

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

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

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WATER RESOURCES RESEARCH CENTER
University of Hawaii at Manoa
Honolulu, Hawaii 96822

SUBSURFACE WATER QUALITY: PESTICIDES CONTAMINATION

PERSONNEL

- Dr. L. Stephen Lau, Director, Water Resources Research Center; and
Professor, Department of Civil Engineering
(Project Principal Investigator)
- Dr. G.L. Dugan, Professor and Chairman, Civil Engineering
Dr. P.C. Ekern, Hydrologist, WRRRC; Professor, Agronomy and Soils
Dr. R.S. Fujioka, Virologist, WRRRC
Mr. H.K. Gee, Environmental Engineering Specialist, WRRRC
Dr. T.W. Giambelluca, Assistant Hydrologist, WRRRC
Dr. R.E. Green, Professor, Agronomy and Soils
Dr. J.W. Hylin, Professor, Agricultural Biochemistry
Dr. R.C. Jones, Associate Professor of Soils
Dr. F.D. Miller, Associate Researcher, WRRRC; Associate Professor,
Public Health
Mr. J.F. Mink, Hydrologist-Geologist; Research Affiliate, WRRRC
Mr. E.T. Murabayashi, Land-Use Specialist, WRRRC
Dr. F.L. Peterson, Professor and Chairman, Geology and Geophysics

COOPERATING AGENCIES

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PREFACE

This report is part of the "Subsurface Water Quality: Pesticides Contamination" project authorized in Act 285, Section 38F, by the Twelfth Legislature, State of Hawaii, and supported by the Office of Environmental Quality Control with the cooperation of several data collecting agencies. Other project activities currently in progress focus on the following topics: geologic factors, mineralogic parameters, chronology of deep water percolation through pineapple fields, leaching properties of fumigants from soils, temporal and spatial distributions of contaminants in basal groundwaters, well and aquifer rehabilitation, and methods of contaminant removal. Forthcoming reports will present the results of these activities.

ABSTRACT

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

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

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

CONTENTS

PREFACE	A-iii
ABSTRACT.	A-v
INTRODUCTION.	A-1
Sorption-Desorption Processes.	A-1
Methodology.	A-2
OBJECTIVES.	A-3
APPROACH AND METHOD DEVELOPMENT	A-3
Measuring Distribution Coefficients—Background.	A-4
Direct Sorption Method	A-4
Indirect Sorption Method	A-7
Purge System	A-9
Column Study	A-11
Selection of Soil Samples for Sorption-Desorption Studies	A-12
ACCOMPLISHMENTS	A-12
Initial Development of Vapor Sampling Techniques	A-12
Using Indirect Sorption Method	A-13
Solving Mass Balance Relations Using Henry's Law	A-13
Results of Henry's Law Experimental Work	A-14
Modification of Application of Henry's Law	A-15
Preliminary K_d Experiment.	A-18
Purge System	A-18
SUMMARY	A-18
REFERENCES CITED.	A-20

Figures

1. Schematic Diagram Outlining Basic Steps in Direct Sorption Method (Batch Equilibration Method).	A-6
2. Schematic Diagram Outlining Basic Steps in Indirect Sorption Method	A-8
3. Diagram of Purge System Used for Collecting Pesticide Vapor Purged from Soil in Solution.	A-10
4. Linear Plot Showing Dependence of K_h on Temperature and Varying Concentrations of DBCP in Solution.	A-16

5. Linear Plot Showing Dependence of K_h on Varying Concentrations of DBCP in Solution.	A-16
6. Logarithmic Plot Showing Linearity of DBCP Vapor Concentrations at Low Solution Concentrations and Deviation from Linearity at High Solution Concentrations.	A-17

Tables

1. Comparison of K_h Values Derived from Measurements of DBCP Vapor in Soil Solution and Tap-Water Samples by Using Indirect Sorption Method.	A-15
2. Data Used to Calculate DBCP Distribution Coefficient (K_d) by Indirect Sorption Method and Calculation Sequence for Soil Sample	A-19

INTRODUCTION

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

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

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

Sorption-Desorption Processes

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

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

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

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

Methodology

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

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

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

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

OBJECTIVES

The objectives of this project are

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

APPROACH AND METHOD DEVELOPMENT

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

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

varying time intervals.

