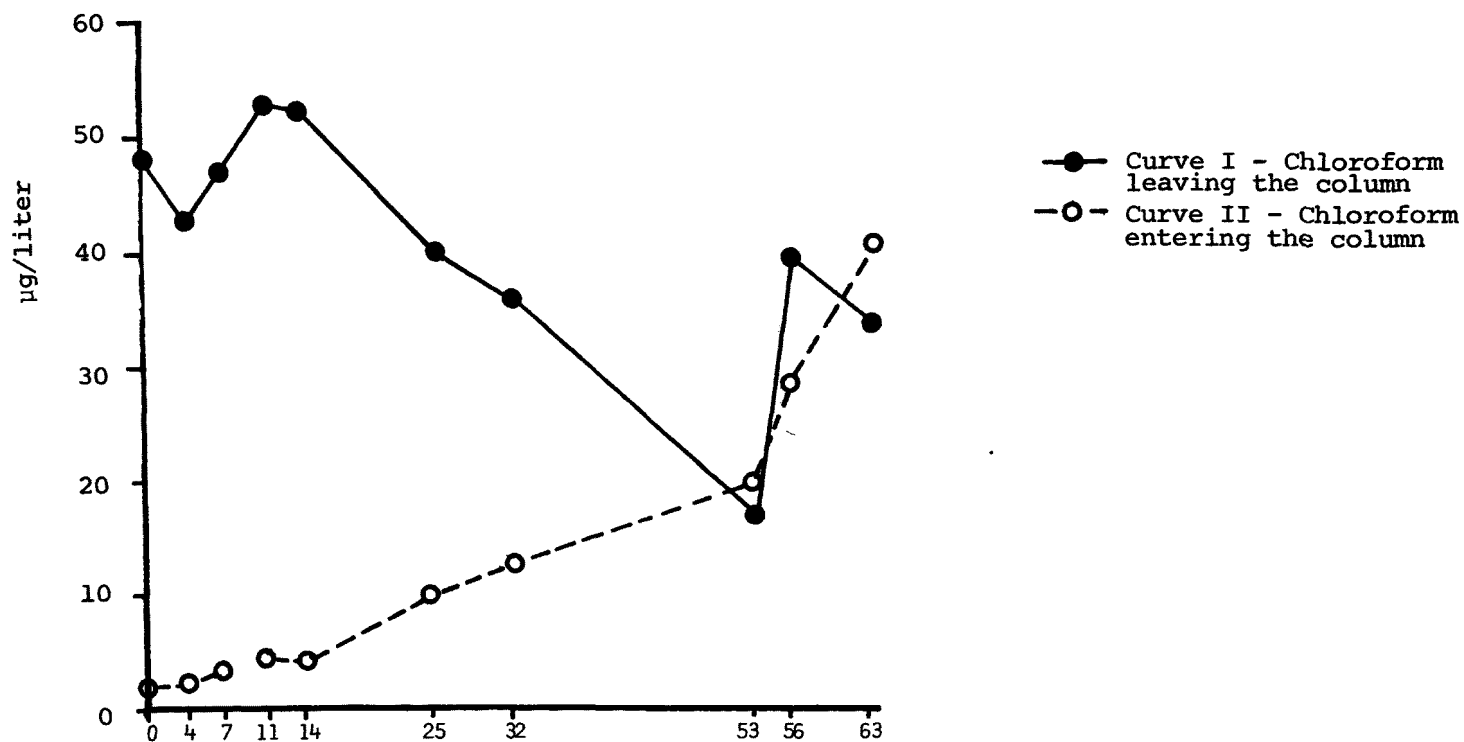


Figure 165. Level of chloroform entering and leaving the partially exhausted 0.76 meter (2.5 feet) deep XE-340 column (ED2).

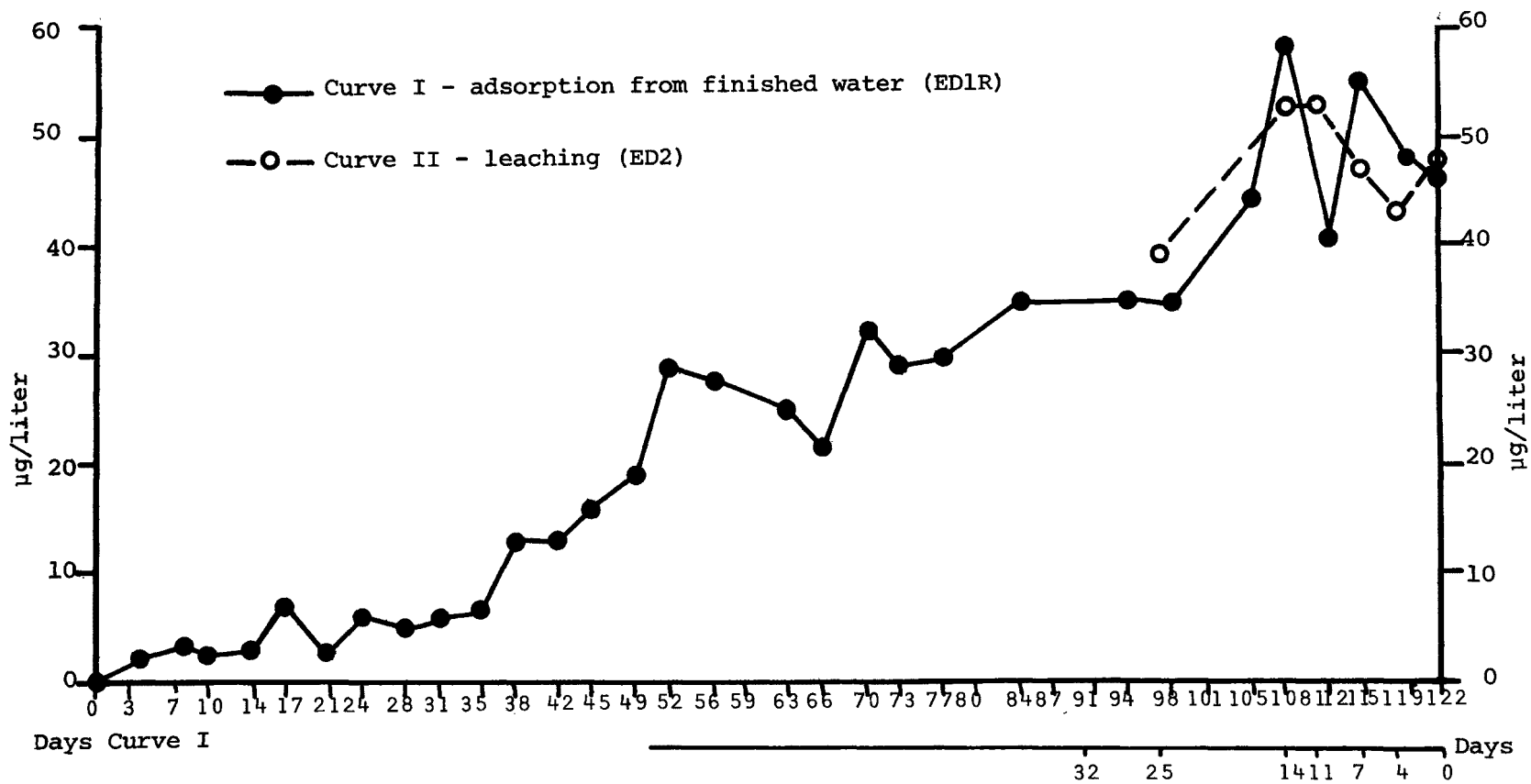


Figure 166. Adsorption and leaching of chloroform on a 0.76 meter (2.5 feet) deep XE-340 column (ED1R and ED2).

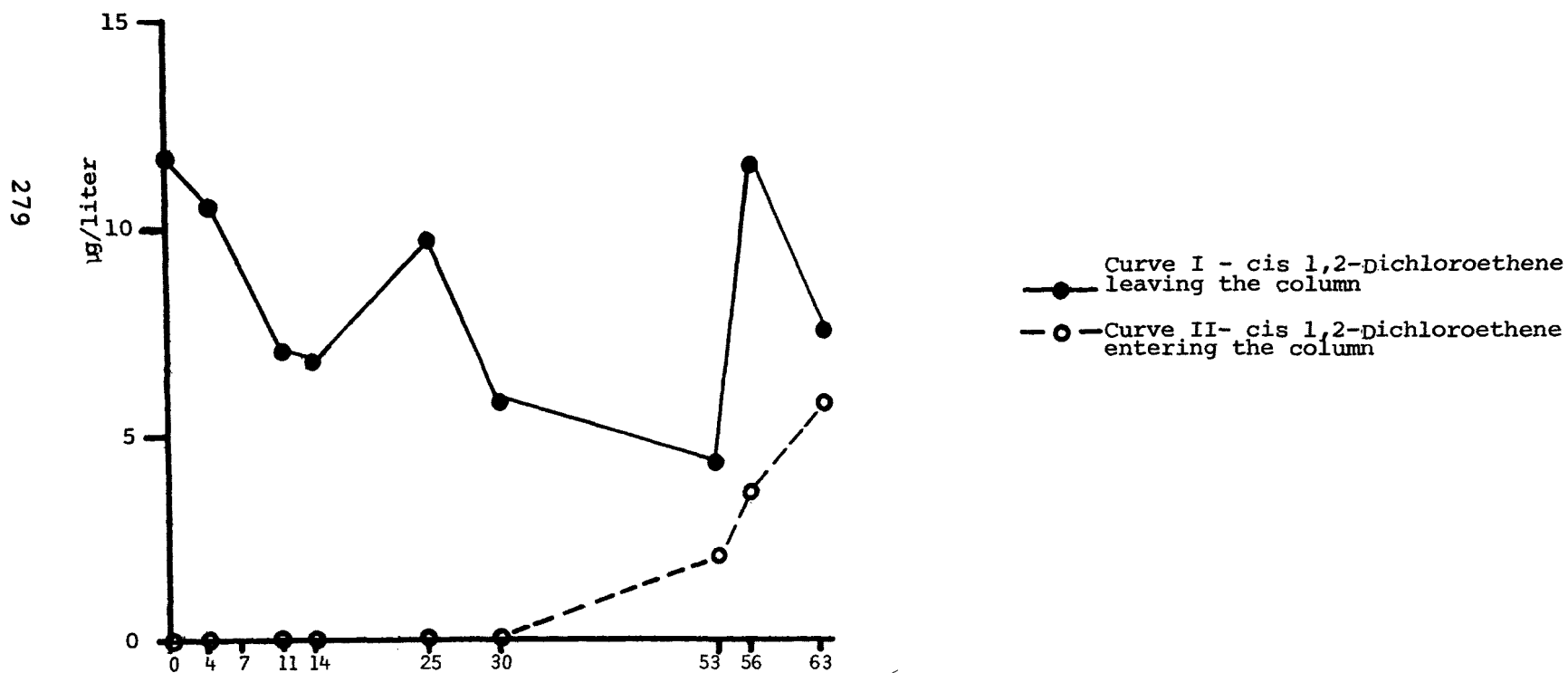


Figure 167. Level of cis 1,2-Dichloroethene entering and leaving the partially exhausted 0.76 meter (2.5 feet) deep XE-340 column (ED2).

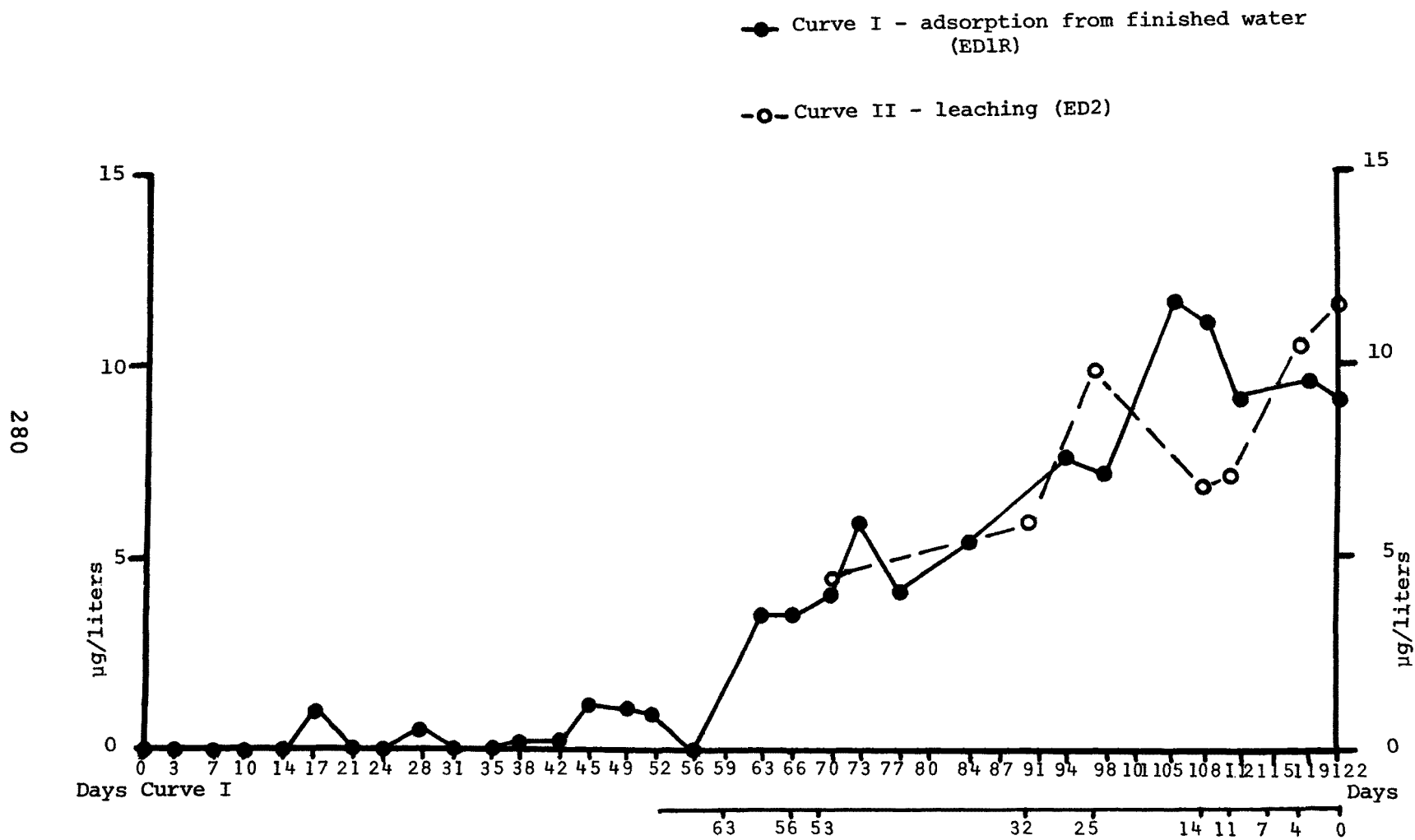


Figure 168. Adsorption and leaching of cis 1,2-dichloroethene on a 0.76 meter (2.5 feet) deep XE-340 column (ED1R and ED2).

Biological Activated Carbon (BAC)

An aquatic microbiology laboratory has been established in the Drinking Water Quality Research Center at Florida International University. At the beginning of ED4, Dr. Frances Parsons began a bacteria profile study of raw and finished water at the Preston Plant and the effluent from each of the four GAC columns. Samples of water from the distribution system were also analyzed. This work was contributed to this project by Florida International University to demonstrate their capability and interest in this area. Two reports by Dr. Parsons are available in Appendix A. It is obvious from this work that we had a BAC system. Since no additional oxygen was added to the water, we call it a partial BAC system to differentiate it from the oxygenated European system. We do not know how our adsorption results would differ if the bacterial growth had not developed. Despite massive bacterial growth that hindered and finally prevented backwashing of the columns, the adsorptive capacity of the GAC for HOC did not seem to be affected. The initial breakthrough and saturation times for each HOC through each column were too consistent to suggest blocking of active sites or the pore openings in the carbon by the bacteria.

The two reports in Appendix A indicate the inadequacy of the standard plate count method in bacterial analysis of drinking water. It stresses the need for longer incubation times at various temperatures and with different media for specific species as first indicated by Van Der Kooij (9).

Conclusion and tentative recommendations from the two reports by Dr. Frances Parsons are as follows:

Report I:

Bacteria that occur in small numbers in raw water survive treatment and colonize granular activated carbon (GAC) columns used to remove organic solutes from treated water. The bacteria multiply, form slime that interferes with column maintenance by preventing backwashing, and slough off in large numbers into the water passing through the columns.

Based on influent and effluent sampling, the size and composition of the microbial populations in GAC columns appear to change with time. The composition of the microbial population of the raw water apparently influenced the population in the columns. Each column had a somewhat different population composition and size on each sample date.

Some of the organisms that multiply in the GAC columns may pose a health hazard because of the vast numbers present if the column effluent is ingested or comes in contact with susceptible body surfaces such as the otic canal or the naso-pharyngeal

mucosa. The possibility of a consumer incurring enteritis, intoxication, and/or an opportunistic infection should be studied. Because of the large numbers of Gram-negative organisms that colonize GAC columns, endotoxin should be assayed using the LAL method. Staphylococci sp. sometimes present in finished water should be tested for coagulase.

The large numbers of noncoliform bacteria found in column effluents will suppress coliform growth and interfere with interpretation of the standard coliform detection test.

Effects of rechlorination of column effluents on the subsequent bacterial population of this water over a period of time is being studied. Preliminary results indicate that entering organisms that survive treatment plant processes become a major component of the microbial population in GAC columns. A count of 300/100 mL of sample of Enterobacter agglomerans was obtained in a GAC column effluent sample two days after rechlorination to 3 ppm. Two colonies of Enterobacter agglomerans per 100 mL of sample were isolated from a sample of effluent that was chlorinated to 10 ppm and held at 25°C for six days. These results suggest that small numbers of bacteria can survive chlorination probably inside of cell aggregates.

Report II:

Chlorination of the effluent from granular activated carbon (GAC) columns apparently kills bacteria that grow on the carbon granules and slough off into the effluent, but the initial dose of chlorine must be adequate to combine with the bacteria and leave sufficient free chlorine to prevent regrowth. The concentration of chlorine necessary would vary with the bacterial biomass and chlorine demand due to all constituents of the water.

This study was of a cursory nature and was only intended to suggest a more complete study. Shorter sampling intervals (daily), for a period of time longer than six days (end point determination), with more than these two concentrations (especially less than 3 ppm free chlorine) of several disinfectants (chlorine, chloramines, chlorine dioxide, ozone, ferrates) should be examined. Certainly, the minimum level of chlorine needed and the time that it is effective for several bacterial population sizes should be determined. All of these factors; i.e., dose size, contact time, regrowth rate and size and composition of the bacterial population should be studied and compared with parallel determination of the bacteriology of the distribution system.

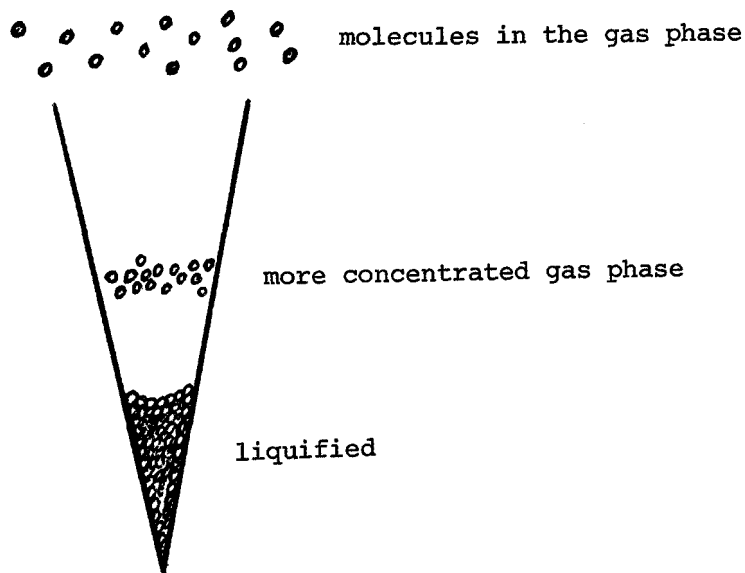
Polanyi-Manes Adsorption Theory

Theory Development--

Theories of adsorption from solution were developed by Polanyi. (10) They were modified by Hansen and Fackler. (11) Manes and Hofer (12) made modifications for predicting relative adsorption potentials from the refractive index of a substance. With these modifications one can estimate the adsorptive capacity at saturation of a variety of miscible organic liquids by activated carbon over a wide concentration range.

