

REPORT DOCUMENTATION FORM
 WATER RESOURCES RESEARCH CENTER
 University of Hawaii at Manoa

¹ Report Number Technical Report No. 157	² COWRR Field-Group 05-A, B, C
³ Title DBCP Volatilization from Soil and Water: A Laboratory Study with Two Hawaiian Soils	⁴ Report Date August 1984
	⁵ No. of Pages ix + 95
	⁶ No. of Tables 30 ⁷ No. of Figures 21
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¹⁰ Grant/Contract No. S-0013	
¹¹ Descriptors: *pesticides, *wells, *water, soil contamination, agricultural chemicals Identifiers: *DBCP, *volatilization, *soil fumigant, *nematicide, Oxisol, Wahiawa soil, Maile soil, Kunia well, central Oahu, Hawaii	
¹² Abstract (Purpose, method, results, conclusions) DBCP (dibromochloropropane) has been used as a soil fumigant for nematode control for decades by the Hawaii pineapple industry. Recent detection (parts-per-trillion range) of the fumigant in potable well water has spurred a study of the behavior of DBCP in its Hawaiian environment. A volatile trapping apparatus was developed which proved to be highly efficient in capturing volatilized DBCP. Rates of DBCP volatilization from water were established for variations in air flow rate, temperature, and DBCP solution concentration. Measurements of cumulative DBCP volatilized at three solution concentrations indicated the applicability of Henry's law for solution concentrations up to 35 µg/ml. A soil cell, patterned after that developed by Spencer and associates, was used to determine volatilization rates for DBCP mixed uniformly in surface soils from the Wahiawa series of Oahu and the Maile series of Hawaii Island. The effect of Wahiawa soil-water content on DBCP volatilization (without water loss) was evaluated at water contents of 2.3, 8.5, 13.5, and 31.6% by volume. DBCP vapor flux was lower at 2.3% water content than at higher water contents for the first three days, possibly because of higher adsorption on the very dry soil. An untreated 0.02 m thick soil layer placed above DBCP-treated soil greatly retarded DBCP volatilization during the first two days. The calculated effective liquid-vapor diffusion coefficient, D_e , for Wahiawa soil increased with soil water content from 6.1×10^{-4} cm ² /s at 2.3% water content to 2.6×10^{-3} cm ² /s at 31.6% water content.	

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DBCP VOLATILIZATION FROM SOIL AND WATER:
A LABORATORY STUDY WITH TWO HAWAIIAN SOILS

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Technical Report No. 157

August 1984

Research Project Completion Report
for

An Investigation of Perched and Underlying Groundwater Bodies
in Relation to Contamination by Pesticides: DBCP Adsorption
and Volatilization in Soils and Saprolites of Central Oahu, Hawaii

Project No. S-0013

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Project Period: 1 July 1983 to 30 June 1984

The work on which this report is based was supported in part by the U.S. Geological Survey, Water Resources Division; the Hawaii State General Fund; and the University of Hawaii at Manoa, Water Resources Research Center.

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ABSTRACT

DBCP (dibromochloropropane) has been used as a soil fumigant for nematode control for decades by the Hawai'i pineapple industry. Recent detection (parts-per-trillion range) of the fumigant in potable well water has spurred a study of the behavior of DBCP in its Hawaiian environment.

A volatile trapping apparatus was developed which proved to be highly efficient in capturing volatilized DBCP. Rates of DBCP volatilization from water were established for variations in air flow rate, temperature, and DBCP solution concentration. Measurements of cumulative DBCP volatilized at three solution concentrations indicated the applicability of Henry's law for solution concentrations up to 35 $\mu\text{g}/\text{ml}$.

A soil cell, patterned after that developed by Spencer and associates, was used to determine volatilization rates for DBCP mixed uniformly in surface soils from the Wahiawa series of O'ahu and the Maile series of Hawai'i Island. The effect of Wahiawa soil-water content on DBCP volatilization (without water loss) was evaluated at water contents of 2.3, 8.5, 13.5, and 31.6% by volume. DBCP vapor flux was lower at 2.3% water content than at higher water contents for the first three days, possibly because of higher adsorption on the very dry soil. An untreated 0.02 m thick soil layer placed above DBCP-treated soil greatly retarded DBCP volatilization during the first two days.

The calculated effective liquid-vapor diffusion coefficient, D_e , for Wahiawa soil increased with soil water content from $6.1 \times 10^{-4} \text{ cm}^2/\text{s}$ at 2.3% water content to $2.6 \times 10^{-3} \text{ cm}^2/\text{s}$ at 31.6% water content.

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INTRODUCTION

Farmlands are complex ecosystems. While only one plant species may be cultivated on a farm, many insects and plants vie for survival within the same ecosystem. One of the main tasks for the modern agriculturist is the control of undesirable pests or weeds. Thus, the many chemical substances developed to meet this need were initially used with great enthusiasm because they were relatively inexpensive, easy to apply, fast-acting, and effective against a wide range of pests. However, these chemicals also kill non-pest species, and may result in the disruption of ecosystems and/or may prove harmful to human health.

Dibromochloropropane (DBCP) is a soil fumigant used by Hawai'i pineapple growers to control nematodes. Besides DBCP, two other alternative nematicides, ethylene dibromide (EDB) and dichloropropene/dichloropropane (Telone or DD), were also used in very large amounts in Hawai'i. At normal temperature, these chemicals are volatile liquids which move through soil pores in the gaseous phase. Although the major portion of the injected DBCP will eventually escape to the atmosphere, a certain residual amount remains in the soil due to soil particle adsorption. This small residual amount may percolate downward with infiltrating water and become a source of groundwater contamination. In the late 1970s, DBCP was found in the groundwater of several states (Severn et al. 1983), thereby prompting regulatory action by the U.S. Environmental Protection Agency (EPA), which banned the agricultural use of DBCP. The continuing use of this chemical by pineapple growers in the state of Hawai'i was permitted on the basis of unique geohydrological characteristics relative to the Hawai'i basal groundwater lens.

The environmental fate of DBCP residuals in soil became an important issue in Hawai'i in mid-1980 when water samples collected from the Kunia well in central O'ahu were found to be contaminated by DBCP as well as EDB. Since then, ground-

water contamination by these chemicals has been discovered in a small number of wells in central O'ahu and Maui.

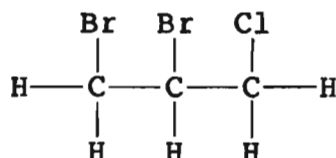
The transport of DBCP residuals in soil has been investigated by system simulation (Liu et al. 1983). Soil is a dynamic system in which numerous physical, chemical, and biological processes are continuously taking place. To simulate the chemical transport in soil, therefore, rate constants and equilibrium process constants which govern these natural processes must first be identified. How long residual DBCP will persist in soil is an important indication of its potential for groundwater contamination. Volatilization of DBCP from the soil to air determines, to a large degree, the chemical persistence in soil. A better understanding of this natural process is one of the most important elements for a successful modeling study. This report provides research findings from an experimental investigation of DBCP volatilization from soils. Preliminary experiments included measurements of DBCP volatilization from water with variable air-flow rates, temperatures and DBCP concentrations.

Physical Properties of DBCP

DBCP (1,2-dibromo-3-chloropropane) is an amber to dark brown, slightly pungent, brominated organochlorine with the following specific chemical characteristics (Babich, Davis, and Stotzky 1981):

Molecular weight	236.36
Boiling point	196°C
Melting point	6°C
Vapor pressure (20°C)	0.8 mm Hg
Specific gravity	2.093.

DBCP is 2.13% H, 15.00% Cl, 15.24% C, and 67.62% Br by weight, with the following structural formula,



and empirical formula, $C_3H_5Br_2Cl$. DBCP is only moderately soluble in water (700 mg/l at 20°C) (Burlinson, Lee, and Rosenflatt 1982), but is miscible with oils, aliphatic and aromatic hydrocarbons, isopropyl alcohol, 1,2-dichloropropane, 1,1,2-trichloroethane, and tetrachloroethylene (Babich, Davis, and Stotzky 1981).

Burlinson, Lee, and Rosenflatt (1982) attribute the persistence of DBCP in the environment to its vapor pressure, moderate solubility in water, resistance to biodegradation, and hydrolytic stability. At 25°C and pH 7, DBCP has an estimated half-life of 38±4 years; however, at 15°C (average groundwater temperature in the United States) and pH 7, the estimated half-life of DBCP is 141 years (Burlinson, Lee, and Rosenflatt 1982).

DBCP as a Nematicide

DBCP has been effectively used since 1955 to combat nematodes, microscopic organisms that feed on the roots, buds, stems, crowns, leaves, or the developing seeds of a plant, causing reduced yield and poor quality of the resultant crop. DBCP's attributes as a nematicide include the fact that it is 8 to 16 times as active as DD (a 100% mixture of 1,3-dichloropropene, 1,2-dichloropropane, 3,3-dichloropropene, 2,3-dichloropropene, and other related chlorinated hydrocarbons) and that it is of such low phytotoxicity that it can be applied at the time of planting or to certain growing crops without damage to the plants (White-Stevens 1976).

The principal techniques for DBCP application to soil include: soil injection, pressure or gravity flow irrigation, sprinkler irrigation, drench application, and granular deposition (EPA 1976b in Babich, Davis, and Stotzky 1981). Once in the soil, the volatilization of DBCP has a fumigating action. When applied to the soil DBCP may follow one of several paths: (1) degradation by microorganisms to n-propanol and bromide (Br) and chloride (Cl) ions (Castro and Belser 1968); (2) uptake and accumulation by agricultural crops; (3) volatiliza-

tion from the soil; and (4) leaching into underground waters (EPA 1979; Babich, Davis, and Stotzky 1981).

Castro and Belser (1968) concluded that because DBCP is not readily hydrolyzed in an aqueous milieu, its persistence in the soil is apparently limited by volatilization rather than by chemical or biological conversions which may occur in the soil matrix.

Health Effects of DBCP

DBCP's effectiveness as a nematicide may be outweighed by recently discovered, potential deleterious effects to human beings. Babich, Davis, and Stotzky (1981) report:

In 1977 many of the employees at the Occidental Chemical Plant in Lathrop, California, who handled DBCP, were found to be either azoospermic or oligospermic. Subsequent surveys of employees handling DBCP at other chemical plants confirmed these findings. In 1977 DBCP per se (rather than just its degradation products, e.g., bromide ions) was detected on edible crops and in 1979 DBCP per se was detected in well waters. As a result of these studies, the Occupational Health and Safety Administration (OSHA) and the Environmental Protection Agency (EPA) in 1977 promulgated regulations restricting the use and handling of DBCP.

In 1979 the EPA unconditionally suspended registration of all pesticide products containing DBCP except for those used on pineapple in the Hawaiian Islands. Babich, Davis, and Stotzky (1981) have summarized the reasons offered by the EPA for its cancellation of all other uses of DBCP:

1. DBCP is a potential carcinogen to human beings.
2. DBCP has harmful testicular effects.
3. DBCP is a genetic toxin, causing chromosome and chromatid breaking, inducing a higher incidence of double Y chromosomes in sperm cells, and is mutagenic to bacteria.
4. DBCP persists in the environment, as is evidenced by the residues of DBCP per se on all agricultural crops tested, by the contamination of drinking water with DBCP, and by atmospheric concentrations of DBCP above

soils treated with the nematicide. LD₅₀ values (defined by Edmonds [1978] as "the concentration [lethal dose] of...substance that is required to kill 50% of the test animals to which the substance...has been administered") have been determined for a number of animals and are presented in Table 1.

TABLE 1. LETHAL DOSE (LD₅₀) VALUES FOR ANIMALS EXPOSED TO DBCP

Animal	Sex	LD ₅₀ (mg/kg)	Source
mouse	F	260-410	Torkelson et al. (1961)
rat	M	170-300	Torkelson et al. (1961)
rat	F	260-410	Torkelson et al. (1961)
rat	M or F	350	Rakhmatullayev (1971)
rabbit	M or F	180	Torkelson et al. (1961)
rabbit	M or F	440	Rakhmatullayev (1971)
guinea pig	M	210	Torkelson et al. (1961)
guinea pig	M or F	316	Rakhmatullayev (1971)
chicken	unsorted	60	Torkelson et al. (1961)
mallard duckling	M or F	66.8	Tucker and Crabtree (1970)

SOURCE: Babich, Davis, and Stotzky (1981).

Thus, there is strong evidence to support DBCP's carcinogenicity to man. Babich, Davis, and Stotzky (1981) have stated:

The estimated dietary intake of DBCP by human beings is in the range of 2.2×10^{-6} to 6.1×10^{-6} mg/kg/day. Assuming DBCP is consumed in the diet over an entire lifetime for 70 years, DBCP will induce 28 to 740 cases of cancer per million exposed people during their lifetime.

DBCP in Hawai'i

DBCP has been used as a soil fumigant for nematode control for decades by the Hawai'i pineapple industry. Kimura and Hurov (1969) have stated:

The use of volatile soil fumigants is much greater in Hawaii than on the mainland, because of the more severe nematode problem. Nematodes mutilate and destroy the roots of many tropical crops and plants, and thrive exceptionally well in Hawaii's frost-free climate. Without nematode control, pineapple and several other Hawaiian crops would almost be complete economic failures.

The use of DBCP in the Hawaiian Islands ranged from a high of 298 472 kg (658,008 lb) in 1970 to a low of 59 617 kg (131,432 lb) in 1981 (Pacific Biomedical Research Center 1982; 1964-1981 data). The estimated use in the United States as a whole has ranged from 13.608×10^5 kg (3,000,000 lb) in 1971 to 5.579×10^6 kg (12,300,000 lb) in 1972 (NIOSH 1978 in Babich, Davis, and Stotzky 1981). The standard field dose for DBCP is $0.009 \text{ m}^3/\text{ha}$ (3 gal/acre) of 85.5%, or 5.49 kg (12.1 lb) of active ingredient/gal, of DBCP (see App. D for Dow Chemical's Fumazone B6 label, and for comparison of this field dose to the dosage used for the volatilization from soil phase of this study). Use of DBCP on O'ahu was voluntarily discontinued by the Hawai'i pineapple industry in 1977, but the substance is still being used on Maui.

On 4 April 1980, after a joint sampling program had been organized by the Pineapple Growers' Association of Hawaii and the Hawaii State Department of Agriculture and Department of Health (DOH), significant amounts of DBCP (11 ppb) and ethylene dibromide (EDB, 92 ppb) were identified in a water sample collected from the Del Monte Corporation's Kunia well (State No. 2703-01) located near Mililani in central O'ahu (Mink 1981). The contamination was initially attributed to a spill of 1.87 m^3 (495 gal) of EDB (probably containing 0.25% DBCP as an impurity) which occurred on 7 April 1977 within 18.3 m (60 ft) of the well. Informed of the accidental spill, DOH analyzed the well water for EDB but found none above the 0.5 ppb detection level (Mink 1981). Mink reported that no analyses were made for DBCP and that it was evidently concluded "that contamination had not reached the deep aquifer." A second potential point source of contamination was later determined in a small gully 15 to 46 m (50-150 ft) north of

the well where DBCP and EDB had been stored in drums on the ground and were transferred to other containers for field use.

Liu et al. (1983) have simulated DBCP transport through the soil and rock formation in the Kunia area with a one-dimensional, time-variable model. Their study suggests that the DBCP present in the Kunia well water is not a result of the 1977 spill near the well, but that contamination of the basal aquifer was likely from the storage area. However, more specific determinations of the rates of adsorption and volatilization of DBCP under various conditions are needed before the assumptions of the Liu et al. (1983) model can be evaluated.

In October 1982 Mililani well No. 5 was closed because of DBCP contamination. In July 1983, eight O'ahu wells (4 at Waipahu, 2 at Kunia, and 2 at Mililani) were closed because of greater than 20 ppt (parts per trillion, as used throughout this report) DBCP and EDB contamination. In that same month the Moloaa well on Kaua'i and the Old Maui High School well were closed (190 ppt and 140 ppt respectively). Mililani well No. 6 was never put into operation because of contamination. The remaining two Mililani wells (Nos. 1, 3) remained open despite slight contamination (approximately 20 ppt and 10 ppt, respectively) revealed in initial testing. J.F. Mink, witness for the Pineapple Growers' Association of Hawaii in the September 1979 EPA proceedings ("Notice of Intent to Suspend Registrations of Pesticide Products Containing Dibromochloropropane [DBCP]") that exempted Hawaii from a national ban of DBCP, in October 1982, urged Governor Ariyoshi to agree to an immediate formal ban of DBCP in Hawaii.*

No federal standard has been established for DBCP in drinking water. In Hawai'i, the Department of Health director, C. Clark, set 20 ppt (the reliable detection limit) as the upper limit for drinking water contamination. By comparison, California's drinking water standard is 1 ppb (parts per

*Honolulu Advertiser, 8 Oct. 1983, "Waterline to Mililani Set," pp. A-1, A-4.

billion).

OBJECTIVES OF STUDY

This study was conducted to investigate DBCP volatilization from water and soil. Rates were first determined for volatilization from water to establish a working experimental procedure and to gain a first approximation of the effects of varying environmental conditions on these rates. Volatilization rates from water derived in this study are also useful information to the design of treatment facilities which clarify DBCP-contaminated water by aeration. Rates were then established for the more intricate case of volatilization from soil to enable more accurate prediction of the fate of DBCP in the subsurface environment. Secondary objectives of this study include (1) an assessment of the applicability of Henry's law; (2) the estimation of effective gas-liquid diffusion coefficients; and (3) determination of the effect of an untreated soil layer above the treated zone on volatile losses of DBCP from the soil surface.

LITERATURE REVIEW

Many researchers have attempted to quantify the effects of varying environmental conditions on the movement of pesticides in and from the soil. The most pertinent of these studies are roughly summarized by category as a framework for this investigation.

Volatilization Studies

Danielson and Genter (1964) analyzed the influence of air movement on the persistence of the preemergence herbicide EPTC (see Glossary for pesticide abbreviations) in silica sand and in potting soil mix. A bioassay technique was utilized in which EPTC was applied to the surface of soils placed in cups

which were then exposed to a given air flow rate. Seed and sand were then added to the soil-cups to determine subsequent plant responses as an indication of pesticide residual in the soil. This methodology has the disadvantage of utilizing plant response as a means to quantify the pesticide remaining in the soil.

Bowman, Schechter, and Carter (1965) investigated the behavior of chlorinated insecticides in a broad spectrum of soil types. A small amount of soil was placed in an oven for a given time increment. A sample of the soil was then analyzed for pesticide concentration by hexane-acetone extraction followed by gas chromatographic analysis. This methodology has the disadvantage of arriving at the amount volatilized indirectly, the difference between the initial and final soil concentration being attributed to volatile loss.

Gray (1965) developed a vapor trapping apparatus for determining the loss of EPTC and other herbicides from soils. A Plexiglas chamber was placed over the soil surface and air withdrawn from the chamber through a series of glass traps immersed in dry-ice acetone baths. Vapor loss from differing types of soils and under different conditions of soil-moisture content, irrigation, and incorporation were studied. The main drawback to this method was the frequency with which the dry-ice acetone baths must be changed.

Parochetti and Warren (1966) analyzed vapor losses of IPC and CIPC from several types of soil. Dry air flow was passed into closed cylinders containing treated soil. The vapors emitted were trapped in dry columns containing Florisil dispersed with glass wool. The authors did not report the efficiency of the trapping apparatus.

Bardsley, Savage, and Walker (1968) studied the volatilization of trifluralin from water and soil. A thin layer of activated charcoal and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ dried on the bottom of a glass beaker was inverted over a polypropylene cup which contained treated water or soil. The influence of concentration, time, soil-moisture content, pesticide incorporation were in-

vestigated. The authors reported that only about 60% of the actual amount of trifluralin volatilized could be recovered from the trap.

Ketchersid, Bovey, and Merkle (1969) studied the rate of volatilization of trifluralin and nitralin from soil. An 11-l jar was placed over pans of treated soil; air samples were removed with a syringe and directly injected into a gas chromatograph. The effects of temperature and soil-moisture content were analyzed. Residual pesticide concentrations in the soil were determined. This methodology does not allow for investigation of the effects of air flow rate on pesticide volatilization, and also assumes a homogeneous distribution of the volatiles in the air space above the soil.

Caro and Taylor (1971) used sets of three glass-fiber furnace filters placed horizontally at three heights above the soil surface to study the volatilization rate of dieldrin. The pesticide was extracted from the filters with hexane which was then analyzed for dieldrin content by using gas chromatography. Dieldrin concentration for soil, runoff water sediment, and plant materials was also determined. In this methodology pesticide vapors are assumed to travel upward only; no provision is made for the entrapment of horizontally moving volatiles.

Ciccioli et al. (1976) studied the concentration of various organic pollutants found in the air of industrial work-sites. Their volatile trap consisted of Tenax GC (a porous polymer) or Carbopack B (a graphitized carbon black absorbent) held in place by glass wool in a vacuum-pumped glass tube. Disadvantages of this methodology are the relatively high cost of the trapping agents coupled with the fact that these agents selectively and barely adsorb some substances while they strongly adsorb others.

Saltzman and Kliger (1979) studied the effects of soil properties and application techniques on the volatilization losses of DBCP from several soils. DBCP was extracted from the soil samples with water and hexane by shaking. After

freezing the extractants, the supernatant hexane was taken off and analyzed by gas liquid chromatography. DBCP not found in the soil samples was assumed to have volatilized. The main drawback of this methodology is the indirectness of the approach for measuring the amount of pesticide volatilized.

RADIOACTIVE TECHNIQUES. Fang, Theisen, and Fried (1961) studied the effects of water evaporation, temperature, and EPTC concentration on the retention of EPTC in various soils. EPTC labelled with radioactive ^{35}S was dissolved in alcohol, then incorporated into the soil prior to the treatment in question. Initial and final radioactivity (corrected for the half-life of ^{35}S) was measured to determine the retention of EPTC. This methodology requires laboratory equipment for the use and detection of radioactive substances.

Guenzi and Beard (1970) analyzed the volatilization of ^{14}C -labeled lindane and DDT from several soil types. Hexane was utilized to trap the volatiles which were quantified using scintillation counting. Soil type, temperature, air flow rate, and irrigation schedule were varied. Again, this methodology requires specialized laboratory equipment.

POLYURETHANE FOAM. Bidleman and Olney (1973) studied chlorinated hydrocarbons found in the Sargasso Sea atmosphere and surface water. To study PCBs, DDT, and chlordane in the atmosphere, they developed a sampler which pulled air through a preliminary glass-fiber filter and then through a polyurethane foam (PUF) plug. The authors report greater than 90% efficiency for the trapping apparatus.

Lewis, Brown, and Jackson (1977) utilized a Syracuse University Research Corporation high-volume air sampler, containing a PUF plug in the lower compartment, to test for concentration of a variety of substances in the air of a rural, non-agricultural environment. They concluded that while PUF was an efficient high-volume air sampling medium for low levels of chlorinated pesticides and PCBs of low volatility, it proved inadequate or only marginally adequate for 24-hr sampling of the more volatile members of these families. Lewis and

MacLeod (1982) studied the concentrations of pesticides and PCBs in indoor air by using a constant flow sampler equipped with a borosilicate cartridge containing a PUF plug. Lewis and Jackson (1982) continued the study of air-borne pesticides and PCBs by sandwiching various granular sorbents with PUF in an aluminum, high-volume air sampling cartridge. This latest apparatus would seem to have considerable promise for low volatility substances in that it combines the trapping capabilities of two frequently used absorbents.

IMPINGERS. Harris and Lichtenstein (1961) investigated the factors affecting the volatilization of a variety of insecticidal residues from several soil types. The treated soil was placed in a glass jar which was attached to a trap, containing a suitable solvent, through which air was pulled at a rate of 1.0 l/min. Soil and vapor were analyzed according to colorimetric methods. Of the literature reviewed for this report, these authors were the first to utilize an impinger as the trapping apparatus. The methodology proved highly successful for the substances tested.

Willis et al. (1969) conducted a field study of the atmospheric concentration of endrin found above sugarcane plots. The system included a stainless steel boom with regularly placed ports, a stainless steel regulating valve, an ethylene glycol impinger, a pressure-vacuum pump, and a flow-meter. Climatological data were not reported in this paper. In 1971 Willis et al. utilized the 1969 methodology to monitor the volatilization of DDT and DDD from flooded and non-flooded field plots. Willis et al. (1972) used the same methodology to examine the volatilization of dieldrin from fallow soil as affected by different soil-water regimes. Here the effects of flooding, sprinkling, and no irrigation aside from natural rainfall were compared. Of the literature reviewed, these authors were the first to report the use of ethylene glycol impingers for the entrapment of pesticide vapors.

Miles, Fetzner, and Pearce (1970) studied water and several low molecular weight hydrocarbon solvents for relative

efficiency as a trapping agent for DDVP, diazinon, parathion, DDT, and dieldrin, and found ethylene glycol to be the superior trapping fluid. They reported that

Packed columns are very efficient for trapping vapors, but recovery of the sample is frequently difficult; the filter systems permit the collection of large volumes of air in short periods of time, but their efficiency for vapors is low and unknown losses of particulate and aerosol samples occur during the sampling period; the scrubbers are good for aerosols and vapors, but the sampling rate is slow and the use of sintered glass precludes the collection of particles; and cold traps are of limited value in field work in view of the maintenance problem. Midget and Greenburg-Smith type impingers seem to offer a compromise in that they can be operated at a reasonably fast rate, they are very efficient for collection of particulate matter, and with proper selection of solvent they can collect aerosols and vapors efficiently.

Stanley et al. (1971) designed a collection train consisting of a glass cloth filter, an impinger containing hexylene glycol, and an adsorbent tube filled with alumina to test for atmospheric contamination and organophosphate pesticides. This methodology was shown to be highly efficient for multi-residue determinations.

