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Land Disposal of Hexachlorobenzene Wastes

Controlling Vapor Movement in Soil

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LAND DISPOSAL OF HEXACHLOROBENZENE WASTES

Controlling Vapor Movement in Soil

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FOREWORD

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

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

This report presents results of a study of the volatilization and vapor phase movement of hexachlorobenzene (HCB) from industrial wastes deposited on land. The work focused on understanding the factors that control movement of HCB in soil. The principal application of the results will be in designing adequate soil covers for land disposal sites receiving HCB wastes.

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ABSTRACT

Hexachlorobenzene (HCB) is a persistent (chemically stable and resistant to microbial degradation), water-insoluble, fat-soluble organic compound present in some industrial wastes. Because of its low water-solubility (6.2 ug/l), transport in water moving through soil will be negligible. Its long term persistence and appreciable vapor pressure (1.91×10^{-5} mm Hg at 25 C) allows significant volatilization to occur. The potential for volatilization indicates a need for disposal site coverings that will reduce the vapor phase transport of HCB into the surrounding atmosphere. Research was initiated to determine the conditions that would control the movement of HCB out of landfills and other disposal/storage facilities into the surrounding atmosphere. The volatilization fluxes of hexachlorobenzene from industrial wastes (hex wastes) were determined using coverings of soil, water, and polyethylene film in a simulated landfill under controlled laboratory conditions. Coverings of water and soil were found to be highly efficient in reducing volatilization. Polyethylene film was less efficient when compared on a cost basis. Volatilization flux through a soil cover was directly related to soil air-filled porosity and was therefore greatly reduced by increased soil compaction and increased soil water content. An organic liquid phase associated with the hex waste was heavier than water and contained 1.4% HCB by weight. The presence of HCB in this liquid phase creates the potential for the rapid transport of HCB in porous media. A procedure is proposed for using the results of this study to design a landfill cover that will limit the volatilization flux of HCB and other compounds.

This report was submitted in fulfillment of Contract No. 68-03-2014 by the University of California, Riverside, under the sponsorship of the U. S. Environmental Protection Agency. The report covers the period from June 14, 1974, to September 13, 1976, and work was completed as of September 13, 1976.

CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables ix
Acknowledgement x

1. Introduction 1
2. Conclusions 6
3. Recommendations 8
4. Materials and Methods 9
   Collection and preparation of hex waste and soil samples . 9
   Recrystallized practical grade HCB 12
   Measurement of HCB solubility and vapor pressure 12
   Simulated landfill volatilization cell 14
   HCB volatilization experiment 15
   Extraction, clean-up, and analysis of HCB 17
5. Results and Discussion 19
   Solubility and vapor pressure of HCB 19
   Volatilization of HCB from simulated landfill 24
      Uncovered hex waste 24
      Hex waste covered with polyethylene film 25
      Hex waste covered with water 28
      Hex waste covered with soil layer 29
      Hex waste covered with a composite layer of soil and polyethylene film 36
   Effect of soil parameters on HCB volatilization 37
   Calculation of HCB vapor phase diffusion coefficient . . . 43
6. Significance of Findings for Some Disposal Practices 49
   Equivalent thickness of polyethylene film 49
   Liquid component of the hex waste 50
7. Application of the Findings in Designing Landfill Covers 52
   Design application 54
   Assessment application 58
   Discussion 59

References 64
Appendix 67
   Column cleanup procedure for volatilization products from hex waste 67