Deviations from the Polanyi Theory and its modifications are ascribable to specific chemical interactions or steric effects. Work on adsorption of miscible liquids from water has been done by Wohleber and Manes. (13,14) Their work has been expanded by Chiou and Manes (15) to include solids from solution. Adsorption of Binary Organic Liquids was studied by Schenz and Manes. (16) The most recent work on competitive adsorption was reported by Rosene and Manes. (17,18,19,20)

Application of the theory usually starts with adsorption in the gas phase. The mechanisms involved are illustrated in the following drawing of a micro pore in a carbon particle.



Two molecules in the gas phase are attracted by Van der Waals forces. The distance between two molecules is "r" and the attracting force decreases by $\frac{1}{r^6}$. As the molecules enter the pore they become more concentrated, and when "r" becomes small enough they will condense into a liquid. Molecules of both gas and liquid are held to the carbon surface molecules by Van der Waals forces.

There are two parts to the driving force responsible for a substance going from the gas to the liquid phase. One is the energy part of the attractive force. It is related to the polarizability. The other part of the driving force is entropy, which is related to solubility. The less soluble a substance is, the easier it is to bring to saturation (condensation). The driving force is expressed as ϵ .

$$\epsilon = RT \ln \frac{P_s}{P}$$

R = ideal gas constant 1.987 cal/deg/mole

T = absolute temperature

P_s = saturated pressure

P = equilibrium pressure

The polarizability of a substance is p^s

$$p^s = \frac{n_i^2 - 1}{n_i^2 + 2}$$

where n_i = refractive index.

The refractive index for all hydrocarbons is about the same, therefore p_b , where b stands for butane, equals 0.236. To determine the adsorption isotherm curve for heptane adsorbed on a particular GAC (gas phase), the volume of heptane adsorbed (cc per 100 gm of GAC) is measured at various concentrations of heptane in the gas phase. This is usually plotted with concentration expressed as $\frac{\epsilon}{4.6V}$ on the horizontal axis.

The natural log is converted to base 10 log by:

$$\ln X = 2.3 \log X$$

$$\epsilon = 1.987 T 2.3 \log \frac{P_s}{P} = 4.6 T \log \frac{P_s}{P}$$

$$\text{molar volume} = V \frac{\text{molecular weight}}{\text{density}}$$

divide both sides of equation by V

divide both sides of equation by 4.6

$$\frac{\epsilon}{4.6V} = \frac{T}{V} \log \frac{p_s}{p}$$

The adsorption isotherm (gas phase) for butane on GAC Filtrasorb 400 is shown in Figure 169. On the horizontal axis, "O" is adsorption on GAC from pure butane in the gas phase. The higher numbers on the axis represent lower concentrations of butane (usually in nitrogen gas). The seven data points making up the Butane Gas Phase curve in Figure 169 (and the four data points for the Butane Gas Phase on XE-340 in Figure 170) were supplied by Rosene at the Calgon Corporation. His data extended to the 0.1 cc range on the "Y" axis. Later he indicated that subsequent work on GAC resulted in data points falling on a tangential straight line extension of the curve below 0.1 cc. This extension is drawn in Figure 169 as a dash line segment. Later in this discussion we will extend this straight line still further for both GAC and XE-340 to get some idea of the behavior of very low concentrations.

To determine how another gas substance, other than hydrocarbon, will adsorb on the same GAC (if it is a substance that follows the modified Polanyi Theory), one can calculate a theoretical adsorption isotherm using a scale factor γ_s , based on the ratio of the polarizability of a given substance p_s^s to the polarizability of butane (p^b).

$$\gamma_s = \frac{p_s^s}{p^b}$$

The theoretical curve is obtained by multiplying any point on the butane curve by γ_s .

Using the Polanyi Theory modifications of Hansen and Fackler, as well as the modifications of Manes and Hofer, one can calculate a theoretical adsorption isotherm curve for a substance from a solution, in our case water, by the following:

$$\frac{\epsilon}{4.6V} = \frac{T}{V} \log \frac{C_s}{C}$$

where C_s = solubility of the substance in water (gm/100cc water).

C = concentration of the substance in the influent water.

The scale factor for a liquid substance (s) adsorbed from another liquid (in our case from water) is γ_{s1} .

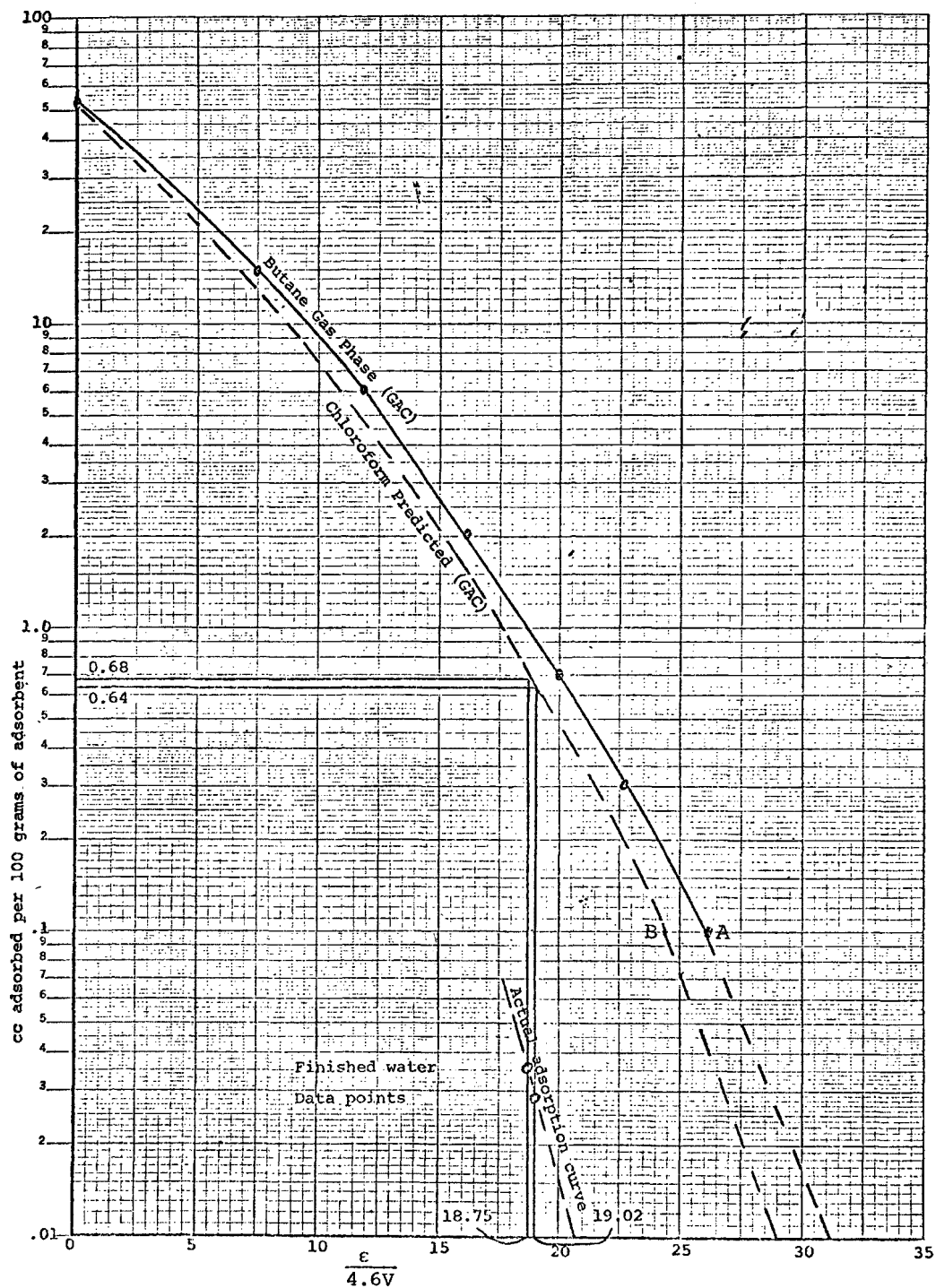


Figure 169. Chloroform adsorption by 0.76 meter (2.5 feet) of GAC.

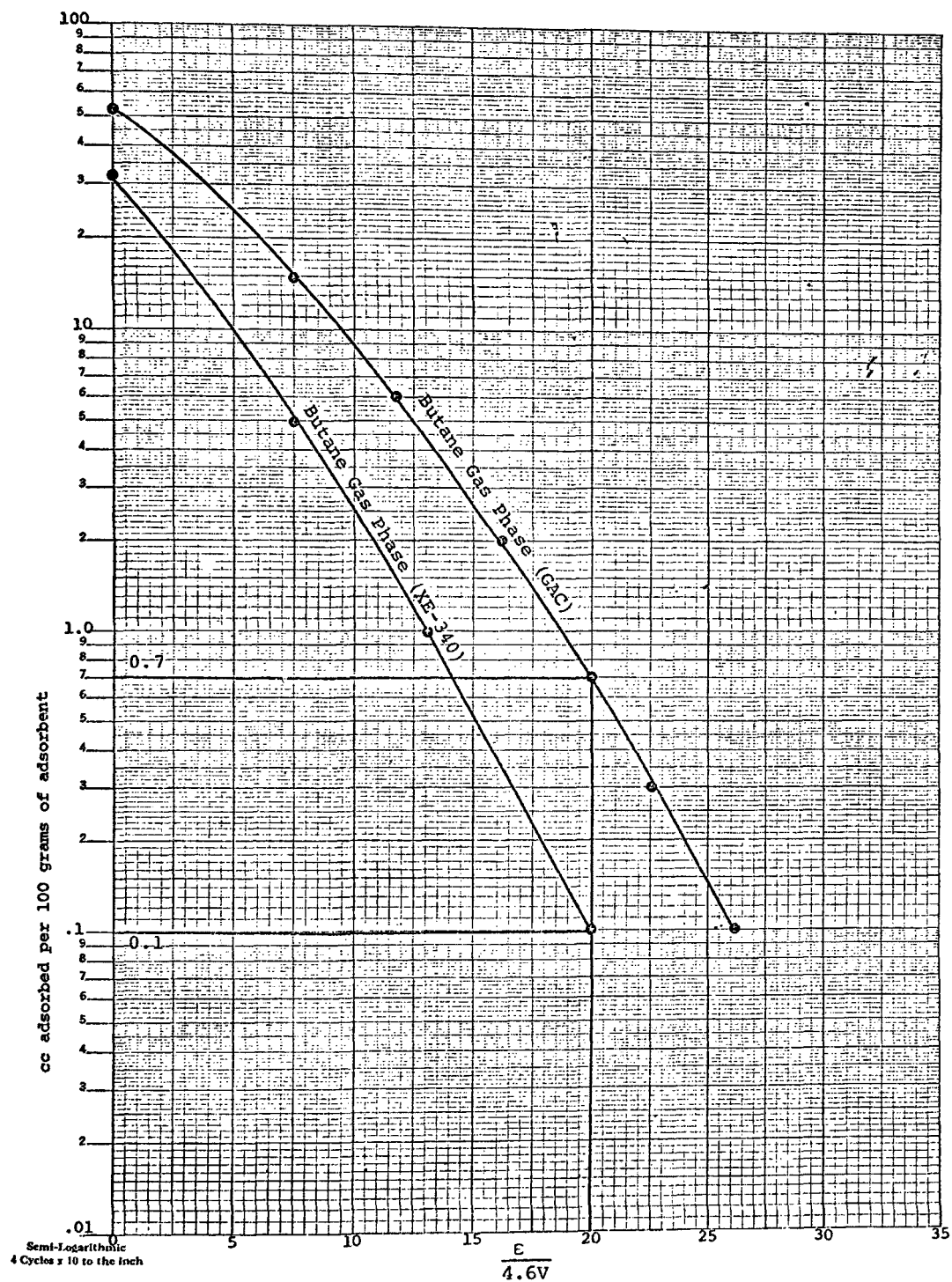


Figure 170. Butane adsorption curves for E-400 GAC and XE-340 resin.

$$\gamma_{sl} = \gamma_s - \gamma_e$$

γ_s = scale factor for substance to be adsorbed

γ_e = scale factor for water

$$\gamma_e = \frac{(1.33281)^2 - 1}{(1.33281)^2 + 2} = 0.206$$

$$\gamma_{sl} = \frac{p^s}{p^b} - 0.206$$

For chloroform the calculated γ_{sl} is:

$$p^s = \frac{n_i^2 - 1}{n_i^2 + 2} = \frac{(1.44643)^2 - 1}{(1.44643)^2 + 2} = .2669$$

(refractive index
from Table 47)

$$\gamma_{sl} = \frac{.2669}{.236} - .206 = .93$$

Using this scale factor (.93), take as many points on the butane curve (Figure 169) as needed to produce the predicted curve for adsorption of chloroform from pure water on Filtrasorb 400. For example, take the lowest data point "A" on the Butane Gas Phase (GAC) curve having coordinates 0.1 cc and 26.2 for $\frac{\epsilon}{4.6V}$. The horizontal coordinate corresponding to 0.1 cc on the predicted chloroform curve is .93 (26.2) = 24.4. This is point "B". Continuing in this manner generates the predicted curve for chloroform shown in Figure 169. This curve indicates the cc of chloroform that will be adsorbed from purified water per 100 grams of Filtrasorb 400. Physical data for the halogenated organic compounds required for application of the Polanyi-Manes adsorption theory are provided in Table 47. As seen in Table 47, the solubility of chloroform is 0.82 grams/100 cc of water.

$$\frac{\epsilon}{4.6V} = \frac{T}{V} \log \frac{C_s}{C}$$

$$T = 295$$

$$V = 80 \text{ (from Table 47)}$$

TABLE 47. PHYSICAL DATA FOR POLANYI-MANES CALCULATIONS

Cpd. No.	Compound	ED4 Conc. in fin. water $\mu\text{g/L}$	ED4 Conc. of cpds. 5,6, 11 & 13 $\mu\text{g/L}$	γ_{sl} Scale Factor	$\frac{\epsilon}{4.6V}$	Solubility in water $\text{gm}/100\text{cc}$	Molecular wt.	Density gm/cc	Molar Volume cc/mole	Dipole Moment	Refractive Index
1	Methylene chloride	ND		.875		2^{20}	84.93	1.325	64.1	1.54	1.424
3	Trans 1,2-dichloroethene	.77		.931	22.68	.63	96.94	1.26	76.9		1.4490
4	1,1-dichloroethane	.4					98.97	1.177	84.1		
5	Cis-1,2-dichloroethene	24.1	24.1	.937	20.17	.35	96.94	1.284	75.5	1.9	1.4519
6	Chloroform	67.3	67.3	.93	18.75	.82 ^{22*}	119.38	1.492	80.0	1.02	1.44643
7	1,1,1-trichloroethane			.906		.82 ¹⁵	133.42	1.338	99.7	1.79	1.4377
8	1,2-dichloroethane	7.7		.928		.869 ²⁰	98.96	1.256	78.8	1.19	1.4448
9	Carbon tetrachloride			.961		.08 ²⁰	153.82	1.594	96.5	0	1.46305
10	Trichloroethylene	.68		.993	20.86	.1	131.39	1.464	89.8	1.22	1.4777
11	Bromodichloromethane	47	47	1.033	18.45	.606 ^{22*}	163.83	2.006	81.7		1.4964
12	Tetrachloroethylene	.003		1.052			165.85	1.623	102.2		1.5055
13	Chlorodibromomethane	33.6	33.6	1.14	18.00	.519 ^{22*}	208.29	2.451	85.0		1.5482
14	Chlorobenzene	.86		1.092	16.68	.0488 ³⁰	112.56	1.106	101.8	1.7(1.55)	1.52479
15	Bromoform	2.5		1.24	21.00	.424 ^{22*}	252.75	2.89	87.5	1.8	1.5980
16	p-chlorotoluene	.1		1.081		.319 ³⁰	126.58	1.07	118.3		1.5193
17	m-dichlorobenzene	nil		1.135		.0123 ²⁵	147.01	1.288	114.1	1.72	1.54570
18	p-dichlorobenzene	.21		1.084	13.88	.0079 ²⁵	147.01	1.241	118.5	0	1.52104
19	o-dichlorobenzene	.14		1.148	15.75	.0145 ²⁵	147.01	1.305	112.7	2.52	1.5518
20	Vinyl chloride	6.2		.752	24.06	.28 ²⁵	62.6 liq.	.9013	69.34		1.370
					17.7	.009	gas	.00279			
	Total	191.6	172								
											90% of Total

ND = not determined

*Our analysis in tap water at 22°C

$$C_s = .82$$

C = concentration of chloroform in water

$$= 67.3 \text{ } \mu\text{g/liter from ED4}$$

$$= 6.73 \text{ } \mu\text{g/100 cc}$$

$$= .00000673 \text{ gm/100 cc}$$

$$\frac{\epsilon}{4.6V} = \frac{295}{80} \log \frac{.82}{.00000673} = 18.75$$

This means that at 18.75 on the horizontal axis (Figure 169) which corresponds to a concentration of 67.3 $\mu\text{g/L}$ of chloroform in purified water, we expect Filtrasorb 400 to adsorb about 0.68 cc (1.015 grams) per 100 grams of GAC. Manes and his associates have studied the adsorption of several halogenated organic compounds, including chloroform, from pure water on GAC. Actual data points on chloroform coincided very well with predicted values.

Theory Application--

Application of the Polanyi-Manes Theory to interpretation of data in this report first considers chloroform adsorption from finished water by 0.76 (2.5 feet) meter deep columns of GAC. Two runs were made, ED3 and ED4, Table 48. In these two ED, average influent levels were 57 $\mu\text{g/L}$ and 67.3 $\mu\text{g/L}$ respectively. Adsorption per 100 grams of adsorbent at saturation were 0.0280 cc and 0.0358 cc respectively. The adsorptive capacity increased as the concentration increased, as predicted by the Polanyi-Manes Theory. These two finished water data points are plotted in Figure 169. The two vertical lines from the "X" axis were drawn from the appropriate $\frac{\epsilon}{4.6V}$ values shown in Table 48. These vertical lines were then projected from their intercept points on the Chloroform Predicted (GAC) curve to the "Y" axis. For ED3 and ED4, respective predicted adsorption values were 0.64cc and 0.68 cc from pure water compared to actual adsorption values of 0.028 cc and 0.0358 cc. Respective actual values are 4.4 percent and 5.3 percent of the predicted values. These data appear in Table 48. This reduction is the result of competitive adsorption by DOM, including other HOC. To construct an actual adsorption curve through the two finished water data points it would be better if the two points were further apart. However, working with what is available, we can calculate the actual γ_{sl} value for these two points from our actual water. Projections horizontally from the two data points to the Butane Gas Phase (GAC) curve indicate $\frac{\epsilon}{4.6V}$ values of 28.8 and 28.4 respectively.