Parmele et al. (1972) collected micrometeorological measurements of pesticide vapor flux from bare soil and corn under field conditions. Air was sampled for dieldrin and heptachlor at five heights above the soil surface by drawing air through hexylene glycol in glass scrubbers mounted on masts. An evaluation of the sources and sinks of pesticide vapors within the crop canopy was conducted, and the system modeled for both vertical and horizontal flux.

Ford et al. (1975) of the USDA National Monitoring and Residue Analysis Laboratory reported preferred methodologies for the sampling and analysis of pesticides in the environment. For air sampling, they recommended machines containing four ethylene glycol filled impingers in series connected to a vacuum pump. This method, although efficient, requires many impingers and much ethylene glycol for multiple analyses.

In 1981 Burkhard and Guth compared calculated results with those determined in a laboratory model system of the rate of volatilization of pesticides from soil. In their laboratory study, they tested the volatilization rates of methidathion, diazinon, isazophos, metolachlor, and metalaxyl from soils by pulling air from a glass volatilization chamber through an impinger filled with ethylene glycol. Variables investigated were concentration, air flow rate, temperature, and organic matter content of the soil. They obtained highly satisfactory correlations between calculated and experimental results.

STUDIES BY SPENCER AND CO-WORKERS. The most long-term and systematic study of the volatilization of pesticides from soil has been conducted by Spencer and his co-investigators. In 1969 Spencer and Cliath investigated the vapor density of dieldrin by passing N_2 gas over the treated soil at a sufficiently slow rate to ensure equilibrium saturation. A first volatile trap contained hexane which removed the volatilized pesticide; a second trap contained transmission fluid which trapped hexane volatilized from the first trap. A gas chromatograph was used to analyze the hexane for dieldrin concentration. Spencer, Cliath, and Farmer (1969) utilized the same methodology, minus the transmission fluid trap, to investigate the vapor density of soil-applied dieldrin as related to soil water content, temperature, and dieldrin concentration. Spencer and Cliath (1970a) next investigated the vapor density and apparent vapor pressure of lindane utilizing the methodology of Spencer, Cliath, and Farmer (1969). The effects of temperature and soil water content were examined. Later, Spencer and Cliath (1970b) studied the desorption of lindane from soil as related to vapor density, again using the 1969 apparatus. The effects of variation of soil water content and temperature were investigated. In 1972 these same authors studied the volatility of DDT and related compounds. The 1969 methodology was utilized to investigate the effects of variation in soil type, temperature, initial soil water content,

and relative humidity. In 1972 Cliath and Spencer studied the dissipation of pesticides from soil by volatilization of degradation products. In their field study the vapor collection system was similar to that used in previous work, but with glass washing bottles containing ethylene glycol as the vapor trapping agent located at two heights above the soil surface. Irrigated vs. nonirrigated conditions were investigated. In 1974 Spencer and Cliath examined the factors affecting vapor loss of trifluralin from soil, again utilizing the 1969 experimental design. Variations in temperature, soil water content, organic matter content, and mode of application were studied.

Farmer et al. (1972) examined the effect of concentration, temperature, air flow rate, and vapor pressure on the volatility of organochlorine insecticides from soil. ¹⁴C-tagged insecticides were placed in a volatilization chamber which was part of a closed air-flow system. Volatiles were collected in ethylene glycol traps and subsequently extracted into hexane which was analyzed using liquid scintillation. Igue et al. (1972) extended this same study in order to determine the effects of relative humidity and soil water content on dieldrin volatility. In 1973 Farmer, Igue, and Spencer utilized the same methodology to investigate the effect of bulk density on the diffusion and volatilization of dieldrin from soil. In 1973 Spencer and Cliath modified the Farmer, Igue, and Spencer (1973) apparatus to include soil water content and relative humidity controls. Lindane and dieldrin were examined for volatility as related to water loss from soil.

In 1979 Spencer et al. investigated the vapor pressure and relative volatility of ethyl and methyl parathion. A rectangular Plexiglas volatilization cell was utilized for the relative volatility measurements. Relative humidity, soil water content, air flow rate, and temperature were controlled. Pesticide vapors were trapped on PUF plugs. Jury et al. (1980) utilized the Spencer et al. (1979) methodology to in-

investigate vapor losses of soil-incorporated triallate. The effects of variation in soil type and relative humidity were investigated. Laboratory values were compared to calculated convective mass flux values.

Soil Studies

Johnson and Lear (1968) evaluated the movement of DBCP through soil by using sectioned Plexiglas columns. After application of the pesticide, the columns were stored for given time intervals, then disassembled and soil samples of each section analyzed for DBCP concentration. Water and solvent were combined with the soil sample in a glass bottle which was placed on a reciprocating shaker for 30 min. The solvent was then removed and analyzed for DBCP concentration by gas chromatography. Time, concentration, soil type, and grade of DBCP were used as variables. Johnson and Lear (1969a) utilized a similar apparatus to investigate the effect of temperature on the dispersion of DBCP in soil. In their 1969b report they describe their method of recovery from soil and analysis by gas-liquid chromatography. Hodges and Lear (1973) studied the effect of time of irrigation on the distribution of DBCP in soil after shallow injection. Here field plots were treated, then sampled and analyzed for DBCP concentration at various time intervals. In 1974 Hodges and Lear examined the persistence and movement of DBCP in three types of soil. Concrete ground-beds were used to compare injection vs. surface-solution application. These authors offer a simple yet efficient methodology for the determination of pesticide concentration in soil samples.

In 1978 the California Department of Food and Agriculture presented an alternate method for the quantification of DBCP concentration in soil. The soil samples were combined with distilled water and ethyl acetate, then distilled. After distillation, sodium sulfate was added to dry the ethyl acetate which was then analyzed for DBCP concentration by gas chromatography.

Summary of Research Trends

Generalizations for the pesticides tested may be summarized from the research results cited in this review:

1. The volatilization rate of a pesticide increases as air flow rate, concentration, and temperature are increased
2. The volatilization rate of a pesticide decreases with increasing organic matter and clay contents of a soil
3. The volatilization rate of a pesticide is greater from wet than from dry soils as water competes for soil adsorption sites causing displacement of the pesticide
4. Injection of the pesticide, incorporation of the pesticide after surface application, or coverage of the treated surface with another soil layer result in a lower volatilization rate than that of only surface application
5. Very small amounts of irrigation cause an increased volatilization rate because water competes with the pesticide for soil adsorption sites; however, when irrigation is increased to significant amounts, the volatilization rate decreases as the pesticide is carried downward by the advancing water front
6. Decreasing barometric pressure and lowering of relative humidity increase the volatilization rate of pesticides.

EXPERIMENTAL TECHNIQUES

Experimental Apparatus

VAPOR TRAP. To quantify the mass of pesticide volatilized from the water or soil, efficient vapor trapping procedures have been developed; however, none have yielded high recovery rates for substances of high volatility. In their 1968 paper on the degradation of DBCP in the soil environment,

Castro and Belser stated:

...the amount of this halide present at the end of a run is more an attribute of its volatility than its biodegradability.

As can be seen in Table 2, DBCP is second only to EDB in vapor pressure among those pesticides whose vapor pressures were given in the literature surveyed for this report. This property is undoubtedly the root of the problems encountered in developing a suitable trapping apparatus for volatilized DBCP.

TABLE 2. VAPOR PRESSURES OF SELECTED PESTICIDES

Substance	Vapor Pressure (mm Hg)	Temp. (°C)	Source
EDB	7.69	..	Saltzman and Kliger (1979)
DBCP	0.80	20	Babich, Davis, and Stotzky (1981)
DBCP	0.58	..	Saltzman and Kliger (1979)
EPTC	1.55×10^{-1}	25	Bardsley, Savage, and Walker (1968)
EPTC	1.97×10^{-2}	..	Burkhard and Guth (1981)
CDA	9.4×10^{-3}	20	Bardsley, Savage, and Walker (1968)
lindane	1.48×10^{-3}	55	Guenzi and Beard (1970)
trifluralin	1.99×10^{-4}	29.5	Spencer and Cliath (1974)
lindane	1.28×10^{-4}	30	Spencer and Cliath (1973)
dieldrin	1.0×10^{-5}	30	Spencer and Cliath (1973)
metolachlor	1.30×10^{-5}	..	Burkhard and Guth (1981)
DDT	2.6×10^{-5}	55	Guenzi and Beard (1970)
parathion	3.79×10^{-5}	..	Burkhard and Guth (1981)
lindane	4.5×10^{-5}	30	Guenzi and Beard (1970)
diazinon	7.28×10^{-5}	..	Burkhard and Guth (1981)
metalaxyl	2.20×10^{-6}	..	Burkhard and Guth (1981)
diuron	3.1×10^{-6}	50	Bardsley, Savage, and Walker (1968)
methidathion	9.98×10^{-7}	..	Burkhard and Guth (1981)
DDT	2.53×10^{-7}	..	Burkhard and Guth (1981)
DDT	7.2×10^{-7}	30	Guenzi and Beard (1970)

Figure 1 details the trapping apparatus ultimately utilized for this study. This trapping apparatus was the result of many trials using other trapping devices which will be briefly described below.

The first substance to be tested as a possible trapping medium was activated charcoal, held in place by glass wool, placed in glass tubing through which air was drawn. Several trials of this medium resulted in no detectable DBCP being recovered in the charcoal trap; apparently the volatilized DBCP was so tightly held on the charcoal that it could not be desorbed by the solvents used.

The second medium to be tested was polyurethane foam (PUF) which replaced the charcoal in the above described trapping system. A single trial of the PUF resulted in less than 30% recovery of the initial DBCP emplaced in the system.

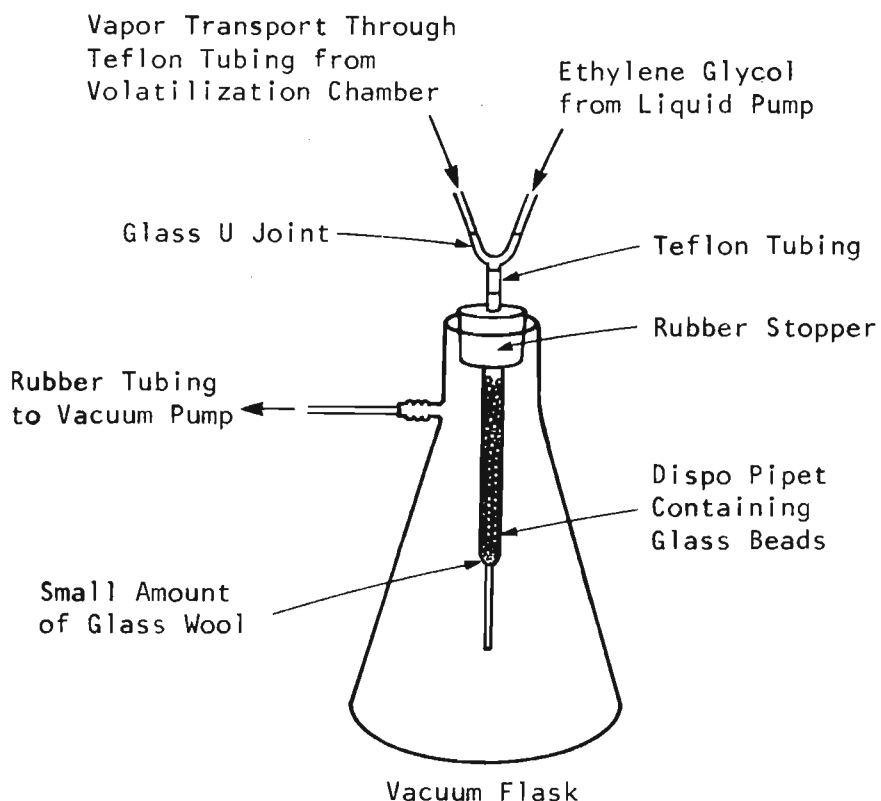


Figure 1. Apparatus for trapping volatilized DBCP

Ethylene glycol-coated glass beads held in place with glass wool and contained in glass tubing were tested as a possible trapping apparatus, but resulted in no detectable DBCP recovery. Apparently, insufficient ethylene glycol was present to effectively trap the DBCP.

Single impingers filled with 100 ml of ethylene glycol were tested next. Six trials resulted in recovery efficiencies ranging from less than 5% to 120%. Single initial volumes of DBCP test solutions placed in the volatilization chamber produced the poorest efficiencies; however, when the DBCP dose was added to the system over the duration of the experiment, recovery efficiency improved. Since volatile fluxes encountered in this study were nearer to the flux resulting from the single initial dose case, it was feared that single impingers would be unsatisfactory as DBCP vapor trapping devices for this study.

The major disadvantage of the impinger is that the trapping reservoir remains in contact with the vapor stream. Therefore volatile pesticides, such as DBCP, may indeed be trapped by the ethylene glycol, but are revolatilized because of the turbulence imposed by the system on the trapping fluid. In addition, contact time may be insufficient for the ethylene glycol to trap a significant percentage of the pesticide as it bubbles through the trapping medium. Impingers are thus often connected in series and filled with larger volumes of ethylene glycol to improve recovery efficiency.

The ideal vapor trap would therefore (1) maximize contact between the vapor stream and the ethylene glycol and (2) minimize contact between the vapor stream and the reservoir of ethylene glycol containing entrapped DBCP. The simple trapping apparatus illustrated in Figure 1 was designed to meet these requirements. In this design, ethylene glycol is pumped into the trap at approximately 0.8 ml/min (50 ml/hr) where it combines with the air being pulled through the glass bead filled column into the vacuum flask. The ethylene glycol and air are in combination only during their passage through the

glass bead-filled pipet, the ethylene glycol experiencing no further turbulence after its deposition in the bottom of the vacuum flask. Excessive loss by revolatilization and escape of DBCP captured by the ethylene glycol is thereby prevented. It should be noted that only common laboratory ware was utilized and that ethylene glycol consumption was minimized, at least for the collection times (30 min-2 hr) used in this study.

Subsequent testing of this apparatus resulted in apparent recovery efficiencies ranging from 90 to 130%, averaging about 106%. In all cases where the impinger and the new vapor trap could be compared, the vapor trap was at least 10 to 20% more efficient than the impinger. Considering this efficiency, combined with ease of use (i.e., simple laboratory apparatus, less ethylene glycol required, no multiple trap samples to analyze), this vapor trap was concluded to be a superior trapping apparatus for this study.

The problems associated with the development of a successful vapor trapping apparatus substantiate the Ford et al. (1975) statement:

Good air sampling machines are still much in question. Some agencies have suspended their air monitoring programs until a reliable method is achieved.

VOLATILIZATION FROM WATER. Figure 2 details the apparatus utilized for the preliminary study of volatilization from water. Twenty milliliters of a DBCP solution of a given concentration were placed in a petri dish beneath a glass funnel. A given temperature was imposed via the water bath and hot plate. Air flow rates were achieved by pulling air through the receiving flask by using a vacuum pump.

All equipment in the experimental chain prior to the ethylene glycol deposition in the receiving flask was either glass or teflon to minimize DBCP adsorption to the apparatus.

All experiments were conducted in duplicate.

VOLATILIZATION FROM SOIL. Volatilization rates of DBCP from soil were measured using the soil cell illustrated in Figure 3 which was adapted from the design developed by

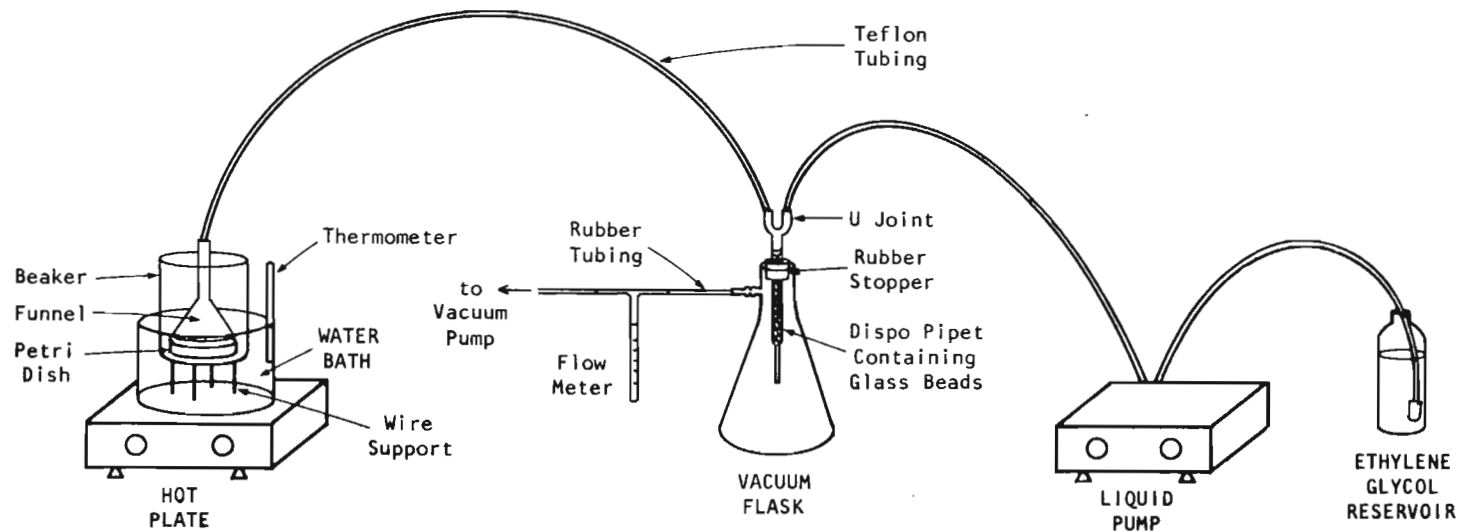


Figure 2. Apparatus used for development of volatilized DBCP trap and in preliminary experiments of volatilization from water

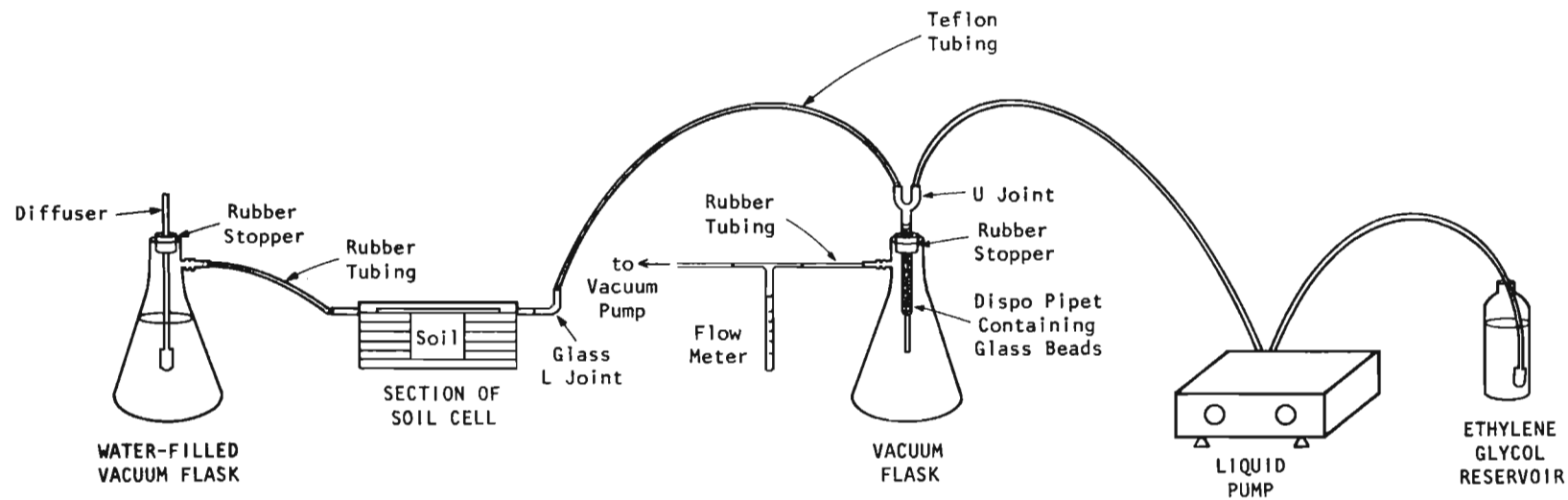


Figure 3. Apparatus for measuring DBCP volatilization from soil

Spencer et al. (1979). The cell was constructed of aluminum with a rectangular chamber (0.03 m wide by 0.10 m long) for inserting soil. The depth of the soil chamber was varied by the addition or deletion of center sections. Each section of the cell was grooved for an O-ring to provide a positive seal between sections. The upper section contained an air chamber (0.002 m deep, 0.03 m wide), which was the same width as the volatilizing surface.

With these dimensions, a flow rate of 250 ml/min through the air chamber provided an air flow rate across the volatilizing surface of about 0.25 km/hr and changed the atmosphere in the space over the surface about 42 times/min. The air chamber extended 75 mm (3 in.) on either side of the volatilizing chamber to allow air to spread out before reaching the soil, thus providing essentially laminar flow across the volatilizing surface. Humidity was kept at 100% by diffusion of incoming air through water prior to entry into the soil chamber to prevent water evaporation from the soil surface. Temperature remained at $23^{\circ}\text{C}\pm 2^{\circ}$ throughout this phase of the study.

Two soils (surface horizons) were used in this phase of the experimentation: Wahiawa silty clay (Oxisol order, Tropeptic Eustrustox; clayey, kaolinitic, isohyperthermic) and Maile silt loam (Inceptisols order, Hydric Dystrandeps, thixotropic, isomesic). Their specific characteristics are given in the data tables for each experimental run (App. C). Before being treated with DBCP, the soils were autoclaved for 1.25 hr at 25 psi and 126°C , twice at 2-day intervals. This prevented microbial degradation of the pesticide during experimentation. Water was added in drops to the soil, and was then thoroughly incorporated with a thin glass pestle to establish the specific soil water content desired. Then, technical grade pesticide in solution (1 ml of 35.0 ppm DBCP solution per 100 g air-dry soil) was added in drops to the soil followed by thorough incorporation. After treatment the soil was placed in the soil cell 0.01 m at a time and tamped

lightly with a glass rod. Descriptions of the methodologies utilized for the determinations of initial soil water content, organic matter content, and bulk density are given in Appendix Table A.1.

After closing the soil cell, air flow was started and continued for five to six days. Collection of volatilized DBCP was accomplished during 1- to 2-hr intervals for the first 10 hr, then for 2 hr each day thereafter. DBCP volatilization flux for each collection period and the flux during the intervening periods were calculated by assuming the flux to be equal to the mean of the fluxes for measurement periods before and after the non-measurement period.

At the end of the volatilization experiment, the soil was removed in slices delineated by corresponding center sections. Each slice was placed in a capped 70 ml glass test tube whose screw cap was aluminum foil lined to prevent sample contamination. The soil samples were analyzed for concentration to establish final DBCP distribution with depth in the cell.

All experiments were conducted in duplicate.

Quantitative Analysis

A quantitative analysis was conducted to establish (1) volatilization rates and (2) initial and final soil concentrations. For both types of samples, an extraction of pesticide into solvent was necessary. The pesticide-laden solvent was then analyzed for concentration by gas chromatography.

EXTRACTION AND DISTILLATION. Extraction and distillation techniques for all samples analyzed are outlined in Figure 4. The techniques for each type of sample is briefly described below.

For volatile samples, following entrapment of the pesticide, the ethylene glycol was combined with 2% sodium sulfate solution (5 parts sodium sulfate solution to 1 part ethylene glycol) and 10 ml of nanograde benzene in a separatory funnel. The mixture was vigorously shaken for 2 min. After allowing

sufficient time for separation (30 min), the benzene was drained off and stored in glass-stoppered centrifuge tubes for subsequent distillation and analysis. If the process was delayed at this point, samples were sealed with Parafilm and stored at 4°C until work was resumed. For distillation, each sample was transferred to a round-bottomed distillation flask which contained 100 ml aerated tap water. The distillation flask was attached to a distilling receiver Barrett trap that was attached to an Allihn condenser. The solution was brought to a boil with a heating mantle and the DBCP-laden benzene collected in the trap. Approximately 5 ml of water was also allowed to distill into the trap to assure maximum recovery of the benzene. The benzene solution was then drained into a clean centrifuge tube, centrifuged at 3500 rpm for 5 min, and any remaining water removed. The sample was then ready for analysis by gas chromatography, the technique utilized for initially testing the ethylene glycol and sodium sulfate solutions for DBCP contamination or interfering impurities.

For soil samples, the soil was placed in a distillation flask with 100 ml of water and 10 ml benzene. The sample was then distilled and centrifuged by the same process as for the volatile samples described above.

Distillation control analyses were conducted to quantify losses that resulted from distilling and centrifuging the samples tested. Distillation controls of two forms were used: DBCP-water solutions (0.35 and 35.0 ppm), and DBCP-benzene solution (1 ng/ μ l). For the case of DBCP-water solutions, 0.5 ml of the solution was used; for the DBCP standard in benzene, 100 μ l were used. In both cases, the control aliquot was added to 100 ml of water in a distillation flask. The procedure that followed was as for the ethylene glycol trapping solvent and soil samples, as described above. It should be noted that any water solution can be analyzed for DBCP concentration by this method.

Extraction controls were run to quantify losses associated with the transfer of the DBCP from ethylene glycol to

benzene. For the extraction controls, 0.5 ml of 0.35 ppm DBCP-water solution was added to 50 ml ethylene glycol. The mixture was agitated, then placed in a separatory funnel with 250 ml sodium sulfate solution. The subsequent extraction and distillation proceeded as given above.

Table 3 presents the summarized results of the control analyses described above. Detailed recounting of the data are in Appendix Tables B.1 and B.2. All three distillation control variations yielded very similar results. It may be therefore concluded, within analytical precision, that recovery efficiency is relatively independent of diluent or solution concentration. Because the extraction control recovery was higher than that for the distillation controls, virtually no loss to the system can be assumed to have occurred in the extraction portion of the analytical process. The mean, weighted inversely with respect to the variance (see Table 3) for all four control groups, yielded 82.4% (± 0.8) recovery (2σ , c.v. = 0.5%). It should be emphasized here that no correction of the data was made in lieu of recovery efficiency except where explicitly noted. All data reported are uncorrected and therefore probably represent only about 82.4% of the quantities actually present.