FIGURES

Number		Page
1	Soil water release curve for soil taken from municipal sanitary landfill used for the disposal of industrial wastes containing hexachlorobenzene.	10
2	Schematic drawing of vapor saturation cell	13
3	Details of volatilization cell used in simulated landfill. . .	14
4	Schematic drawing of closed air flow system for collecting volatilized HCB from a simulated landfill operation.	15
5	Effect of temperature on the vapor pressure of hexachlorobenzene. Extrapolated data are from Sears and Hopke (1949).	23
6	Volatilization vapor flux of hexachlorobenzene from hex waste A covered with 0.015 cm (0.006 in) polyethylene film in contact with waste which had been filtered only (Experiment I)	26
7	Volatilization flux of hexachlorobenzene from hex waste A covered with 0.025 cm (0.01 in) polyethylene film in contact with waste which had been filtered only (Experiment II).	27
8	Effect of liquid phase in hex waste on volatilization of hexachlorobenzene from polyethylene film covered hex waste which had been filtered only (Experiment I) and film covered waste which had been air-dried (Experiment XII). The thickness of the films were each 0.015 cm (0.006 in). Volatilization from uncovered hex waste is shown for comparison	28
9	Volatilization vapor flux of hexachlorobenzene from untreated soil at bulk density of 1.19 g/cm^3 and 17% (w/w) soil water content. The soil was initially collected from a landfill used for the disposal of HCB containing wastes	30
10	Volatilization vapor flux of hexachlorobenzene from hex waste A covered with 2.5 cm (1.0 in) soil at bulk density of 1.19 g/cm^3 (Experiment III). The hex waste	

Number Page

used in this experiment had been filtered only and contained considerable quantities of the liquid waste component. 32

11 Volatilization vapor flux of hexachlorobenzene from hex waste A covered with 1.8 cm (0.75 in) soil at bulk density of 1.19 g/cm^3 (Experiment V). The hex waste used in this experiment had contacted several layers of soil and therefore did not contain significant amounts of the liquid waste. . . 34

12 Volatilization of hexachlorobenzene from two hex wastes collected from separate industrial sources and covered with 1.8 cm soil (Experiments V and VII) 35

13 Volatilization vapor flux of hexachlorobenzene from hex waste A covered with a composite layer of 1.8 cm soil and 0.01 cm polyethylene film (Experiment IV). The hex waste used in this experiment had been filtered only and contained considerable quantities of the liquid waste component 36

14 Volatilization vapor flux from hex waste A covered with a composite layer of 1.8 cm soil and 0.01 cm polyethylene film (Experiment VI). Results of duplicate experiments. The hex waste used in this experiment had contacted several layers of soil and therefore did not contain significant amounts of the liquid waste. 38

15 Effect of soil water content on the volatilization of hexachlorobenzene from recrystallized HCB covered with 1.8 cm soil at bulk density of 1.15 g/cm^3 (Experiments VIII and XI) 39

16 Effect of soil water content on the specific HCB volatilization flux through a soil cover 40

17 Effect of soil bulk density on the volatilization of hexachlorobenzene from recrystallized HCB covered with 1.8 cm soil cover (Experiments VIII, IX, and X) 41

18 Effect of soil bulk density on the specific HCB volatilization flux through a soil cover 42

19 Effect of air-filled porosity on the specific HCB volatilization flux through a soil cover 44

20 Linear regression line for the relationship between the specific HCB volatilization flux and the ratio $P_a^{10/3}/P_T^2$. . . 46

21 Predicted HCB volatilization flux through a soil cover as a function of soil water content and soil bulk density at 25 C. Soil thickness is 100 cm 48

Number | Page

22 The equivalent thickness of polyethylene film to soil assuming a soil bulk density of 1.19 g/cm^3 and a soil water content of 20% (w/w) 51

23 Flow diagram for predicting depth of soil cover required to limit vapor flux through soil cover to an acceptable value . 57

24 Predicted HCB volatilization fluxes through a soil cover of various soil bulk densities and soil thicknesses at 25 C. The soil was assumed to be dry (zero soil water content) in order to yield a maximum flux. 60

25 Predicted HCB volatilization fluxes through a soil cover of various soil water contents and soil thicknesses at 25 C. Soil bulk density is 1.2 g/cm^3 61

26 Predicted HCB volatilization fluxes through a soil cover as a function of soil thickness and temperature. A bulk density of 1.2 g/cm^3 and a water content of 17% (w/w) is assumed . . 62