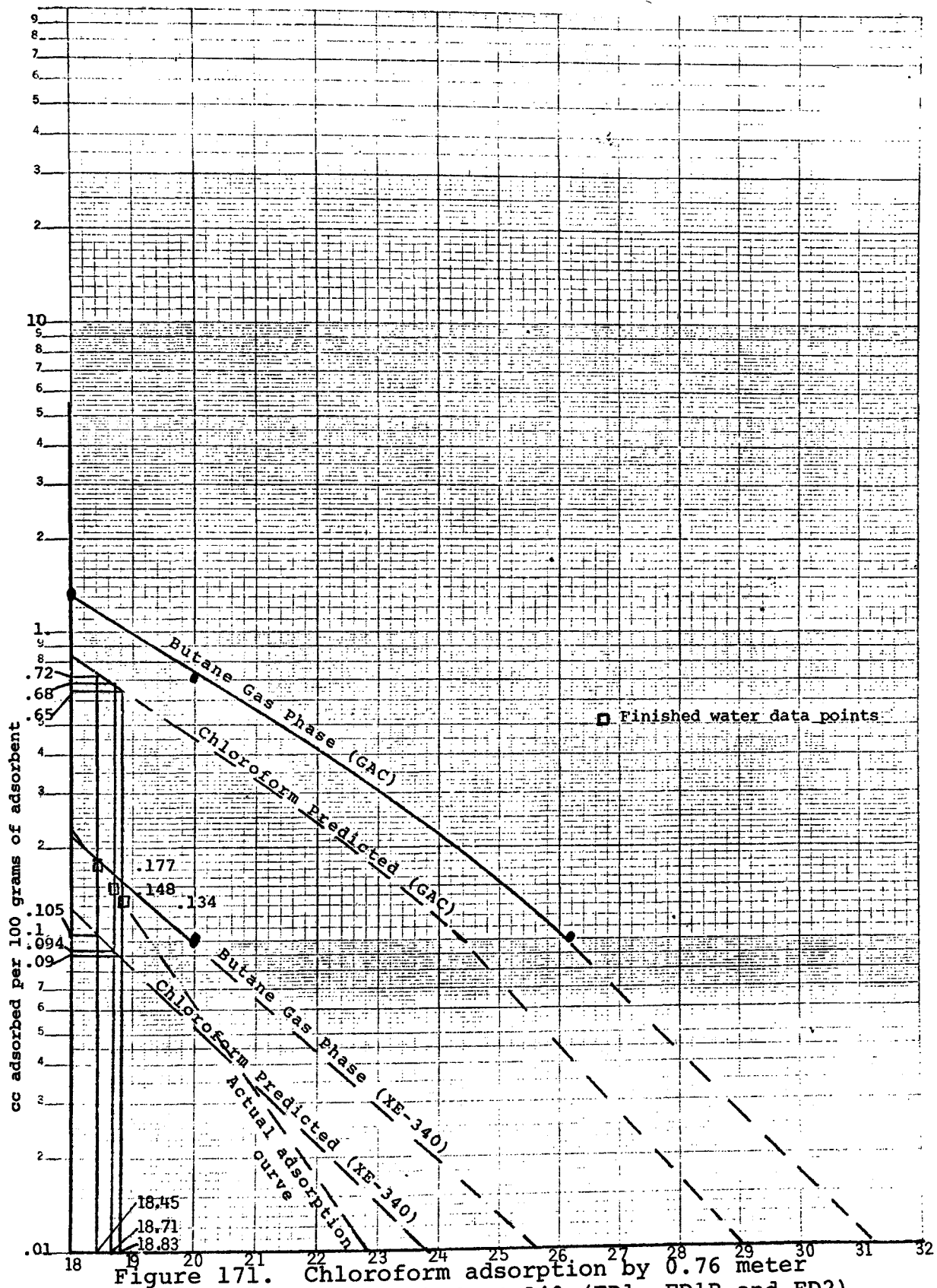
TABLE 48. CHLOROFORM ADSORPTION DATA
FROM FINISHED WATER

ED	Bed depth Feet	Adsorbent	Average influent µg/L	Adsorption per 100 grams adsorbent at saturation Grams	CC	$\frac{\epsilon}{4.6V}$	Predicted Polanyi- Manes adsorption for GAC CC	Percent adsorption of predicted value for GAC %
1	2.5	XE- 340	80.2	.265	.177	18.45		
1R	2.5	XE- 340	69.3	.22	.148	18.71		
2	2.5	XE- 340	64	.2	.134	18.83		
3	2.5	GAC	57	.042	.028	19.02	.64	4.4
3	2.5	904	57					
4	2.5	GAC	67.3	.0534	.0358	18.75	.68	5.3
4	5	GAC	67.3	.067	.049	18.75	.68	7.2
4	7.5	GAC	67.3	.071	.048	18.75	.68	7.1
4	10	GAC	67.3	.073	.049	18.75	.68	7.2

2.5 feet=0.76 meter
5 feet=1.52 meters
7.5 feet=2.29 meters
10 feet=3.05 meters

Respective actual γ_{s1} values are 0.660 and 0.660. Using this γ_{s1} value, the actual adsorption curve, shown in Figure 169, was generated, and it passed through the two data points. We predict that for our water, this generated actual chloroform adsorption curve can be used to predict chloroform results on our water over the entire chloroform concentration range we will experience. To generate this curve, only one actual data point is required to calculate the actual γ_{s1} value. Since there was nil chloroform in our raw water, we cannot test this prediction from our data on chloroform. In the discussion on XE-340 which follows we will show that it appears to work down to a very low chloroform level. The curves in Figure 169 are a log-log plot since the equation for $\frac{\epsilon}{4.6V}$ contains a log function. In our water, the concentrations of HOC are within the tangential straight line portion of the adsorption curve, therefore the log-log plot of data points mentioned earlier in this report, fall on a straight line and the line can be used to predict adsorption values at different concentrations.

Chloroform adsorption from finished water by 0.76 (2.5 feet) meter deep columns of XE-340 were studied in three runs, ED1, ED1R, and ED2, Table 48. The Butane Gas Phase (XE-340) curve and the generated Chloroform Predicted (XE-340) curve for pure water appear in Figure 170. The predicted curve was again generated from the gas phase curve by using the 0.93 γ_{s1} scale factor (Table 47) for chloroform. The average influent level varied from 80.2, 69.3 to 64 $\mu\text{g/L}$. For these three runs, compare the grams of chloroform adsorbed per 100 grams of adsorbent at saturation with their respective average influent level. The adsorptive capacity of XE-340 for chloroform decreases (0.177 cc, 0.148 cc and 0.134 cc) as the influent concentration decreases, as predicted by the Polanyi-Manes Theory. Using $\frac{\epsilon}{4.6V}$ values (from Table 48) corresponding to the three chloroform concentrations of 80.2, 69.3 and 64 $\mu\text{g/L}$, the three levels of cc's adsorbed per 100 grams of adsorbent at saturation (also shown in Table 48) are plotted in Figure 171. The three vertical lines from "X" axis correspond to the three $\frac{\epsilon}{4.6V}$ values. The three finished water data points are replotted in Figure 172 on an expanded "X" and "Y" axis scale for greater accuracy to show that they fall approximately on a straight line. To minimize drawing error the slope of this was transferred to the scale in Figure 171 and the actual adsorption curve drawn as shown through the three finished water data points. It is apparent that the actual adsorption curve is not parallel to the Butane Gas Phase (XE-340) curve nor to the Chloroform Predicted (XE-340) curve. The predicted curve predicts adsorption from pure water of 0.105 cc, 0.094 cc and 0.09 cc instead of the 0.177 cc, 0.148 cc and 0.134 cc actually adsorbed from our finished water. Obviously, the Polanyi-Manes Theory does not apply to XE-340, an adsorbent



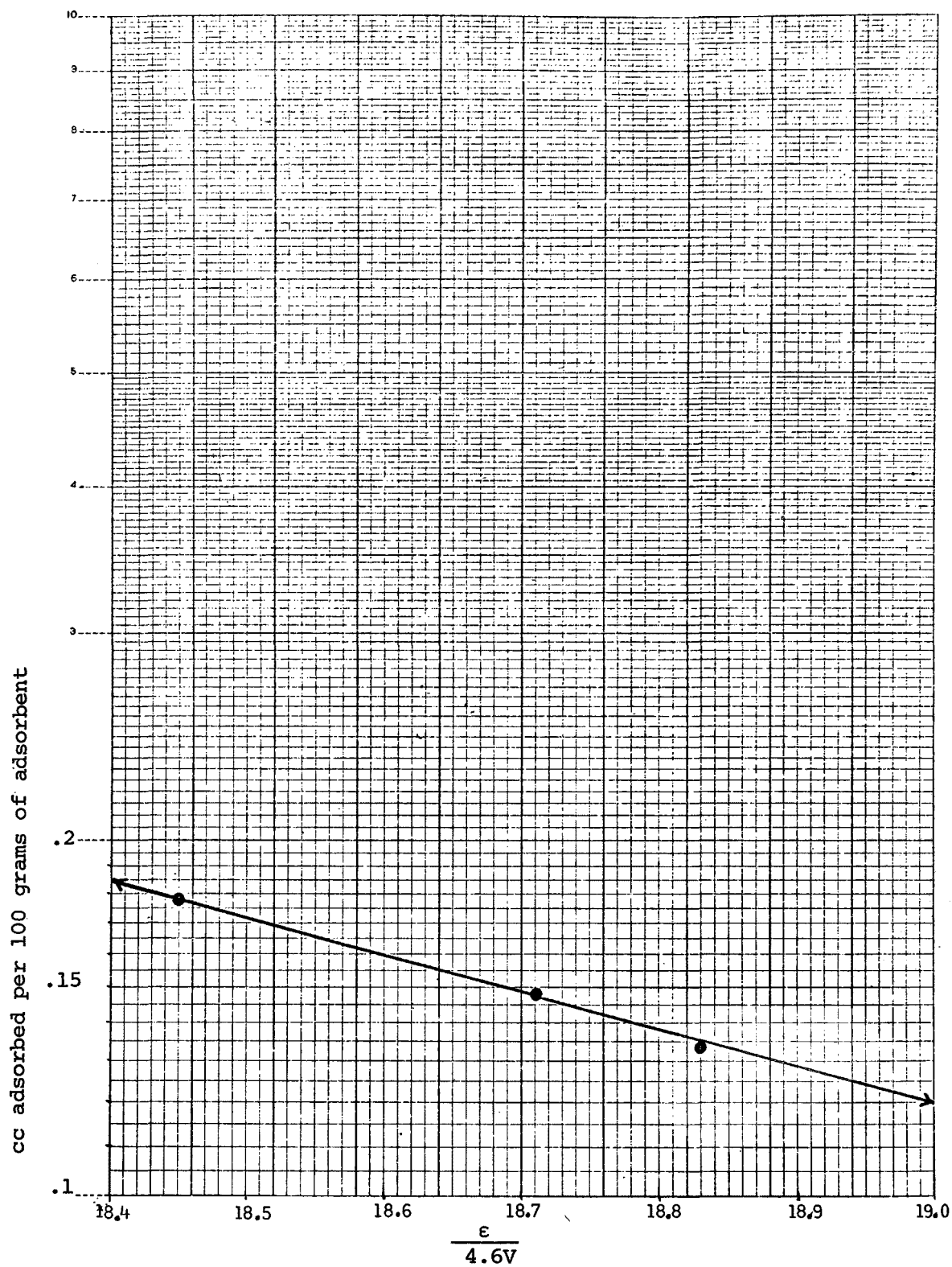


Figure 172. Chloroform adsorption by 0.76 meter (2.5 feet) of XE-340.

that not only allows micropore surface adsorption but adsorption into the polymer matrix. However, if at least two actual adsorption data points are obtained on a water system, the actual adsorption curve could be drawn to predict adsorption at some other concentration on the straight line portion of the curve. We do not have finished water experimental data to test this possibility but we do have a data point on H.T. water in ED1R, Table 19. Competitive adsorption by HOC and TOC will be different in H.T. and finished water so one cannot expect too much from this comparison. The H.T. data point is plotted in Figure 173 at the appropriate $\frac{\epsilon}{4.6V}$ value of 25.2. From the prediction

curve we predict an adsorptive capacity of 0.0023 cc and we reported an observed capacity of 0.0027 cc. Granted, error possibilities are great, but at least even at this very low concentration (1.2 $\mu\text{g/L}$ of chloroform) adsorption does occur, can be measured and the adsorptive capacity predicted with some degree of success.

Adsorption of cis 1,2-dichloroethene on 0.76 (2.5 feet) meter of XE-340 was studied in ED1, ED1R and ED2. The Butane Gas Phase (XE-340) curve appears in Figure 174. From this curve, the cis 1,2-dichloroethene predicted (XE-340) curve was generated by using the scale factor γ_{s1} of 0.937 appearing in Table 47. As with chloroform adsorption on XE-340, Figure 171, plotted cis 1,2-dichloroethene adsorption points in Figure 174 lie above the predicted curve and, in the case of raw and H.T. data points, lie above the Butane Gas Phase (XE-340) curve. Lines drawn through the data points are not parallel to the predicted curve. As with chloroform XE-340 data, the Polanyi-Manes Theory does not apply to adsorption of cis 1,2-dichloroethene by XE-340. Again however, two actual data points on raw, H.T. and finished water should be sufficient to generate an actual adsorption curve for our samples. In Figure 174, notice how adsorption data points from raw and H.T. water fall nearly on the same straight line. Notice also how adsorption points for finished water fall on a displaced straight line, indicating considerably less adsorptive capacity per 100 grams of adsorbent. This reduction in adsorption of about 30 percent is due, we believe, to increased competitive HOC adsorption, as was discussed for chloroform on page 112 and for cis 1,2-dichloroethene on pages 113 and 193. The adsorptive capacity of XE-340 is about the same from raw and H.T. water, indicated by the actual data points falling on almost the same curve. The capacity of XE-340 to adsorb from finished water was less. The competition of TOC adsorption decreased from raw to H.T. to finished water, corresponding to TOC values of 8.3, 5.8, and 5.4 mg/L. This would indicate possibly greater adsorptive capacity of cis 1,2-dichloroethene from finished water. The level of HOC in finished water is approximately 150 $\mu\text{g/L}$ compared to cis 1,2-dichloroethene levels 25 $\mu\text{g/L}$ in raw and H.T. water. The competitive adsorption of other HOC would indicate less adsorption capacity

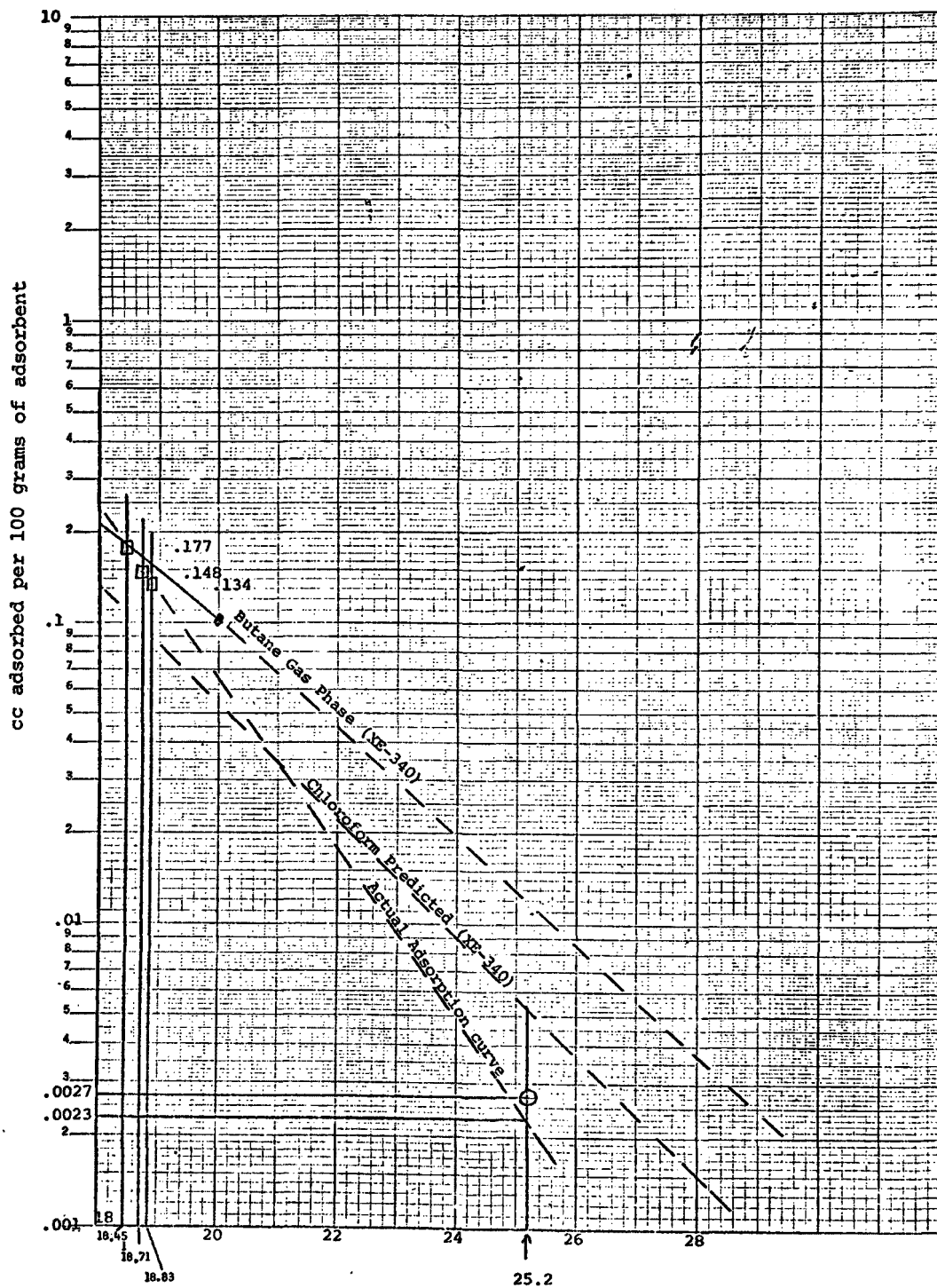


Figure 173. Chloroform adsorption by 0.76 meter (2.5 feet) of XE-340 (ED1, ED1R and ED2).

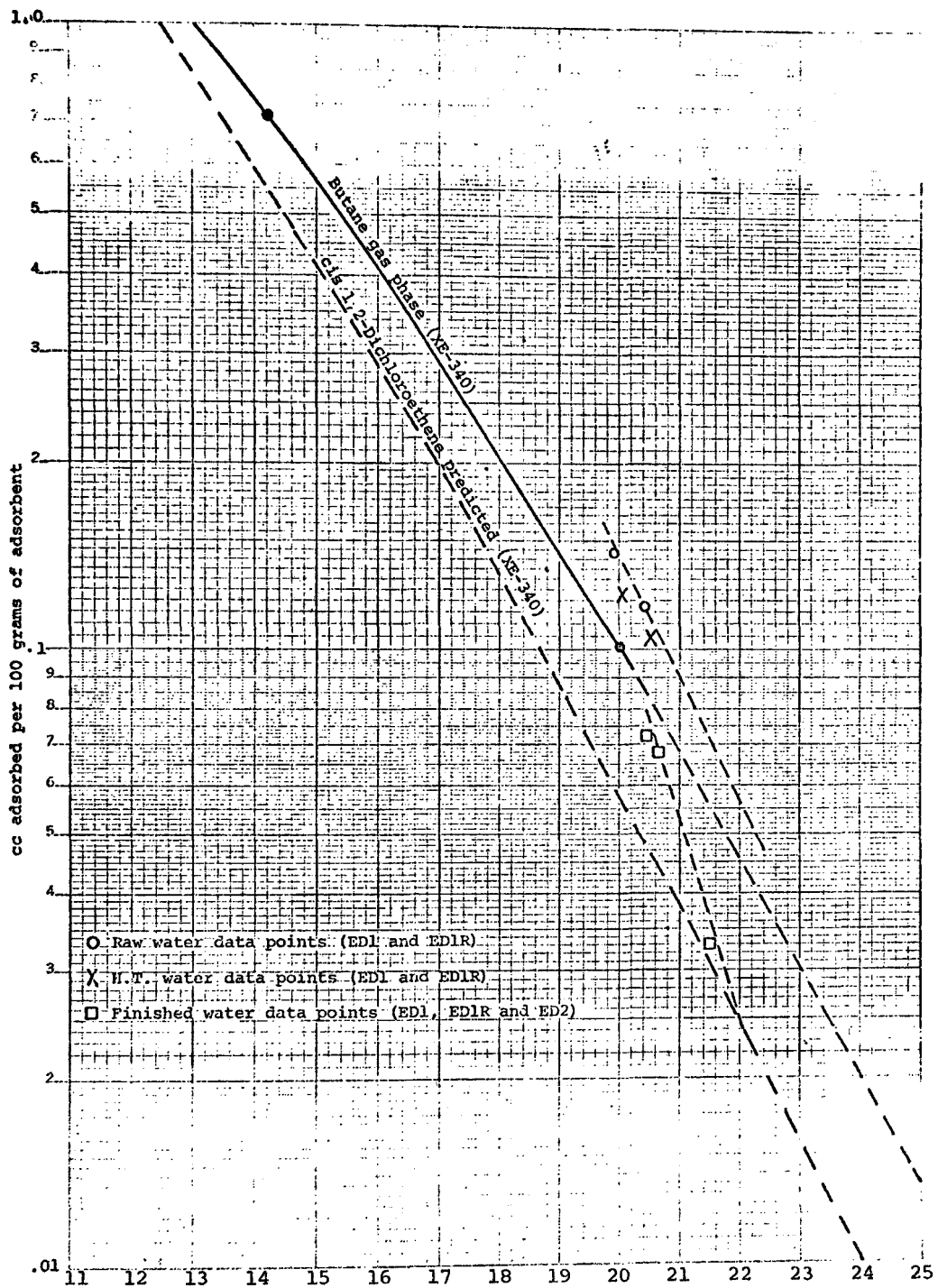


Figure 174. cis 1,2-Dichloroethene adsorption by 0.76 meter (2.5 feet) of XE-340 (ED1, ED1R and ED2).

in finished water. The data showed less adsorption; therefore, this may suggest that competitive adsorption of HOC has a greater influence than TOC competitive adsorption from finished water.

Adsorption of cis 1,2-dichloroethene on 0.76 (2.5 feet) meter of GAC was studied in ED3 and ED4. Plotted curves and actual data points appear in Figure 175. Raw and finished water data points, as with XE-340 in Figure 174, fall on displaced lines, indicating again the reduction in adsorptive capacity due to increased competitive HOC adsorption. The lines through the actual data points in Figure 175 were drawn through the points by sight and by calculating the γ_{s1} value for each point and generating the line from Butane Gas Phase (GAC) curve. Since the two methods produced the same lines, on GAC columns, one actual data point is enough to generate an actual adsorption curve. The predicted Polanyi-Manes adsorptive capacities for GAC in ED1, ED1R, ED3 and ED4 appear in Table 49. The percent of actual adsorption in our water is also shown. In two separate runs, columns 0.76 (2.5 feet) meter deep on raw water both adsorbed 8.8 percent of the predicted adsorption value from pure water. On finished water two runs at the same bed depth adsorbed 6.4 and 6.5 percent of the predicted adsorption value from pure water. In ED4, as bed depth increased, the adsorptive capacity increased as expected due to less competitive HOC adsorption with increasing bed depth.