STANDARDS, EXPERIMENTAL SOLUTIONS, AND BLANKS. DBCP standards used for this study were from a parent standard acquired from the U.S. Environmental Protection Agency (Quality Assurance Section, Analytical Chemistry Branch ETC/HERTL [MD-69], U.S. EPA, Research Triangle Park, North Carolina 22711) and diluted in benzene.

Experimental DBCP-water solutions were made from an aliquot of technical grade DBCP obtained from the Maui Land and Pineapple Company. A blank was run with each set of samples. Each blank consisted of 10-ml benzene added to 100 ml tap water and the mixture then distilled, centrifuged, and analyzed for DBCP concentration. Nondetectable concentrations resulted in all cases.

GAS CHROMATOGRAPHY. DBCP concentration of sample solutions were quantified by gas chromatography. For this study,

TABLE 3. DBCP DISTILLATION AND EXTRACTION RECOVERY EFFICIENCY

	CONTROL SAMPLE	PROCEDURE	TOTAL DBCP ADDED (ng)	RECOVERY EFFICIENCY		
				%	% c.v.	n
Distillation	100 μ l, 1.0 ppm*	Added to 10 ml benzene and 100 ml water in distillation flask	100	83.1	9.2	7
	0.5 ml, 0.35 ppm†	Added to 100 ml water in distillation flask, 10 ml benzene added	175	83.0	11.6	18
	0.5 ml, 35.0 ppm†	Added to 100 ml water in distillation flask, 10 ml benzene added	17,500	78.6	9.0	10
Extraction	0.5 ml, 0.35 ppm†	Shaken with 50 ml ethylene glycol, extracted with 250 ml 2% Na ₂ SO ₄ into 10 ml benzene, added to 100 ml water in distillation flask	175	88.4	11.4	15

*EPA standard dissolved in benzene.

†Technical grade DBCP.

$$\ddagger \text{Weighted mean} = \frac{\left[\sum_{i=1}^n (x_i / \sigma_i^2) \right]}{\left[\sum_{i=1}^n 1 / \sigma_i^2 \right]}$$

in which x_i and σ_i^2 are the mean recovery and variance for the i th set of data, with n data sets.

$$\text{Weighted variance} = \frac{\left[\sum_{i=1}^n \frac{(x_i - \bar{x})^2}{\sigma_i^2} \right]}{\left[\sum_{i=1}^n \frac{n-1}{n\sigma_i^2} \right]}$$

§Excluding extraction control, weighted mean = 81.2 ± 0.6 .

$$\text{Weighted mean}^\ddagger = 82.4 \pm 0.8^{\S} \\ (2\sigma, \text{ c.v.} = 0.5\%)$$

a Tracor model No. MT-220 electron-capture gas chromatograph was used. The carrier gas utilized was nitrogen (70 ml/min) and the column packing was 4% SE30, 6% OV-210. The column temperature was maintained at 115°C and the detector at 250°C.

In this study, the practical lower limit of DBCP detection for the above described gas chromatograph was about 2 ng of DBCP in 10 ml benzene, or approximately 0.2 ppb. Concentration of samples was not possible because of the volatility of DBCP.

In practice, two injections of each sample were made and the pair bracketed by standards. If values obtained for the sample differed by more than 5%, the sample was reexamined. In the concentration range used for this study, there appeared to be a fairly linear relationship between concentration and peak height. However, an effort was made to match the peak heights of standard and sample by adjustment of shot-volume or by dilution to minimize problems of nonlinearity.

Safety Precautions

Throughout this study, care was taken to avoid inhaling the fumes emitted from the pesticide solutions. Dilutions and soil treatments were conducted under a fume hood. Disposable surgical gloves were worn when handling DBCP solutions or treated soil samples to prevent skin contact.

The Georgia Cooperative Extension Service (1978) gives the following short-term symptoms of acute exposure to DBCP:

1. Inhalation (nausea, irritation of the eyes and respiratory tract)
2. Ingestion (acute distress of stomach and intestine, with congestion and fluid in the lungs)

The following procedures were suggested for accidental contact with the pesticide:

1. In case of inhalation, remove victim from source of exposure
2. For accidental eye contact, flush eyes with clean water for 10 to 15 min

3. For skin contact, thoroughly wash skin with detergent and water
4. In case of ingestion, make victim drink 3 to 4 glasses of water; induce vomiting only if the victim is conscious and sitting up.

EXPERIMENTAL RESULTS

Volatilization of pesticides from water differs from volatilization from soil in the length and complexity of the pathway. In the case of volatilization from water, the transfer pathway is directly from water to air. This movement is dependent on the chemical and physical properties of the pesticide in question, the presence and absence of other contaminants, and the physical properties of the water body and overlying air mass (Thomas 1982). In this study, the effects of variation in temperature, initial DBCP solution concentration, and air flow rate were investigated. In addition, an attempt was made to determine the dependence of DBCP volatilization from water on solution concentration in relation to the assumptions of Henry's law.

For the case of volatilization from soil, the primary pathway is desorption from soil-sorbed sites to soil water, volatilization to soil-air, and finally escape to the atmosphere. In addition to the factors that affect the rate of direct volatilization from water, the chemical and physical properties of the soil must be considered. Particularly important are the organic matter, clay, and initial soil water contents of the soil in question. Environmental factors, such as irrigation rate, if any, and type of surface coverage (e.g., crop, mulch), if any, also affect the rate of volatilization from the soil environment. In this study, the effects of the variation of soil type (i.e., differing organic matter and clay contents) and initial soil water content, and the addition of a soil cover layer were studied. For each condition imposed, when the volatilization rate became insignifi-

cant, the soil column was sectioned and analyzed for pesticide concentration distribution to determine the effective depth at which volatilization and, thus, escape of DBCP essentially ceases.

Volatilization from Water

The effects of variation in the parameters of air flow rate, initial DBCP solution concentration, and temperature were investigated in the volatilization from water phase. The preliminary laboratory study suggested the following base conditions of 250 ml/min air flow rate, 0.35 ppm initial DBCP solution concentration, and 23°C temperature. These conditions are presented in all tables and graphs as standards of comparison for the data obtained with experimental variations, and the results of each variation discussed separately in the text to follow.

Each set of experimental conditions was run in duplicate. The mean and percent error for each set are presented in Table 4. Table 5 presents the experimental results in terms of units of vapor flux. Figures 5 to 10 graphically present these data.

A mass balance for each case was attempted by comparing total nanograms of DBCP recovered (total ng volatilized + total ng in residual solution) to the total nanograms of DBCP supplied initially to the system (Table 6, Fig. 11). The values presented in Table 6 have not been corrected for recovery efficiency in this report. Also, nondetectable concentrations were assumed to be zero for the calculation of mass balance. These two factors adversely affected percent recovery in all cases.

In general, flux from the system was highest during the first time increment, decreasing exponentially throughout the duration of the experiment. Thus, the curves for cumulative nanograms (plotted on semi-log paper) increased exponentially, flattening with increasing time. It is apparent from the analysis of the residual solutions that, for each case, more

TABLE 4. DBCP VOLATILES RECOVERED FROM WATER FOR VARIOUS TIME INTERVALS AND CONCENTRATION OF RESIDUAL SOLUTION

CONDITIONS			VOLATILES RECOVERED (ng)												RESIDUAL SOLUTION		
Temp. (°C)	Conc.* (ppm)	Air Flow Rate (ml/ min)	30 min			1 hr			2 hr			3 hr			Mean No. 1 No. 2 (ng/ml)	% Error	Mean Vol. Rcvd. (ml)
			No. 1 No. 2	Mean	% Error	No. 1 No. 2	Mean	% Error	No. 1 No. 2	Mean	% Error	No. 1 No. 2	Mean	% Error			
23	0.35	250	1134 1734	1434	41.8	723.5 1130.0	926.75	43.8	813.9 693.0	753.45	16.0	345.7 337.0	341.35	2.5
23	0.35	500	1264 1699	1481.5	29.3	767.9 1536	1152	66.7	397.1 1436	916.5	113.3	117.8 495.2	306.5	123.1	19.0
23	0.35	100	340.5 97.0	218.8	111.3	395.6 627.2	511.4	45.3	190.9 401.1	296.0	71.0	119.1 127.8	123.5	7.0	20.5	33.0	19.5
23	35.0	250	189 800 151 000	170 400	22.7	79 210 64 430	71 820	20.6	63 960 61 300	62 630	4.2	35 730 30 170	32 950	16.9	1 422	8.5	19.0
23	0.0035	250	12.28 7.55	9.92	47.7	6.43 3.01	4.72	72.5	ND [†] ND	ND	...	ND ND	ND	ND	...	19.0
33	0.35	250	882.2 1432	1157.1	47.5	218.2 113.8	166.0	62.8	125.1 106.1	115.6	16.4	31.2 22.9	27.05	30.6	ND	...	17.3
43	0.35	250	549.2 949.4	749.3	53.4	80.4 97.2	88.8	18.9	11.0 22.4	16.7	68.3	3.1 8.9	6.0	96.7	ND	...	15.3

*Initial solution volume, 20 ml.

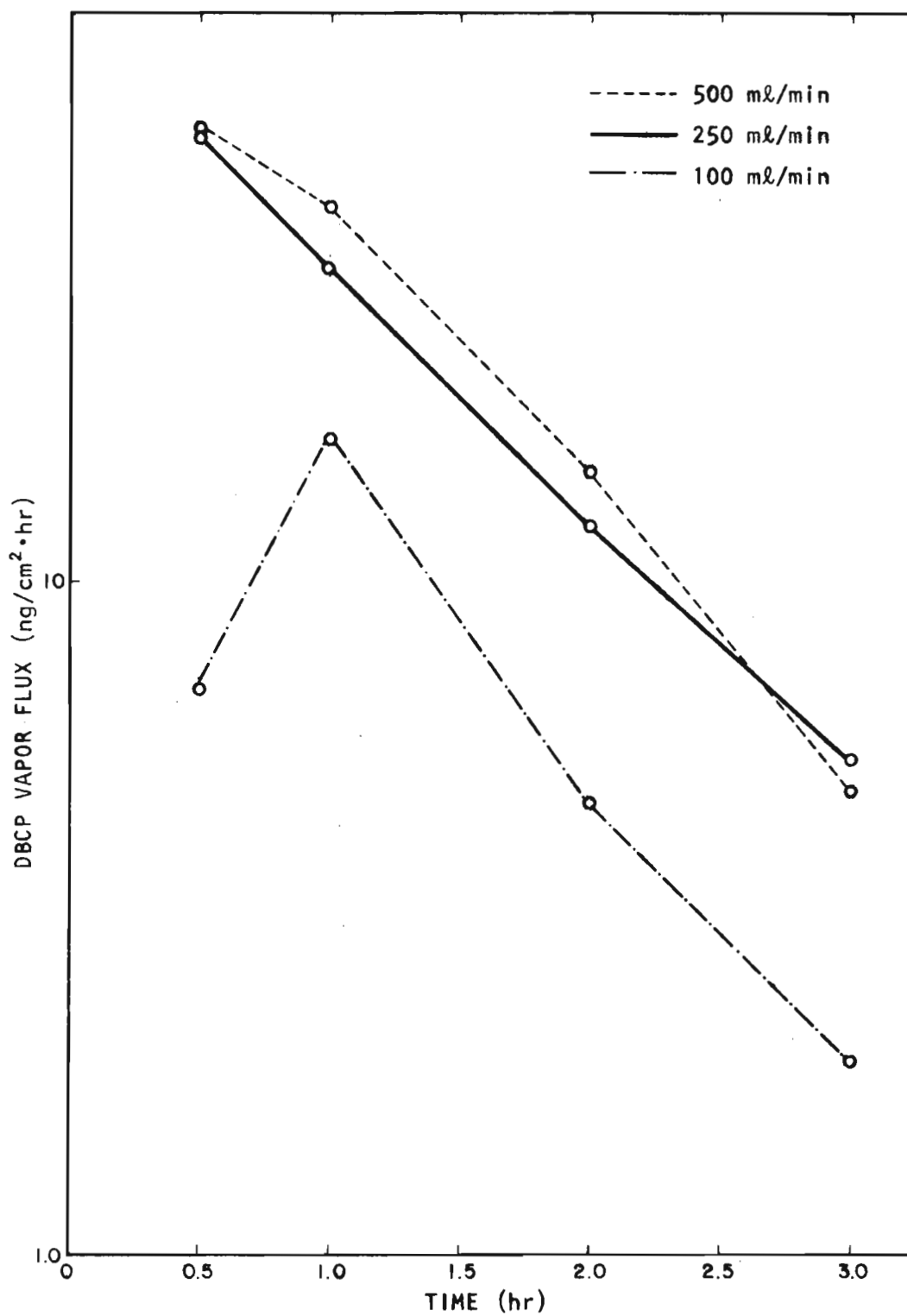
†Nondetectable.

TABLE 5. VAPOR FLUX OF DBCP FROM WATER FOR VARIOUS TIME PERIODS

CONDITIONS			VAPOR FLUX (ng/hr/cm ²)*							
Temp. (°C)	Conc. (ppm)	Air Flow Rate (mL/min)	30 min		1 hr		2 hr		3 hr	
			No. 1 No. 2	Mean	No. 1 No. 2	Mean	No. 1 No. 2	Mean	No. 1 No. 2	Mean
23	0.35	250	35.64 54.51	45.08	22.75 35.52	29.14	12.79 10.90	11.85	5.43 5.30	5.37
23	0.35	500	39.74 53.41	46.58	24.14 48.29	36.22	6.24 22.57	14.41	1.85 7.78	4.82
23	0.35	100	10.71 3.05	6.88	12.44 19.72	16.08	3.00 6.30	4.65	1.87 2.01	1.94
23	35.0	250	5967 4749	5358	2490 2026	2258	1005 963.6	984.3	561.7 474.3	518.0
23	0.0035	250	0.39 0.24	0.32	0.20 0.09	0.15	ND [†] ND	ND	ND ND	ND
33	0.35	250	22.73 45.01	33.87	6.86 3.58	5.22	1.97 1.67	1.82	0.49 0.36	0.43
43	0.35	250	17.27 29.85	23.56	2.53 3.05	2.79	0.17 0.35	0.26	0.05 0.14	0.10

*Petri dish radius: $r = 4.5$ cm
 $A = \pi r^2 = 63.62$ cm².

[†]Nondetectable.



NOTE: In ml/min of air over water surface.

Figure 5. DBCP volatilization flux from water for three rates of air flow

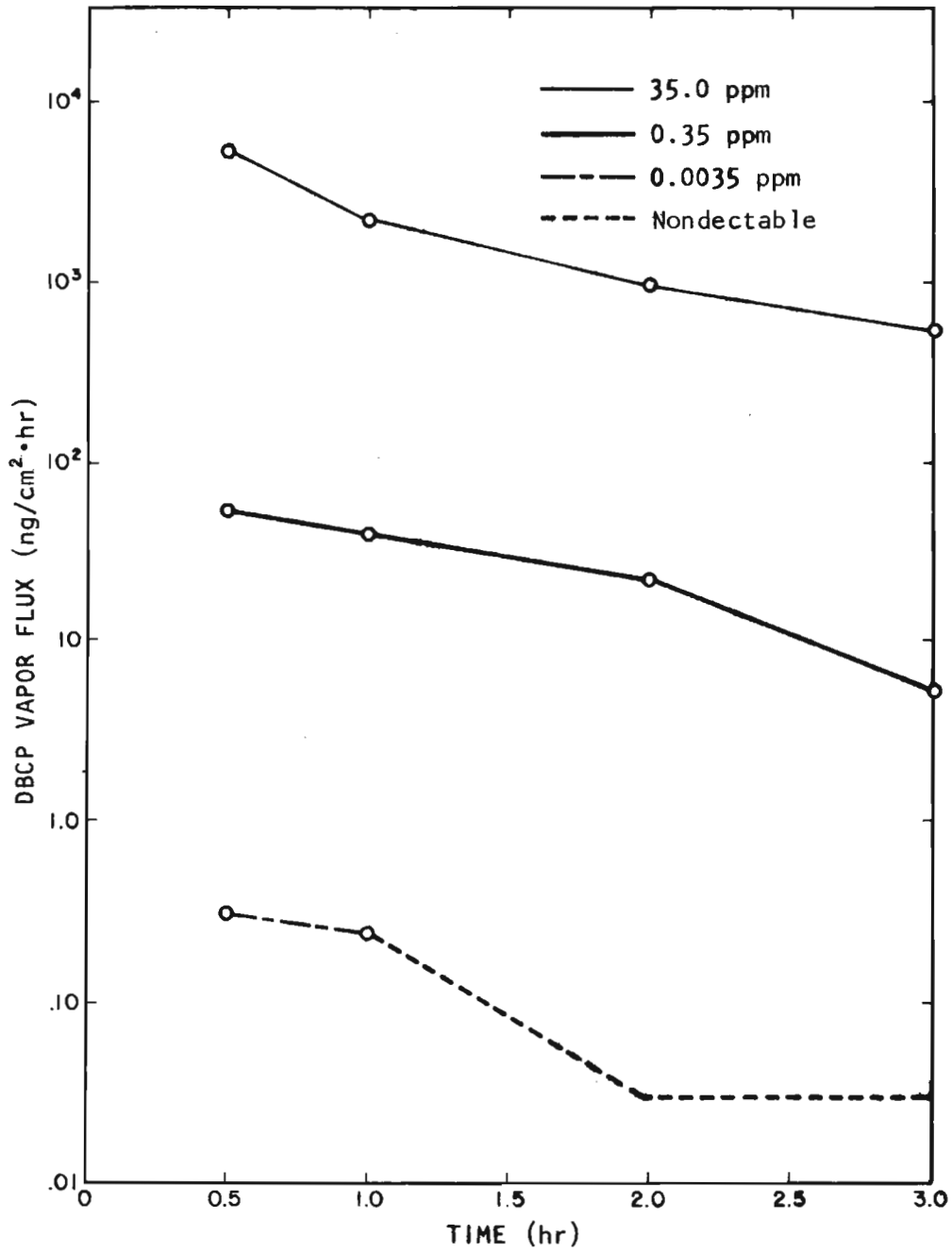


Figure 6. DBCP volatilization flux from water with three initial concentrations

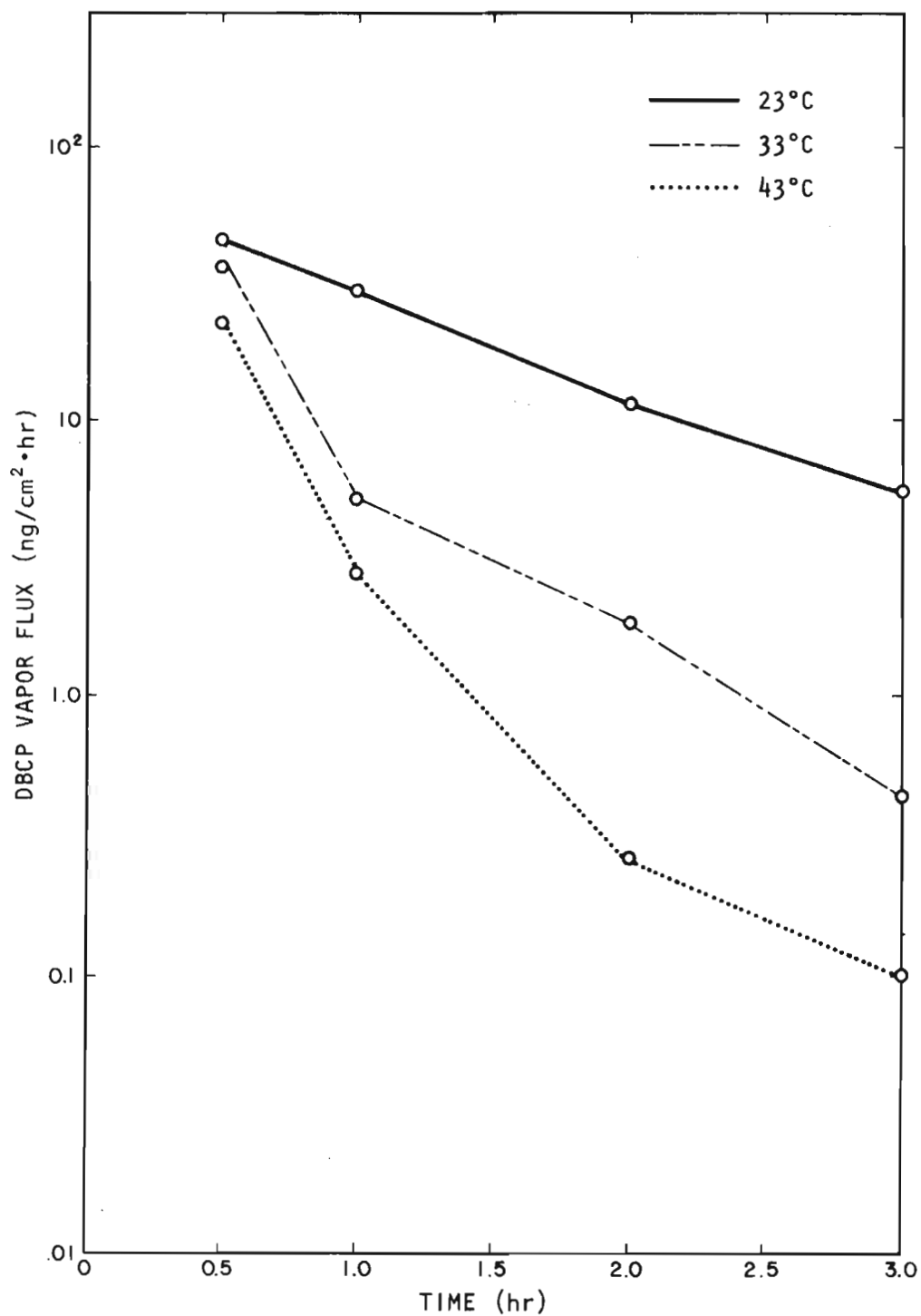


Figure 7. DBCP volatilization flux from water with three temperatures

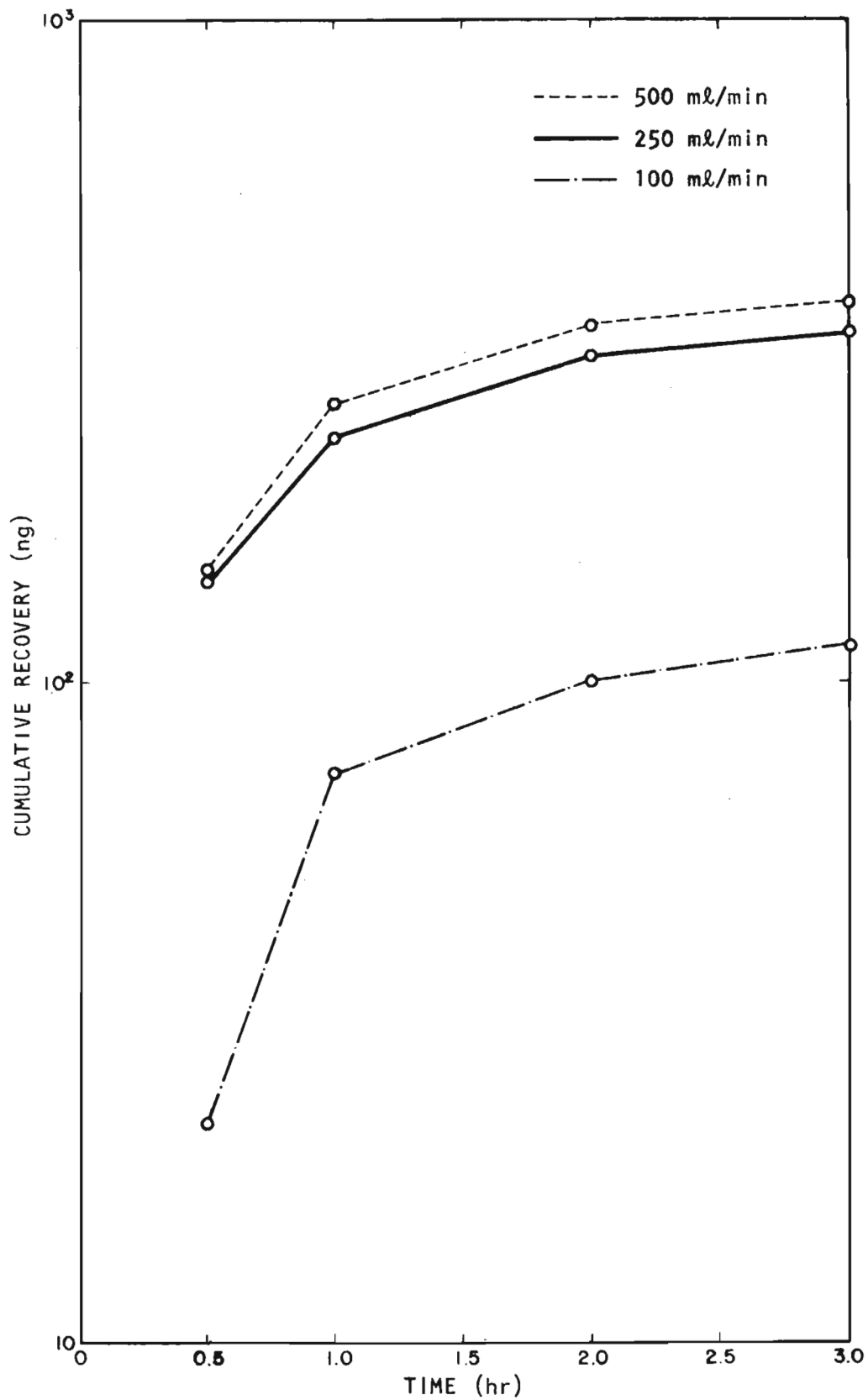


Figure 8. Cumulative recovery of DBCP volatilized from water with three rates of air flow