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

Measuring Distribution Coefficients—Background

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

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

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

The amount of pesticide sorbed onto soil particles is given by

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

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

Direct Sorption Method

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

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

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

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

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

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

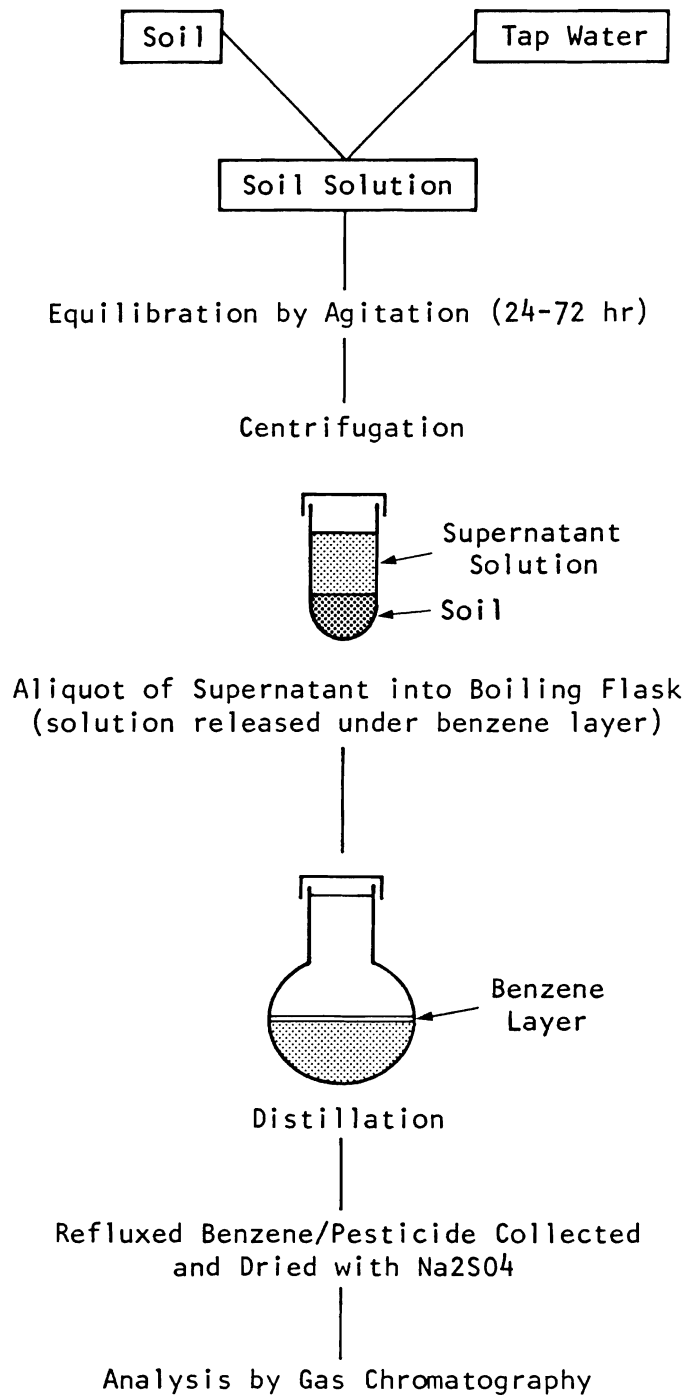


Figure 1. Schematic diagram outlining basic steps in direct sorption method (batch equilibration method)

tion at any given time can be measured.