TABLES

Number | Page

1 Summary of Variables Used in the Volatilization Studies. . . . 16

2 HCB Saturation Vapor Densities from Practical Grade HCB and Hex Waste at 15, 25, 35, and 45 C. 21

3 Vapor Pressure of HCB at 15, 25, 35, and 45 C. 22

4 HCB Vapor Density and Vapor Flux from Uncovered Hex Waste A. The Data are for Consecutive Time Periods After Start of the Experiment 24

5 HCB Vapor Density and Vapor Flux from Hex Waste A Covered With Water. The Data are for Consecutive Time Periods After Start of the Experiment. 29

6 Conversion Factors 53

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SECTION 1

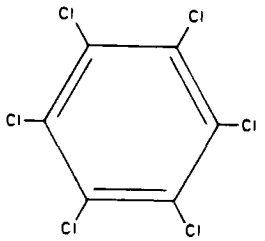
INTRODUCTION

Large quantities of synthetic compounds are being continuously added to the land either intentionally or accidentally. The intentional additions may be for beneficial purposes as in the case of fertilizers and pesticides or more or less casually as in the case of land as a disposal medium. Regardless of the reason for their presence, when the properties of these compounds are ill-defined, their potential distribution in the environment becomes of considerable concern. Properties which must be considered include toxicity, persistence, solubility, concentration, volatility or combinations of them.

Hexachlorobenzene (HCB) is a compound whose presence in the environment has caused much concern due to the large quantities being released into the environment, its extreme persistence, and potential toxicity. The toxicity of hexachlorobenzene first became widely apparent after approximately 5,000 people developed a condition called porphyria cutanea tarda in Turkey in the 1950's due to the accidental consumption of wheat treated with HCB as a protective fungicide. The wheat contained 20 parts per million HCB (Cam and Nygogosyan, 1963; Ochner & Schmid, 1961).

However, the present environmental concern is not over the use of HCB as a fungicidal seed treatment, which is minimal, but over the disposal of large quantities of HCB produced annually as a by-product of several manufacturing processes. Hexachlorobenzene is present in industrial waste as a by-product in the commercial production of various chlorinated solvents such as perchloroethylene and carbon tetrachloride. In addition significant quantities of HCB have been present as impurities or by-products in the production of certain pesticides such as PCNP, dacthal, mirex, simazine, atrazine, and propazine. By far the largest quantities of HCB appear to be produced as the waste product of the chlorinated solvent industry (Quinlivan, Ghassemi and Santy, 1976).

Hexachlorobenzene is a stable persistent compound of low water solubility and moderate vapor pressure. It exists as a white powder at room temperature. Its empirical formula is C_6Cl_6 and its structural formula is:



Hexachlorobenzene (HCB)

HCB has a melting point of 230 C and sublimes at 322 C (Handbook of Chemistry & Physics, 1973). Little information is available in the literature on HCB solubility, but it is essentially insoluble in water. We have measured its solubility in water to be 6.2 ug/l. Sears and Hopke (1949) reported a vapor pressure for HCB of 2.10 x 10^{-5} mm Hg at 25 C. We have measured its vapor pressure to be 1.91 x 10^{-5} mm Hg at 25 C. HCB is soluble in several organic solvents such as benzene and hexane and is soluble in fats and oils. Hence it tends to accumulate in the fatty tissues of animals. HCB should not be confused with the organochlorine insecticide lindane which is hexachlorocyclohexane ($C_6H_6Cl_6$). Lindane has the common name BHC (benzene hexachloride).

This study was initiated because of a specific instance of HCB contamination of beef cattle in December, 1972 in southern Louisiana. Beef cattle to be slaughtered for consumption were quarantined from sale in a 200-square mile area because of high levels of HCB in their fat tissue. Following extensive investigations by local, state and federal agencies and the cooperation of HCB-producing industries in the area, the source of the HCB was traced to the disposal of waste containing HCB (hex waste) in a municipal landfill. Uncovered trucks had been used to haul hex waste from the industrial source to the landfill. This led to spillage and contamination along the pathways followed by the trucks. Additionally, waste material deposited at the landfill sites was left uncovered and was, in some cases, being used as a covering over municipal waste to repel flies. Disposal of hex waste in municipal landfills has ceased in affected areas in southern Louisiana. The uncovered waste at these landfills has been collected into a small area of the landfill and covered with 4 to 6 feet of soil, with a 10-mil thick sheet of polyethyelene film buried approximately midway in the soil cover.