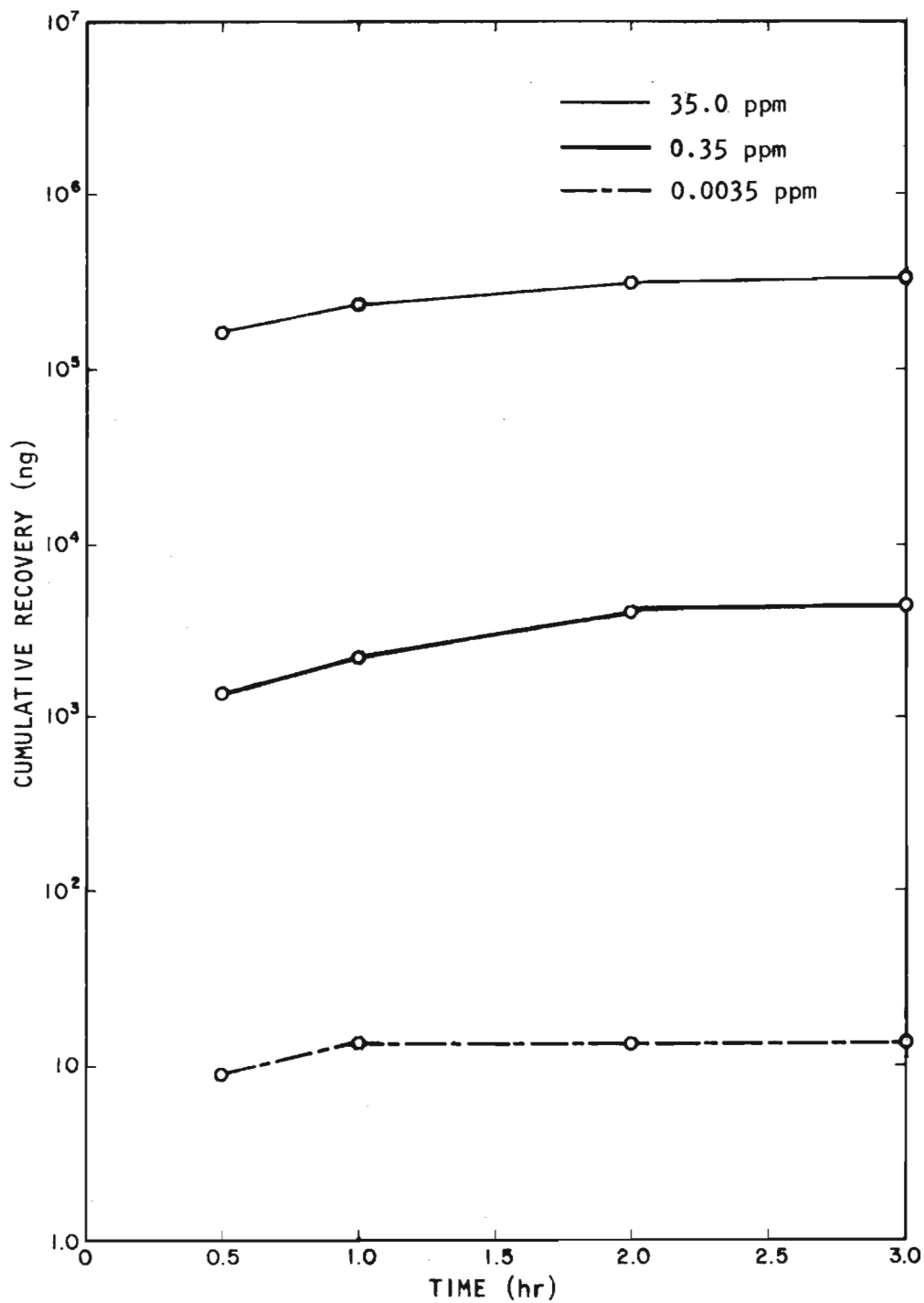


Figure 9. Cumulative recovery of DBCP volatilized from water with three initial concentrations

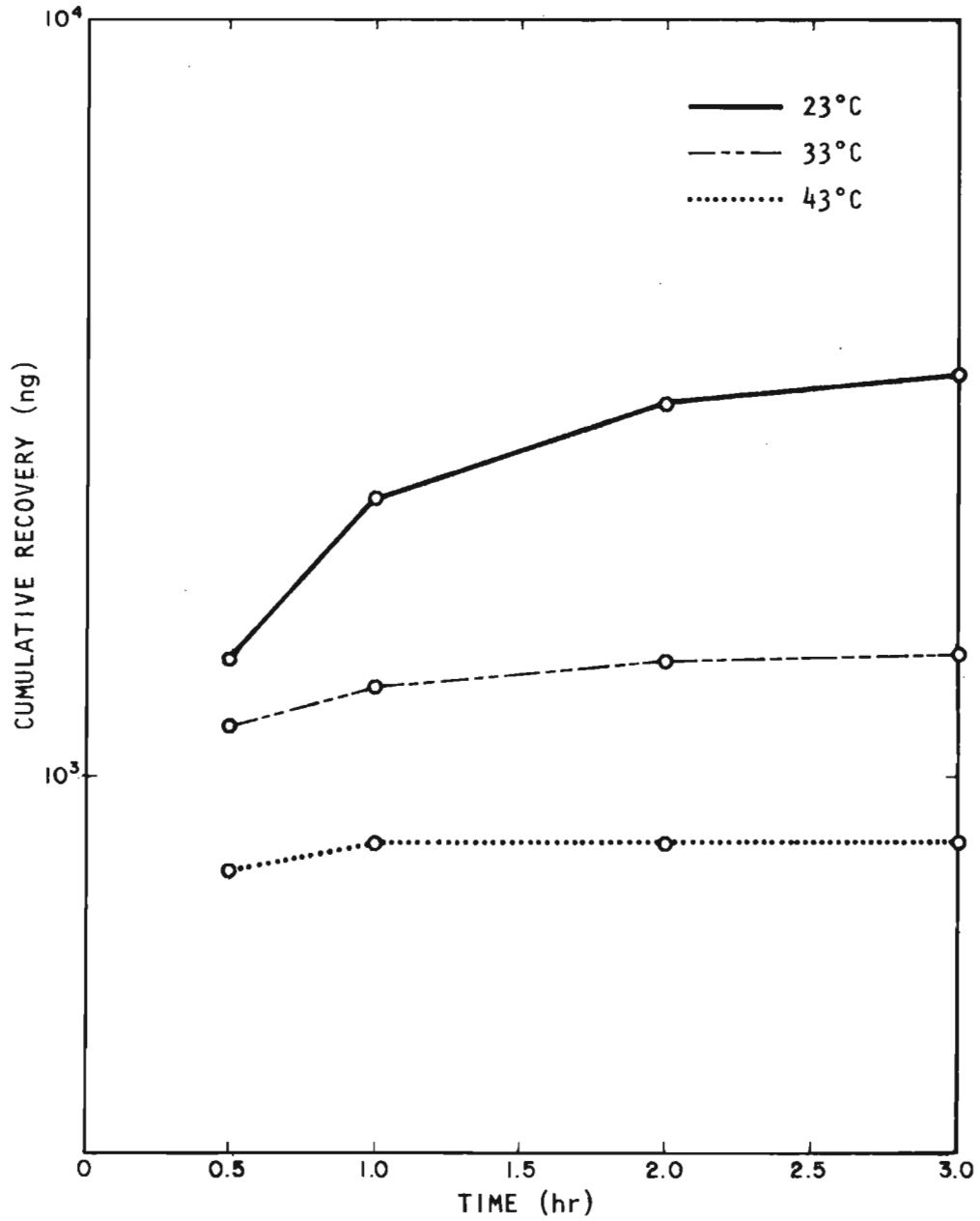
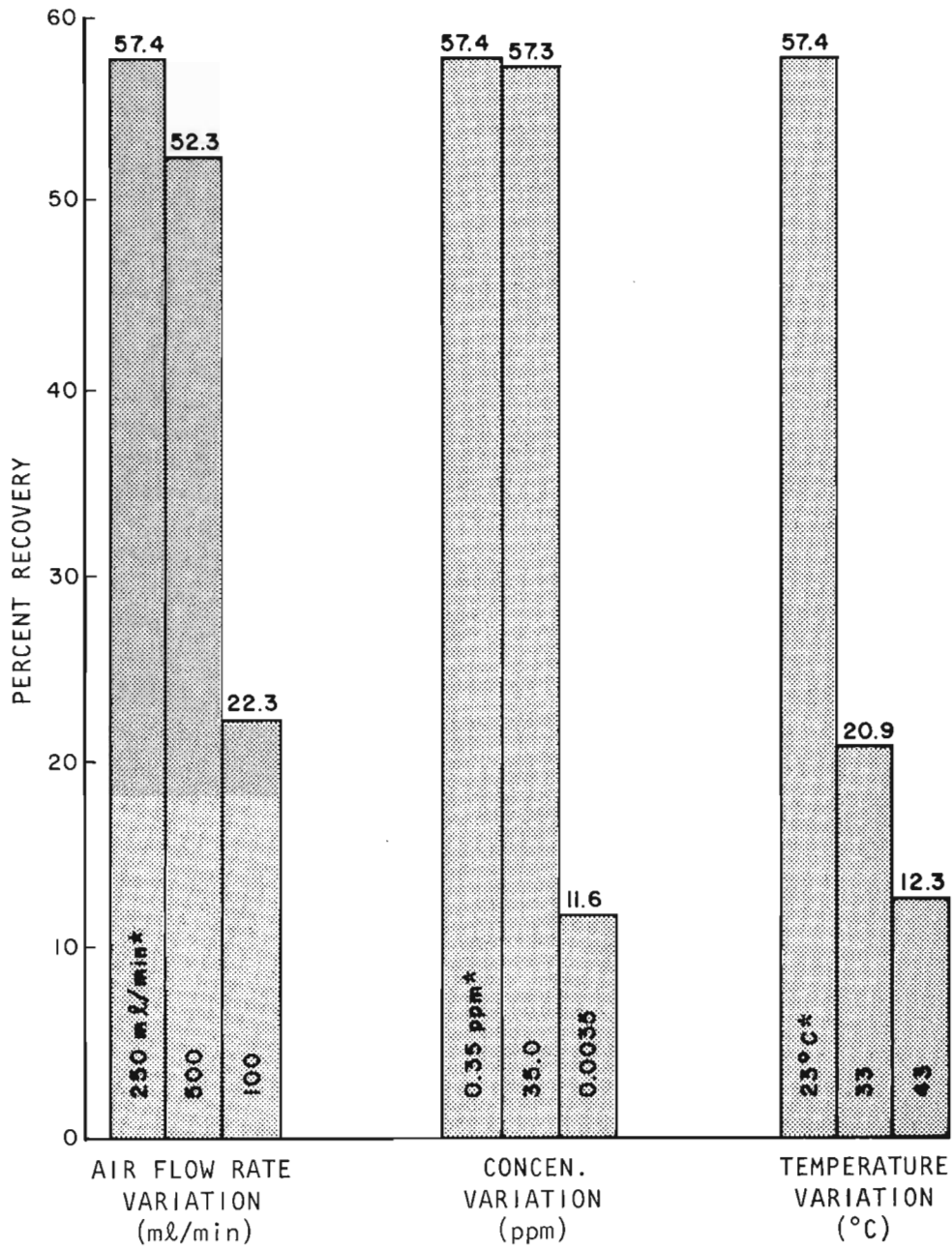


Figure 10. Cumulative recovery of DBCP volatilized from water with three temperatures

TABLE 6. CUMULATIVE DBCP VOLATILES RECOVERED FROM WATER FOR VARIOUS TIME INTERVALS AND MASS BALANCE ANALYSIS

CONDITIONS			CUMULATIVE VOLATILES RECOVERED (ng)								RESIDUAL SOLUTION		MEAN MASS BALANCE	
Temp. (°C)	Conc. (ppm)	Air Flow Rate (ml/min)	30 min		1 hr		2 hr		3 hr		No. 1 No. 2	Mean Total ng Rcvrd.	(Volatile + Resid.) Initial (ng)	% Recov- ered
			No. 1 No. 2	Mean	No. 1 No. 2	Mean	No. 1 No. 2	Mean	No. 1 No. 2	Mean				
23	0.35	250	1 134	1 434	1 857	2 361	2 671	3 114	3 017	3 456	533.9	3 989	57.0
			1 734		2 864		3 557		3 894		28.1		7 000	
23	0.35	500	1 264	1 467	2 032	2 634	2 429	3 550	2 547	3 857	ND*	144.0	4 001	57.2
			1 669		3 235		4 671		5 166		15.2		7 000	
23	0.35	100	340.5	218.8	736.1	730.2	927.0	1 026	1 046	1 150	23.9	399.8	1 550	22.1
			97.0		724.2		1 125		1 253		17.1		7 000	
23	35.0	250	189 800	170 400	269 000	242 250	333 000	304 900	368 700	337 900	1361	27,010	364 800	52.1
			151 000		215 500		276 800		307 000		1482		700 000	
23	0.0035	250	12.28	9.92	18.71	14.64	18.71	14.64	18.71	14.64	ND	ND	14.64	20.9
			7.55		10.56		10.56		10.56		ND		70	
33	0.35	250	882.2	1 157	1 100	1 323	1 226	1 439	1 257	1 466	ND	ND	1 466	20.9
			1 432		1 546		1 652		1 675		ND		7 000	
43	0.35	250	549.2	749.3	629.6	838.3	640.6	854.8	643.7	860.9	ND	ND	860.8	12.3
			949.4		1 047		1 069		1 078		ND		7 000	

*Nondetectable.



NOTE: Data uncorrected for analytical recovery efficiency. Nondetectable values assume to be zero; ∴ both factors contribute to lowered percent recovery in all cases.

*Base condition.

Figure 11. Mass recovery of DBCP volatilized under various environmental conditions

than 90% of the initial DBCP present in the solution volatilized in the 3-hr test period.

For base conditions (presented in Figs. 5-10 for comparison purposes), the distribution was as expected, with the greatest amount of DBCP volatilizing in the first 30 min, followed by stepwise decreases in the amount captured per time period. Fifty-seven percent of the DBCP placed in the system was accounted for in the mass balance (Table 6, Fig. 11).

AIR FLOW RATE. Air flow rate was the first parameter to be varied in this phase of the study (Fig. 5). When the air flow rate was doubled to 500 ml/min from the base condition, very little difference in final results was observed. Recovery was slightly higher for the first three time-increments, and slightly lower for the fourth (Table 4). The 500-ml/min run showed increasing percent error with each subsequent collection time compared to a basic decrease in percent error with time in the 250-ml/min case.

When the air flow rate was lowered to 100 ml/min, the results varied significantly from the 250- and 500-ml/min cases (Fig. 5). The DBCP mass recovered in the first 30 min was approximately one-seventh of that recovered in the 250- and 500-ml/min runs (Table 4). This recovery increased to approximately one-half of that achieved in the 250 and 500 ml/min air flow rate experiments for the remaining time increments. No particular trend in percent error with time was demonstrated. Only 19.5% of the initial DBCP placed in the petri dish could be accounted for in this experiment (Table 4). In the 100-ml/min case, DBCP was assumed to have escaped from the system because the air flow rate was insufficient to capture all the DBCP as it volatilized. This argument is supported by the small amount of DBCP captured in the first 30 min, followed by the much greater amount captured in the second 30 min. Significant vapor loss from the system seems highly possible. These results suggest the need for air movement of sufficient rate to insure the transfer of DBCP vapor from the source into the recovery system. A more desirable alternative

would be to use a closed system, thereby preventing DBCP loss, regardless of the air flow rate used.

INITIAL SOLUTION CONCENTRATION. The second parameter to be varied was the initial concentration of the DBCP solution (Fig. 6). Concentrations two orders of magnitude above and below the base conditions were tested. Total recovery for the 35.0-ppm solution was 52.1% (Table 6), only slightly less than that achieved with base conditions. The pattern of recovery closely parallels that of the base conditions, both showing an exponential decrease with time.

The initial concentration was then lowered to 0.0035 ppm. For the last two time increments of this run, as well as for the residual solution, concentrations of the DBCP in solvent analyzed were below the detection limit of the gas chromatograph used in this study. Non-detection of DBCP in these samples might help explain the poor mass balance results at this concentration. If these undetectable concentrations are assumed to be zero, total recovery for the run was only 20.9% (Table 6). The low percent recovery might also be attributable to some systematic loss, such as DBCP adsorption to the apparatus. Such a loss may have occurred for all runs, but would have only proven significant at such low concentrations.

The concentration variation segment of this study indicated that as concentration was increased, so was the precision of the capture and recovery of the pesticide. This relationship is graphically shown in Figure 12. Figure 13 is taken from the American Chemical Society's 1981 Symposium Series No. 160, and although not directly comparable to Figure 12, it clearly illustrates the problem of decreasing certainty with decreasing concentration.

TEMPERATURE. The third parameter varied was temperature (Fig. 7). Two higher temperatures, 33 and 43°C, were tested in addition to the baseline temperature of 23°C. In both cases of increased temperature, the recovery efficiency dropped considerably. Only 20.9% of the original 7 000 ng was recovered in the 33°C run, and 12.3% in the 43°C run

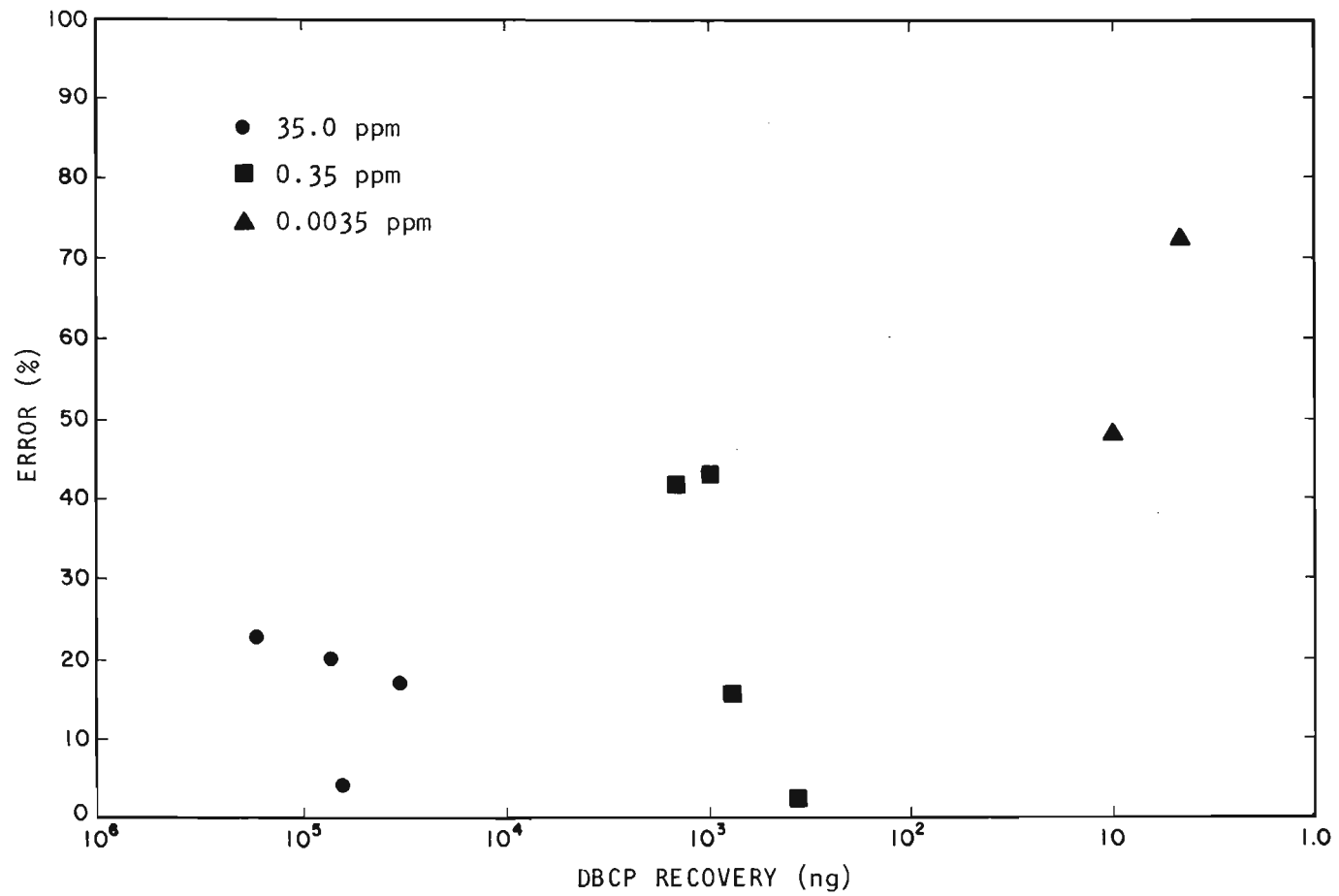
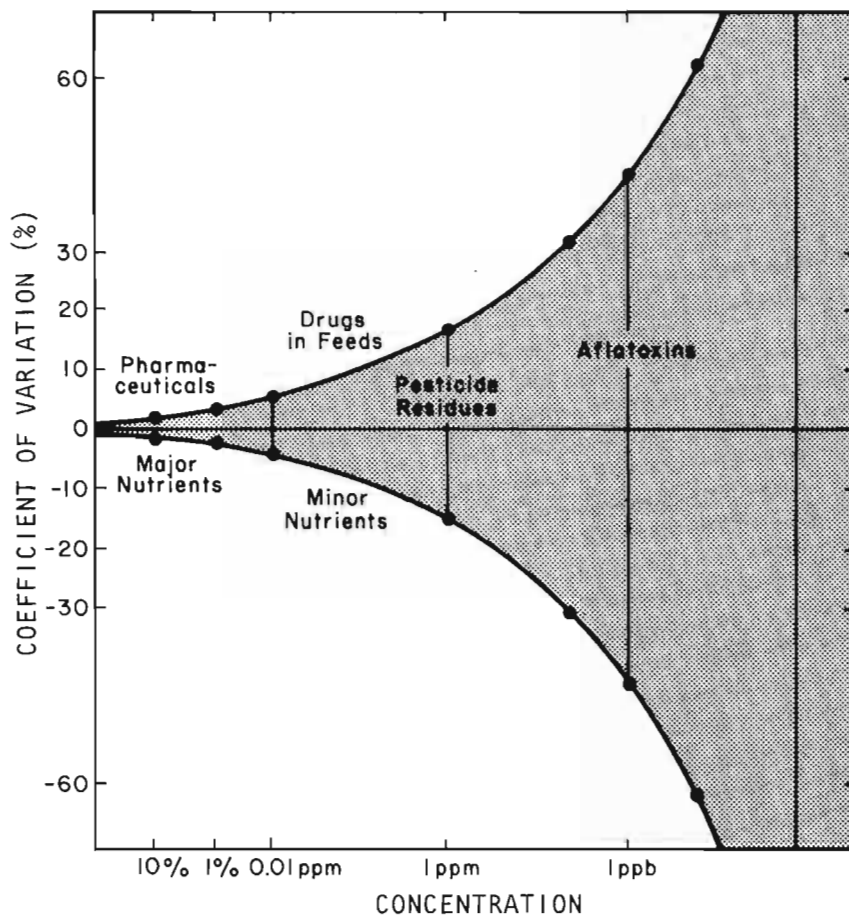


Figure 12. Error analysis vs. DBCP recovery



SOURCE: American Chemical Society Symposium Series (1981) No. 160.

Figure 13. Coefficient of variation for inter-laboratory analytical results as a function of initial concentration

(Table 6). The decrease in the recovery efficiency is probably the result of extreme vapor flux from these increases in temperature. The loss of DBCP is extremely rapid, either through the volatile trap itself, or to the open air before reaching the collection apparatus. The patterns of recovery for the higher temperature run roughly parallel to those of the baseline conditions, although mass values are consistently lower for each time increment as temperature is increased. Percent error for each time increment increased with rising temperature in all cases except for 43°C at 1 hr (Table 4). This indicated a decrease in the precision of the capture and

recovery of the pesticide with increasing temperature.

EVALUATION OF SOLUTION CONCENTRATION EFFECT IN RELATION TO HENRY'S LAW. Henry's law is assumed valid if, for equilibrium conditions at a given temperature, the ratio of the concentration of a given constituent in the vapor phase to the concentration of the same constituent in the liquid phase remains constant for any liquid concentration. Examining the application of Henry's law to dynamic conditions is important for the concentration range in question if Henry's constant is to be used in calculations of a predictive nature.

The results of the concentration variation portion of the preliminary study reported above indicate a direct relationship between liquid concentration and DBCP vapor loss from the liquid (Table 7). By dividing the total nanograms per milliliter of air for the first 30 min of the experiment by the mean concentration of the liquid for the same time period, the ratio of the average gas phase concentration to the average solution phase concentration is obtained. The approximate equality of these ratios implies that Henry's law is approximately valid for the concentration range in question. It is suspected that the value for the 0.0035-ppm run (3.5 ng/ml) would be closer if the recovery efficiency for the run were improved.

A more conclusive investigation of vapor loss from water at three solution concentrations was conducted utilizing the apparatus designed for the volatilization from soil described on pages 21 to 24. Fifty milliliters of DBCP-water solution were placed in the cell, using only a single center section whose chamber volume was 60 cm³, and an air flow rate of 250 ml/min was applied for 30 min. Laboratory temperature remained at 23°C±2°C. Initial and residual solutions were tested for DBCP concentration. Results of this experimentation are presented in Table 8. By again dividing the total nanograms per milliliter of air for the 30-min experiment by the mean concentration of the liquid for the same time period, the constancy of the ratio of vapor loss to solution concen-

TABLE 7. VOLATILIZATION OF DBCP FROM WATER: PRELIMINARY EXPERIMENT

SOLUTION PHASE		VAPOR PHASE		RATIO <u>DBCP Conc. in Vapor</u> <u>DBCP Conc. in Solution</u>
Initial Concn. (ng/ml)	Corrected Mean Conc.* (ng/ml)	Cum. Loss to Air in 30 min (ng)	Concentration in Air [†] (ng/ml)	
3.5	2.62	9.92	1.32×10^{-3}	5.00×10^{-4}
350	262.2	1,434	191.2×10^{-3}	7.29×10^{-4}
35 000	26 220	170 400	$22 720 \times 10^{-3}$	8.67×10^{-4}
Mean				6.99×10^{-4}

NOTE: Preliminary experiment using apparatus shown in Fig. 2.

