

WATER RESOURCES RESEARCH CENTER
UNIVERSITY OF HAWAII AT MANOA
Holmes Hall 283 • 2540 Dole Street
Honolulu, Hawaii 96822

SUBSURFACE WATER QUALITY:
ORGANIC CHEMICAL CONTAMINATION OF O'AHU GROUNDWATER

First Progress Report

L. Stephen Lau

Special Report 7.0:85

December 1985

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University of Hawaii at Manoa
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SUBSURFACE WATER QUALITY: PESTICIDE CONTAMINATION

PERSONNEL

- *Dr. L. Stephen Lau, Director, Water Resources Research Center;
Professor, Civil Engineering;
Project Principal Investigator
- *Dr. G.L. Dugan, Professor and Chairman, Civil Engineering
Dr. P.C. Ekern, Hydrologist, WRRC; Professor, Agronomy and Soils
- *Dr. R.S. Fujioka, Virologist, WRRC
- *Mr. H.K. Gee, Environmental Engineering Specialist, WRRC
- *Dr. T.W. Giambelluca, Assistant Hydrologist, WRRC
- *Dr. R.E. Green, Professor, Agronomy and Soils
- *Ms. K.R. Green, Junior Researcher, Agronomy and Soils
Dr. J.W. Hylin, Professor, Agricultural Biochemistry
- *Dr. R.C. Jones, Associate Professor, Agronomy and Soils
Dr. C.C.K. Liu, Associate Professor, Civil Engineering
Dr. F.D. Miller, Associate Researcher, WRRC; Associate Professor
Public Health
- *Mr. J.F. Mink, Hydrologist-Geologist; Research Affiliate, WRRC
Mr. E.T. Murabayashi, Land-Use Specialist, WRRC
- *Mr. J.N. Ogata, Assistant Chemist, Agricultural Biochemistry
- *Dr. F.L. Peterson, Professor and Chairman, Geology and Geophysics
- *Mrs. B.S. Yoneyama, Research Associate, WRRC
Dr. R.H.F. Young, Associate Dean, College of Engineering;
Professor, Civil Engineering
- *Ms. D.S. Buxton, graduate student, Geology and Geophysics
- *Mr. D.S. Oki, graduate student, Civil Engineering
Mr. C. Lao, Hydrologist-Geologist, Board of Water Supply,
City and County of Honolulu
- *Mr. O.T. Narikawa, project chemist
- *Contributing authors.

COOPERATING AGENCIES

Federal

U.S. Department of the Navy
U.S. Geological Survey

State of Hawaii

Department of Agriculture

City and County of Honolulu

Board of Water Supply

Private

Del Monte Corporation, Dole Process Foods, The Estate of James Campbell, Honolulu International Country Club, Maui Land and Pineapple Company, Oahu Sugar Company, Pacific Concrete and Rock Company, Waialua Sugar Company

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PREPARED FOR

Hawaii State Legislature
Office of Environmental Quality Control
Department of Health
State of Hawaii

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EXECUTIVE SUMMARY

This progress report is a study of the unprecedented problem of low-level organic chemical contaminants discovered principally in 1983 in potable groundwater sources on O'ahu. A number of immediate and serious concerns are (1) extent of the contaminated basal water, (2) treatments capable of removing such low level contaminant concentrations, and (3) health effects to drinking water consumers. Short-term actions were undertaken by the Hawaii State Department of Health (DOH) regarding the potability question of the contaminated water and the associated health risk. (The DOH subsequently proposed 20 ppt as the maximum limit of EDB and DBCP in drinking water and none for TCP, despite controversies and lack of definitive scientific basis.) As a result of closing water wells exceeding these limits, immediate action was needed and taken by the major water purveyors (City and County of Honolulu Board of Water Supply [BWS] and U.S. Navy) to replace the closed water sources and/or to treat the contaminated water to below the maximum level. The BWS and U.S. Navy decided on treatment plants and the State drilled two new wells. Expediency was the priority for these actions.

Another set of questions became quickly apparent: (1) how persistent would the water sources remain contaminated, (2) would the contaminated groundwater contaminate other sources by migration, (3) would the residual pesticides in soils, an obvious suspect of contamination source, be a source for continued contamination of the basal water, (4) can the cost of treatment be reduced by improving the process or using alternative methods, and (5) can new wells be drilled in a suspected contaminated area and yet with reasonable assurance produce water below the maximum organic limit? These questions should be of special concern to water purveyors.

This project is planned to address these questions:

1. Extent and migration of contaminated groundwater on O'ahu, especially in southern, central, and northern O'ahu.
2. Potential of residual organics in soils and saprolites to contaminate the underlying groundwater (basal water).
3. Technology for water wells located in a contaminated aquifer to permit continued development of groundwater of potable quality.
4. Alternative methods of treatment for removing low-level organics pumped from the contaminated water.

The project will contribute to the overall effort of protecting and rehabilitating the all-important Pearl Harbor aquifer which is the most important potable water source for the island of O'ahu.

The project approach is multidirectional and multidisciplinary, and includes eight coordinated activities, each having its own scientific objectives and direction to attain pertinent information. Some activities are of a research nature, others are evaluative and interpretative. Many activities were completed within a year, while others required two or three years because of their interrelation with the results of other activities. The most highly competent University of Hawaii faculty and staff were selected for the project. Numerous agencies cooperated in the conduct of the project. Several companion WRRC projects contributed to the study. Concurrent and recently completed actions by other agencies are geared to produce immediate effects and to provide regular monitoring which is not duplicated by but useful to the project.

The project was conceptualized in December 1983 and has been in progress for 12 months (January-December 1985). Because the project is still continuing, it appears prudent to defer conclusions. However, some interim findings appear significant at this time.

Regarding the extent of contaminated groundwater, a coincidence is apparent between the location of contaminated wells and the location of land used for pineapple cultivation. However, the occurrence of fuel pipeline leaks of aviation fuels containing EDB was also located in the vicinity of several of the contaminated Waipahu wells. No significant variation is evident in the level of contamination of selected wells in southern O'ahu over a 12-month period (September 1983-August 1984). The thickness of contaminated basal water is not determinable at this time. Taking each chemical species individually, EDB appears only in the Waipahu area between the Waikele and Panakuahi gulches. DBCP and TCP occur in the Koolau aquifer beneath and down gradient of pineapple fields but have not been detected in the Waianae aquifer. Detection of DBCP is always accompanied by detection of TCP but TCP may also appear alone and, thus, is most widely distributed.

Groundwater contamination potential of residual pesticides in soils is undeterminable at this time. The project focused its effort on the supposition that the residual pesticides are leachable from the soils by the percolating water. Progress made thus far includes a completed compilation of pertinent geologic information, drilling of deeper boreholes (up to 146 ft) to

delineate the penetration of residual fumigants in soils, and development of two new laboratory methods needed to characterize desorption (leaching). A spatially detailed evaluation of the time series of deep percolation of water under pineapple fields in southern O'ahu is in progress. Evaluation of pipeline leaks of aviation fuels containing EDB is not a part of the project objective. But the project-produced information should be useful for similar evaluation by other agencies.

Water well technology for contaminated aquifers was under study through planning well drilling and pumping tests in upper Honouliuli scheduled for Spring 1986, courtesy of The Estate of James Campbell. An alternative objective by testing a contaminated well for retrofitting purpose was discussed with the Board of Water Supply.

Laboratory studies of treatment methods of low level contaminated waters by the project indicated that the use of granular activated carbon is a very effective method at controlled loading rates. Certain carbon materials were more effective than others. The use of ultraviolet light in conjunction with ozone or hydrogen peroxide showed considerable promise as an alternative method. On the other hand, chlorine and chlorine dioxide did not. Boiling water is effective but the cost would be prohibitive for large-scale operations. A thin-layer volatilization method proved effective and lends itself to household use. Large-scale operations will require further innovative research.

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INTRODUCTION

The Situation

The high quality of Hawai'i's groundwater has been a principal reason for its extraordinary development and utilization as a potable water source for more than a century since its discovery. Safeguarding its quality against contamination by the underlying seawater has been and still is of paramount concern to water consumers and agencies in Hawai'i. Investigative studies and research projects have produced remarkable advancement in Hawai'i's groundwater knowledge and technologies and related geohydrologic environments as documented by the University of Hawaii Water Resources Research Center (WRRC) (Fujimura and Chang 1981).

Protection of groundwater from contamination began in 1929 with the formation of the City and County of Honolulu Board of Water Supply (BWS). With foresight the BWS in the 1920s designated the principal natural groundwater recharge areas as watersheds within the forest reserves, thus restricting these areas from man's entry and development. At the same time, the BWS instituted a water quality monitoring program of physical, chemical, and microbiological water quality parameters. These actions virtually assured that only potable groundwater would be delivered to consumers. Thus, the quality of the municipal water supply as provided by the BWS has been regarded as exceptionally pure by known standards.

Prior investigative research studies on other sources of contamination of groundwater have uncovered no real threats to the groundwater quality. These sources include cesspools, sugarcane irrigation return flow, and sanitary landfill leachate which have been investigated in a series of research projects conducted since 1966. The nearly 60,000 cesspools still in use on O'ahu and other islands would appear to constitute a potential nonpoint pollution source; however, laboratory studies on selected water quality factors and typical soils have not produced conclusive evidence of polluting consequences (Koizumi, Burbank, and Lau 1966). Another study concentrated on agricultural fertilizers transmitted by irrigation return water from sugarcane culture (Mink 1962). Subsequent WRRC research in the early 1970s on O'ahu and Maui revealed conclusive evidence of a layer of water of lower quality at the top of the basal lens located beneath cane fields (Tenorio, Young, and Whitehead 1969; Tenorio et al. 1970). Research efforts focused on inorganic chemicals (Cl^- , NO_3^- , SO_4^{2-} , SiO_2), of which chloride and nitrate nitrogen were of pot-

ability concern; however, no regulatory actions were deemed warranted. Still another potential pollution source is sanitary landfill leachate for which WRRC research efforts were directed to ascertain the water quality of leachate and to monitor the receiving groundwater quality (Chun and Dugan 1981). Serious problems were not indicated. It should be noted that few landfills are located directly over potable groundwater sources on O'ahu.

Agricultural chemicals, including fertilizers, have been used for almost a century by the sugarcane and pineapple industries in fields overlying groundwater sources. Studies of pesticides must have been made by private agricultural research institutes to meet regulatory agencies' requirements for use permits in terms of the interaction of the pesticides with pests and soils, persistence in the field, and possible toxic effects to field workers. However, it should be noted that the analytic capabilities detecting low level of pesticides were then limited to the parts per million (ppm) and, at best, parts per billion (ppb) range in comparison to the present-day parts per trillion (ppt) detection range.

Prior to 1979, limited studies were made at higher concentrations (ppm and ppb) by public institutions concerning the possible transmission of refractory organic chemicals (pesticide) used in agriculture through the soils (Eto et al. 1967; Fischer, Green and Burbank 1977). These studies revealed that trace organics were generally retained in the soil columns and only trace amounts of the more refractory materials might break through and be transported to the basal lens. A 1971 survey of the major municipal water sources on O'ahu showed the presence of carbon chloroform extracts (OCE) but in amounts less than the applicable standards (Zaidi 1976). A 1979 review paper showed the need for more baseline data on refractory constituents (e.g., heavy metals and trace organics, especially chlorinated hydrocarbons) and the need for better understanding of the interaction of such refractory materials with aquifer materials and aquifer waters (Young 1981). The author suggested:

It may be shown that through sheer dilution in the aquifers or through physicochemical interactions with aquifer materials, the health hazard of pollution potential of these trace substances is severely diminished. If such be the case, then continued development and utilization of our aquifers with minimum treatment for potable and other uses is warranted. If not, then appropriate treatment measures will have to be employed to allow continued use/or future development.

Unfortunately, these insightful comments seem to have escaped the attention of action agencies and to have prophesied the realities in Hawai'i

today—ignorance and uncertainty.

In 1971 a major water recycling research program was launched dealing, in part, with the potential groundwater quality consequences of recycling treated (secondary) municipal wastewater for sugarcane irrigation. This six-year pilot field study showed that the water quality of the percolate below the vegetative root zone contained no pathogenic viruses and did not exceed other potable water quality standards (Lau et al. 1980). Nevertheless, continued monitoring for viruses was recommended. Checking for heavy metals and pesticides in the effluent before application was also recommended as a requirement. Beginning in November 1983, the Pearl Harbor aquifer located west of Waikale Stream has been monitored for viruses, heavy metals, and pesticides by the WRRC and the City and County Department of Public Works as a four-year program. The program was undertaken in conjunction with a research and development wastewater recycling project performed under quality-control conditions.

The recharge-discharge relation and flow pattern in groundwater in the Honolulu and Pearl Harbor areas, long recognized by hydrologic and geologic evidences, were reaffirmed and refined by analyzing tritium and radiocarbon traces, two environmental isotopes in the hydrologic cycle (Hufen, Eyre, and McConachie 1980). This technique presents a potential adjunct method for subsurface water quality investigations.

In addition to those noted previously, concern for viruses reaching the groundwater was investigated at sites at Makakilo, O'ahu (Fujioka and Lau 1985) and at Haina, Hawai'i (Fujioka and Lau 1983) in connection with the seepage of sewage from an unlined ditch and cesspools. Negative results were reported for both cases.

In the late 1970s Hawai'i's public attention was captured by concern over the availability of water supplies—water quantity rather than water quality—in reaction to a prolonged period of dry weather, dropping of groundwater levels to all-time lows on O'ahu, call for voluntary cutbacks of water use by county water developments, and other concurrent events. The Governor's State Water Commission, which was created to study the problem, projected an island-wide water shortage by the turn of the century and made a number of policy recommendations. One action by the state was the full allocation of the entire quantity of the groundwater resources in the Pearl Harbor aquifer among the several major water purveyors. The water quality situation, being por-

trayed as relatively problem-free, was submerged below the water supply concern and activities at that time.

The turning point occurred in 1980 when a Kunia water supply well was shut down because of contamination by DBCP and EDB. However, it was not until 1983 that a series of stunning events took place after the discovery of apparent contamination of many water wells at Waipahu and Mililani by pesticides (DBCP, EDB, TCP) at the low level (parts per trillion [ppt]) range with the apparent sources being fumigants used by the pineapple industry. These events included the shutdown of a number of municipal water supply wells, the uncertainty over the health risk of consuming water containing pesticides at the ppt range, and the very expensive measures (up to \$9 million) to replace water wells or to treat the contaminated water. Thus, a crisis atmosphere prevails.

The current crisis is, to a large extent, caused by the lack of necessary scientific information on multiple aspects of subsurface water quality, treatment technologies of the contaminated water, and health implications to consumers.

The pesticides DBCP, EDB, and TCP are volatile organic chemicals. DBCP and EDB are soil fumigants. TCP is an impurity in a soil fumigant, but EDB and TCP have nonagricultural uses. EDB is an additive to leaded aviation fuels for military and commercial uses. TCP is found in paint and varnish removers and is a solvent and a degreasing agent. Given this information, the discovery of EDB and TCP in groundwater can mean other than just the impact of agriculture on groundwater, and not just the contamination caused by their use as pesticides. An accurate but generic reference should be organic chemical contamination of groundwater. However, purely for convenience, the term pesticide contamination is used in this report.

Rationales for Project

RELATION OF LAND USE TO SUBSURFACE WATER QUALITY. Groundwater quality is governed by several parameters: the quality of water that recharges into the ground, the chemical properties of the soils and rock formations through which the water passes, the residence time of the water in aquifer formations, and the quality of the resident waters with which it may mix. For instance, limestone aquifer waters are expected to have characteristic calcium carbonate composition, and basalt aquifer waters will have moderately high silica.

Under natural conditions, the ambient groundwater quality is fairly well protected from abrupt alterations and can be expected to be maintained over time for a given aquifer system.

Certain anthropogenic activities, such as agricultural irrigation and wastewater injection practices, can significantly change the groundwater quality. Moderate concentrations of nitrate, chloride, sulfate, and silica have been identified in certain groundwater bodies as a result of prolonged furrow irrigation of sugarcane on O'ahu and Maui.

Has Hawai'i used land management as a strategy to protect groundwater quality? The answer is affirmative. The first example is the kapu signs posted for over 50 years in the high rainfall Ko'olau Range which is zoned into conservation districts. These areas have not only been kept in their natural undeveloped state and as prime groundwater recharge areas for our vital groundwater sources, but have also protected the purity of that portion of the rainwater percolating and replenishing our groundwater aquifers. The second example is the recent state regulation governing Underground Injection Control (UIC) (Department of Health 1984, chap. 23). A line (pass-no-pass) sets off that part of the aquifer to be protected by prohibiting direct injection of wastewater effluent. Injection is allowed for the remainder of the aquifer containing water of low quality.

Between these two lines, however, is the vast land area that overlies the mostly geologically unconfined aquifer that contains potable water sources and that are potentially vulnerable to contamination. This vast land area, by necessity, has been and will be used for various kinds of anthropogenic activities. The question is which land areas, and to what degree, should be given protection from potential groundwater polluting activities? A short watchlist of pollution suspects would include pesticide-using agriculture; large manufacturing industries; service industries, including dry cleaners, service stations, and garages; storage, handling, and disposal sites of chemicals; landfills; and transporting routes.

Although not a part of this study, an aquifer classification effort is underway by the WRRC and supported by the Hawaii State Department of Health. The effort is based on the rationale that groundwater quality can be significantly protected or degraded by anthropogenic activities through land use and land development practices.

IMPORTANCE OF PEARL HARBOR AQUIFER. The Pearl Harbor aquifer is the most

important potable water source for the island of O'ahu. By the 1980 state water allocation, major water purveyors were issued certified water permits (daily average) in the following amounts: City and County of Honolulu Board of Water Supply 77 million gallons per day (mgd), Oahu Sugar Company 115 mgd, U.S. Navy 21 mgd, U.S. Army 6 mgd; and others, 6 mgd, for a total of 225 mgd, the sustainable yield recognized at that time for the Pearl Harbor aquifer. To the BWS, the closing of nine wells because of organics totaling approximately 13 mgd, means more than a significant percent of its total water sources. The lack of alternative potable water sources that are already developed and available in the proximity of some of these wells poses an unusually difficult situation for the BWS and water consumers.

The Pearl Harbor aquifer provides the greatest sustainable yield of potable water among all sources on O'ahu. The aquifer's sustainable yield was fully allocated in 1980. In 1984 when the Oahu Sugar Company (OSC) withdrew 5000 acres of land from sugarcane culture, the Hawaii State Department of Land and Natural Resources reduced the OSC allocation by 22.5 mgd.

It is clear that the Pearl Harbor aquifer requires not only continued protection from further groundwater contamination to maintain the future water supply, but also rehabilitation of the contaminated portion of the aquifer and the affected water wells to regain its full source. This project will help fulfill these goals by providing the necessary knowledge and technologies for action agencies to formulate management alternatives for both water and land resources.

Objectives of Project

Cognizant of the relation of land use to groundwater quality and of the importance of the Pearl Harbor aquifer as a major water source, the project objectives are formulated to help answer the following questions:

1. Extent and migration of contaminated groundwater on O'ahu, especially in southern, central, and northern O'ahu
2. Potential of residual organics in soils and saprolites to contaminate the underlying groundwater (basal water)
3. Technology for water wells located in contaminated aquifer to permit continued development of groundwater of potable quality
4. Alternative methods of treatment for removing low-level organics from the pumped contaminated water.

Organization of Project

The four broad project objectives require a multidirectional and multidisciplinary approach. Thus, the project consists of a number of coordinated project activities, each having its own scientific objectives and direction to attain information pertinent and useful to one or more of the project objectives. Some project activities are of a research nature, others are evaluative or interpretative.

Project responsibility is vested in its Principal Investigator whose duty, beyond any project activity he leads, is to assure that the project is in line with its stated objectives, to manage its budget, to call project personnel together for progress meetings, and to apprise project sponsors and major agencies of research progress.

Many of the eight activities require one year for completion, while some require two or even three years to coordinate information produced by other activities, such as the following:

1. Statewide contaminated subsurface water and soil computerized data base (completed; see UH WRRC Special Rep. 7:85, 1985)
2. Compilation and mapping of assembled information, agricultural and nonagricultural uses (yr 1)
3. Deep percolation of water below the root zone of pineapple growing areas (yr 1)
4. Desorption and leachability of residual fumigants in soils and saprolites (yrs 1, 2)
5. Characterization of geological and mineralogical parameters (yrs 1, 2)
6. Transport of contaminated groundwater (yrs 1, 2, 3)
7. Methods for rehabilitation of contaminated wells and construction of new wells in contaminated aquifers (yrs 1, 2)
8. Alternative methods for treating low-level contaminated water (yrs 1, 2).

There are other related concurrent and recently completed actions by other agencies, including the Hawaii State Department of Land and Natural Resources, Department of Agriculture, and Department of Health; and the City and County of Honolulu Board of Water Supply. Their actions are to produce immediate effects. This project is aimed at providing the base information needed for the near future and over a broader geographic extent, thus com-

plementing other companion studies being conducted by WRRC, other University units, and other agencies.

The Hawaii State legislature recognized the significance of the environmental impact of organics contamination at Mililani and Wahiawa, and the importance of safeguarding the public health by appropriating funds in fiscal year 1984-1985 (Act 285, Sec. 38F) and again in FY 1985-1986 for the University of Hawaii Water Resources Research Center (WRRC) for "research on mitigation and degradation of contaminants in groundwater." The Hawaii State Office of Environmental Quality Control (OEQC) and the Department of Health provided supplemental funds.

Nature and Scope of Report

This report is a progress report of the project whose activities were initiated in January 1985. Thus, the information provided herein is interim in nature. Subsequent research and investigative results will complete, confirm, refine, or revise the findings of this report.

This report is accompanied by a data base report entitled, "Subsurface Water and Soil Quality Data Base for State of Hawai'i" (Parts 1 and 2, by D.S. Oki and T.W. Giambelluca, WRRC Special Report 7:85, July 1985).

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Companion projects which contribute to the overall study include:

1. DBCP Volatilization from Soil and Water: A Laboratory Study with Two Hawaiian Soils (Pringle, Liu, and Green 1984)
2. Desorption and Leachability of Residual Pesticides in Soils and Saprolites (UHM-WRRC project funded by U.S. Dept. of Interior, Geological Survey; in progress)
3. Activated Carbon Adsorption of Low Concentration Organic Pesticides in Water (UHM-WRRC project funded by City and County of Honolulu Board of Water Supply; see Dugan et al. 1984)

4. Low Level Organic Pesticide Removal (UHM-WRRC project funded by U.S. Dept. of Interior, Geological Survey; in progress).

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GENERAL SETTING

Geology and Hydrology

The island of O'ahu is formed primarily from the lavas of the Koolau and Waianae shield volcanoes. The Koolau dome and the lower portion of the Waianae dome consist mainly of thin basaltic flows (generally less than 3 m [10 ft] in thickness). The Wahiawa Plateau, which lies between the two volcanoes, consists of lavas from the younger Koolau volcano ponded against the eroded lower slopes of the Waianae volcano. Terrestrial and marine sedimentary deposits created coastal plains during the quiescent period following the formation of the two volcanoes. The permeability of the coastal plain sediments is considerably lower than the permeability of the underlying basalt aquifers. Thus, the sedimentary deposits act as a caprock restraining the seaward movement of the fresh groundwaters. The caprock boundaries for O'ahu are presented in Figure 1.

The basal aquifers of O'ahu (Fig. 1) consist of a body of fresh water floating on seawater. Based on the Ghyben-Herzberg principle, the depth of the basal lens below sea level is approximately 40 times the freshwater head above sea level. The permeability of the unweathered rock that forms the basal aquifers of O'ahu is generally high. The high permeability is a result of the presence of clinker layers, lava tubes, irregular openings within and between the surface of flows, and contraction joints that formed on solidification (Visher and Mink 1964). The hydraulic conductivity of the Koolau lava flows is on the order of 204 to 815 m/day (670-2670 ft/day) in the Meinzer index. The gross porosity may range from 10 to 25% (Wentworth 1951).

Rainfall is the ultimate source of recharge to the basal waters. Water for recharge also occurs as a result of inflow from dike compartments at higher elevations, inflow from streams, and deep percolation of irrigation return water. Discharge from the aquifers occurs as a result of well withdrawals and the natural discharge of fresh water as springs and seepage to the ocean. Groundwater flows from areas of high hydraulic head to areas of lower head. The general flow patterns for selected aquifers within the study area are presented in Figure 1.

Land Use and Management

Land use is a critical factor affecting recharge. On agricultural lands, irrigation and suppressed evapotranspiration (pineapple) can contribute sig-

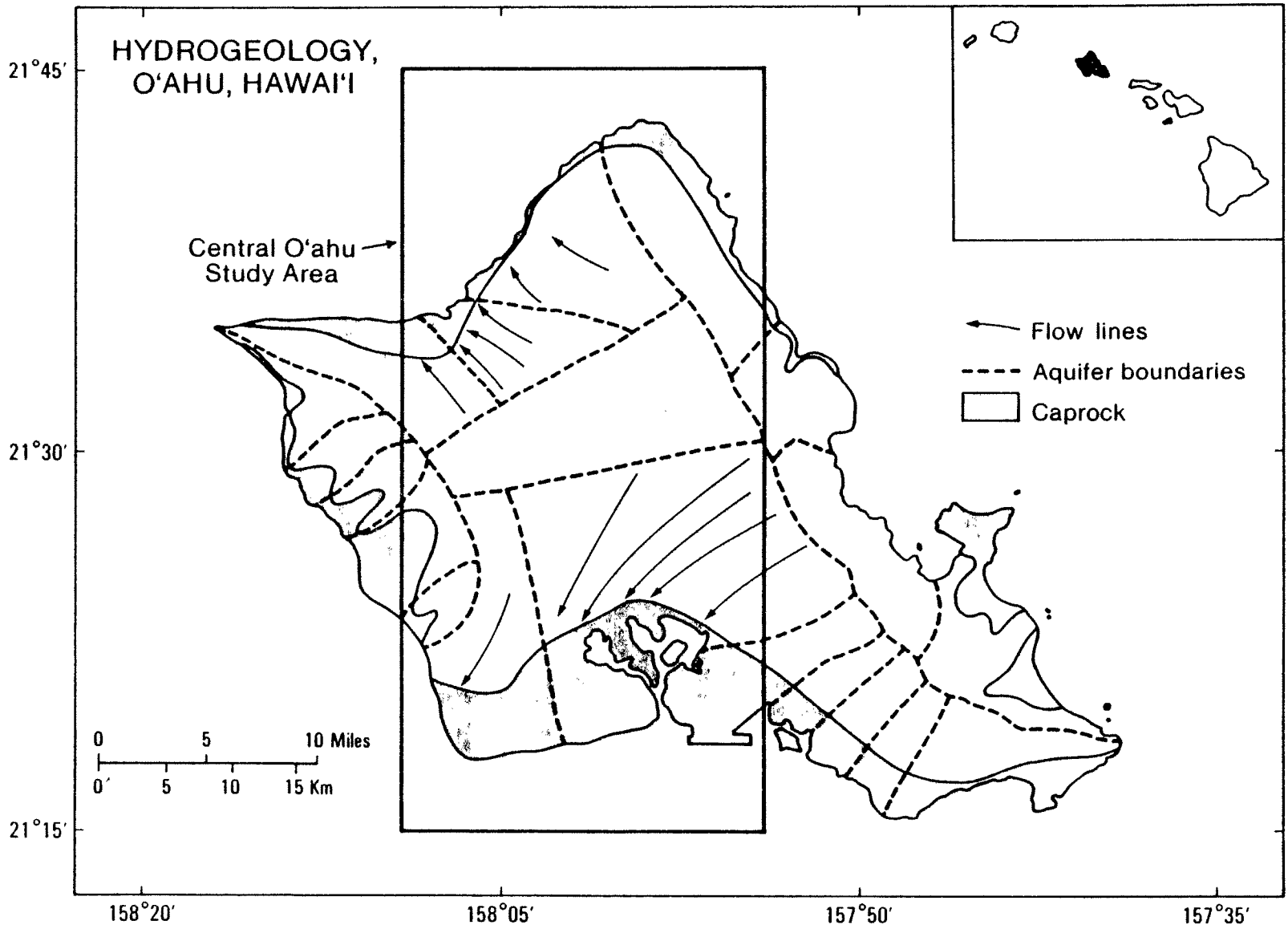


Figure 1. Aquifer and caprock boundaries for O'ahu, Hawai'i

nificantly to recharge (Giambelluca 1983). The leaching of pesticide residues may be accelerated as a result of high percolation rates in agricultural areas. The compounds DBCP, EDB, and TCP have all been associated with the cultivation of pineapples. Areas of past and present pineapple cultivation (1940-1985) are shown in Figure 2. It should be noted that some of these areas were converted from pineapple cultivation to sugarcane cultivation. This change in land use would enhance the opportunity for leaching of pesticide residues because of the large amount of water used for sugarcane irrigation.

Dole Process Foods and Del Monte Corporation are now the two pineapple growers on O'ahu. A third company, Libby, was involved with pineapple cultivation until the early 1960s.

Agricultural Uses of Volatile Organic Chemicals

1,2-DIBROMO-3-CHLOROPROPANE (DBCP). DBCP is a soil fumigant introduced in 1955 by the Dow Chemical Company and the Shell Development Company. This fumigant, which is used to control nematodes that attack the roots of pineapple crops, is effective in controlling a particularly hardy strain of root-worm called the reniform nematode. DBCP is injected into the soil at a depth of approximately 203 to 254 mm (8-10 in.) beneath a polyethylene film prior to planting. The application rate is approximately 0.028 to 0.037 m³/ha (3-4 gal active/acre). It is generally applied with another fumigant, such as DD (a dichloropropane-dichloropropene mixture) or Telone (a dichloropropene mixture). The volumetric application ratio of DBCP to DD or Telone is about 1:10 (Yim and Dugan 1975).

Records are not available to indicate the precise date on which DBCP was first used on a commercial basis by pineapple growers on O'ahu; however, the pesticide was probably first used between 1955 and 1964 on O'ahu pineapple fields. Dole phased out the use of DBCP in the 1977 planting season. Del Monte has not used DBCP on O'ahu except on an experimental basis (Dept. of Agriculture 1983).

1,2-DIBROMOETHANE (EDB). The use of EDB as a fumigant was first reported in 1925. It was later introduced by the Dow Chemical Co. in 1946 (Worthing 1979). The Environmental Protection Agency (EPA) reported in 1983 that over 20 million pounds (9.07 million kg) of ethylene dibromide were being used in this country every year with soil fumigation accounting for 90% of the volume

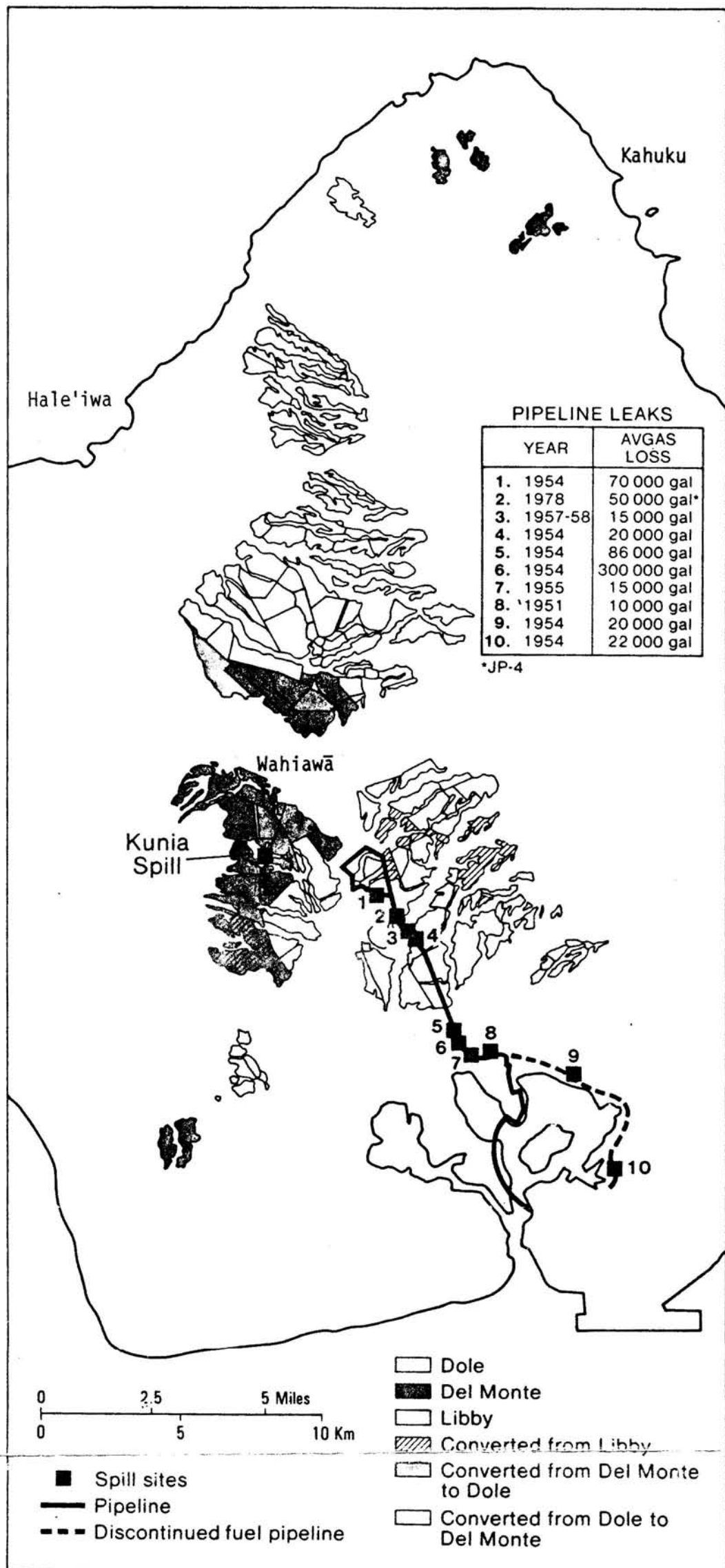


Figure 2. Spill sites and areas previously and presently under pineapple cultivation, central O'ahu, Hawai'i

used (EPA 1983). Although EDB has been used as a quarantine fumigant for papayas in Hawai'i, its major use in the state has been for the soil fumigation of pineapple fields to control nematodes. As a soil fumigant for pineapple fields, EDB is injected into the ground at a depth of approximately 203 to 254 mm (8-10 in.) prior to planting. It is applied at a rate of 0.094 to 0.112 m³/ha (10-12 gal active/acre). A polyethylene film is placed over the soil at the time of application to retain the volatile fumigant and thereby improve nematode control. The film also helps to retain moisture and to increase soil temperature which improve early plant growth. Planting generally takes place 48 hr or more after fumigation (Dept. of Agriculture 1983).

On O'ahu, EDB was the primary soil fumigant of Del Monte for approximately 35 years prior to the EPA notice of cancellation and emergency suspension of registrations in September 1983. Dole only began using EDB on O'ahu in 1978 after it phased out use of DBCP in 1977 (Dept. of Agriculture 1983). By the terms of the cancellation order, the use of EDB on pineapple fields in Hawai'i was allowed until 1 September 1984. Dole chose not to use up its remaining stocks and discontinued use of EDB at the time of the order. Del Monte continued use of EDB until its remaining supply was completely depleted by the end of 1983.*

1,2,3-TRICHLOROPROPANE (TCP). TCP is used as a paint and varnish remover, a solvent, and a degreasing agent (EPA 1980). It also occurs as an impurity during the manufacturing process of the Shell Chemical Co. product DD which was introduced in 1942. The first use of DD as a soil fumigant was described in 1943 (Worthing 1979). Estimates of the amount of trichloropropanes in the DD mixture vary from 0.4% by weight (Dept. of Agriculture 1984) to 6 to 7% by weight (Carter 1954). The actual amount of trichloropropanes in the mixture, however, may have deviated greatly from these values at times.

The soil fumigant DD was commonly used in conjunction with DBCP by Dole on O'ahu. It is also believed that Libby used a DD formulation with a high TCP content on its fields. Where the reniform nematode was not present, DD (or Telone) was used alone at the rate of 0.374 to 0.561 m³/ha (40-60 gal/acre) (Yim and Dugan 1975). Records are not available to determine when DD was first used on a commercial basis; however, it was most likely first used/

*"Pine Growers Drop Fight for EDB," Hono. Star-Bull., 13 Feb. 1984, pp. A-10.

on O'ahu in the 1940s or 1950s. It has not been used on pineapple fields on O'ahu since 1977.*

Nonagricultural Uses of Volatile Organic Chemicals

EDB IN AVIATION GASOLINE. Tetraethyl lead was introduced in 1922 and leaded gasoline was sold commercially by Standard Oil of New Jersey in 1923. The potential of using tetraethyl lead to boost octane rating of gasoline led to the formation of the Ethyl Corporation by Standard Oil and General Motors. The sole use of tetraethyl lead caused fouling of spark plugs and sticking of valves through the deposition of metallic lead upon them. To remedy this problem, ethylene dibromide, EDB, was added to anti-knock motor fuels containing tetraethyl lead to form lead bromide in the cylinder upon combustion.

Lead bromide was discharged with other gases in the exhaust system. EDB accounted for 77% of the bromine produced in the U.S. in 1963 but is decreasing because of the EPA regulation on lead emission in automobile exhausts (Kirk-Othmer 1978). Production in 1966 of EDB amounted to 200 million lb (Shreve 1967). The composition of the tetraethyl lead fluid (Ethyl fluid) varies according to the literature. Some of the compositions and sources of information are as follows:

| | | |
|-------------------------|--------|--------------------------------|
| tetraethyl lead | 63.30% | |
| EDB | 25.74% | (Kalichevsky and Stagner 1942) |
| ethylene dichloride | 8.73% | |
| dye and impurities | 2.23% | |
| tetraethyl lead | 61.42% | |
| EDB | 35.68% | (Van Winkle 1944) |
| kerosene and impurities | 2.65% | |
| dye | 0.25% | |
| tetraethyl lead | 61-62% | |
| EDB | 35-36% | (Kirk-Othmer 1978) |
| dye, solvent, inhibitor | 3% | |

*"EDB May Be in Mililani's Water Wells," Hono. Adv., 6 Oct. 1983, pp. A-1, -4.

Aviation fuel uses tetraethyl lead mixtures that contain only bromides. Various amounts of tetraethyl lead mixtures are added to obtain different grades of aviation gasoline:

Detailed Requirements for Aviation Gasoline (ASTM 910-63T)
(Bland and Davidson 1967)

| | Grade | 80-87 | 91-98 | 100-130 | 108-135 | 115-145 |
|----------------------------|--------|-------|-------|---------|---------|---------|
| tetraethyl lead maximum | ml/gal | 0.5 | 2.0 | 3.0 | 3.0 | 4.6 |

Specifications on Aviation Gasoline
(Van Winkle 1944)

| | Octane No. | 73 | 91 | 100 |
|-----------------|------------|-----|-----|-----|
| tetraethyl lead | ml/gal max | 1.0 | 4.0 | 3.0 |

Peak production of aviation gasoline was in 1944 with 192,440,000 bbl produced. In 1946 it dropped to 14,480,000 bbl but gradually increased to 95,774,000 in 1958.

SUMMARY. EDB in tetraethyl lead additive ranges from 35 to 36% in aviation gasoline. For 100 octane fuel, 3.0 ml per gallon of gasoline of tetraethyl lead is added or 1.05 to 1.08 ml of EDB is contained in each gallon of aviation gasoline. The concentration of EDB in aviation gasoline would be 277 to 285 ppm by volume or 602 to 620 mg/l. Aviation uses tetraethyl lead additive with only bromide.

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EXTENT OF CONTAMINATED GROUNDWATER

Among the objectives of the subsurface water quality project is determination of the geographical extent of detectable concentrations of DBCP, EDB, and TCP in groundwater. Starting in 1980 a general sampling program was initiated by the Hawaii State Department of Health and Department of Agriculture in cooperation with Dole Process Foods and Del Monte Corporation; the Board of Water Supply and the U.S. Navy later joined the effort. The first collection of samples included a rough estimate of the extent of contamination, but the detectable levels were considerably greater than 20 ppt, which became standard a year later. Subsequently, the goal of most sampling was to identify the concentration levels in potable sources. As a result, the geographical boundaries of the contaminated area were not defined for the 20 ppt detection limit.

Over the past several decades, large amounts of pesticides have been used by the pineapple industry in the southern and central portion of O'ahu, Hawai'i (Fig. 1). During that time, application of pesticides continued based on the belief that the great distance (hundreds of meters) between the ground surface and the basal lens of the aquifer was adequate to protect the groundwater body from pesticide residue leachate. It was further argued that if any residues did reach the basal aquifer, the concentrations would be so dilute as to be undetectable and presumably harmless.

In recent years, however, several pesticide-related contaminants have been detected in the basal waters of southern and central O'ahu aquifers. Dibromochloropropane (DBCP) and ethylene dibromide (EDB), two soil fumigants which were previously used by pineapple growers in southern and central O'ahu, have been discovered in several wells in the area. In fact, 10 wells were closed by the Hawaii State Department of Health in the central O'ahu area as a result of DBCP or EDB contamination (Fig. 3). A third contaminant, trichloropropane (TCP), which is an impurity of the soil fumigant DD, has also been detected in a number of wells. DBCP, EDB, and TCP have been of particular concern because of their associated health effects, both known and unknown. This is especially true for the Pearl Harbor aquifer, which is the major potable water source for Honolulu. Thus, it is imperative to understand the extent and movement of the contamination.

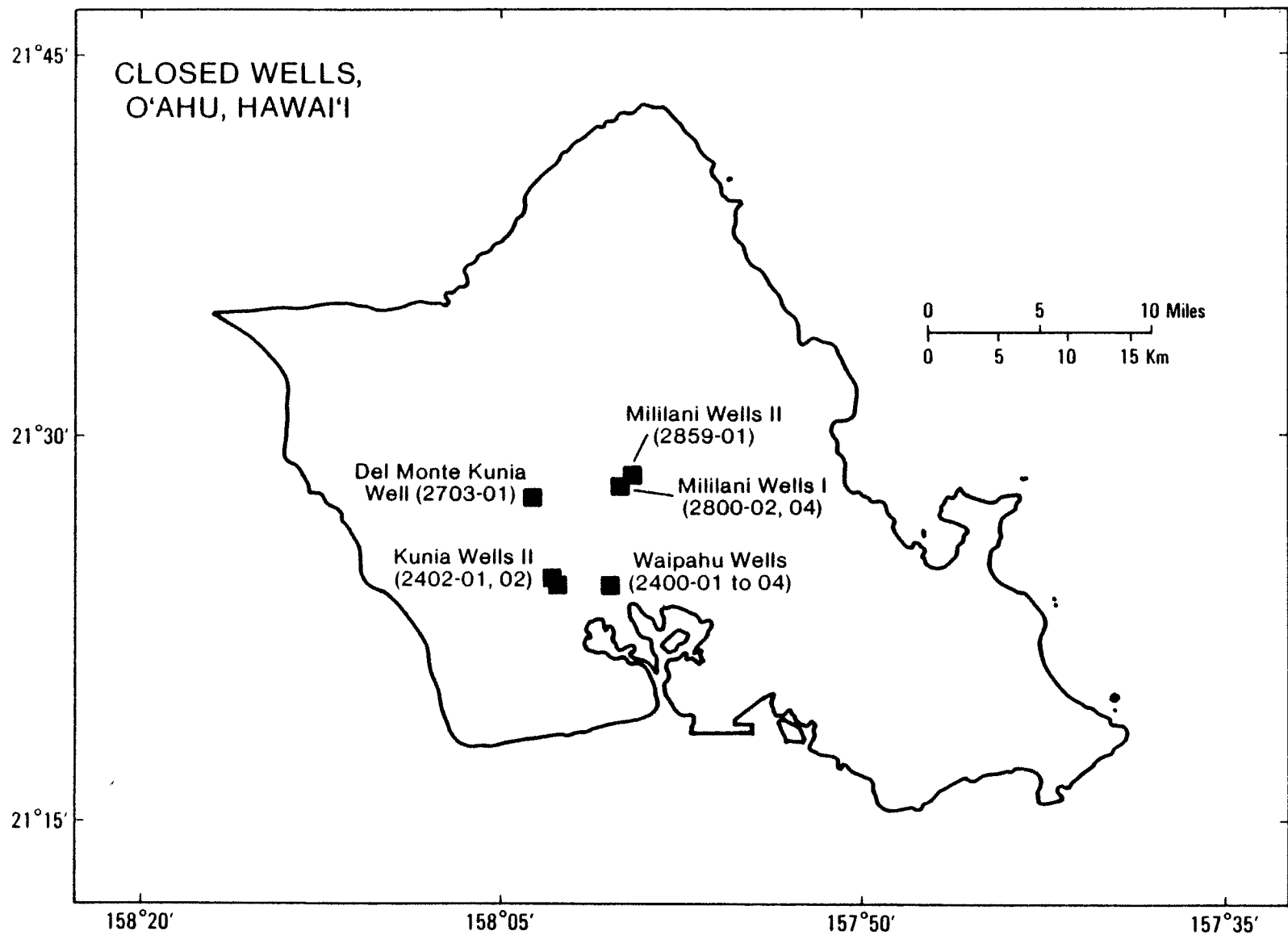


Figure 3. Closed well sites on O'ahu, Hawai'i

Subsurface Water and Soil Contamination Data Base

Various agencies and companies in Hawai'i have been monitoring the groundwater quality with regard to dibromochloropropane (DBCP), ethylene dibromide (EDB), and trichloropropane (TCP), while others have been investigating their movement through the soil at various sites on O'ahu and Maui. The Data Base and its accompanying report represent an effort to compile all available results from water and soil contamination tests and to organize the data into a uniform, computer readable format to facilitate research on the extent, movement, and persistence of contaminants in the soil and groundwater of Hawai'i.