Adsorption data from Table 50 for bromodichloromethane by 0.76 (2.5 feet) meter of XE-340 from H.T. and finished water are plotted in Figure 176. Since the H.T. water data point is probably not on the same straight line as the finished water data points, the dashed line drawn in Figure 176 represents only an approximate actual adsorption curve for this HOC in our system. Adsorption data from Table 50 for bromodichloromethane by 0.76 (2.5 feet) meter of GAC from finished water are plotted in Figure 177. In this case the bromodichloromethane predicted (GAC) curve lies above the Butane Gas Phase (GAC) curve because the γ_{s1} value for this HOC in Table 47 is 1.033. The calculated γ_{s1} value for both data points, obtained from the curves, was 0.652. This indicated that the two points fall on a straight line parallel to the Butane Gas Phase (GAC) curve. Thus, one data point would have been sufficient to generate the actual adsorption curve as shown. The actual adsorption of this HOC in our water is only about 3.6 percent of the predicted value from pure water.

Adsorption data from Table 51 for chlorodibromomethane by 0.76 (2.5 feet) meter of XE-340 from H.T. and finished water are plotted in Figure 178. The approximate actual adsorption curve is shown. Adsorption data from Table 51 for adsorption by 0.76 (2.5 feet) meter of GAC from finished water are plotted in Figure 179. The calculated γ_{s1} value for both data points, obtained from the curves, were 0.602 and 0.598, averaging 0.6.

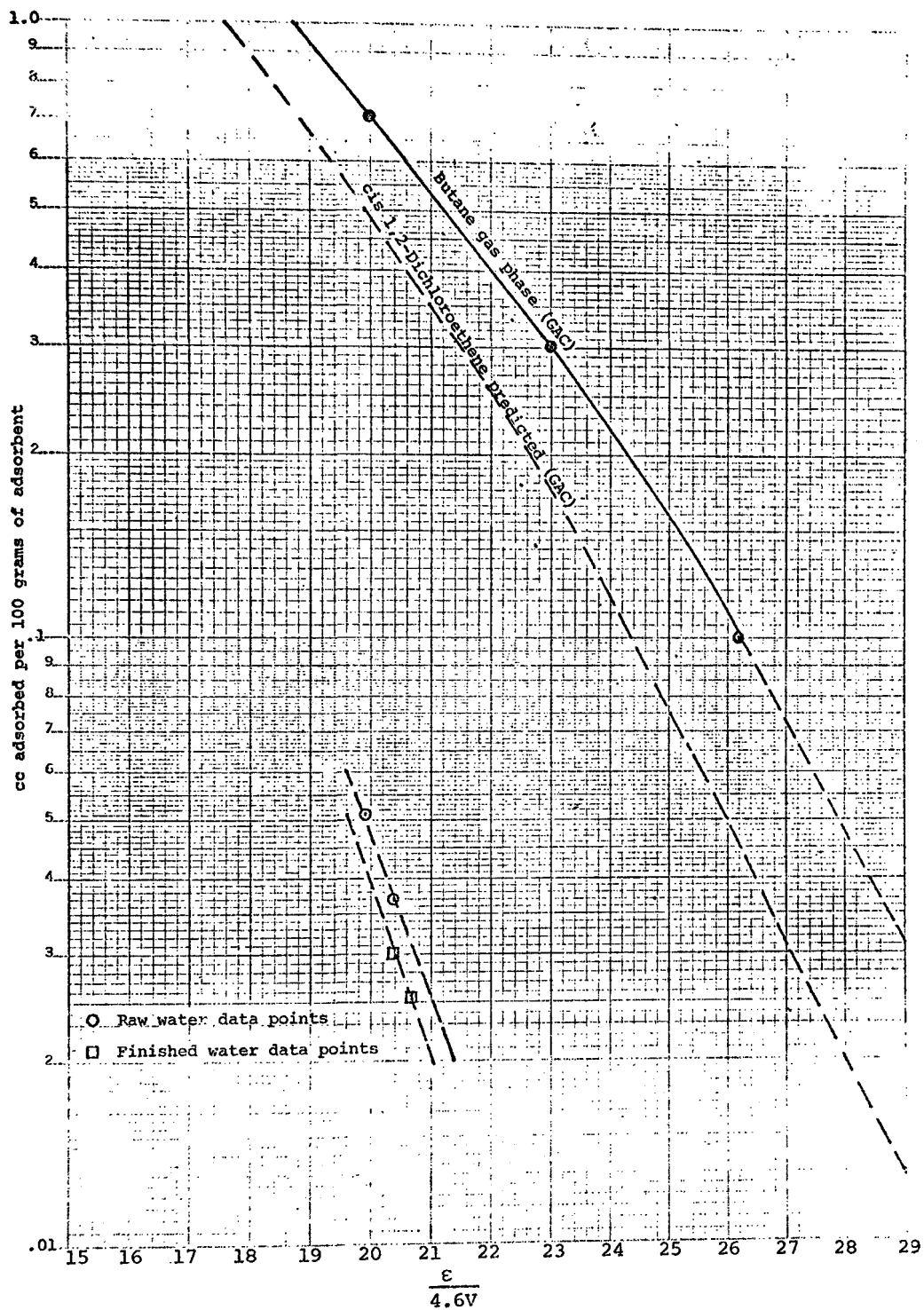


Figure 175. cis 1,2-Dichloroethene adsorption by 0.76 meter (2.5 feet) of GAC (ED3 and ED4).

TABLE 49. CIS 1,2-DICHLOROETHENE ADSORPTION DATA FROM
RAW, H.T., AND FINISHED WATER

ED	Bed depth feet	Adsorbent	Average influent µg/L	Adsorption per 100 grams adsorbent at saturation		$\frac{E}{4.6V}$	Predicted Polanyi adsorption CC	Percent adsorption of predicted value
				Grams	CC			
RAW WATER								
1	2.5	GAC	21	.048	.037	20.4	.42	8.8
1R	2.5	XE-340	21	.15	.117	20.4		
1R	2.5	GAC	29	.065	.0509	19.36	.58	8.8
1R	2.5	XE-340	29	.181	.141	19.86		
H.T. WATER								
1	2.5	XE-340	20	.134	.104	20.49		
1R	2.5	XE-340	25.4	.157	.122	20.08		
FINISHED WATER								
1	2.5	XE-340	10.9	.043	.003			
1R	2.5	XE-340	19.4	.093	.0724			
2	2.5	XE-340	18.4	.087	.068			
3	2.5	GAC	18.3	.033	.0257	20.57	.4	6.4
4	2.5	GAC	19.9	.039	.03	20.17	.46	6.5
4	5	GAC	19.9	.045	.035	20.17	.46	7.6
4	7.5	GAC	19.9	.049	.0357	20.17	.46	7.8
4	10	GAC	19.9			20.17		
2.5 feet=0.76 meter 5 feet=1.52 meters 7.5 feet=2.29 meters 10 feet=3.05 meters								

TABLE 50. BROMODICHLOROMETHANE ADSORPTION DATA FROM
H.T. AND FINISHED WATER

ED	Bed depth feet	Adsorbent	Average influent µg/L	Adsorption per 100 grams adsorbent at saturation		$\frac{\epsilon}{4.6V}$	Predicted Polanyi adsorption CC	Percent adsorption of predicted value
				Grams	CC			
H.T. WATER								
1	2.5	XE-340	variable see Fig. 39		.0028	23.1		
1R	2.5	XE-340	erratic see Fig. 40			26.9		
FINISHED WATER								
1	2.5	XE-340	37.1	.182	.0907	18.82		
1R	2.5	XE-340	42.7	.204	.1017	18.60		
2	2.5	XE-340	42.4					
3	2.5	GAC	39	.069	.0344	18.74	1.13	3.04
4	2.5	GAC	47	.084	.0419	18.45	1.21	3.46
4	5	GAC	47	.083	.0414	18.75	1.14	3.63
4	7.5	GAC	47	.084	.0419	18.75	1.14	3.68
4	10	GAC	47			18.75		
2.5 feet=0.76 meter								
5 feet=1.52 meters								
7.5 feet=2.29 meters								
10 feet=3.05 meters								

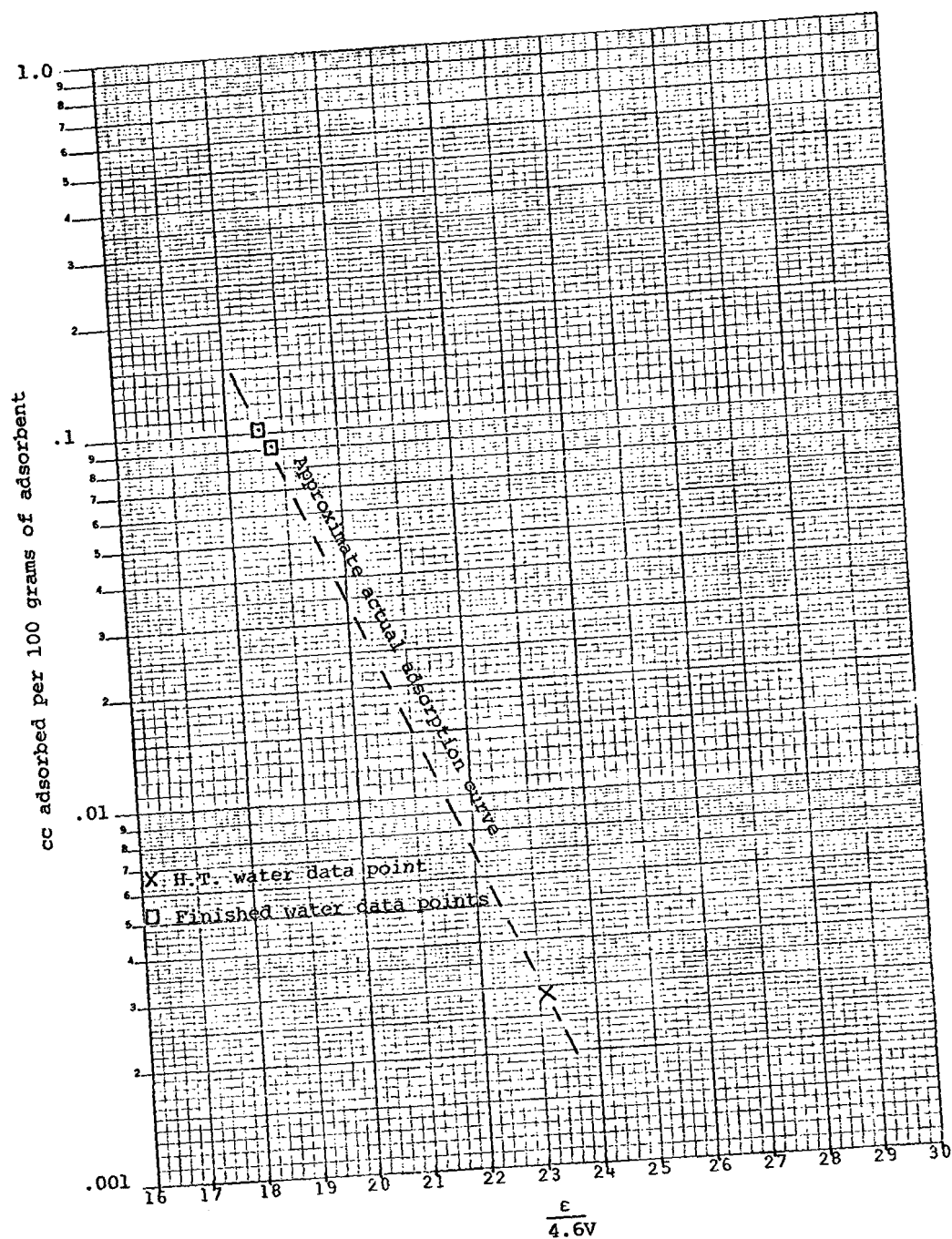


Figure 176. Bromodichloromethane adsorption by 0.76 meter (2.5 feet) of XE-340 (ED1 and ED1R).

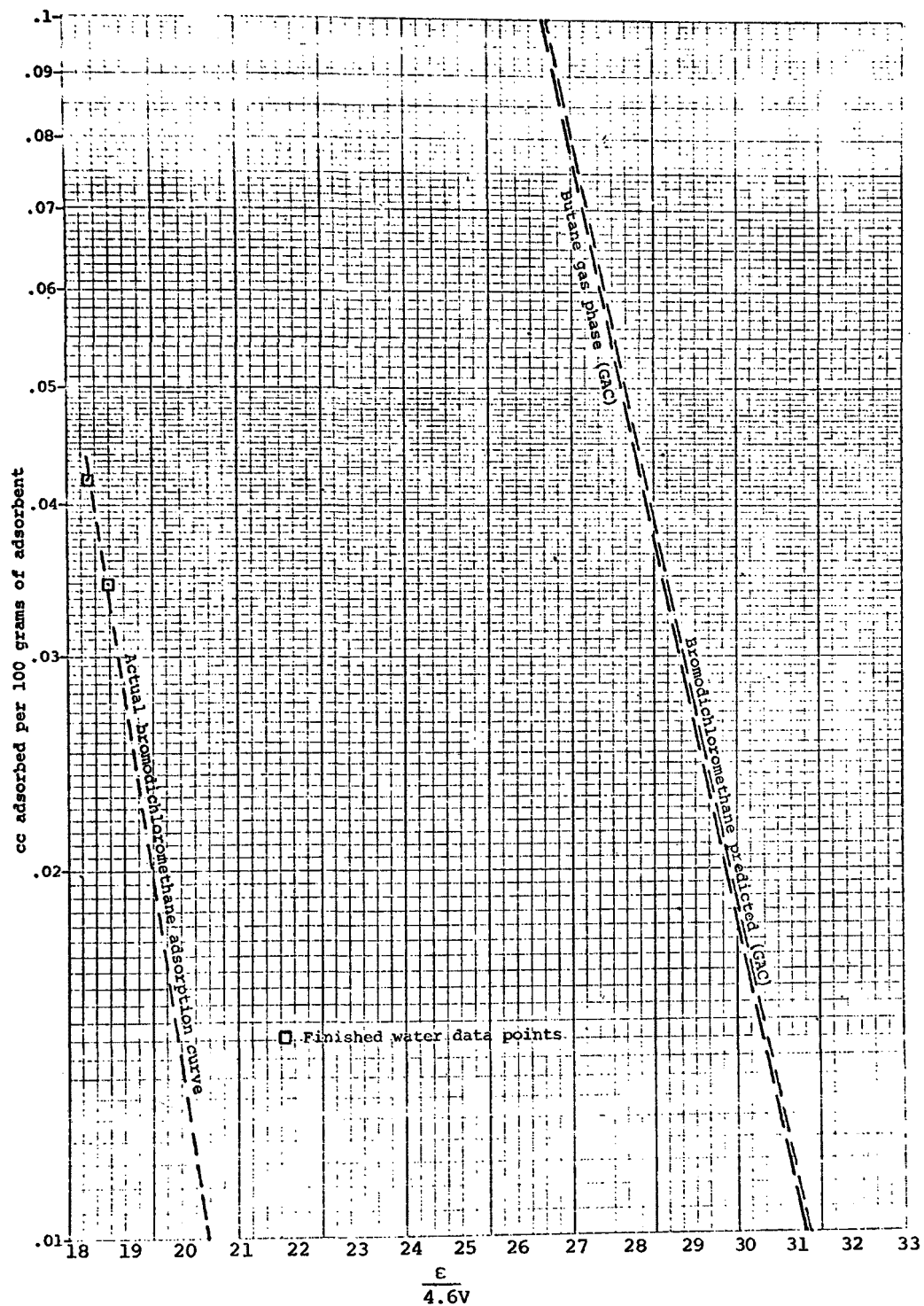


Figure 177. Bromodichloromethane adsorption by 0.76 meter (2.5 feet) of GAC (ED3 and ED4).

TABLE 51. CHLORODIBROMOMETHANE ADSORPTION DATA
FROM H.T. AND FINISHED WATER

ED	Bed depth feet	Adsorbent	Average influent µg/L	Adsorption per 100 grams adsorbent at saturation		$\frac{\epsilon}{4.6V}$	Predicted Polanyi adsorption CC	Percent adsorption of predicted value
				Grams	CC			
H.T. WATER								
1	2.5	XE-340	1.0		.0009	23.31		
1R	2.5	XE-340	.25		.0005	25.39		
FINISHED WATER								
1	2.5	XE-340	12	.077	.031	19.56		
1R	2.5	XE-340	24.5	.155	.063	18.48		
2	2.5	XE-340	26.7					
3	2.5	GAC	27	.067	.027	18.34	2.2	1.2
4	2.5	GAC	33.6	.104	.042	18.01	2.3	1.8
4	5	GAC	33.6	.1	.041	18.01		
4	7.5	GAC	33.6					
4	10	GAC	33.6					
2.5 feet=0.76 meter 5 feet=1.52 meters 7.5 feet=2.29 meters 10 feet=3.05 meters								

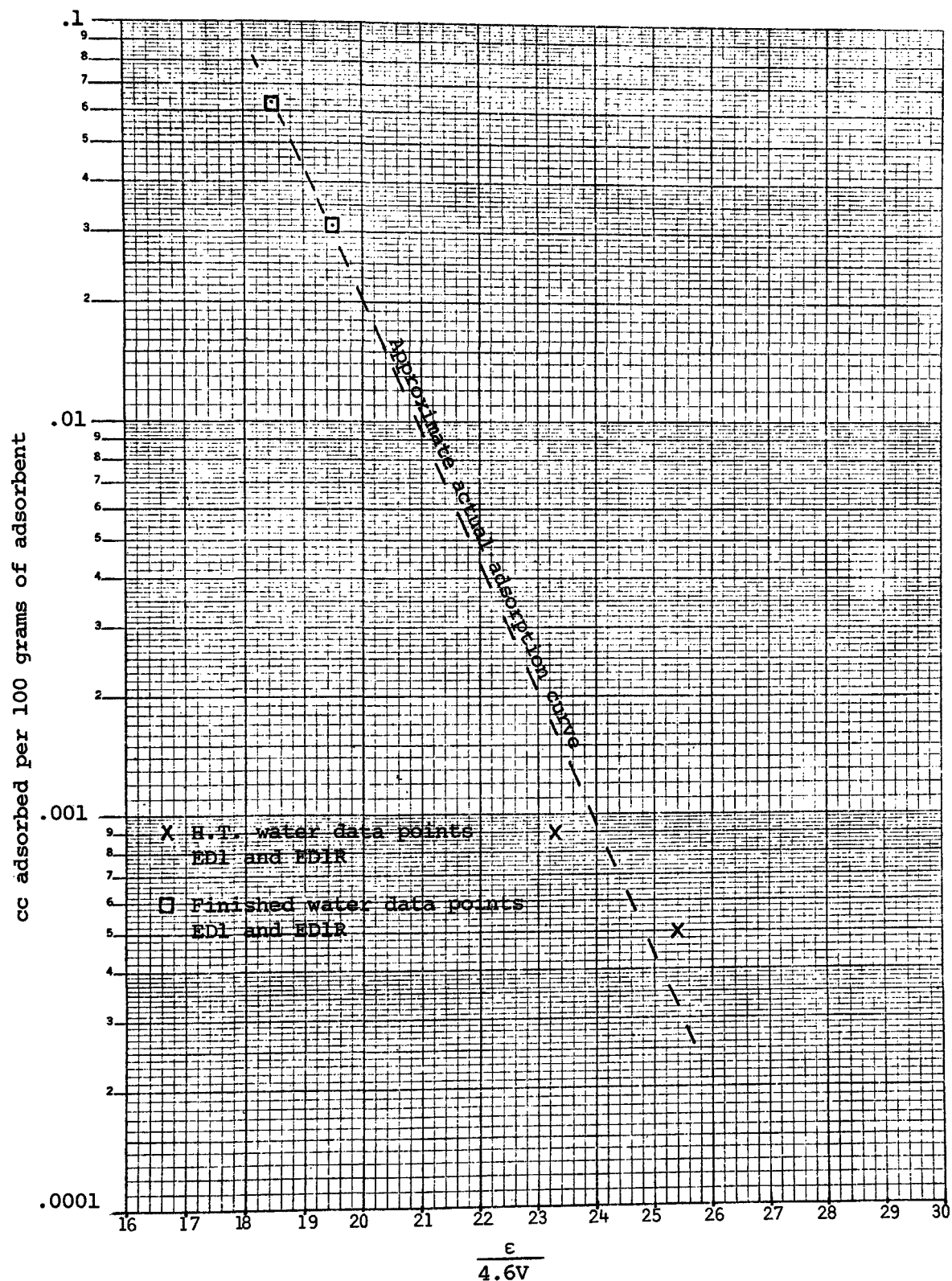


Figure 178. Chlorodibromomethane adsorption by 0.76 meter (2.5 feet) of XE-340 (ED1 and ED1R).