*Corrected for extraction and distillation efficiency (82.4% recovery) and for solution concentration decrease. A 10% decrease in solution concentration for first 30 min assumed (based on Table 8 data); therefore corrected value is $(x/1.1)(0.824)$ where x is initial solution concentration.

[†]Average concentration for 30-min period with 250 ml/min air flow.

tration was evaluated.

Table 9 summarizes the vapor phase to solution phase ratios obtained under dynamic (non-equilibrium) conditions. The mean ratio was 6.96×10^{-4} (ng/ml air)/(ng/ml water). Thomas (1982) discusses a method of approximating Henry's constant by dividing the vapor pressure (atm) of the substance in question by the solubility (mol/m³) of that substance. Using the Thomas method, the approximate Henry's constant for DBCP is 3.56×10^{-4} (atm-m³)/mol or 1.48×10^{-2} (ng/ml vapor)/(ng/ml liquid). The lower value of the ratio obtained experimentally relative to the theoretical Henry's constant is not surprising due to the dynamic nature of vaporization associated with the high air flow rate of the experiments. The relative constancy of the experimentally measured ratio suggests the applicability of Henry's constant to modeling efforts.

In the section on Experimental Techniques (p. 17), the high vapor pressure of DBCP in relation to other selected pesticides was discussed. Figure 14 (Thomas 1982) plots the vapor pressure of selected chemicals vs. solubility, resulting in the Thomas approximation of Henry's constant. Other chemi-

TABLE 8. VOLATILIZATION OF DBCP FROM WATER: CONCENTRATION DEPENDENCE OF THE RATIO OF VOLATILIZED DBCP TO SOLUTION PHASE DBCP

WATER PHASE			VAPOR PHASE		DBCP RATIO (ng/ml Air)/ (ng/ml H ₂ O)	MASS BALANCE				
Initial	Final (ng/ml)	Mean	ng in 30 min	ng/ ml Air [†]		Initial Solution	Final Solution [‡]	Final Volatilized (ng)	Final Total	% Re- covery
234.9	229.4	232.2	1 117	0.149	6.42×10^{-4}	17 500	11 470	1 117	12 587	71.9
2 884*	2 264	2 574	13 570	1.809	7.03×10^{-4}	175 000	113 200	13 570	126 770	72.4
30 680	25 060	27 870	154 300	20.570	7.38×10^{-4}	1 750 000	1 253 000	154 300	1 407 300	80.4
Mean					6.94×10^{-4}					74.3

NOTE: Experiment conducted with apparatus shown in Fig. 3.

*Sample lost; extrapolated value used.

[†]250 ml/min air flow rate used.

[‡]50 ml.

TABLE 9. SUMMARY OF RATIOS OF VOLATILIZED DBCP TO SOLUTION DBCP OBTAINED UNDER NON-EQUILIBRIUM CONDITIONS

INITIAL SOLUTION CONCENTRATION (ng/ml)	RATIO Conc. in Vapor/ Conc. in Liquid
2.88*	5.00×10^{-4}
234.9†	6.40×10^{-4}
288.4*	7.29×10^{-4}
2,884†	7.03×10^{-4}
28,840*	8.67×10^{-4}
30,680†	7.38×10^{-4}
Mean	6.96×10^{-4}

*Water phase apparatus values corrected for extraction and distillation efficiency (82.4%).

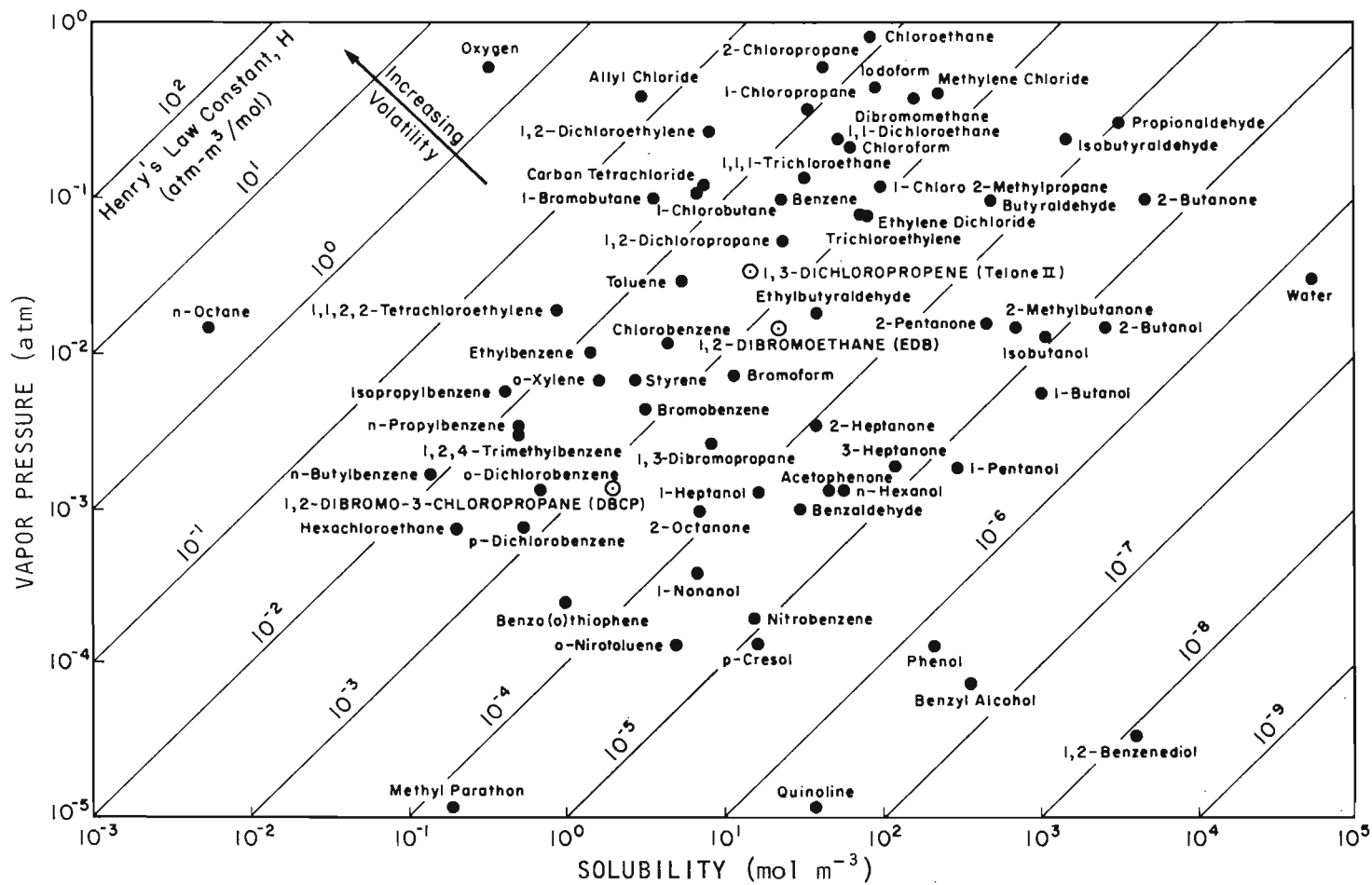
†Measured soil phase apparatus values.

cals pertinent to the current O'ahu groundwater situation have been added to the Thomas illustration.

Although their vapor pressures and solubilities differ, DBCP and EDB (1,2-dibromoethane) have almost identical values for the Thomas approximation of Henry's constant. Therefore, these substances could be expected to volatilize from water to the same extent. The Thomas approximation of Henry's law was determined for Telone II (1,3-dichloropropene) by utilizing vapor pressure and solubility data taken from the Farm Chemicals Handbook.* The H' value thus determined for 1,3-dichloropropene, 4.05×10^{-3} atm-m³/mol, was added to Figure 14. Telone II is currently used as a soil fumigant and will be increasingly important as a pineapple nematicide in Hawai'i. Based on the above approximation, Telone II shows an order of magnitude of higher volatility than DBCP and EDB, thereby posing less of a threat to groundwater quality.

SUMMARY. The air flow rate portion of this study clearly indicated the need for a closed system to prevent vapor loss

*1983 (Willoughby, Ohio: Meister Publishing).



SOURCE: Thomas (1982).

Figure 14. Solubility, vapor pressure, and Henry's law constant for selected chemicals

at low air flow rates. A closed system was utilized for the volatilization from soil phase of this study. This variation also demonstrated that air flow rates in excess of that required to maintain low vapor densities at the air-water interface do not significantly affect the vapor flux from the system. Because no significant improvement in collection efficiency was noted by raising the air flow rate from 250 to 500 ml/min, the lesser value was used for the volatilization from soil phase of this study.

The concentration variation portion of this study first pointed out the inability of the gas chromatograph employed to detect DBCP solution concentrations lower than approximately 2 ppb. The parallel results of the 0.35- and 35.0-ppm studies imply that flux increases proportionately to increases in concentration. The validity of Henry's law was shown for the concentration range selected for this study when the water and soil phase apparatuses were used. In comparing percent recovery for the water- and soil-phase apparatuses used in verifying Henry's law, a 30% difference was noted in the 35.0-ppm portion of the study. The water phase apparatus recovered only 50% of the original mass, whereas the 80% recovery by the soil phase apparatus demonstrated the superior efficiency of a closed system.

The temperature variation demonstrated the more extreme vapor flux rates incurred at higher temperatures from the system. Much of the DBCP added initially to the system was undoubtedly lost either through the volatile trap itself or to the atmosphere before reaching the collection apparatus. Because all the temperature curves are generally parallel, flux is assumed to increase in proportion to temperature increase.

Volatilization from Soil

The effects of variation in initial soil water content, the addition of a soil cover layer, and variation in soil type were investigated. The volatilization rate and the DBCP dis-

tribution in the soil column were examined.

Each experimental variation was conducted in duplicate. The mean and percent error for each data set are presented in Tables 10 through 15. For the soil phase apparatus, precision was generally markedly improved over that for the apparatus used in preliminary experiments.

A mass balance was computed for each case. Percent recovery for the soil phase apparatus was significantly improved over that for the water phase apparatus. Mass balance was calculated for two initial concentrations of DBCP in the soil: first, using experimentally measured values for initial soil concentration; and second, using the known volume of DBCP solution and the measured concentration of the applied solution to calculate the initial soil concentration. It was thought that measured initial soil concentrations could be lower than the actual initial concentration value for the soil packed into the cells because of DBCP volatile losses from the soil during packing of the cell and during storage before analysis. After the cells were packed, the remaining treated soil was kept in a covered jar, with a substantial head space above the soil, while the cells were secured and attached to the trapping system. As the volatile results will show, flux of DBCP from treated soil is highest during the time period immediately following application. Significant volatilization (1-30%) could have occurred during the time the sample was unattended, thus lowering the initial soil concentration values. Theoretical initial concentration values were calculated assuming (1) a homogeneous application of a known mass of DBCP and (2) a recovery efficiency of 78.6% (extrapolated from distillation control recovery efficiency for the soil phase). The true initial soil concentration undoubtedly lies between the theoretical and measured values--probably much closer to the theoretical concentration.

Effects of Experimental Variations

INITIAL SOIL WATER CONTENT VARIATION. For this phase, only the Wahiawa soil (Tropeptic Eustrtox) of the Oxisol

TABLE 10. DBCP SOIL CONCENTRATION AND VOLATILIZATION RATES AT
2.3% INITIAL SOIL WATER CONTENT FOR WAHIAWA SOIL

DBCp IN SOIL										DBCp VOLATILIZED									
Depth (cm)	Initial				Depth (cm)	Final				Day	Hr	Volatilization Rate			Flux				
	No. 1	No. 2	Mean	%		No. 1	No. 2	Mean	%			No. 1	No. 2	Mean	No. 1	No. 2	Mean	%	
	(ng/cm ³)					(ng/cm ³)						(ng/hr)			(ng/hr/cm ²)				
				Error					Error									Error	
0-2	253.7	271.8	262.8	6.9	0-2	52.4	57.2	54.8	8.8	1	0-1	383.1	335.2	359.2	12.77	11.17	11.97	13.4	
2-4	253.7	271.8	262.8	6.9	2-4	*	233.0	233.0 [†]	...		1-2	315.2	391.0	353.1	10.51	13.03	11.77	21.5	
4-6	253.7	271.8	262.8	6.9	4-6	418.7	400.8	409.8	4.4		2-3	346.5	348.4	347.5	11.55	11.60	11.58	0.4	
6-8	253.7	271.8	262.8	6.9	6-8	339.0	313.6	326.3	7.8		3-4	339.3	267.4	303.4	11.31	8.91	10.11	23.7	
8-10	253.7	271.8	262.8	6.9	8-10	382.1	†	382.1 [†]	...	2	0-2	124.6	115.1	119.9	4.15	3.84	4.00	7.8	
SOIL CHARACTERISTICS: Wahiawa (Tropeptic Eutrustox; Oxisol)										3	0-2	128.2	117.1	123.0	4.27	3.90	4.09	9.0	
Bulk Density (g/cm ³)... 1.05					Initial Soil Water					4	0-2	95.0	75.2	85.1	3.17	2.51	2.84	23.2	
Organic Matter					Content (cm ³ /cm ³)... 2.3					5	0-2	87.1	69.9	78.5	2.90	2.33	2.62	21.8	
Content (%)..... 2.6																			

*No. 2 value used for total residual value.

[†]No. 1 value used for total residual value.

[‡]Single analysis used as mean.

TABLE 11. DBCP SOIL CONCENTRATION AND VOLATILIZATION RATES AT
8.5% INITIAL SOIL WATER CONTENT FOR WAHIAWA SOIL

DBCp IN SOIL										DBCp VOLATILIZED									
Depth (cm)	Initial				Depth (cm)	Final				Day	Hr	Volatilization Rate			Flux				
	No. 1	No. 2	Mean	%		No. 1	No. 2	Mean	%			No. 1	No. 2	Mean	No. 1	No. 2	Mean	%	
	(ng/cm ³)					(ng/cm ³)						(ng/hr)			(ng/hr/cm ²)				
				Error					Error									Error	
0-2	251.4	275.1	263.3	9.0	0-2	57.0	40.8	48.9	33.1	1	0-2	1227	1301	1264	40.89	43.37	42.13	5.8	
2-4	251.4	275.1	263.3	9.0	2-4	117.9	156.4	137.2	28.1		2-4	642.5	849.3	745.9	21.42	28.31	24.87	27.7	
4-6	251.4	275.1	263.3	9.0	4-6	245.2	215.2	230.2	13.0		8-10	502.3	446.9	474.6	16.74	14.90	15.82	11.6	
6-8	251.4	275.1	263.3	9.0	6-8	281.7	283.4	282.6	0.6	2	0-2	216.8	212.7	214.8	7.23	7.09	7.16	2.0	
8-10	251.4	275.1	263.3	9.0	8-10	306.7	275.5	291.1	10.7	3	0-2	130.8	129.8	130.3	4.36	4.33	4.35	0.7	
SOIL CHARACTERISTICS: Wahiawa (Tropeptic Eutrustox; Oxisol)										4	0-2	154.9	141.0	148.0	5.16	4.70	4.93	9.3	
Bulk Density (g/cm ³), No. 1... 1.08					Initial Soil Water					5	0-2	107.9	98.7	103.3	3.60	3.29	3.45	9.0	
No. 2... 1.01					Content (cm ³ /cm ³)... 8.5					6	0-2	93.5	97.4	95.5	3.12	3.18	3.15	1.9	
Organic Matter Content (%).... 2.6																			

TABLE 12. DBCP SOIL CONCENTRATION AND VOLATILIZATION RATES AT 8.6% INITIAL SOIL WATER CONTENT FOR UNTREATED TOP LAYER OF WAHIAWA SOIL

DBCP IN SOIL										DBCP VOLATILIZED								
Depth (cm)	Initial				Depth (cm)	Final				Volatilization Rate				Flux				
	No. 1	No. 2	Mean	% Error		No. 1	No. 2	Mean	% Error	Day	Hr	No. 1	No. 2	Mean	% Error	No. 1	No. 2	Mean
	(ng/cm ³)					(ng/cm ³)				(ng/hr)				(ng/hr/cm ²)				
0-2	1.41	1.48	1.45	4.8	0-2	46.2	50.9	48.6	9.7	1	0-2	ND*	ND	ND	ND	ND	ND
2-4	218.4	208.0	213.2	4.9	2-4	141.2	148.5	144.9	5.0		2-4	ND	ND	ND	ND	ND	ND
4-6	218.4	208.0	213.2	4.9	4-6	230.4	211.8	221.1	8.4		8-10	52.4	42.5	47.5	1.75	1.42	1.59	20.8
6-8	218.4	208.0	213.2	4.9	6-8	233.3	231.8	232.6	0.6	2	0-2	81.9	84.7	83.3	2.73	2.82	2.78	3.2
8-10	218.4	208.0	213.2	4.9	8-10	263.5	284.7	274.1	7.7		8-10	94.1	102.8	98.5	3.14	3.43	3.29	8.8
SOIL CHARACTERISTICS: Wahiawa (Tropeptic Eutrustox; Oxisol)										3	0-2	92.0	94.2	93.1	3.07	3.14	3.11	2.3
Bulk Density (g/cm ³)..... 1.06					Initial Soil Water Content (cm ³ /cm ³).... 8.6					4	0-2	82.6	80.8	81.7	2.75	2.69	2.72	2.2
Organic Matter Content (%)... 2.6										5	0-2	60.2	70.4	65.3	2.01	2.35	2.18	15.6
											8-10	81.5	87.3	84.4	2.72	2.91	2.82	6.7

*ND = Nondetectable.

TABLE 13. DBCP SOIL CONCENTRATION AND VOLATILIZATION RATES AT 13.5% INITIAL SOIL WATER CONTENT FOR WAHIAWA SOIL

DBCP IN SOIL										DBCP VOLATILIZED								
Depth (cm)	Initial				Depth (cm)	Final				Volatilization Rate				Flux				
	No. 1	No. 2	Mean	% Error		No. 1	No. 2	Mean	% Error	Day	Hr	No. 1	No. 2	Mean	% Error	No. 1	No. 2	Mean
	(ng/cm ³)					(ng/cm ³)				(ng/hr)				(ng/hr/cm ²)				
0-2	249.0	266.9	258.0	6.9	0-2	47.6	51.2	49.4	7.3	1	0-2	1622	1647	1635	54.07	54.89	54.48	1.5
2-4	249.0	266.9	258.0	6.9	2-4	140.4	128.5	134.5	8.8		2-4	767.2	791.8	779.5	25.57	26.39	25.98	3.2
4-6	249.0	266.9	258.0	6.9	4-6	213.7	182.4	198.1	15.8		8-10	504.0	483.6	493.6	16.80	16.12	16.46	4.1
6-8	249.0	266.9	258.0	6.9	6-8	252.0	218.2	235.1	14.4	2	0-2	226.0	211.6	218.8	7.53	7.05	7.29	6.6
8-10	249.0	266.9	258.0	6.9	8-10	261.4	235.0	248.2	10.6	3	0-2	150.8	153.6	152.2	5.03	5.12	5.08	9.5
SOIL CHARACTERISTICS: Wahiawa (Tropeptic Eutrustox; Oxisol)										4	0-2	119.4	129.7	124.6	3.98	4.32	4.15	8.2
Bulk Density (g/cm ³)..... 1.05					Initial Soil Water Content (cm ³ /cm ³).. 13.5					5	0-2	105.7	107.7	106.7	3.52	3.59	3.56	2.0
Organic Matter Content (%).. 2.6										6	0-2	94.2	97.2	95.7	3.14	3.24	3.19	3.1

TABLE 14. DBCP SOIL CONCENTRATION AND VOLATILIZATION RATES AT
31.6% INITIAL SOIL WATER CONTENT FOR WAHIAWA SOIL

DBCP IN SOIL										DBCP VOLATILIZED								
Depth (cm)	Initial				Depth (cm)	Final				Day	Hr	Volatilization Rate			Flux			
	No. 1 (ng/cm ³)	No. 2 (ng/cm ³)	Mean	%* Error		No. 1 (ng/cm ³)	No. 2 (ng/cm ³)	Mean	% Error			No. 1 (ng/hr)	No. 2 (ng/hr)	Mean (ng/hr)	No. 1 (ng/hr/cm ²)	No. 2 (ng/hr/cm ²)	Mean (ng/hr/cm ²)	% Error
0-2	203.8	162.4	183.1	22.6	0-2	24.5	22.4	23.5	8.9	1	0-2	1426	1468	1448	47.54	48.94	48.25	2.9
2-4	203.8	162.4	183.1	22.6	2-4	46.5	56.1	51.3	18.7		2-4	774.7	891.9	833.3	25.82	29.73	27.77	14.0
4-6	203.8	162.4	183.1	22.6	4-6	80.1	92.5	86.3	14.4		8-10	367.0	500.1	433.6	12.23	16.67	14.45	30.7
6-8	203.8	162.4	183.1	22.6	6-8	111.7	123.6	117.7	10.1	2	0-2	250.0	281.3	265.7	8.33	9.38	8.86	11.9
8-10	203.8	162.4	183.1	22.6	8-10	138.5	128.9	133.7	7.2	3	0-2	166.7	186.3	176.5	5.56	6.21	5.88	11.1
SOIL CHARACTERISTICS: Wahiawa (Tropoctic Eutrastox; Oxisol)										4	0-2	103.7	126.1	114.9	3.46	4.20	3.83	19.3
Bulk Density (g/cm ³), No. 1... 0.90					Initial Soil Water					5	0-2	82.6	82.6	82.6	2.75	2.75	2.75	0.0
					Content (cm ³ /cm ³)... 31.6					6	0-2	62.7	58.8	60.8	2.09	1.96	2.03	6.4
Organic Matter																		
Content (%)..... 2.6																		

TABLE 15. DBCP SOIL CONCENTRATION AND VOLATILIZATION RATES AT
29.9% INITIAL SOIL WATER CONTENT FOR MAILE SOIL

DBCP IN SOIL										DBCP VOLATILIZED								
Depth (cm)	Initial				Depth (cm)	Final				Day	Hr	Volatilization Rate			Flux			
	No. 1 (ng/cm ³)	No. 2 (ng/cm ³)	Mean	%* Error		No. 1 (ng/cm ³)	No. 2 (ng/cm ³)	Mean	% Error			No. 1 (ng/hr)	No. 2 (ng/hr)	Mean (ng/hr)	No. 1 (ng/hr/cm ²)	No. 2 (ng/hr/cm ²)	Mean (ng/hr/cm ²)	% Error
0-2	181.4	162.1	171.8	11.2	0-2	14.58	21.48	18.03	38.3	1	0-2	1950	1864	1907	65.00	62.12	63.56	4.5
2-4	181.4	162.1	171.8	11.2	2-4	43.17	51.43	47.30	17.5		2-4	920.9	1157	1039	30.70	38.57	34.63	22.7
4-6	181.4	162.1	171.8	11.2	4-6	76.98	68.72	72.85	11.3		8-10	609.7	580.2	595.0	20.32	19.34	19.83	4.9
6-8	181.4	162.1	171.8	11.2	6-8	96.68	117.69	107.19	19.6	2	0-2	283.8	285.4	284.6	9.46	9.51	9.49	0.5
8-10	181.4	162.1	171.8	11.2	8-10	113.76	102.13	107.95	10.8	3	0-2	182.6	192.7	187.7	6.09	6.43	6.26	5.4
SOIL CHARACTERISTICS: Maile (Hydric Dystrandeps; Inceptisols)										4	0-2	180.4 [†]	180.4 [†]	6.01 [†]	6.01 [†]	...
Bulk Density (g/cm ³)..... 0.63					Initial Soil Water					5	0-2	142.9	144.8	143.9	4.76	4.83	4.80	1.5
Organic Matter Content (%).. 5.5					Content (cm ³ /cm ³)... 29.9					6	0-2	126.4	131.8	129.1	4.21	4.39	4.30	4.2

*Percent error is obtained from the difference between two replicates divided by the mean value.

[†]No. 1 value used for total volatilized value.

[†]Single analysis used as mean.

only the Wahiawa soil (Tropeptic Eutruxtox) of the Oxisol order, typical of the central O'ahu region, was used. Initial soil water content was varied from 2.3 to 31.6% (determined on a volumetric basis).