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

Indirect Sorption Method

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

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

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

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

Mass balance in a soil-pesticide system is defined as

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

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

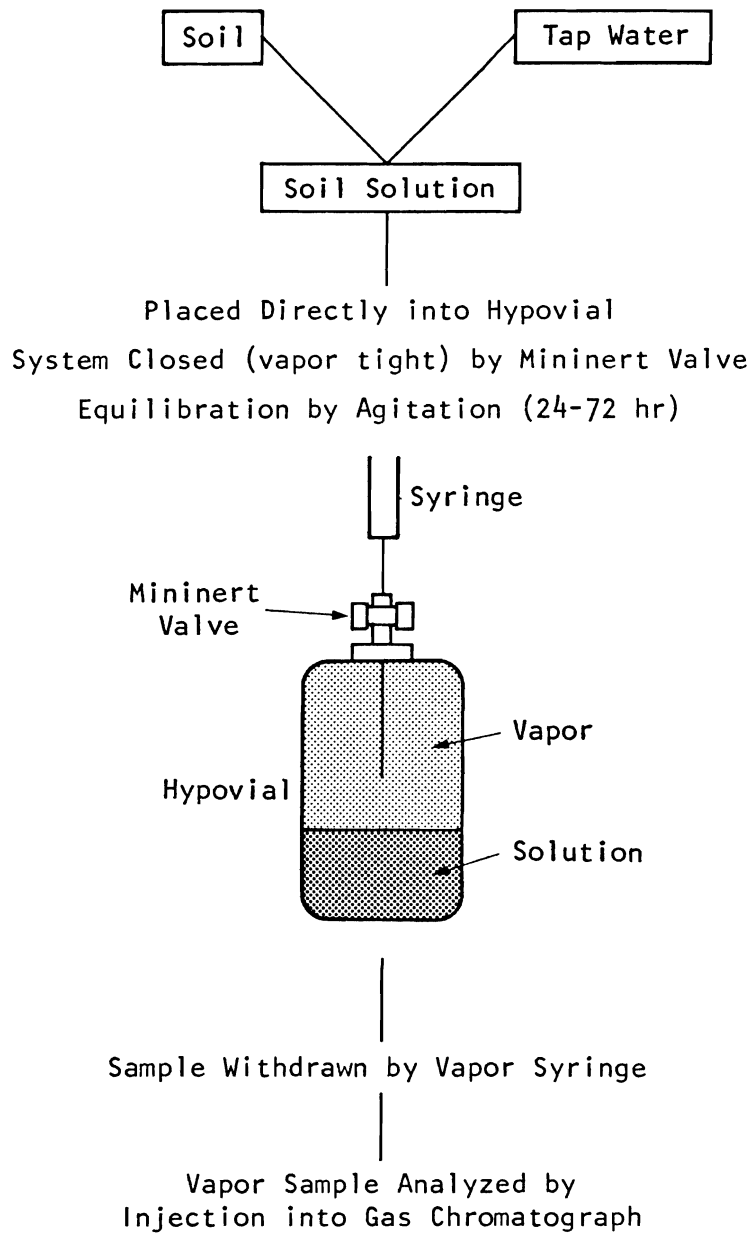