METHODOLOGY. All sources of information regarding the chemical concentrations of DBCP, EDB, and TCP in the groundwaters and soils of Hawai'i were sought, tabulated in a standardized format, keypunched for computer entry, and stored on magnetic tape. Included in the report are a description of the chronology of contaminant discovery; maps of well, spring, and soil-bore sites; and tables of variable descriptions, laboratory notes, abbreviations, computer storage specifications, and data summaries. The Data Base spans a period from 15 April 1977 to 30 October 1984.

The Data Base, issued as a separate report in two parts (Oki and Giambelluca 1985), is a contribution to several on-going projects regarding the contamination of subsurface water and soil in Hawai'i. Specifically, the compilation of data into a coherent form is expected to facilitate the tracking of contaminated subsurface water, the assessment of the potential for continued contamination by chemical residuals in the soil, and the search for well and aquifer rehabilitation strategies.

Data Base Indicated Extent of Contaminated Groundwater

OBJECTIVES. The objective is to examine available groundwater quality data to identify spatial and temporal patterns of DBCP, EDB, and TCP contamination. In addition, possible sources of DBCP, EDB, and TCP will be identified to establish a general relationship between the spatial distribution of contamination and the potential sources of contamination.

METHODOLOGY. Water quality data compiled by the Water Resources Research Center (Oki and Giambelluca 1985) were utilized to determine the extent of the contamination in southern and central O'ahu aquifers. Additional results from recent analysis performed by the University of Hawaii were utilized to supple-

ment the existing WRRC Data Base. Separate maps were drawn to depict spatial distributions of DBCP, EDB, and TCP contamination. On each map, all well sites tested for the particular compound of interest are shown. The contaminated well sites are identified on these maps. In addition, those contaminated well sites with sufficient available data were analyzed for temporal variations in contaminant levels from 1 September 1983 to 1 September 1984.

SPATIAL DISTRIBUTION OF CONTAMINATION. Well and spring sites tested for DBCP, EDB, and TCP contamination in relation to areas of pineapple cultivation are respectively presented in Figures 4, 5, and 6. The locations of the contaminated well sites appear to be correlated with the areas of past and present pineapple cultivation when the ambient groundwater flow patterns (Fig. 1) are taken into consideration. That is, the contaminated well sites are located directly within or hydraulically down gradient from areas of pineapple cultivation. The Del Monte Kunia Well No. 2703-01 is not down gradient from any fields which received regular applications of DBCP. DBCP contamination at that well site has been attributed to a spill of 1.87 m³ (495 gal) of EDB occurring on 7 April 1977 and sporadic leakage of DBCP and EDB on bare ground in the storage area (it was believed that the EDB contained a small amount of DBCP as an impurity) (Mink 1981). All other sites contaminated with either DBCP or TCP are within or hydraulically down gradient from fields which received applications of DBCP or DD. The EDB contamination occurring in the Waipahu area of southern O'ahu may or may not be the result of soil fumigation on upgradient Dole fields inasmuch as several significant pipeline leaks of petroleum products (aviation fuels) in the vicinity may have contributed to the EDB contamination (Fig. 2).

TEMPORAL VARIATION OF CONTAMINATION. The temporal variation of the contamination can be seen with the formation of a time series. Such a time series was formed when sufficient data were available. Several contaminated well sites were not analyzed due to an insufficient amount of quantitated results at these sites. In general, the time series presented in Appendix A do not indicate any distinct temporal variations of contaminant levels. The one year of record utilized may have been insufficient to reveal any significant trends. The one exception to this generalization is at Mililani Well II Pump 5 (2859-01). From October 1983 to April 1984, DBCP concentrations at this site rose steadily from 25 to 70 parts per trillion (ppt). This may have been due to the continual introduction of DBCP from some source or the aquifer

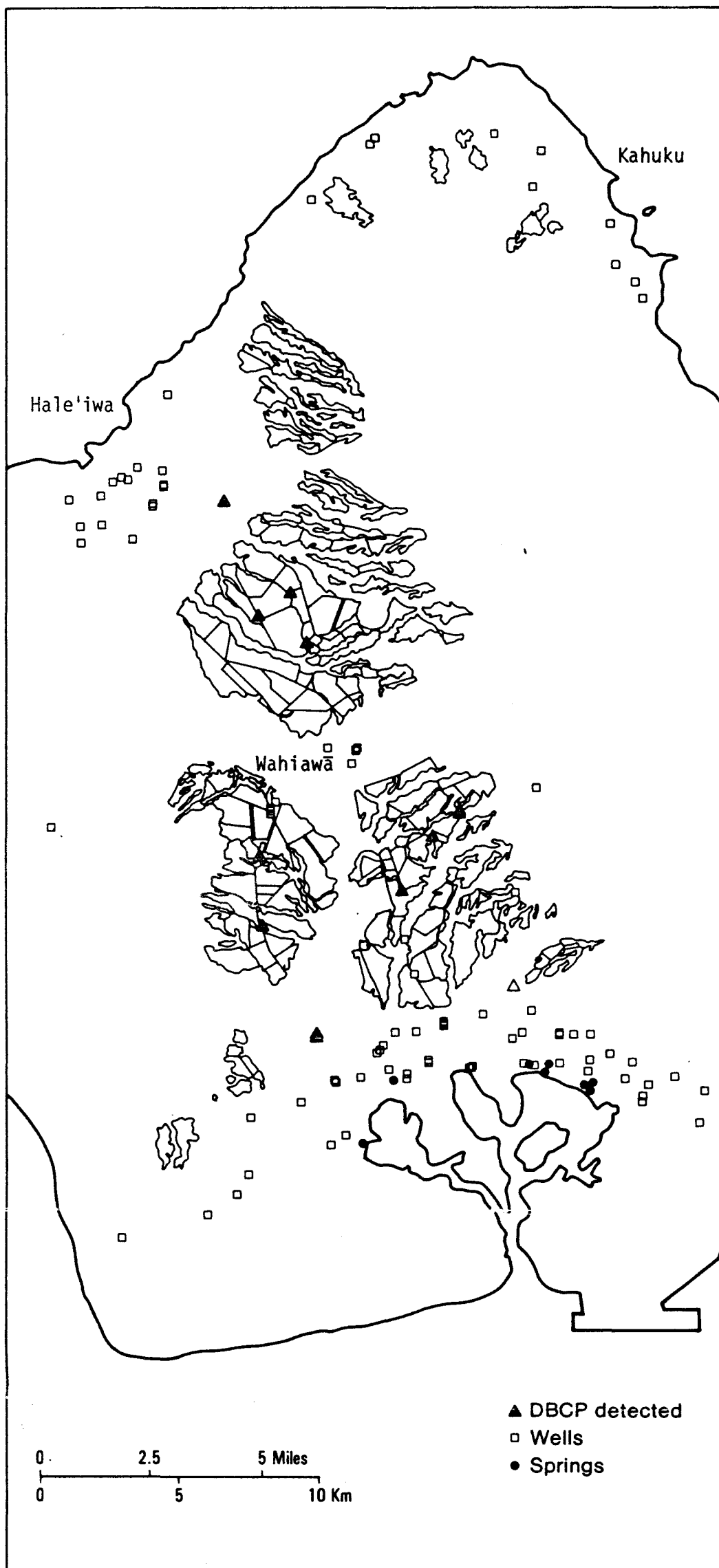


Figure 4. Well and spring sites tested for DBCP contamination in relation to areas of pineapple cultivation, central O'ahu, Hawai'i

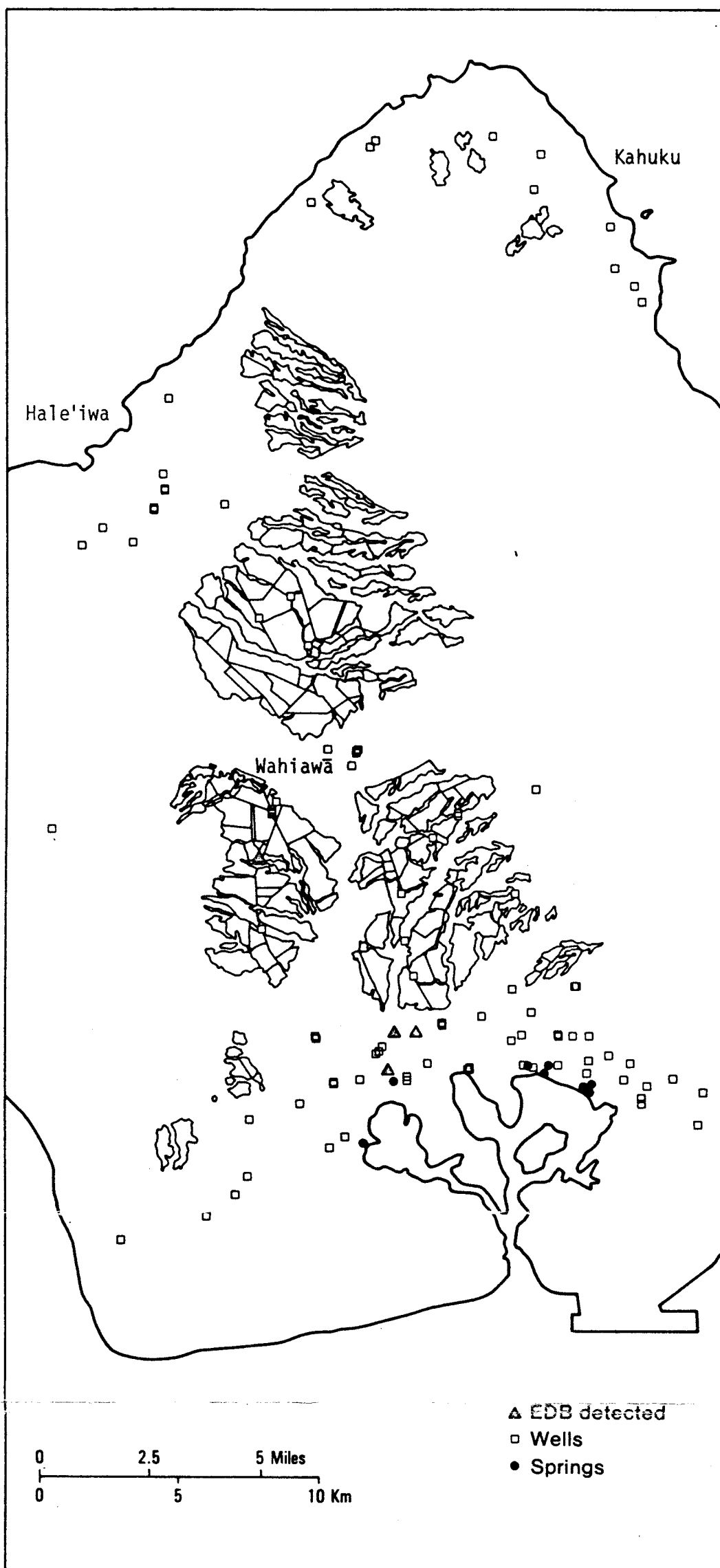


Figure 5. Well and spring sites tested for EDB contamination in relation to areas of pineapple cultivation, central O'ahu, Hawai'i

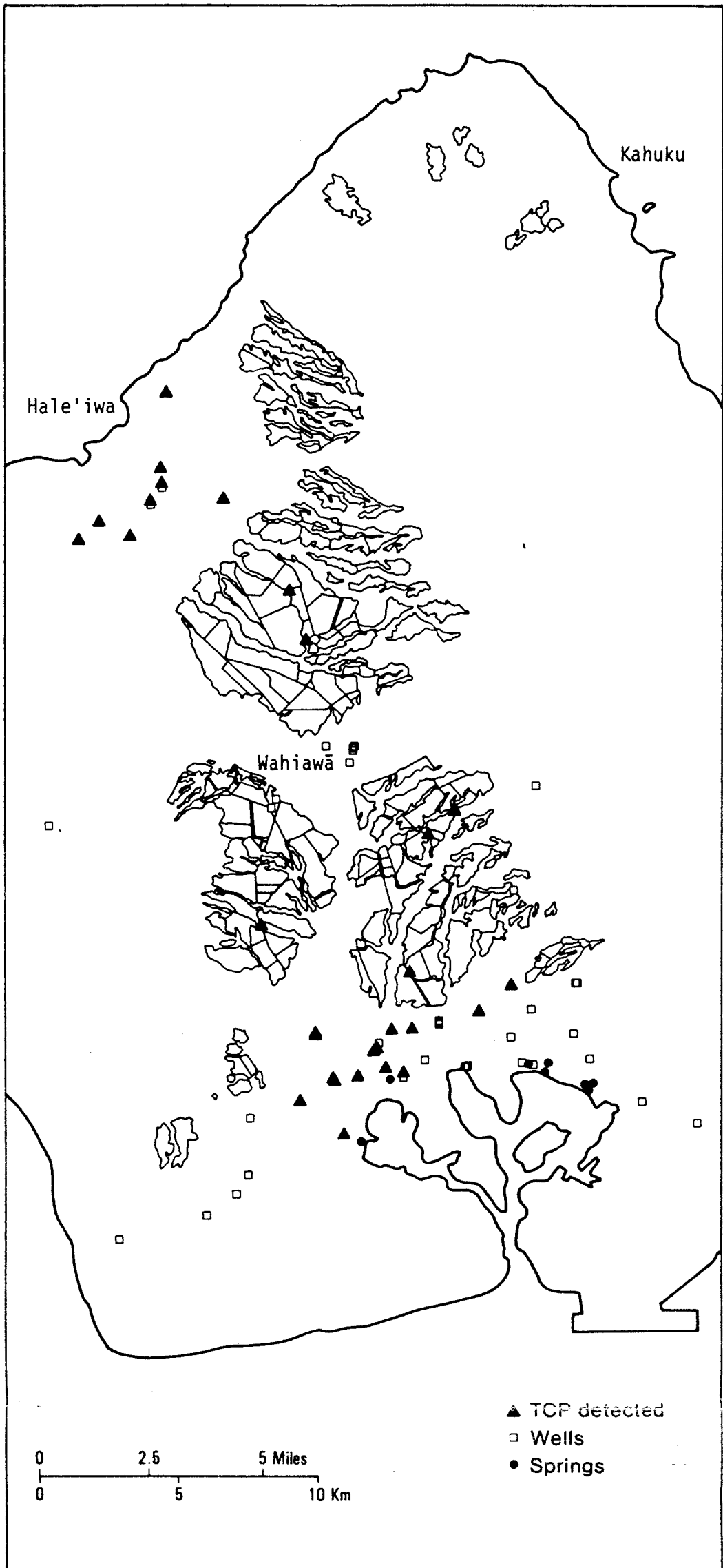


Figure 6. Well and spring sites tested for TCP contamination in relation to areas of pineapple cultivation, central O'ahu, Hawai'i

response to variable well pumping rates.

Project Groundwater Contamination Investigative Sampling

The project sampling program was designed to estimate the reach of contamination in and beyond the pineapple areas by including a variety of sampling sites in southern, central, and northern O'ahu. Sites were selected to supplement the extensive analytical data generated by the State, BWS, and U.S. Navy. Samples were collected at the Pearl Harbor Springs from orifices and shallow artesian wells, from plantation wells, springs in northern O'ahu, and BWS wells. The sampling net included sites in the Koolau and Waianae basal aquifers of southern and northern O'ahu and in the Wahiawa high level aquifer.

PEARL HARBOR SPRINGS. The springs at the inland margin of Pearl Harbor are the discharge front of the basal lens of the Koolau aquifer of southern O'ahu. They occur where the sediments of the coastal plain abut against and lie as a thin cover over the residuum-rock of the Koolau volcanic series. The largest discharges take place directly from saprolite overlying the unweathered basaltic aquifer, and smaller individual orifices and seepages break through the sediments where they are thin and unconfining.

A transect of discharges from the inner edge of the coastal plain to the harbor reflects a vertical section of the lens inland of the discharge front. The uppermost flow lines of the lens discharge furthest inland and lower ones break out toward the coast. By selecting individual orifices it is possible to obtain an image of the quality of flow lines at their relative position in the lens.

In a lens in which infiltrating water does not mix throughout with the resident water, some flow lines, normally the higher ones, may carry contaminants while others may not. The lens in southern O'ahu is so thick that it is unlikely that complete mixing of infiltrate and resident water takes place.

Four major spring areas and a smaller one drain into Pearl Harbor. The most easterly, Kalauao, is now remote from plantation agriculture, but at one time, until about 1960, it was directly down gradient from irrigated sugarcane fields. Next westward, the Waiiau-Waimano complex is probably outside the flow path from either pineapple or sugarcane cultivation, but the large drainage beyond it, Waiawa Springs, may be on the periphery of the flow net. Still further westward, the very large springs in the Waipahu depression and in Waikele Valley are the most likely candidates to exhibit contamination from

agricultural chemicals. Beyond Waikele, groundwater discharges as diffused seepage in the lower reach of the Honouliuli flood plain.

Where wetland agriculture is practiced on the coastal plain, farmers have drilled shallow artesian wells to add to the flow of natural springs. As sampling sites these wells are not as informative as spring orifices because they integrate many flow lines rather than represent a small interval of them.

In only one spring area, and there at a single site, was contamination detected. EDB (160 ppt) and TCP (120 ppt) were found in a combined spring and tunnel discharge from the east bank of Waikele Gulch. This appearance is consistent with the detection of EDB in the BWS Waipahu wells and the new Amfac wells in the same area. It is noteworthy that EDB has not been detected anywhere but in the facet between Waikele Valley and Panakuahi Gulch.

SOUTHERN AND CENTRAL O'AHU. Since 1980 numerous wells in the Pearl Harbor sector of southern O'ahu have been sampled by the Hawaii State Department of Health (DOH) and the Board of Water Supply (BWS) in a program aimed at detecting the limits and levels of contamination of the groundwater. Most of the wells sampled are in the Koolau basal aquifer where the BWS has its principal pumping stations. The program has focused on monitoring contaminant concentrations in the Board's wells.

The Waianae aquifer of the Pearl Harbor sector has not been comprehensively nor regularly sampled, even though it is down gradient of a large portion of Del Monte's pineapple fields. No BWS wells obtained water from this aquifer until recently when the Campbell well (200-04) was put on stream. The U.S. Navy, however, supplies the Barbers Point Naval Air Station with water from Shaft 14 (2103-03), an infiltration gallery in Waianae basalt.

The high level water in the Wahiawa aquifer of central O'ahu has been sampled to some extent but, apparently, sporadically rather than routinely. A considerable acreage of pineapple overlies the high level aquifer.

In the WRRC sampling of wells in the sugarcane area on the Koolau basalt of southern O'ahu, neither DBCP nor EDB were detected, but TCP was found in all of the Koolau aquifer wells. No detectable concentrations of EDB, DBCP, and TCP have yet been found in the Waianae basalt aquifer. At a private well (Honolulu International Country Club) just down gradient of pineapple, a DBCP concentration of 16 ppt, which is less than the standard limit of 20 ppt, was found along with 130 ppt TCP.

DBCP and TCP were detected in the northern portion of the Wahiawa high level aquifer, confirming results earlier obtained by the DOH. No levels were

found at the BWS pumping station in the southern part of the aquifer. Evidently the northern part, which lies under pineapple fields, drains toward Waialua.

NORTHERN O'AHU. DBCP in less than the standard detection limit was found in Waialua Sugar Company's large infiltration gallery pumping station (Pump 17) in combination with a large quantity of TCP (530 ppt). Nowhere else in northern O'ahu was DBCP detected, but at all sites in the Koolau aquifer significant quantities of TCP were measured. In the Waianae aquifer at Mokuleia no concentrations of the contaminants appeared. To date, the Waianae aquifers in northern and southern O'ahu seem to be free of contamination.

Summary

Based on the Data Base, a correlation is apparent between the location of the contaminated wells and the location of areas used for pineapple cultivation. However, the occurrence of fuel pipeline leaks of aviation fuels containing EDB was also located in the vicinity of several contaminated Waipahu wells. No significant temporal variation has occurred in the contamination of selected wells in southern O'ahu from 1 September 1983 to 1 September 1984.

Based on WRRC sampling in and beyond pineapple areas, preliminary conclusions include the following:

1. EDB. Only in the Waipahu area between Waikele and Panakuahi gulches has EDB been detected in groundwater.
2. DBCP. Detectable concentrations of DBCP occur in the Koolau aquifer beneath and down gradient of pineapple fields, but have not been detected in the Waianae aquifer.
3. TCP. TCP is widely distributed in the Koolau aquifer beneath and down gradient of pineapple fields but has not been detected in the Waianae aquifer. Detection of DBCP is always accompanied by detection of TCP, but TCP may also appear alone.

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GROUNDWATER CONTAMINATION POTENTIAL OF RESIDUAL PESTICIDES IN SOILS

For a number of years various pesticides have been applied to surface soils of central O'ahu in an attempt to reduce nematode infestation of pineapple plants. Pesticides have since been detected in groundwater drawn from the underlying aquifer. The compounds being detected are classified as fumigant nematicides, dibromochloropropane (DBCP) and ethylene dibromide (EDB), both halogenated hydrocarbons. Although these compounds have been successful in controlling nematode populations, they have been banned from use in pineapple cultivation because of their carcinogenicity and presence in groundwater.

Besides detection in groundwater, DBCP and EDB residues have been detected in soils and underlying saprolite, despite their discontinued use on O'ahu some years ago (Dept. of Agriculture 1983). Another contaminant, trichloropropane (TCP), which originated in the nematicide DD applied over 30 years ago, has also been detected in groundwater samples taken from several locations on central O'ahu. Acceptable levels for DBCP and EDB, set by the Environmental Protection Agency and the State of Hawaii, are in the parts per trillion (ppt) range. Both DBCP and TCP have been detected at the parts per billion (ppb) level in water and soil samples obtained from the Wahiawa Plateau in central O'ahu.

The overall objective is to examine the leachability of sorbed pesticide residues and to assess the possibility that continued groundwater contamination can result from the desorption of these residues. Leachability can be studied through the analysis of soil-pesticide systems. More specifically, leachability can be assessed by sorption distribution coefficients and by characterizing the kinetics of sorption-desorption processes.

Characterization of Geologic and Mineralogic Parameters

PROBLEM AND RESEARCH OBJECTIVES. Geologic parameters, especially those related to the occurrence, mineralogy, and hydrologic characteristics of the soil and saprolite zones, in the Wahiawa Plateau area of southern O'ahu are of critical importance to the movement of subsurface water and pesticides. A fair amount of geologic information from southern O'ahu is available, however, little of it is directly pertinent to problems of pesticide transport. In 1983 the Hawaii State Department of Agriculture collected soil and saprolite

core samples for pesticide analysis from several boreholes beneath pineapple fields in the Wahiawa Plateau. These core samples have been stored on the University of Hawaii campus and are available for further mineralogical analysis. Furthermore, a companion WRRC Subsurface Water Quality subproject has been undertaken for the purpose of collecting additional soil and saprolite core samples for pesticide analysis and mineralogical and hydrological testing.

The research objectives are (1) to summarize applicable geologic information presently available for the Wahiawa Plateau area, (2) to analyze core samples collected in 1983 to characterize their mineralogy, and (3) to use the findings from objectives 1 and 2 to guide a new borehole drilling and core sample collection program.

METHODOLOGY. The project was divided into three sub-tasks corresponding to the three objectives listed above. Approximately the first three months were devoted to collecting and compiling previously existing pertinent geologic data. This task has been completed. The second sub-task, which is still in progress, is devoted to mineralogic analysis of existing soil and saprolite core samples. A reconnaissance program of qualitative analysis using x-ray diffraction is intended to provide a general picture of the soil and saprolite mineralogy. This is to be followed by more detailed analyses, concentrating especially on the fine-grained and amorphous fractions. X-ray diffraction is being used for qualitative analysis and x-ray fluorescence for quantitative analysis. Some electron microscopy also will be undertaken. The third sub-task is to provide guidance for the drilling of additional sample boreholes. Results from the first two sub-tasks will be used to plan the location and sampling depths of additional soil and saprolite core samples which will be analyzed for pesticide concentrations as well as mineralogical and hydrological characteristics.

PRINCIPAL FINDINGS AND SIGNIFICANCE. Sub-task 1, the compilation of pertinent geological information has been completed. The information consists of a generalized description of the geology of the Wahiawa Plateau area, and more detailed geologic/mineralogic data from the eight borehole sites where core samples were collected in 1983 and 1985 for pesticide and mineralogical testing. Data have been compiled on borehole location, sampling intervals, geologic province, soil types, detailed mineralogy, presence of perched water, and saprolite occurrence.

Sub-task 2, analysis of mineralogical characteristics from the 1983 Department of Agriculture borehole core samples, has been essentially completed. Sixty-two core samples from nine different boreholes were analyzed by x-ray diffraction and the results plotted as mineral concentration versus depth. More detailed results of this sub-project have been described elsewhere (see attached Mineralogical Analysis summary in Appendix A). To summarize from Jones, with the exception of samples from one borehole (Dole field 4111-A) only secondary minerals were detected. This indicates that weathering apparently has been severe in the samples analyzed. It is recommended that deeper samples be collected to investigate the depth to which this complete weathering takes place (note that this suggestion has been implemented in the 1985 drilling sub-project).

Sub-task 3, which is to utilize the findings from sub-tasks 1 and 2 to provide guidance for locating additional borehole sampling sites, has been completed. Based primarily on the findings from this study, five additional boreholes were drilled and core samples collected for pesticide, mineralogical, and hydrological analyses. Thus far all boreholes have been drilled into materials derived from Koolau basalts. One or two additional boreholes remain to be drilled. Permission has recently been obtained from Del Monte Corp. to allow drilling the holes in their fields, thus penetrating soil and saprolite materials derived from Waianae rocks.

Project Borehole Drilling

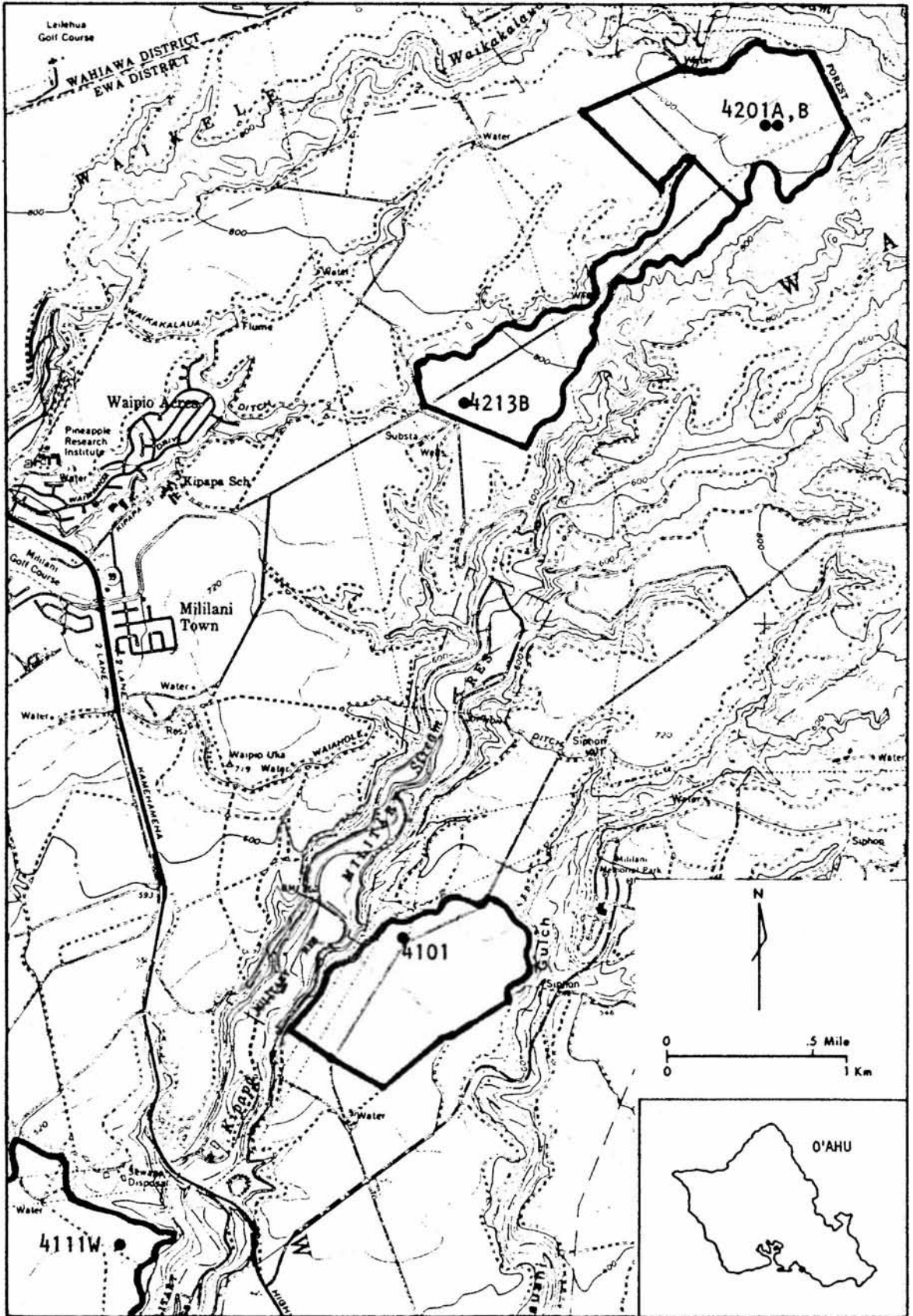
PROBLEM AND RESEARCH OBJECTIVES. During the past several years information has been collected on the vertical and areal distribution of pesticides within the soil and saprolite layers in central and southern O'ahu. During the summer of 1983, the Hawaii State Department of Agriculture supervised the drilling of several boreholes in Dole and Del Monte pineapple fields from which samples were collected for EDB and DBCP analysis. Additional drilling is desirable to expand the existing sampling base and also to resample in the vicinity of several of the more interesting 1983 sampling sites.

The activity has as its primary objective to further delineate the vertical distribution of residual fumigants in the soil and saprolite and their rates of movement. To do this several boreholes in Wahiawa Plateau pineapple fields will be drilled to obtain core samples that will be analyzed for EDB, DBCP, TCP, clay mineralogy, and various geohydrological parameters.

METHODOLOGY. Some 6 to 8 boreholes will be drilled in Dole and Del Monte pineapple fields to collect core samples for pesticide, mineralogical, and physical testing. The holes, which will range in depth from 75 to 150+ ft, will be drilled in Dole fields 4201, 4213, 4111, and 4101, and if permission is granted in Del Monte fields 8, 9, or 13. To avoid contamination of sample material special precautions will be used in the drilling and sample collection operations. Drilling for the first 100 ft will be done with a hollow-stem auger and core samples collected inside the auger tube with a split spoon sampler. So-called "undisturbed" samples for physical testing will be collected with a Shelby tube. Drilling and sampling below 100 ft will be done with foam or air rotary. All sampling tools will be thoroughly washed with water and detergent between each sampling run.

Samples collected for pesticide testing will be chilled immediately and analyses conducted within 24 hr. Samples will be tested for EDB, DBCP, and TCP in the University of Hawaii Agricultural Biochemistry Laboratory. The core samples will also be subjected to several additional tests including the following: EDB and DBCP desorption and leachability testing; determination of clay mineralogy; and determination of physical geohydrologic parameters such as porosity, pore size distribution, pore structure, and hydraulic conductivity. All these analyses will be conducted in the Department of Agronomy and Soil Sciences under the supervision of R.E. Green and R.C. Jones.

PRINCIPAL FINDINGS AND SIGNIFICANCE. Approximately 75% of the drilling and pesticide analysis work is completed. None of the other testing work including interpretation of data has begun. Five boreholes have been drilled (Fig. 7), ranging in depth from 70 to 146 ft. A total of 106 samples were collected and analyzed for pesticides and 80 "undisturbed" core samples collected for later physical and mineralogical testing. EDB, DBCP, and TCP were all detected in Dole fields 4201 and 4213, but were not detected in Dole fields 4111 and 4101 (see attached plots).

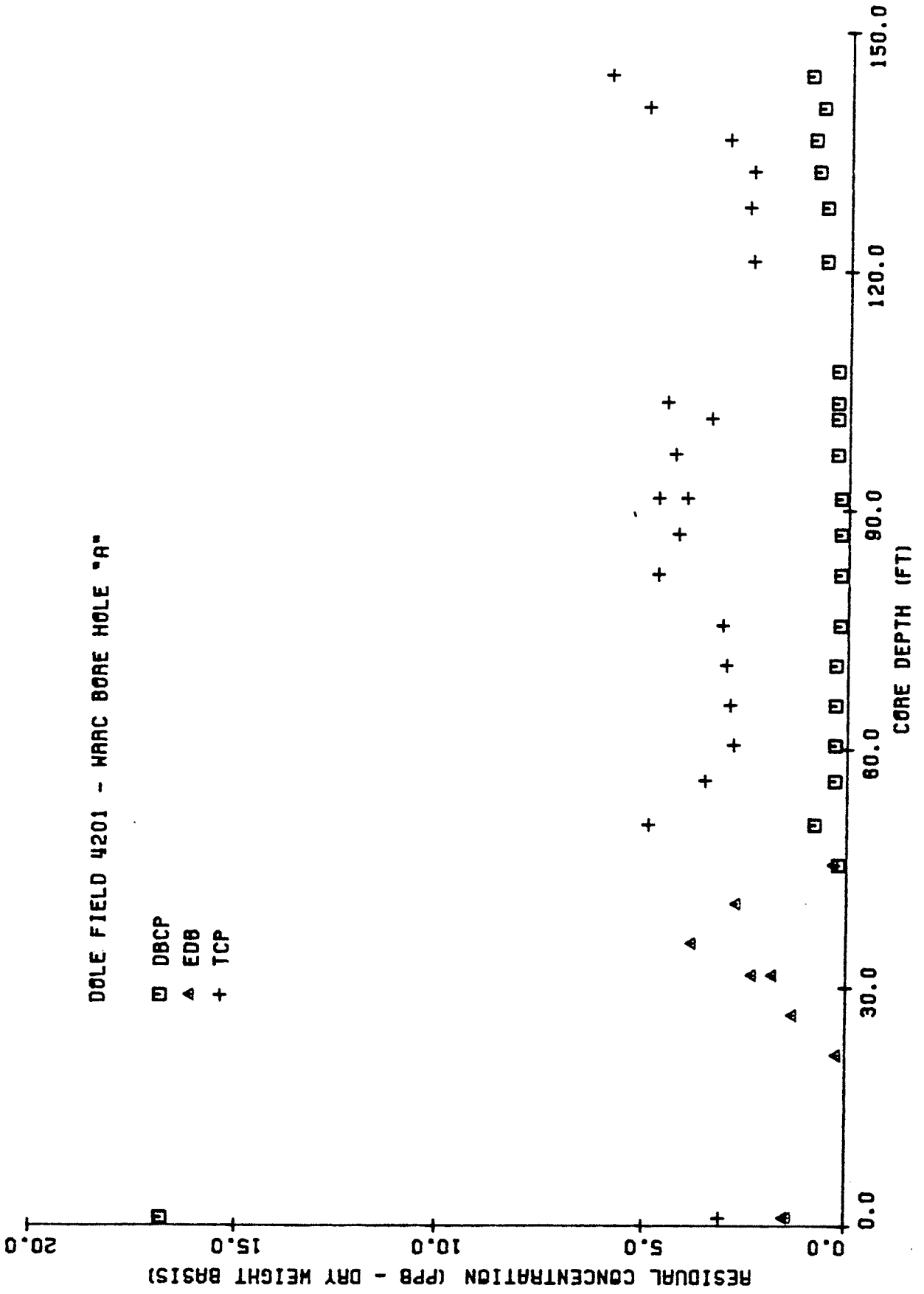


Base Map: USGS Waipahu 1:24,000 scale quadrangle.

Figure 7. Location of borehole sampling sites in central O'ahu

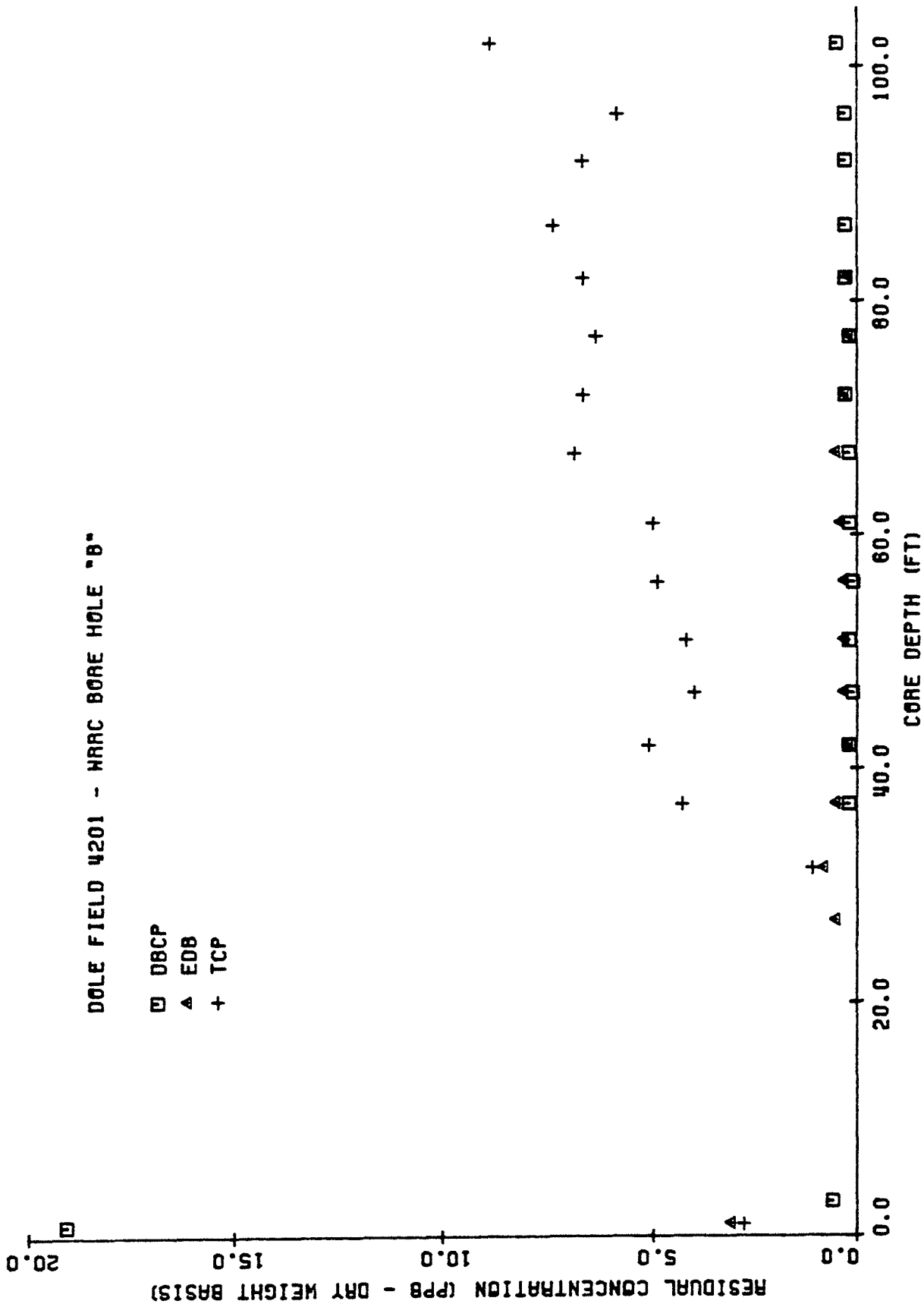
DOLE FIELD 4201 - WARC BORE HOLE "A"

□ DBCP
▲ EDB
+ TCP



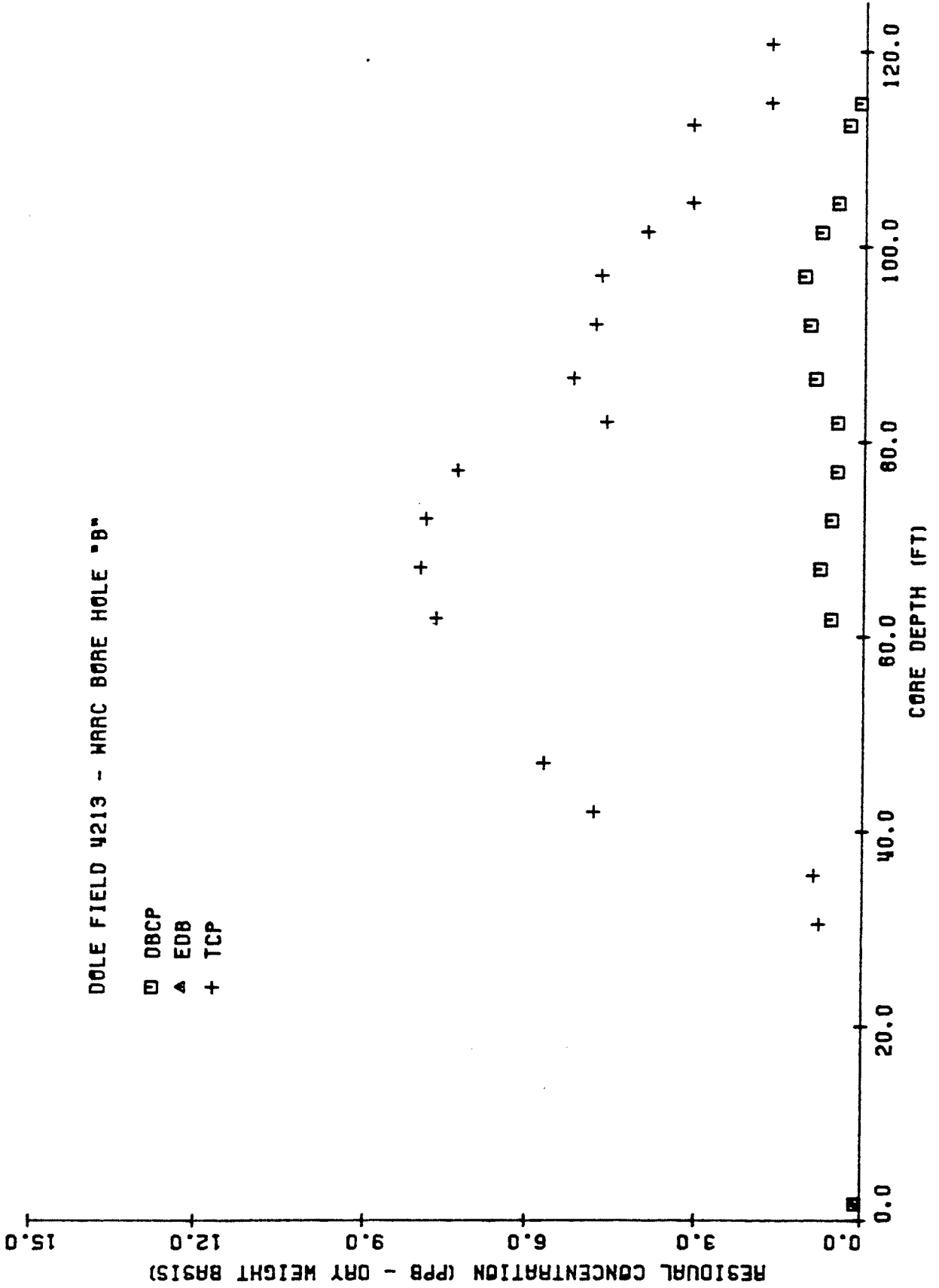
DOLE FIELD 4201 - WARC BORE HOLE "B"

- DBCP
- △ EDB
- + TCP



DOLE FIELD 4213 - WARC BORE HOLE "B"

- DBCP
- ▲ EDB
- + TCP



Desorption and Leachability of Residual DBCP and EDB from Soils and Saprolite

PROBLEM AND RESEARCH OBJECTIVES. There is evidence that nematicides applied to pineapple soils in Hawai'i may move great distances through the soil, saprolite, and underlying rock, and eventually reach the basal aquifer. Although the major portion of applied DBCP and EDB dissipates from the root zone by volatilization, the pesticide residue in the soil profile is a potential source of groundwater contamination. Such residues exist in both the sorbed and solution phases, the relative amounts in each phase depending principally on the soil organic matter content. The amount of pesticide remaining in the soil profile after application diminishes exponentially with time during the first few weeks; subsequently, the residue may be present at concentrations ranging from a few parts per billion (ppb, dry soil basis) to a few thousand ppb. The "leachability" of this residue is not known, that is, we do not know to what extent residues of DBCP and EDB in the soil profile and the underlying saprolite may move with percolating water to greater depths.