The data presented in Tables 10, 11, 12, 13, and 14 and the curves of Figure 15 show that initial soil water content affects the rate of DBCP volatilization, at least for the time period immediately following application. After the initial 2-hr period, however, the flux for 8.5, 13.5, and 31.6% initial soil water content cases were basically identical. Only the low 2.3% initial soil water content case had a significantly lower volatilization rate for the first two days. Total percentages volatilized of the initial DBCP soil treatments for the 8.5, 13.5, and 31.6% soil water content cases were respectively 29.3, 30.8, and 34.4% (Table 16). These percentages are similar because of their distinct difference from the 15.2% volatilized for the 2.3% initial soil water

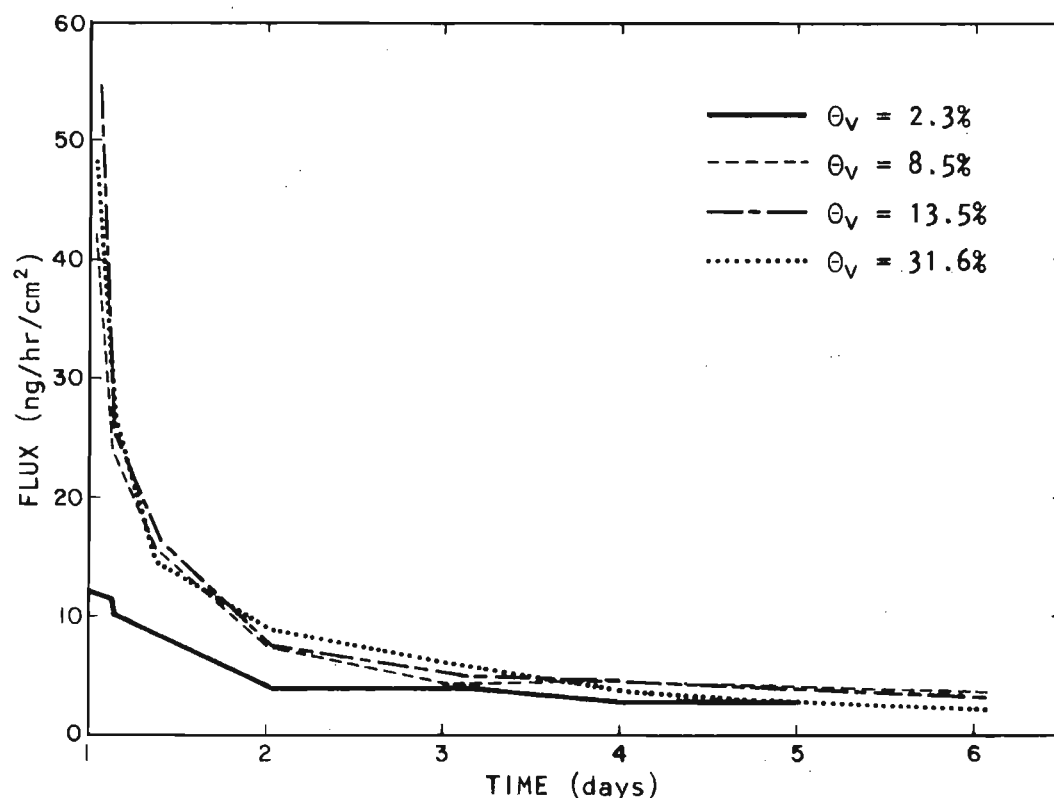


Figure 15. DBCP volatilization from Wahiawa (Tropeptic Eutruxtox) soil at various initial water contents, θ_v

TABLE 16. MASS BALANCE DETERMINATIONS USING QUANTITY OF DBCP APPLIED AS BASIS FOR INITIAL SOIL CONCENTRATIONS FOR WAHIAWA AND MAILE SOILS

SOIL TYPE	WATER CONTENT (cm ³ /cm ³)	INITIAL SOIL TREATMENT*	TOTAL SOIL RESIDUAL (ng)	TOTAL VOLATILIZED	TOTAL RECOVERY	% INITIAL TREATMENT ACCOUNTED FOR	TOTAL RECOVERY	
							% Soil Residual	% Volatilized
Wahiawa	2.3	86 630	84 360	13 160	97 520	113.0	97.4	15.2
	8.5	86 630	61 200	25 430	86 630	100.0	70.6	29.3
	8.6 [†]	69 960	55 270	7 993	63 260	90.4	79.0	11.4
	13.5	86 630	51 910	26 640	78 550	90.7	59.9	30.8
	31.6	75 900	24 750	26 080	50 820	67.0	32.6	34.4
Maile	29.9	51 980	21 200	34 170	55 370	106.5	40.7	65.7

NOTE: Recovery values are means for duplicate volatilization cells.

*Based on 27 500 ng/100 g soil; see Table 17 for distillation standard calculations.

[†]This experiment included an untreated layer of soil over the soil treated with DBCP.

TABLE 17. DISTILLATION STANDARDS RUN CONCURRENTLY
WITH VOLATILIZATION FROM SOIL STUDY

Soil Type	Water Content (cm ³ /cm ³)	Initial DBCP (Total ng)*	Final DBCP (Total ng)	% Re-covered
Wahiawa	2.3	17 500	11 025	63.0
		17 500	15 140	86.5
	8.5	17 500	13 785	78.8
		17 500	13 550	77.4
	8.6	17 500	{ 10 280 9 105 }	58.7
		17 500		52.0
13.5	17 500	12 550	71.7	
	17 500	14 635	83.6	
Maile	29.9	17 500	15 115	86.4
		17 500	13 450	76.9
Mean			3 730	78.5
			(N = 10, c.v. = 9.0)	

*17 500 ng = 0.5 m 35.0 ppm in water.

†Excluded in mean calculations; significant deviation.

content case. It could be argued that there is a trend toward greater volatilization at higher initial soil water contents, but the trend is slight for the higher values herein measured. It is noteworthy that volatilization was greatest over the first two hours for the intermediate case (13.5% initial soil water content). These data indicate that, for very low initial soil water contents, flux is inhibited, possibly because of adsorption. Above some initial soil water content (lying between 2.3 and 8.5%), this effect is overridden, and increases in initial soil water content beyond this value seem to have little, if any, effect.

All flux values were essentially the same by the beginning of the third day, decreasing only slightly during the following three days. This implies that, regardless of ini-

tial soil water content, some common minimally decreasing flux is ultimately achieved for all cases.

A comparison of the initial and final soil concentration distributions (Fig. 16) demonstrates fairly similar results for all four variations. In all cases, volatilization occurred mainly from the upper 0.02 m, with a lesser loss from the 0.02- to 0.04-m section, and a minimal loss from the 0.04- to 0.06-m section. There appeared to be a trend toward greater loss from the lower sections with increasing initial soil water content, but volatilization from the bottom 0.08- to 0.10-m section was only significant in the highest water content case of 31.6% (near field capacity). These results imply that diffusion-controlled volatilization effectively occurs only from the top 0.04 to 0.06 m of the soil column over the 5- to 6-day course of the experiments. However, for studies concerned with high water contents, and/or long time-frames, a deeper soil column would be necessary.

ADDITION OF A SOIL COVER LAYER. The effect of the addition of an untreated soil cover layer to the DBCP-treated soil column was examined. The soil cell was packed with 0.08 m of treated Wahiawa soil, then topped with 0.02 m of untreated Wahiawa soil. The 8.6% initial soil water content determined for the layered case was intended to match the 8.5% initial soil water content case described in the previous section.

The pattern of DBCP flux from the soil surface for the layered case was significantly different from that for the unlayered case (Fig. 17); for the former case the flux was non-detectable until the 8 to 10 hr volatile measurement. The flux value detected at this time changed little over the remaining four days of the run. Thus, less total volatilization occurred for the layered case (11.4%) than for the unlayered case (29.3%) with respect to the initial soil treatment (Table 16).

Significant similarities occurred between the two cases. In the layered and unlayered cases, the slightly decreasing flux observed for the other Wahiawa cases was ultimately

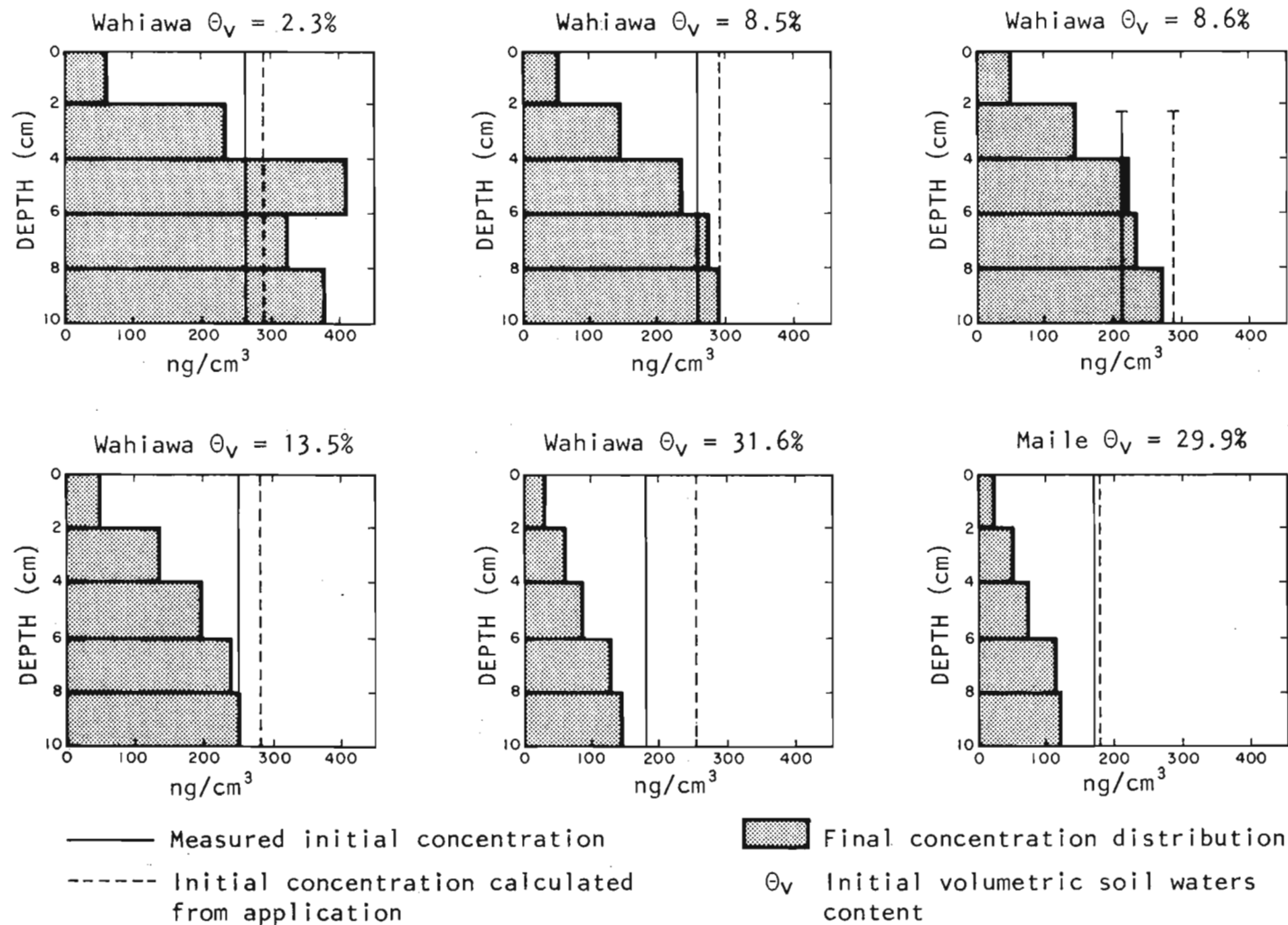


Figure 16. DBCP concentrations with depth initially and after volatilization for five to six days, Wahiawa (Tropeptic Eustrustox) and Maile (Hydric Dystrandeps) soils

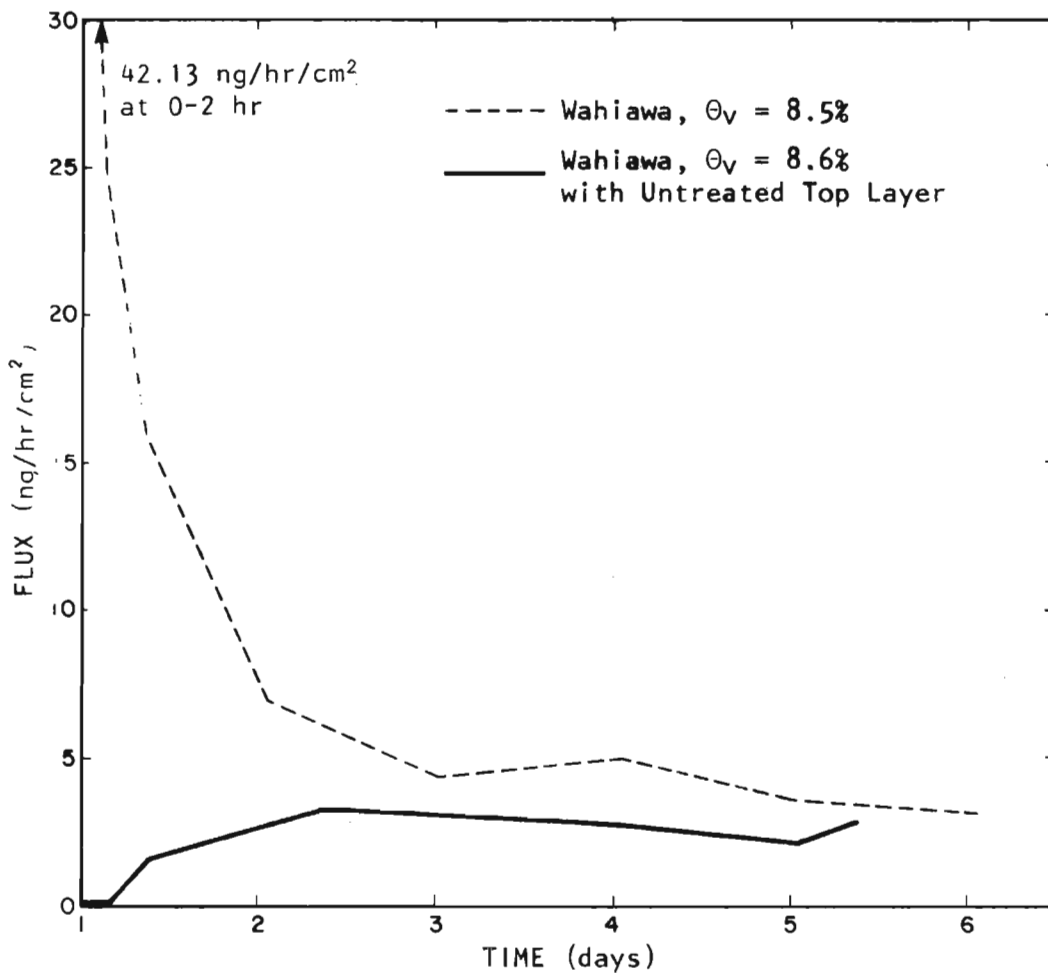


Figure 17. DBCP volatilization from Wahiawa soil with and without cover layer at comparable initial soil water content

approached. A more striking similarity was observed in the final distribution of DBCP concentration in the soil column when the layered and the unlayered cases seemed to approach the same diffusion-controlled equilibrium state.

The above results demonstrate the effectiveness of a soil cover layer in preventing excessive initial loss of the pesticide to the atmosphere. These results also illustrate the upward diffusion of DBCP which must have occurred to cause the measured flux of DBCP from the soil surface and the final distribution of the pesticide in the soil column.

SOIL TYPE VARIATION. Two soil types (Wahiawa and Maile) with similar initial soil water contents (31.6 and 29.9% re-

spectively) were compared. Although mineralogical and structural soil characteristics are very different for the two soils (see App. B), the soil type variation was conducted to compare contrasting soil types.

The Maile silt loam (Hydric Dystrandepsts of the Inceptisols order) had a significantly higher volatilization rate during the first four hours of the study, and remained higher, but to a lesser degree, for the remainder of the experimental run (Table 15, Fig. 18). Total percent volatilized, with respect to total recovery and initial soil treatment, was higher for the Maile soil than for the Wahiawa silty clay (Tables 16, 18). Final distribution of the DBCP concentration in the soil

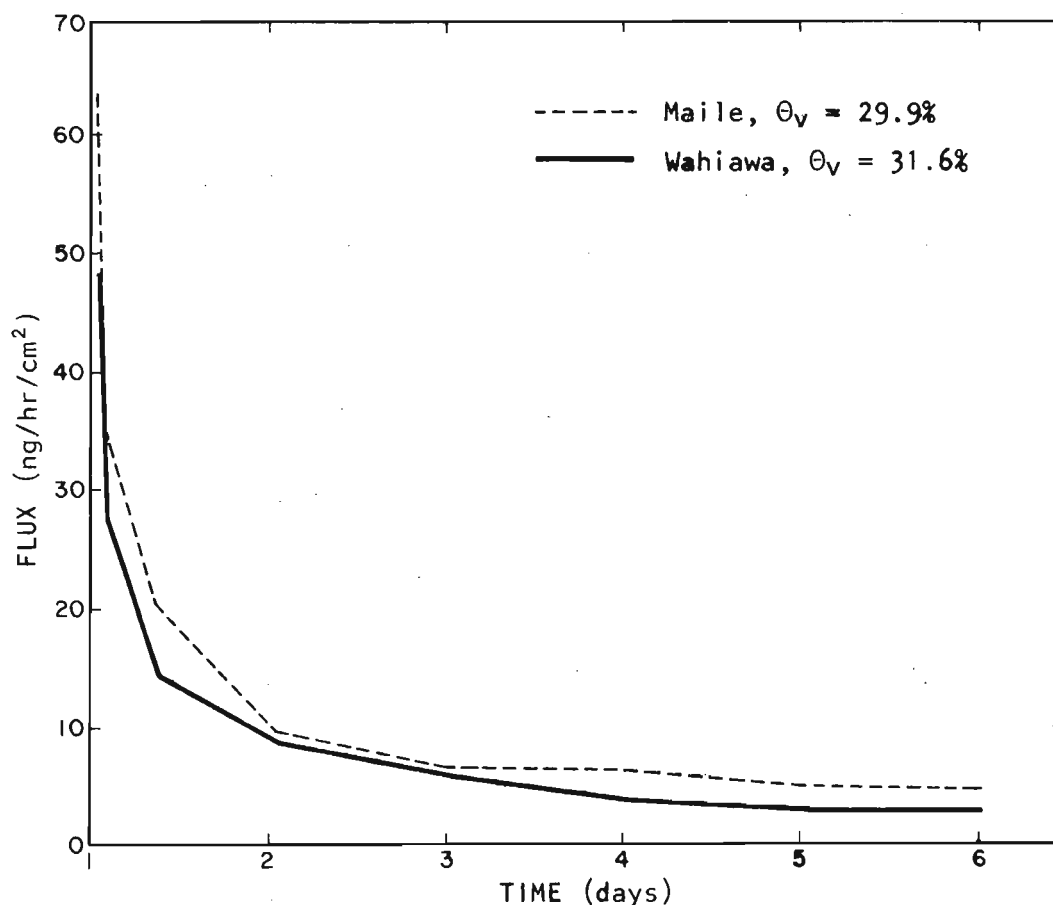


Figure 18. DBCP volatilization from Maile and Wahiawa soils at similar initial water contents

TABLE 18. MASS BALANCE DETERMINATIONS USING MEASURED INITIAL SOIL CONCENTRATIONS FOR WAHIAWA AND MAILE SOILS

SOIL TYPE	WATER CONTENT (cm ³ /cm ³)	INITIAL SOIL TREATMENT	TOTAL SOIL RESIDUAL (ng)	TOTAL VOLATILIZED*	TOTAL RECOVERY	% INITIAL TREATMENT ACCOUNTED FOR	TOTAL RECOVERY	
							% Soil Residual	% Volatilized
Wahiawa	2.3	78 820	84 360	13 160	97 520	123.7	86.5	13.5
	8.5	78 980	61 200	25 430	86 630	109.7	70.6	29.4
	8.6	51 250	55 270	7 993	63 260	123.4	87.4	12.6
	13.5	77 380	51 910	26 640	78 550	101.5	66.1	33.9
	31.6	54 920	24 750	26 080	50 820	92.5	48.7	51.3
Maile	29.9	51 530	21 200	34 170	55 370	107.5	38.3	61.7

*See Appendix B for sample calculation.

column was very similar to the pattern observed for the Wahiawa soil, but with a slightly greater decrease in the lower sections (Table 13). Both of the trials with higher water contents demonstrated measurable pesticide loss from the bottom 0.08 to 0.10 m soil section.

It is difficult to determine exactly to what these higher flux rates from the Maile soil may be attributed. Undoubtedly, mineralogy (particularly clay type and content), structure, and organic matter content, as well as initial soil water content, contribute to the difference in behavior. A more thorough comparison would have to be made before results could be meaningfully discussed.

SUMMARY. The initial soil water content variation portion of this study demonstrated that initial soil water content did indeed affect the rate of volatilization of DBCP. During the time period immediately following the application of the pesticide, the initial rapid loss of DBCP from the system was generally observed to be greater for higher initial soil water contents. This effect was particularly noticeable for the 2.3% initial soil water content case when compared to the remaining runs. For very low soil water contents, upward diffusion appears to remain minimal, probably due to increased adsorption. After the initial rapid loss of DBCP from the system, the effect of variation in initial soil water content is greatly diminished. Apparently, above some critical soil water content, upward diffusion ultimately becomes steady, creating a common minimally decreasing flux regardless of initial soil water content.

The addition of a soil cover layer to the system caused significant differences in the initial pattern of DBCP volatilization. The initial release of DBCP from the soil column was precluded, demonstrating the effectiveness of a cover layer in preventing excessive initial loss of the pesticide to the atmosphere. Upward diffusion of the DBCP through the untreated layer continued until a flux from the soil surface was observed during the 8- to 10-hr period of the first day. The

flux value detected at this time changed very little during the remainder of the experiment, indicating the relatively quick establishment of steady vapor loss. Similarities between the two systems were also observed. For the layered and the unlayered cases, the same slightly decreasing flux was ultimately approached. More striking was the similarity of the final DBCP distribution in the soil column for the two cases. The layered and the unlayered systems seem to have approached some diffusion-controlled steady state.

The Maile soil had a significantly greater volatilization rate for the first 4 hr of the study than did the Wahiawa soil, remaining slightly higher for the remainder of the study. The substantial differences in soil characteristics were undoubtedly the cause of this difference; however, a more detailed study would have to be conducted before individual factors could be weighed as to cause and effect.

Diffusion Coefficients

Effective diffusion coefficients for DBCP from Wahiawa and Maile soils were calculated using the methodology proposed by Jury et al. (1980). The following equilibrium assumptions and simplifications were made: (1) gas and liquid concentrations are related by Henry's law, (2) the adsorption isotherm is linear over the range of concentrations encountered in the experiment, (3) the diffusion coefficient is constant during an experiment, (4) the water flux is zero for diffusion experiments, (5) the gas concentration is zero at the surface of the column, and (6) the column is assumed to behave identically as though it were infinitely deep during the experiment. Details of this calculation are presented in Table 19. A diffusion coefficient was not calculated for the layered 8.6% initial soil water content case as the pesticide was not homogeneously incorporated throughout the soil column and was therefore not applicable to the case solved by Jury et al. (1980). All values in Table 19, except the adsorption coefficient, were determined by the methodologies previously dis-

TABLE 19. EFFECTIVE LIQUID-VAPOR DIFFUSION COEFFICIENT FOR DBCP, AND ASSOCIATED SOIL AND PESTICIDE PROPERTIES, WAHIWA AND MAILE SOILS

Soil Type	Bulk Density ρ_b (g/cm ³)	Volumetric Water Content, θ (cm ³ /cm ³)	Air Content, η^*	Adsorption Coef., K_d^\dagger (ml/g)	Dimensionless Henry's Constant, K'^\ddagger (cm ³ Liquid / cm ³ Vapor)	Initial Conc. C_T at $t = 0$ (μg / cm ³ Soil)	Time, t (s)	Cumulative Surface Loss, $M(t)$ ($\mu\text{g}/\text{cm}^2$)	Effective Liquid-Vapor Diffusion Coef., D_e^S (cm ² /s)
Wahiwa	1.05	0.023	0.615	1.65	1.48×10^{-2}	0.289	3.53×10^5	0.44	6.15×10^{-4}
	1.05	0.085	0.553	1.65	1.48×10^{-2}	0.289	4.39×10^5	0.85	1.91×10^{-3}
	1.05	0.135	0.503	1.65	1.48×10^{-2}	0.289	4.39×10^5	0.89	2.15×10^{-3}
	0.92	0.316	0.367	1.65	1.48×10^{-2}	0.253	4.39×10^5	0.87	2.63×10^{-3}
Maile	0.63	0.299	0.459	1.04	1.48×10^{-2}	0.173	4.39×10^5	1.14	5.04×10^{-3}

*See Table 20.

†See Table 21; K_d here corresponds to α of Jury et al. (1980).

‡Using the Thomas (1982) approximation, in which K' , the Henry's constant, equals the reciprocal of K_H of Jury et al. (1980).

§Effective liquid-vapor diffusion coefficient was determined using the Jury et al. equation (1980):

$$D_e = \{ [M(t)/2(C_{T_0} - \gamma)]^2 (\pi \epsilon) \} / t$$

where

$$\gamma = \rho_b \beta \quad (\beta \text{ considered to equal } 0)$$

$$\epsilon = (\rho_b K_H \alpha + \theta K_H + \eta), \text{ in cm}^3/\text{cm}^3.$$

cussed in this report. Table 20 shows the determination of air-filled porosity. Adsorption coefficients were determined by the methodology described by Liu et al. (1983). Details of the adsorption coefficient calculation are given in Table 21.

Table 22 presents a comparison of the diffusion coefficients calculated to the percent of the initial soil treatment volatilized. The diffusion coefficients for the Wahiawa soil ranged from 0.002 to 0.006 cm²/s, with only the 2.3% initial soil water content case being significantly lower than the remaining three values which clustered fairly closely, paralleling the total volatilization results. The calculated diffusion coefficients again imply that, for very low soil water contents, upward diffusion is inhibited, but that above some critical soil water content, diffusion becomes a more prominent mechanism. However, further increases in soil water content above this critical level appear to have a minimal effect, i.e., diffusion coefficients are relatively constant over a wide range of water contents (Fig. 19).

The higher diffusion coefficient for the Maile soil (Table 22, Fig. 19) is in keeping with the higher percent of the initial soil treatment volatilized (Table 22). Specific reasons as to why diffusion from this soil is greater than for the Wahiawa soil are unknown; however, the principal reason may be the lower adsorption coefficient for the Maile soil ($K_d = 1.04$ ml/g) than for the Wahiawa ($K_d = 1.65$). Care should be taken in interpreting the coefficients determined for the two high water content cases, since some measurable DBCP loss did occur from the bottom soil sections--a violation of one of the boundary conditions for the Jury et al. (1980) solution.