Figure 2. Schematic diagram outlining basic steps in indirect sorption method

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

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

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

Purge System

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

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

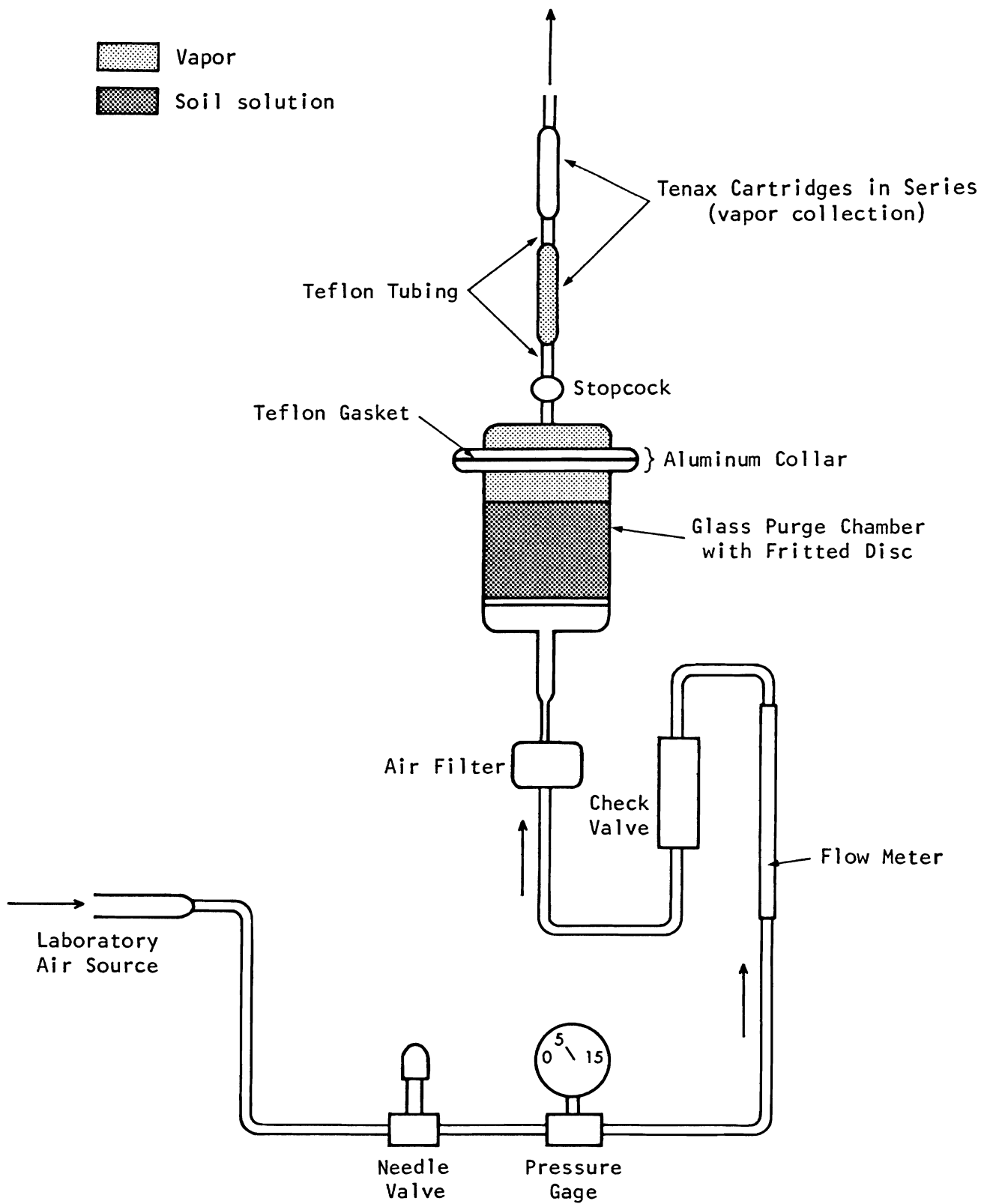


Figure 3. Diagram of purge system used for collecting pesticide vapor purged from soil in solution