Research objectives are (1) to determine the rate and extent of DBCP and EDB desorption from soils in relation to soil properties, (2) to determine the relationship between the hydraulic properties of soils and the displacement of residual pesticides by transient water movement, and (3) to assess the potential of groundwater contamination by residual DBCP and EDB in soils in central O'ahu.

METHODOLOGY. To determine the rate of release of pesticide from the sorbed state into the soil solution, we need methods which provide a means of monitoring the change in concentration of pesticide in solution over time during desorption. The conventional batch equilibration method is not satisfactory for this purpose. Thus, we have developed methods which exploit the tendency of DBCP and EDB to volatilize. By measuring the gas phase in a sealed vessel which contains contaminated soil and water, we can deduce the concentration of pesticide in solution from an experimentally derived relationship between solution and vapor concentrations of the pesticide. A mass balance calculation then allows a determination of the sorbed quantity over time. A second method will measure cumulative removal of sorbed pesticide over time in a purge system. Soil samples will be taken from a number of field sites on O'ahu (for EDB) and on Maui (for DBCP) to examine the rate of desorption (or leachability) of residual pesticide. Measurements will be

made on (1) suspensions of soil, (2) packed columns of sieved soil (imposed uniformity of pore space), and (3) field-structured soil. The displacement of recently applied pesticides versus long-term residual pesticide will be evaluated to provide an experimental basis for developing a methodology to predict the mobility of both recently applied and residual pesticides. Attempts will be made to obtain undisturbed core samples of saprolite if possible. Soil samples will be characterized for key chemical and physical properties if the properties are not already known. Organic carbon will be determined on all samples by dry combustion.

PRINCIPAL FINDINGS AND SIGNIFICANCE. In this study, leachability is assessed by sorption-desorption measurements and is characterized by distribution coefficients and the kinetics of release of sorbed residues.

Two methods for characterizing sorption-desorption processes have been developed that exploit the tendency of these fumigant pesticides to vaporize. Both methods analyze the vapor phase of a soil-pesticide system. The indirect sorption method results in a determination of distribution coefficients; the purge system results in a characterization of the kinetics of desorption.

Preliminary experiments using the indirect sorption method to determine distribution coefficients for a surface soil obtained from central O'ahu gave results which compare favorably with those from a conventional batch equilibration method, and revealed that the pesticide residues are highly sorbed. The new sorption-desorption methods will be used to determine the leachability of DBCP and EDB residues in soil and saprolite obtained from central O'ahu.

This activity is principally reported in the UHM-WRRC companion project, "Desorption and Leachability of Residual Pesticides in Soils and Saprolites."

Deep Percolation of Water from Pineapple Fields

Efforts are now being made to identify the sources, concentrations, spatial extent, movements, and rates of degradation of the O'ahu groundwater contaminants, DBCP, EDB, and TCP. A spatially detailed evaluation of the time series of water percolation is required so that leaching from the top soil, downward transport through the profile, and eventual movement of the pesticides within the basal groundwater may be estimated. The purpose of this activity is to provide an estimate of downward percolating water in high spatial and temporal detail for present and former pineapple growing areas of central O'ahu.

METHODOLOGY. The water balance method is used in this study to estimate the sequence of downward percolating water for each location of interest. The study area includes all areas overlying the principal groundwater bodies of central O'ahu which have been used for pineapple cultivation at any time between 1946 and 1983. The water balance is computed separately for each major pineapple field on a monthly time interval for the entire study period, 1946 through 1983, regardless of whether the area remained in pineapple. Thus, the model should be adaptable for handling various alternative land uses.

Using principles developed by Thornthwaite (1948), and Thornthwaite and Mather (1955), and others, a model of the water balance was devised in which the influences of land use are described by certain variables. Other variables in the model account for the climatic influences and site factors unaffected by land use. With such a model, the appropriate climatic sequence and land use parameters can be used to estimate the water balance for a particular time and place.

MODEL. The model used in this study is a variant of the Thornthwaite and Mather (1955) bookkeeping procedure. For a given location, the model keeps account of the moisture exchanges that occur within the soil-plant system during each time interval. To do so, the state variable X_i is first computed. (Variables are expressed as the average equivalent water depth over the entire area unless otherwise noted.) X_i is determined as

$$X_i = S_{i-1} + (P_i - RO_i)G^{-1} + I_i + U_i - E_i$$

where S_{i-1} is available soil moisture at beginning of time interval i , (unpaved area only); P_i is precipitation during time interval i ; RO_i is surface runoff during time interval i ; G is ratio of unpaved area to total area; I_i is agricultural irrigation during time interval i , U_i is urban irrigation during time interval i (applied to a portion of unpaved area depending on degree of urbanization); and E_i is actual evapotranspiration during time interval i . On the basis of X_i , the end-of-interval soil moisture and percolation are determined as

$$\begin{aligned} S_i &= 0 && \text{For } X_i < 0 \\ Q_i &= 0 \\ E_i &= -X_i \end{aligned}$$

$$\begin{array}{ll}
 S_i = X_i & \text{For } 0 < X_i < \phi \\
 Q_i = 0 & \\
 S_i = \phi & \text{For } X_i > \phi \\
 Q_i = G(X_i - \phi) &
 \end{array}$$

where S_i is available soil moisture content at the end of time interval (unpaved area only); Q_i is downward percolation beyond the root zone during time interval i ; and ϕ is soil available moisture capacity (unpaved area only). Note that when X_i is negative, E_i is also adjusted.

Each input variable in the model is evaluated by direct measurement or by estimation from physical or empirical relationships. The evaluation of input variables is described below.

PRECIPITATION. Monthly precipitation is estimated at each node of a 10 by 10 grid superimposed over the study area by computer interpolation. The monthly precipitation sequence for each pineapple field is assumed equal to that of the nearest node.

RUNOFF. Runoff in the water balance model is defined to include overland flow, interflow, and high level spring flow. Streamflow data are insufficient for estimating runoff at the spatial resolution required for this study. Runoff curve numbers have been derived experimentally for Hawai'i pineapple and sugarcane fields (Cooley and Lane 1980) for use in the Soil Conservation Service (SCS) (U.S. Department of Agriculture 1972) runoff model. A modified version of the SCS method (Giambelluca 1983) is used to estimate monthly runoff for each pineapple field.

AGRICULTURAL IRRIGATION. Sugarcane irrigation is estimated on the basis of well pumpage, ditch flow, and stream diversion records. Pineapple in Hawai'i is traditionally irrigated only at planting time and during extreme drought. The amounts had a negligible effect on the water balance. In recent years, drip irrigation systems have been installed in some fields, and these now receive a significant amount of irrigation. Pineapple irrigation is estimated from water source records.

URBAN IRRIGATION. Seasonal fluctuation in municipal water consumption on O'ahu has been attributed to variations in outdoor uses, primarily lawn sprinkling (Yamauchi 1981). Assuming that the lowest observed water use represents a period of no lawn sprinkling (an extended rainy period), the volume of water used for urban irrigation was computed for each month of a 10 yr sample period. The area over which this irrigation occurred was estimated and

monthly depths of lawn sprinkling determined (Giambelluca 1983, Table 9). Monthly means from the 10 yr sample period are used as input to the water balance model for residential and park land uses.

EVAPOTRANSPIRATION. Evapotranspiration (ET) is evaluated using the concept of potential evapotranspiration (PE) (Thorntwaite 1948). Evaporative demand (PE) is first determined. Actual evapotranspiration (E) is estimated as a fraction of PE according to the prevailing soil moisture content. PE is estimated on the basis of recently prepared annual pan evaporation maps (Ekern and Chang 1985). Average monthly PE is estimated from the annual figure and seasonal patterns at individual pan stations. Adjustments are made for surface type and vegetation density. The relationship between E and soil moisture for Hawai'i developed by Giambelluca (1983) depends on soil type, root depth, and evaporative demand (PE).

INTERIM RESULTS. Thus far, work on this project has focused on land-use identification, parameter evaluation, and gathering of necessary hydrological data. As such, no percolation figures are yet available. However, based on previous studies using the same model (Giambelluca 1983), it appears that ET-suppression by pineapple causes percolation to be significantly higher than that experienced under a natural vegetative cover. This fact has important implications regarding the leaching of pesticides and may account for the unexpected movement of these chemicals through the great thickness separating the pineapple fields from the basal water.

Summary

The potential of groundwater contamination by residual pesticides in soils presupposes that the residual pesticides are leachable from the soils in significant amount and rate, and that the transport agent is principally deep percolation of water from the apparent sources of pineapple fields. Similar leaching processes would occur for EDB that was contained in pipeline leaks of aviation fuels and that came into contact with soils.

In order to accomplish these objectives, it is necessary to be able to determine the amount and rate of percolation of water below the soil and saprolites, and the concentration of pesticides in the percolating water. This information will be used subsequently by another WRRRC project task to model the transport downward in the several hundred feet of basaltic rock to the basal water table and then the lateral migration from one part to the

other parts in the basal water itself. To the regulatory agencies and the major water purveyors, these transport information should be useful for designing an effective monitoring system and groundwater management which includes phasing in and out of water treatment plants for constructed and operated for low-level pesticide removal. The necessary tasks and progress made thus far include:

1. Completion of compiling pertinent geologic information including generalized geologic description and existing borehole geology and mineralogy.
2. Initiation of drilling additional deeper holes that will delineate vertical distribution of residual fumigants in soils and saprolites. Five holes have been drilled in Dole fields to depths 70 to 146 feet and core samples analyzed for pesticides, mineralogy, and hydrologic parameters. Additional boreholes are planned in Del Monte fields in Waianae volcanic rocks.
3. Development of two needed new laboratory methods which will characterize the desorption leaching process and help predict the concentration of pesticides in percolating water over time. Leaching testing of contaminated soil samples has been planned.
4. A spatially detailed evaluation of the monthly time series of water percolation for each past and present pineapple field in central O'ahu. Works have focused on land-use identification, parameter evaluation, and gathering of necessary hydrologic data.

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WATER WELL TECHNOLOGY FOR CONTAMINATED AQUIFERS

The boundaries of the contaminated groundwater above the action level are poorly delineated in both areal extent and depth. These three well fields are widely scattered in the vast Pearl Harbor aquifer. Further, there is a remarkably non-uniform distribution of other wells in this aquifer, being very sparse in the upper and middle parts and concentrated in the lower part near Pearl Harbor.

The thickness of the contaminated water is not determinable with the presently available data. All such data are obtained under pumping condition. Among the very few monitoring wells, none of them was suited for the monitoring of the upper portion of the freshwater lens affected by the contamination. For the case of non-pumping condition, virtually no data are available to characterize the depth of contamination. One such test was performed by WRRC at Amfac's Waipahu Well No. 228-1 in February 1984. The EDB concentration was found identical at 25 ppt for the two water depths, 85 and 145 ft below the water table. However, EDB was nondetectable at the 5-ft depth below the water table. Inasmuch as the casing is inserted 46 ft below the water table, creating a column of static water within it, evaporation of the volatile chemical EDB could have taken place after nine months of exposure in the well casing and may account for the result of the surface water sample. Depth profiling of BWS Mililani Wells 7 and 9 and DLNR Mililani wells have been reported. Data are presently being collected.

Typically, Hawai'i water wells consist of a cased section in the upper part and an open hole of varied length in the basaltic flows in the lower part. The casing extends usually to a shallow depth below the water table. Under pumping condition, the pumped water is drawn from but not limited to the basaltic flows in contact with the open hole. How much of the aquifer above and below these basaltic flows actually contributing to the pumped water is unknown. Also, unknown is the relative amount of water contributed by the individual basaltic flows. The present water quality data base can only infer the minimum thickness of the contamination to be the bottom of the hole by assuming the aquifer water drawn into the well occurs no deeper than the hole.

Additional constraints are imposed on investigative programs of groundwater contamination in Hawai'i basaltic aquifers and remedial actions: expensive drilling in hard volcanic rock, hydrologic nature of the basaltic flows,

and presence of the underlying seawater. Drilling cost at \$300 to \$400 per foot and depth to water in hundreds of feet virtually rule out drilling monitoring wells. The difference in hydraulic conductivity among clinker, pahoe-hoe, and dense aa is vast (Mink 1980). As a result, deepening a contaminated well and casing off sections of the open hole as rehabilitative measures will experience considerable uncertain effectiveness. The presence of the underlying seawater poses a limit on the extent of deepening a contaminated water well as a rehabilitative measure.

It should be mentioned that some other rehabilitation methods of contaminated aquifer and wells have been used elsewhere. These include containment of the contaminated groundwater by constructing physical barriers, in-aquifer biodegradation of contaminants (bio-reclamation) by introducing suitable microorganisms that feed on the contaminants, and prolonged pumping to extract the contaminated water. Considerations have been given to these and other methods but none of them appear feasible at this time for the southern O'ahu situation.

Artificial recharge by wells or by surface spreading of uncontaminated water appears to be an effective but long-term method. With or without the occurrence of the present organic chemical contamination, artificial recharge should be seriously considered for groundwater management for O'ahu.

In spite of the aforementioned problems and uncertainties, it is desirable to explore various possibilities, or at least to develop necessary information, to rehabilitate the contaminated water wells. The incentive is an economic one since treatment of the pumped water for removing volatile organic chemicals (VOC) is expensive (GMP 1985).

The information should also be useful in reducing the uncertainties associated with drilling new wells to provide water having acceptable VOC concentrations.

New Water Wells

The objective is to develop a set of water well technology guidelines (design, construction, completion, development, testing, monitoring) tailored to the on-site VOC quality of the groundwater and aquifer characteristics for the purpose of producing a pumped water having acceptable VOC concentrations.

Two wells (Upper Honouliuli Wells I and II) in the Koolau basalt aquifer are planned by Campbell Estate at about the 400-ft elevation in upper

Honouliuli. The wells will increase the potable water supply for southwestern O'ahu. They are located in an area where contamination by volatile organic chemicals is suspected but has not been demonstrated. Drilling and testing the wells present an opportunity to determine whether contamination occurs, and if it does, whether it varies with depth and rate of pumping.

A preliminary agreement includes the following testing protocol:

1. Stage 1
 - a. Drill to 125 ft below sea level
 - b. Obtain salinity profile (DLNR or BWS)
 - c. Collect three static samples with thief sampler: one at the top of the saturated aquifer, the second in the middle, and the third at the bottom of the hole; analyze for chloride, nitrate, silica and sulfate
 - d. Conduct step pump test at 500, 1000, and 1750 gpm, holding each rate for 2 hr
 - e. Collect two samples per step rate for volatile chemical analyses, the first after 30 min of pumping, the last at the end of the step. These samples to be analyzed for TCP, EDB, DBCP, TCE, PCE and Atrazine; total of six samples
 - f. Collect a pumping sample for a complete standard water analysis at the end of the last step (BWS)
 - g. For the above, a total of ten samples will be taken.
2. Stage 2
 - a. Continue drilling to 250 ft below sea level
 - b. Place packer at -125 ft; repeat above protocol.

For both stages the total number of samples collected and analyzed is 20, of which twelve are for volatile organics and eight for inorganics. Analyses will be done through WRRC, except stage 1f. Maximum turn around time for the results will be ten days to enable expeditious well completion decisions. The salinity profiles will have to be open for inspection even sooner.

Drilling specifications will allow either rotary or cable tool, but drilling fluid will be specified as "foam". Mud will not be permitted, and strict requirements to prevent contamination by surface will be stated.

Retrofitted Water Wells

The objective is to develop a set of guidelines for modifying the pumping

regime of water wells and retrofitting water wells for the purpose of producing a pumped water having acceptable VOC concentrations from existing wells.

Wells in the same well field may not penetrate the same basaltic flows; therefore, they may draw water from somewhat different sources. Thus, a question may be posed as to whether the contamination may vary with the rate of pumping.

A testing protocol may be drawn up similar to that for Objective 1 for the upper Honouliuli wells. The essence is to conduct a step pump test at different pumping rates for a selected well, collect water samples, and analyze them for organics and other chemicals. The same test is repeated for another well in the same well field which is known to have most different water quality from the first well. The two sets of data will be interpreted. The end results are the effect of varying the pumping rates and the feasibility for deepening and casing the wells. Inasmuch as the Upper Honouliuli wells offer much greater flexibility for testing, this objective is held in abeyance as an alternative.

Summary

The activity objectives have been identified and the methodology prepared for the Campbell upper Honouliuli wells. An alternative objective and associated methodology have been prepared for BWS wells to be selected. The Campbell well construction and testing are tentatively scheduled for the spring of 1986.

The well technology to be developed can be useful for mitigating the effects of the contaminated groundwater. Further, the data and information to be obtained should help understand the migratory behavior of the contaminated groundwater body and will strengthen the groundwater data base.

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ALTERNATIVE TREATMENT METHODS OF LOW-LEVEL CONTAMINATED WATERS

Water treatment offers a traditional technology to reduce objectional water quality parameters to acceptable concentration. For EDB and DBCP, such technology is available, tested, and in operation elsewhere. However, a major unknown element is how well the technology can treat the low-level concentrations (ppt) that occur in Hawai'i groundwater and what modifications of the available technology need to be made or what alternative treatment methods can be developed to reduce the concentration to less than 20 ppt.

A recently completed BWS contracted study for Mililani and Waipahu water wells provided some positive answers on the effectiveness of three treatment methods and their capital and operating costs (GMP 1984). The treatments tested at Mililani were activated carbon, packed tower, and cooling tower. The first two treatments were also tested at Waipahu. These treatments demonstrated their effectiveness for both sites. The capital costs are on the order of 1.0 to 1.8 million dollars to meet the Mililani capacity requirement (4 mgd daily average) and 1.7 to 2.5 million dollars to meet the Waipahu capacity requirement (5 mgd daily average). The BWS selected activated carbon treatment, and a water treatment plant utilizing this method is presently under construction at each site.

A portion of the project is dedicated to explore alternative treatment methods to assess their feasibilities (practical and economic) and to further improve the effectiveness of the activated carbon treatment.

The pesticides of concern have been primarily EDB (ethylene dibromide) and DBCP (dibromochloropropane), generally found at < 100 ppt (parts per trillion). Also of concern is TCP (trichloropropane) at concentrations up to approximately 3 ppb. Although these pesticides were only found in well waters of central O'ahu at very low concentrations and the U.S. Environmental Protection Agency has not as yet established maximum concentration limits, the Hawaii State Department of Health has proposed that EDB and DBCP be limited to 20 ppt. Despite the concern over TCP, the Hawaii State Department of Health has not proposed an upper limit, although concern is being voiced in some areas that it may be a potential health hazard. For this activity TCP removal is not considered; however, its easy removal by activated carbon has been demonstrated.

Water Disinfectants

An exploratory project was designed to assess the feasibility of using chlorine, chlorine dioxide, hydrogen peroxide, ultraviolet (UV) light or UV light plus hydrogen peroxide to oxidize EDB in water and thus reduce its concentration. A full progress report of this activity is given in Appendix D.

METHODOLOGY. Purified EDB was added to clean water with 100 ppt to 20 ppb and this sample extracted with benzene using the liquid-liquid partitioning technique. The extract was analyzed for concentrations of EDB using gas chromatography. This same water sample containing EDB was then treated with various doses of disinfectants (chlorine, chlorine dioxide, hydrogen peroxide, UV light, and UV light plus hydrogen peroxide). These treated samples were similarly extracted using the liquid-liquid partitioning technique and the concentrations of EDB in these extracts determined by gas chromatography. The capacity of the various disinfectants to remove EDB from the water was determined by comparing the concentrations of EDB in the untreated water and the concentrations of EDB in the water after being treated with the various disinfectants. A full description of the methodology is given in Appendix D.

CONCLUSIONS. The object of this study was to determine whether disinfectants used to treat drinking water (chlorine, chlorine dioxide, hydrogen peroxide, UV, UV + hydrogen peroxide) were capable of reducing (oxidizing) the concentrations of EDB in clean water. The results of this study show that treatment of water with 5 to 5,000 mg/l chlorine was ineffective in reducing the concentrations of EDB. Moreover, treatment of water with chlorine resulted in the formation of numerous additional peaks detected by gas chromatography analysis indicating the formation of various subspecies of chlorinated organic compounds. These additional peaks masked the EDB peak and made interpretation of the results difficult. However, gas chromatography plus mass spectroscopy resolved this problem and indicated that EDB was not being oxidized by chlorine. Many of these additional peaks may represent other species of halogenated hydrocarbon which may differ from EDB but may also be toxic or carcinogenic. Thus treatment of water with chlorine as a means of oxidizing EDB is not recommended.

Treatment of EDB with 2 to 50 mg/l of chlorine dioxide was also ineffective in reducing the concentrations of EDB. Like chlorine but to a lesser degree, an increase occurred in the number of additional peaks detected by gas

chromatography analysis. Thus, evidence was obtained that chlorine dioxide was also capable of forming other products with unknown properties. Treatment of water with chlorine dioxide as a means of oxidizing EDB is not recommended.

Treatment of water with 3% and 10% hydrogen peroxide resulted in sporadic (0 to 45%) reductions in EDB concentrations in water. The 10% hydrogen peroxide concentration did not appear to be more effective than the 3% hydrogen peroxide treatment. Significantly, the formation of other peaks detected by gas chromatography analysis was minimal, indicating that many intermediate products were not being formed. Based on these results, further exploratory studies involving the use of hydrogen peroxide as a means of reducing the concentrations of EDB in clean water is encouraged.

Treatment of water with UV plus 3% and 10% hydrogen peroxide resulted in 33 to 75% reduction in EDB. The addition of 10% hydrogen peroxide was not substantially more effective than 3% hydrogen peroxide. UV alone reduced the EDB concentrations by 10%. It should be noted that the UV plus hydrogen peroxide system used in this experiment was crude in design and required an open system to allow volatilization to occur. Commercially available systems which use UV and an oxidant, such as ozone or hydrogen peroxide, are enclosed and allow for better control of the dose of UV and the oxidant. The UV lamp used in our system was old and its output of UV light is suboptimal. However, the evidence obtained strongly indicated that UV plus hydrogen peroxide was effective in reducing the concentrations of EDB in water. This appeared to be the most promising method and further studies to determine the effectiveness of UV plus an oxidant is highly recommended.

It should be noted that hydrogen peroxide is available as a liquid at concentrations of 3% and 30%. As a result, large volumes of this stock hydrogen peroxide must be used to treat large volumes of water, thus making the use of hydrogen peroxide impractical on a large scale. Hydrogen peroxide was selected for two reasons: first, it is readily available and easy to use; second, it is chemically similar to ozone which requires expensive generators for its production. However, the technology for generating and using ozone to treat large volumes of water is available. Thus in subsequent studies, the use of ozone may be more applicable than the use of hydrogen peroxide. The most highly recommended method to remove the concentrations of EDB in water would be to use UV and ozone. Equipment to produce UV and ozone to treat water are commercially available.

Other Treatment Methods (Granular Activated Carbon, Volatilization at Elevated Temperature, Thin-Layer Volatilization)

The purpose of the research involves studying practical and economic measures that could be implemented by water action agencies to eliminate or significantly decrease organic pesticide levels of local health concern (EDB and DBCP) in O'ahu's groundwater supply. Methods of pesticide removal to be explored include: (1) the use of various forms of granular activated carbon (GAC) at different hydraulic flow ratios to remove different concentrations of EDB and DBCP, (2) the volatilization of the pesticides at elevated temperatures, and (3) thin layer volatilization of the pesticides.

METHODOLOGY. All testing was conducted in the Water Resources Research Center and Sanitary Engineering laboratories in Holmes Hall, University of Hawaii at Manoa campus. Testing for pesticides was performed on a Hewlett Packard Model 5700A (electron capture) gas chromatograph with a specialized glass column. Pesticide removal by GAC involved the passage of EDB at concentration ranges of approximately 2,200 to 10,000 ppt and DBCP at about 5,000 ppt through fine-sized and standard grained calgon (F300) and Darco (12- to 20-mesh) at various hydraulic flow rates. The second pesticide removal method, volatilization of EDB and DBCP at elevated temperatures involved pesticide analysis over fixed intervals of time of relatively high concentrations of EDB and DBCP (20,000-22,000 ppt) in waters that were maintained at boiling (100°C) and at a mid-range temperature (60°C). The third pesticide removal technique, thin layer volatilization, consists of pumping pesticide-laden water (< 1,000 ppt) over surfaces in such a way as to enhance the surface area to volume ratio and consequently promote volatilization.

PRINCIPAL FINDINGS AND THEIR SIGNIFICANCE. Based on a series of thirty separate experimental runs in which EDB and/or DBCP within concentration ranges of approximately 2,200 to 10,000 ppt in water were treated by different amounts of both standard and fine-grained calgon and Darco GAC at varying hydraulic loading rates, it was determined that (1) no detectable concentrations of EDB occurred at the 10-ppt level when the flow-through GAC loading rate was 307 gal/lb·day (≤ 1.78 ml/g min); (2) calgon is more efficient than Darco in removing EDB and DBCP; (3) fine-grained GACs are more efficient than standard GACs; (4) EDB is removed more efficiently than DBCP; (5) mixtures of EDB and DBCP have a lower removal efficiency through the same GAC than when

individual concentrations of these same pesticides are passed through GAC (based on fine-grained calgon); and (6) initial start-up carbon loss through GAC columns is considerably less than 1%.

At the relatively high EDB and/or DBCP concentrations of 20,000 to 22,000 ppt both pesticides were reduced to below the detectable limit within 60 min when the temperature of the pesticide-spiked water was maintained at boiling 100°C, whereas at 60°C only approximately 60% of the pesticides were removed within the 60 min time period.

The results of the thin layer volatilization technique clearly demonstrated that EDB has a higher volatilization potential than DBCP, and that the removal percentage characteristics of pesticide concentrations near 1,000 ppt is similar to concentrations one order of magnitude less, for single pass-through conditions. Thus, it appears that recirculation could be employed to reduce EDB below the detectable limit (10 ppt). At a flow-through loading of approximately $-0.5 \text{ gal/ft}^2\text{-hr}$ for a single pass through situation EDB was decreased to $< 10 \text{ ppt}$ and DBCP to $< 20 \text{ ppt}$ from original concentrations of 155 and 112 ppt, respectively. This relates to a required surface area of approximately $85,000 \text{ ft}^2/\text{mgd}$ $\left(1.802 \times 10^5 \frac{\text{m}^2}{\text{m}^3/\text{s}}\right)$.

This activity is reported in two UHM-WRRC companion projects: (1) Activated carbon adsorption of low concentration organic pesticides in water, and (2) Low level organic pesticide removal. A full report of the first project is published by WRRC (Dugan et al. 1984); the second project has resulted in an M.S. thesis (Oshiro 1985).

Summary

Based on the research conducted, some findings appear significant at this time:

1. The use of ultraviolet light plus 3% or 10% hydrogen peroxide consistently reduced (33-75%) the concentration of EDB in water. Thus, the method of using ultraviolet light plus an oxidant, such as hydrogen peroxide or ozone, should be further explored as a practical mean of reducing the concentrations of EDB detected in groundwater supplies.
2. Chlorine (5-5,000 mg/l) and chlorine dioxide (2-50 mg/l) are incapable of removing low concentration EDB in water, whereas 3% and 10% hydrogen peroxide occasionally removed up to 45% of the EDB in water.

3. The use of GAC at controlled loading rates is confirmed as a very effective method of decreasing the concentration of pesticides to less than not only 20 ppt but also to the 10 ppt detectable limit.
4. Boiling water for EDB and DBCP is effective, but the cost would be prohibitive for large-scale water operations.
5. Thin layer volatilization proved effective at low hydraulic flow in surface area, which lends itself to household use, especially since the line pressure could be used to force the pesticide-laden water over a thin layer. For large-scale operations innovative surface area exposure means would have to be devised to be competitive with other volatilization type equipment.

References Cited

- Dugan, G.L.; Gee, H.K.; Oshiro, K.M.; and Lau, L.S. 1984. Activated carbon adsorption of low concentration organic pesticides in water. Tech. Rep. No. 166, Water Resources Research Center, University of Hawaii at Manoa, Honolulu. 53 pp.
- GMP Associates, Inc. 1984. Treatment study for ground water supply. Submitted to the Board of Water Supply, City and County of Honolulu, Hawaii.
- Oshiro, K.M. 1985. "Treatment of drinking waters contaminated by trace levels of pesticides." Master's thesis (Civil Engineering), University of Hawaii at Manoa, Honolulu.

CONCLUSIONS

The project was conceptualized in December 1983 and has been in progress for 12 months since funded in January 1985. Inasmuch as many project activities are still in progress, it appears prudent to defer conclusions. However, some findings appear significant at this time and are summarized as follows.

Extent of Contaminated Groundwater

Based on the subsurface water and soil contamination Data Base, a coincidence is apparent between the location of the contamination wells and the location of land used for pineapple cultivation. However, the occurrence of fuel pipeline leaks of aviation fuels containing EDB was also located in the vicinity of several contaminated Waipahu wells. No significant temporal variation has occurred in the contamination of selected wells in southern O'ahu from 1 September 1983 to 1 September 1984.

Based on WRRC sampling in and beyond pineapple field areas, preliminary conclusions are as follows:

1. EDB. Only in the Waipahu area between Waikele and Panakuahi gulches has EDB been detected in groundwater
2. DBCP. Detectable concentrations of DBCP occur in the Koolau aquifer beneath and down gradient of pineapple fields, but has not been detected in the Waianae aquifer
3. TCP. TCP is widely distributed in the Koolau aquifer beneath and down gradient of pineapple fields but has not been detected in the Waianae aquifer. Detection of DBCP is always accompanied by detection of TCP, but TCP may also appear alone.

Groundwater Contamination Potential of Residual Pesticides in Soils

The potential of groundwater contamination by residual pesticide in soils presupposes that the residual pesticides are leachable from the soils in significant amount and rate, and that the transport agent is principally deep percolation of water from the apparent sources of pineapple fields. Similar leaching processes would occur for EDB that was contained in the pipeline leaks of aviation fuels and that came into contact with soils.

The project progress made thus far include the following:

1. Completion of compiling pertinent geologic information, including

generalized geologic description and existing borehole geology and mineralogy.

2. Initiation of drilling additional deeper holes to delineate vertical distribution of residual fumigants in soils and saprolites. Five boreholes have been drilled in Dole fields to 70 to 146 ft depths and core samples analyzed for pesticides, mineralogy, and hydrologic parameters. Additional boreholes into Waianae volcanic rocks are planned in Del Monte fields.
3. Development of two new laboratory methods which are needed to characterize the desorption (leaching) process and to enable the prediction of pesticides concentration in the percolating water over time. Leaching tests of contaminated soil samples has been planned.
4. A spatially detailed evaluation of the monthly time series of water percolation for each past and present pineapple field in southern O'ahu. Works have focused on land-use identification, parameter evaluation, and compilation of necessary hydrologic data.

Water Well Technology for Contamination Aquifer

The activity task objectives have been identified. The protocol for drilling and testing has been prepared for the Campbell upper Honouliuli wells. The well construction is tentatively scheduled for Spring 1986. An alternative objective by testing contaminated wells for retrofitting purpose was discussed with the Board of Water Supply.

Alternative Treatment Methods of Low Level Contaminated Waters

The project progress made thus far indicates:

1. The use of ultraviolet light plus 3% or 10% hydrogen peroxide consistently reduced (33-75%) the concentration of EDB in water. Thus, the method of using ultraviolet light plus an oxidant, such as hydrogen peroxide or ozone, should be further explored as a practical mean of reducing the concentrations of EDB detected in groundwater supplies.
2. Chlorine (5-5,000 mg/l) and chlorine dioxide (2-50 mg/l) are incapable of removing low concentration EDB in water, whereas 3% and 10% hydrogen peroxide occasionally removed up to 45% of the EDB in water.
3. The use of granular activated carbon at controlled loading rates is confirmed as a very effective method of decreasing the concentration

of pesticides to less than not only 20 ppt but also to the 10 ppt detectable limit.

4. Boiling water for EDB and DBCP is effective, but the cost would be prohibitive for large-scale water operations.
5. Thin-layer volatilization proved effective at low hydraulic flow to surface area, which lends itself to household use, especially since the line pressure in the municipal water pipe system could be used to force the pesticide-laden water over a thin layer. For large-scale operations innovative surface area exposure means would have to be devised to be competitive with other volatilization type equipment.

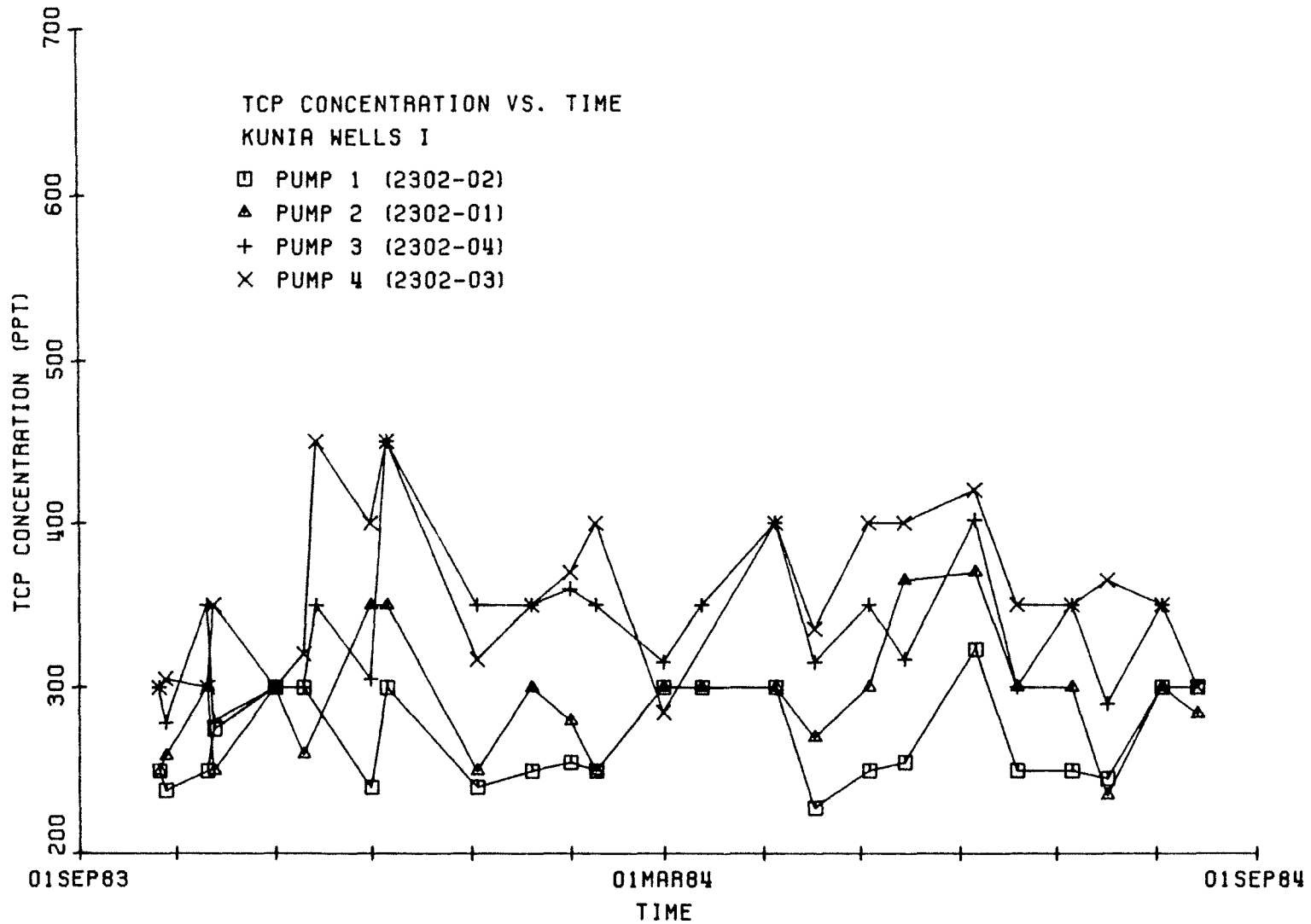
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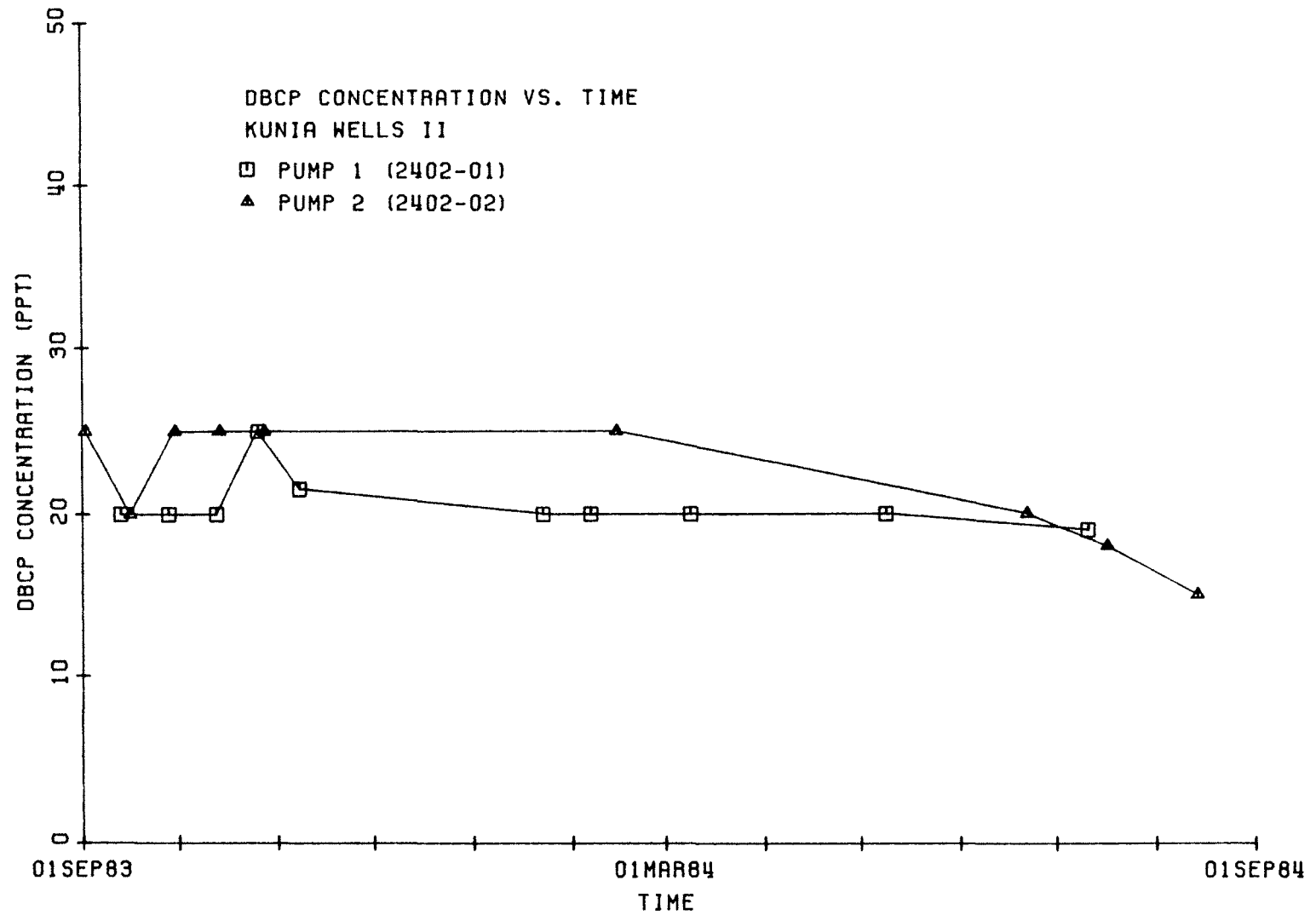
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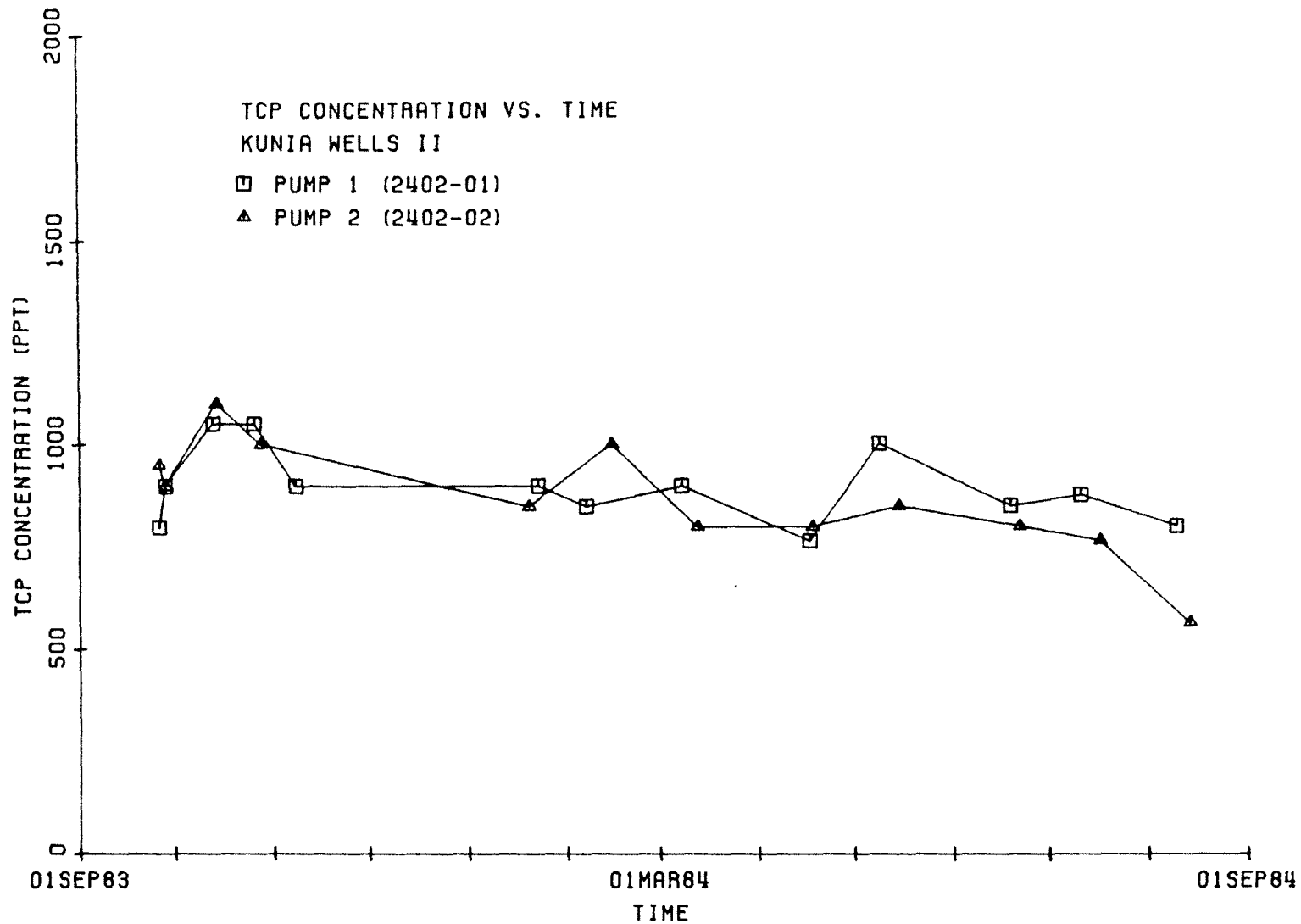
APPENDIX A. TIME SERIES OF PESTICIDE CONCENTRATION IN SELECTED WELLS