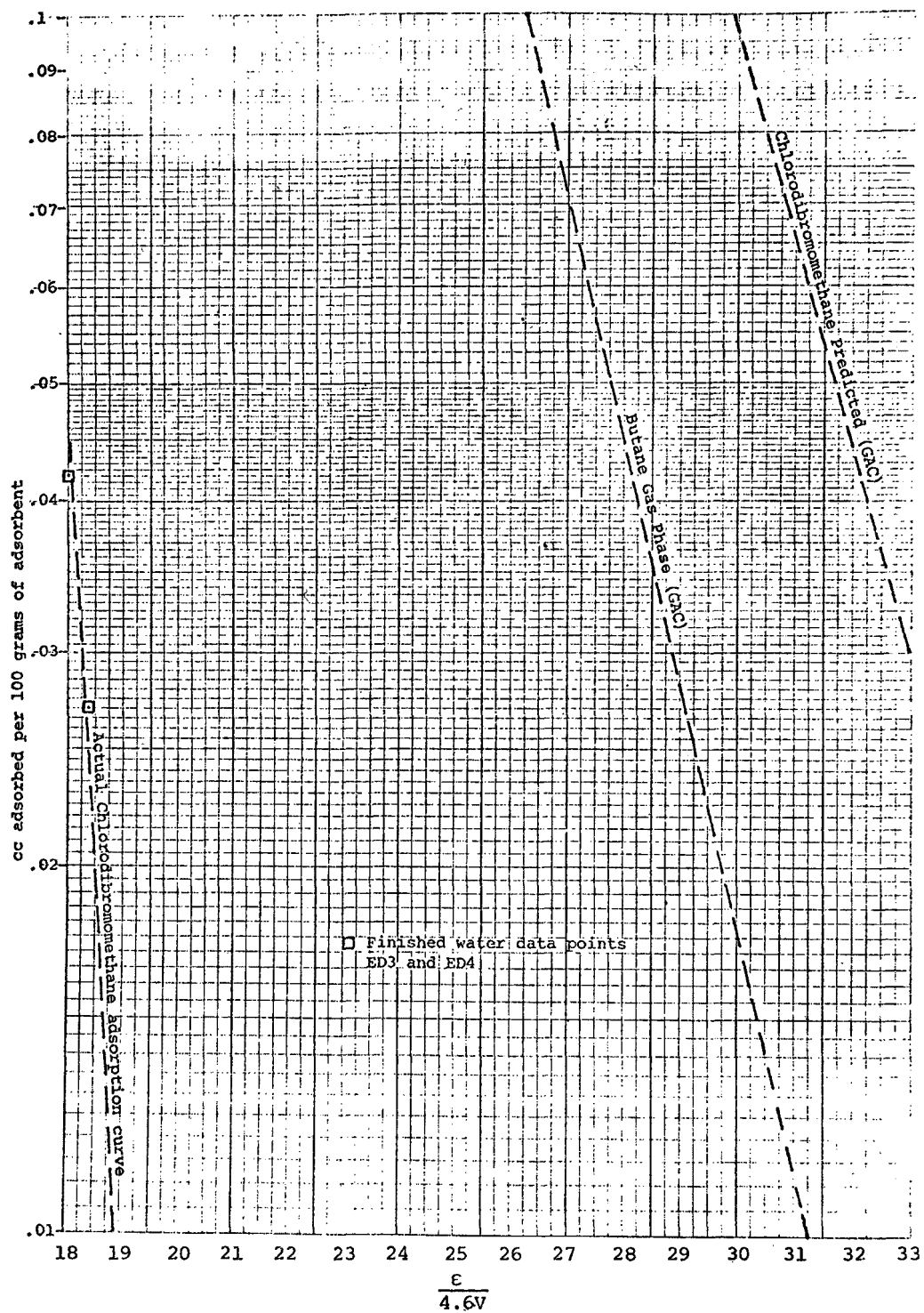


Figure 179. Chlorodibromomethane adsorption from 0.76 meter (2.5 feet) of GAC (ED3 and ED4).

Once again, this indicated that both points lie on the same straight line parallel to the predicted curve. The actual adsorption of this HOC in our water is only about two percent of the predicted value from pure water.

Adsorption data in this part of the report for the HOC discussed above and for additional HOC appear in Table 52. The chemical identification number given in Table 8, for each HOC studied correspond to their elution time on a GC through a Tenax column (except for vinyl chloride, Chem. No. 20, which elutes first). Chemical No. 3 is eluted first (after vinyl chloride), and 17, 18, and 19 are eluted last. In Table 52, it is seen that the γ_{sl} values in most cases predict this order of elution from a Tenax column. This table supports and adds to the data in Table 37, which is discussed beginning on page 193.

We have found the Polanyi-Manes Adsorption Theory useful in interpreting and explaining the data we have obtained. It is obvious that more fundamental research is needed in the laboratory to determine the actual adsorption of all our HOC from pure water. This will indicate whether or not our observed reduction in adsorption as the molecular weight of the HOC increased, is due to steric exclusion or largely to competitive HOC adsorption. We found the Theory useful in predicting results in a given system where the concentration of dissolved substances change in magnitude but not in ratio.

TABLE 52. SUMMATION OF ADSORPTION PARAMETERS BY GAC

Cpd. No.	Chemical	Column Bleed Time Days	Column Saturation Time Days	MT _z Inches	Y _{sl}	Polanyi-Manes Predicted Capacity cc	Observed Capacity cc	Percent of Predicted
3	Trans 1,2-dichloroethene	52	?	16+?	.931	.03	.002	6.7
5	Cis-1,2-dichloroethene	18	65	22	.937	.46	.029	6.5
6	Chloroform	7	23	21	.93	.68	.032	5.0
7	1,1,1-trichloroethane				.906			
8	1,2-dichloroethane	29	76	18	.928			
9	Carbon tetrachloride				.961			
10	Trichloroethylene	38	56	9.6	.993	.65	.0012	.19
11	Bromodichloromethane	15	54	21	1.003	1.14	.04	3.6
13	Chlorodibromomethane	21	89	22	1.14	2.2	.04	1.8
15	Bromoform	42	94	16.6	1.24	1.7	.002	.12
17	m-dichlorobenzene				1.135			
18	p-dichlorobenzene	none	>122	<10	1.084	4.9		
19	o-dichlorobenzene				1.148			
						Total	.1462	

GC/MS HOC Confirmation Data

Periodically during the two-year study, GC/MS determinations were made on both raw and finished water to confirm GC peaks of HOC. All nineteen HOC have been confirmed. Sample dates and results are summarized in Table 53. Analyses on sample dates August and November 4, 1976; and May 3 and May 20, 1977 were determined on a Hewlett-Packard Mass Spectrograph, Model 5981, with a Model 5933 Dual Disc Inter-Active Data System. The data on October 11, 1977 were obtained by EPA Laboratories in Cincinnati. Analyses on sample dates March 11 and April 17, 1978 were made on a Varian MAT Model 112S Magnetic Sector, double-focusing, high resolution mass spectrograph coupled to a MAT 166 data system.

TABLE 53. GC/MS HOC CONFIRMATION DATA

	4/17/78				3/11/78				10/11/77**				5/20/77		5/3/77				11/4/76				8/8/76			
Chem No.	Raw µg/	Wtr. MS*	Fin. µg/	Wtr. MS	Raw µg/	Wtr. MS	Fin. µg/	Wtr. MS	Raw µg/	Wtr. MS	Fin. µg/	Wtr. MS	Raw µg/	Wtr. MS	Raw µg/	Wtr. MS	Fin. µg/	Wtr. MS	Raw µg/	Wtr. MS	Fin. µg/	Wtr. MS	Raw µg/	Wtr. MS	Fin. µg/	Wtr. MS
20	14.2	Y	11.3	Y	12.8	Y	11.7	Y	10.8	Y	14.1	Y	.33	Y	1.1	Y	.62	Y	NR	NR	NR	NR	NR	NR	NR	NR
1	.45	Y	int. std.	NR	.52	Y	int. std.	NR	.13	Y	int. std.	Y	.06	Y	.06	Y	.07	Y	.19	ND	.16	Y	NR	Y	NR	Y
3	1.6	Y	.87	Y	1.3	Y	.78	Y	2.1	Y	.5	Y	.7	Y	1.8	Y	.79	Y	.33	Y	.24	Y	NR	Y	NR	Y
4	.6	Y	.5	Y	.7	Y	.61	Y	1.0	Y	nil	Y	.25	Y	.43	Y	.15	Y	.14	ND	.11	ND	NR	Y	NR	Y
5	24.3	Y	22.1	Y	27.4	Y	25.2	Y	19.8	Y	27.6	Y	19.4	Y	33.7	Y	20.6	Y	21.2	Y	15.7	Y	22.7	Y	16.8	Y
6	nil	ND	69	Y	nil	ND	73	Y	nil	ND	79	Y	82	Y	nil	ND	83.4	Y	nil	ND	53.5	Y	nil	ND	98.2	Y
7		ND		Y		ND		Y		ND		ND		ND		ND		ND		ND		ND		ND		ND
8	.13	Y	8.1	Y	.17	Y	7.8	Y	.16	Y?	3.6	ND	.27	ND	.08	ND	2.16	Y	.11	ND	.14	ND	NR	ND	NR	ND
9		Y		Y		Y		Y		ND		Y		Y		ND		Y		ND		ND		ND		ND
10	.37	Y	.63	Y	.41	Y	.72	Y	.58	Y	ND	Y	.11	Y	.06	Y	.43	Y	.32	Y	.37	Y	NR	ND	NR	ND
11	nil	Y	46	Y	nil	ND	43.4	Y	nil	ND	60.1	Y	29.7	Y	nil	ND	38.5	Y	nil	ND	29.4	Y	nil	ND	25.1	Y
12	.003	Y	.003	Y	.003	Y	.002	Y	nil	ND	ND?	ND	.08	Y	nil	ND	nil	ND	.1	ND	.08	ND	NR	ND	NR	ND
13	nil	ND	34.3	Y	nil	ND	37.2	Y	nil	ND	36.7	Y	9.9	Y	nil	ND	20.6	Y	nil	ND	13.4	Y	nil	ND	20.2	Y
14	1.2	Y	.81	Y	1.3	Y	1.1	Y	1.4	Y	.51	Y	.07	Y	.11	Y	.04	ND	.18	Y	.16	Y	NR	ND	NR	ND
15	nil	ND	2.7	Y	nil	ND	2.9	Y	nil	ND	1.84	Y	1.01	Y	nil	ND	.59	Y	nil	ND	.8	Y	NR	ND	NR	ND
16	.03	Y	.11	Y	.04	Y	.13	Y	.87	A	ND	A	nil	ND	nil	ND	nil	ND	.16	Y	.18	Y	NR	ND	NR	ND
17-18 19	nil .57, .19	ND Y/Y	nil .23, .15	ND Y/Y	nil .63, .21	ND Y/Y	nil .37, .19	ND Y/Y	1.2	A	.25	A	1.4	Y	2.24	Y	1.22	Y	1.1	Y	1.3	Y	NR	Y	NR	Y
ben- zene	NR	Y	NR	Y	NR	Y	NR	Y	ND	Y	ND	Y	ND	Y									NR	Y	NR	Y
tol- uene	NR	Y	NR	Y	NR	Y	NR	Y																		

*GC/MS - confirmation ND - none detected **Analysis by EPA Lab. Cinn. A - does not elute on GC column used
Y - Yes NR - not run

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MICROBIAL FLORA OF GRANULATED ACTIVATED CARBON
COLUMNS USED IN WATER TREATMENT
(Part I)

by

Frances Parsons
Drinking Water Quality Research Center
Florida International University
Tamiami Campus
Miami, Florida

ABSTRACT

Differential bacteria counts were made on samples of effluents of granulated activated carbon (GAC) columns used to remove dissolved organic material from drinking water. The membrane filter procedure, four primary media, and incubation at 25°C for six days were used to isolate colonies. Identification was done using Roche Diagnostics systems and additional diagnostic tests. Most of the growth occurred on tryptone glucose extract agar and Czapek Dox agar after four days incubation at 25°C. Most bacterial growth was not detected when standard methods were used.

Raw water organisms, which apparently can survive existing treatment plant processes, colonized the initially bacteria-free GAC columns, and released vast numbers of bacteria into the water flowing through the columns. Some of the organisms, though innocuous in small numbers, may pose a threat to human health when they are present in drinking water in large numbers. These organisms include Pseudomonas-like bacteria, Acinetobacter, Alcaligenes faecalis, Moraxella, Enterobacter agglomerans, and Flavobacterium (probably aquatile).

The development of bacterial growth in the GAC columns interfered with backflushing the columns. Preliminary results indicate that the GAC system provides an ecological advantage for entering organisms that survive treatment plant processes. Enterobacter agglomerans in GAC column effluent survived exposure to 3ppm chlorine. This suggests that at least in our subtropical environment a careful study is required to insure proper bacterial control before installing GAC adsorbers in treatment plants.

CONCLUSION AND RECOMMENDATIONS (TENTATIVE)

Bacteria that occur in small numbers in raw water survive treatment and colonize granulated activated carbon (GAC) columns used to remove organic solutes from treated water. The bacteria multiply, form slime that interferes with column maintenance by preventing backflushing, and slough off in large numbers into the water passing through the columns.

The size and composition of the microbial populations in GAC columns changed with time. The composition of the microbial population of the raw water apparently influenced the population in the columns. Each column had a somewhat different population composition and size on each sample date.

Some of the organisms that multiply in the GAC columns may pose a health hazard because of the vast numbers present if the column effluent is ingested or comes in contact with susceptible body surfaces such as the otic canal or the naso-pharyngeal mucosa. The possibility of a consumer incurring enteritis, intoxication, and/or an opportunistic infection should be studied. Because of the large numbers of Gram-negative organisms that colonize GAC columns, endotoxin should be assayed using the LAL method. Staphylococci sp. sometimes present in finished water should be tested for coagulase.

The large numbers of noncoliform bacteria found in column effluents will suppress coliform growth and interfere with interpretation of the standard coliform detection test.

Effects of rechlorination of column effluents on the subsequent bacterial population of this water over a period of time is being studied. Preliminary results indicate that entering organisms that survive treatment plant processes become a major component of the microbial population in GAC columns. A count of 300/100 ml of sample of Enterobacter agglomerans was obtained in a GAC column effluent sample two days after rechlorination to 3 ppm. When the concentration of chlorine was increased to 10 ppm, two colonies of Enterobacter agglomerans were recovered from 100 ml of sample held for six days at 25°C. This experiment was repeated and supplementary survival tests using organisms isolated from chlorinated column effluent were done to verify these results. cursory examination of results of these experiments indicate that small numbers of bacteria can survive in

water containing 3 ppm chlorine for as long as six days, probably inside of cell aggregates.

The Standard Plate Count method (APHA, AWWA, WPCF 1975) is inadequate for enumerating these aquatic bacteria. Longer incubation time and lower temperatures than specified by Standard Methods are needed. New media that would support more kinds of heterotrophic organisms should be developed and tested. Better methods for identification of these organisms need to be devised.

INTRODUCTION

Granulated activated carbon (GAC) columns that are capable of retaining organic material and removing chlorine from water can be expected to diminish the bacteriocidal property of treated water passed through them and to provide metabolic substrate for microorganisms that survive chlorination. Controlling bacterial populations in treated water is important because bacteria that may be harmless in small numbers may be capable of causing disease under certain conditions (Geldreich 1973, Peterson and Favero 1975). Wallis et al. (1974) pointed out that charcoal filters used in domestic water supplies released large numbers of bacteria to water flowing through them. Allen et al. (1977) demonstrated that excessive bacterial populations mask coliform growth in the standard method for determining potability of water. Fiore and Babineau (1977) stated that activated carbon filters in household use had no effect on bacteria counts in water passed through them. They used the pour plate method and incubated the cultures at 30°C for a 48-hour period. Klotz et al. (1976) demonstrated that 48 hours was inadequate for the slow-growing micro flora that developed on activated carbon filters, and incubated their cultures at 27°C for seven days. Our work supports that of Klotz.

Although American workers in the field of water quality are concerned about the increase in numbers of bacteria in water filtered through GAC columns, European workers encourage bacterial growth in carbon filters used at various points in the treatment process (Eberhart 1976). By doing so, adsorbed carbon material is mineralized and soluble inorganic ions are immobilized in bacterial biomass. This can be an attractive feature to American designers of water systems. Van der Kooij (1976), Klotz et al. (1976), and Eberhardt (1976) described the development of bacterial populations on carbon filters in Europe and their activity in mineralizing organic substances from the water flow.

This study is being done to determine the changes in microbial population composition and size in treated water subjected to filtration through GAC beds of various depths. It is necessary to determine successional changes in bacterial populations to determine if a potential health hazard can result 1) from development of massive populations of ordinarily harmless bacteria, and 2) from a change in kind of bacteria multiplying in the carbon filters from innocuous species to chlorine resistant

pathogenic species that ordinarily may be present in small numbers in raw water.

It will also become increasingly important to understand how bacterial growth on carbon filter material can be controlled to facilitate maintenance of the filters. Bacterial growth tends to develop slime within the carbon granules, which makes back-flushing difficult, and after a time impossible.

METHODS AND MATERIALS

The bench model column adsorption system used in Experimental Design No. 4 of EPA Grant Project R804521-01 (Wood et al. 1979) is shown diagrammatically in Figure 1. Sample dates and bed depths are shown also. The four 1" ID columns were connected in series and packed with 2.5 feet of GAC Filtrasorb 400 to give bed depths of 2.5, 5, 7.5, and 10 feet. Sample ports were located at the effluent end of each column. Two-liter samples were collected on the dates shown and analyzed within two hours. The membrane filter technique was used to isolate bacteria from water samples (APHA, AWWA, WPCF 1975). Figure 2 is a flow diagram of the procedure used. Table 1 is a list of diagnostic tests and media used in identification. Membranes used to filter water samples were placed on several primary media, incubated at 25°C, and read at 1-, 2-, 3-, and 6-day intervals as this temperature and these incubation times were shown previously to yield higher counts and greater diversity of bacteria than those specified by Standard Methods (APHA, AWWA, WPCF 1975).

When the primary cultures were examined, every recognizable different colony type on each primary medium was described, assigned a number, and counted. At least two colonies of each type were picked and each was streaked on a new plate of medium to insure isolation. Dissimilar colonies were expected to be sometimes identical as bacteria express different morphologies on different media. Gram stains were made of each colony type and examined for purity of cell morphology. When the purity of the isolates was assured, they were inoculated into differential media (Figure 2), incubated at 25°C, and examined daily for six days. The pattern of biochemical reactions for each colony type was compared with those listed in Bergey's Manual (1974), and names were assigned.

To determine the bacterial flora of the carbon granules used to fill the filter columns, a 250 ml volume of new carbon granules in 500 ml sterile, buffered, deionized water was shaken for one hour and then allowed to settle. Two hundred ml of the rinse water was passed through each of two membranes, which were then placed on TGE and Endo's media.

When it became apparent that large numbers of bacteria were being generated in the granulated activated carbon columns, it was necessary to determine the effect of rechlorination of the effluent to control this bacterial growth. One-liter samples of

effluent from the end of the series of columns (10 feet of granulated activated carbon) were collected and treated as follows:

- 1) effluent plated on primary media following membrane filtration;
- 2) effluent plus 3 ppm chlorine plated after one hour contact time;
- 3) effluent plus 3 ppm chlorine aged for two days before plating to simulate residence time of water in a distribution system with the possibility of depletion of residual chlorine;
- 4) effluent plus 10 ppm chlorine aged for six days to simulate a condition of overabundance of chlorine, assured residual chlorine, and a lengthy residence time in a distribution system.

RESULTS

Table 2 lists the numbers of different kinds of microorganisms isolated from raw and finished water from the treatment plant prior to sampling the GAC columns. Table 3 gives total colony counts on the different primary media obtained from raw, finished, and filtered water samples on 11/21/77 after the GAC columns had been in use for 19 days. Counts are reported for 100 ml of filtered sample because the low numbers of bacteria isolated would result in fractional values if they were expressed per ml as Standard Methods (APHA, AWWA, WPCF 1975) specifies. No bacteria were isolated from water in which new carbon granules had been shaken. Table 4 lists all the different colonies picked for identification, shows the primary medium and system location where each colony was found, and the colony number assigned for reference during the identification process. Table 5 is a list of groups of colonies with similar biochemical reactions that resulted from growth in differential media. Table 6 lists the different identified organisms and their population size in raw and finished water and column effluents. Values given in Table 6 are the counts obtained from the most favorable medium. Each medium favors a different population of microorganisms and no single medium can yield an accurate estimate of population size.