The disposal of hex waste in landfill sites in southern Louisiana as described above has resulted in HCB contamination of residents in the area, operators of the municipal landfills, beef cattle, and soil, plant and air samples (Burns and Miller, 1975; Louisiana Air Control Commission, 1973; U.S.D.A., 1973; U.S.-E.P.A., 1973). Soil and plant samples taken from near landfill areas used for disposal of hex waste showed decreasing HCB contents as distance from the landfill increased (Louisiana Air Control Commission, 1973).

Burns and Miller (1975) reported high levels of HCB in the plasma of individuals exposed through the transportation and disposal of hex waste in southern Louisiana. In a sampling of 29 households situated along the route of trucks transporting hex waste, the average plasma level of HCB was 3.6 ppb with a high of 23 ppb. The range for landfill workers was 2 to 345 ppb plasma HCB. The average plasma HCB level in a control group was 0.5 ppb with a high of 1.8 ppb.

Presently there is no information to indicate that significant degradation of HCB occurs in the environment. This means that HCB persists long enough that even with its moderate vapor pressure, significant quantities can escape into the atmosphere and can be redistributed by moving air currents. Based on the pattern of HCB contamination of soils and plants in the Louisiana incident, and the moderate vapor pressure, low water solubility, and long-term persistence of HCB, it was concluded that volatilization and subsequent transport by moving air currents is the principal mechanism by which HCB moves in the environment.

Since storage or disposal of hex wastes on land is currently a common practice, information on movement of HCB in soil is needed as a basis for improving the safety of future disposal practices and for remedying problems with existing landfills. This study was initiated to determine the optimum soil conditions for limiting movement of HCB and to show how this information could be used in designing covers for hex wastes disposed of on land. Although this study was conducted with wastes containing HCB, the results will apply, in general, to any waste material containing organic compounds of moderate vapor pressure and persistence. In conducting this study, it was assumed that vapor phase movement to the soil surface and subsequent volatilization from the soil surface would be the only significant pathway for movement of HCB out of wastes deposited on land. Consequently, the effectiveness of various coverings - soil, water, and polyethylene film - in reducing vapor movement of HCB was investigated. The study, and this report also, was divided into several phases: theory, design and construction of a simulated landfill, sample collection, measurement of essential chemical and physical properties of samples, laboratory evaluation of covers for controlling volatilization, calculation of vapor phase diffusion coefficients, and application of the findings in designing landfill covers.

The theoretical treatment of volatilization losses from a landfill is based on our knowledge of vapor phase diffusion. The volatilization of HCB from a landfill will be a diffusion controlled process. The rate at which HCB is lost to the atmosphere from the surface of a soil cover will be determined by how fast the HCB molecules diffuse through the soil cover over the waste. Volatilization through a soil cover can thus be predicted by use of the flux equation for steady state diffusion and expressed as:

$$J = -D_s \ (C_2 - C_s)/L \qquad (1)$$

where J is the volatilization vapor flux through the soil cover ($ng/cm^2/day$),

D_s is the apparent steady state diffusion coefficient (cm^2/day),

C_2 is the concentration in the air at the surface of the soil layer (ng/cm^3).

C_s is the concentration in the air at the bottom of the soil layer (ng/cm^3), and

L is the depth of the soil layer (cm).

Experiments were designed in this project to evaluate the utility of Equation (1) in predicting the volatilization flux of HCB and other compounds through a soil layer. As will be shown in this report, the pertinent parameter in Equation (1) to be evaluated is the effect of soil factors on D_s, the apparent steady state diffusion coefficient. The other parameters can be readily measured or ascertained as will be discussed.