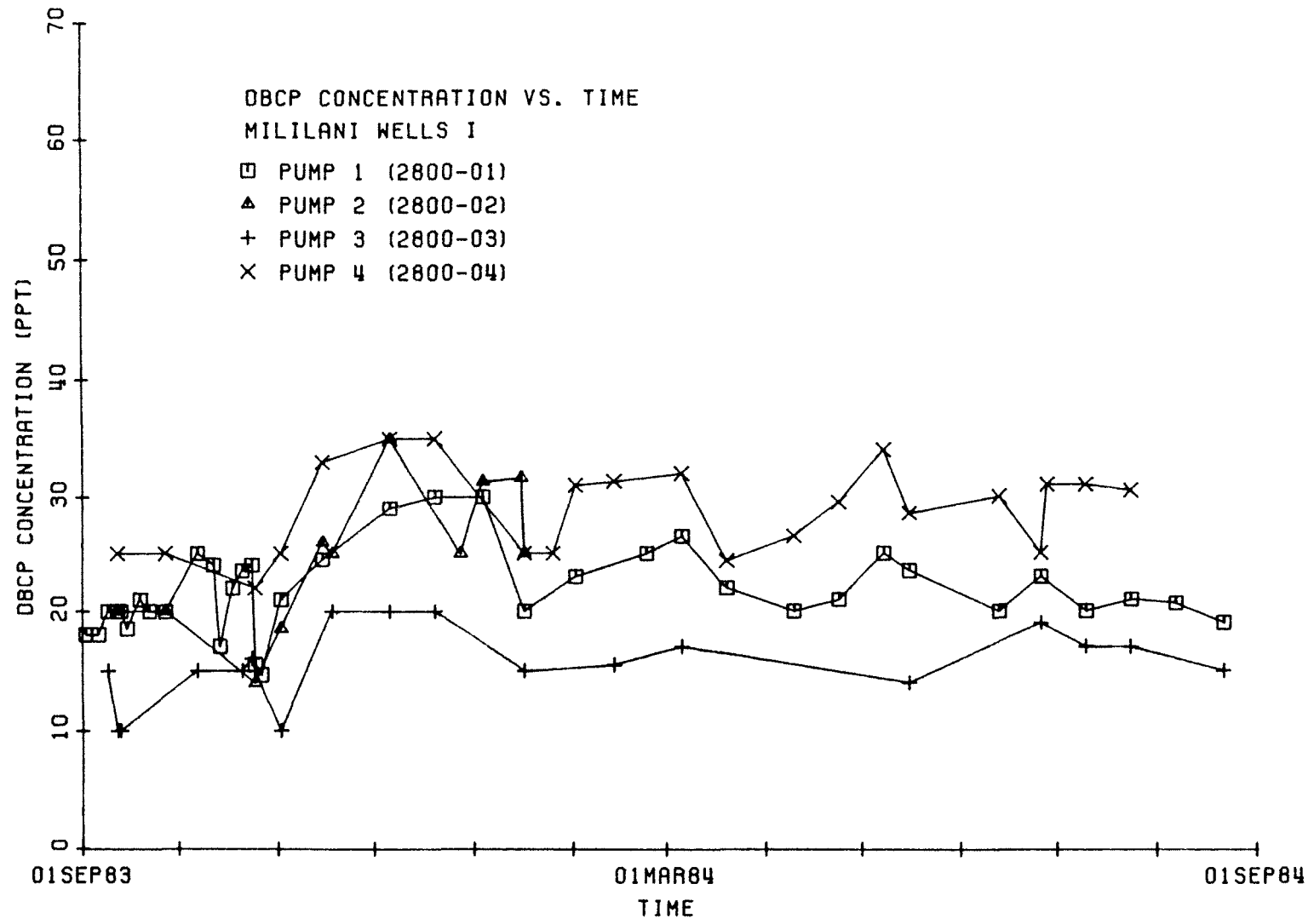
Appendix Figure A.1. TCP concentration vs. time, Kunia Wells I, O'ahu



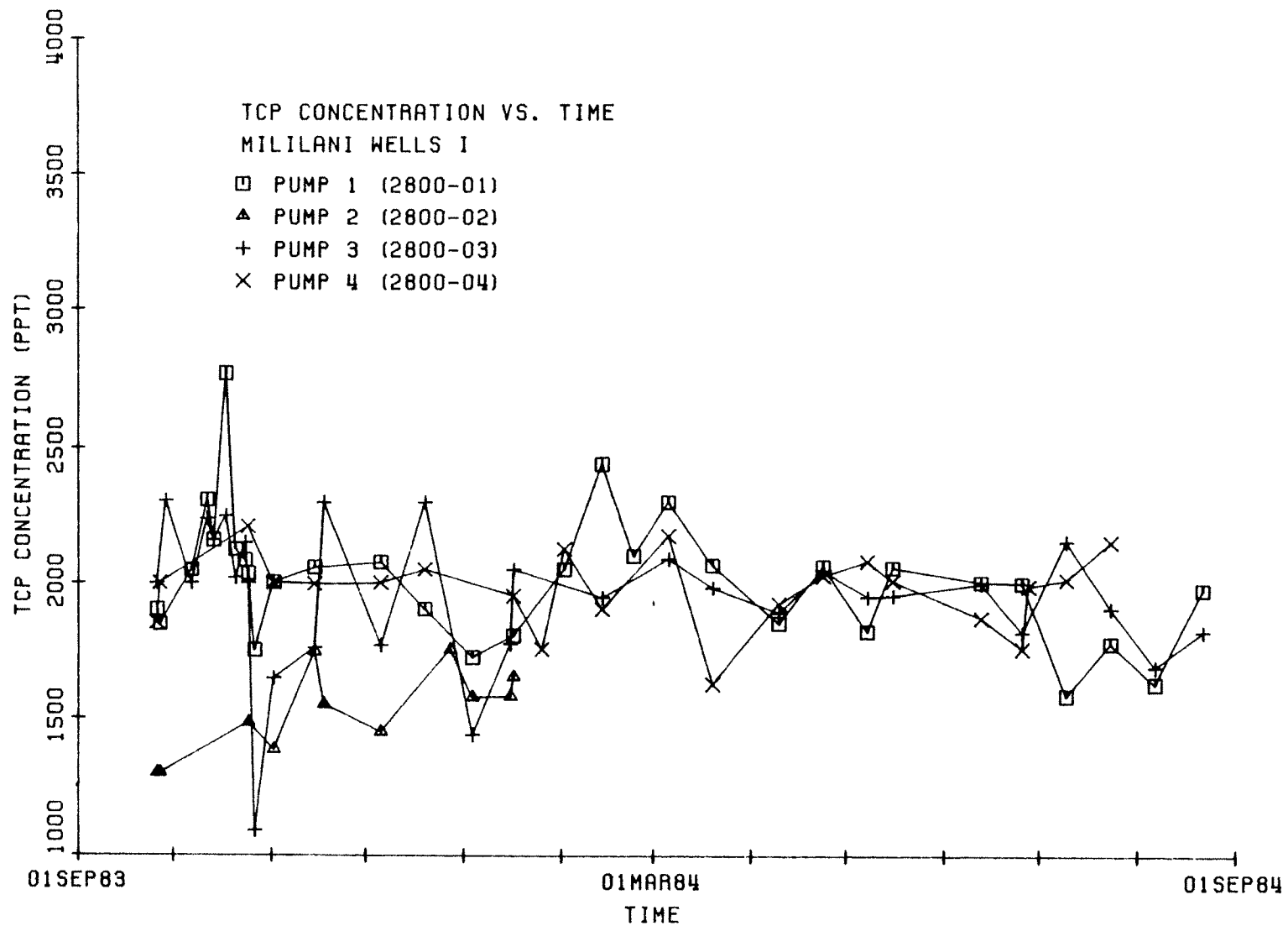
Appendix Figure A.2. DBCP concentration vs. time, Kunia Wells II, O'ahu



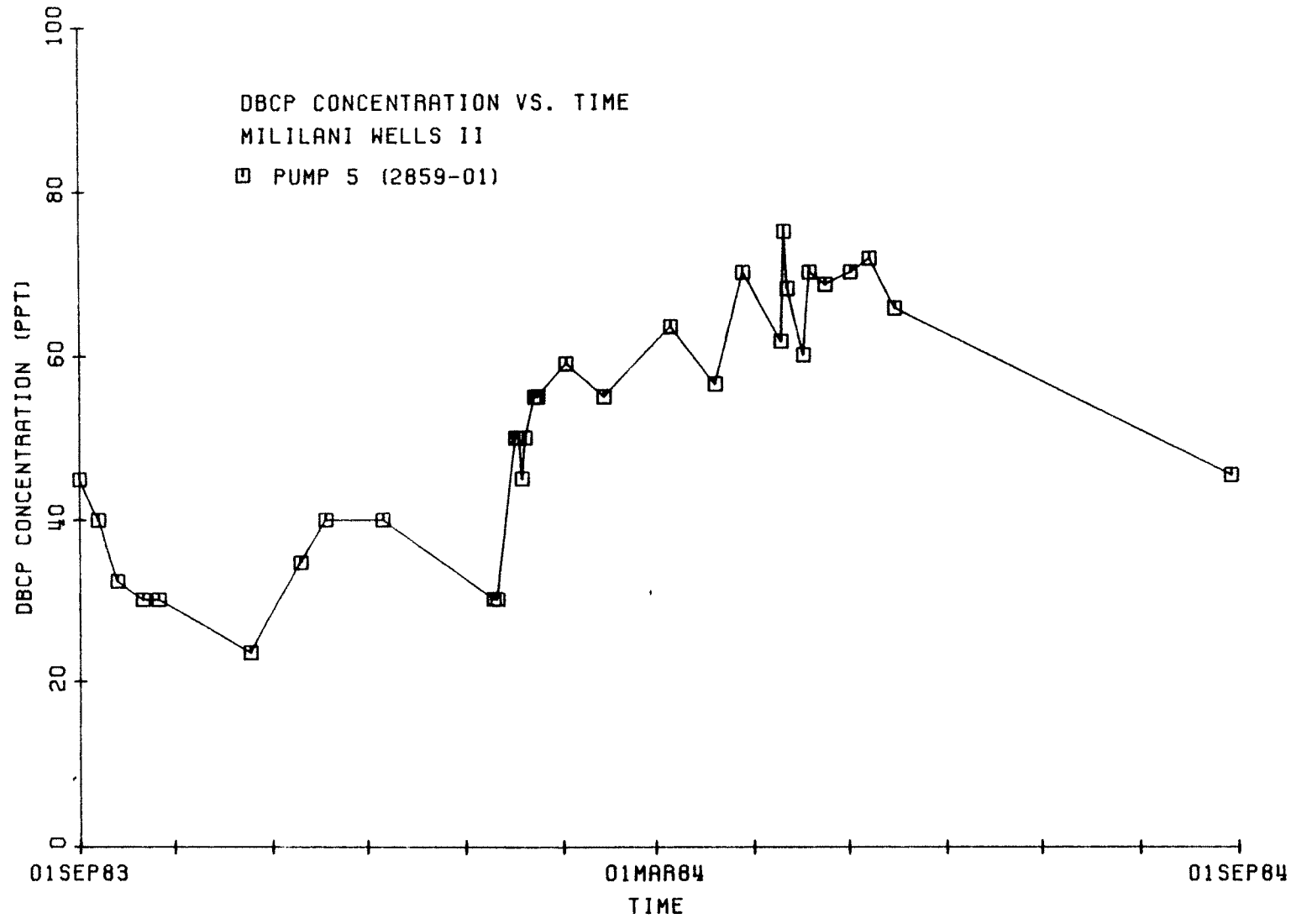
Appendix Figure A.3. TCP concentration vs. time, Kunia Wells II, O'ahu



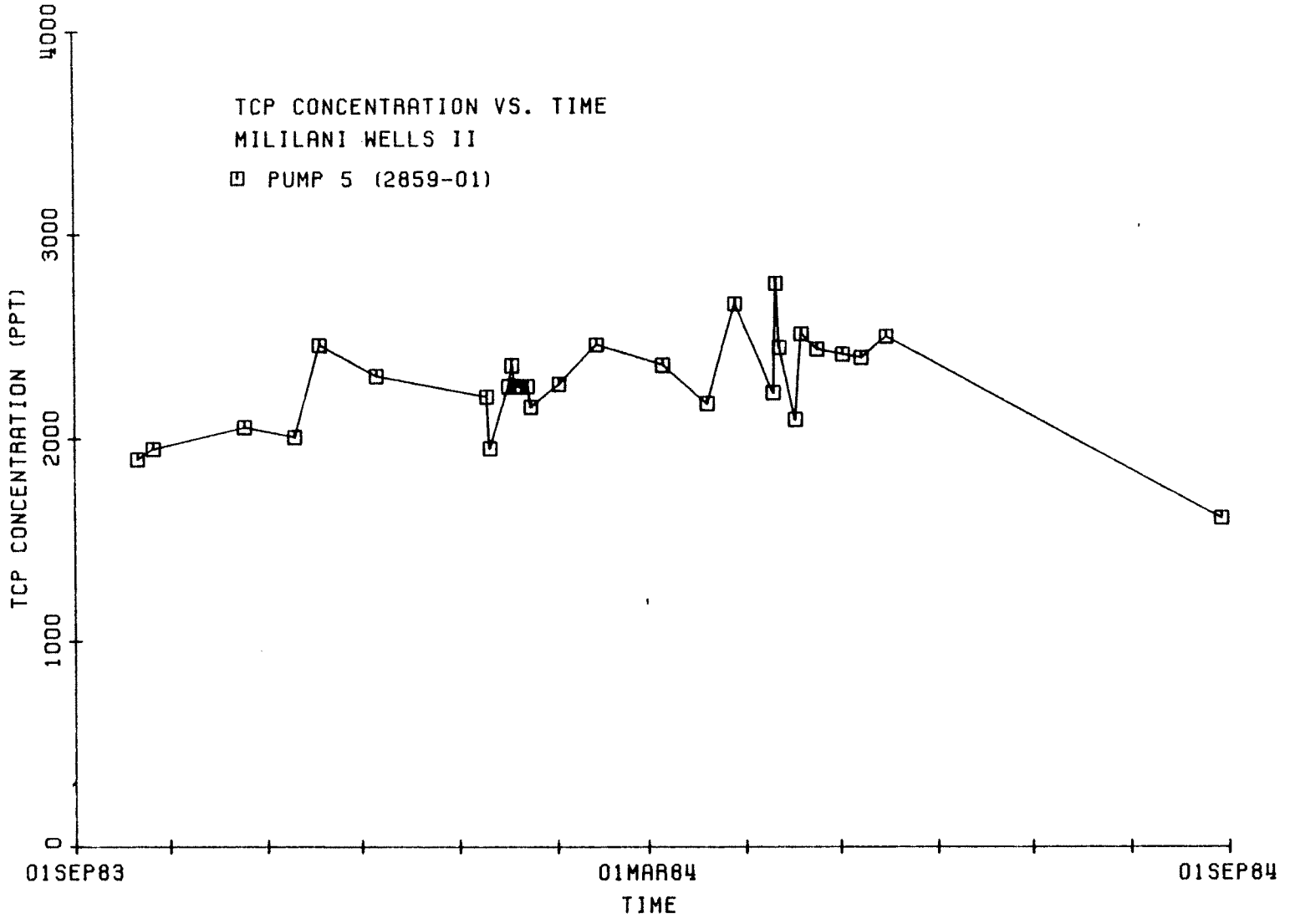
Appendix Figure A.4. DBCP concentration vs. time, Mililani Wells I, O'ahu



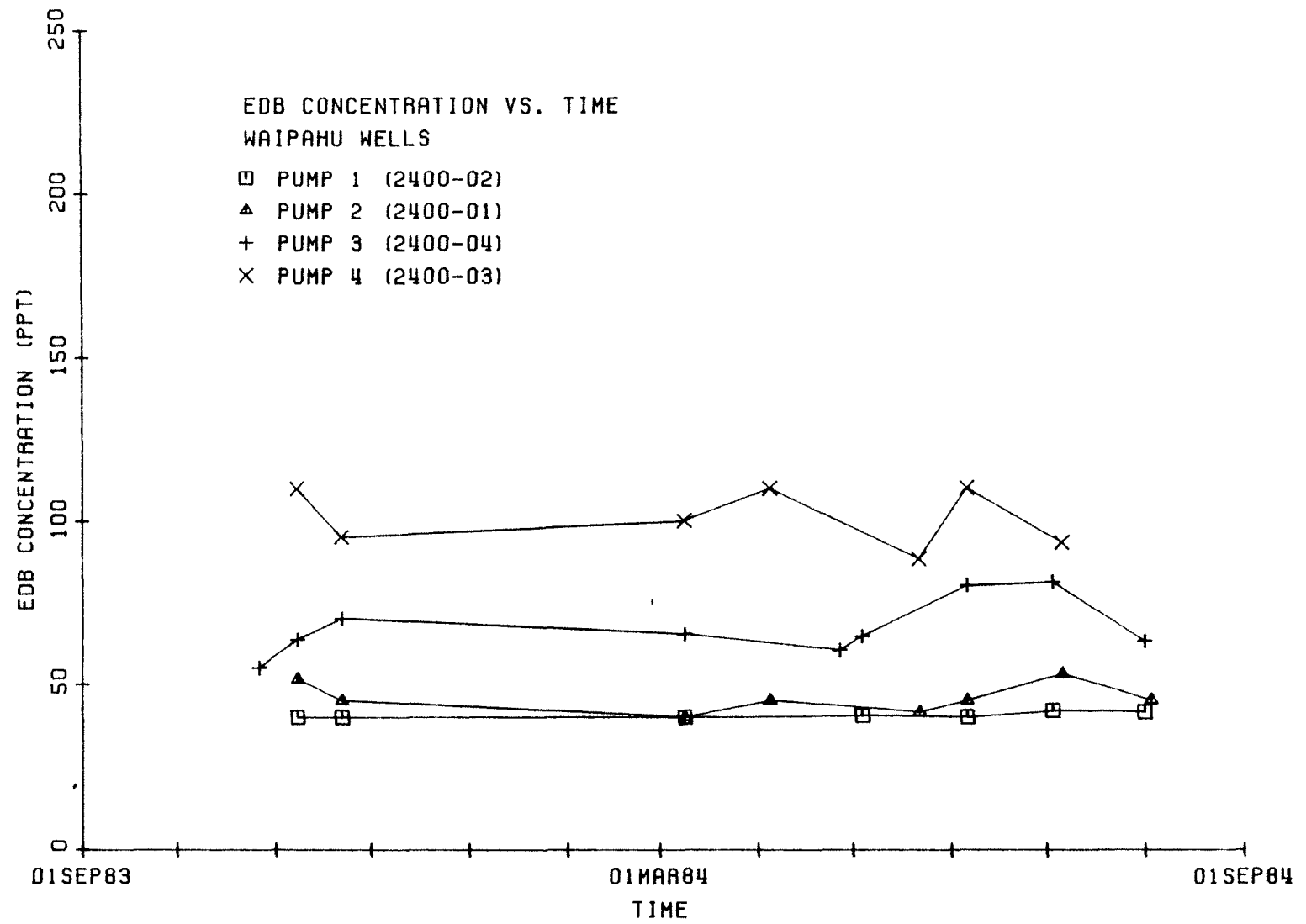
Appendix Figure A.5. TCP concentration vs. time, Mililani Wells I, O'ahu



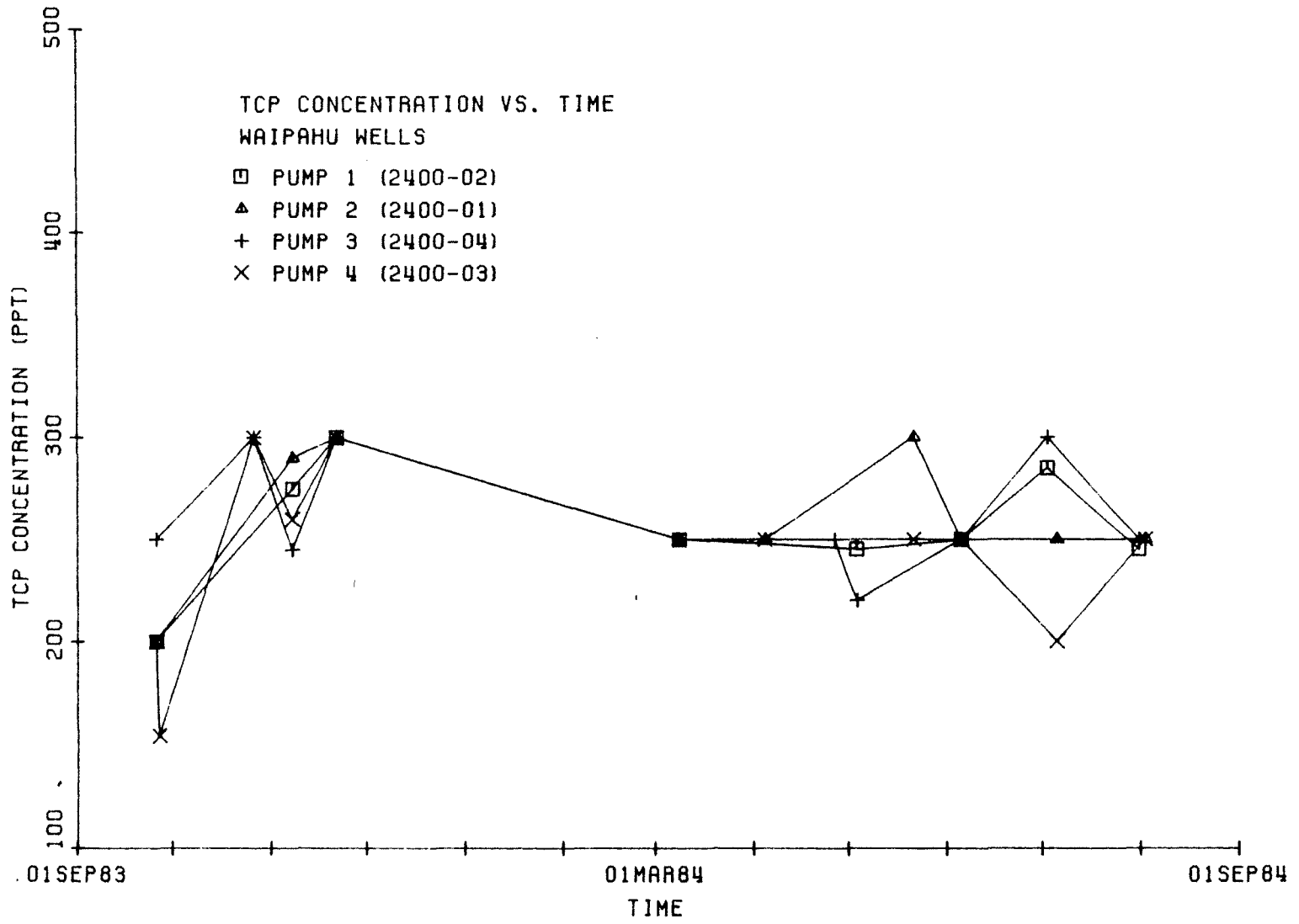
Appendix Figure A.6. DBCP concentration vs. time, Mililani Wells II - Pump 5, O'ahu



Appendix Figure A.7. TCP concentration vs. time, Mililani Wells II - Pump 5, O'ahu



Appendix Figure A.8. EDB concentration vs. time, Waipahu Wells, O'ahu



Appendix Figure A.9. TCP concentration vs. time, Waipahu Wells, O'ahu

APPENDIX B. MINERALOGICAL ANALYSIS OF EXPLORATORY BOREHOLE
SOIL SAMPLES IN WAHIAWA PLATEAU

Sixty-two selected soil samples from nine exploratory boreholes drilled on the Wahiawa Plateau were sieved to 120 mesh and analyzed by x-ray diffraction. Samples from Well 4111-A were also analyzed by transmission electron microscopy in order to characterize a smectite (nontronite) layer which centered at a depth of 37 ft (11.3 m).

The plots of mineral concentrations vs. depth are based on visual estimations of integrated mineral peak intensities (area under the peak) and have a best case validity of $\pm 25\%$ of the amount of each mineral present. The sum of mineral concentrations at each well depth is $100\% \pm 3\%$. A more precise quantitative analysis can be accomplished by computer processing the the x-ray diffraction data. Computer processing was not done as these analyses were considered preliminary.

With the exception of Well 4111-A, no primary minerals were found. A primary mineral is one that is found in the unweathered parent material. Secondary minerals are those that have formed as a weathering product of primary minerals. Well 4111-A contained cristobalite which exhibits an inverse relationship to feldspar. Cristobalite was found above and below the primary smectite layer while feldspar was found in the smectite layer. It is apparent that for Well 4111-A there is an accumulation of silica, magnesium, and iron at a depth of 30 to 55 ft (9-16.8 m). The sample taken at 55 ft contained approximately 45% smectite. Unfortunately, no samples were taken below 55 ft; thus, we were unable to determine the full extent of the smectite layer. However, the smectite layer most probably continues below 55 ft. Since smectite carries a strong net negative charge, it would repel substances that also carry a negative charge and it would absorb substances that carry a positive charge. Furthermore, because smectite has a very large specific surface (about $600 \text{ m}^2/\text{g}$) it is an effective absorber of substances that carry no charge.

Most wells contained halloysite in various degrees of hydration. If, however, the samples were allowed to dry in the sun or were placed near a heat source of 30°C or more, the degree of hydration that was observed by x-ray diffraction analysis is not representative of the condition of the halloysite that was collected from the wells. Since the Well 4701-D samples submitted to us were dry, none of the samples contained hydrated halloysite—only dehy-

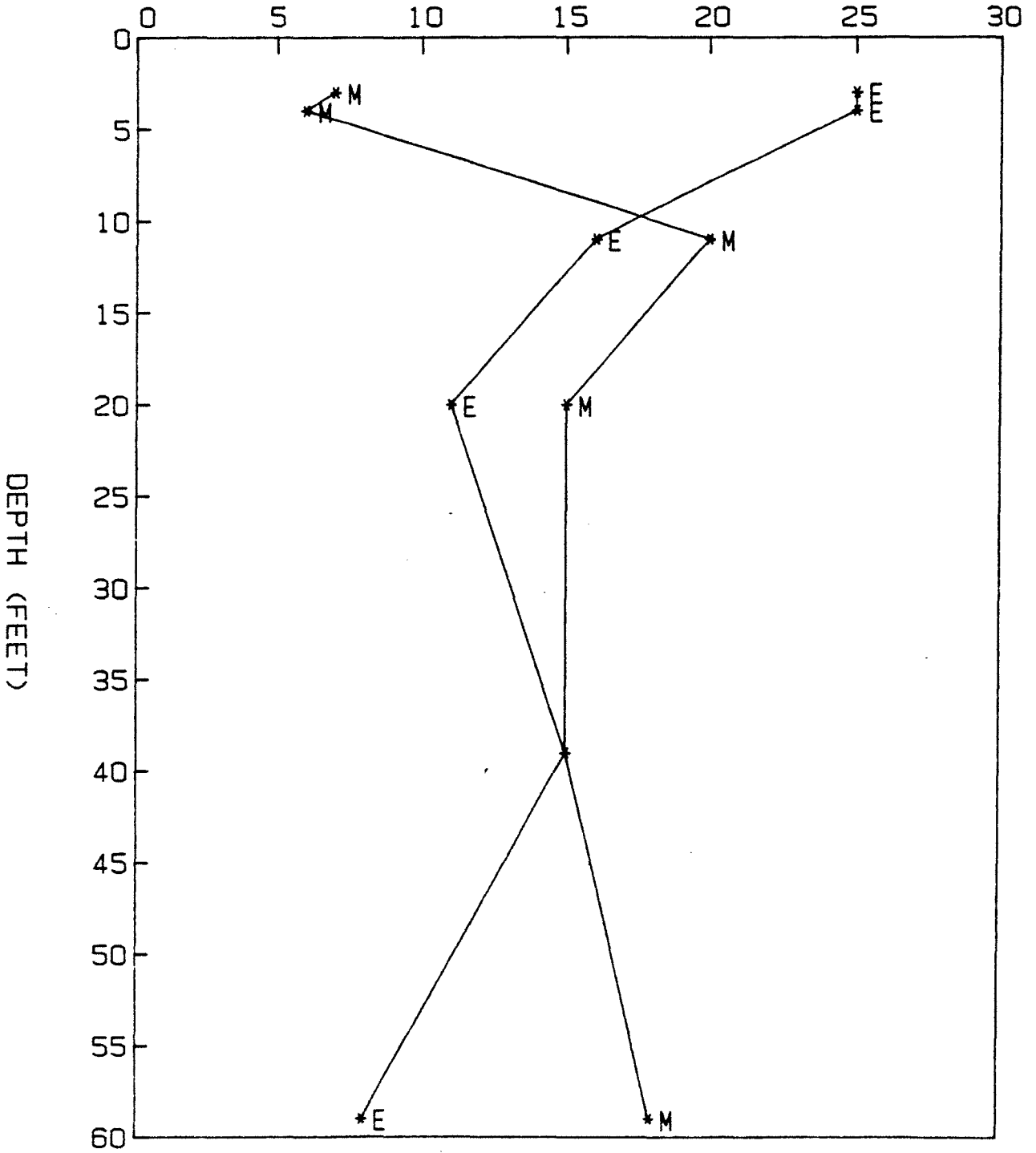
drated halloysite. Because kaolinite and dehydrated halloysite both have 001 peaks at about 7.2A, the presence of halloysite can only be determined by the asymmetry of the 7A peak or by electron microscopic examination. It is for this reason that in most cases halloysite/kaolinite is reported rather than separately as halloysite or kaolinite. Since halloysite carries approximately an order of magnitude more net negative charge than kaolinite, it is important to distinguish between the two minerals.

The conclusion that is drawn from this preliminary mineralogical analysis is that the samples exhibited more of a soil-like character rather than a rock-like character. Weathering has apparently been severe as each layer was deposited. Weathering has continued to the maximum depths of the wells to varying degrees as indicated by the differences in layering. Samples taken from shallow depths reflect the approximate mineral composition of the surface soils. The layers at greater depths show an accumulation of iron and titanium minerals that may have accumulated during surface weathering prior to burial. The aluminum bearing mineral, gibbsite, was found only near the surface of all wells. The absence of gibbsite at depth indicates that resilication has most likely taken place with the result of the formation of halloysite. Resilication will occur as the result of silica leaching from upper layers to lower layers as water moves through the profile. Following the movement of silica through the profile is a means by which water movement over long periods of time can be related.

It is suggested that deeper wells be drilled in the future and that the samples be stored at field moisture and protected from heat. Also, for continuing studies the distribution between kaolinite and halloysite should be made by electron microscopy. In addition to spade samples, core samples should be collected to enable a scanning electron microscopy examination of the nature of the pores and their contents.

WELL 0002-A

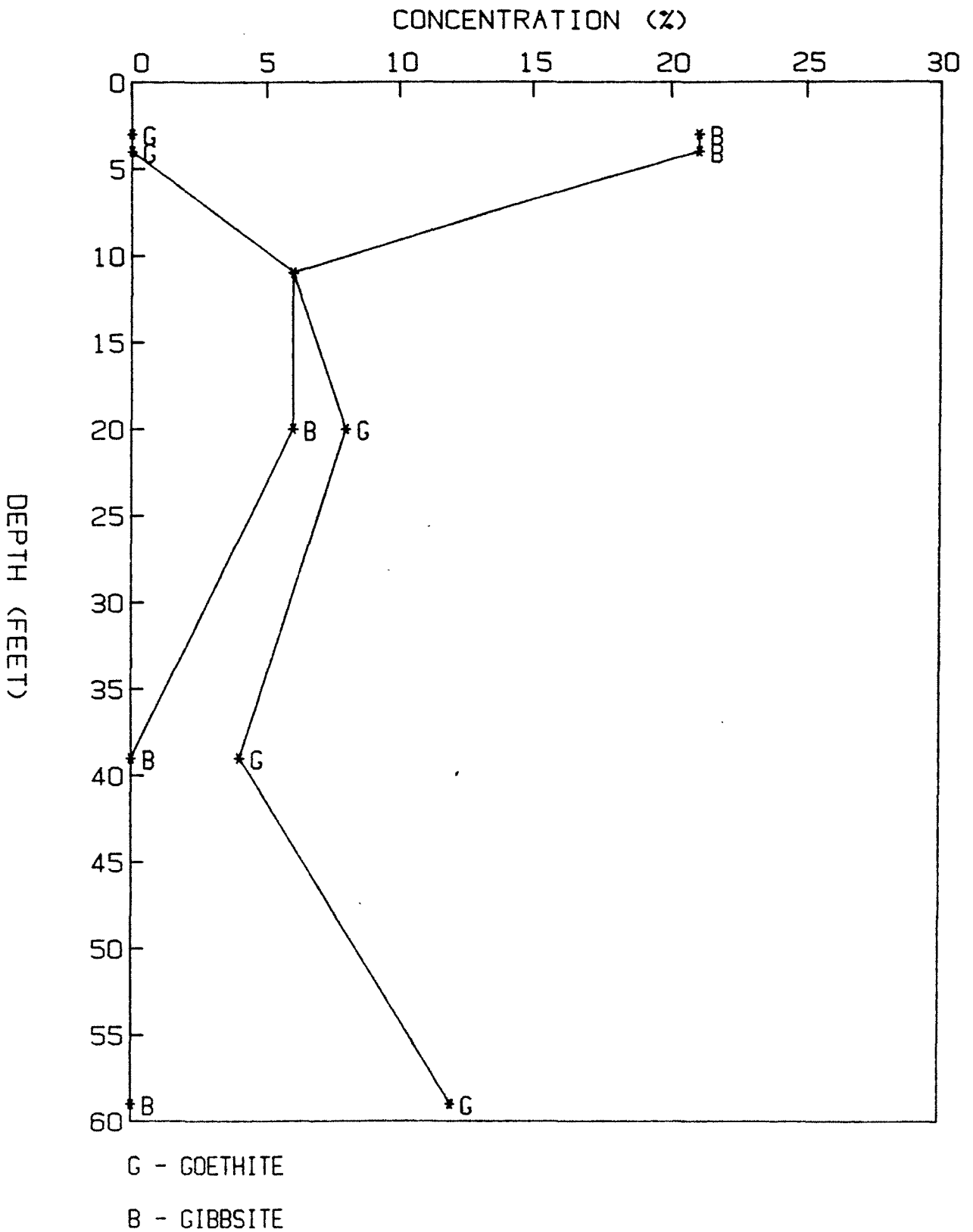
CONCENTRATION (%)



E - HEMATITE

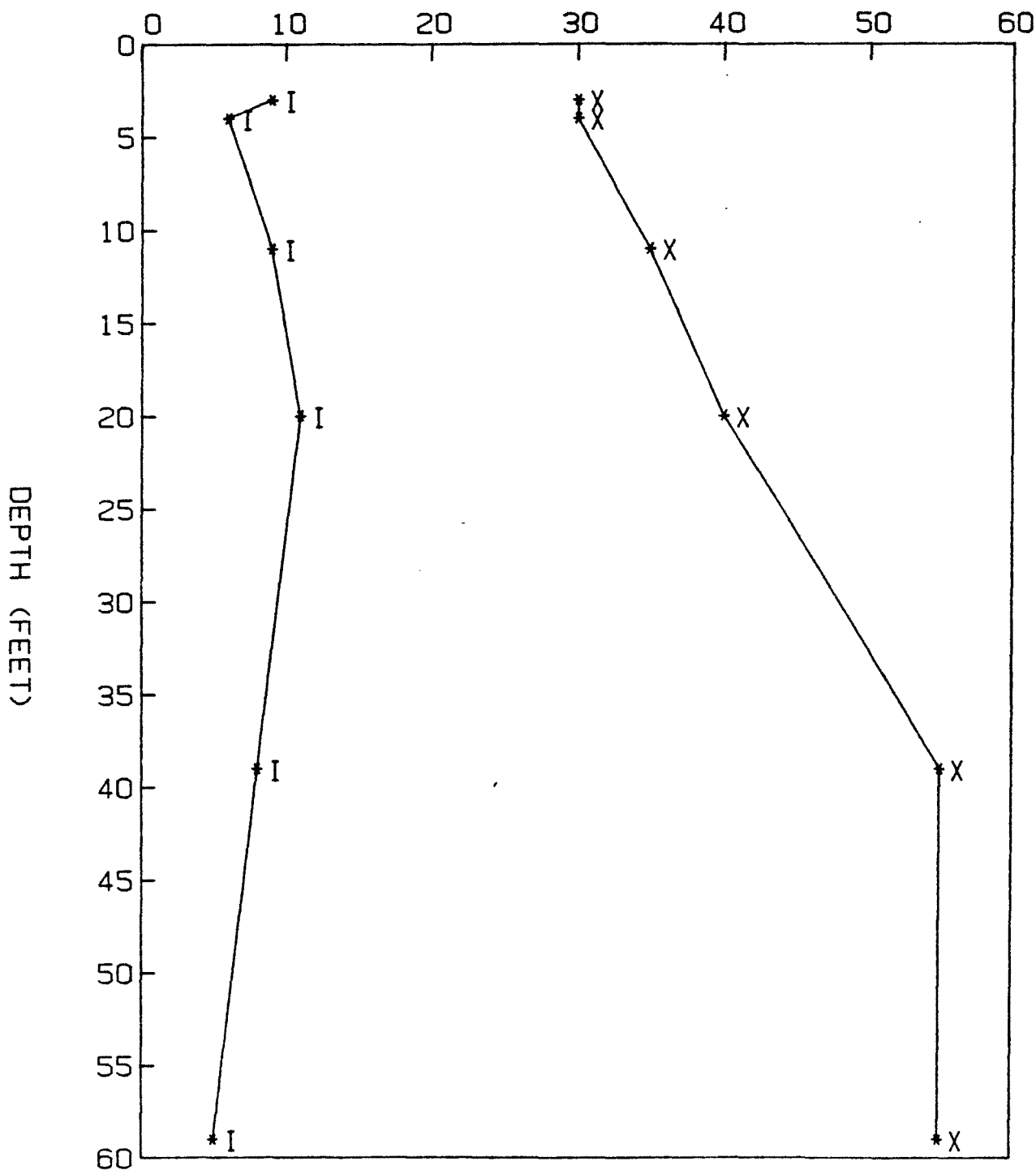
M - MAGNETITE

WELL 0002-A



WELL 0002-A

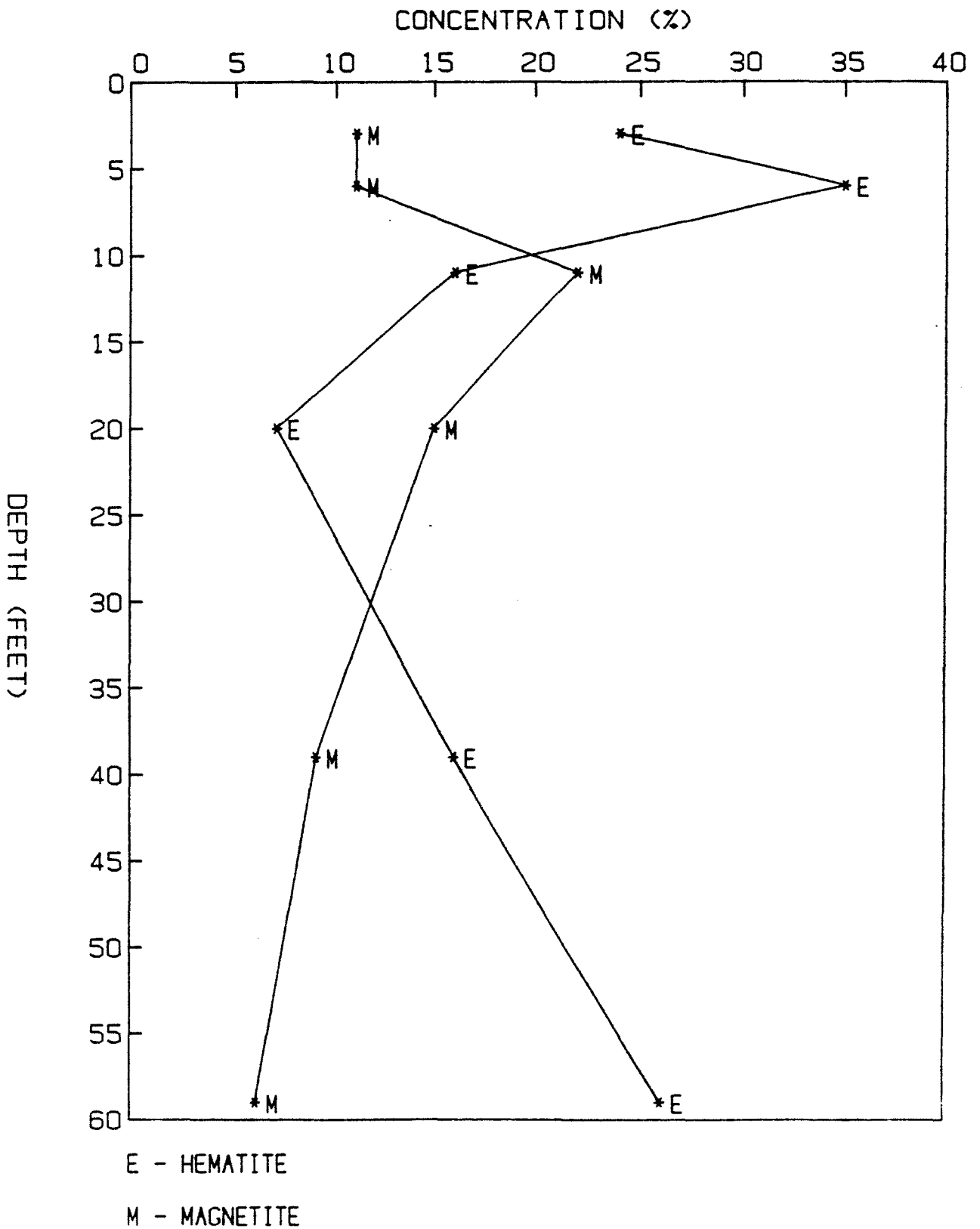
CONCENTRATION (%)