Table 7 gives total counts on different primary media obtained from raw, finished, and effluent samples taken on 12/5/77. Table 8 is the initial description of colonies isolated from samples taken on 12/5/77. The original 11 colonies were mixed cultures; they were streaked on agar plates to separate the cohabitants, and resulted in 29 colonies that were subjected to identification procedures. Table 9 shows the identification process, including colony number assigned during the identification process, colony description, identity, and population size in each part of the GAC system. Table 10 shows the numbers of identified organisms isolated from samples taken on 12/5/77 in each part of the GAC system. Table 11 is the initial description of colonies isolated from samples taken on 1/6/78, their numbers and location in the GAC system. Table 12 shows the number of identified organisms isolated on 1/6/78 from each part of the GAC system.

Group (genus) names only were assigned in the tables showing organism identification (Tables 6, 10, 12) as many of the organisms isolated fit no single taxonomic category with the

diagnostic tests used. Where species epithets are used in the tables, identification is reasonably certain. Several organisms were identified to genus only and some to group; e.g., "Pseudomonas-like," "pseudomonad," and Alcaligenes-like."

Orange colonies that constituted a majority of the population on 12/5/77 (Table 8) and a large proportion of the population on 1/6/78 (Table 12), were composed of Flavobacterium sp. (red colonies) and Enterobacter agglomerans (yellow colonies). The orange colonies were streaked repeatedly to separate the cohabitants in order to identify them. The values given for population size of each of these two organisms is the same as the number of orange colonies that they originally formed. Enterobacter agglomerans also appeared by itself.

Results of one test for regeneration of chlorine resistant bacteria are given in Tables 17, 18, and 19. Table 17 shows residual total and free chlorine concentrations after a one-hour contact time, two days aging, and six days aging of rechlorinated column effluent. Table 18 is a descriptive list of colonies isolated from unchlorinated and chlorinated column effluent samples. Table 19 shows the distribution of identified organisms.

DISCUSSION

Organisms found in the effluent from GAC columns (Tables 6, 10, and 12) are those normal to raw water sources and finished water degraded by standing in distribution systems as described by Geldreich (1973). The bacteria survived the treatment plant process and colonized the initially bacteria-free activated carbon granules. Their numbers in raw water and in treated drinking water are often too few to detect when relatively small volumes (100-200 ml) of water are examined by membrane filter techniques (Tables 3, 6, 7, and 12), but they multiply on the carbon granules in the columns and many then slough off into the water stream. Some of the organisms isolated may have health significance because of kind and/or number (Geldreich 1973, Wallis 1974). Pseudomonas aeruginosa, a possible health threat (Hoadley 1977), was present in numbers too few to be detected in raw and finished water, but multiplied to give counts of 25 per 100 ml of column effluent on 11/21/77 (Table 6). Whether this concentration constitutes an infectious dose to people would depend on the circumstances of exposure. Other Pseudomonas species that may have clinical significance (von Graevenitz and Grehn 1977) are present in greater numbers (120/100 ml sample on 11/21/77). Acinetobacter, Alcaligenes, Moraxella, Flavobacterium and Enterobacter, which constituted a great part of the population in column effluent on 11/21/77, with more than one million colonies per 100 ml of sample, were present in raw and finished water in small numbers when 100-200 ml samples were filtered (Table 14).

Population size in each column and in raw water is not static. Although the total colony counts obtained from column effluents increased within 19 days after the columns were put into use (11/1/77 to 11/21/77), counts in those columns decreased in the following 14 days (Table 13). Klotz et al. (1976) reported a rapid increase in bacterial populations followed by a decline to a lower and stable level in carbon beds they studied. They suggested that the decrease in bacterial numbers may have been due to an increase in numbers of bacteria that do not contribute to the plate count. This may be more a reflection of culture technique that favor some portion of the population than an actual shift in proportion of the population held by any one species in the population.

The decrease in bacterial numbers (Table 13) from 11/21/77 to 12/5/77 occurred when sampling was done four days after back-

flushing of the columns. Backflushing during this period was routinely done twice a week. As time passed, backflushing became impossible because of formation of bacterial slime in the carbon columns. The columns were last backflushed on 12/8/77. Increased numbers of bacteria were isolated from samples collected on 1/6/78 when backflushing had not been done for 29 days prior to sampling. It has been assumed that backflushing only removed surficial deposits of calcium carbonate; its effect, if any, on the resident bacterial culture is unknown.

The populations sampled on different dates were not composed of the same organisms (Table 14). There was an apparent increase in population size with increasing length of carbon bed, but the organisms isolated from samples at different points along the length of the bed were not always the same (Table 15). Klotz et al. (1976) stated that changes in the bacterial population composition of the raw water influences the character of the bacterial populations in the carbon beds they studied. The bacterial composition of the raw water was not always the same as that of the GAC columns in this study (Table 15). In most cases the bacterial population composition in the GAC columns did change with time and with the bacterial composition of the raw water. Flavobacterium, Staphylococcus, Moraxella, Alcaligenes, Citrobacter, Klebsiella, Pseudomonas sp. were found in the effluents from the columns when they appeared in the raw water. Pseudomonas aeruginosa was found in raw water once on 11/2/77 and was always found in column effluent. Erwinia was found in column effluents, but not in raw water. Aeromonas was found in raw water, but not in column effluents. Enterobacter agglomerans was found in column effluents when it was not found in raw water on 12/5/77, but on 1/6/78 it was found in raw water as well as in column effluent. Enterobacter cloacae was found in raw water on 12/5/77 and on 1/6/78; it was found in column effluent on 12/5/77, but not on 1/6/78. Acinetobacter was found in raw water and in column effluents on 11/21/77. It was not found at all on 12/5/77. On 1/6/78 Acinetobacter was not found in raw water, but was present in column effluents. Raw water bacteria apparently do affect the composition of populations in the columns, and these resident bacteria apparently determine which of the incoming organisms can colonize and coexist with them. In most cases the bacteria count in raw water was smaller than in column effluent. Finished water had detectable bacteria only on 11/2/77 and 12/5/77 (Table 15).

The population size of Acinetobacter, Moraxella, Pseudomonas, Alcaligenes, Enterobacter agglomerans, and Flavobacterium increased with increasing bed length (from Column 1 to Column 4). This suggests that increasing distance from the point of chlorination may affect the numbers and kinds of bacteria able to colonize the carbon bed. Table 16 gives residual chlorine values in parts-per-million of water passed through the columns for the period of this study. Dates on which samples were taken for

bacterial analysis are shown inserted in Table 16. The finished water entering the first column had from 0.2 to 3.3 ppm free chlorine, which was taken up by the first column. Combined chlorine, however, passed through the first column in consistent quantities. The amount of combined chlorine entering the first column ranged from 0.5 to 3.2 ppm. Effluent from the first column, after the initial 10 days of negligible quantities (0.05 ppm), had from 0.15 to 0.20 ppm combined chlorine. The column retained from 0.3 to 3.0 ppm total chlorine, which may account for the lower bacteria counts in the effluent from Column 1. This suggests that combined chlorine may be used to control bacterial growth in carbon columns. Column 1 on occasion did have greater numbers of several bacteria species than subsequent columns; these were Staphylococcus on 12/5/77, Flavobacterium on 1/6/78, and Erwinia on 1/6/78 (Table 15).

The microorganisms exhibit succession of species as do most dynamic plant communities. The conditions supporting this succession have not yet been studied. It probably depends on overgrowth and death of a pioneer species, which supplies necessary metabolites for the succeeding species.

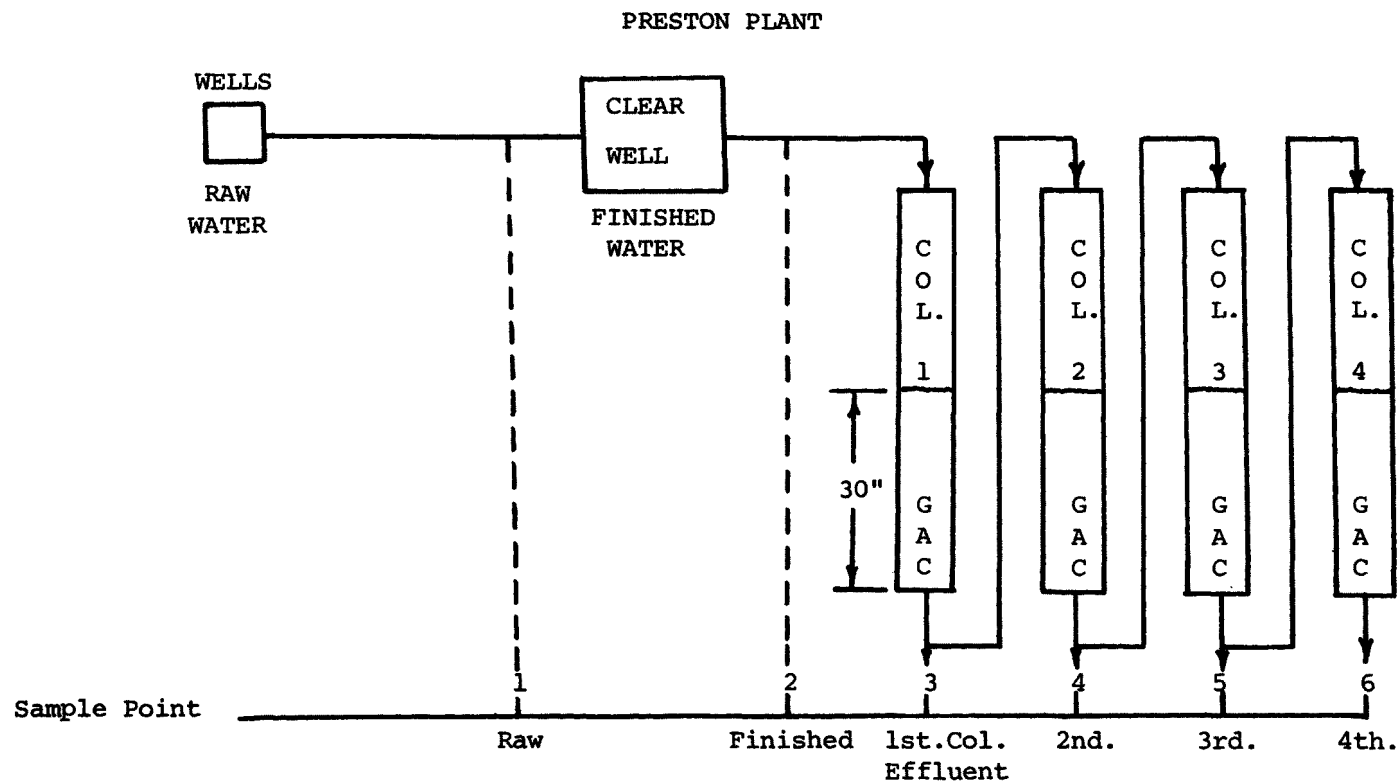
Only Enterobacter agglomerans was found in chlorinated column effluent (Table 19). Column effluent chlorinated to 3 ppm had its population of Enterobacter agglomerans greatly reduced within one hour. These regenerated within two days (300/100 ml sample), as residual chlorine was depleted within 24 hours (Table 17). Column effluent with 10 ppm chlorine added had 4.5 ppm free and 6.3 ppm total chlorine remaining at the end of six days (Table 17). Enterobacter agglomerans was found in this highly chlorinated effluent at the end of six days; however, only three were isolated from 100 ml of sample. The rechlorination experiment is being repeated to determine if the isolated colonies were indeed survivors or if they were merely contaminants. Additionally, a survival experiment is being done to determine if selection and adaptation is taking place in this species. In this experiment chlorinated finished water is seeded with organisms to give a concentration of about 10,000/ml. The suspension is held at room temperature (25°C) for various periods of time and filtered to isolate and enumerate the surviving bacteria.

Enterobacter agglomerans was not found in finished water during this study even though 200 ml volumes (twice the volume suggested by Standard Methods) were passed through membrane filters.

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Sampled:

11/2/77 Raw and Finished Water (Columns installed and flow begun)

11/21/77 All Points

12/5/77 " "

1/6/78 " "

Figure 1. Bench scale column adsorption unit (Experimental Design No. 4). Sampling points and date of sampling at each point are indicated.

TABLE 1. PRIMARY MEDIA AND DIAGNOSTIC TESTS USED TO ISOLATE AND IDENTIFY BACTERIA IN RAW, FINISHED, AND FILTERED WATER

<u>Primary media*</u>	
Endo's broth (Endos)	Pseudosal agar (Ps)
Desoxycholate lactose agar (DES)	Brain heart infusion broth (BHI)
Tryptone glucose yeast extract agar (TGE)	Czapeck agar (Cz)
<u>Diagnostic tests</u>	
Roche Oxiferm system	Hanging drop/motility
Gram stain	Motility agar
Triple Sugar Iron agar	Flagella stain
Oxidase	Casein digestion
Nitrate reduction	Catalase
Roche Enterotube system	Starch digestion

*TGE and Cz gave highest counts; other media used with poor results were Simmons citrate agar, potato dextrose agar, nutrient agar, PA agar, and milk agar.

TABLE 2 BACTERIAL POPULATION COUNTS (COLONIES/100ml SAMPLE) OBTAINED FROM RAW AND FINISHED WATER SAMPLES COLLECTED ON 11/2/77

Name	Raw	Finished
<u>Acinetobacter</u>	120	12
<u>Moraxella</u>	4	2
<u>Pseudomonas aeruginosa</u>	2	3
<u>Pseudomonas</u> sp. (other than <u>P. aeruginosa</u>)	22	0
<u>Penicillium</u>	0	85

TABLE 3. BACTERIAL POPULATION COUNTS (COLONIES/100ml SAMPLE) OBTAINED FROM SAMPLES OF RAW AND FINISHED WATER AND COLUMN EFFLUENTS COLLECTED ON 11/21/77

Medium	Raw	Finished	Col. 1	Col.2	Col.3	Col.4
TGE	96	0	972	10 ^{6*}	10 ^{6*}	10 ^{6*}
Endo's coliform	0	0	0	0	0	0
non-coliform	41	0	27	100	120	131
Ps	27	0	0	520	25	171
Cz	None was evident in 24, 48, 72 hours, but when growth developed in four to five days, the plates were overgrown with minute yellow colonies. Finished water had none.					
DES	58	0	92	208	420	240
BHI	62	0	120	480	640	483

*estimated by counting 10cm²

TABLE 4 . BACTERIAL POPULATION (COLONIES/100ml SAMPLE) OF RAW AND FINISHED WATER* AND COLUMN EFFLUENTS COLLECTED ON 11/21/77.

Colony type	Colony number	Colony group	Raw	Col. 1	Col. 2	Col. 3	Col. 4
<u>Endo's</u>							
2mm, dark red	1	2	37				
0.7mm, dark red	2	1	4			2	
<0.3mm, lt. red	3,6,7,8,9	11,13		27	100	120	111
2mm, lt. red	4,5	10					21
<u>DES</u>							
3mm, gray	10	6	4		2		
2mm, tan	11,13	3,4	54		80		2
2mm, black	12	10				1	25
<1mm, yellow	14	7		92	126	413	213
2mm, yellow	15	14				6	
<u>BHI</u>							
2mm, ivory	16	1	19			7	
1mm, yellow	17	7	43			10	
2mm, green	18	10					15
<1mm, dk. yellow	19	7			475	623	468
3mm, yellow	20	7			1		
3mm, white	21	7			4		
1mm, white	22	7		120			
<u>TGE</u>							
2mm, tan	23	8	28			7	
4mm, rough white	24	7	1				
3mm, yellow	24A	7	67				
2mm, green	25	10				1	24
<1mm, yellow	26	7		970	>10 ^{6**}	>10 ^{6**}	>10 ^{6**}
1mm, white	27	1		2			
<u>Ps</u>							
3mm, gray	28	12	2				
1mm, yellow	29	5	25				
1mm, green	30	10					11
<1mm, yellow	31	7			520	19	160
2mm, yellow	32	5				6	

*No growth was obtained from 200ml volumes of finished water on any medium.
Blanks opposite colony description indicate no growth.

**Estimated by counting 10cm²

TABLE 5 . GROUPING OF COLONIES WITH SIMILAR BIOCHEMICAL REACTIONS, ISOLATED FROM SAMPLES TAKEN 11/21/77

Group number	Identity	Includes colony number
1	<u>Acinetobacter</u>	2, 16, 27
2	<u>Aeromonas</u>	1, 2
3	<u>Alcaligenes</u>	13
4	<u>Citrobacter</u>	11
5	<u>Enterobacter</u>	29, 32
6	<u>Klebsiella</u>	10
7	<u>Moraxella-like</u>	14, 17, 19, 20, 21, 22, 24, 24A, 26, 31
8	<u>Pleisomonas</u>	23
9	<u>Proteus</u>	0
10	<u>Pseudomonas</u> <u>aeruginosa</u>	4, 5, 12, 18, 25, 30
11	<u>Pseudomonas</u> sp.	3, 6, 9
12	<u>Pseudomonas</u> <u>maltophila</u>	28
13	<u>Pseudomonas</u> <u>stutzeri</u>	7, 8
14	<u>Pseudomonas-like</u> group 5E-1	15

TABLE 6. DISTRIBUTION OF IDENTIFIED BACTERIA (COLONIES/100ml SAMPLE) ISOLATED FROM WATER SAMPLES TAKEN ON 11/21/77

Group name	Sample					
	Raw	Finished	Col. 1	Col. 2	Col. 3	Col. 4
<u>Acinetobacter</u>	19	0	2	1000	670	630
<u>Aeromonas</u>	37	0	0	0	0	0
<u>Alcaligenes</u>	54	0	0	80	0	2
<u>Citrobacter</u>	54	0	0	80	0	2
<u>Enterobacter</u> <u>agglomerans</u>	25	0	0	0	6	0
<u>Klebsiella</u>	4	0	0	2	0	0
<u>Moraxella</u>	67	0	970	>10 ⁶	>10 ⁶	>10 ⁶
<u>Pseudomonas</u> <u>aeruginosa</u>	0	0	0	0	1	25
<u>Pseudomonas</u> spp. (other than <u>Ps. aeruginosa</u>)	2	0	27	100	120	110

TABLE 7 BACTERIAL POPULATION COUNTS (COLONIES/100ml SAMPLE) OBTAINED FROM RAW AND FINISHED WATER AND COLUMN EFFLUENT SAMPLES COLLECTED ON 12/5/77

Medium	Sample					
	Raw	Finished	Col. 1	Col. 2	Col. 3	Col. 4
TGE	179	5	15,180	20,000	25,000	25,000
Endo's coliforms	0	0	0	0	0	0
Endo's noncoliform	10	0	0	0	0	8
Ps	3	0	0	0	4	17
Cz	40	0	2,100	8,160	6,950	8,880

TABLE 8. INITIAL DESCRIPTION OF COLONIES COUNTED AND
SELECTED FOR ISOLATION AND IDENTIFICATION
FROM SAMPLES TAKEN 12/5/77

Colony no.	Source sample	Primary medium	Colony description	Gram stains
1 a,b	1	TGE	2mm,yellow	G- mixed sizes
2	1	TGE	1mm,white	G+,staph
3 a,b,c	5	TGE	<.3mm,yellow	G- mixed?
4	5	TGE	5mm, light yellow	G-
5 5b	1	Endos	3mm red, mucoid	G- mixed sizes & shapes
6 a,b,c,d,e	1	Endos	5mm,light red, wrinkled	G- mixed sizes & shapes
7 a,b,c	1	Ps	3mm, cream-yellow	G- mixed sizes & shapes
7a (a) (b)	1	Ps	3mm, creamy, mucoid, stinks	G- mixed sizes & shapes
8 a,b	5	Ps	5mm, green	G- mixed sizes & shapes
8a (a) (b)	6	Ps	3mm, green soh., fruity odor	G- mixed sizes & shapes
9 a,c	1	Cz	3-5mm, white	G- mixed sizes & shapes
10 a,b,c	6	TGE	3-5mm, (greenish, yellow)	G- mixed sizes & shapes
11 a,b, 12,13,14	6	TGE	<.3mm yellow	mixed sizes & shapes
Tiny Orange= Yellow + Red	6	Cz	<.3mm orange, developed 6 days after plating	mixed sizes & shapes

*Colony numbers followed by letters were suspected of being composed of more than one species when the Gram stain was examined. They were streaked on TGE and SMA to effect separation and subcultures were made of several isolated colonies.