A simulated landfill was designed to evaluate Equation (1) and was constructed for use in the laboratory. The simulated landfill had to meet several constraints. It had to represent what would happen in the field as closely as possible. At the same time it had to be subject to close temperature and wind speed control as required when working with gaseous compounds. Such control could only be readily attained in the laboratory. In addition, the simulated landfill needed to be versatile in order to accommodate several types of covers and the thickness of any soil covers used had to remain small to allow completion of the project in a reasonable time period.

An important phase of the project was the collection and characterization of soil and hex waste samples from actual land disposal operations. The collection of the samples accomplished two things. We were able to observe actual methods being used and hopefully make our laboratory methods representative. Secondly, the samples collected at the disposal sites were used in the laboratory experiments. The samples were collected from locations in the southern and midwestern United States. These samples were taken to our laboratories for determination of chemical and physical properties as needed for predicting volatilization. These properties included soil water content, soil bulk density, HCB vapor pressure, and HCB aqueous solubility.

The major portion of the report was the evaluation of the various covers for their potential for controlling HCB volatilization. The covers evaluated were water, polyethylene film, soil, and a composite of soil and polyethylene film. These covers were evaluated because each are being used in land disposal procedures for HCB-containing wastes.

In a final section the results of this project were used to develop a proposed procedure to design a landfill cover to limit the vapor phase transport of HCB into the environment.

There is another aspect to this report peripheral to the central theme of controlling vapor movement in soil. Although originally described as a solid, the hex waste samples were found to contain an organic liquid component. One sample, referred to in the report as fresh hex waste, was found to be approximately 75% organic liquid. Even the wastes which appeared solid contained some amount of this liquid. This organic liquid would not affect the volatilization of HCB from hex waste when covered by several feet of soil but it did exhibit some interesting properties. HCB was highly soluble in the organic liquid and the performance of polyethylene film was affected by the presence of the organic liquid when the film was used as a barrier for hex waste. Therefore, our experiences with the organic liquid are presented in detail throughout the report and some discussions presented on its possible consequences for hex waste disposal.

SECTION 2

CONCLUSIONS

The volatilization flux of hexachlorobenzene (HCB) through a soil cover over wastes containing HCB can be predicted assuming that diffusion in the vapor phase is the only transport process operating. Transport of HCB by mass flow or by nonvapor phase diffusion will be insignificant. Covering waste with soil was found to be highly effective in reducing HCB volatilization. Air-filled porosity is the significant soil parameter affecting the final steady state HCB flux through a soil cover. The bulk density and volumetric water content of a soil determine its air-filled porosity. Consequently, highly compacted wet soil covers are most effective in reducing volatilization. Other soil parameters such as soil organic matter content and soil texture, which may affect the extent to which HCB is adsorbed by soil, will influence the time for the flux to arrive at a steady state but will not affect the magnitude of the final flux except as they influence soil bulk density.

Polyethylene film when used at a reasonable thickness (e.g., 10 mil) is relatively inefficient as a barrier against the movement of HCB in the vapor phase. Polyethylene film is more effective than an equal thickness of soil and about as effective as as equal thickness of water in reducing HCB flux. However, the cost of polyethylene film precludes its use in layers thick enough to significantly retard HCB flux.

The use of a water cover in a temporary storage lagoon for waste containing hexachlorobenzene (hex waste) is a highly effective means of reducing HCB volatilization. The solubility of HCB in water is extremely low (6.2 ug/l) and there is no hazard of HCB movement by leaching with water. However some hex wastes contain a dense (1.67 g/cm^3) organic liquid in which HCB is highly soluble (about 23,400 ug/ml). If this liquid fraction drains from or is washed out of the waste, the potential would be created for transmission of substantial amounts of HCB through soil. Fresh hex waste from a typical perchloroethylene production site contained significant quantities (about 75% by volume) of organic liquids which wetted polyethylene film and caused partial dissolution and swelling of the film. The liquid fraction of the waste thus increased the HCB transmission properties of the film.