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

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

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

Column Study

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

Selection of Soil Samples for Sorption-Desorption Studies

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

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

ACCOMPLISHMENTS

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

Initial Development of Vapor Sampling Techniques

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

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

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

Using Indirect Sorption Method

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

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

Solving Mass Balance Relations Using Henry's Law

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

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

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

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

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

Results of Henry's Law Experimental Work

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

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

The vapor pressure of a volatile compound is a temperature dependent

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

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

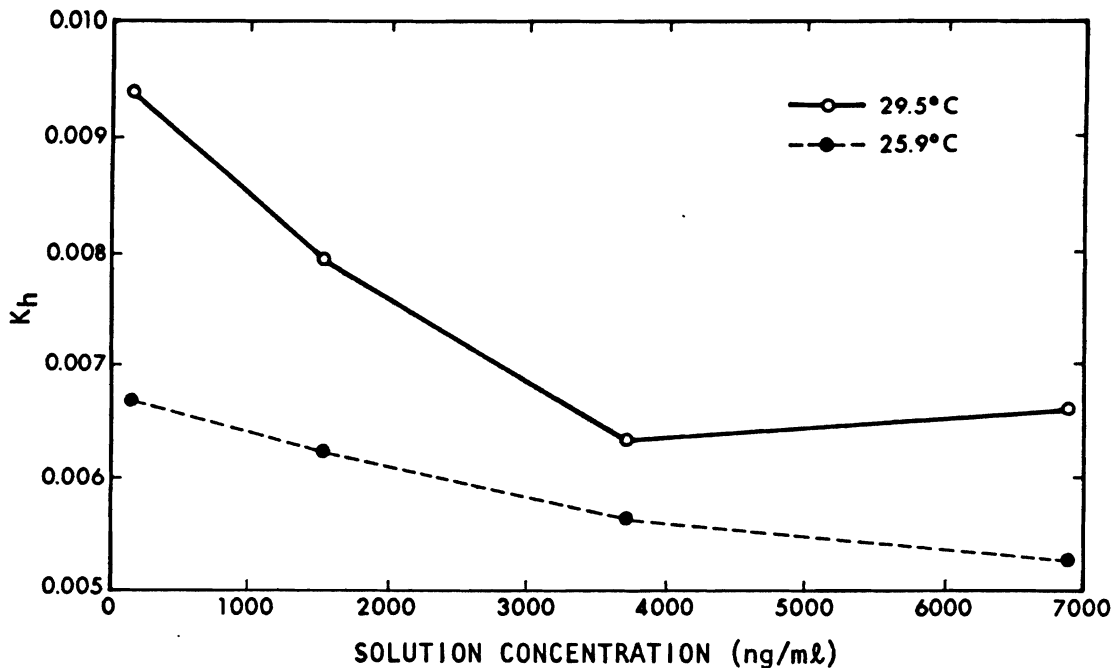
property (MacKay et al. 1982). This behavior was examined experimentally for DBCP by equilibrating and analyzing solutions in a laboratory that was not temperature controlled. Figure 4 shows the results of duplicate samples analyzed at different times (and temperatures) during a single day. K_h values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

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

Modification of Application of Henry's Law

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

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



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

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

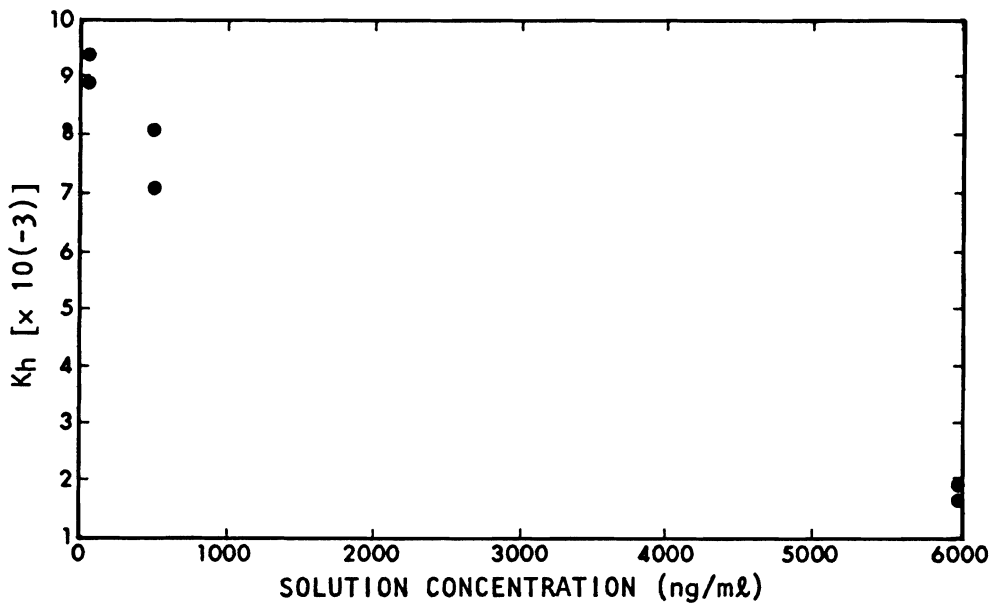


Figure 5. Linear plot showing dependence of K_h on varying concentrations of DBCP in solution