TABLE 9. POPULATION DISTRIBUTION (COLONIES/100ml SAMPLE)* AND COLONIES SELECTED FOR ISOLATION AND IDENTIFICATION FROM SAMPLES TAKEN 12/5/77

Colony old no.	Includes new no.	Sample source	Colony description	Identity	Raw	Fin.	Col. 1	Col. 2	Col. 3	Col. 4
<u>TGE</u> 1	1	Raw	2mm,yellow	Group, 2K-1	14	2				
2	2	Raw	3mm,white	<u>Pseu.-like</u>						
3	3a 3b 3c	Col.3	3mm,yellow-green	<u>Staph. (saprophyticus)</u>	144	3	180 15,000	30 20,000	40 25,000	60 25,000
4	4	Col.3	3mm,yellow-green	<u>Enterobacter agglomerans</u>						
				<u>Ps.aeruginosa</u>					1	3
<u>Endo's</u>										
5	5a 5b	Raw	3mm,lt.red	<u>Ps.putida</u>	4					
6	6a 6b	Col.4	2mm,med.red	<u>Ent.cloacae</u>						
				<u>Serratia marcescens</u>	6					8
<u>Ps</u> 7	7 (SMA) 8 (7TSM) 9 (7A)	Col.3	2mm,white	<u>Alcaligenes faecalis</u>					3	
				<u>Enterobacter cloacae</u>						
				<u>Enterobacter cloacae</u>						
8	10 (a&b) 11	Col.3	3mm,green	<u>Pseudomonas aeruginosa</u>					1	17
<u>Cz</u> 9	12	Raw	2mm,white	<u>Ps.cepacia</u>						
10	13	Col.4	3-5mm,green	<u>Enterbacter cloacae</u>	40	1	3			
11	14	Col.4	<0.3mm, yellow	<u>Ps.aeruginosa</u>						3
				<u>Enterobacter agglomerans</u>			8	57	250	380
<u>Tiny Orange</u> (6 days later) yellow red		Col.4	<1mm,orange	<u>Enterobacter agglomerans</u>			2,140	8,100	6,000	8,500
				<u>Flavobacterium (aquatile)</u>						

*Blank spaces indicate none was isolated

TABLE 10. BACTERIAL POPULATION DISTRIBUTION (COLONIES/100ml)
SAMPLE OF ALL ORGANISMS ISOLATED FROM RAW AND
FINISHED WATER AND COLUMN EFFLUENTS COLLECTED ON
12/5/77

Group name/specie*	Raw	Finished	Col. 1	Col. 2	Col. 3	Col. 4
<u>Alcaligenes faecalis</u>					3	
<u>Enterobacter agglomerans</u>			15,000	20,000	25,000	25,000
<u>Enterobacter cloacae</u>	40		1	3	3	
<u>Pseudomonas aeruginosa</u>					1	17
<u>Pseudomonas cepacia</u>					1	17
<u>P. putida</u>	4					
<u>Pseudomonas-like, Group 2K-1</u>	14	2				
<u>Serratia marcescens</u>	6					8
<u>Staphylococcus (saprophyticus)</u>	144	3	180	30	30	60
<u>Flavobacterium (aquatile)</u>	20		2,140	8,100	6,700	8,500

*Species names given are accurate within the limits of the Roche system and additional media and tests listed in Table 1.
Blank spaces in columns opposite organism name indicates none was isolated.

TABLE 11. INITIAL DESCRIPTION OF COLONIES COUNTED AND SELECTED FOR ISOLATION AND IDENTIFICATION ON 1/6/78

Colony number	Colony description	Sample source	Primary med. (vol.)	Colonies isolated/100 sample					
				Raw	Fin.*	Col. 1	Col. 2	Col. 3	Col. 4
1	3mm, light red	Raw water	Endos (10)	5					
2	3mm, rose beige	"	TGE (100)	20					
3	1mm, yellow	"	TGE (10)	780					
4	1mm, white	"	TGE (10)	100					
5	4mm, white	"	Cz (100)	100					
6	1mm, yellow	Column 1	TGE (10)			60,000			
7	<1mm, white	Column 1	TGE (10)			3,000			
8	3mm, white	Column 2	TGE (10)				2,800	2,600	
9	<1mm, yellow	Column 2	TGE (10)				400		
10	<1mm, white	Column 2	TGE (10)				70,800		
11	<1mm, yellow	Column 3	TGE (10)					2,040	
12	<1mm, white	Column 3	TGE (10)					80,000	
13	3mm, greenish yellow	Column 4	Ps (10)						2
14	1mm, yellow	Column 4	TGE (10)						1,500
15	3mm, white	Column 4	TGE (10)						1
16	1mm, yellow	Column 4	TGE (10)						1,500
17	1mm, white	Column 4	TGE (10)						850,000
18	<1mm, yellow	Column 4	Cz (100)						42
19	<1mm, white	Column 4	Cz (100)						41
20	Tiny orange	Column 4	Cz (10)	{ 10Cz 90TGE		1,730	910	610	8,000
21	Cream color (white?)	Column 2	TGE (10)				300		

*No growth was obtained from finished water. Blank spaces opposite colony descriptions indicate no growth

TABLE 12 . POPULATION DISTRIBUTION (COLONIES/100ml SAMPLE)* OF ALL ORGANISMS ISOLATED FROM RAW AND FINISHED WATER COLUMN EFFLUENTS TAKEN ON 1/6/78

Organism isolated	Raw	Finished	Col. 1	Col. 2	Col. 3	Col. 4
<u>Enterobacter agglomerans</u>	780		1,730	910	610	8,000
<u>Enterobacter cloacae</u>	100					
<u>Acinetobacter</u>				2,800	80,000	850,000
<u>Erwina (stewartii)</u>			60,000		2,040	
<u>Pseudomonas aeruginosa</u>						2
Group, 5A-2, <u>Pseudomonas-like</u>			3,000	70,800		
<u>Pseudomonas (syringae)</u>	20					
<u>Flavobacterium</u> <u>(aquatile)</u>	90		1,730	910	610	8,000

*Blank spaces opposite organism name indicates none was isolated.

TABLE 13 BACTERIAL POPULATION (COLONIES/100ml SAMPLE) GROWN ON MOST FAVORABLE MEDIUM IN EACH COLUMN EFFLUENT, RAW, AND FINISHED WATER (TOTALS OF TABLES 2, 6, 12)

Sample date	Raw	Finished	Col. 1	Col. 2	Col. 3	Col. 4
11/2/77	148	17 (+85 moulds)	a	a	a	a
11/21/77	96	0	999	>10 ⁶	>10 ⁶	>10 ⁶
12/5/77	179	5	15,180	20,000	25,000	25,000
1/6/78 ^b	990	0	66,460	75,820	83,260	866,000

^a No growth was obtained from 200ml of water taken from 500ml water shaken for one hour with a 250ml volume of dry unused carbon granules.

^b Backflushed 30 days prior to sampling. Other samples were taken four days after backflushing.

TABLE 14 . BACTERIAL POPULATION (COLONIES/100ml SAMPLE) OF THE SAMPLE POINT GIVING THE HIGHEST VALUE FOR THE LISTED SPECIES ON THE DIFFERENT SAMPLE DATES COMPARED WITH POPULATION OF INCOMING RAW WATER*

Organism	Date sampled			
	11/2/77	11/21/77	12/5/77	1/6/78
<u>Acinetobacter</u>	(120) 12	(90) 1,000		(0) 850,000
<u>Moraxella</u>	(4) 2	(67) $>10^6$		
<u>Ps. aeruginosa</u>	(2) 3	(0) 25	(0) 17	(0) 2
<u>Pseudomonas sp.</u>	(22) 0	(2) 120	(4) 0	(20) 0
<u>Penicillium</u>	(0) 85			
<u>Aeromonas</u>		(37) 0		
<u>Alcaligenes</u>		(54) 80	(0) 3	
<u>Citrobacter</u>		(54) 80		
<u>Klebsiella</u>		(4) 2		
<u>Enterobacter agglomerans</u>		(25) 6	(0) 25,000	(780) 8,000
<u>Enterobacter cloacae</u>			(40) 3	(100) 0
<u>Pseudomonas-like</u>			(14) 3	(0) 70,000
<u>Serratia marcescens</u>			(6) 8	
<u>Staphylococcus</u>			(144) 180	
<u>Flavobacterium</u>			(20) 8,500	(90) 8,000
<u>Erwinia</u>				(0) 60,000

*Raw water values given in parentheses

TABLE 15. DISTRIBUTION OF ORGANISMS ISOLATED FROM
COLUMN EFFLUENTS

Organism	S a m p l e	Sample date			
		11/2/77	11/21/77	12/5/77	1/6/78
<u>Acinetobacter</u>	R	120 (12) *	19	0	0
	1	-	2	0	0
	2	-	1000	0	2800
	3	-	670	0	80,000
	4	-	630	0	850,000
<u>Moraxella</u>	R	4 (2) *	67	0	0
	1	1	970	0	0
	2	-	>10 ⁶	0	0
	3	-	>10 ⁶	0	0
	4	-	>10 ⁶	0	0
<u>Pseudomonas aeruginosa</u>	R	2 (3) *	0	0	0
	1	-	0	0	0
	2	-	0	0	0
	3	-	1	1	0
	4	-	25	17	2
<u>Pseudomonas species</u>	R	22 (0) *	2	4	20
	1	-	27	0	0
	2	-	100	0	0
	3	-	120	1	0
	4	-	110	17	0
<u>Aeromonas</u>	R	0	37	0	0
	1	-	0	0	0
	2	-	0	0	0
	3	-	0	0	0
	4	-	0	0	0
<u>Alcaligenes</u>	R	0	54	0	0
	1	-	0	0	0
	2	-	80	0	0
	3	-	0	3	0
	4	-	2	0	0
<u>Citrobacter</u>	R	0	54	0	0
	1	-	0	0	0
	2	-	80	0	0
	3	-	0	0	0
	4	-	2	0	0

(continued)

TABLE 15. (continued)

<u>Organism</u>	S a m p l e	Sample date			
		11/2/77	11/21/77	12/5/77	1/6/78
<u>Klebsiella</u>	R	0	4	0	0
	1	-	0	0	0
	2	-	2	0	0
	3	-	0	0	0
	4	-	0	0	0
<u>Enterobacter</u>	R	0	25	0	780
<u>agglomerans</u>	1	-	0	15,000	1730†
	2	-	0	20,000	910
	3	-	6	25,000	610
	4	-	0	25,000	8000
<u>Enterobacter</u>	R	0	0	40	100
<u>cloacae</u>	1	-	0	1	0
	2	-	0	3	0
	3	-	0	3	0
	4	-	0	0	0
<u>Pseudomonas-like</u>	R	0	0	14(2)*	0
	1	-	0	0	3000
	2	-	0	0	70,800
	3	-	0	0	0
	4	-	0	0	0
<u>Serratia</u>	R	0	0	6	0
<u>marcescens</u>	1	-	0	0	0
	2	-	0	0	0
	3	-	0	0	0
	4	-	0	8	0
<u>Staphylococcus</u>	R	0	0	144(3)*	0
	1	-	0	180 †	0
	2	-	0	30	0
	3	-	0	40	0
	4	-	0	60	0
<u>Flavobacterium</u>	R	0	0	20	90
	1	-	0	2140	1730†
	2	-	0	8100	910
	3	-	0	6700	610
	4	-	0	8500	8000

(continued)

TABLE 15. (continued)

<u>Organism</u>	S a m p l e	Sample date			
		11/2/77	11/21/77	12/5/77	1/6/78
<u>Erwinia stewarti</u>	R	0	0	0	0
	1	-	0	0	60,000†
	2	0	0	0	0
	3	-	0	0	2040
	4	-	0	0	0

*Values in parentheses are for finished water, all other values for finished water were less than 1. Zero values indicate less than 1, - indicates not done, R = raw water, 1 through 4 are column numbers.

†Column 1 effluent had higher counts than following columns.

TABLE 16. CONCENTRATIONS OF RESIDUAL FREE AND TOTAL CHLORINE IN FINISHED WATER AND COLUMN EFFLUENT FOR THE STUDY PERIOD

Date	11 Finish		19 Col. 1		21 Col. 2		23 Col. 3		25 Col. 4		17 M. Lakes	
	Free	Total	Free	Total	Free	Total	Free	Total	Free	Total	Free	Total
11/1/77 ^a	2.25	3.25	0	0.05	0	0.05	0	0.05	0	0.05		
11/2/77 ^b												
11/3											0.10	0.55
11/4	1.60	2.30	0	0.05	0	0.05	0		0	0.05		
11/7 ^a												
11/8	1.80	2.60	0	0.05	0	0.05	0	0.05	0	0.05		
11/10 ^a											0.05	0.50
11/11	1.60	2.40	0	0.10	0	0.05	0	0.05	0	0.05		
11/14												
11/15	1.20	2.10	0	0.10	0	0.05	0	0.05	0	0.05		
11/17 ^a											0.05	0.40
11/18	2.00	2.65	0	0.10	0	0.05	0	0.05	0	0.05		
11/21 ^b												
11/25	1.35	1.85	0	0.15	0	0.05	0	0.05	0	0.05		
11/29	1.75	2.40	0	0.15	0	0.05	0	0.05	0	0.05		

(continued)

TABLE 16. (continued)

Date	11 Finish		19 Col. 1		21 Col. 2		23 Col. 3		25 Col. 4		17 M. Lakes	
	Free	Total	Free	Total	Free	Total	Free	Total	Free	Total	Free	Total
12/1 ^a											0.05	0.45
12/2	2.00	2.65	0	0.15	0	0.05	0	0.05	0	0.05		
12/5 ^b	1.90	2.50	0	0.20	0	0.05	0	0.05	0	0.05		
12/8 ^a											0.10	0.50
12/9	1.40	2.10	0	0.20	0	0.05	0	0.05	0	0.05		
12/13	1.95	2.40	0	0.15	0	0.05	0	0.05	0	0.05		
12/15											.05	.40
12/16	1.70	2.10	0	0.15	0	0.05	0	.05	0	.05		
12/20	3.30	6.55	0	0.15	0	.05	0	.05	0	.05		
12/22											.05	.50
12/23	2.40	2.90	0	.20	0	.05	0	.05	0	.05		
12/27/77	0.20	2.70	0	0.15	0	0.05	0	0.05	0	.05		
1/6 ^b												

^aBackflushed columns^bSamples taken for bacterial analysis

TABLE 17 . RESIDUAL FREE AND TOTAL CHLORINE CONCENTRATIONS
IN GAC COLUMN EFFLUENT AFTER AGING

Sample	Rechlorination concentration	Age of sample (Contact time)	Chlorine, ppm	
			Free	Total
Col. 4 effluent	3ppm	24 hours	0.05	0.2
Col. 4 effluent	3ppm	48 hours	0.05	0.3
Col. 4 effluent	10ppm	6 days	4.5	6.3

TABLE 18. INITIAL COLONY DESCRIPTION AND IDENTITY OF BACTERIAL ISOLATES FROM RECHLORINATED, AGED GAC COLUMN EFFLUENT

Medium	Colony number	Sample*	Colony description	Colonies/ 100ml sample	Identity
Endo's	E1	4+0 (0)	3mm, white, moist	2	<u>Acinetobacter</u>
Endo's	E2	4+0 (0)	2mm, red, domed	3	<u>Pseudomonas-like</u>
Endo's	E3	4+0 (0)	2mm, white/halo	2	<u>Pseudomonas-like</u>
Endo's	E4	4+0 (0)	<0.3mm, red	1,500	<u>Moraxella</u>
Endo's	4	4+2 (3)	2mm, red	2	<u>Enterobacter agglomerans</u>
TGE	1	4+0 (0) 4+3 (3) 4+6 (10)	<1mm, yellow	20,000	<u>E. agglomerans</u>
TGE	2	duplicate of 1			<u>E. agglomerans</u>
TGE	3	4+2 (3) 4+6 (10)	<1mm, yellow	5	<u>E. agglomerans</u>
TGE	5	4+0 (3)	<1mm, yellow	1	<u>E. agglomerans</u>
TGE	6	4+0 (0)	1mm, orange	39,000	<u>E. agglomerans</u>
TGE	10	4+0 (0)	<1mm, white	48,000	<u>Moraxella</u>
TGE	11	4+0 (0)	1mm, orange	(like 6)	<u>E. agglomerans</u>
Cz	7	4+0 (0) 4+0 (3) 4+2 (3) 4+6 (10)	1mm, yellow	3,600	<u>E. agglomerans</u>
Cz	8	4+0 (3)	1mm, orange	16,800	<u>E. agglomerans</u>
Cz	9	4+0 (0)	1mm, white	600	<u>Acinetobacter</u>

*4+0 (0) = Column 4 effluent, no chlorine added, analyzed one hour after collection; 4+0 (3) = Column 4 effluent with 3ppm chlorine added, analyzed one hour after collection; 4+2 (3) = Column 4 effluent with 3ppm chlorine added, aged 2 days before analysis; 4+6 (10) = Column 4 effluent with 10ppm chlorine added, aged 6 days before analysis.

TABLE 19 . BACTERIAL POPULATION (COLONIES/100 ml SAMPLE) OF GAC COLUMN EFFLUENT CHLORINATED AND AGED TO SIMULATE DISTRIBUTION SYSTEM CONDITIONS

Organism	Sample			
	4+0 ^a (0)	4+0 ^b (3ppm)	4+2 ^c (3ppm)	4+6 ^d (10ppm)
<u>Acinetobacter</u> (lwoffi)	600	0	0	0
<u>Enterobacter</u> <u>agglomerans</u> ^e	59,000	4	300	3
<u>Moraxella</u>	48,000	0	0	0
<u>Pseudomonas-like</u>	5	0	0	0

^aEffluent from Column 4, no chlorine added, analyzed one hour after collection.

^bEffluent from Column 4, 3ppm chlorine added, analyzed one hour after collection.

^cEffluent from Column 4, 3ppm chlorine added, aged 2 days before analysis.

^dEffluent from Column 4, 10ppm chlorine added, aged 6 days before analysis.

^eMore than one-half (55,800) of the colonies identified as Enterobacter agglomerans were orange. Previously orange colonies yielded Flavobacterium sp. as well, but Flavobacterium was not isolated from orange colonies that developed from these samples.

CHLORINATION OF GRANULATED ACTIVATED CARBON (GAC)
COLUMN EFFLUENT TO CONTROL BACTERIA
(Part II)

by

Frances Parsons
Drinking Water Quality Research Center
Florida International University
Tamiami Campus
Miami, Florida

ABSTRACT

Granulated activated carbon (GAC) columns used in water treatment produce effluents with bacteria counts up to 10,000/ml. A cursory examination was made of the effect of chlorination of effluents on these bacteria. Samples of GAC column effluent chlorinated to 3 ppm and 10 ppm were held at 25°C and plated at two-day intervals for six days to test for survival and regrowth of bacteria. At 3 ppm, chlorine killed most of the bacteria (none recovered initially) and controlled regrowth to less than 500/ml for up to five days. When the 3 ppm chlorine initially added to GAC column effluent was depleted during aging for six days, bacterial regrowth reached 36,000/ml or greater than half that of six-day-old unchlorinated GAC column effluent, which was 62,000/ml. When GAC column effluent had 10 ppm chlorine added, residual free chlorine was 3 ppm throughout the aging period (1.0 ppm in one sample on the sixth day), and no bacteria were recovered.

Finished water to which 8,000 bacteria per ml and 10 ppm chlorine was added, which retained 3 ppm residual free chlorine, had three colonies per ml after six days. Finished water to which 8300 bacteria per ml and 10 ppm chlorine was added, which had less than 0.4 ppm residual free chlorine, had 83,000 colonies per ml after five days aging.

CONCLUSION

Chlorination of the effluent from granulated activated carbon (GAC) columns apparently kills bacteria that grow on the carbon granules and slough off into the effluent, but the initial dose of chlorine must be adequate to combine with the bacteria and leave sufficient free chlorine to prevent regrowth. The concentration of chlorine necessary would vary with the bacterial biomass and chlorine demand due to all constituents of the water.

This study was of a cursory nature and was only intended to suggest a more complete study. Shorter sampling intervals (daily), for a period of time longer than six days (end point determination), with more than these two concentrations (especially less than 3 ppm free chlorine) of several disinfectants (chlorine, chloramines, chlorine dioxide, ozone, ferrates) should be examined. Certainly the minimum level of chlorine needed and the time that it is effective for several bacterial population sizes should be determined. All of these factors; i.e., dose size, contact time, regrowth rate and size and composition of the bacterial population should be studied and compared with parallel determinations of the bacteriology of the distribution system.