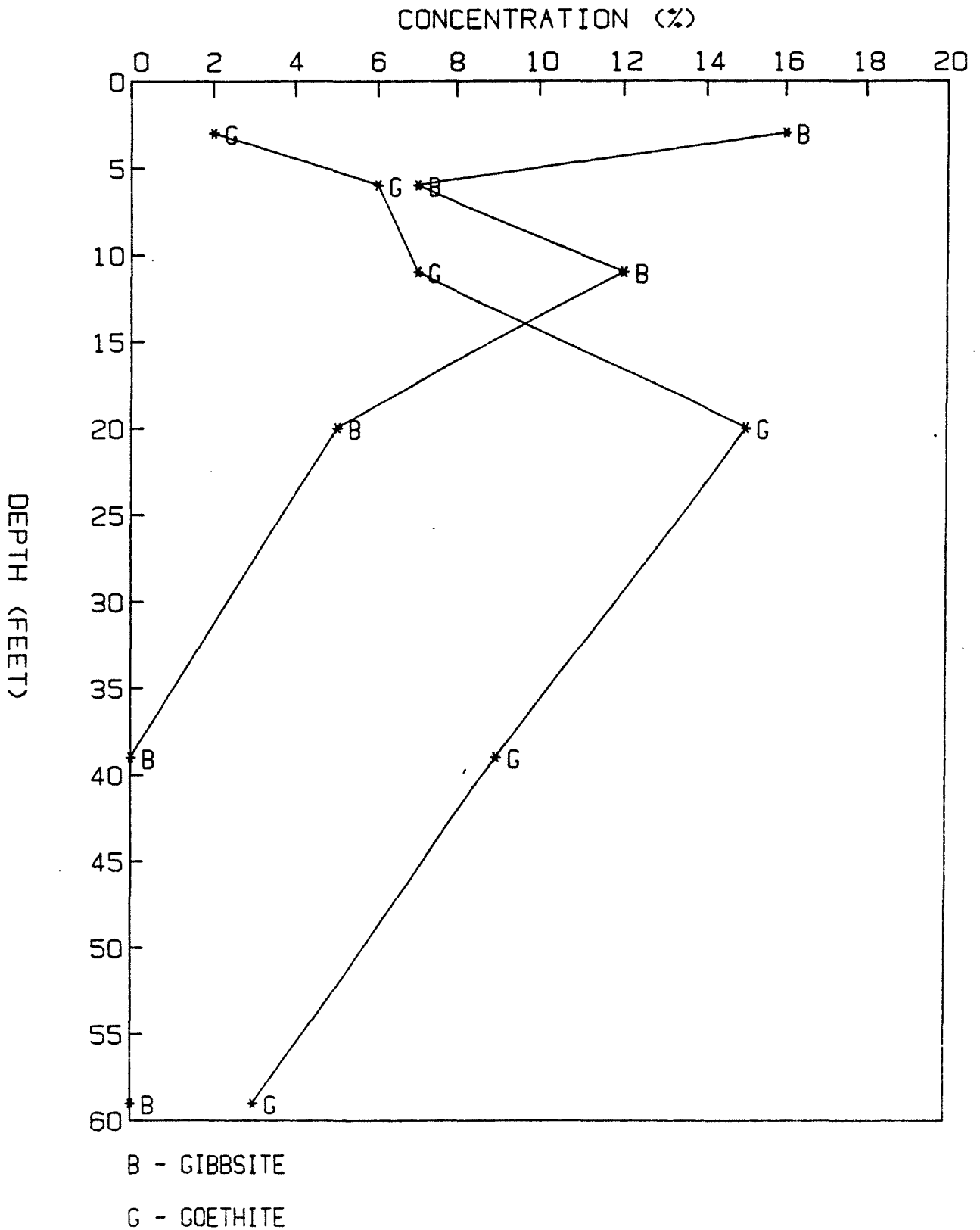
X - HALLOYSITE/KAOLINITE

I - ILMENITE

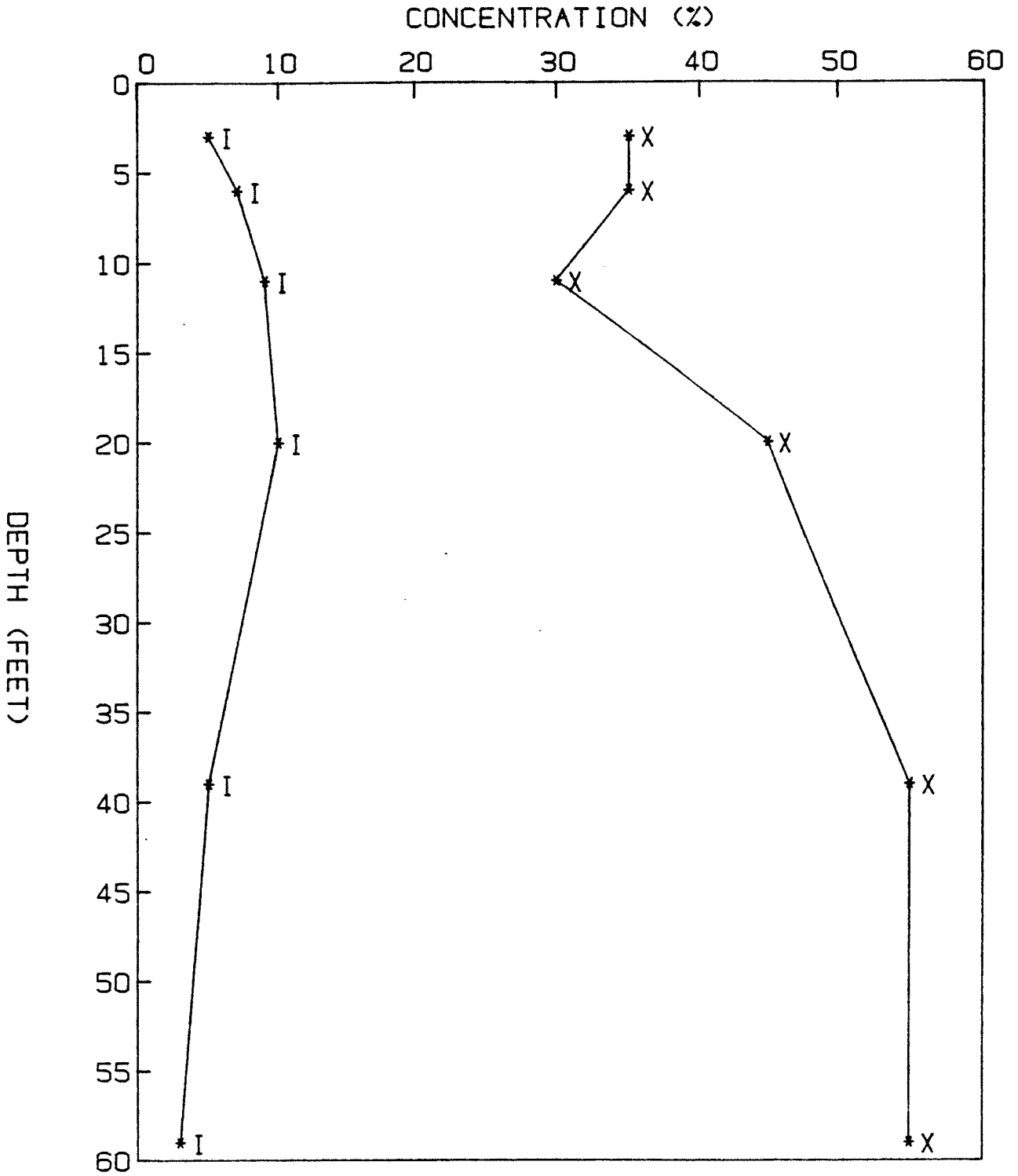
WELL 2013-A



WELL 2013-A



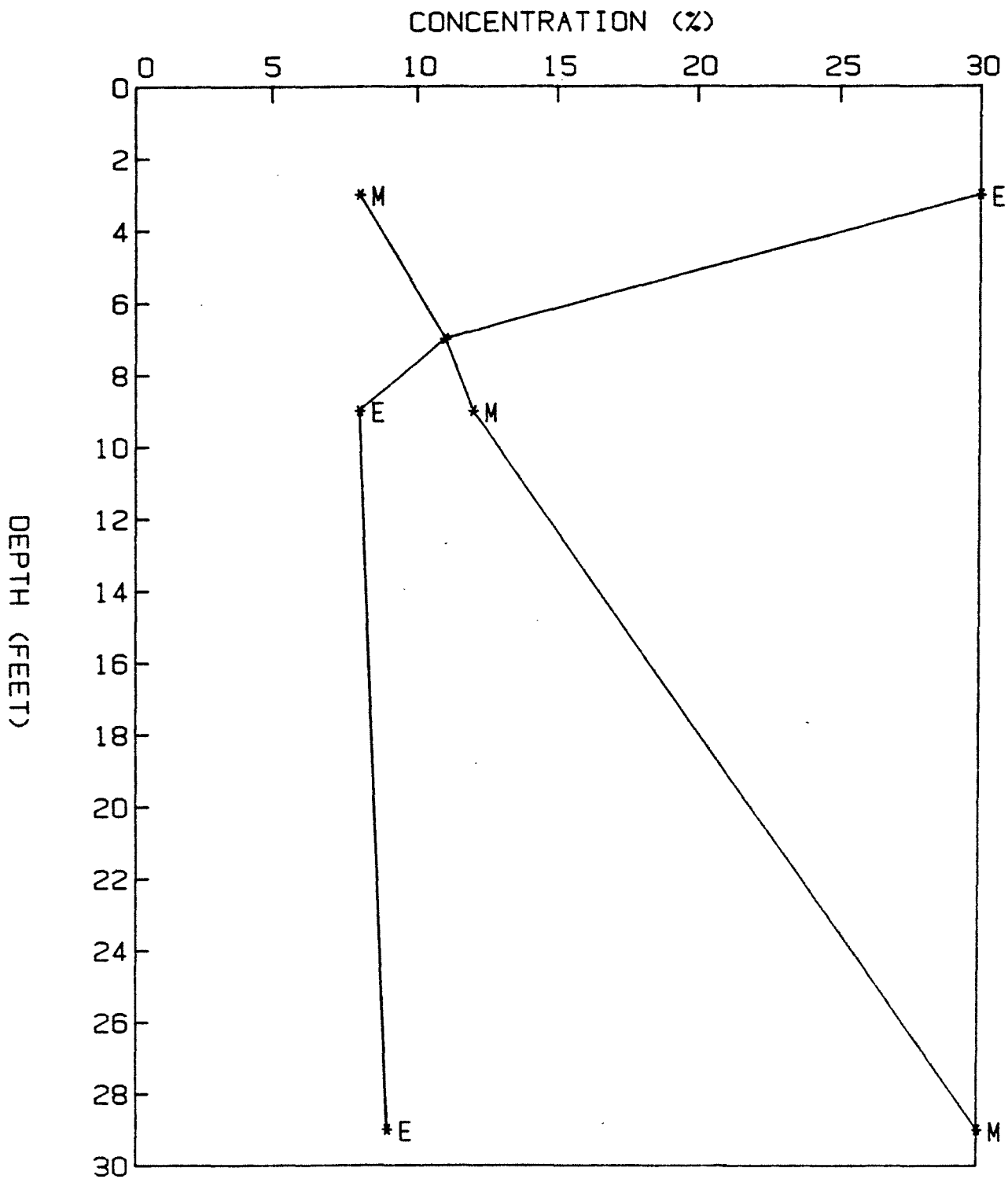
WELL 2013-A



X - HALLOYSITE/KAOLINITE

I - ILMENITE

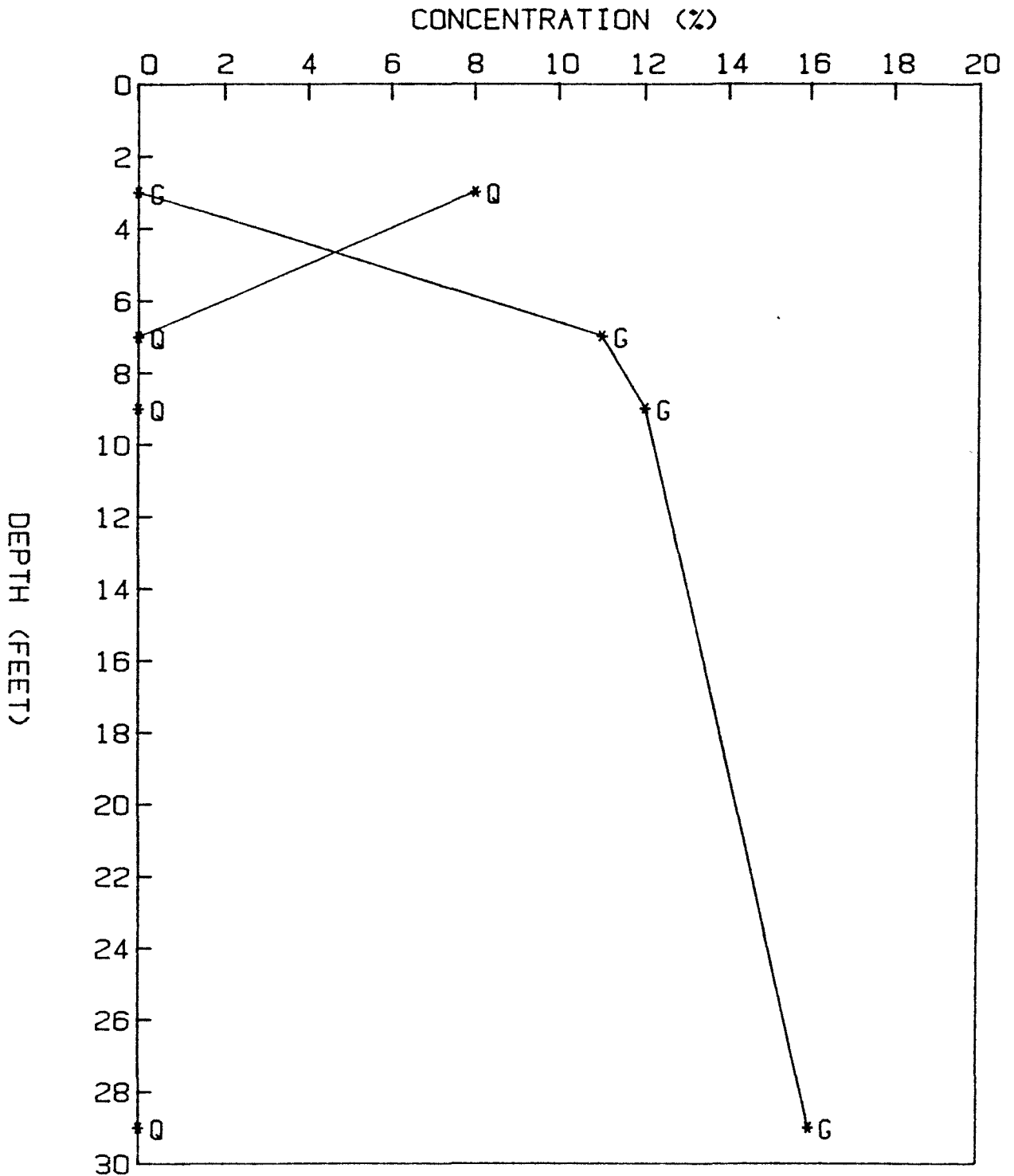
WELL 4107-B



E - HEMATITE

M - MAGNETITE

WELL 4107-B

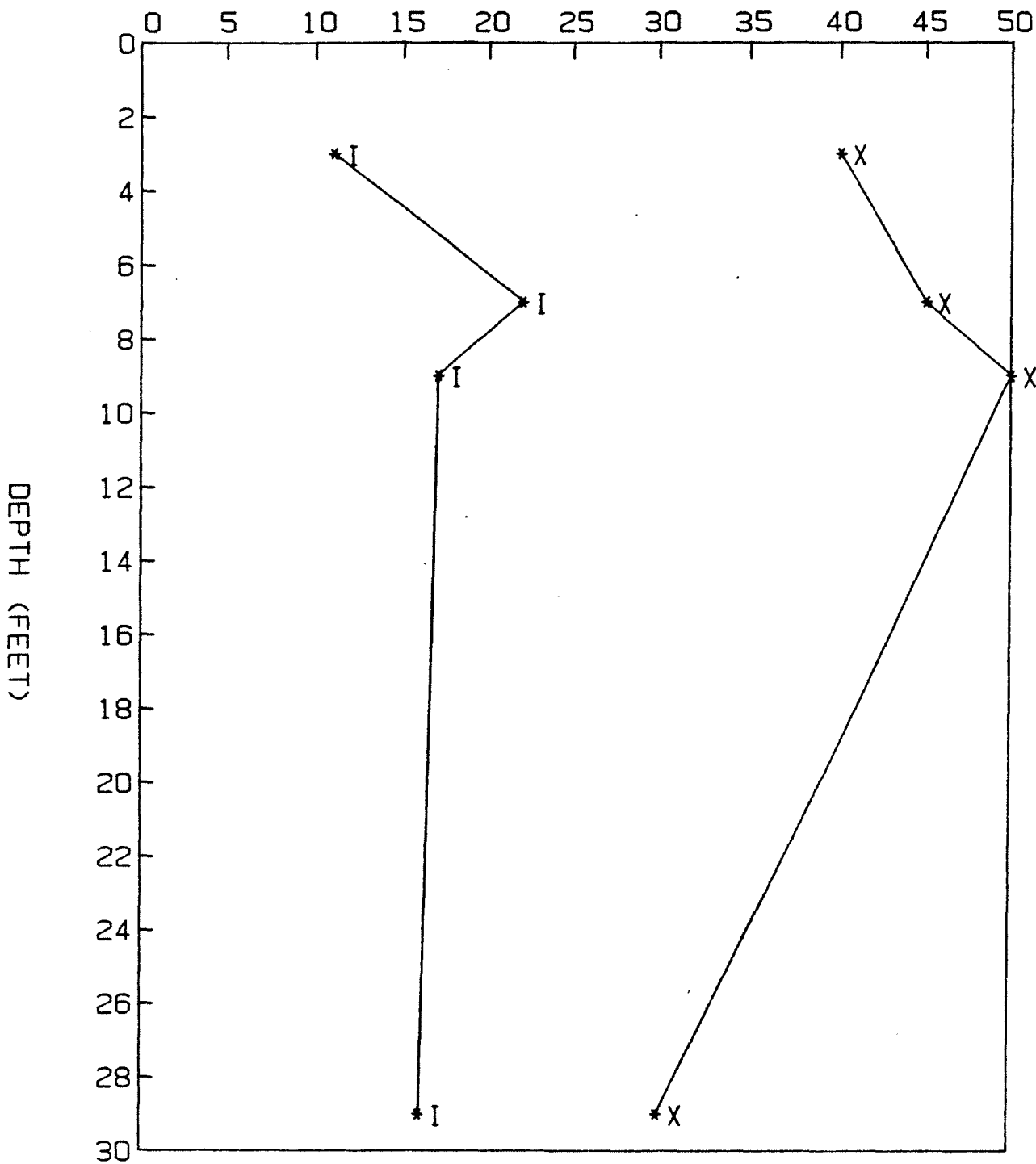


G - GOETHITE

Q - QUARTZ

WELL 4107-B

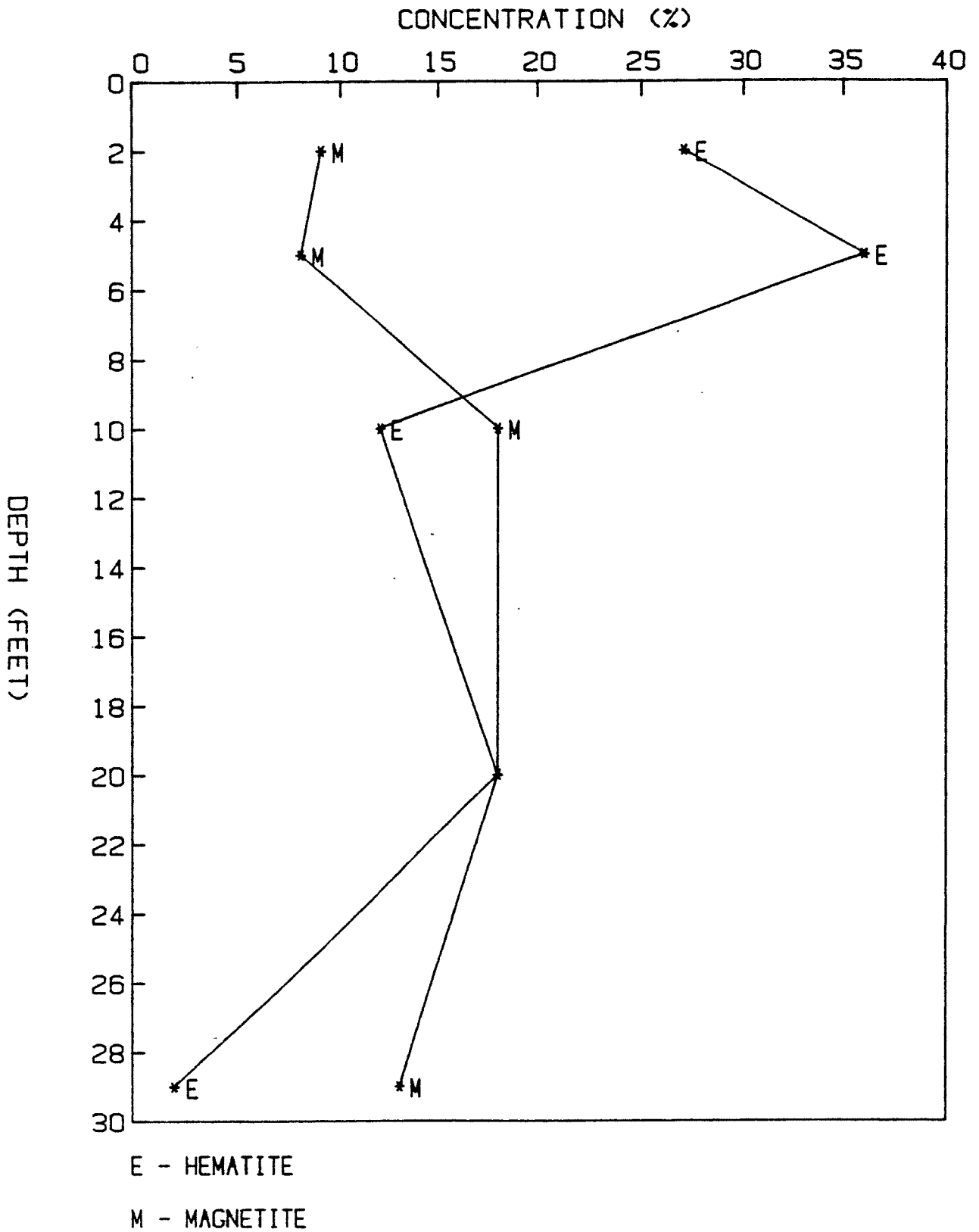
CONCENTRATION (%)



X - HALLOYSITE/KAOLINITE

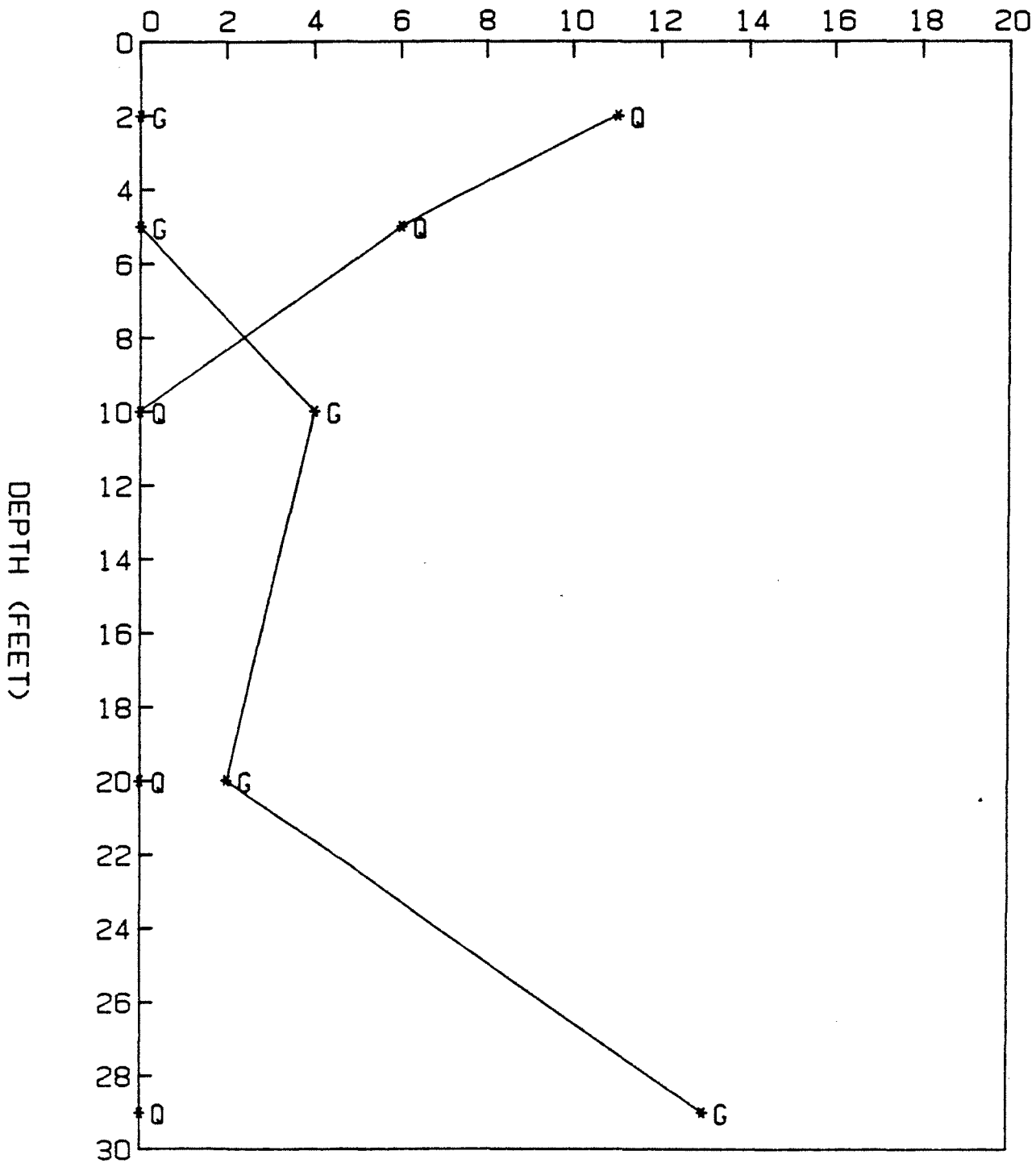
I - ILMENITE

WELL 4107-C



WELL 4107-C

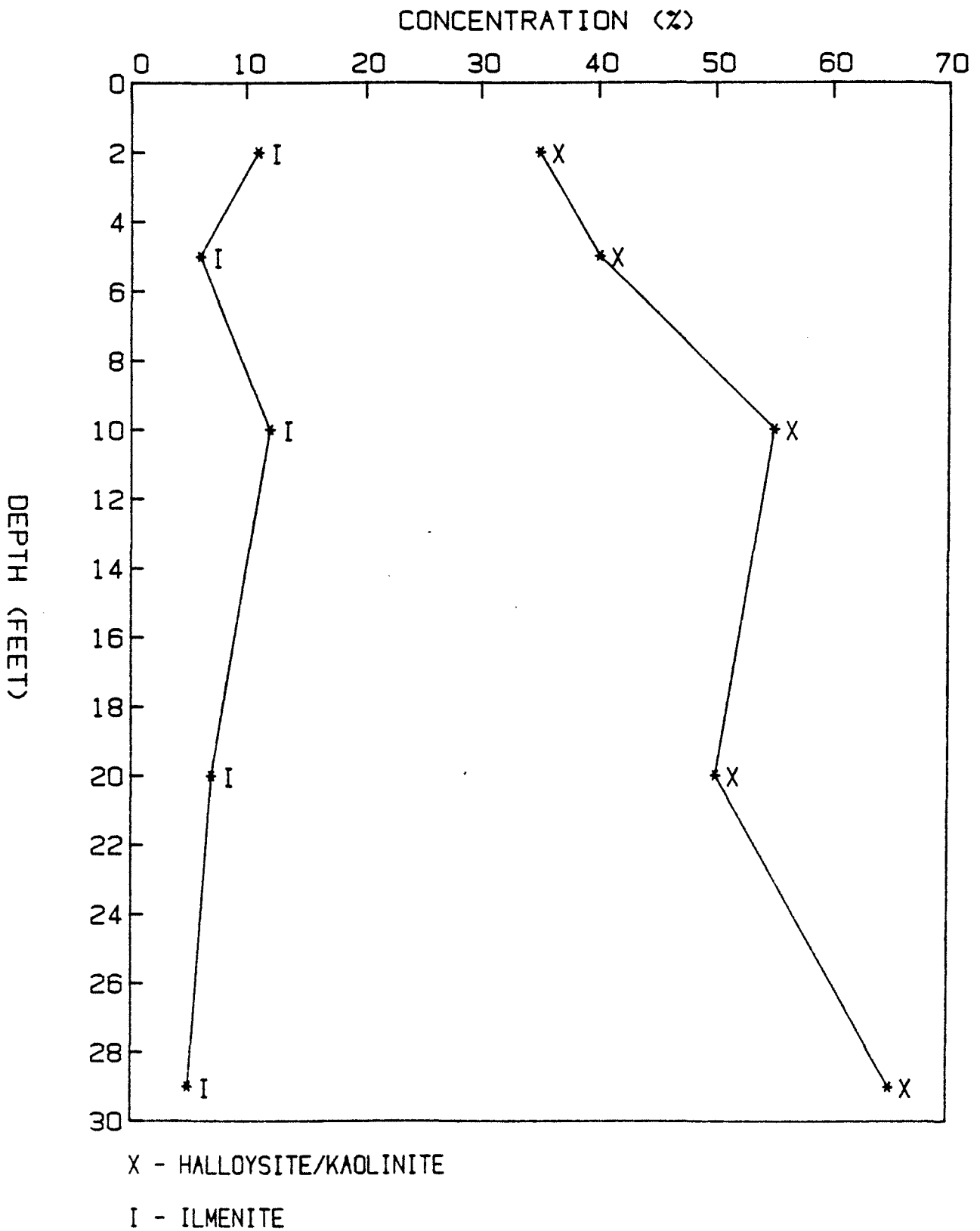
CONCENTRATION (%)



G - GOETHITE

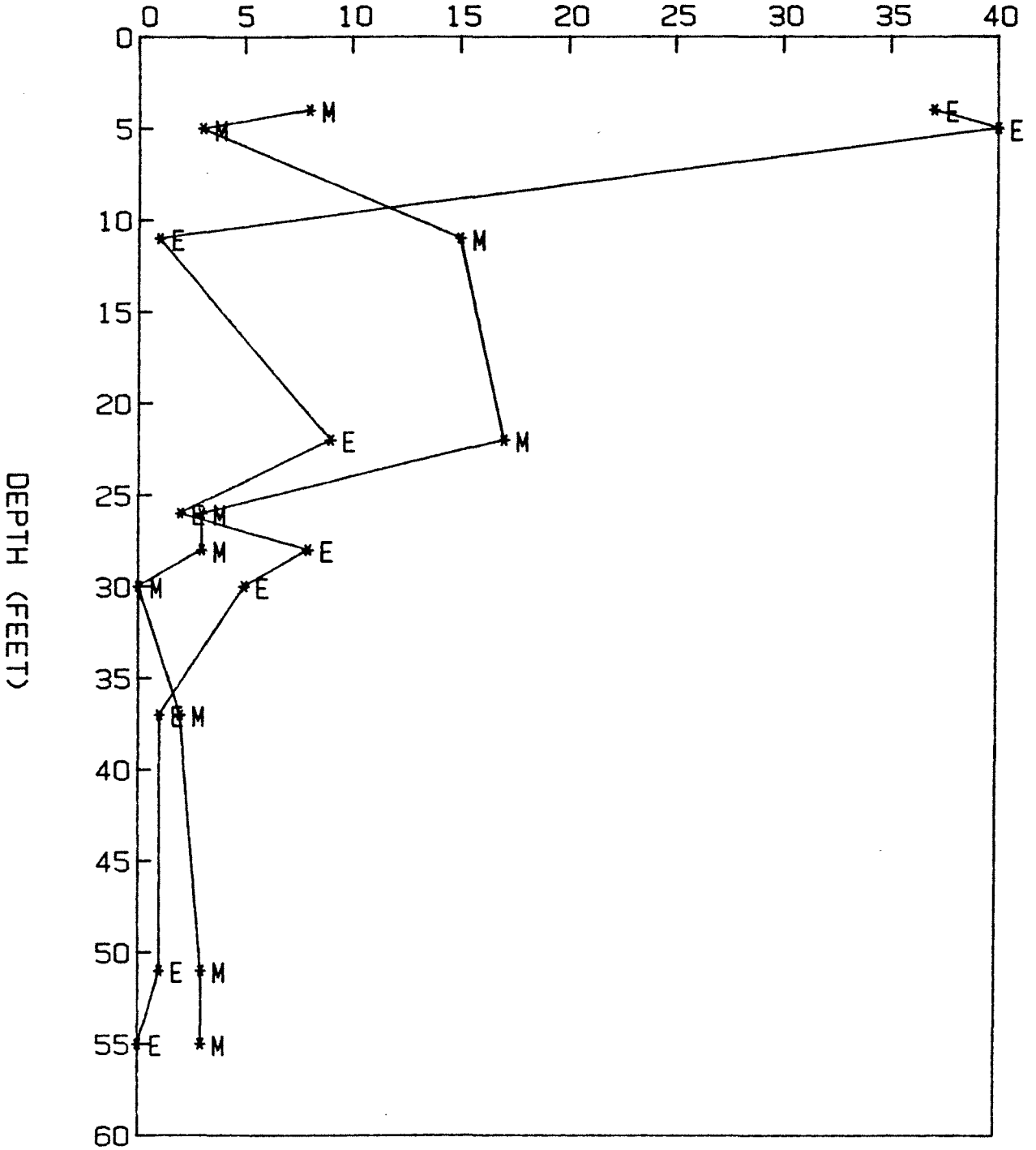
Q - QUARTZ

WELL 4107-C



WELL 4111-A

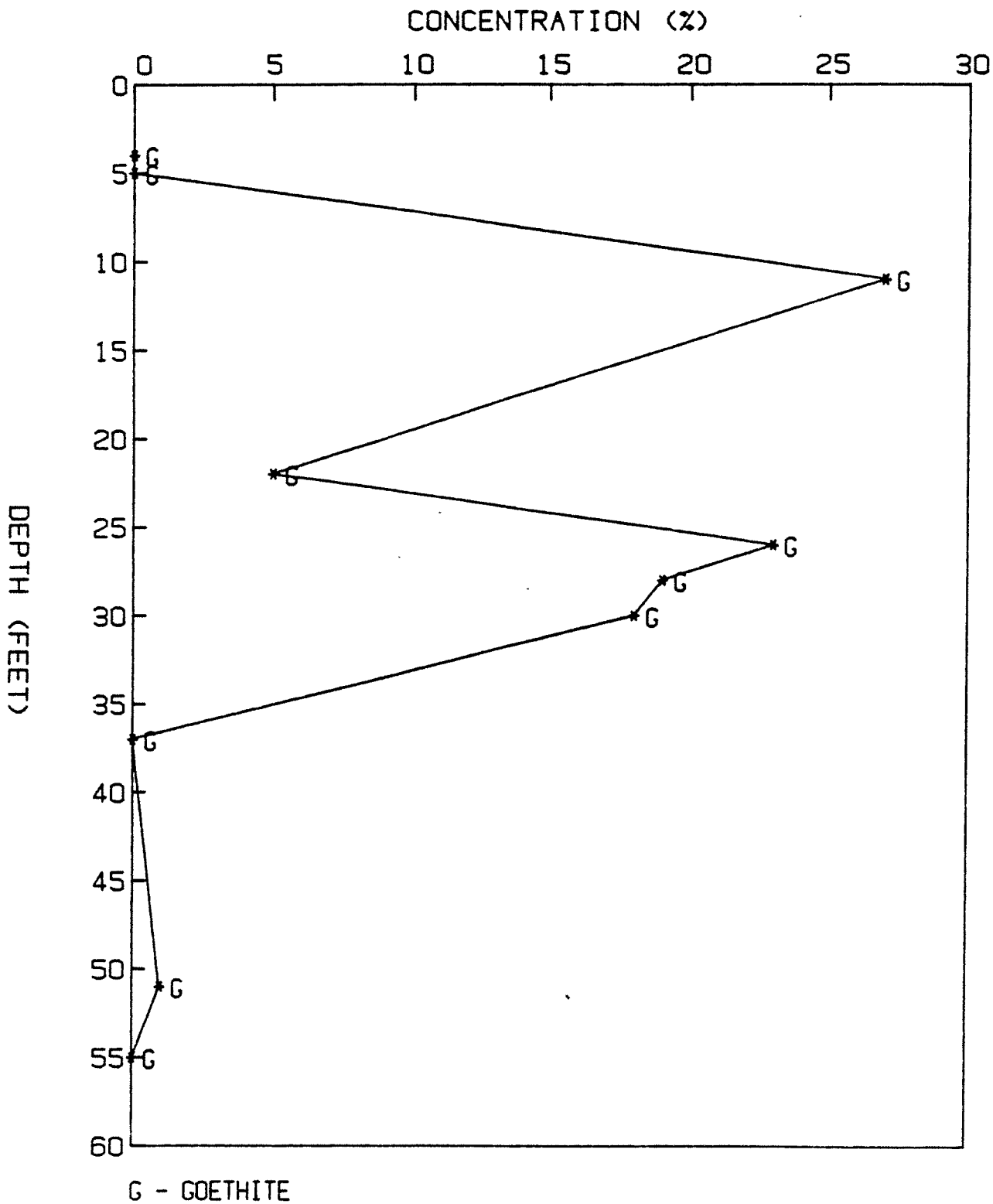
CONCENTRATION (%)



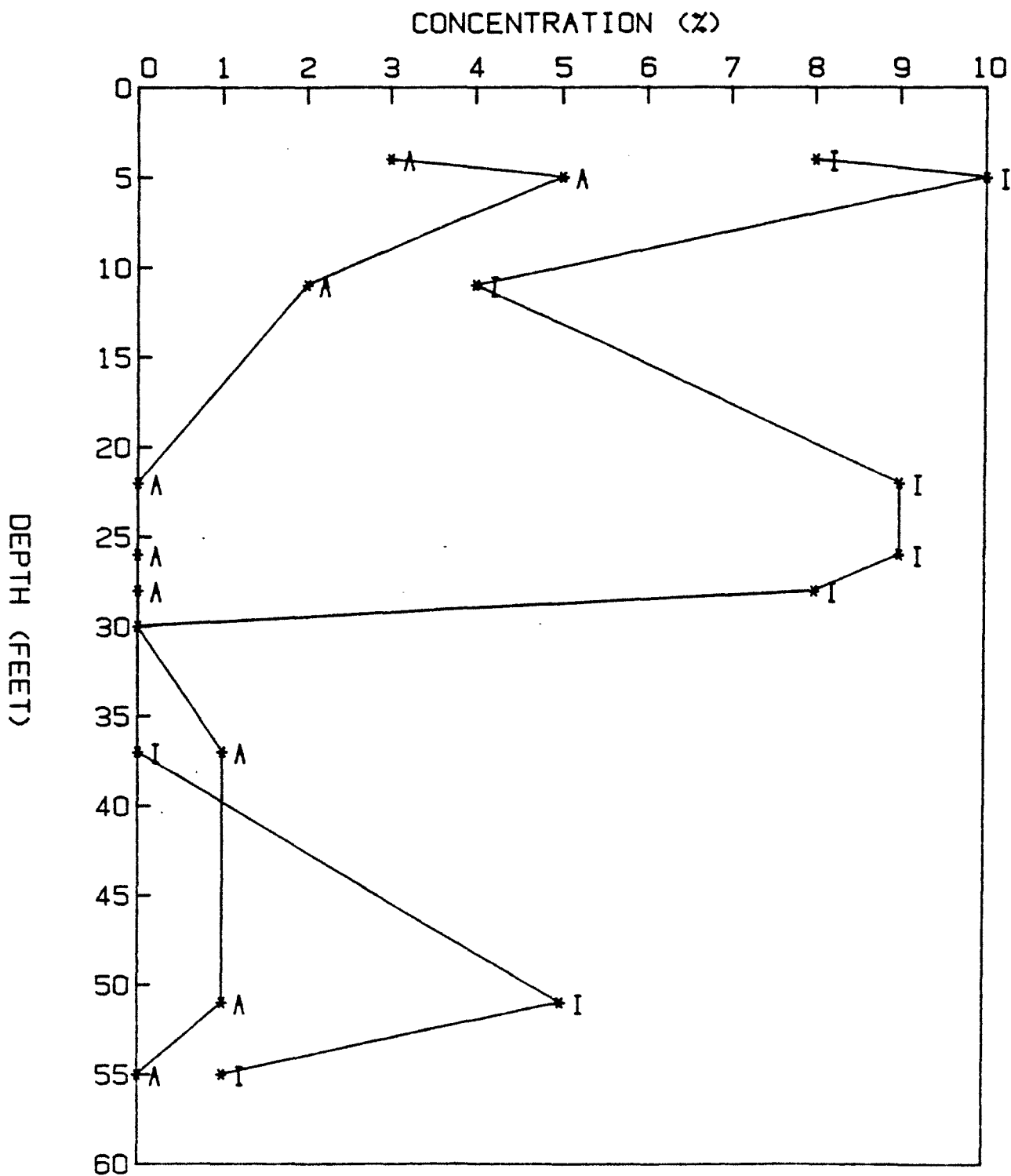
E - HEMATITE

M - MAGNETITE

WELL 4111-A



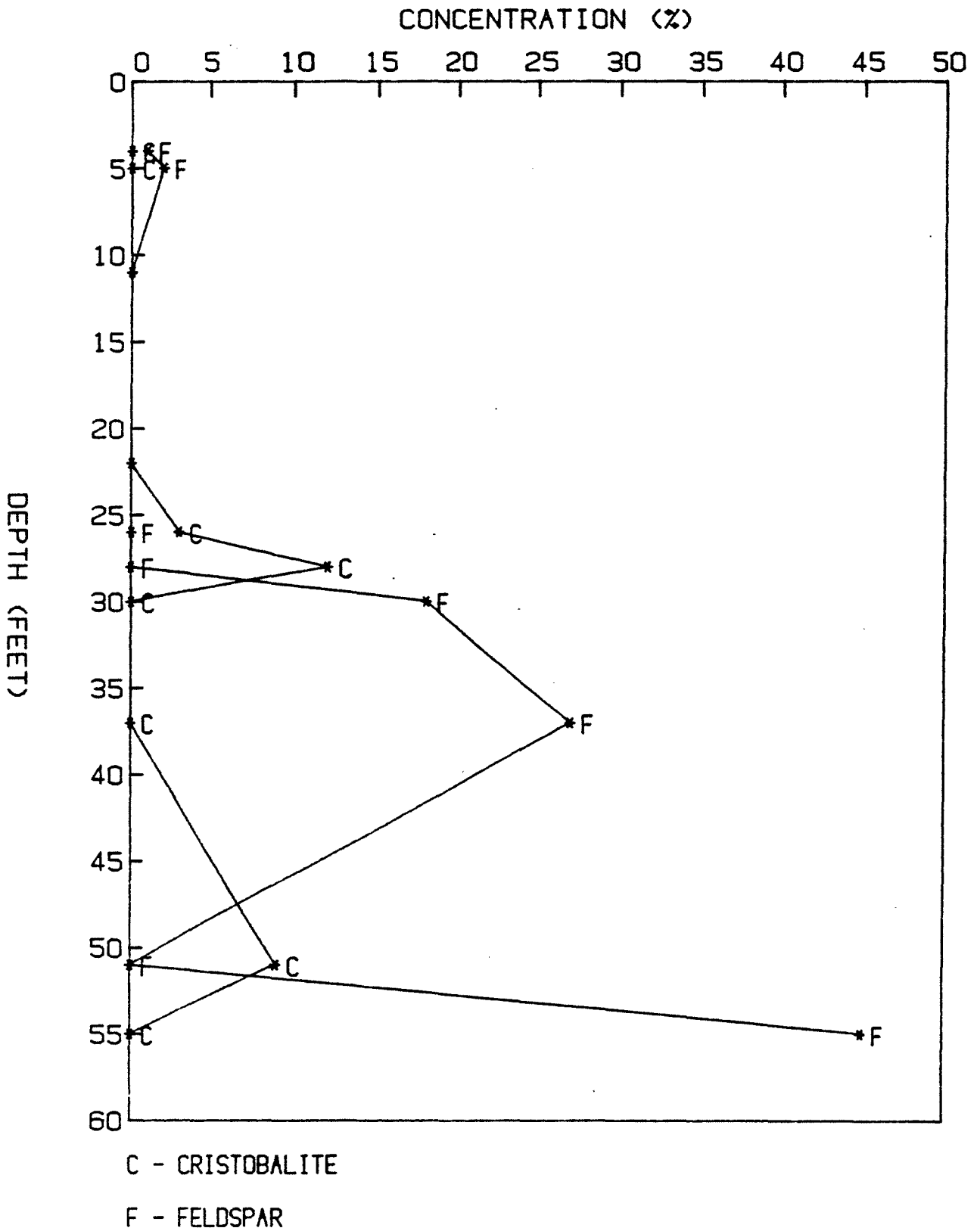
WELL 4111-A



A - ANATASE

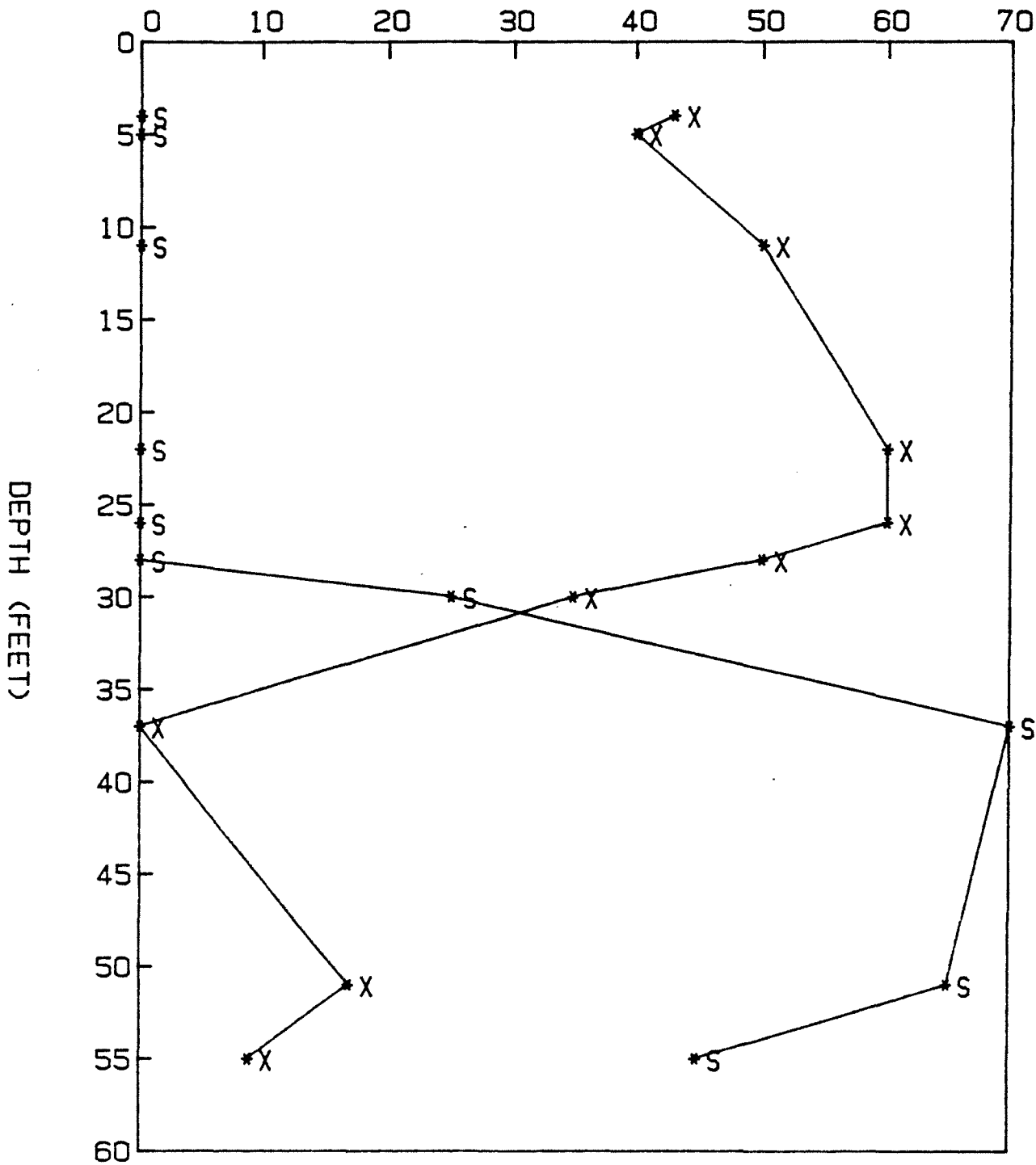
I - ILMENITE

WELL 4111-A



WELL 4111-A

CONCENTRATION (%)