Saltzman and Kliger (1979) reported diffusion coefficients for DBCP applied in water to three air-dried soils. Twenty micrograms of DBCP in water were added to 2 g soil samples contained in glass-stoppered centrifuge tubes. The tubes were stored at 22°C and periodically tested for DBCP. Saltzman and Kliger do not explain how the amount of DBCP volatilized was determined. Diffusion coefficients reported

TABLE 20. DETERMINATION OF THE AIR CONTENT OF WAHIAWA
AND MAILE SOILS AT VARIOUS WATER CONTENTS

Soil Type	Bulk Density (g/cm ³)	Particle Density (g/cm ³)	Porosity (%)	Volumetric Soil Water Content (%)	Air Content (%)
Wahiawa	1.05	2.9	63.8	2.3	61.5
	1.05	2.9	63.8	8.5	55.3
	1.06	2.9	63.4	8.6	54.8
	1.05	2.9	63.8	13.5	50.3
	0.92	2.9	68.3	31.6	36.7
Maile	0.63	2.6	75.8	29.9	45.9

Solution:

$$P = (1 - \rho_b/\rho_p) \times 100$$

$$\rho_p = 2.9 \text{ g/cm}^3 \text{ (Wahiawa soil)}$$

$$2.6 \text{ g/cm}^3 \text{ (Maile soil)}$$

$$P - \theta = \eta$$

where

P = porosity (%)

ρ_b = bulk density (g/cm³)

ρ_p = particle density (g/cm³)

θ = volumetric soil water content (cm³/cm³)

η = air content (%)

TABLE 21. DBCP ADSORPTION ON WAHIAWA AND MAILE SOILS

SOIL TYPE	FINAL SOLUTION CONCENTRATION		SOLUTION VOLUME V (ml)	SOIL MASS M (g)	ADSORBED S (µg/g)	K _d , SLOPE OF LINEARIZED SORPTION ISOTHERM	
	Blank	Soil				Mean	
	—— (ng/ml) ——					—— (ml/g) ——	
Wahiawa	492.3	225.9	20	15	0.355	1.39	1.65
		214.4	20	15	0.371	1.73	
		206.8	20	15	0.381	1.84	
Maile	492.3	296.6	19.5	15	0.254	0.86	1.04
		234.0	15	15	0.258	1.10	
		229.6	15	15	0.263	1.15	

NOTE: Methodology from Liu et al. (1983):

$$S = (C_i - C_e) \cdot V/M \quad K_d = S/C_e$$

$$S = K_d C_e$$

where

K_d = slope of linearized sorption isotherm

C_i = solution concentration of blank

C_e = final solution concentration after equilibration with soil

TABLE 22. COMPARISON OF DIFFUSION COEFFICIENTS AND PERCENT OF APPLIED DBCP VOLATILIZED FOR WAHIAWA AND MAILE SOILS UNDER VARIOUS INITIAL WATER CONTENTS

Soil Type	Initial Soil Water Content (%)	Effective Liquid-Vapor Diffusion Coefficient (cm ² /s)	Percent Volatilized of Initial DBCP in Soil*
Wahiawa	2.3	6.15 x 10 ⁻⁴	15.2
	8.5	1.91 x 10 ⁻³	29.3
	13.5	2.15 x 10 ⁻³	30.8
	31.6	2.63 x 10 ⁻³	34.4
Maile	29.9	5.04 x 10 ⁻³	65.7

*See Table 16.

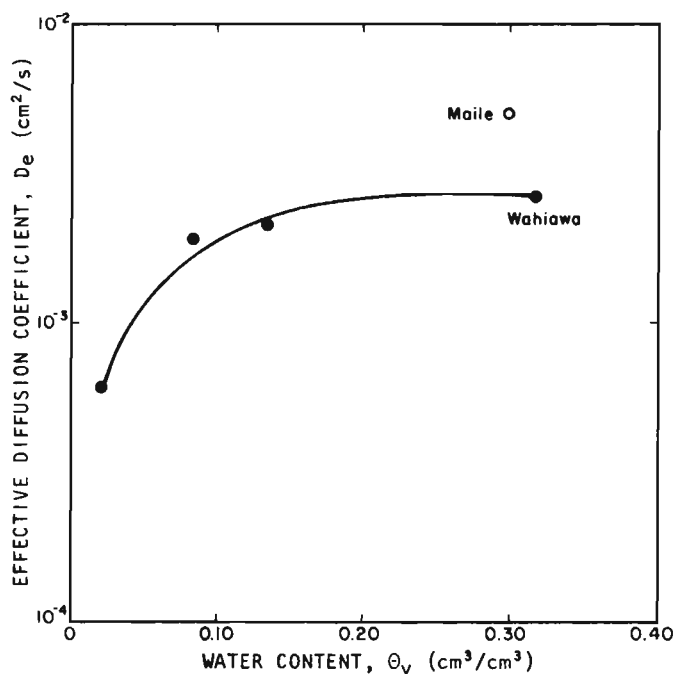


Figure 19. Effective diffusion coefficient of DBCP as a function of soil water content

were 5.43 , 5.45 , and $5.18 \times 10^{-5} \text{ cm}^2/\text{s}$ for a sandy clay loam hamri, a silty loam loessial sierozem, and a reddish-brown grumusol, respectively. These diffusion rates were much lower than those herein determined; however, in their study the samples were stored in a stagnant environment and are therefore actually not comparable to the diffusion coefficient determination described by Jury et al. (1980), even though the two analytical solutions are quite similar. The existence of a volatile concentration gradient above the soil surface, and a nonzero concentration at the soil-air interface, would explain why upward diffusion remained substantially lower in the Saltzman and Kliger (1979) study.

SUMMARY AND CONCLUSIONS

A volatile trapping apparatus was developed which proved to be highly efficient in capturing DBCP as it volatilized from either water or soil. The shortcomings of the volatilization chamber used in the preliminary study of volatilization from water were acknowledged, and an air-tight volatilization cell, patterned after that of Spencer and associates, was used for subsequent experiments on volatilization of DBCP from soil. This soil cell proved highly successful in that it was functional on a practical level, produced numbers of high precision, and was designed so that boundary conditions were readily definable.

One goal was to establish physical coefficients for DBCP in soils of central O'ahu as input to quantitative modeling efforts, such as that of Liu et al. (1983). The following physical coefficients appear to be appropriate for the Wahiawa soil of central O'ahu:

Theoretical Henry's law constant:	$H = 1.48 \times 10^{-2} \text{ (ng/m}^3 \text{ air) / (ng/m}^3 \text{ water)}$
Adsorption coefficient:	$K_d = 1.65 \text{ ml/g}$
Effective liquid-vapor diffusion coefficient:	$D_e = (0.61 \text{ to } 2.63) \times 10^{-3} \text{ cm}^2/\text{s, dependent on soil water content.}$

An experimentally measured ratio of vapor concentration to liquid concentration under dynamic flow conditions was lower than the theoretical value because a complete equilibrium between the liquid and vapor phases was not achieved. By using the numerical analysis of Jury et al. (1980), and the experimental design with well-defined initial and boundary conditions, the effective diffusion coefficient reported herein is undoubtedly a more valid determination than that of Saltzman and Kliger (1979), which differed by more than two orders of magnitude. In addition, the effective diffusion coefficient was shown to be relatively constant over a wide range of water contents.

The establishment of experimentally determined physical coefficients, volatilization fluxes, and soil concentration profiles, not only allows for their use in modeling efforts, but also for their use in testing the validity of analytically derived predictive models, such as that of Liu et al. (1983) and Spencer and Farmer (1983). Given these experimental and theoretical tools, the predetermination of undesirable characteristics should be possible prior to widespread use of the chemicals and later discovery of their adverse effects. In Hawai'i this screening would be particularly applicable for potential successors to DBCP.

ACKNOWLEDGMENTS

Our sincere thanks to Mr. Karl Pfenninger of the Pacific Biomedical Research Center, University of Hawaii at Manoa, for his assistance in the development of the volatile trap and in the laboratory analytical work associated with the gas chromatograph, and to Mr. C. Chow Lee of the Department of Agronomy and Soil Science, University of Hawaii at Manoa for his assistance with soil adsorption measurements and soil characterization. The assistance of Dr. W.F. Spencer (Univ. of California, Riverside) in the design of the soil cell is greatly appreciated.

Support of the USGS Water Resources Division, Hawaii District in the conduct of this project and their many useful suggestions are gratefully acknowledged.

GLOSSARY

CDA	N,N-diallyl-2-chloroacetamide; trade name Radox; selective preemergence herbicide
CIPC	isopropyl m-chlorocarbanilate, or isopropyl-N-m-chlorophenyl-carbamate; common names chloro IPC and chlorpropham; preemergence herbicide
2,4-D	2,4-dichlorophenoxyacetic acid (including esters and salts); selective herbicide
DBCP	dibromochloropropane; 1,2-dibromo-3-chloropropane; soil fumigant for nematode control
DDD (TDE)	1,1-dichloro-2,2 bis (p-chlorophenyl) ethane, insecticide
o,p'-DDT	1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)-ethane
p,p'-DDT	dichloro diphenyl trichlorethane; 1,1,1-trichloro-2,2-bis (p-chlorophenyl)-ethane; organochlorine insecticide
EDB	1,2-dibromoethane; fumigant (insecticide, nematocide)
EPTC	ethyl-N,N-di-n-propylthiolcarbamate; common name Eptam, S-ethyl dipropylthiocarbamate; selective herbicide
IPC	isopropyl carbanilate; preemergence and post-emergence herbicide
PCB	polychlorinated biphenyls; arochlors; mixture of terphenyls; nonspecific insecticide

SOURCE: Farm Chemicals Handbook (1983; Meister Publishing, Ohio).

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APPENDIX A. DETERMINATION OF SOIL PROPERTIES

BULK DENSITY. Bulk density was determined by dividing the mass (g) of the treated soil packed into the soil cell by the volume of the cell (cm³). This "wet" bulk density was converted to standard bulk density by using the calculations outlined in Appendix Table C.1.

VOLUMETRIC SOIL WATER CONTENT. Initial soil water content was determined by weighing treated soil samples before and after drying in a 105°C oven for 24 hr. The volumetric soil water content was calculated by dividing the volume of water initially contained in the soil sample by the dry weight of the soil. Five values were determined and averaged for each soil water content herein reported.

ORGANIC MATTER CONTENT. Organic matter content was derived by conversion from organic carbon content determined by the Walkley-Black wet combustion method without external heating. Percent organic carbon was multiplied by 1.724 to yield percent organic matter (Nelson and Sommers 1982).

APPENDIX TABLE A.1. CONVERSIONS OF WET TO DRY BULK DENSITIES AND INITIAL TO VOLUMETRIC SOIL WATER CONTENT

$$\theta_{wt} = \text{water content} = x/y$$

where

$$x = \text{water}$$

$$y = \text{dry soil}$$

$$\rho_b = \text{dry bulk density} = y/\text{vol}$$

$$\rho_{\text{total}} = \text{wet or total bulk density} = (x + y)/\text{vol}$$

$$= [(\theta_{wt} + 1)y]/\text{vol}$$

therefore

$$\rho = \rho_{\text{total}}/(\theta_{wt} + 1)$$

$$\theta_v = \theta_{wt} \rho_b$$

Soil Type	θ_{wt} (%)	ρ_{total} (g/cm ³)	ρ_b (g/cm ³)	θ_v (%)
Wahiawa	2.2	1.07	1.05	2.3
	8.1	1.17	1.08	8.7
		1.09	1.01	8.2
	8.1	1.15	1.06	8.6
	12.9	1.21	1.05	13.5
	34.5	1.21	0.90	31.1
1.25		0.93	32.1	
Maile	47.2	0.93	0.63	29.9

APPENDIX TABLE A.2. SOIL STUDY: DBCP APPLIED AS DETERMINED
BY GC ANALYSIS OF SOIL EXTRACT

SOIL TYPE	VOL. WATER CONTENT (%)	UNTREATED SOIL		TREATED SOIL*		APPARENT TOTAL DBCP APPLIED (ng)
		Mean (ng/g)		Mean (ng/g)		
Wahiawa	2.3	2.10	2.70	237.1	245.6	77 364
		3.23		254.0		
	8.5	1.63	2.10	214.9	233.7	73 616
		2.47		252.4		
	8.6	1.25	1.25	188.3	187.0	47 573
....		185.7				
13.5	210.4	218.6	68 859	
		226.8			
31.6	168.4	149.2	41 179	
		129.9			
Mean		2.02 [†]		206.98 [§]		
Maile	29.9	ND [†]	ND	195.0	184.7	34 908
				174.3		
Mean		ND		184.7		

*275 ng/g DBCB added.

[†]Nondetectable.

[‡]N = 3, c.v. = 40.

[§]N = 10, c.v. = 19.0.

APPENDIX TABLE A.3. SOIL STUDY: DBCP APPLIED, ASSUMING NO
VAPOR LOSS DURING SETUP

Soil Type	Vol. Water Content (%)	Dry Bulk Density (g/cm ³)	Tot. Soil Dry Wt. (g)	DBCP Added (ng)
Wahiawa	2.3	1.05	315.0	86 630
	8.5	1.05	315.0	86 630
	8.6	1.06	254.4*	69 960
	13.5	1.05	315.0	86 630
	31.6	0.92	276.0	75 900
Maile	29.9	0.63	189.0	51 980

*Based on only 240 cm³ treated soil and 60 cm³ untreated top layer.

APPENDIX TABLE B.1. VOLATILIZATION FROM WATER—DBCP RECOVERY EFFICIENCY

INITIAL DBCP (ng)	VOLATILIZATION FROM WATER			DISTILLATION CONTROL		EXTRACTION CONTROL		
	Temp. (°C)	Conc. (mg/l)	Air Flow (ml/min)	DBCP Recovered (ng)	(%)	DBCP Recovered (ng)	(%)	
175 (0.5 ml 0.35 ppm in water)	Initial Investigations			155	88.6	153	86.4	
				189.6	108.3	
				161.3	92.2	178.6	102.1	
				149.6	85.5	171.7	98.1	
				146.8	83.4	148.0	84.5	
				117.5	67.1	
		23	0.35	250	165.8	94.7	152.3	86.9
					159.5	91.1	140.3	80.1
		23	0.35	500	138.5	79.1
					145.6	83.2	156.4	89.3
		23	0.35	100	135.5	77.4	139.3	79.6
					147.2	84.1	169.6	96.9
		23	35.0	250	126.9	72.5	184.4	105.2
				
		23	0.0035	250	141.8	81.0	118.5	67.7
					130.5	74.5	138.3	79.0
		33	0.35	250	138.8	75.3	150.2	85.8
					136.0	77.7	171.6	98.0
	43	0.35	250	129.4	73.8	148.6	85.9	
				
			Mean	145.3	83.0	154.7	88.4	
				(N = 18, c.v. = 11.8%)		(N = 15, c.v. = 11.4%)		

APPENDIX TABLE B.2. VOLATILIZATION FROM SOIL—DBCP RECOVERY EFFICIENCY, WAHIAWA AND MAILE SOILS

INITIAL DBCP (ng)	VOLATILIZATION FROM SOIL		DISTILLATION CONTROL		
	Soil	θ (cm^3/cm^3)	DBCP (ng)	Recovered (%)	
17 500 (0.5 ml 35 ppm in water)	Wahiawa	2.3	11 025	63.0	
				15 140	86.5
		8.5	13 785	78.8	
				13 550	77.4
		8.6	{ 10 280	58.7	
			{ 9 105	52.0	
		13.5	12 550	71.7	
			14 635	84.6	
		31.6	14 025	80.1	
			14 025	80.1	
	Maile	29.9	15 115	86.4	
			13 450	86.4	
		Mean	13 730	78.6	
			(N = 10, c.v. = 9.0%)		

*Excluded in mean calculations; significant deviation.

APPENDIX TABLE C.1. DATA AND DESCRIPTION FOR WAHIWA SOIL (TROPEPTIC EUTRUSTOX), O'AHU, HAWAII

SOIL FAMILY Tropeptic Eutrustox, clayey, kaolinitic, imahyperthermic U.S. DEPARTMENT OF AGRICULTURE SOIL CONSERVATION SERVICE
 SOIL SERIES Wahiwa silty clay SOIL Nos. S61Ha-7-7 LOCATION Honolulu County, Hawaii
 Beltsville Lab Nos. 61492 - 61497

Depth (cm)	Horizon	Mineralogical Analysis																
		Ailo-phane	Mont-morillonites	Micas	Kdd ^{7A3} lin-ites	7A3 Gibbs-ite	Boehm-ite	Goeth-ite	Amor-phous SiO ₂	Amor-phous Al ₂ O ₃	Mag-netite etc.	Ana-tase	Quartz	Vol-canic glass	Feld-spor	Cliv-ine	Pyrox-ene	Py-rite
Percent of Whole Soil																		
0-15	Ap1				40	-												
15-30	Ap2				43	-												
30-40	B21				53	-												
40-83	B22				55	-												
83-113	B23				53	-												
113-150	B24				50	-												

Depth (cm)	Total Chemical Analysis											Extractable iron 6C1a		Carbonate as CaCO ₃ 6E1b	0.5N NaOH Soluble		
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO ₂	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	L.O.I.	Total	Fe	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	
Percent of Whole Soil																	
0-15	Ap1													8.8	12.6		
15-30	Ap2													9.0	12.8		
30-40	B21													8.5	12.2		
40-83	B22													10.0	14.3		
83-113	B23													9.7	13.9		
113-150	B24													9.8	14.0		

Depth (cm)	6A1a Organic carbon Pct.	6B2a Nitrogen Pct.	C/N	Extractable bases 5B1a				Sum of bases	Extr. acidity 6H2a	Cation exch. capacity		NH ₄ OAc extr. SO ₄ 6G1D	KCl extr. Al ⁺⁺⁺ 6G1D	Base saturation		pH		
				6N2a Ca	6O2b Mg	6P2a Na	6Q2a K			5A1a NH ₄ OAc	5A3a Sum			5C1 NH ₄ OAc	5C3 Sum	8C1a H ₂ O	8C1c KCl	
				Meq./100 g.											Percent		1:1	1:1
																	Percent	
0-15	1.65	0.204	8	5.4	2.9	0.27	0.75	9.3	16.4		25.7	0.2		36	5.3	4.5		
15-30	1.10	0.183	6	6.4	3.7	0.22	0.13	10.5	13.8		24.2	<0.1		43	5.9	5.0		
30-40	0.78	0.130	6	4.9	3.6	0.21	0.08	8.8	7.7		16.5			53	6.4	5.4		
40-83	0.22			4.1	3.3	0.18	0.05	7.6	5.5		13.1	<0.1		58	6.4	5.6		
83-113	0.19			4.3	3.2	0.32	0.05	7.9	5.6		13.5	<0.1		58	6.3	5.9		
113-150	0.23			4.4	2.6	0.52	0.07	7.6	5.2		12.8			59	6.3	6.0		

Depth (cm)	Size class and particle diameter (mm) 3A1			Coarse fragments >2mm pct. of whole soil	Atterberg limits			Bulk density			Particle density	Water content		Extensibility	
	Sand (2-0.05)	Silt (0.5-0.002)	Clay (<.002)		Plastic limit	Liquid limit	Plastic index	1/3 bar	Oven dry	Field moist		1/3 bar	432 bar	COLE	COLE
	Pct. of 2mm.							g/cc				Pct. of whole soil		cm/cm	
0-15													24.4		
15-30													25.1		
30-40													25.1		
40-83													24.3		
83-113													24.6		
113-150													24.7		

APPENDIX TABLE C.1.—Continued

WAHIAWA SILTY CLAY

S61Ha-7-7

LOCATION: Island of O'ahu, Honolulu County, Hawai'i. Dole Corporation field No. 4101-02, plot No. B-30, about 300 m (1000 ft) east of main road.
 SAMPLING DATE: 1961.

DESCRIPTION: D. Womack. COLLECTORS: D. Womack and J.M. Williams.

CLASSIFICATION: Tropeptic Eustrustox, clayey, kaolinitic, isohyperthermic.

VEGETATION: Pineapple. CLIMATE: Average annual precipitation 1 016 mm (40 in.); mean annual temperature 21.7°C (71°F), mean January temperature 20.6°C (69°F), mean July temperature 22.8°C (73°F). PARENT MATERIAL: Olivine basalt.
 TOPOGRAPHY: Low, nearly level upland; relief about 2% convex to west.
 ELEVATION: 150 m (500 ft). DRAINAGE: Well drained; moderate to moderately rapid permeability; slow runoff. SOIL MOISTURE: Dry.

REMARKS: Textures are apparent field textures. Colors are for moist soil unless otherwise noted. Upper solum dry when described. Paired sample number S61Ha-7-8.

HORIZONDESCRIPTION

Ap1 BSL No. 61492	0 to 15 cm (0-6 in.), very dusky red (2.5YR 2/2) silty clay, dusky red (2.5YR 3/2) dry; moderate medium, fine and very fine granular structure; very hard, friable, sticky, plastic; many roots, many medium, fine and very fine pores; many 3 to 5 mm (1/8-1/4 in.) black concretions; violent effervescence with hydrogen peroxide; medium acid (pH 5.6); abrupt, smooth boundary.
Ap2 BSL No. 61493	15 to 30 cm (6-12 in.), dusky red (2.5YR 3/2) moist and dry silty clay; common dark reddish brown (2.5YR 3/4) material from B horizon mixed by cultivation; moderate coarse subangular blocky structure; hard, firm, sticky, plastic; compact in place; many roots; few fine and very fine tubular pores; many black concretions; violent effervescence with hydrogen peroxide; medium acid (pH 5.8); abrupt, wavy boundary.
B21 BSL No. 61494	30 to 40 cm (12-16 in.), dark reddish brown (2.5YR 2/4) silty clay, dark reddish brown (2.5YR 3/4) dry; moderate fine and very fine subangular blocky structure; hard, firm sticky, plastic; common roots, common fine and very fine pores, few coarse tubular pores; many black concretions; strong effervescence with hydrogen peroxide; medium acid (pH 5.6); gradual, wavy boundary.
B22 BSL No. 61495	40 to 83 cm (16-33 in.), dark reddish brown (2.5YR 2/4) silty clay, dark reddish brown (2.5YR 3/4) dry; moderate and strong fine and very fine subangular blocky structure; hard, friable, sticky, plastic; few roots; common fine and very fine tubular pores; nearly continuous pressure faces; many fine distinct black stains; few black concretions; strong effervescence with hydrogen peroxide; slightly acid (pH 6.5); diffuse wavy boundary.
B23 BSL No. 61496	83 to 113 cm (33-45 in.), dark reddish brown (2.5YR 2/4) silty clay, dark reddish brown (2.5YR 3/4) dry; moderate and strong very fine subangular blocky structure; hard, friable, sticky, plastic; common fine and very fine tubular pores; nearly continuous pressure faces; many fine distinct black stains; few black concretions; moderate effervescence with hydrogen peroxide; neutral (pH 7.1); diffuse, wavy boundary.
B24 BSL No. 61497	113 to 150 cm (45-60 in.), dark reddish brown (2.5YR 2/4) silty clay, dark reddish brown (2.5YR 3/4) dry; moderate and strong very fine subangular blocky structure; hard, friable, sticky, plastic; common fine and very fine tubular pores; few fine black stains; thin patchy clay films; continuous pressure faces; many distinct slickensides up to 5 cm (2 in.) long; very few black concretions; slight effervescence with hydrogen peroxide; neutral (pH 6.9).