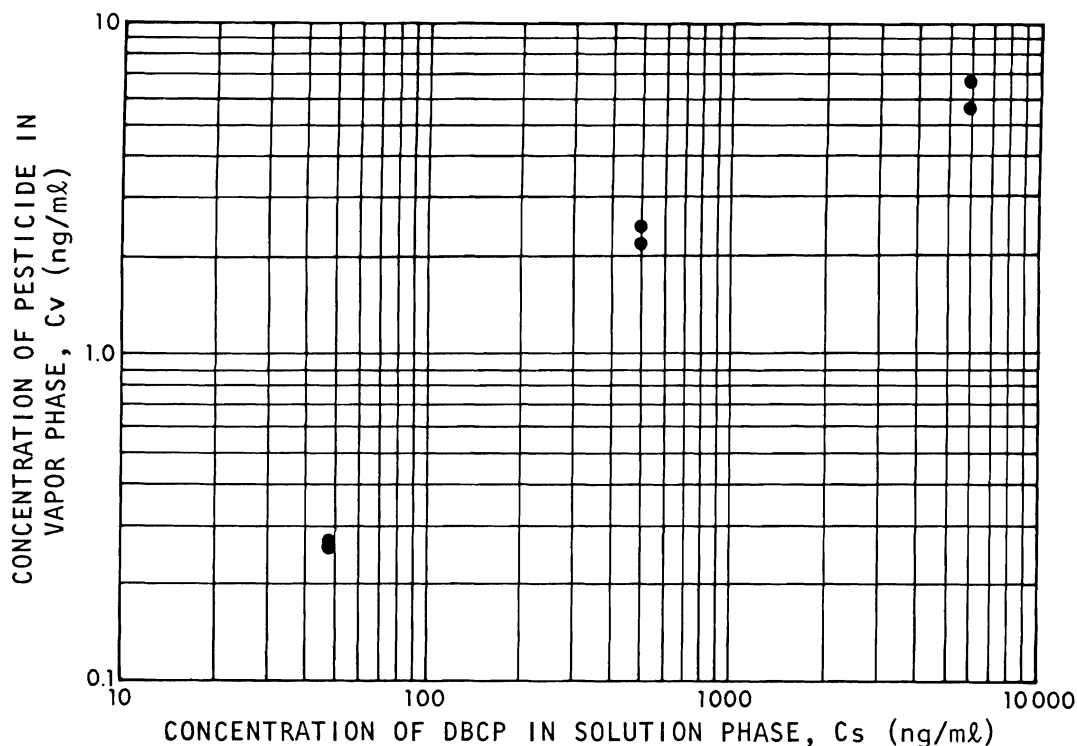


Figure 6. Logarithmic plot showing linearity of DBCP vapor concentrations at low solution concentrations and deviation from linearity at high solution concentrations

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

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

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

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

Preliminary Kd Experiment

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

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

Purge System

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

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

SUMMARY

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

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

Sample	Cv	Cs	S	Kd
	Measured ————— (ng/ml)	Calculated —————	Calculated (ng/g)	Calculated (ml/g)
1	0.2077	24.39	5.00	0.205
2	0.2048	23.87	6.74	0.282

Calculation Sequence for Soil Sample 1:

$$\text{Step 1 (eq. [5]): } C_v = 0.0258 C_s^{(0.653)}$$

or

$$C_s = \left(\frac{0.2077}{0.0258} \right)^{(1/0.653)} = 24.39$$

$$\text{Step 2 (eq. [3]): Total = sorbed phase + solution phase + vapor phase}$$

or

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

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

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

GLOSSARY

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

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