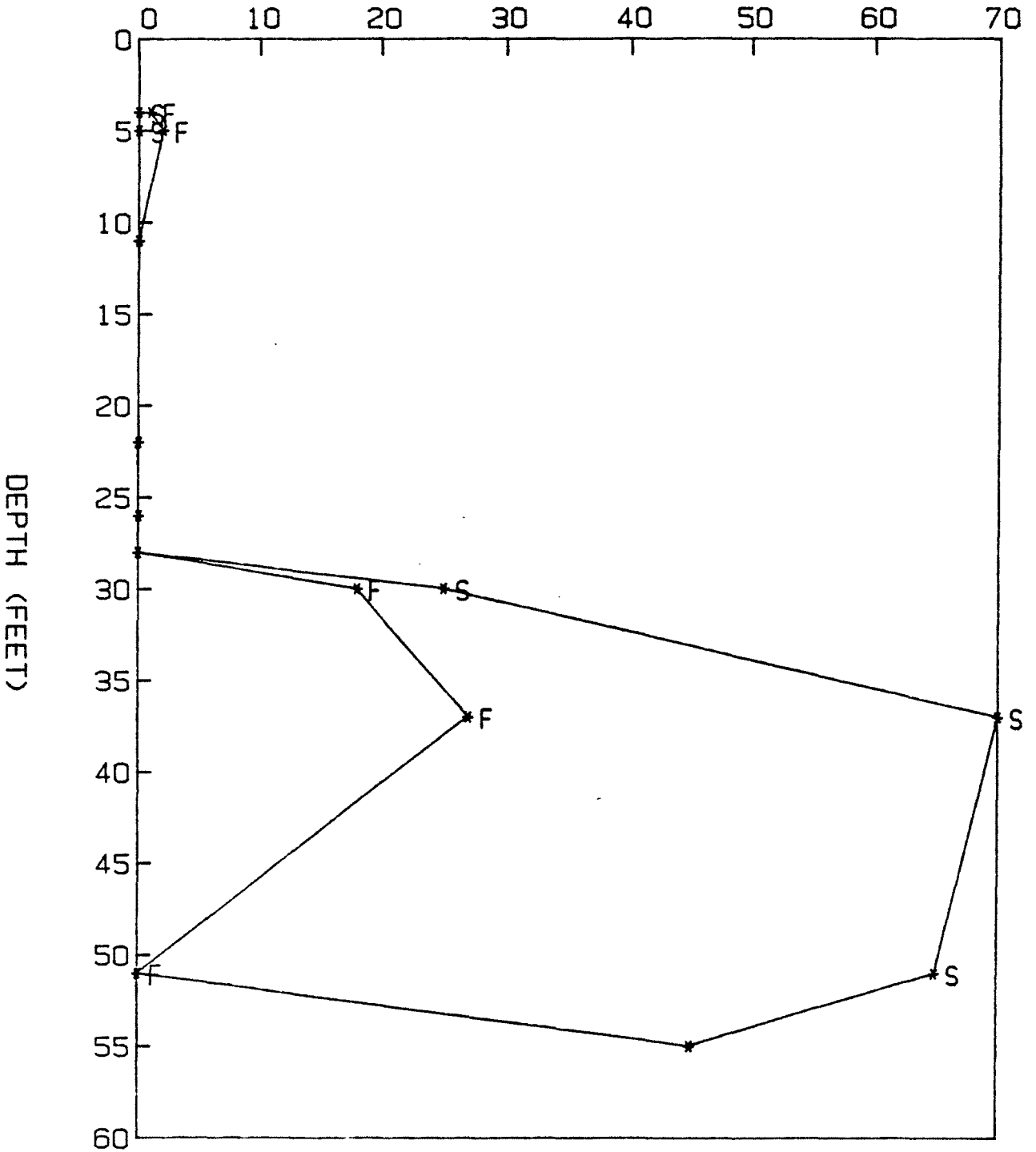


X - HALLOYSITE/KAOLINITE

S - SMECTITE

WELL 4111-A

CONCENTRATION (%)

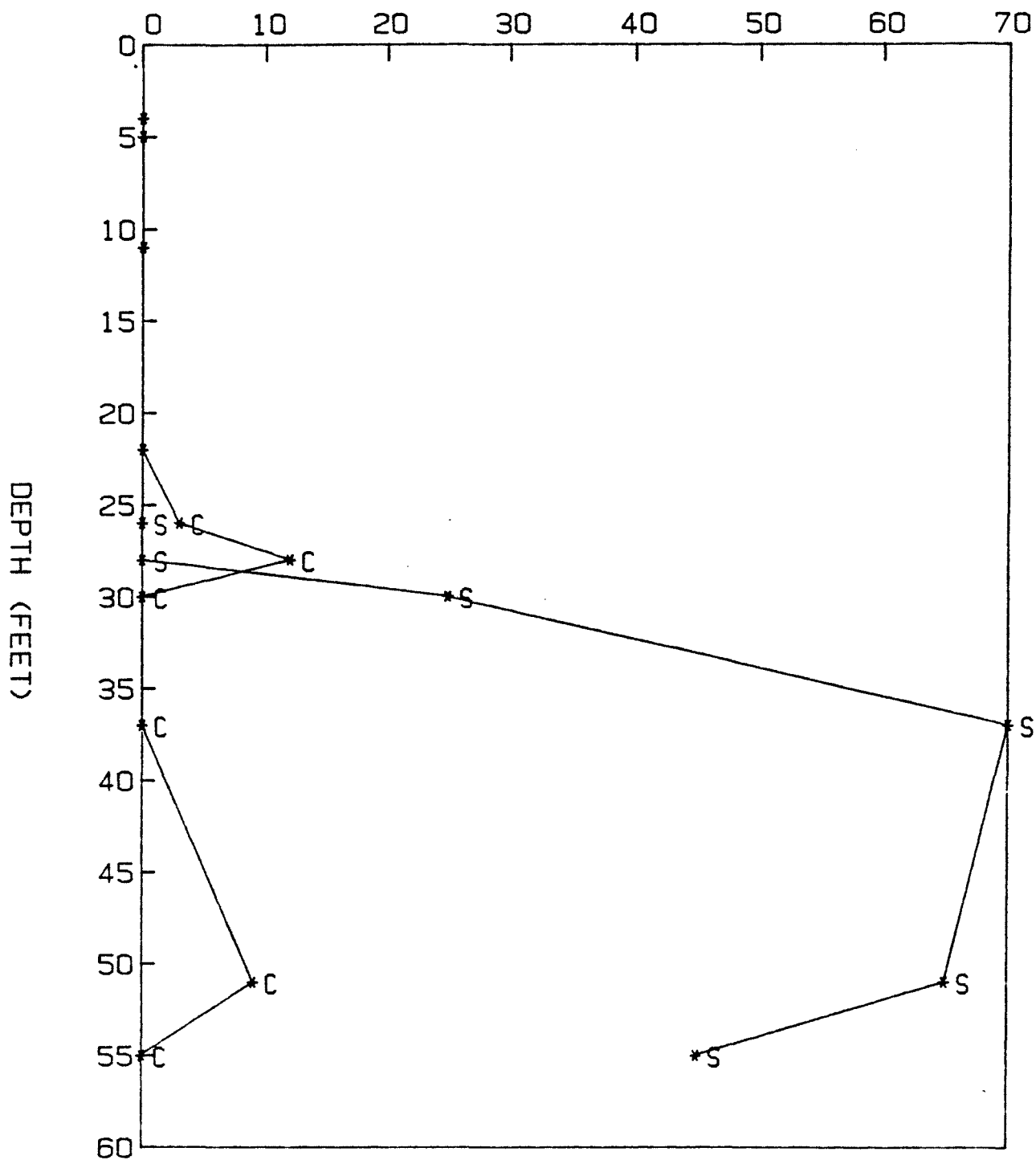


S - SMECTITE

F - FELDSPAR

WELL 4111-A

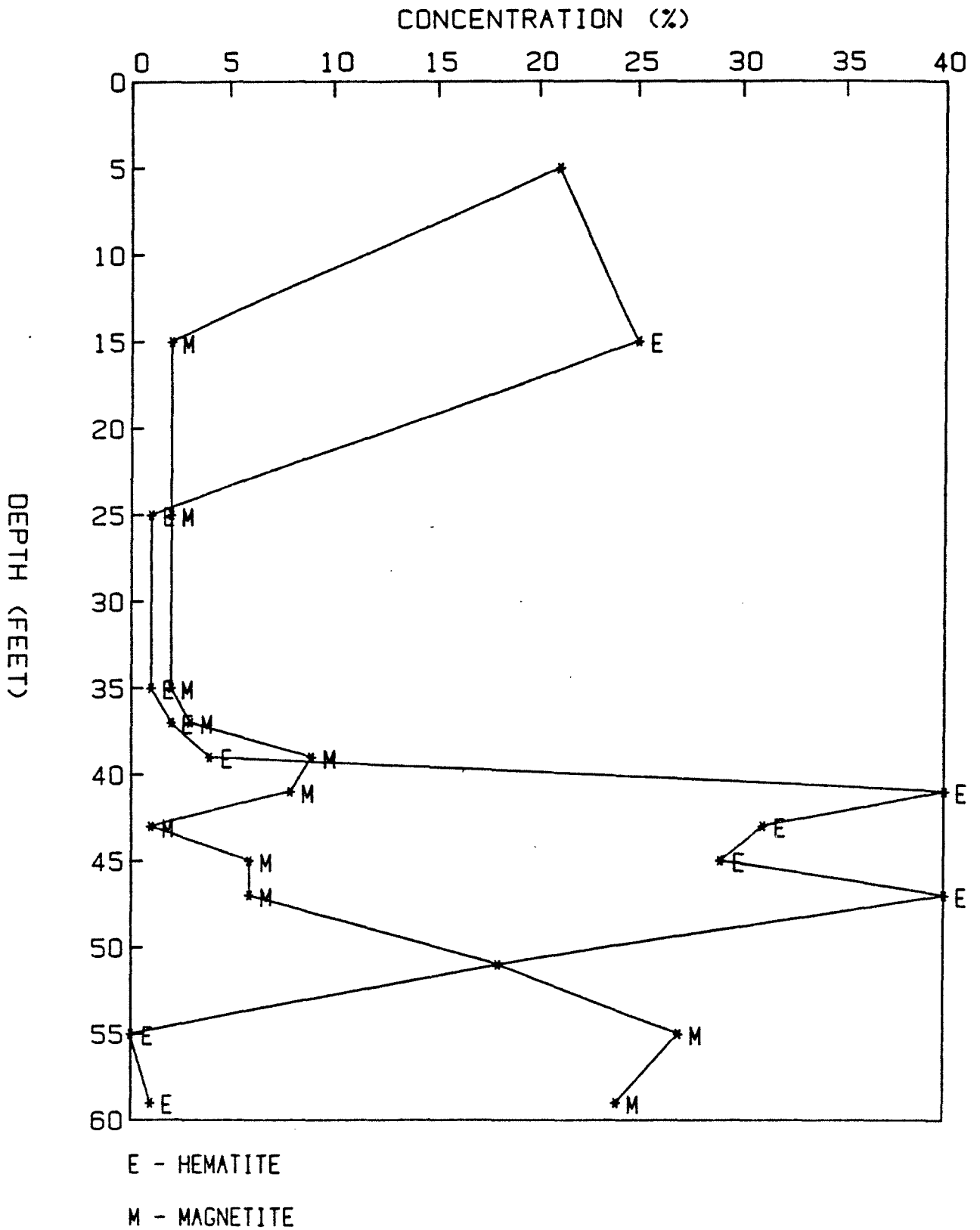
CONCENTRATION (%)



S - SMECTITE

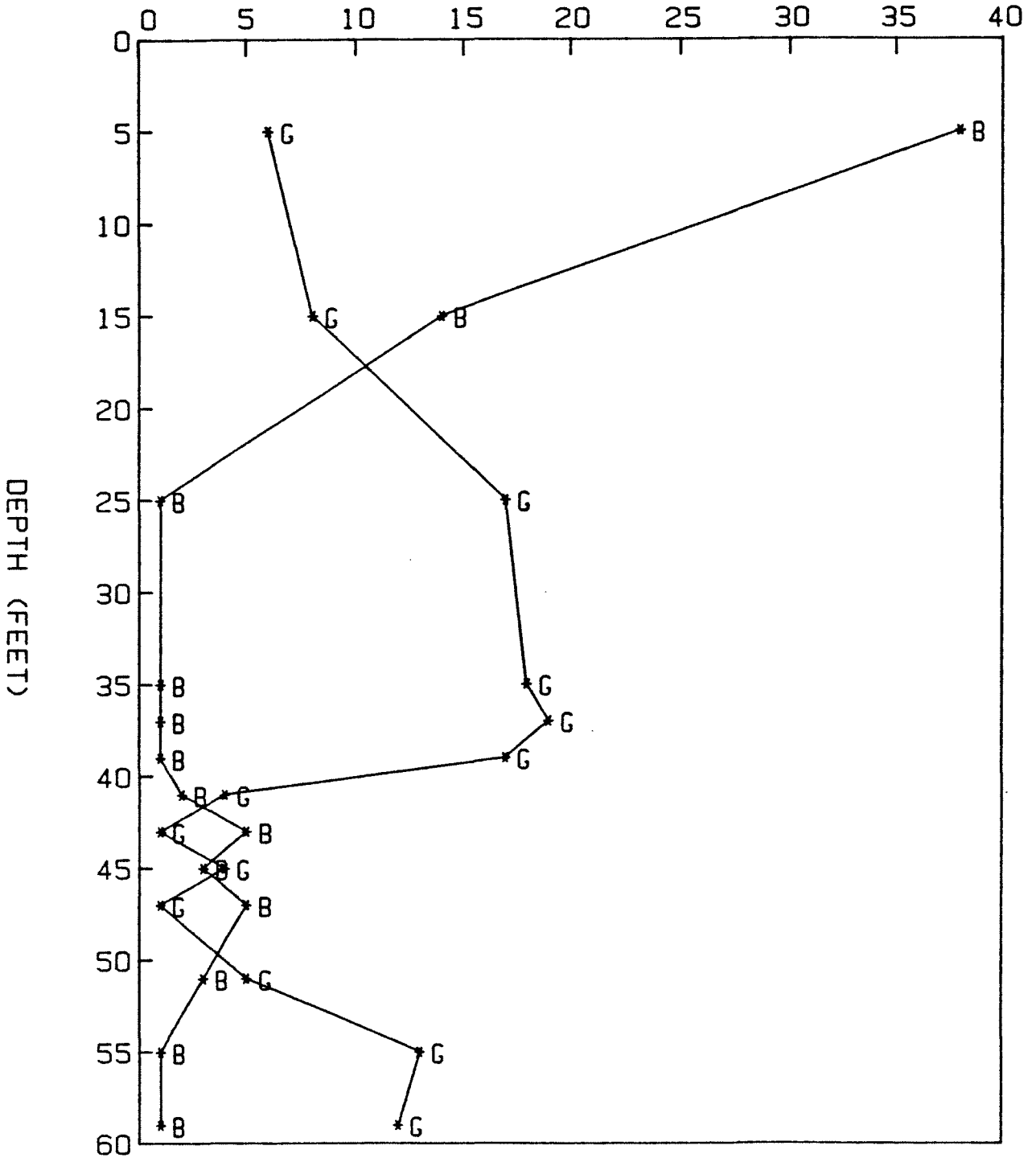
C - CRISTOBALITE

WELL 4201-B



WELL 4201-B

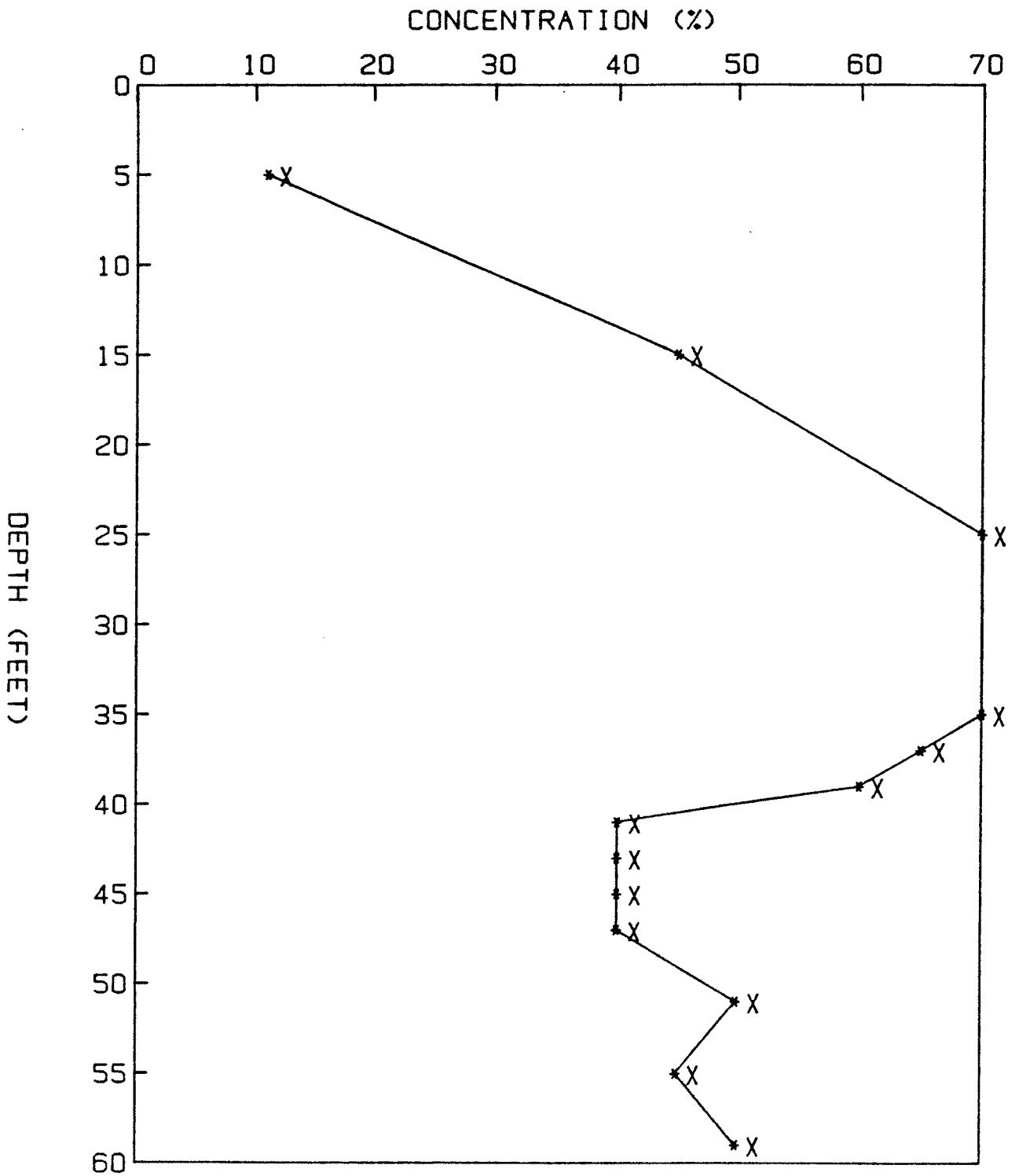
CONCENTRATION (%)



G - GOETHITE

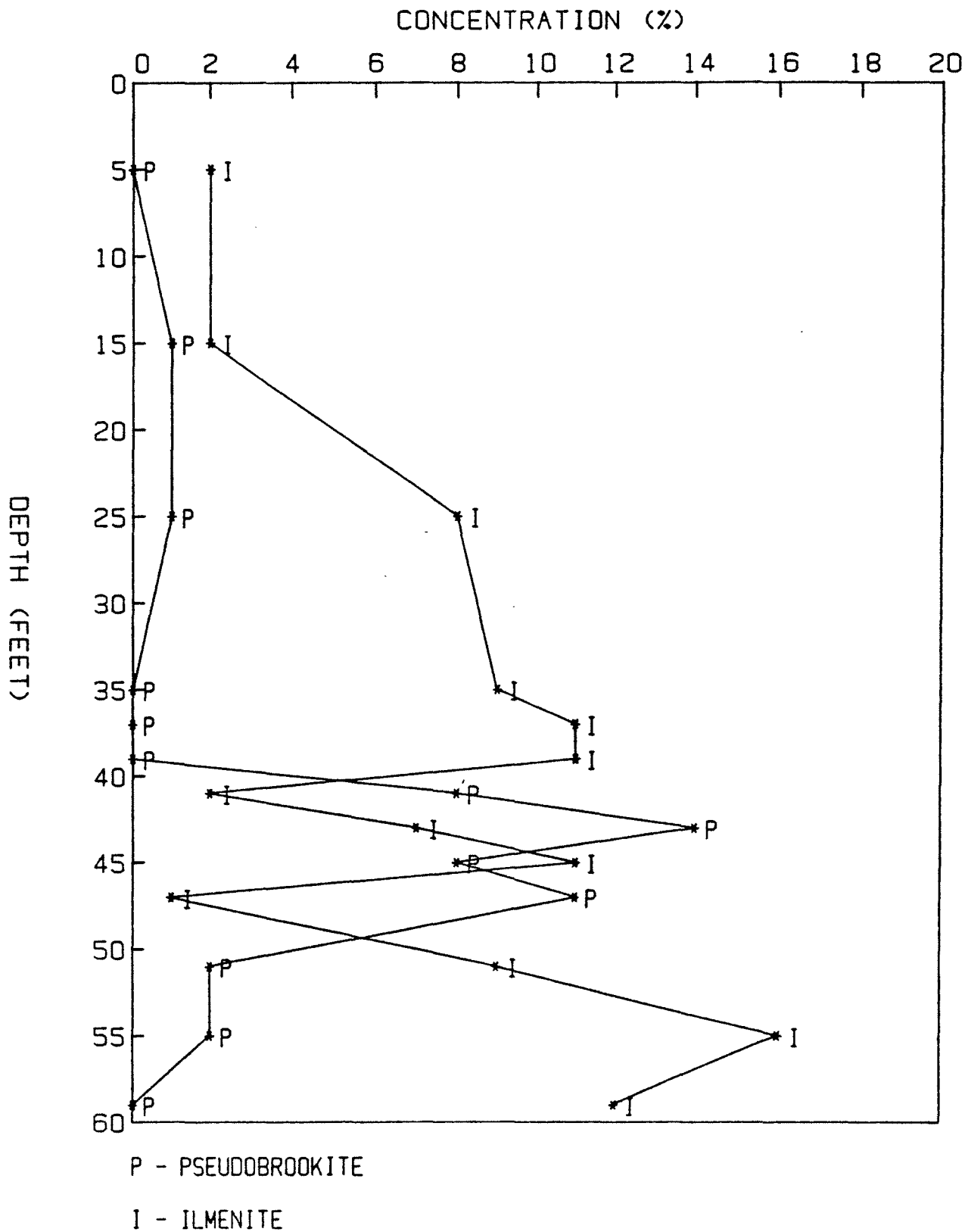
B - GIBBSITE

WELL 4201-B



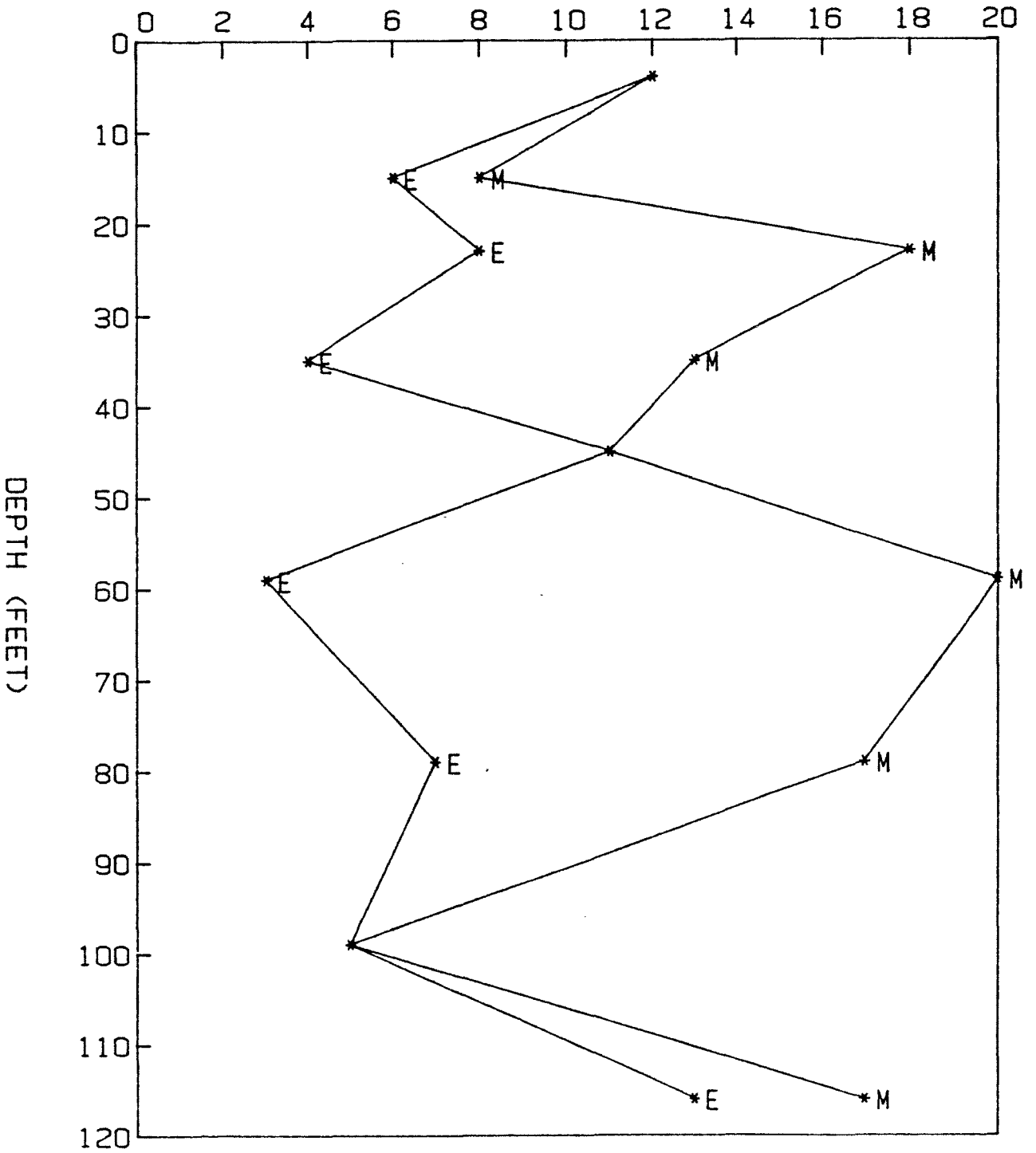
X - HALLOYSITE/KAOLINITE

WELL 4201-B



WELL 4201-D

CONCENTRATION (%)

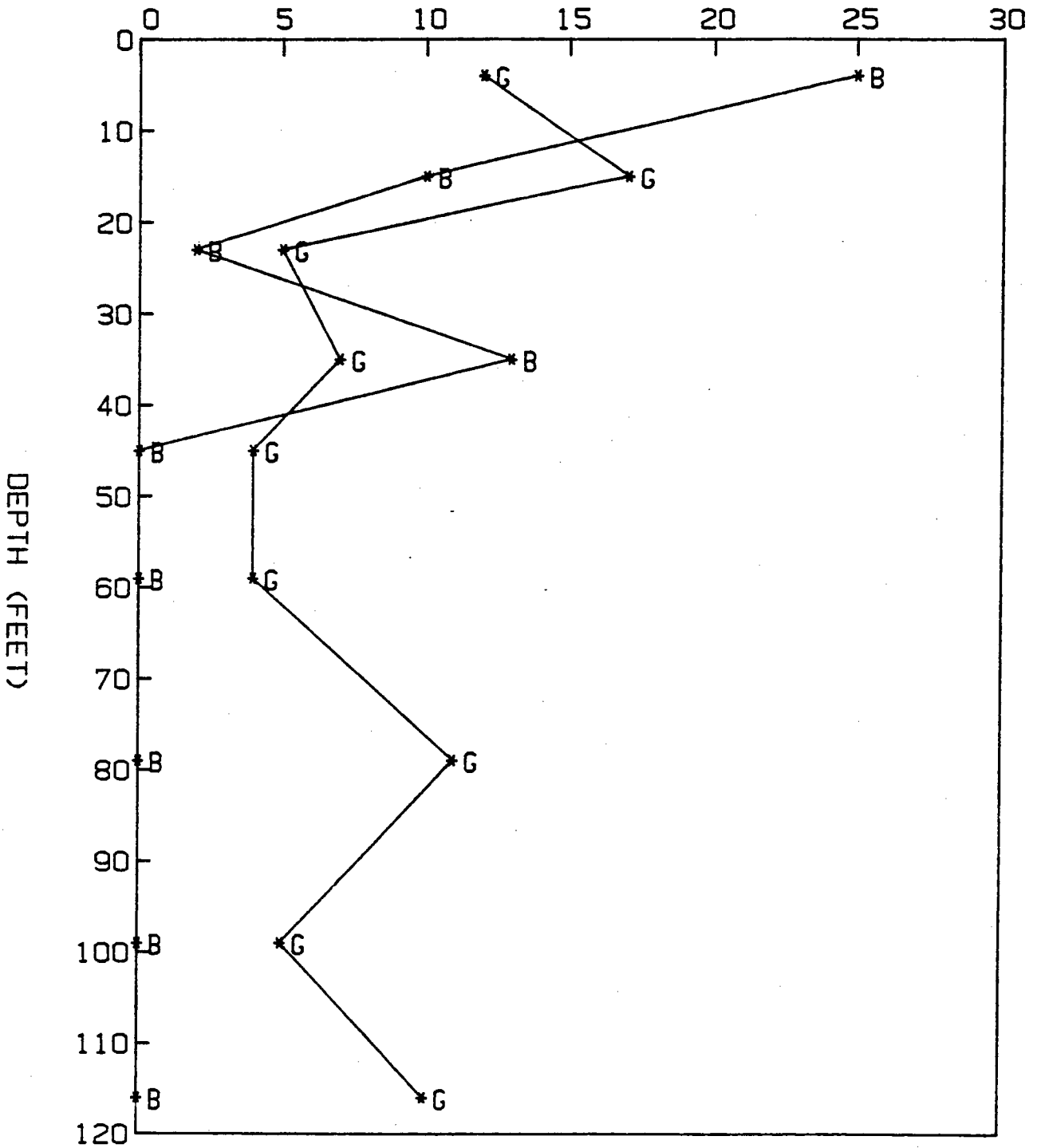


E - HEMATITE

M - MAGNETITE

WELL 4201-D

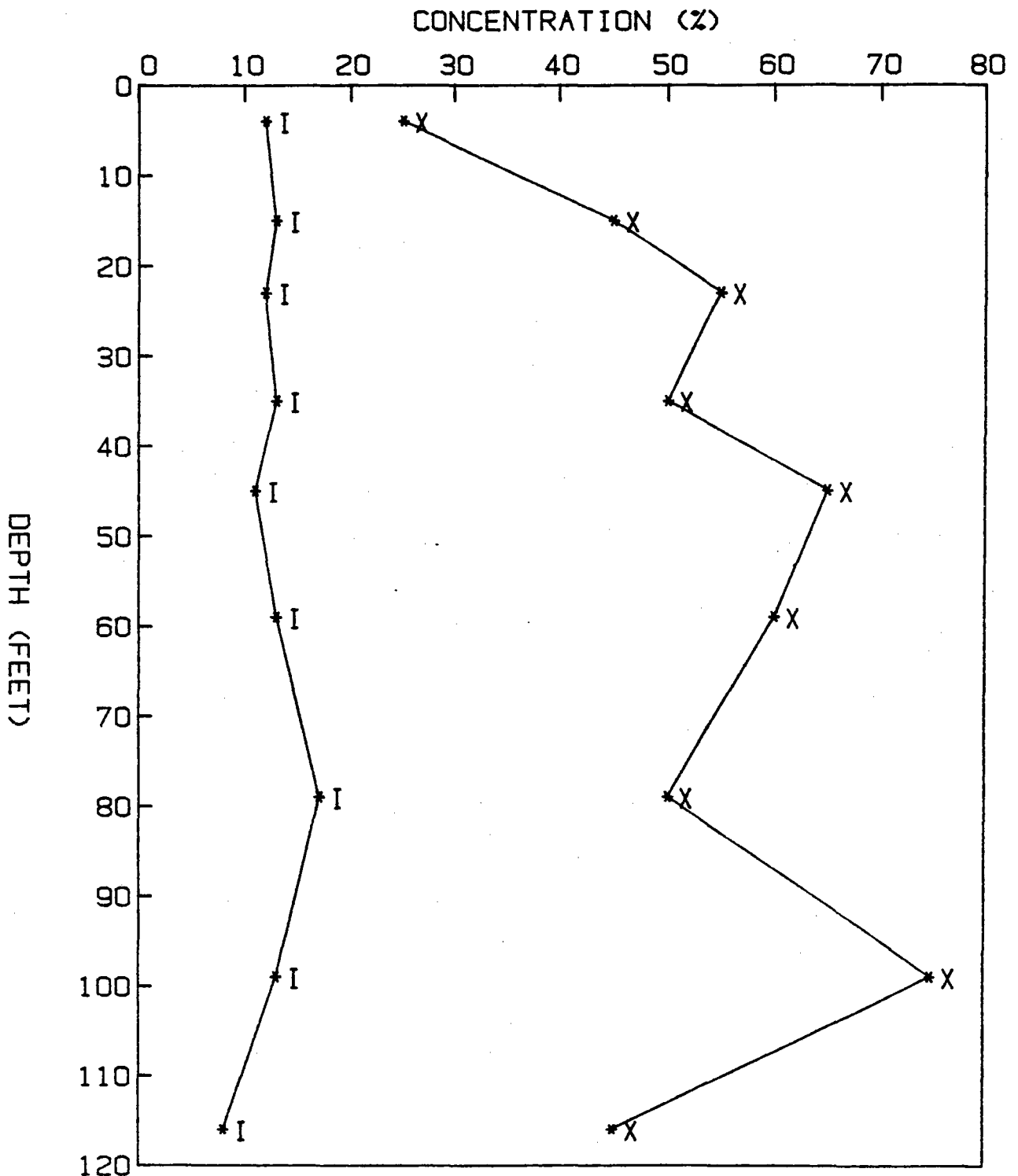
CONCENTRATION (%)



G - GOETHITE

B - GIBBSITE

WELL 4201-D

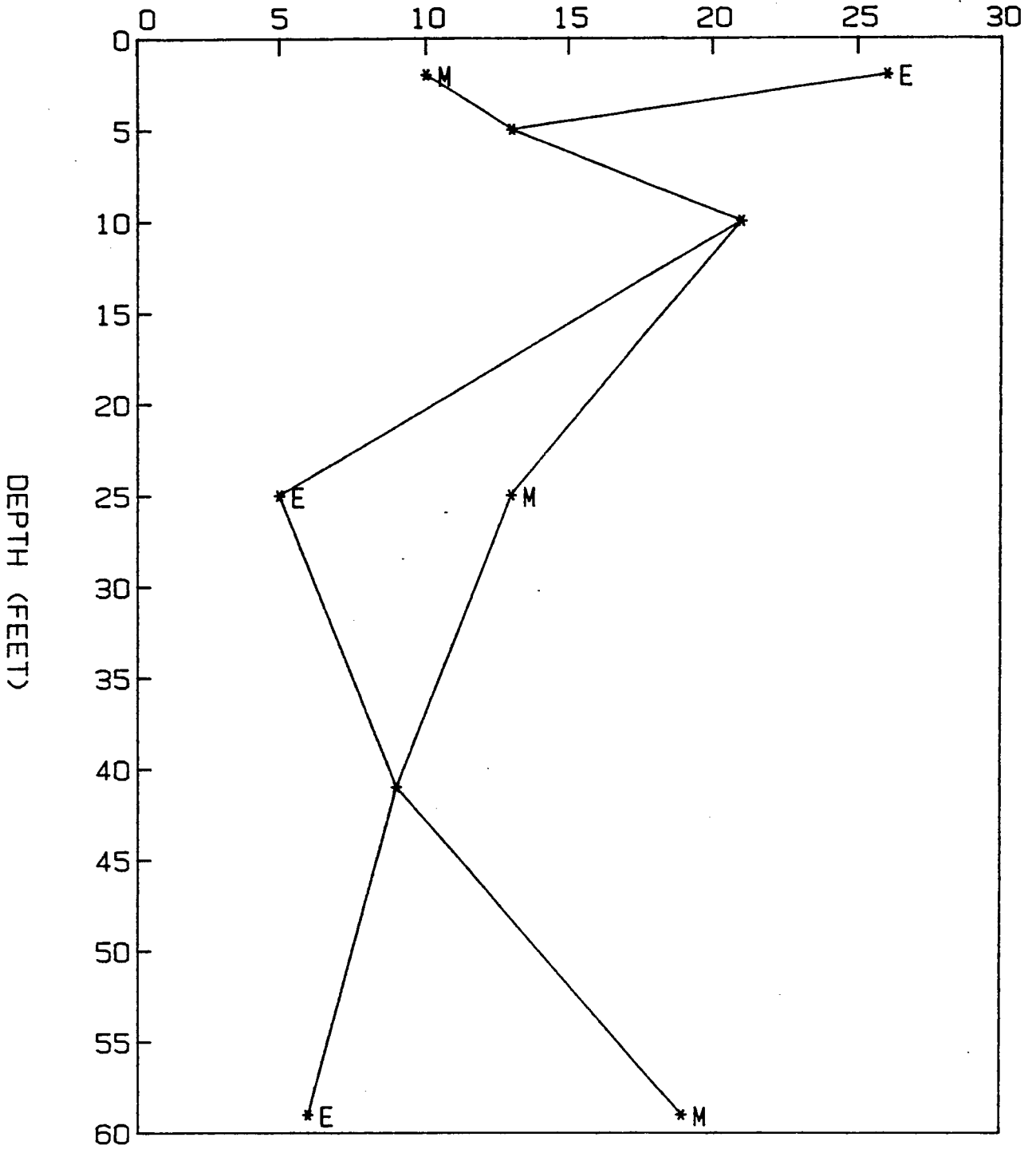


X - HALLOYSITE/KAOLINITE

I - ILMENITE

WELL 4213-A

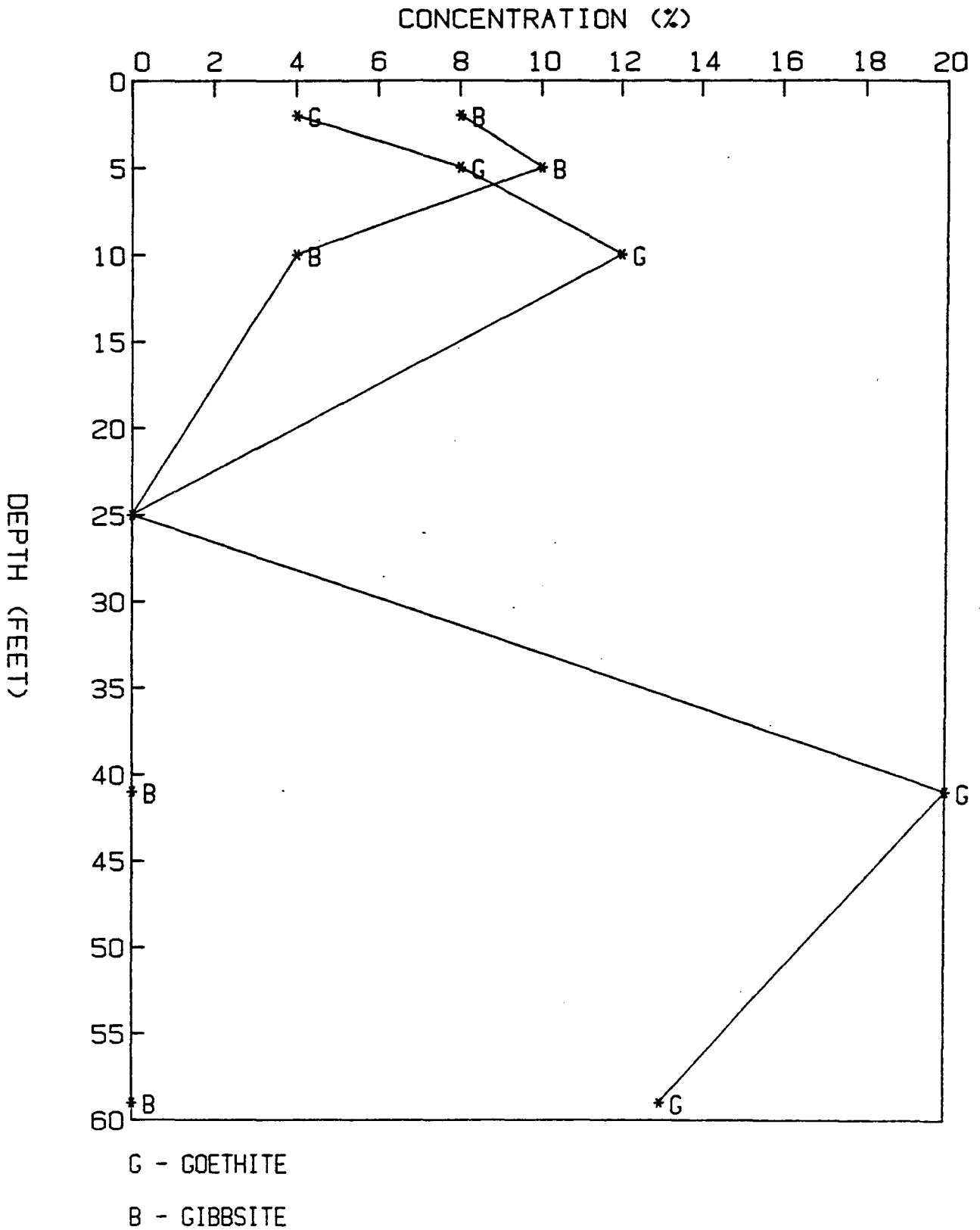
CONCENTRATION (%)