INTRODUCTION

Granulated activated carbon (GAC) columns used to remove organic substances from water are colonized by bacteria that survive water treatment plant processes. Large populations of these bacteria develop on the carbon granules and slough off into the water flowing through them. Some of these bacterial populations have been characterized (Parsons 1978). In an attempt to find a way to control bacterial numbers, GAC column effluent was chlorinated and analyzed for bacterial survivors and for regrowth

Finding Enterobacter agglomerans in highly chlorinated (10 ppm) GAC column effluent prompted this study to determine if the few colonies isolated represented selection of a resistant strain or survived because of protection offered by cell aggregation or slime.

METHODS AND MATERIALS

The following samples were taken from the water treatment plant and from the bench scale model GAC system described earlier (Wood et al. 1979):

Finished water (containing 3 mg/l chlorine)	referred to as: Finished
Column 4 effluent (with no added chlorine)	referred to as: Column 4 (0)
Column 4 effluent (with 3 mg/l chlorine added)	referred to as: Column 4 (3)
Column 4 effluent (with 10 mg/l chlorine added)	referred to as: Column 4 (10)
Finished water (with 10 mg/l chlorine added) (bacteria were added to this sample in the laboratory)	referred to as: Finished Water + Bacteria (10)

The samples were taken to the laboratory where bacteria were added to the sample of finished water containing 10 mg/l chlorine to give a concentration of approximately 10,000 cells per ml. A culture of Enterobacter agglomerans isolated from chlorinated Column 4 effluent was used to seed the chlorinated (10 ppm) finished water on 2/2/78. An Acinetobacter isolated from the 2/2/78 samples was used on 2/17/78 when the experiment was repeated. Chlorine contact time for this sample was approximately ten minutes as plating was begun shortly after addition of the bacteria to the water. The time interval (contact time) for the other samples on 2/2/78 was approximately three hours after collection. The remainders of the samples, after initial plating, were stored at room temperature (25°C) to simulate conditions in a distribution system, and plated for bacteria at intervals during the following six days. The samples were aged to determine bacterial regrowth potential of chlorinated GAC column effluent.

Enumeration and isolation of bacteria from the water samples were done by the membrane filter technique (APHA 1976). Volumes from 0.01 to 200 ml were passed through Gelman GN6 (0.45 µm pore size) filter membranes, which were then placed on tryptone glucose extract (TGE) agar in petri dishes. Volumes less than 100

ml were diluted with 100 ml sterile, buffered, glass-distilled water to assure uniform distribution of the organisms on the surface of the membrane. The cultures were incubated at 25°C and examined daily. Cumulative colony counts were made daily for six days of all different types of colonies observed. Different colony types were described, assigned numbers, and picked for identification. The API system (Analytab Products, Division of Ayerst Laboratories, Inc., Plainview, NY), and supplementary media and tests (Parsons 1978) were used in identification. Gram positive cocci were planted in glucose OF medium. Staphylococci were tested for coagulase.

Residual chlorine was determined at the time of plating using a Taylor Basic 2000 test kit (DPD).

RESULTS

Table 1 is a summary table of total bacteria counts obtained from samples taken on 2/2/78. Concentrations of residual free chlorine are also given. The distribution of the different kinds of bacteria isolated in the samples is shown in Table 2. Table 3 lists the original colony description, the sample from which it was isolated, the estimated population size, and the identity of the bacterial isolates from samples taken 2/2/78.

Table 4 is a summary table of bacteria counts and free chlorine concentrations for samples taken 2/17/78. Table 5 shows the different kinds of bacteria isolated and the sample from which they came. Table 6 is a list of colonies, with their description, chosen for isolation. Their final identity is also given.

Comparison of large numbers and small numbers precludes uniform rounding. Small numbers (less than 100) are not rounded; large ones are.

DISCUSSION

Three mg/l added chlorine was sufficient to reduce the bacteria count in Column 4(3) effluent to the level found in treatment plant Finished Water when both were plated shortly after chlorination. Table 1 shows that both samples had 0 colonies per ml isolated on 2/2/78. Table 4 shows that Finished Water had one colony per ml and Column 4(3) effluent had none on 2/17/78. After four days aging of the samples taken on 2/2/78, Column 4(3) had 330 colonies per ml and Finished Water had 22 colonies per ml. After five days aging of samples taken on 2/17/78, Column 4(3) effluent had 250 colonies per ml and Finished Water had four colonies per ml. These numbers have little health significance as there is no standard for noncoliform bacteria, but do indicate regrowth potential when chlorine is depleted by initially high bacteria counts. The initial bacteria counts for Column 4 effluent with no added chlorine, 4(0), were 1100 colonies per ml on 2/2/78 (Table 1) and 8300 on 2/17/78 (Table 4).

On 2/2/78 Column 4 effluent with 3 ppm chlorine added initially had less than 0.4 mg/l free chlorine three hours later when initial plating was done. Finished water, which had 3 ppm chlorine added by the treatment plant process, had 0.5 mg/l (Table 1). At four days age, Column 4(3) had ten times more bacteria than finished water, but the count was only 330/ml (Table 1). On 2/17/78 when finished water had less than 0.4 mg/l free chlorine at the time of initial plating, it had a higher bacterial count (though still a small number: 42/ml) at the end of three days age than did Column 4(3) effluent (Table 4). Column 4 effluent without added chlorine had high counts (83,000/ml) initially that became larger (120,000/ml) with aging. When the concentration of chlorine added to Column 4 effluent was increased to 10 ppm, it effectively killed bacteria; one per ml was recovered after a contact time of 3 hours, none after six days aging. There was sufficient chlorine at this level (10 ppm) to sustain a residual of 1 ppm at the end of six days after sample preparation on 2/2/78 (Table 1). Only one colony was recovered from this sample initially. Chlorine residual was 3 ppm at the end of five days after sample preparation on 2/16/78 (Table 4). No bacteria were recovered from this sample. No attempt was made to determine the products formed by the action of chlorine on bacteria.

Bacteria added to finished water (Finished Water + Bacteria

(10) to determine if chlorine-resistant bacteria were developing in GAC columns bathed in chlorinated finished water were effectively controlled when 3 ppm residual free chlorine was present. Three colonies/ml were recovered after six days (Table 1). When free chlorine was initially depleted in column effluent rechlorinated to 10 ppm on 2/17/78, regrowth occurred and reached 83,000 colonies per ml in five days (Table 4).

Staphylococcus sp. and Acinetobacter sp. grew in Finished Water + Bacteria (10) although only Enterobacter agglomerans was added to the sample (Tables 2, 3), which suggests that these organisms, survivors of the treatment plant processes, survived the subsequent rechlorination to 10 ppm because the added Enterobacter agglomerans cells (approximately 10,000 cells/ml were added to the Finished Water) combined with and depleted the available free chlorine in the sample. On 2/17/78 only Acinetobacter sp. was added to the Finished Water + Bacteria (10) sample and only Acinetobacter sp. was recovered (Tables 5, 6).

Bacteria in GAC column effluent could deplete chlorine, which in turn could allow pathogenic survivors of the treatment process to grow in the distribution system.

The results do not follow uniform patterns. Cell aggregates examined briefly by microscope, make it exceedingly difficult to obtain ten-fold counts from Log₁₀ dilutions.

There seems to be a tendency among water bacteria to form mixed-culture colonies that appear well isolated on solid medium and for them to have similar cellular morphologies. For example, colonies that first appear as small, white, and entire become yellow after two or three days. Staining only discloses Gram-negative rods of sizes and shapes within the range of individual variability. When diagnostic media are inoculated, the results often indicate a mixed culture. Upon re-isolation by streaking from a diagnostic medium and from the original colony, a mixed culture often results. Succession of species, as often occurs in higher plants, is suspected.

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TABLE 1. BACTERIAL POPULATIONS (COLONIES ISOLATED/ml SAMPLE) OBTAINED IN SAMPLES OF FINISHED WATER AND GRANULATED ACTIVATED CARBON (GAC) COLUMN EFFLUENT TREATED IN SEVERAL WAYS. SAMPLES TAKEN 2/2/78

	Finished water (3) ^a	4 (3)	4 (10)	Bact. + fin. (10) ^c	4 (0)
<u>Initial^b</u>					
Residual Cl ₂ ^d	0.5	<0.4	3	3	0
Colonies/ml	0	0	1	8000	1100
<u>2 days</u>					
Residual Cl ₂	ND ^e	ND	ND	ND	
Colonies/ml	0	29	0	130	1600
<u>4 days</u>					
Residual Cl ₂	<0.4	<0.4	3.0	<0.4	
Colonies/ml	22	330	0	1	19000
<u>6 days</u>					
Residual Cl ₂	ND	ND	1.0	ND	
Colonies/ml	330	36000	0	3	62000

^aNumber in parenthesis is ppm (mg/l) Cl₂ added initially.

^bContact time about 3 hours. Plating was done two hours after sample collection.

^cContact time, 10 minutes. Bacteria were added in the laboratory just prior to plating.

^dInitial residual chlorine values, mg/l, determined at plating time.

^eND = not done

TABLE 2. DISTRIBUTION OF BACTERIA BY TYPES IN SAMPLES TAKEN
2/2/78.* ONLY COUNTS GREATER THAN 1/ml ARE GIVEN

	Finished (3)	Col.4 (3)	Col.4 (10)	Bact.+ Col.4(10) Fin.
<u>Day 1</u>				
<u>Acinetobacter</u>				940
<u>Enterobacter</u> <u>agglomerans</u>			1	8000 140
<u>Aged 2 days</u>				
<u>Acinetobacter</u>		1	10	1300
<u>Enterobacter</u> <u>agglomerans</u>		28	120	300
<u>Pseudomonas-like</u>				260
<u>Staphylococcus</u>			3	
<u>Aged 4 days</u>				
<u>Acinetobacter</u>			1	
<u>Enterobacter</u> <u>agglomerans</u>	22**	330		19000
<u>Aged 6 days</u>				
<u>Acinetobacter</u>		36000	3	62000
<u>Moraxella</u>	330			

*Blank spaces in table indicate no growth.

**These colonies were initially white and developed a yellow pigment after two days. It is suspected that the Enterobacter agglomerans overgrew and replaced another organism.

TABLE 3. COLONIES CHOSEN FROM ISOLATION MEDIUM FOR IDENTIFICATION. SAMPLES COLLECTED 2/2/78

Colony number	Description	Sample source	Colonies/ml	Identity
<u>Samples initial</u>				
1a	1mm,yellow	Col.4(10)	1	<u>Enterobacter agglomerans</u>
2a	1mm,golden	Fin.Water	<1	<u>Staphylococcus</u>
3a	1mm,lemon	Fin.Water	<1	<u>Staphylococcus</u>
4a	1mm,white	Fin.Water	<1	<u>Staphylococcus</u>
5a	<1mm,white malodorous	Col.4(0)	1100	<u>Acinetobacter</u>
6a	5mm,white slimey, malodorous	Col.4(0)	1	<u>Acinetobacter</u>
7a	1mm,yellow	Col.4(0)	140	<u>Enterobacter agglomerans</u>
8a	<1mm,white turns yellow,malodorous	Fin.+Bact.	8000	<u>Enterobacter agglomerans</u> (<u>Acinet. overgrown?</u>)
<u>Samples aged 2 days</u>				
1	5mm,white,mucoid	Col.4(3)	<1	<u>Acinetobacter</u>
2	1mm,yellow	Col.4(3)	27	<u>Enterobacter agglomerans</u>
3	<1mm,white	Col.4(3)	<1	<u>Acinetobacter</u>
4	1mm,white	Col.4(10)	<1	Gram + cocci
5	1mm,yellow	Col.4(10)	<1	Gram + rods
6	1mm,golden	Col.4(10)	<1	Gram + cocci
7	1mm,yellow	Fin.+Bact. (10)	120	<u>Enterobacter agglomerans</u>
8	1mm,white	Fin.+Bact. (10)	10	<u>Acinetobacter</u>
9	1mm,lemon	Fin.+Bact. (10)	1	<u>Staphylococci</u>

(continued)

TABLE 3. (continued)

Colony number	Description	Sample source	Colonies/ml	Identity
10	1mm, golden	Fin.+Bact. (10)	1	<u>Staphylococci</u>
11	1mm, white	Fin.+Bact. (10)	1	<u>Staphylococci</u>
12	5mm, white, mucoid	Col.4 (0)	1300	<u>Acinetobacter</u>
13	1mm, yellow	Col.4 (0)	260	Ve2
14	<1mm, white	Col.4 (0)	1300	<u>Acinetobacter</u>
<u>Samples aged 4 days</u>				
15	<1mm, white turns yellow	Fin.Water	22	<u>Enterobacter agglomerans</u> (?overgrown?)
16	1mm, white turns yellow, malodorous	Col.4 (3)	30	<u>Enterobacter agglomerans</u>
17	5mm, white, malodorous	Col.4 (10)	<1	<u>Acinetobacter</u>
18	2mm, mucoid, white	Bact.+Fin.	<1	Ve2
19	4mm, mucoid, white, malodorous	Col.4 (0)	19000	<u>Acinetobacter</u>
<u>Samples aged 6 days</u>				
20	1mm, white, malodorous	Fin.Water	330	<u>Moraxella</u>
21	<1mm, white, mucoid, malodorous	Col.4 (3)	36000	<u>Acinetobacter</u>
22	1mm, mucoid, white	Col.4 (10)	<1	<u>Acinetobacter</u>
23	1mm, lemon	Col.4 (10)	<1	Gram + cocci
24	1mm, gold	Col.4 (10)	<1	Gram + cocci (continued)

TABLE 3. (continued)

Colony number	Description	Sample source	Colonies/ml	Identity
25	1mm,white, mucoid,malodorous	Fin.+Bact.	3	<u>Acinetobacter</u>
26	2mm,white, mucoid,malodorous	Fin.+Bact.	10000	<u>Acinetobacter</u>
27	2mm,white, mucoid,malodorous	Fin.+Bact.	62000	<u>Acinetobacter</u>

TABLE 4. BACTERIAL POPULATIONS (COLONIES ISOLATED/ml SAMPLE) OBTAINED IN SAMPLES OF FINISHED WATER AND GRANULATED ACTIVATED CARBON (GAC) COLUMN EFFLUENT TREATED IN SEVERAL WAYS. SAMPLES TAKEN 2/17/78

	Finished water (3) ^a	4 (3)	4 (10)	Bact. + fin. (10) ^c	4 (0)
<u>Initial^b</u>					
Residual Cl ₂ ^d	<0.4	<0.4	3	<0.4	
Colonies/ml	1	0	0	8300	8300
<u>Aged 3 days</u>					
Residual Cl ₂	ND ^e	ND	3	ND	
Colonies/ml	42	0	0	2	25000
<u>Aged 5 days</u>					
Residual Cl ₂	ND	ND	3	ND	
Colonies/ml	4	250	0	83000	12000

^aNumber in parenthesis is ppm (mg/l) Cl₂ added initially.

^bContact time about 3 hours. Plating was done two hours after sample collection.

^cContact time, 10 minutes. Bacteria were added in the laboratory just prior to plating.

^dInitial residual chlorine values, mg/l, determined at plating time.

^eND = not done

TABLE 5. DISTRIBUTION OF BACTERIA (COLONIES/ml) BY TYPES IN
 SAMPLES TAKEN 2/7/78.* ONLY COUNTS GREATER THAN
 1/ml ARE GIVEN

	Finished (3)	Col.4 (3)	Col.4 (10)	Bact.+ Fin. (10)	Col.4 (0)
<u>Day 1</u>					
<u>Acinetobacter</u>				8300	8300
<u>Aged 3 days</u>					
<u>Acinetobacter</u>	42			2	25000
<u>Aged 5 days</u>					
<u>Acinetobacter</u>		250		83000	7500
<u>Enterobacter</u>					
<u>agglomerans</u>					4150
<u>Staphylococci</u>	2				
II K 2	2				

*Blank spaces in table indicate no growth.

TABLE 6. COLONIES CHOSEN FROM ISOLATION MEDIUM FOR IDENTIFICATION. SAMPLES COLLECTED 2/17/78

Colony number	Description	Sample source	Colonies/ml sample	Identity
<u>Samples initial</u>				
1	2mm, white, mucoid	Fin. Water	<1	<u>Acinetobacter sp.</u>
2	1mm, white, entire	Fin. Water	<1	<u>Staphylococcus</u>
3	2mm, golden, entire	Fin. Water	<1	<u>Staphylococcus</u>
4	1mm, lemon, entire	Fin. Water	<1	<u>Staphylococcus</u>
5	<1mm, orange	Fin. Water	<1	<u>Pseudomonas-like (Ve2)</u>
6	<1/2mm, white malodorous	Bact.+ Fin.	8300	<u>Acinetobacter</u>
7	1mm, runny white malodorous	Col.4(0)	8300	<u>Acinetobacter</u>
<u>Sample aged 3 days</u>				
8	1mm, white, mucoid	Fin. Water	42	<u>Acinetobacter</u>
9	4mm, white	Col.4(3)	<1	<u>Acinetobacter</u>
10	2mm, white	Bact.+Fin.	2	<u>Acinetobacter</u>
11	<1mm, white, mucoid, stringy, malodorous	Col.4(0)	25000	<u>Acinetobacter</u>
<u>Sample aged 5 days</u>				
12	2mm, golden	Fin. Water	2	<u>Staphylococcus</u>
13	<1mm, orange	Fin. Water	<1	<u>Staphylococcus</u>
14	1mm, lemon	Fin. Water	<1	<u>Staphylococcus</u>

(continued)

TABLE 6. (Continued)

Colony number	Description	Sample source	Colonies/ml sample	Identity
<u>Sample aged 5 days</u>				
15	<1/2mm, orange	Fin. Water	<1	II K 1
16	1mm, yellow	Fin. Water	<1	II K 2
17	<1mm, white	Col. 4 (3)	250	<u>Acinetobacter</u>
18	1mm, yellow	Col. 4 (10)	1	<u>Enterobacter</u> <u>agglomerans</u>
19	<1mm, white	Bact. + Fin.	83000	<u>Acinetobacter</u>
20	5mm, white	Col. 4 (0)	700	<u>Acinetobacter</u>
21	<1mm, white, malodorous	Col. 4 (0)	6800	<u>Acinetobacter</u>
22	1mm, yellow	Col. 4 (0)	4150	<u>Enterobacter</u> <u>agglomerans</u>

TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i>		
1. REPORT NO. EPA-600/2-80-130a	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE REMOVING POTENTIAL ORGANIC CARCINOGENS AND PRECURSORS FROM DRINKING WATER Volume I and Appendix A	5. REPORT DATE August 1980 (Issuing Date)	
	6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Paul R. Wood, Daniel F. Jackson, James A. Gervers, Doris H. Waddell, and Louis Kaplan	8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Drinking Water Quality Research Center Florida International University Miami, Florida 33199	10. PROGRAM ELEMENT NO. 61CLC, SOS #1, TASK 42	11. CONTRACT/GRANT NO. R-804521
12. SPONSORING AGENCY NAME AND ADDRESS Municipal Environmental Research Laboratory--Cin., OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED Final 6/22/76-6/30/80	
	14. SPONSORING AGENCY CODE EPA/600/14	
15. SUPPLEMENTARY NOTES See also Volume II, EPA-600/2-80-130b Project Officer: Jack DeMarco (513) 684-7282		
16. ABSTRACT Feasible and economical methodologies were needed to remove existing organic contaminants--specifically, four trihalomethanes (chloroform, bromodichloromethane, chlorodibromomethane, and bromoform)--from and prevent development of potential carcinogens in the public water supplies in Dade County, Florida. A four-phase study was designed to evaluate the efficiency of three adsorbents in removing 19 individual halogenated organics and trihalomethane precursors. These adsorbents were XE-340--a carbonized polymeric macroreticular resin; IRS-904--a strong base cationic resin designed to remove large molecular weight substances such as precursors from water; and granular activated carbon (GAC). Adsorbent columns were placed at various stages in the water processing system: the raw-water, the lime-softened at the up-flow Hydrotreator effluent, and the finished water stage. Four 0.76-meter-deep GAC Filtrasorb 400 columns, arranged in series on the finished water line, were most effective in reducing the level of the trihalomethanes present in the finished water. The Polanyi-Manes theory of adsorption was applied and found helpful in interpreting results. Appendix A contains the preliminary studies made of the bacterial profile of raw and finished water and effluent from four GAC columns from the Preston Water Treatment Plant. Raw water organisms, which apparently can survive existing treatment plant processes, colonized the initially bacteria-free GAC columns and released vast numbers of bacteria into the water flowing through the columns. The development of bacterial growth in the GAC columns interfered with backflushing the columns. Appendix B (Volume II of this report) contains the supporting data for the study.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Adsorbents, Granular Activated Carbon Treatment, Synthetic Resin Treatment, Potable Water, Organics Control	Adsorption, Specific Organic compounds, General Organic Parameters	13B
18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 389
	20. SECURITY CLASS (This page) Unclassified	22. PRICE