APPENDIX TABLE C.2. DATA AND DESCRIPTION FOR MAILE SOIL
(HYDRIC DYSTRANDEPTS), HAWAII I ISLAND

SOIL FAMILY Hydric Dystrandept, thixotropic, isomesic

U.S. DEPARTMENT OF AGRICULTURE
SOIL CONSERVATION SERVICE

SOIL SERIES Maile silt loam

SOIL Nos. 365Ha-1-7

LOCATION Hawaii County, Hawaii

Riverside Lab Nos. 6590 - 65101

Depth (cm)	Horizon	Mineralogical Analysis																	
		Allo- phane	Mont- moril- lonites	Micas	Kao- lin- ites	Gibbs- ite	Boehm- ite	Goeth- ite	Amor- phous SiO ₂	Amor- phous Al ₂ O ₃	Mag- netite etc.	Ana- tase	Quartz	Vol- canic glass	Feld- spar	Oli- vine	Pyrox- ene	Py- rite	
Percent of Whole Soil																			
0-5	A11																		
5-10	A12																		
10-35	A13	3X		2	2			15				5	5	2X		1X			
35-43	B21																		
43-50	B22																		
50-60	B23																		
60-73	IIC																		
73-90	IIIB24b	3X		5	2			20				1	5	1X		1X			
90-120	IIIB25b																		
120-150	IIIB26b	3X		2				10				10	5	tr.		1X			
0-10	A11/A12																		
35-73	B21/IIC																		
Depth (cm)	Total Chemical Analysis													Extractable iron 6C2a		Carbonate as 6E1b		0.5N NaOH Soluble	
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO ₂	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	L.O.I.	Total	Fe	Fe ₂ O ₃	CoCO ₃	SiO ₂	Al ₂ O ₃		
Percent of Whole Soil																			
0-5	A11																		
5-10	A12																		
10-35	A13	9.07	4.43	24.32	17.52	0.37	1.81	0.10	0.09	0.16	1.25	41.14	100.3	17.2	24.6				
35-43	B21													10.4	14.9				
43-50	B22													10.9	15.6				
50-60	B23													12.5	17.9				
60-73	IIC													9.1	13.0				
73-90	IIIB24b	11.08	4.12	24.38	21.33	0.31	1.43	0.06	0.10	0.30	1.17	35.90	100.2	14.4	20.6		4.32	4.53	
90-120	IIIB25b													8.6	12.3				
120-150	IIIB26b	15.15	4.27	29.19	17.51	0.29	3.48	0.67	0.19	0.14	1.49	28.04	100.4	6.5	9.3		8.61	6.02	
0-10*	A11/A12													21.8	31.2				
35-73*	B21/IIC													11.1	15.9				
Depth (cm)	6A1a Organic carbon Pct.	6B1a Nitro- gen Pct.	C/N	Extractable bases 5B1a				Sum of bases	Extr. acidity 6H2a	Cation exch. capacity		NH ₄ OAc 6L2a extr. SO ₄	KCl extr. Al ⁺⁺⁺ 6G1D	Base saturation			pH		
				6N2a Ca	6O2a Mg	6P2a Na	6Q2a K			5A1a NH ₄ OAc	Sum			5C1 NH ₄ OAc	5C3	8C1a H ₂ O	8C1c KCl		
Meq./100 g.																			
0-5	18.00	1.220	15	9.2	1.8	0.6	0.7	12.3		56.2		0.8	1.2	22			1:5	1:5	
5-10	5.12	0.464	11	0.7	0.3	0.2	0.1	1.3		25.5		0.4	1.1	5			5:4	4:5	
10-35	11.74	0.654	18	-	0.1	0.1	0.1	0.3		56.1		1.2	0.7	1			5:2	4:9	
35-43	10.55	0.581	18	-	0.2	0.1	0.1	0.4		43.2		4.4	0.2	1			5:3	5:1	
43-50	9.79	0.545	18	-	0.1	0.4	0.1	0.6		38.2		6.1	0.2	2			5:4	5:3	
50-60	9.04	0.498	18	-	tr.	0.1	0.1	0.2		43.6		6.6	0.2	tr.			5:4	5:3	
60-73	8.32	0.429	19	-	tr.	0.1	0.1	0.2		36.7		5.5	-	1			5:3	5:3	
73-90	8.89	0.436	20	-	0.2	0.1	0.1	0.4		42.2		8.7	-	1			5:1	5:3	
90-120	9.15	0.422	22	-	-	0.1	0.1	0.2		50.5		7.5	0.2	tr.			5:2	5:3	
120-150	4.66	0.192	24	-	0.1	0.1	0.1	0.3		31.1		7.3	0.1	1			5:2	5:5	
0-10		0.631		1.1	0.4	0.3	0.2	2.0		36.8		0.7	1.4	5			5:4	4:5	
35-73		0.578		-	0.1	0.2	0.1	0.4		37.6		6.8	0.2	1			5:3	5:2	
Depth (cm)	Size class and particle diameter (mm) 3A1			Coarse fragments >2mm pct. of whole soil	Atterberg limits			Bulk density			Particle density	Water content		Extensibility					
	Sand (2-0.05)	Silt (0.05-0.002)	Clay (<0.002)		Plastic limit Pct.	Liquid limit Pct.	Plastic index Pct.	1/3 bar	Oven dry	Field moist		1/3 bar	15 bar	4D1	COLEf	COLE			
g/cc																			
0-5																			
5-10										0.52	3.12			65.9	41.9				
10-35										0.41	2.60			160.4	131.8				
35-43										0.32	2.56			198.1	161.1				
43-50										0.32									
50-60										0.34									
60-73					158	190	32			0.30									
73-90										0.26	2.62			242.4	193.9				
90-120					226	280	54			0.30	2.63			234.2	192.7				
120-150					N.P.	N.P.	N.P.			0.45	2.73			159.0	126.4				
0-10																			
35-73					214	240	26												

* Composite bulk samples
 a/ 34.3 kg of organic carbon per square meter to a depth of 1 meter.
 b/ These samples were not allowed to dry prior to analysis.

APPENDIX TABLE C.2.—Continued

MAILE SILT LOAM
S65Ha-1-7

LOCATION: Island of Hawai'i, Hawai'i County, Hawai'i. USGS Umikoa Quadrangle, lat. 19°59'00" N. long. 155°32'32" W; 0.8 km (½ mile) NE of Kukaiiau Ranch headquarters at point about 90 m (100 yd) west of ranch road. SAMPLING DATE: 7 April 1965.

DESCRIPTION BY: H. Sato and L. Giese. COLLECTORS: L. Giese, K. Flach, L. Swindale, H. Sato, R. Smythe, G. Yamamoto, and W. Subica.

CLASSIFICATION: Hydric Dystrandepts, thixotropic, isomesic.

VEGETATION: Ohia-grass cover; kikuyu (*Pennisetum clandestinum*), white clover (*Trifolium repens*), ohia (*Metrosideros collina*), and tree fern (*Cibotium menziesii*). CLIMATE: Average annual precipitation 1 524 to 2 286 mm (60-90 in.); mean annual temperature 14°C (57°F), January mean 12°C (54°F), July mean 17°C (63°F). PARENT MATERIAL: Volcanic ash. TOPOGRAPHY: Intermediate windward mountain slopes of Mauna Kea, convex 10% slope, north aspect. ELEVATION: 1 020 m (3400 ft). DRAINAGE: Well drained; slow runoff; moderately rapid permeability. SOIL MOISTURE: Moist.

REMARKS: Textures are apparent field textures. Paired sample number S65Ha-1-8.

<u>HORIZON</u>	<u>DESCRIPTION</u>
A11 RSL No. 6590	0 to 5 cm (0-2 in.), dark reddish brown (5YR 2/2) silt loam, black (2.5YR 2/1) dry; moderate fine subangular blocky structure; hard, friable, slightly plastic; many roots; many fine pores; medium acid (pH 6.0); abrupt, smooth boundary.
A12 RSL No. 6591	5 to 10 cm (2-4 in.), dark reddish brown (5YR 2/2) cindery sandy loam, dark brown (10YR 3/3) dry; moderate fine subangular blocky structure, hard, friable; many roots; common, fine black cinders and charcoal; medium acid (pH 6.0); abrupt, smooth boundary.
A13 RSL No. 6592	10 to 35 cm (4-14 in.), very dark brown (10YR 2/2) silty clay loam, dark brown (10YR 3/3) dry; strong fine subangular blocky structure; extremely hard, friable, slightly sticky, plastic, smeary, many roots; many fine pores; slightly acid (pH 6.1); clear, wavy boundary.
B21 RSL No. 6593	35 to 43 cm (4-14 in.) very dark brown (10YR 2/2) silty clay loam, dark brown (7.5YR 3/3) dry; weak coarse prismatic structure breaking to moderate fine subangular blocky structure; very hard, friable, slightly sticky, plastic, weakly smeary; many roots; many fine pores; slightly acid (pH 6.2); clear, smooth boundary.
B22 RSL No. 6594	43 to 50 cm (17-20 in.), dark brown (10YR 3/3) silty clay loam, very dark brown (10YR 2/2) dry; weak coarse prismatic structure breaking to moderate fine subangular blocky structure; very hard, friable; sticky, plastic, weakly smeary; common roots; many fine pores; slightly acid (pH 6.2); clear, smooth boundary.
B23 RSL No. 6595	50 to 60 cm (20-24 in.), dark yellowish brown (10 YR 3/4) silty clay loam, very dark brown (10YR 2/2) dry; weak coarse prismatic structure breaking to moderate fine subangular blocky structure; very hard, friable, sticky, plastic weakly smeary, few roots; slightly acid (pH 6.5); clear, smooth boundary.
IIC RSL No. 6596	60 to 73 cm (24-29 in.), dark brown (10YR 3/3) silty clay loam, very dark brown (10YR 2/2) dry; structureless, massive, hard, firm, slightly sticky, slightly plastic, weakly smeary; tuff band, few roots; many fine pores; slightly acid (pH 6.5); abrupt, smooth boundary.
IIIB24b RSL No. 6597	73 to 90 cm (19-36 in.), dark brown (7.5YR 3/4) silty clay loam, very dark brown (10YR 2/2) dry; weak medium and fine subangular blocky structure; very hard, friable, sticky, plastic, moderately smeary; few roots, many fine pores, common patchy glaze; neutral (pH 6.6); abrupt, smooth boundary.
IIIB25b RSL No. 6598	90 to 120 cm (36-48 in.), very dark brown (10YR 2/2) silty clay loam, (10YR 2/2) dry; weak coarse and medium prismatic structure breaking to moderate medium and fine subangular blocky structure; very hard, friable, sticky, plastic, moderately smeary; few roots; many fine pores; common patchy gelatin-like coatings on peds; tuff band about 5 cm (2 in.) thick; neutral (pH 6.6); abrupt, smooth boundary.
IIIB26b RSL No. 6599	120 to 150 cm (48-60 in.), very dark brown (10YR 2/2) silty clay loam, very dark grayish brown (10YR 3/2) dry; weak medium subangular blocky structure; friable, sticky, plastic, moderately smeary; few roots; many fine pores; neutral (pH 6.6).

APPENDIX TABLE C.3. COMPARISON OF DBCP QUANTITIES APPLIED IN
THE FIELD AND IN THE LABORATORY FOR SOIL
VOLATILIZATION STUDY

Field Application: 3 gal/acre of 85.5% DBCP

$$(3 \text{ gal/acre}) (0.855) = 2.4 \times 10^{-4} \text{ ml/cm}^2$$

which is equivalent to $5.33 \times 10^{-6} \text{ ml/cm}^3$ in 45 cm soil layer
or $10.9 \text{ } \mu\text{g/cm}^3$

Laboratory Dosage: 1.0 ml of 35.0 $\mu\text{g/ml}$ DBCP solution/100-cm³
soil = $0.35 \text{ } \mu\text{g/cm}^3$

ASSUMPTIONS:

1. DBCP density of 2.05 g/ml
 2. Field application achieves uniform distribution of DBCP throughout a 45 cm deep soil layer
-



FUMAZONE* 86

NEMATICIDE

FUMAZONE 86 is intended for application to mineral soil to control plant parasitic nematodes such as awl, citrus, cyst, dagger, lance, lesion or meadow, pin, ring, root-knot, spiral, sting, stubby root, stunt and symphylians in land to be planted to crops listed in the accompanying "Dosage and Use Recommendation" table. NOTE: DO NOT ATTEMPT TO DILUTE WITH WATER FOR CHISEL APPLICATION — THIS IS NOT AN EMULSIFIABLE FORMULATION

DIRECTIONS FOR USE

Apply FUMAZONE 86 when soil temperature at a depth of not less than 5 inches is between 40° and 80° F. Soil should be in seedbed condition with adequate moisture for good seed germination. Work plant remains into the soil and allow time to decompose before treating. Do not treat extremely wet or dry soils. Read the entire label before making application.

OVERALL APPLICATION

Apply FUMAZONE 86 when soil temperature at a depth of not less than 5 inches is between 40° and 80° F. Soil should be in seedbed condition with adequate moisture for good seed germination. Work plant remains into the soil and allow time to decompose before treating. Do not treat extremely wet or dry soils. Read the entire label before making application.

METHOD: Either chisel equipment, with chisels 12 inches apart or plowshare equipment may be used to apply the fumigant. With this equipment release the fumigant at a depth of 5 to 8 inches. Overall application may also be accomplished by introducing the fumigant into irrigation water through centrifugal pumps.

SOIL SEALING: Immediately after chisel application, seal and compact the soil by using a roller, cultipacker, or similar device or flood with water. After plowshare application, disk the land, then compact by rolling.

EXPOSURE PERIOD: After overall preplant application, leave soil undisturbed for 7 to 14 days.

Aeration and Preparation of Soil Before Planting: After overall preplant application, the soil should be aerated by deep cultivation at the end of the exposure period. If heavy rains occur, accompanied by low temperatures during the exposure period, additional aeration is required. Working the soil several times before planting will aid in aeration which is usually adequate when the fumigant odor is gone. Shallow-rooted crops can usually be planted about one week after the end of the exposure period. For deep rooted trees and shrubs, the aeration period after preplant treatments should be 4 to 6 weeks.

ROW APPLICATION

For Use as Preplant and at Planting Time: Use two or more chisels per row depending upon the width of the area to be treated. Set chisels 12 inches apart and inject the fumigant 5 to 8 inches below the final soil surface planting level. For preplant applications the treated rows may be marked by bedding or lining, and by tractor or press wheels.

For Use as Postplant Application: Use two or more chisels per row and in such a manner as to treat both sides of the row, with the chisel injection lines no closer to the plant line than 4 inches.

Planting Instructions with Row Application: Direct seeding may be done at the time the fumigant is applied or at any time after a preplant application. Keep seed at least 4 inches away from chisel injection furrow to avoid poor stands due to loose soil in the area.

When setting transplants use following instructions: (1) Preplant treatment with 14 day wait, plant anywhere, or (2) Preplant treatment with less than 14 day wait, set plants at least 4 inches from chisel injection furrow, or (3) Fumigated at planting time, set plants at least 4 inches from chisel injection furrows.

For best control of nematodes, seal all row treated soil immediately after application and after any subsequent disturbing of the soil within 7 days after treatment. This can be done by tractor wheels and by lining or bedding followed by ring rollers, press wheels or flooding with water.

IRRIGATION APPLICATION

FUMAZONE 86 is recommended for use at the rate of 30 ppm of the active ingredient in sufficient water to give penetration to the desired depth. 0.561 gallons of FUMAZONE 86 per acre inch of irrigation water will provide 30 ppm by weight of active ingredient. For the irrigation treatment, multiply 0.561 gallons by the number of acre inches of water to be applied by the number of acres to be fumigated. For example, if an irrigation of 5 acre inches of water is planned, and 10 acres are to be treated, the following calculation will give the number of gallons of FUMAZONE 86 required: Example: 0.561 x 5 x 10 = 28.05 gallons. In this case the dosage is equivalent to 2.805 gallons of FUMAZONE 86 per acre.

Irrigation Application Equipment: For best results FUMAZONE 86 should be applied by introducing the fumigant into the intake side of a centrifugal pump having a minimum output of not less than 4% of the total gallons of water of the irrigation system. The fumigant should be metered directly into the pump from its original container through a simple gravity flow applicator. There are several excellent applicators of this type commercially available.

Water Requirements to Bring Soil Moisture from the Wilting Point to Field Capacity: It has been determined that this fumigant in irrigation water will penetrate the soil to approximately one half of the depth of the water penetration. Therefore, sufficient water should be applied to bring the field capacity to a depth about twice that desired to be fumigated. On deep sandy soils this will require about 4 to 6 acre inches of water. The following table is offered as a guide to estimate the water requirements to bring soil moisture from the wilting point to field capacity.

Type of Soil	Acre Inches of Water Required For:	
	Top 6 to 8 inches of soil	Each additional foot of soil depth
Sand	1/2 to 1	1/2 to 1
Loam	1 to 2	1 to 2
Clay	2 to 3	2 to 3

APPLICATION SUGGESTIONS:

1. Apply the fumigant in all the water used in a given irrigation.

2. Do not use more treated water per acre in one irrigation than will provide the maximum dosage of FUMAZONE 86 recommended for each crop listed in the accompanying "Dosage and Use Recommendations" table.
3. Always determine the water delivery rates of the pump and canal or ditch before irrigation. This determination is necessary to assure accurate dosage which is based on total volume of irrigation water.
4. Irrigate with a maximum amount of water in a minimum period of time. Best results are obtained when irrigation time is two hours or less.
5. For best results, cover as much of the soil surface as possible with the treated irrigation water.
6. The necessity for treatment of perennial crops is dependent upon reestablishment of damaging nematode populations. Over-all treatment will usually give 2 to 4 years control of nematodes. To avoid the possibility of exceeding the residue tolerances of food crops, do not treat by irrigation more often than once a year.

DOSAGE AND USE RECOMMENDATIONS

Crops	Application		Dosage (a)	
	Time	Type	Gallons Per Acre	#1 Oz./1000 ft Row Per Chisel
Vegetables: Broccoli, brussels sprouts, cabbage, cauliflower, carrots, celery, egg plant, endive (escarole), lettuce, okra, parsnips, radishes, snapbeans (c)	Preplant	Overall (b)	1.5 to 2.0	4.4 to 5.9
	At Planting	Row (d)		
Cucurbits: Melons, cucumbers and summer squash	Preplant	Overall (b)	1.5 to 2.0	4.4 to 5.9
	At Planting	Row (d)		
Lima beans: (a)	Preplant	Overall (b)	1.0 to 1.7	2.9 to 5.0
	At Planting	Row (d)		
Tomatoes:	Direct Seeded	Overall (b)	1 to 1.5	2.9 to 4.4
		Row (d)		
	Transplants	Overall (b)	1.0	2.9
		Row (d)		
Soybeans: (a) Southeastern States Only (q)	Preplant	Row (p)	0.5 to 1.0 (42" row)	5.1 to 10.3
	At Planting	Row (d)	1.0 to 2.0	2.9 to 5.9
Cotton:	Preplant	Overall (b)	1.5 to 4.5	4.4 to 13.2
	At Planting	Row (d)		
Bananas:	Preplant	Overall (b)	1.5	4.4
	At Planting	Row (d)		
Pineapple:	Preplant	Irrigation (h)	3.0 to 11.0	8.8 to 32.3
	At Planting	Row (d)		
Berries: Blackberries, boysenberries, dewberries, loganberries, raspberries and strawberries (i)	Preplant	Overall (b)	2.0	5.9
	At Planting	Row (d)		
	Postplant (j)	Irrigation		
Citrus Fruit (k): Grapefruit, lemons, limes, oranges, tangerines	Preplant	Overall	3.0 to 7.0	8.8 to 20.6
	At Planting	Row (d)		
Deciduous Fruit and Nuts: Apricots, cherries (l, h), figs (l), grapes, nectarines, peaches, plums (prunes) (l, h), almonds (m), English walnuts (m)	Preplant	Irrigation	3.0 to 7.0	8.8 to 20.6
	At Planting	Row (d)		
	Postplant	Overall (b)		
Ornamentals: flowers, shrubs, trees, etc. Tolerant species (n)	Preplant	Overall (b)	3.0	8.8
	At Planting	Row (d)		
	Postplant	Irrigation		
Moderately Tolerant species (n)	Preplant	Overall (b)	1.5	4.4
	At Planting	Row (d)		
	Postplant	Row (d)		
Turf:	Preplant	Overall (k)	3.0	8.8
	At Planting	Row (d)		
Peanuts (r)	Preplant	Overall (b)	1.4 to 2.1	4.1 to 6.2
	At Planting	Row (d)		

* Any forage crops grown on soil treated with a bromide containing fumigant should not be used as a feed for dairy animals, or animals being finished for slaughter, until 2 years after row treatments and 3 years following overall treatments.

NOTE: All references to gallons are to U.S. gallons.

(a) Use dosages in the lower range in light sandy soil and dosages in the higher range on heavier mineral soil or where deeper penetration is desired. Do not exceed maximum dosage per acre in a single year.

(b) Overall application may be made with injection equipment or by irrigation.

(c) Do not feed food plant remains to dairy cattle or animals being finished for slaughter.

(d) For row applications where 2 or more chisels are used per row apply at the same rate per chisel as for overall. As the distance between rows is increased, the amount of fumigant applied per acre will decrease and vice versa. For crop planting see label directions under "Planting Instructions with Row Applications."

(e) Make the postplant application as soon as the plants become firmly established.

(f) Do not apply more than once in each 9 to 12 month period following initial application.

(g) Do not apply within 9 months of harvest.

(h) Apply in about 1/2 inch of irrigation water.

(i) Two postplant applications are recommended, the first as soon as the plants become established the second 4 to 6 weeks later. Note: Do not treat any of the bumble fruits within 48 days of harvest.

(j) Do not apply within 55 days of harvest.

(k) Apply no more often than once each 3 years.

(l) Do not apply within 30 days of harvest. Do not use more than 3 gallons per acre (14.7 lb. oz. per 1,000 feet row per chisel).

(m) Do not apply within 30 days of harvest.

(n) Before application, to determine tolerant and moderately tolerant species, consult manufacturer's literature, "FUMAZONE NEMATICIDE—A Check List for Use on Ornamental Plants."

(o) Soybean hay and plant remains from lima beans grown on treated soil may contain bromide residues greater than those resulting from natural sources. Accordingly, do not graze treated areas or feed soybean hay or lima bean plant remains to meat or dairy animals. Do not sell such plant parts to another party or otherwise introduce into commerce.

(p) Use a single chisel per row and apply at the same flow rate per 1000 feet row per chisel as given in table, regardless of row spacing. Gallons per acre will increase as row spacing decreases and vice versa.

(q) Ala., Ark., Del., Fla., Ga., Ky., La., Md., Miss., N.C., S.C., Va., Tenn. and the southern third of Ill. and Mo.

(r) Do not feed, sell or introduce into commerce hay or hulls taken from treated soil.

Figure D.1. Dow Chemical Company DBCP Label No. 1



SYMPHYLANS: To control symphylians use only over-all applications at the dosages indicated in the table. Apply during late summer or early fall when the soil is warm.

USE PRECAUTIONS

Caution — Note Carefully: Fumigation may temporarily raise the level of ammonia nitrogen and of soluble salts in the soil. This is most likely to occur when heavy rates of fertilizer and fumigant are applied to soils that are either cold, wet, acid or high in organic matter. To avoid injury to roots of ammonia sensitive plants, fertilize as indicated by soil tests made **after** fumigation. To avoid ammonia injury or nitrate starvation, or both, avoid using fertilizers containing ammonium salts, and use only fertilizers containing nitrates until after the crop is well established and the soil temperature is above 65°F. Certain crops, including cotton and pineapple, are tolerant to ammonia; the above rule does not apply to them. Liming highly acid soils before fumigation stimulates nitrification and may reduce the possibility of ammonia toxicity.

Attention: To avoid reinfestation of treated soil, do not use transplants, tools or crop residues that may be contaminated with soil borne pests.

If foliage of plants is contacted with the fumigant, wash off immediately with water. FUMAZONE 86 is not recommended for use on extremely heavy mineral or muck soils.

Do not use containers, pumps or other transfer equipment made

of aluminum, magnesium or their alloys, as under certain conditions FUMAZONE 86 may be severely corrosive to such metals.

Store in tightly closed containers in cool place away from dwellings and out of reach of children. Not for use or storage in or around the home.

This product is toxic to wildlife. Keep out of lakes, streams and ponds. Birds and other wildlife in treated areas may be killed.

Rinse equipment and containers and dispose of wastes by burying in non-crop lands away from water supplies. Containers should be disposed of by punching holes in them and burying with wastes.

NOTICE: Seller warrants that the product conforms to its chemical description and is reasonably fit for the purposes stated on the label when used in accordance with directions under normal conditions of use, but neither this warranty nor any other warranty of MERCHANTABILITY or FITNESS FOR A PARTICULAR PURPOSE, express or implied, extends to the use of this product contrary to label instructions, or under abnormal conditions, or under conditions not reasonably foreseeable to seller, and buyer assumes the risk of any such use.

Patented U.S. No. 3,049,472. This product licensed for use according to methods of U.S. Patent 3,049,472.

10690-002-1

M577

THE DOW CHEMICAL COMPANY

AND SUBSIDIARIES

MIDLAND, MICHIGAN 48640, USA Horgen, SWITZERLAND HONG KONG
CORAL GABLES, FLORIDA 33134, USA SARNIA, ONTARIO, CANADA

*Trademark of THE DOW CHEMICAL COMPANY



FUMAZONE* 86

NEMATICIDE

SOIL FUMIGANT FOR CONTROLLING SOIL BORNE PLANT PARASITIC NEMATODES and FOR USE IN THE MANUFACTURE OF OIL SOLUTIONS, EMULSIFIABLE LIQUIDS, AND GRANULATED NEMATOCIDAL FORMULATIONS

ACTIVE INGREDIENT:†

1,2-dibromo-3-chloropropane and related halogenated C₃ aliphatics 85.5%
 INERT INGREDIENT 14.5%

†Contains 12.1 Pounds Active Ingredient per Gallon.

E.P.A. Registration No. 464-313-ZA

E.P.A. EST. 464-AR-1

AGRICULTURAL CHEMICAL

Do Not Ship or Store with Food, Feeds, or Clothing

PRECAUCION AL USUARIO: Si usted no lee inglés, no use este producto hasta que la etiqueta le haya sido explicada ampliamente.

TRANSLATION: (TO THE USER: If you cannot read English, do not use this product until the label has been fully explained to you.)

WARNING

**KEEP OUT OF REACH OF CHILDREN • HARMFUL LIQUID AND VAPOR • COMBUSTIBLE MIXTURE • CAUSES SKIN IRRITATION AND BLISTERS ON CONTACT • CAUSES IRRITATION OF EYES, NOSE AND THROAT • MAY BE ABSORBED THROUGH SKIN
 MAY BE HARMFUL OR FATAL IF SWALLOWED**

**Do Not Breathe Vapor • Keep Container Closed • Do Not Get in Eyes, on Skin, or on Clothing • Do Not Take Internally • Use Only in a Well-Ventilated Area
 Wash Thoroughly with Soap and Water After Handling and Before Eating and Smoking • Do Not Contaminate Feed and Foodstuffs • Keep Children and Pets Off Treated Area until This Material Has Been Washed into Soil • Keep Away From Heat and Open Flame**

In case of contact, immediately remove contaminated shoes and clothing and wash skin with soap and water. Flush eyes with plenty of water for at least 15 minutes and get medical attention. Do not wear shoes or clothing until ABSOLUTELY free of all chemical odor. If illness results from inhalation, remove to fresh air and call a doctor. If swallowed, call a doctor. Induce vomiting by giving an emetic such as 2 tablespoons of table salt in a glass of warm water.

18.93 L / 5 GAL

86-1075 PRINTED IN U.S.A. IN MAY, 1977.

REPLACES SPECIMEN LABEL 86-1075 PRINTED MARCH, 1975.

DISCARD PREVIOUS SPECIMEN LABELS

REVISIONS INCLUDE: (1)REVISED PRECAUTIONARY FORMAT.

(2)ADDED DOT FLAMMABLE DIAMOND AND THE WORDS

FLAMMABLE LIQUID N.O.S. (Contains Allyl Chloride)

(3)REVERSED ENGLISH/METRIC UNITS

(4)DROPPED PATENT # 2,937,936