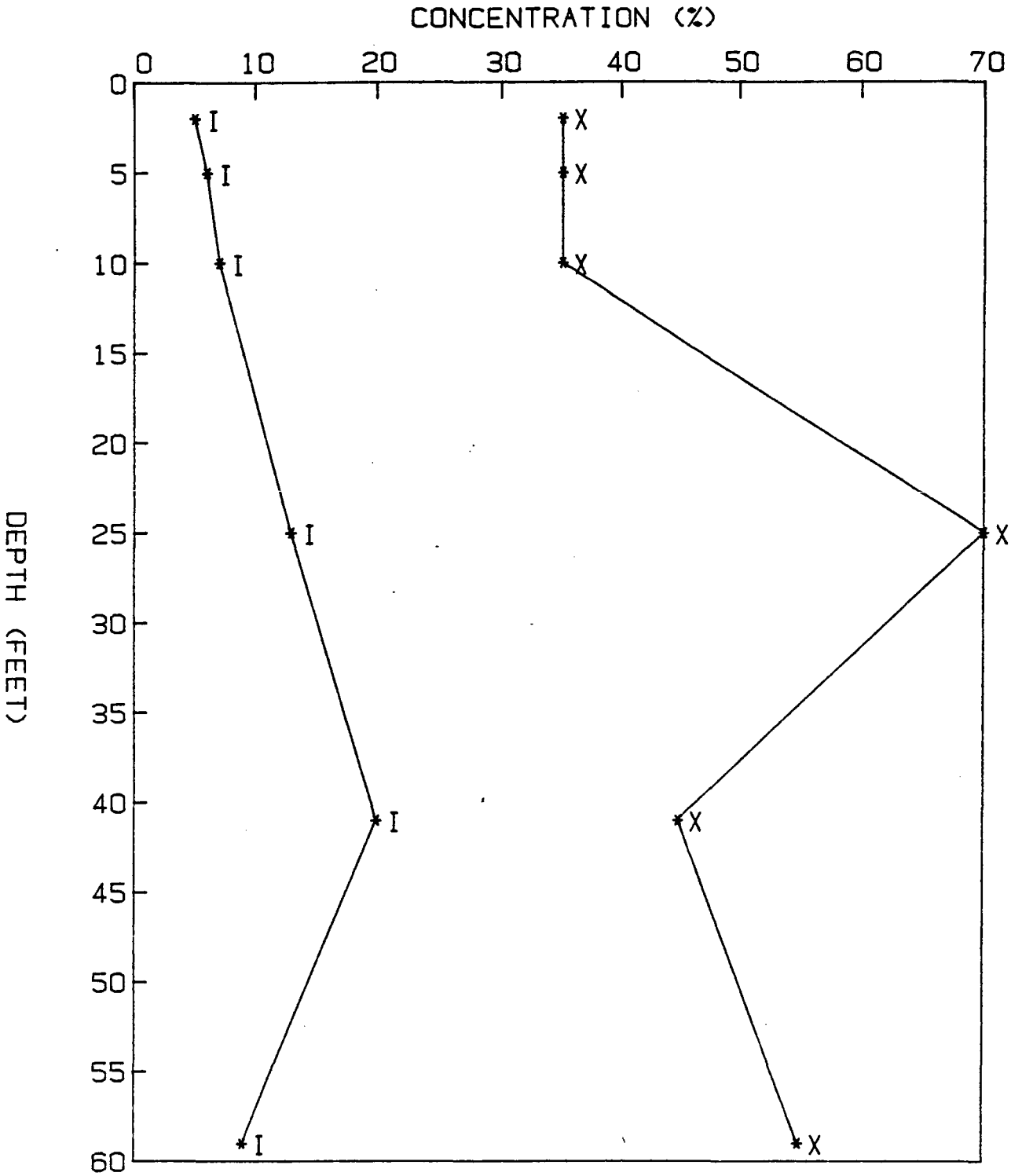
E - HEMATITE

M - MAGNETITE

WELL 4213-A



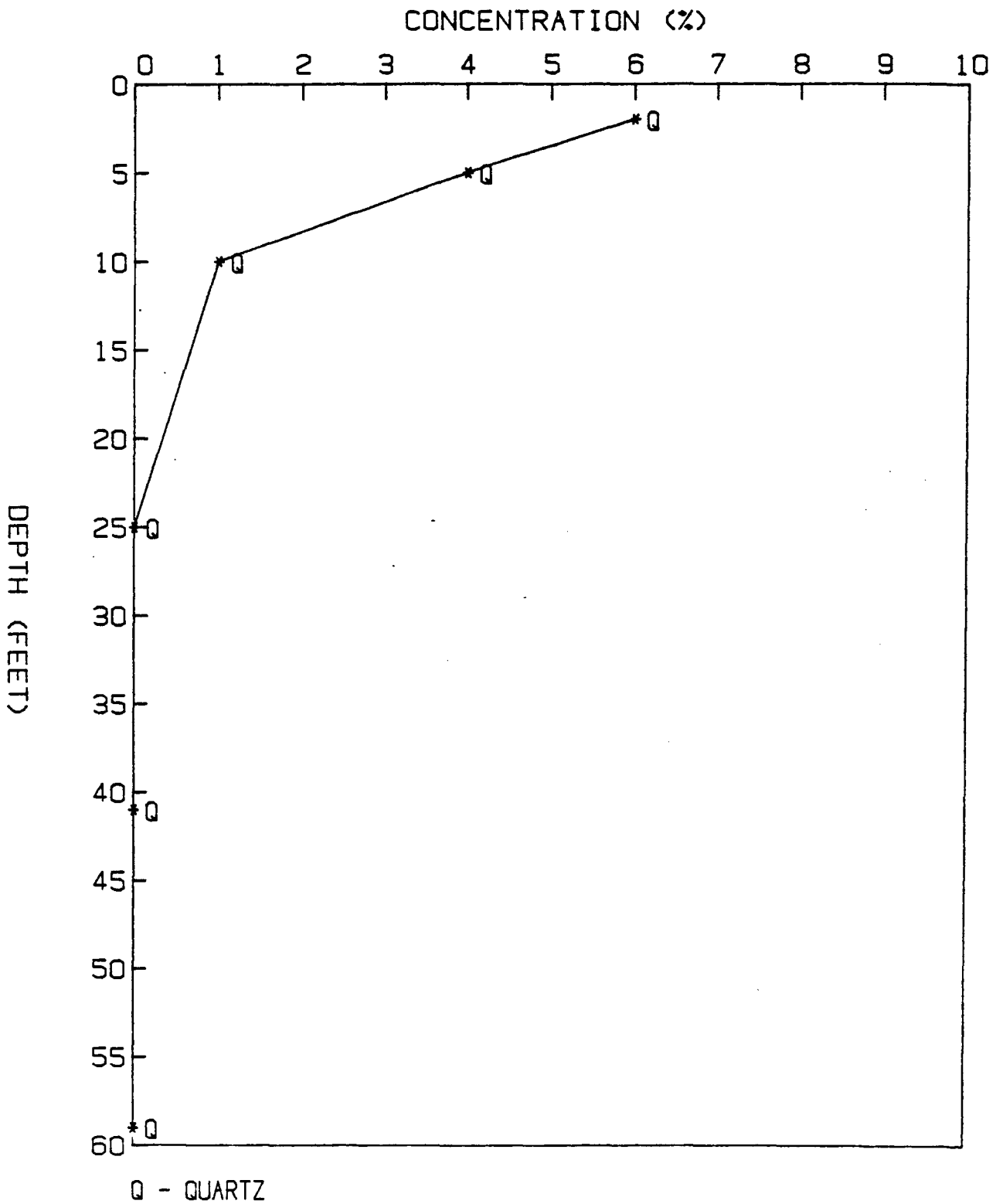
WELL 4213-A



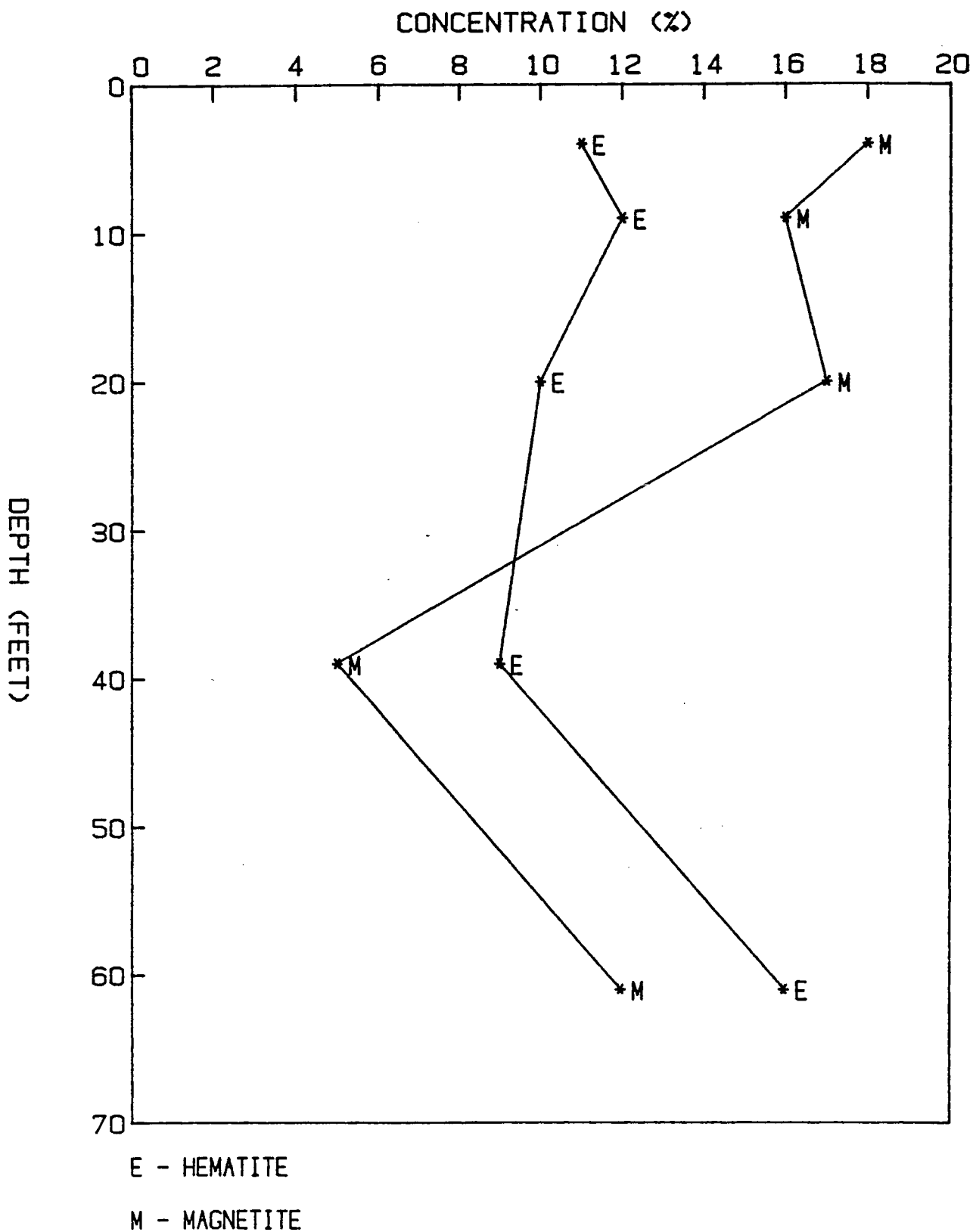
X - HALLOYSITE/KAOLINITE

I - ILMENITE

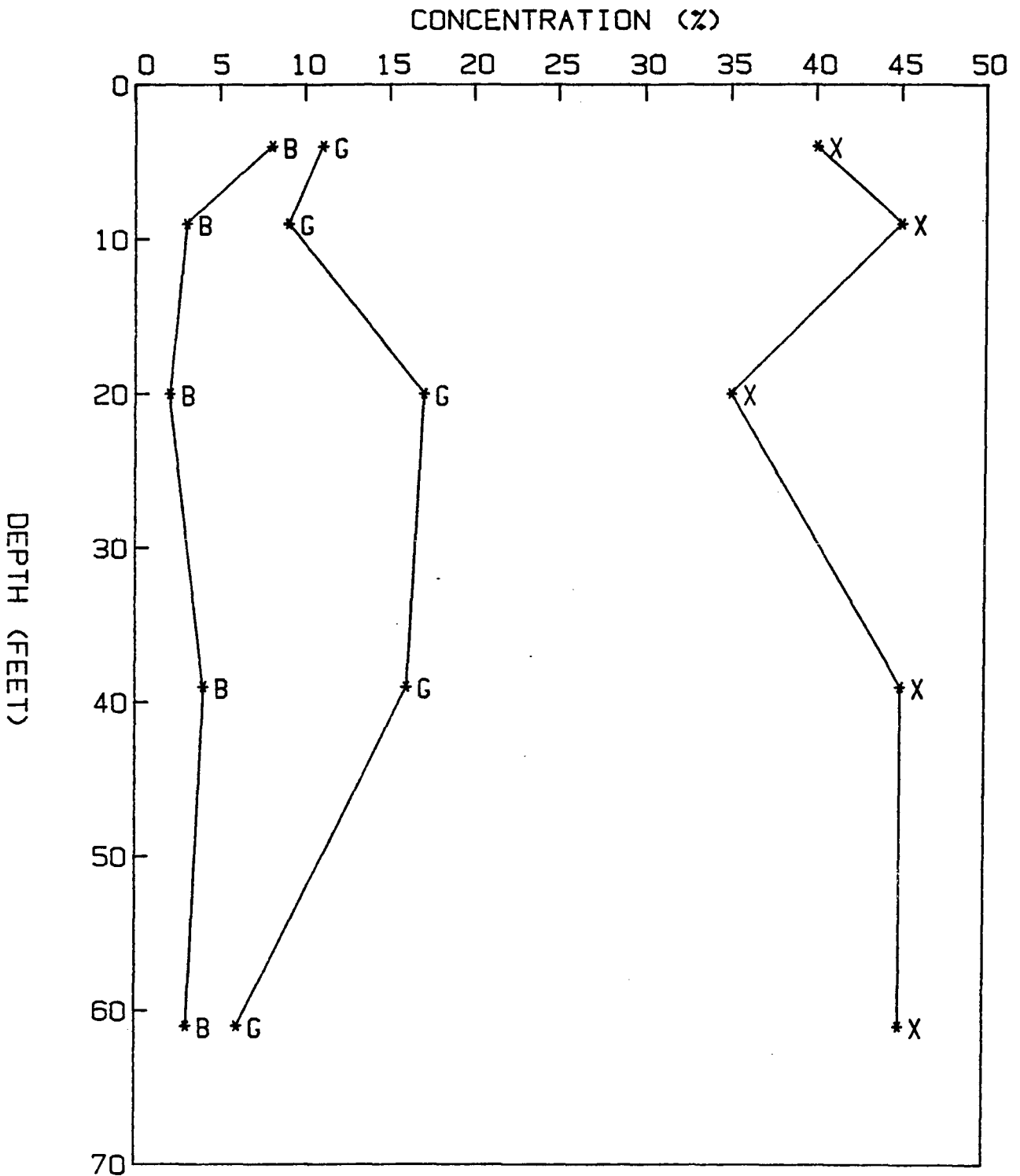
WELL 4213-A



WELL 9060-C



WELL 9060-C



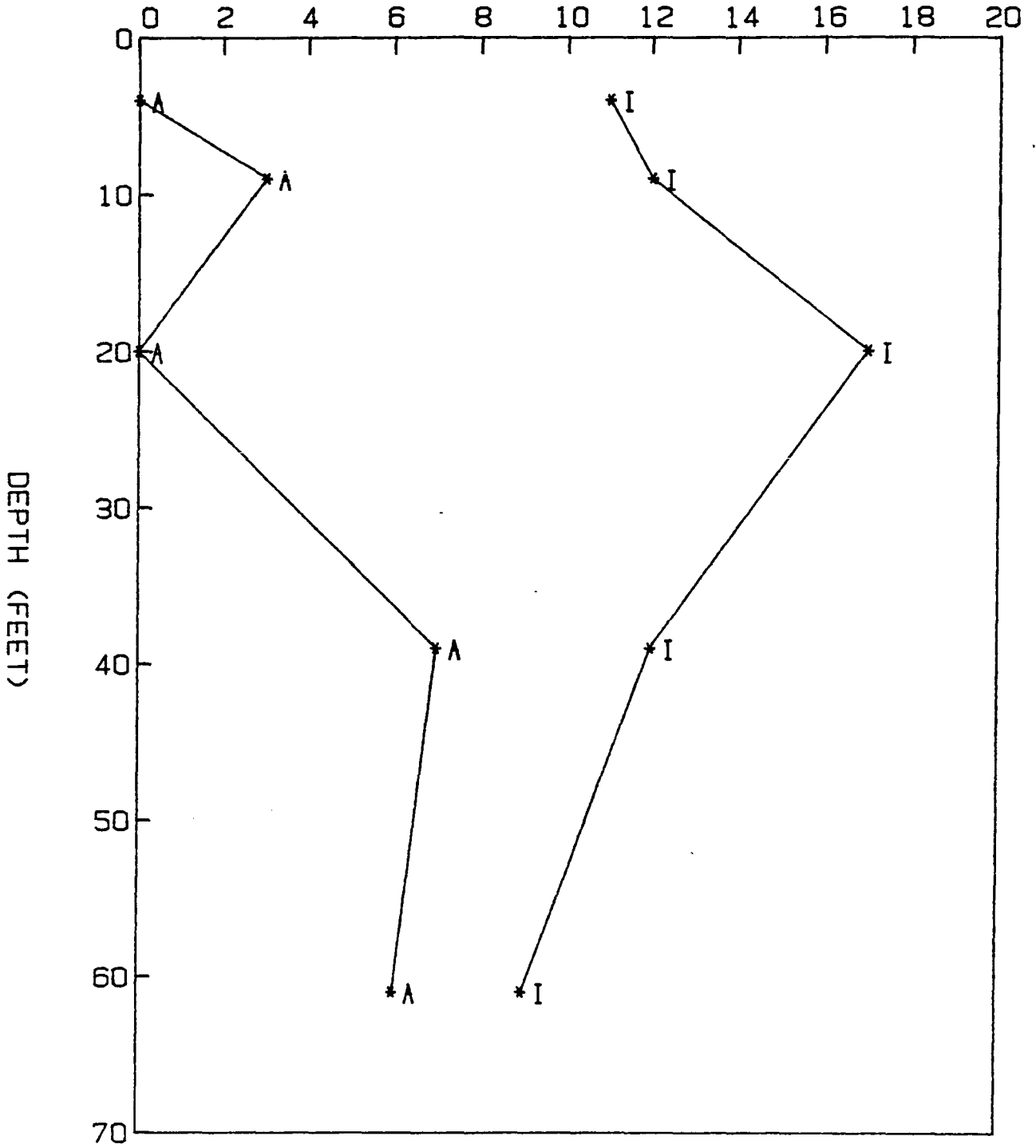
X - HALLOYSITE/KAOLINITE

G - GOETHITE

B - GIBBSITE

WELL 9060-C

CONCENTRATION (%)



A - ANATASE

I - ILMENITE

APPENDIX C
DESORPTION AND LEACHABILITY OF RESIDUAL DBCP AND EDB
FROM SOILS AND SAPROLITE

Richard E. Green
Frank L. Peterson
Donna S. Buxton

ABSTRACT

Pesticides applied to pineapple fields in central O'ahu to control nematode populations have been detected in groundwater drawn from the underlying aquifer. These nematicides have persisted in surface soils and deep saprolite despite their discontinued use. The leachability of these pesticide residues from soil and their subsequent movement will determine whether or not they constitute a continued threat to groundwater quality. In this study, leachability is assessed by sorption-desorption measurements and is characterized by distribution coefficients and the kinetics of release of sorbed residues.

Two methods for characterizing sorption-desorption processes have been developed that exploit the tendency of these fumigant pesticides to vaporize. Both methods analyze the vapor phase of a soil-pesticide system. The indirect sorption method results in a determination of distribution coefficients and the purge system results in a characterization of the kinetics of desorption.

Experiments using the indirect sorption method to determine distribution coefficients for a surface soil obtained from central O'ahu have been initiated. Preliminary work using the purge system is also underway. The new sorption-desorption methods will be used to determine the leachability of DBCP and EDB residues in soil and saprolite obtained from central O'ahu.

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INTRODUCTION

For a number of years various pesticides have been applied to surface soils of central O'ahu in an attempt to reduce nematode infestation of pineapple plants. Pesticides have since been detected in groundwater drawn from the underlying aquifer. The compounds being detected are classified as fumigant nematicides, dibromochloropropane (DBCP) and ethylene dibromide (EDB), both halogenated hydrocarbons. Although these compounds have been successful in controlling nematode populations, they have been banned from use in pineapple cultivation because of their carcinogenicity and presence in groundwater.

Besides detection in groundwater, DBCP and EDB residues have been detected in soils and underlying saprolite, despite their discontinued use on O'ahu some years ago (Dept. of Agriculture 1983). Another contaminant, trichloropropane (TCP), which originated in the nematicide DD applied over 30 years ago, has also been detected in groundwater samples taken from several locations on central O'ahu. Acceptable levels for DBCP and EDB, set by the Environmental Protection Agency and the State of Hawaii, are in the parts per trillion (ppt) range. Both DBCP and TCP have been detected at the parts per billion (ppb) level in water and soil samples obtained from the Wahiawa Plateau in central O'ahu.

The overall objective is to examine the leachability of sorbed pesticide residues and to assess the possibility that continued groundwater contamination can result from the desorption of these residues. Leachability can be studied through the analysis of soil-pesticide systems. More specifically, leachability can be assessed by sorption distribution coefficients and by characterizing the kinetics of sorption-desorption processes.

Sorption-Desorption Processes

The extent of contamination of a water resource is related to the leachability of sorbed compounds (i.e., their removal from the soil by percolating water). The leachability of a pesticide depends on the sorption-desorption process, a phenomenon that involves two-way exchange of soluble components. Sorption describes the process by which soil particles take up pesticide; desorption is the process by which soil particles release sorbed pesticide to soil solution.

Partitioning of a pesticide between soil solution and soil particles at equilibrium is expressed in terms of a distribution coefficient, K_d . This distribution coefficient is defined as the ratio of the concentration of the sorbed phase to the concentration of the solution phase for a system at equilibrium. At low solution concentrations (e.g., one-tenth the solubility in water for DBCP and EDB), sorption K_d values are relatively constant, i.e., the sorption isotherm is linear. The magnitude of K_d values reveals information concerning both sorption and desorption processes. For instance, a relatively large desorption K_d value indicates a pesticide may be "highly" sorbed or is not readily or easily leached from the soil site, whereas a relatively small value suggests that the pesticide is quite easily leached.

Previously, a single K_d value determined from sorption experiments was applied to both sorption and desorption processes. K_d values of sorption and desorption have been shown to differ significantly (Green, Liu, and Tamrakar 1986). This implies the importance of determining K_d values for the appropriate processes.

To understand the rates of release of a pesticide from soil particle surfaces and subsequent movement, it is important to characterize the kinetics of desorption. Previous studies by DiToro and Horzempa (1982) and Karickhoff and Morris (1985) have shown that the initially desorbed portion of the total amount of pesticide in a soil system is easily removed while the remainder is more resistant to desorption.

Methodology

Conventional methods used to obtain distribution coefficients (K_d) involve measuring a compound in the solution phase. However, due to the volatile nature of these nematocides, methodologies were developed that exploit the tendency of these particular compounds to vaporize.

Two different methods were developed that quantify the volatile component of DBCP and EDB. The first method, a simple "headspace analysis" technique, is referred to as the indirect sorption method. It involves characterizing desorption processes within a closed soil-water-pesticide system that reaches equilibrium (given sufficient time) between the sorbed, solution, and vapor phases of the pesticide. The second method, referred to as a "purge system" and which is modeled after the approach of Karickhoff and Morris (1985), characterizes desorption in an open system under dynamic conditions. Both

methods require an analysis of the vapor phase and allow the determination of the rates and the extent of desorption. The indirect sorption method is capable of determining sorption distribution coefficients. The purge system provides data which can yield kinetic coefficients for the desorption process.

Soil properties, such as organic carbon content, pH, and moisture content, will also be determined for soil samples. Using the techniques developed in this study, relationships between soil properties, sorption distribution coefficients, and desorption kinetics will be thoroughly examined. Such relationships will enable an assessment of the potential for leaching of pesticide residues and the possible contamination of groundwater underlying the study area.

OBJECTIVES

The objectives of this project are

1. To determine the rate and extent of DBCP and EDB desorption from soils in relation to soil properties
2. To determine the relationship between hydraulic properties of soils and the displacement of residual pesticides by transient water movement
3. To assess the potential of groundwater contamination by residual DBCP and EDB in soils in central O'ahu.

APPROACH AND METHOD DEVELOPMENT

The development of methods used to determine sorption coefficients (K_d) and to characterize the kinetics of release are described. The batch equilibration method is a traditional method used to obtain K_d values, and involves analysis of pesticide in the solution phase. Two additional techniques have been developed in this study to characterize sorption-desorption processes from measurements of pesticide in the vapor phase in a soil system.

The first technique, the indirect sorption method, relates the vapor phase to the solution phase, the concentration of which is used to calculate K_d . The second technique developed in this study, the purge system, characterizes the kinetics of desorption via measurements of the amount of pesticide in the vapor phase purged from a soil solution, analyses being conducted at

varying time intervals.

In this study, the conventional batch equilibration method has been used to determine sorption coefficients for comparison with results obtained by the more versatile indirect sorption method. The indirect sorption method has been applied to determine the relationship between the vapor phase pesticide in equilibrium with a pesticide in the solution phase in a solution-vapor system. Preliminary measurements have also been made using a soil-solution-vapor system to obtain sorption coefficients for a surface soil sample by the indirect sorption method.

Measuring Distribution Coefficients—Background

A major effort in this study will be directed toward measuring distribution coefficients, whether for a system at equilibrium or at various stages in the equilibration process. K_d values can be calculated from the change in concentration of a pesticide in a soil solution before and after equilibration. By definition,

$$K_d = S/C_e \quad (1)$$

where S is the amount of pesticide sorbed onto soil particles (ng/g) and C_e is the concentration of pesticide in the soil solution after equilibration (ng/ml). K_d is expressed in units of ml/g of oven-dry soil.

The amount of pesticide sorbed onto soil particles is given by

$$S = \frac{(C_i - C_e)V}{M} \quad (2)$$

where C_i is the initial concentration of pesticide in the soil solution (ng/ml), C_e is as defined above, V is the total volume (ml) of solution (the amount added containing pesticide plus that amount existing as soil moisture), and M is the mass of soil expressed as oven-dry weight (g). The methods used in this project involve either a direct measurement of C_i and C_e , as with the batch equilibration method, or an analysis of the vapor phase which can be used to determine the concentration of pesticide in the solution phase, as with the indirect sorption method.

Direct Sorption Method

The batch equilibration method is a conventional method that has been used to determine K_d values in the study of sorption-desorption processes. It

is also referred to here as the direct sorption method since the pesticide released to solution is determined by a direct analysis of the equilibrium solution phase. A schematic diagram that outlines the steps in the procedure is shown in Figure 1.

To measure the desorption K_d value, a soil sample is weighed directly into a screw-cap teflon centrifuge tube into which tap water is also weighed. The ratio of solution to soil is variable. The tube is agitated for 24 to 72 hr to insure full contact between tap water and sorbed pesticide residue, resulting in a well-mixed soil solution. The agitated solution phase is then separated from soil particles by centrifugation.

An aliquot of this supernatant solution phase is pipetted into a boiling flask containing tap water and benzene; the supernatant is added to the flask under a layer of benzene so that pesticide loss due to volatilization is minimized. The benzene solution is left to sit (with periodic agitation) to encourage the partitioning of the pesticide into the benzene. After one hour, the system is distilled. The refluxed benzene/pesticide azeotrope is collected and dried with sodium sulfate. An aliquot of this azeotrope is injected into a gas chromatograph to determine the concentration of the pesticide in the original soil solution sample.

The same procedure is followed to determine sorption information except that the tap water initially added to the soil sample contains a known pesticide concentration. During the sorption process, the pesticide is taken up by the soil system instead of being released to solution.

The direct sorption method has the advantage of being a traditional procedure, one that has been tested numerous times, and is fairly simple to conduct. However, the method has certain disadvantages. It can take up to five days to complete depending on the equilibration time and each sample provides only one measured value. Pesticide losses can be substantial due to the number of times the supernatant solution is transferred to various containers according to the steps in the procedure. More importantly, however, the efficiency of this procedure depends principally on pesticide losses in the distillation step. Numerous distillations with both water and soil samples conducted in this laboratory resulted in 87% (5%) recovery, a value comparable to others obtained from the literature. Also, desorption rates cannot be measured accurately because of the difficulty in interrupting the desorption process at specific stages of equilibration; only the extent of desorp-

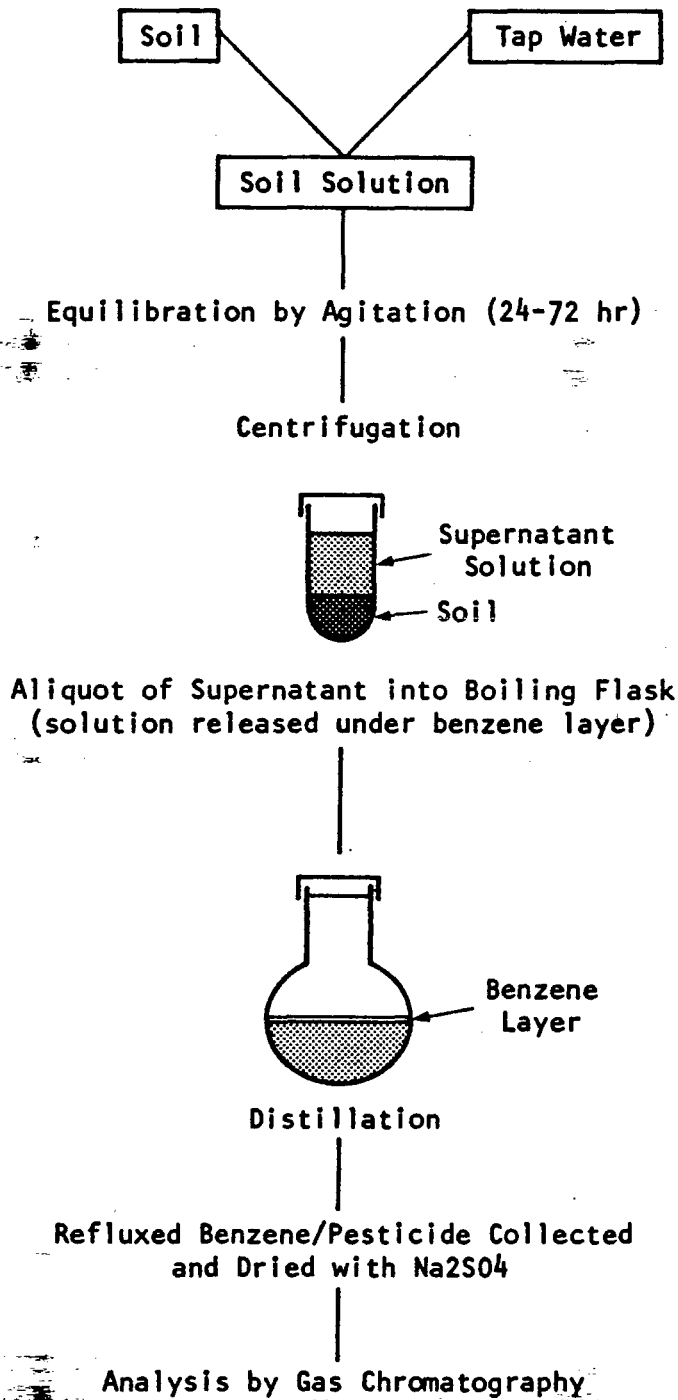


Figure 1. Schematic diagram outlining basic steps in direct sorption method (batch equilibration method)

tion at any given time can be measured.

These disadvantages encouraged the development of new methodologies—the indirect sorption method and the purge system—to improve the quantification of pesticide distribution in various phases within a soil system.

Indirect Sorption Method

The indirect sorption method was developed for the specific purpose of inferring solution phase concentration from measured pesticide in the vapor phase. A generalized schematic diagram is shown in Figure 2 that outlines the basic steps to the procedure.

An amount of soil containing sorbed pesticide residues is weighed directly into a 160-ml Hypovial, a glass bottle with a very narrow neck that is closed (stopper fashion) by a tight-fitting teflon "mininert" valve that can be accessed by a syringe needle. Tap water is then added by weight until the total volume of solution is 60 ml, leaving a total headspace volume of 100 ml. The system is immediately closed with a mininert valve.

The contents of the Hypovial are agitated on a gyrotory shaker for 24 to 72 hr after which time a vapor sample (maximum volume 0.5 ml) is drawn. This vapor sample is injected directly into a gas chromatograph and its concentration determined.

Two equations are applied in the indirect sorption method that result in a determination of the amounts of pesticide coexisting in the sorbed, the solution, and the vapor phases. The first equation makes use of simple mass balance relations. The second equation is empirically derived and states the relationship between the vapor concentration of a particular pesticide and its concentration in the solution phase as determined for a solution-vapor system only (i.e., no soil particles present). The application of these equations is described more fully in the Accomplishments section of this report although a brief description is given here.

Mass balance in a soil-pesticide system is defined as

$$\begin{aligned} \text{Total amount of pesticide} = \\ \text{sorbed phase} + \text{solution phase} + \text{vapor phase.} \end{aligned} \quad (3)$$

The total amount of pesticide is determined by codistillation of a portion of the soil sample with benzene. The amount in the vapor phase is measured from another portion of the same soil sample contained in a closed Hypovial. The

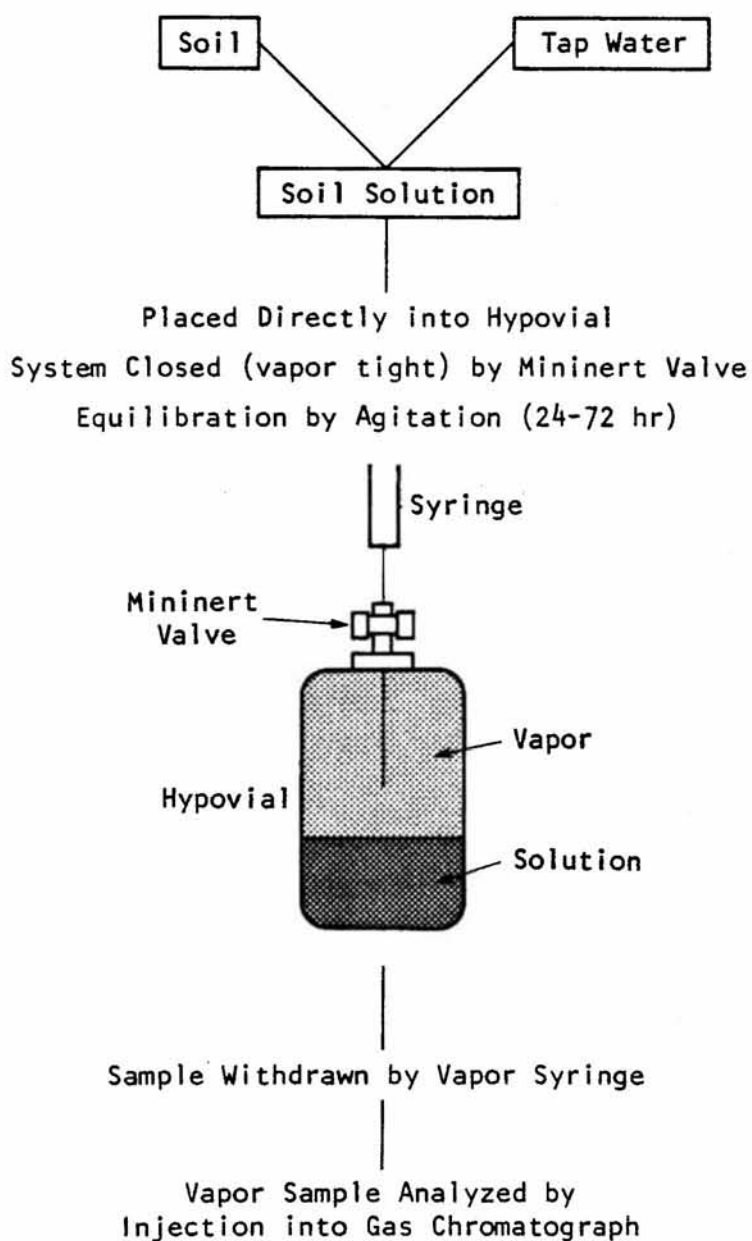


Figure 2. Schematic diagram outlining basic steps in indirect sorption method

concentration of the solution phase is calculated from the previously determined empirical equation that relates the concentrations of the vapor and solution phases of the particular pesticide system. The only unknown term remaining in the mass balance equation, the amount present in the sorbed phase, is then calculated. K_d is determined by dividing the sorbed phase concentration by the solution phase concentration.

As with the direct sorption method, the indirect sorption method has advantages and disadvantages. The disadvantages include having to experimentally derive the relationship between the vapor and solution phases of a particular pesticide (solution-vapor) system. Another disadvantage lies in the propagation of errors in the calculations required to obtain a K_d value from a measurement of the vapor phase. Advantages of this method include reduction of pesticide loss under vapor-tight conditions, and minimal handling of the soil sample once the procedure is underway. Also, a single sample is able to provide many data points; the examination of multiple measurements taken at various time intervals enables the rate and the extent of sorption and desorption to be determined.

Additionally, vapor samples result in a clean, distinct peak on gas chromatograms. The small number of components in a vapor sample decreases the chance of column contamination occurring during gas chromatographic analyses. It is not unusual for samples obtained from soil or solution extractions to contain components derived from the extracted medium that cause contamination of a gas chromatographic column or erroneous peaks on a gas chromatogram. Peaks other than those of concern make interpretation of gas chromatograms more difficult than need be.

Purge System

A second method, the purge system, was developed to measure the instantaneous release of sorbed pesticide over time. This approach has been used by others to study the desorption of highly hydrophobic organic compounds (Karickhoff and Morris 1985; Garbarini and Lion 1985; and Oliver 1985). Figure 3 is a schematic diagram of the purge system developed for our studies.

Filtered laboratory air forced through a fritted glass disc results in a continuous supply of fine air bubbles that stream through a soil solution contained within the glass purge chamber. This constant supply of uncontaminated air heightens the effect of concentration gradients between the sorbed,

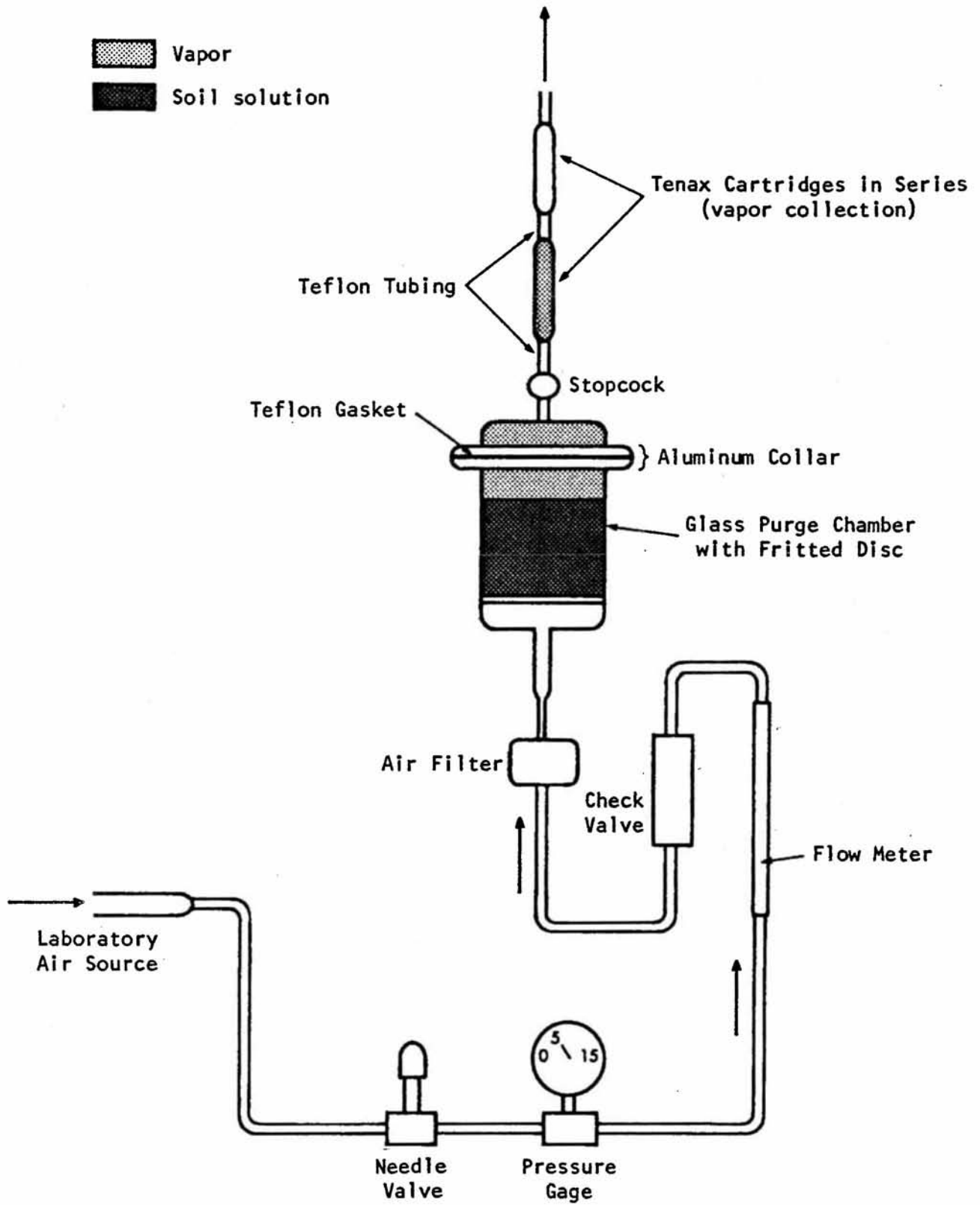


Figure 3. Diagram of purge system used for collecting pesticide vapor purged from soil in solution

solution, and vapor phases (i.e., the continuous flushing of pesticide-laden vapor out of the system causes pesticide in the solution phase to diffuse/disperse out which in turn encourages the diffusion of sorbed pesticide from soil sorption sites into the solution phase). A series of Tenax cartridges (consisting of the same components as in a gas chromatographic column—diatomaceous earth and silica gel) capture the pesticide in the vapor phase as it is forced out of the purge system.

After several minutes to hours of purging, the cartridges are removed from the system. Their contents are emptied into aliquots of benzene which are then analyzed by gas chromatography. This analysis reveals the amount of pesticide purged from the soil system in the vapor phase for a given time interval. The soil system is assumed to be completely purged of leachable sorbed residues when no pesticides are detected on the Tenax cartridges. With this method as well as with the indirect sorption method, a small number of components present in the analyzed vapor sample results in a clean gas chromatogram.

By removing and replacing spent cartridges at different time intervals throughout the purge, rates of desorption as well as the extent can be determined. A plot showing amount of pesticide released per time interval versus elapsed time will provide data required for analysis of desorption kinetics. How readily and at what rates sorbed pesticide residues are released from soil sites is directly related to the leachability of a particular compound. We are particularly interested in determining why pesticide residues in surface soils resist leaching and volatilization over long periods of time (years).

Column Study

A fourth method, not yet developed, will serve to correlate sorption information obtained from the methods outlined above with pesticide movement through a soil layer as a function of flow velocity and soil properties. This study will be conducted on recently applied pesticides as well as long-term sorbed residues already present in field samples. Attempts will be made to acquire undisturbed field-structured columns (surface soils) once laboratory packed columns have been analyzed. This portion of the project will provide an important link to future modeling efforts.

Selection of Soil Samples for Sorption-Desorption Studies

Soil and saprolite samples will be taken from pineapple fields where EDB and DBCP have been applied in the past. High priority will be given to areas associated with the ongoing deep drilling project conducted by the UHM Water Resources Research Center. The three compounds of interest (EDB, DBCP, TCP) have been detected in various locations and at various depths in soil cores taken from central O'ahu. Soil samples containing the highest concentrations of these pesticides will be analyzed in this study.

It has been stated that the leachability of a compound can be characterized by desorption distribution coefficients and kinetic measurements of the release of sorbed pesticides. All of the above methods accomplish these goals by providing information about the partitioning of pesticide into each of the three phases (sorbed, solution, and vapor) present in a soil system.

ACCOMPLISHMENTS

Several months were committed to refining vapor sampling and injection techniques for use in gas chromatographic analyses. During this phase, several difficulties were encountered that had to be worked through before the studies could continue.

Initial Development of Vapor Sampling Techniques

It was found that the vapor phase sample of a soil solution had to consist solely of vapor for consistent gas chromatographic results to be obtained, i.e., no moisture could be present in the syringe used to inject the vapor sample into the gas chromatograph (GC). This necessitated construction of an apparatus to prevent condensation from occurring on the mininert valves used to close the Hypovials. Ultraviolet light and a cooling fan were added to the apparatus used for agitating the samples to prevent the occurrence of both condensation and excessive heating of samples in the Hypovials during the equilibration period.

The technique of removing a vapor sample from the Hypovial also required refinement. It was found that the barrel of the glass syringe used for obtaining a vapor sample became coated with pesticide molecules so that a portion of the sample was sorbed within the syringe after its contents had been

expelled, thus reducing the measured vapor concentration. This problem was overcome by fully exposing the syringe barrel to pesticide vapor before sample analysis. This was done by flushing the syringe with three volumes of vapor prior to injection of a final sample into the GC.

Using Indirect Sorption Method

Initial experiments with the indirect sorption method involved the equilibration of aqueous DBCP solutions of varying concentrations with the resulting vapor phase. The original intention was to apply the concepts of Henry's law to derive a constant equilibrium value calculated as the ratio of the vapor phase concentration to the solution phase concentration. The resulting ratio, a theoretical constant as predicted by Henry's law, could then be applied to solving mass balance relations (eq. [3]).

However, it was found that for DBCP the Henry's law ratio is not constant over a range of solution concentrations, thereby invalidating its use in the indirect sorption method. As a result, the application of the Henry's law ratio was modified into the application of an empirically derived equation that expresses the relationship between a compound's vapor and solution phases as measured after the equilibration of a solution-vapor system. But since much of the initial work with the indirect sorption method was completed with the assumption of a constant vapor concentration to solution concentration ratio, this topic will be discussed briefly.

Solving Mass Balance Relations Using Henry's Law

Henry's law states basically that the ratio of a solute's vapor pressure to its solubility in aqueous solution, under temperature controlled conditions, is constant. For this study, the Henry's law constant was represented by the ratio of the vapor phase concentration to the solution phase concentration at equilibrium within a solution-vapor system. This ratio (K_h) was calculated as follows:

$$K_h = \frac{C_v \cdot V_v}{C_s \cdot V_s - C_v \cdot V_v} \quad (4)$$

where C_v and C_s are respectively the concentrations of the vapor and the solution phases (ng/ml), and V_v and V_s are respectively the volumes (ml) of vapor (headspace) and solution. Here, C_s is the concentration of solution when it

is placed in the Hypovial before equilibration with the vapor phase.

The purpose of defining the K_h ratio was to provide terms necessary for solving the mass balance equation that accounts for all three phases coexisting in the system at equilibrium (eq. [3]). The total amount of pesticide in the system was determined by refluxing a soil sample with benzene and water followed by co-distillation of benzene and the pesticide. Equation (4) was rearranged to solve for the solution concentration given a predetermined K_h value and the vapor concentration as measured by the indirect sorption method and GC analysis. Application of the total, solution, and vapor phase concentrations in equation (3) left only the sorbed phase as an unknown. This "sorbed phase value" divided by the concentration of solution at equilibrium yielded the value of the distribution coefficient, K_d (eq. [1]).

Results of Henry's Law Experimental Work

The application of Henry's law to indirect sorption measurements was evaluated using DBCP. First, the behavior of the vapor phase was found to be unaffected by the presence of organic solutes in the solution phase. Second, K_h was found to be dependent on the concentration of pesticide in solution and on temperature. Third, it was found that a relationship between the concentrations of the vapor phase and the solution phase of a solution-vapor system at equilibrium could be expressed by a mathematical equation derived by interpolation of a logarithmic plot of the solution and vapor concentration values. These findings are discussed more fully below.

Initial experiments using the indirect sorption method involved separate equilibrations of DBCP-spiked soil solutions and DBCP-spiked tap water samples to see if soluble organic components in soil solutions significantly affected the concentration of DBCP in the vapor phase at equilibrium. Table 1 compares K_h values derived from soil solution and tap water samples for two different concentrations of DBCP. No statistically significant difference occurred between K_h values obtained from DBCP-spiked tap water solutions or from DBCP-spiked soil solutions. This result shows that soluble organic material does not significantly affect the behavior of sorbed DBCP as it is released to the vapor phase. This conclusion enabled vapor studies to be conducted with tap water solutions instead of soil solutions which saved considerable time in experimental procedures.

The vapor pressure of a volatile compound is a temperature dependent

TABLE 1. COMPARISON OF HENRY'S LAW CONSTANT (K_h) VALUES DERIVED FROM MEASUREMENTS OF DBCP VAPOR IN SOIL SOLUTION AND TAP-WATER SAMPLES BY USING INDIRECT SORPTION METHOD

| DBCP SOLUTION CONCENTRATION (ng/ml) | MEASURED K_h | |
|--|------------------|--------------|
| | Soil Solution | Tap Water |
| 2,348 | 0.00575 | 0.00571 |
| 628 | 0.00963 | 0.00969 |

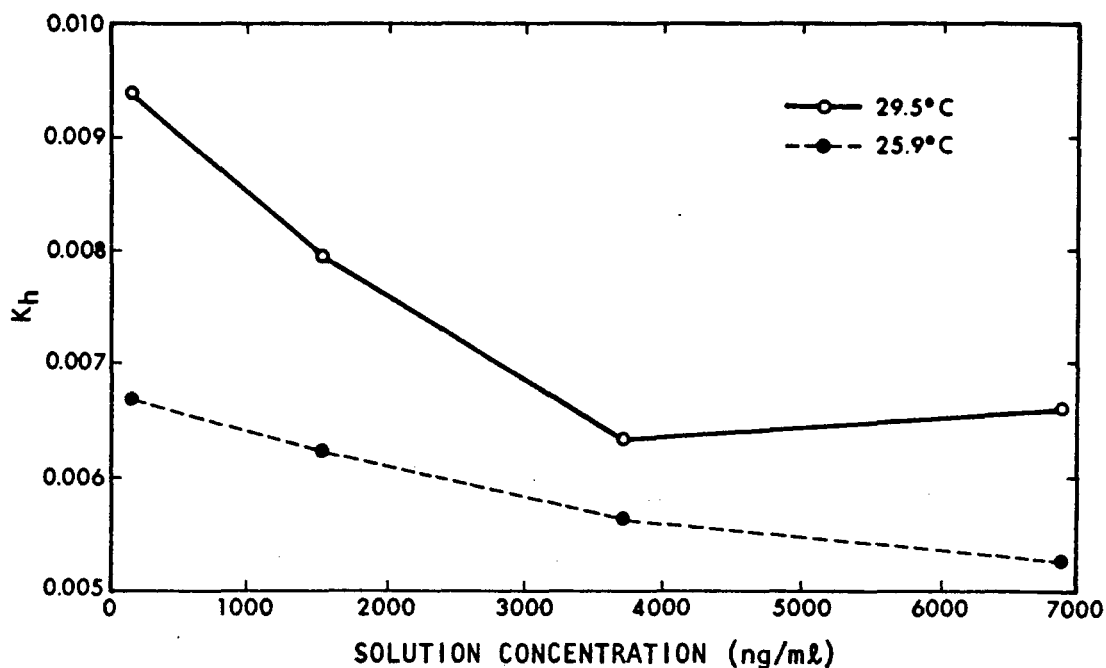
property (MacKay et al. 1982). This behavior was examined experimentally for DBCP by equilibrating and analyzing solutions in a laboratory that was not temperature controlled. Figure 4 shows the results of duplicate samples analyzed at different times (and temperatures) during a single day. K_h values are plotted against the corresponding solution concentrations. The temperature of the room was coolest (average of 25.9°C) in the morning when the first set of samples was analyzed and warmest (average of 29.5°C) in the afternoon when the second set was analyzed. The differences in K_h values for a single solution concentration are statistically significant. This conclusion demonstrated the importance of conducting vapor studies under temperature-controlled conditions.

Figure 4 also shows a dependence of K_h on solution concentration. The value of K_h decreases significantly as solution concentration increases. To remove the effects of fluctuating temperature, an experiment identical to that which resulted in Figure 4 was conducted under temperature controlled conditions. The same trend in variation of K_h with solution concentration was revealed as shown in Figure 5.

Modification of Application of Henry's Law

Nonconstancy of the K_h ratio might appear to invalidate the use of an equilibrium relationship between the vapor and solution phases to determine sorption by the indirect sorption method. Yet closer inspection of the data shows that the equilibrium relationship between a solution phase and its vapor phase can be applied with confidence.

A logarithmic plot of DBCP vapor concentrations versus corresponding aqueous solution concentrations is shown in Figure 6. The graph shows that



NOTE: Data is for duplicate samples in a single day.

Figure 4. Linear plot showing dependence of K_h on temperature and varying concentrations of DBCP in solution

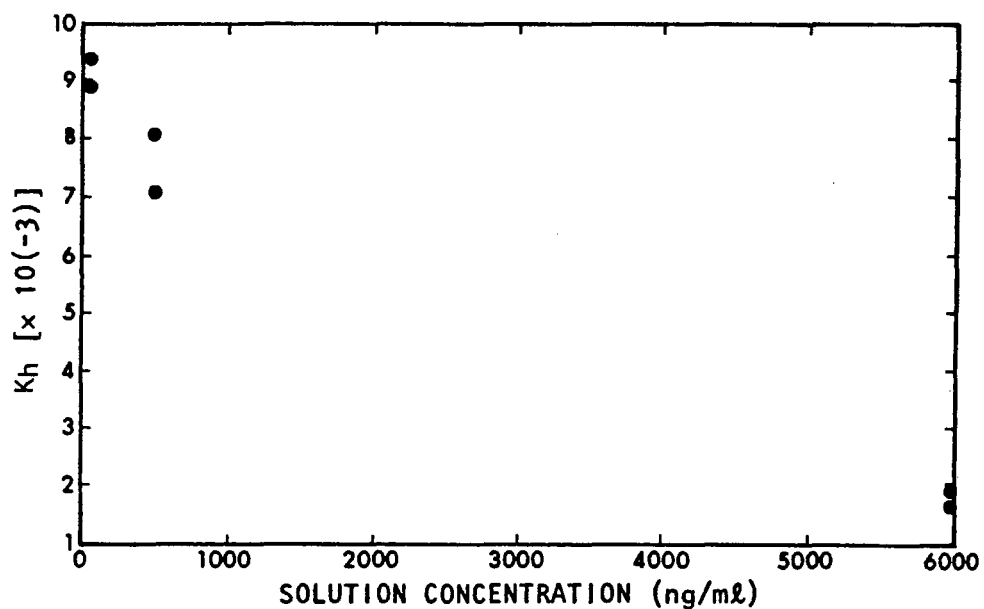


Figure 5. Linear plot showing dependence of K_h on varying concentrations of DBCP in solution

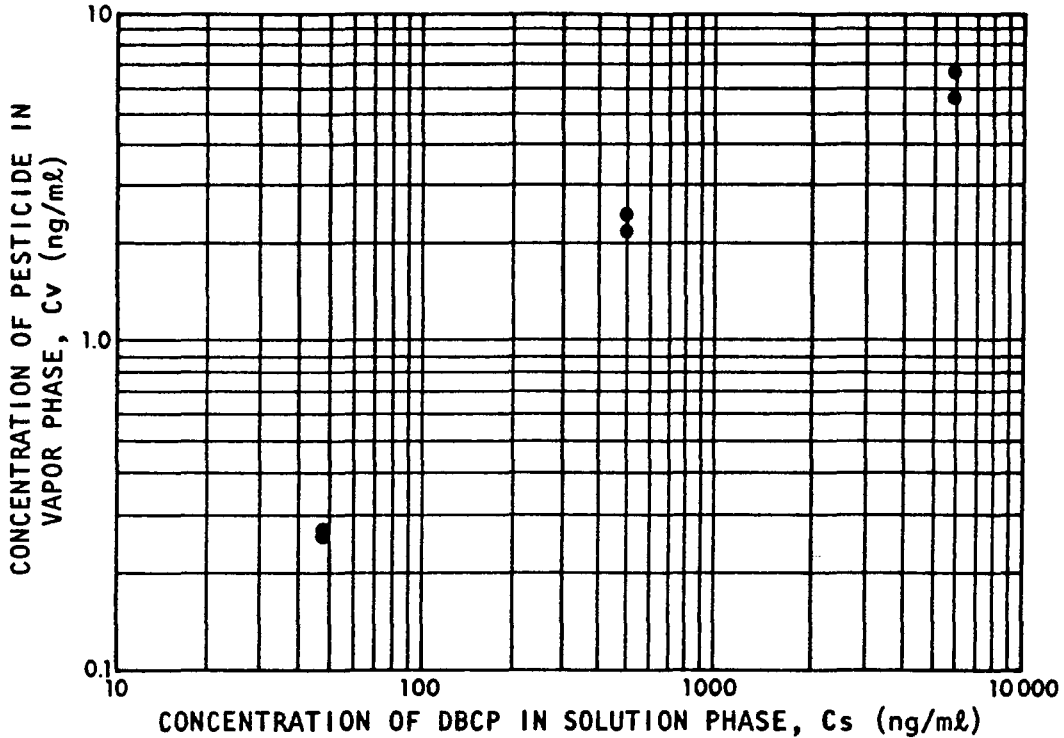


Figure 6. Logarithmic plot showing linearity of DBCP vapor concentrations at low solution concentrations and deviation from linearity at high solution concentrations

vapor concentration deviates from linearity at high solution concentrations but is approximately log-linear at low solution concentrations. This trend is consistent with theories that describe the nonideal behavior of the vapor phase as the solubility limit of a compound is approached. A linear interpolation of the data plotted in Figure 6 results in an equation relating C_s and C_v as

$$C_v = a C_s^b \quad (5)$$

where C_v and C_s are respectively the concentrations of pesticide in the vapor and solution phases in (ng/ml); for DBCP a is 0.0258 and b is 0.653.

The fact that the soils of the Wahiawa Plateau contain relatively low levels of total pesticide (tens of ppb) places the concentration of pesticide in the solution phase at the dilute solution end and in the linear region of the graph. Thus, for analyzing soils that contain residual pesticide concentrations within the range over which this equation applies, the application of the empirical relationship (eq. [5]) is justified.

Preliminary K_d Experiment

A single experiment was conducted using the indirect sorption method to determine desorption K_d values for a surface soil obtained from Dole Field 4201 located near Mililani Town in central O'ahu. Two samples from a depth of 170 to 360 mm were analyzed in duplicate.

Soil and tap water in a ratio of 2:1 were equilibrated for 72 hr in Hypovials after which time vapor measurements were taken. The soil samples as obtained from the field contained a total of about 59 ppb of long-term sorbed pesticide residues. Table 2 shows the data that were used in calculating K_d from a vapor measurement and an application of equations (5), (3), and (1) (in that order). The resulting K_d values are less than expected compared to values previously determined in this laboratory by the direct sorption method (unpublished data). We plan to conduct more solution-vapor equilibration studies to confirm the reproducibility of the a and b terms in equation (5). The indirect sorption method will be run concurrently with the direct sorption method to assess the applicability of the indirect sorption method.

Purge System

Duplicate setups of the purge system have recently been completed and checked to be vapor tight. However, no soil solutions have yet been tested, nor has the efficiency of the apparatus been evaluated. Therefore, no definitive results are available to date.

The purge system will be initially tested using aqueous solutions to determine the efficiency of the apparatus. Mass balance relations will be applied in which the total amount of pesticide in the initial solution will be compared to the amount in the final solution plus that amount of pesticide captured on the Tenax cartridges after a period of purging.

SUMMARY

Development of the indirect sorption method and the purge system is complete and much of the preliminary work has been refined. Experiments are being conducted using the indirect sorption method that estimates the pesticide concentration in solution from a vapor concentration measurement, allowing determination of sorption K_d values.

TABLE 2. DATA USED TO CALCULATE DBCP DISTRIBUTION COEFFICIENT (Kd) BY INDIRECT SORPTION METHOD AND CALCULATION SEQUENCE FOR SOIL SAMPLE

| Sample | Cv Measured <hr/> (ng/ml) | Cs Calculated <hr/> | S Calculated (ng/g) | Kd Calculated (ml/g) |
|--------|---------------------------------|---------------------------|---------------------------|----------------------------|
| 1 | 0.2077 | 24.39 | 5.00 | 0.205 |
| 2 | 0.2048 | 23.87 | 6.74 | 0.282 |

Calculation Sequence for Soil Sample 1:

Step 1 (eq. [5]): $C_v = 0.0258 C_s$ (ass)

or

$$C_s = \left(\frac{0.2077}{0.0258} \right)^{(1/0.853)} = 24.39$$

Step 2 (eq. [3]): Total = sorbed phase + solution phase + vapor phase

or

$$\begin{aligned} \text{sorbed phase} &= [(total)(g \text{ soil}) - (C_s)(ml \text{ solution}) \\ &\quad - C_v (ml \text{ vapor})] / (g \text{ soil}) \\ &= (59 \cdot 22.78 - 24.39 \cdot 49.58 \\ &\quad - 0.2077 \cdot 100) / 22.78 \\ &= 5.00 \end{aligned}$$

Step 3 (eq. [1]): $K_d = \left(\frac{5.00}{24.39} \right) = 0.205$

The application of these techniques and the information they are designed to provide in terms of distribution coefficients and kinetics of desorption will be used to correlate desorption processes with soil properties (particularly organic carbon). Investigations of pesticide behavior in soil systems aid in defining the leachability of a sorbed pesticide and the related potential for groundwater contamination.

GLOSSARY

- a intercept of logarithmic plot of C_v and C_s determined experimentally
- b slope of logarithmic plot of C_v and C_s determined experimentally
- C_e equilibrium (final concentration (ng/ml) of pesticide in solution phase
- C_i initial concentration (ng/ml) of pesticide in solution phase before equilibration with vapor phase
- C_s concentration (ng/ml) of pesticide in solution phase
- C_v concentration (ng/ml) of pesticide in vapor phase
- K_d distribution coefficient; defines partitioning of a pesticide between sorbed and solution phases of a soil system
- K_h ratio of C_v in equilibrium with C_s (based on Henry's law)
- M mass (g) oven-dry soil
- S concentration (ng/g) of pesticide in sorbed phase (sorbed onto soil particles)
- V volume (ml) of moisture in soil system (preexisting soil moisture plus additional solution containing pesticide)
- V_v volume (ml) of vapor phase (headspace)
- V_s volume (ml) of solution phase

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APPENDIX D
EXPLORATORY STUDY USING WATER DISINFECTANTS
TO REMOVE EDB FROM CLEAN WATER

Roger S. Fujioka
Owen T. Narikawa
Bunnie S. Yoneyama

ABSTRACT

A reliable and practical method is required to reduce the concentrations of hazardous chemicals (EDB, DBCP, TCP) which have been detected in some of the groundwaters used for drinking on O'ahu. This study evaluates the feasibility of using high concentrations of water disinfectants to oxidize (reduce) the concentrations of EDB in water. Water seeded with 100 ppt to 20 ppb of EDB were treated with various doses of disinfectants (chlorine, chlorine dioxide, hydrogen peroxide, ultraviolet light, ultraviolet light plus hydrogen peroxide). The concentrations of EDB in water samples before and after treatment with these disinfectants were determined using liquid-liquid partitioning to extract the EDB and gas chromatography to measure the concentrations of EDB. The results of this study indicated that 5 to 5,000 mg/l of chlorine and 2 to 50 mg/l of chlorine dioxide are incapable of reducing the concentrations of EDB in water. The ability of 3% and 10% hydrogen peroxide to reduce the concentrations of EDB in water was erratic. In some experiments, no reduction of EDB was observed while in other experiments up to 45% of the EDB was apparently oxidized. Ultraviolet (UV) light alone removed only 10% of the EDB. The most promising system was the use of UV light plus 3% or 10% hydrogen peroxide. When this system was used, 33 to 75% of the EDB in the water was reduced. Thus, further studies assessing the feasibility of using UV light and hydrogen peroxide to remove EDB and other toxic chemicals in water is recommended. However, hydrogen peroxide is available in a liquid state at 30% and therefore it is impractical to treat large volumes of water with high concentrations of hydrogen peroxide. In this regard, ozone is chemically similar to hydrogen peroxide but is more reactive. Ozone can also be generated as a concentrated gas and apparatus for the treatment of large volumes of water with UV light and ozone is commercially available. It is therefore recommended that further studies be done to determine the feasibility of using UV light and ozone to remove the concentrations of EDB in water.

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Our thanks to Mr. Sidney Kansako, Laboratory Director and Mr. Reginald Goo, Special Chemist, of the Water Quality Laboratory, Division of Wastewater Management, City and County of Honolulu for their technical support. We appreciate Mr. Goo's skillful analysis of one set of our samples using the gas chromatography and mass spectroscopy technique. We also are grateful to Dr. John Hylin, Professor and Chairman of Agricultural Biochemistry at the University of Hawaii for giving us the EDB standard which was used in this study.

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INTRODUCTION

The detection of hazardous chemicals (EDB, DBCP, TCP) in groundwaters obtained from the Mililani-Waipahu area resulted in the closing of wells used to provide drinking water for the area. Although the levels of these chemicals are very low (parts per million [ppm], parts per trillion [ppt]), these chemicals are highly carcinogenic and therefore should be removed from drinking water sources. The Honolulu Board of Water Supply (BWS) initially determined that aeration of the groundwater through a cooling tower could be used to remove most of these chemicals from the water. More recently, GMP Associates (1984), obtained preliminary data demonstrating that these chemicals could be removed by treating the water by aeration through a packed tower or by filtration through activated carbon. The BWS is currently analyzing the cost-effectiveness and reliability of these three methods.

It should be noted that all three of the above methods rely on the principle of maximum contact of the groundwater with man-made substances involving a large surface area. Any surface area constantly bathed in liquid can be expected to be colonized by bacteria and other microorganisms; therefore, the product water of these three treatments can be expected to contain elevated concentrations of bacteria which would have to be reduced before the water is distributed to consumers. Thus, the disinfection of product water will probably be a cost factor for any of the three methods currently being considered.

Chlorine, chlorine dioxide, ozone, hydrogen peroxide, and bromine chloride are chemical oxidants used at very low concentrations (ppm) to destroy the infectivity of microorganisms in water. Under these conditions, these chemicals are called disinfectants. However, at higher concentrations these same chemicals are used as oxidants to oxidize (reduce/destroy) color, odor, taste, and organic molecules from water. Treatment of water with high concentrations of these chemical disinfectants as a means of removing low concentrations EDB and DBCP or TCP from water has not been properly evaluated.

It should be noted that many of the organic toxins detected in waters persist because they are resistant to microbial degradation (biorefractory compound) and often to chemical and physical factors present in the environment. Thus, these persistent pollutants or toxins are sometimes called recalcitrant chemicals. One method which has been successfully used in industry to degrade hazardous, recalcitrant chemicals is the use of ultraviolet (UV) light

plus an active oxidant, such as ozone or hydrogen peroxide (Glaze et al. 1980). The mechanism by which this method works has not been determined. However, the prevailing evidence suggests that UV light excites the oxidant to form short-lived but super active OH radicals which degrade any organic molecule. An alternative hypothesis suggests that UV light excites the molecular configuration of organic molecules which sensitizes the organic compound to the oxidation reaction of the disinfectant.

PROJECT GOALS AND OBJECTIVES

This study was designed as a short-term (3 mo) exploratory project to assess the feasibility of using high concentrations of some established water disinfectant to oxidize (reduce) the concentrations of pesticides found in groundwater. The goal of this study was not to conduct an in-depth analysis for each of the selected methods, but rather to quickly assess which methods should or should not be further evaluated in a subsequent study.

The specific objectives of this study were to evaluate and compare the feasibility of using the following five water disinfectant/oxidant to reduce the concentrations of ethylene dibromide (EDB) in water:

1. Oxidation by chlorine (Cl_2)
2. Oxidation by chlorine dioxide (ClO_2)
3. Oxidation by hydrogen peroxide (H_2O_2)
4. Ultraviolet (UV) light irradiation
5. Ultraviolet light irradiation in the presence of hydrogen peroxide ($\text{UV} + \text{H}_2\text{O}_2$).

MATERIALS AND METHODS

Extraction of EDB from Water by Liquid-Liquid Partitioning. The test sample (25 ml) containing EDB was first poured into a clean separatory funnel to which 5 ml of benzene were added. This mixture was vigorously mixed, vented, and set aside to allow for phase separation. The water phase was drained off and the benzene phase collected in a test tube. Anhydrous sodium sulfate (0.5 g) was added to the benzene extract to remove residual water. Using a microsyringe, 5 μl of this benzene extract containing EDB were inject-

ed into the gas chromatograph for analysis.

Extraction of EDB from Water by Benzene Distillation. The test sample (25 ml) containing EDB was first poured into a clean distillation flask containing 5 ml of benzene and several glass beads. This mixture was then distilled at 70 to 80°C until approximately 5 ml of benzene were recovered. Anhydrous sodium sulfate (0.5 g) was added to 5 ml of this distillate and this sample injected into the gas chromatograph for analysis.

Analysis by Gas Chromatography. All samples were analyzed by a Hewlett Packard Model 5700-A gas chromatograph (GC). The oven temperature was set at 60°C and the carrier gas (argon 90%, methane 10%) was maintained at a flow rate of 40 c³/min. The retention time (min) or the time for the EDB to be eluted from the column in the gas chromatograph was first detected by analyzing a sample containing measured concentrations of EDB in water. This peak was called the standard EDB peak, which served as a comparison for the presence and concentrations of EDB in test samples. All peaks were plotted and the areas under the peak automatically integrated/calculated using the Hewlett Packard Model 3390A integrator. Percent removal of EDB in each treated sample was calculated by comparing the integrated peak areas recovered from the treated sample with the integrated peak area of the EDB standard.

Chemicals used in the study were

1. Benzene, reagent grade, thiophene free, Mallinckrodt
2. Chlorine dioxide, laboratory generated from H₂SO₄ and Na chlorite as per Standard Methods (APHA, AWWA, and WPCF 1980)
3. Commercial chlorox bleach, sodium hypochlorite 5.25%
4. Ethylene dibromide (EDB)
5. Hydrogen peroxide, 30% solution, stabilized analytical reagent, Mallinckrodt
6. Sodium sulfate, anhydrous, Baker analyzed reagent.

Experimental Design. To measure the capacity for Cl₂, ClO₂, and H₂O₂ to remove EDB from water, various concentrations of each oxidant were added to 25 ml of distilled water containing a known concentration of EDB. This mixture was then allowed to react for 15 min at room temperature in a closed flask. To measure the effects of UV light, 25 ml of EDB in water were poured into the lid of a 100 mm glass petri dish and exposed for 15 min to a 15 W germicidal lamp at a distance of 101.6 mm (4 in.). To measure the effects of UV plus H₂O₂, 25 ml of EDB in water containing the H₂O₂ were poured into the lid of a 100 mm glass petri dish and then exposed to UV as described above.

In the UV experiments, the petri plates were not covered. The treated water samples were then extracted by either the liquid-liquid partitioning technique or the benzene distillation technique. Since the liquid-liquid partitioning technique was determined to be more efficient than the benzene distillation technique, all of the definitive studies were carried out using the liquid-liquid partitioning technique. The concentrations of EDB in these samples were determined using the gas chromatograph as described above.

GC-Mass Spectroscopy Analysis. Although the GC method is very effective in separating out the various organic molecules in a sample, the recovered peak cannot be positively identified as one specific compound since other compounds may have a similar peak. Some of the oxidized samples resulted in several multiple peaks near or overlapping the EDB peak area. To identify these peaks, the use of GC plus mass spectroscopy (MS) is recommended. One sample was analyzed using the GC-MS by the Water Quality Laboratory, Department of Public Works, City and County of Honolulu.

RESULTS AND DISCUSSION

Chemical Oxidants

In the initial experiment, water was seeded with 100 ppt EDB and treated with various doses of chlorine (Cl_2) and hydrogen peroxide (H_2O_2). These samples were then extracted and the residual concentrations of EDB determined using gas chromatography. The results (Table 1) show that the 100 ppt EDB standard resulted in a small peak at a retention time (RT) of 3.22 min and a calculated area under that peak of 11,456. When these samples were treated with 3 and 10% H_2O_2 , well defined peaks with a respective RT of 3.23 and 3.21 min were observed. In the sample treated with 3% H_2O_2 , the area of the EDB peak was 23,881 or greater than the input EDB peak. Based on these results, it was concluded that 3% H_2O_2 was incapable of reducing (oxidizing) the concentrations of EDB in the water. However, in the sample treated with 10% H_2O_2 , the area of the EDB was only 8,026 indicating that 30% of the input EDB was oxidized. When this same sample was treated with 5 to 500 mg/l of Cl_2 , numerous peaks were detected by gas chromatography with some of the peaks overlapping and masking the EDB peak with a RT of 3.22 min. This was reflected in the major peak at 3.39 min RT in samples treated with 50, 100 and 500 mg/l of Cl_2 . It was not clear whether the recorded area under the 3.39 RT

TABLE 1. TREATMENT OF WATER CONTAINING 100 ppt EDB WITH CHLORINE (Cl₂) AND HYDROGEN PEROXIDE (H₂O₂)

| Oxidant Used | Oxidant Concentration | EDB Added (ppt) | Retention Time:EDB Peak (min) | Area Under Peak | EDB Removed (%) |
|-------------------------------|-----------------------|-----------------|-------------------------------|-----------------|-----------------|
| None | — | 100 | 3.22 | 11,456 | — |
| H ₂ O ₂ | 3% | 100 | 3.23 | 23,881 | 0 |
| H ₂ O ₂ | 10% | 100 | 3.21 | 8,026 | 30 |
| Cl ₂ | 5 mg/l | 100 | 3.22 | 15,497 | 0 |
| Cl ₂ | 50 mg/l | 100 | 3.39* | 10,413 | † |
| Cl ₂ | 100 mg/l | 100 | 3.39* | 15,412 | † |
| Cl ₂ | 500 mg/l | 100 | 3.39* | 13,573 | † |

*Major peak observed; EDB peak masked at RT of 3.22 min.

†Percent EDB removal could not be determined since unknown peak at 3.39 overlapped EDB peak at 3.22.

peak indicated concentrations of EDB or some intermediate product.

The masking of the EDB peak was believed to be complicated by the fact that only low concentrations of standard EDB (100 ppt) were used. This resulted in a very small EDB peak which could easily be masked by other chemicals present in the sample. In an attempt to resolve this problem, a second experiment was conducted by seeding water with a higher concentration (5 ppb) of EDB. This water sample was treated with various doses of chlorine dioxide (ClO₂) and Cl₂, and the residual concentrations of EDB in these treated waters determined. The results (Table 2) show that 5 ppb EDB resulted in a larger peak with a RT of 3.92 min and an area under the curve of 31,161. When this water sample was treated with 2, 5, and 50 mg/l of ClO₂, no reduction of the EDB peak at 3.91 min RT was observed, indicating that ClO₂ was incapable of oxidizing EDB. The chlorine samples again showed numerous multiple peaks, with a peak at 3.94 and 3.95 min RT which masked the EDB peak at 3.92 min RT. Based on these results, it was not possible to clearly conclude whether Cl₂ was capable of reducing the concentrations of EDB. It was clear that Cl₂ was highly reacted and formed many intermediate products, presumably chlorinated by-products which were detected by gas chromatography.

TABLE 2. TREATMENT OF WATER CONTAINING 5 ppb EDB WITH CHLORINE DIOXIDE (ClO₂) AND CHLORINE (Cl₂)

| Oxidant Used | Oxidant Concentration (mg/l) | EDB Added (ppb) | Retention Time:EDB Peak (min) | Area Under Peak | EDB Removed (%) |
|------------------|------------------------------|-----------------|-------------------------------|-----------------|-----------------|
| None | - | 5 | 3.92 | 31,161 | - |
| ClO ₂ | 2 | 5 | 3.92 | 33,797 | 0 |
| ClO ₂ | 5 | 5 | 3.92 | 35,085 | 0 |
| ClO ₂ | 50 | 5 | 3.92 | 49,823 | 0 |
| Cl ₂ | 200 | 5 | 3.95* | 59,741 | † |
| Cl ₂ | 500 | 5 | 3.94* | 39,316 | † |
| Cl ₂ | 5,000 | 5 | 3.94* | 57,418 | † |

*Major peak observed; EDB peak masked at RT of 3.22 min.

†Percent EDB removal could not be determined since unknown peak at 3.39 overlapped EDB peak at 3.22.

Gas Chromatography/Mass Spectroscopy

Treatment of water with Cl₂, and to a lesser degree ClO₂, resulted in numerous peaks when analyzed by gas chromatography. These results prevented a clear interpretation of the results and raised doubts as to the effect of Cl₂ and even ClO₂ on EDB. To resolve this question, the same water samples treated with Cl₂ and ClO₂ were analyzed for the fate of the EDB molecules in these water samples using gas chromatography and mass spectroscopy. This complementary analysis was provided by the Water Quality Laboratory, Division of Wastewater Management, Department of Public Works, City and County of Honolulu. The results of the mass spectroscopy data alongside our gas chromatography data are summarized in Table 3 and show that the concentration of EDB molecules was 3,276. The concentrations of EDB in waters treated with 200, 500, and 5,000 mg/l Cl₂ ranged from 3,396 to 7,763 indicating that Cl₂ had not degraded the EDB molecules. The concentration of EDB following ClO₂ treatment was slightly reduced (2,672 to 2,933) indicating that only slight (11-18%) reduction of EDB molecules resulted after treatment with ClO₂. Based on these results and the results of analyzing these same samples with gas chromatography, it was concluded that both Cl₂ and ClO₂ were not effectively reducing (oxidizing) the molecules of EDB present in the water samples.

TABLE 3. MASS SPECTROSCOPY ANALYSIS OF EDB SAMPLES TREATED WITH CHLORINE (Cl₂) AND CHLORINE DIOXIDE (ClO₂)

| Oxidant Used | Oxidant Concentration (mg/l) | EDB Added (ppb) | Area Under Peak* | Concentration of EDB Molecules |
|------------------|------------------------------|-----------------|------------------|--------------------------------|
| None | — | 5 | 31,161 | 3,276 |
| Cl ₂ | 200 | 5 | 59,741 | 7,763 |
| Cl ₂ | 500 | 5 | 39,316 | 3,408 |
| Cl ₂ | 5,000 | 5 | 57,418 | 3,396 |
| ClO ₂ | 2 | 5 | 33,797 | 2,897 |
| ClO ₂ | 5 | 5 | 35,085 | 2,672 |
| ClO ₂ | 50 | 5 | 49,823 | 2,933 |

*Major peak observed; EDB peak masked at RT of 3.22 min.

UV + H₂O₂ Treatment

The use of UV plus an oxidant such as ozone or H₂O₂ has been reported to be effective in reducing the concentrations of recalcitrant chemicals in water. As a result, the next experiment was designed to determine whether UV plus H₂O₂ could be relied on to degrade EDB in water. In this experiment, a water sample containing 5 ppb of EDB was treated with 3% and 10% H₂O₂ as well as UV plus 3 and 10% H₂O₂. All water samples were extracted and analyzed for EDB using gas chromatography as reported earlier. The results (Table 4) show that 5 ppt EDB corresponded to a peak with 4.13 min RT and an area under that peak of 17,120. Treatment of these samples with H₂O₂ and UV plus H₂O₂ resulted in a clearly defined peak with a RT of 4.12 min, with no interfering similar peaks as observed when water was treated with Cl₂. All treatments resulted in a reduction of EDB peak. Based on these results, it was concluded that 3% and 10% H₂O₂ can be expected to oxidize 11% and 18%, respectively, of the EDB. When the same sample was treated with UV plus 3% H₂O₂ or UV plus 10% H₂O₂, 74% and 37% reductions of EDB were observed. These results suggest that H₂O₂ is capable of oxidizing some of the EDB. However, UV and H₂O₂ are much more effective in reducing the concentrations of EDB in water.

To verify the results that H₂O₂ and in particular UV and H₂O₂ will oxidize EDB, the experiment was repeated. However, in this subsequent experiment, the concentration of EDB added to the water was increased to 20 ppb. The results of this experiment are summarized in Table 5 and show that 20 ppb

TABLE 4. TREATMENT OF WATER CONTAINING 5 ppb EDB WITH HYDROGEN PEROXIDE (H₂O₂) AND ULTRAVIOLET (UV) LIGHT PLUS H₂O₂

| Oxidant Used | Oxidant Concentration (%) | EDB Added (ppb) | Retention Time:EDB Peak (min) | Area Under Peak | EDB Removed (%) |
|------------------------------------|---------------------------|-----------------|-------------------------------|-----------------|-----------------|
| None | - | 5 | 4.13 | 17,120 | — |
| H ₂ O ₂ | 3 | 5 | 4.12 | 15,313 | 11 |
| H ₂ O ₂ | 10 | 5 | 4.12 | 14,080 | 18 |
| UV + H ₂ O ₂ | 3 | 5 | 4.12 | 4,425 | 74 |
| UV + H ₂ O ₂ | 10 | 5 | 4.12 | 10,722 | 37 |

TABLE 5. TREATMENT OF WATER CONTAINING 20 ppb EDB WITH HYDROGEN PEROXIDE (H₂O₂) AND ULTRAVIOLET (UV) LIGHT PLUS H₂O₂

| Oxidant Used | Oxidant Concentration (%) | EDB Added (ppb) | Retention Time:EDB Peak (min) | Area Under Peak | EDB Removed (%) |
|------------------------------------|---------------------------|-----------------|-------------------------------|-----------------|-----------------|
| None | - | 20 | 5.76 | 58,589 | - |
| H ₂ O ₂ | 3 | 20 | 5.76 | 50,867 | 0 |
| H ₂ O ₂ | 10 | 20 | 5.77 | 62,977 | 0 |
| UV + H ₂ O ₂ | 3 | 20 | 5.74 | 14,782 | 75 |
| UV + H ₂ O ₂ | 10 | 20 | 5.74 | 21,400 | 63 |

correlated to a peak with RT of 5.76 min and area of 58,589. In this experiment, 3% and 10% H₂O₂ did not result in reduction of EDB. Treatment of this same water with UV plus 3% H₂O₂ and UV plus 10% H₂O₂ resulted in 75 and 63% reductions of EDB.

One of the limitations of experiments using UV is the need to run the reaction in an open dish. Since EDB is volatile, some of the measured reduction of EDB could be from the volatilization rather than the oxidation of EDB. To resolve this question, another experiment was run. This time the standard EDB in water solution was held in an open dish for 15 min so that any volatilization of EDB would have taken place in this standard. The results of this experiment summarized in Table 6 show that 20 ppb EDB correlated with a peak (5.49 min RT) area of 99,218. After treatment with 3% and 10% H₂O₂, the area of the EDB peak was reduced by 35% and 45% indicating that EDB was oxi-

TABLE 6. TREATMENT OF WATER CONTAINING 20 ppb EDB WITH HYDROGEN PEROXIDE (H₂O₂) AND ULTRAVIOLET (UV) LIGHT PLUS H₂O₂

| Oxidant Used | Oxidant Concentration (%) | EDB Added (ppb) | Retention Time:EDB Peak (min) | Area Under Peak | EDB Removed (%) |
|------------------------------------|---------------------------|-----------------|-------------------------------|-----------------|-----------------|
| None | - | 20 | 5.49 | 99,218 | — |
| H ₂ O ₂ | 3 | 20 | 5.49 | 66,974 | 35 |
| H ₂ O ₂ | 10 | 20 | 5.51 | 54,489 | 45 |
| UV + H ₂ O ₂ | 3 | 20 | 5.49 | 64,627 | 35 |
| UV + H ₂ O ₂ | 10 | 20 | 5.50 | 66,882 | 33 |
| UV | 0 | 20 | 5.49 | 88,917 | 10 |

dized by H₂O₂ treatment. When the sample was simply UV irradiated, the EDB peak had an area of 88,917 indicating that UV alone could reduce 10% of the EDB. When the same sample was treated with UV plus 3% H₂O₂ and UV plus 10% H₂O₂, 35% and 33% reductions in EDB was observed.

CONCLUSIONS

The object of this study was to determine whether disinfectants used to treat drinking water (chlorine, chlorine dioxide, hydrogen peroxide, UV, UV + hydrogen peroxide) were capable of reducing (oxidizing) the concentrations of EDB in clean water. The results of this study show that treatment of water with 5 to 5,000 mg/l chlorine was ineffective in reducing the concentrations of EDB. Moreover, treatment of water with chlorine resulted in the formation of numerous additional peaks detected by gas chromatography analysis indicating the formation of various subspecies of chlorinated organic compounds. these additional peaks masked the EDB peak and made interpretation of the results difficult. However, gas chromatography plus mass spectroscopy resolved this problem and indicated that EDB was not being oxidized by chlorine. Many of these additional peaks may represent other species of halogenated hydrocarbon which may differ from EDB but may also be toxic or carcinogenic. Thus treatment of water with chlorine as a means of oxidizing EDB is not recommended.

Treatment of EDB with 2 to 50 mg/l of chlorine dioxide was also ineffec-

tive in reducing the concentrations of EDB. Like chlorine but to a lesser degree, an increase occurred in the number of additional peaks detected by gas chromatography analysis. Thus, evidence was obtained that chlorine dioxide was also capable of forming other products with unknown properties. Treatment of water with chlorine dioxide as a means of oxidizing EDB is not recommended.

Treatment of water with 3% and 10% hydrogen peroxide resulted in sporadic (0 to 45%) reductions in EDB concentrations in water. The 10% hydrogen peroxide concentration did not appear to be more effective than the 3% hydrogen peroxide treatment. Significantly, the formation of other peaks detected by gas chromatography analysis was minimal, indicating that many intermediate products were not being formed. Based on these results, further exploratory studies involving the use of hydrogen peroxide as a means of reducing the concentrations of EDB in clean water is encouraged.

Treatment of water with UV plus 3% and 10% hydrogen peroxide resulted in 33 to 75% reduction in EDB. The addition of 10% hydrogen peroxide was not substantially more effective than 3% hydrogen peroxide. UV alone reduced the EDB concentrations by 10%. It should be noted that the UV plus hydrogen peroxide system used in this experiment was crude in design and required an open system to allow volatilization to occur. Commercially available systems which use UV and an oxidant, such as ozone or hydrogen peroxide, are enclosed and allow for better control of the dose of UV and the oxidant. The UV lamp used in our system was old and its output of UV light is suboptimal. However, the evidence obtained strongly indicated that UV plus hydrogen peroxide was effective in reducing the concentrations of EDB in water. This appeared to be the most promising method and further studies to determine the effectiveness of UV plus an oxidant is highly recommended.

It should be noted that hydrogen peroxide is available as a liquid at concentrations of 3% and 30%. As a result, large volumes of this stock hydrogen peroxide must be used to treat large volumes of water, thus making the use of hydrogen peroxide impractical on a large scale. Hydrogen peroxide was selected for two reasons: first, it is readily available and easy to use; second, it is chemically similar to ozone which requires expensive generators for its production. However, the technology for generating and using ozone to treat large volumes of water is available. Thus in subsequent studies, the use of ozone may be more applicable than the use of hydrogen peroxide. The most highly recommended method to remove the concentrations of EDB in water

would be to use UV and ozone. Equipment to produce UV and ozone to treat water are commercially available.

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