The volatilization of HCB is independent of the origin of hex waste as long as the HCB concentration in the hex waste is sufficiently high (about 0.3% by weight) to yield an HCB vapor pressure equal to that of pure HCB. Hexachlorobenzene volatilization from soils will increase

exponentially with increases in soil temperature due to the effect of increasing temperature on HCB vapor pressure. Each 10 C rise in soil temperature will increase HCB flux about 3.5 times.

The chemical stability and resistance to microbial degradation of HCB dictates that when deposited on land it will remain and continue to volatilize at a maximum rate for long periods of time. Calculations of vapor flux through a soil cover over hex waste assuming no degradation, a soil bulk density of 1.2 g/cm^3 (74.9 lb/cu ft), a soil depth of 122 cm (4 ft) covering hex wastes 91 cm (3 ft) in depth with a HCB concentration of 54.9% (by weight) indicate that HCB would continue to volatilize at its maximum rate from that soil for several million years. Although no one would attempt to predict over such a time frame, it is obvious that extremely long periods are involved. Secure storage for such a period will require institutional arrangements that are beyond the scope of this study.

This study has developed sufficient information to allow the design of soil covers that will limit HCB vapor flux to a specified value. However, because small cracks or other openings will appreciably increase the flux of HCB through a soil cover, placement of hex waste with any materials, such as municipal solid waste, that are subject to gradual settling will likely impair the integrity of a soil cover.

SECTION 3

RECOMMENDATIONS

If hex wastes are placed on land, the air-filled porosity of soil covers should be minimized and placement with materials (such as municipal solid waste) that are subject to settlement should be avoided.

If hex wastes are placed on land, consideration should be given to the need for long-term arrangements for insuring the integrity of soil covers.

Lagoons for storage of hex wastes should be covered, at all times, with as great a depth of water as possible and should be constructed of low permeability materials.

The organic liquid fraction of hex wastes should be removed or reduced as much as possible before storage or disposal of the waste.

Further research is needed on movement of HCB in soil in the organic liquid fraction of hex waste.

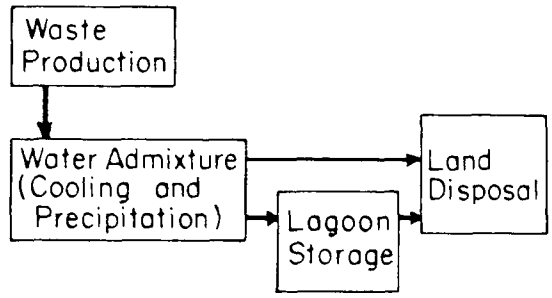
SECTION 4

MATERIALS AND METHODS

COLLECTION AND PREPARATION OF HEX WASTE AND SOIL SAMPLES

Samples of waste containing hexachlorobenzene (hex wastes) were collected from two chlorinated solvent industries. Hex wastes A and B were collected from the southeastern and midwestern United States respectively. A third sample of waste containing hexachlorobenzene was collected from the same location as hex waste A and is described below as fresh hex waste. Soil samples for use in the laboratory were obtained from the actual landfill site used for the disposal of waste A.

In order to more fully understand the nature of the wastes discussed in this study, a brief discussion of procedures used in handling these wastes by industry is given. A typical operation where land disposal of hex waste is used is as follows:



The solid phase remaining after the water admixture step may be either hauled directly to the final land disposal site or temporarily remain in a lagoon storage site. In cases where lagoon storage is used, the cooling and crystallization step (water admixture) and lagooning are one and the same. That is, the waste stream from the production process is fed directly below the water surface of a water lagoon. Cooling and precipitation take place and the solid phase is stored under water in the lagoon. Periodically, the lagoon is emptied and the hex waste carried by truck to the land disposal site. Hex wastes A and B were obtained after the cooling and precipitation step. The sample referred to above as fresh hex waste was collected prior to the cooling and precipitation step. Detailed descriptions of the materials and procedures used in the laboratory are given below.

Soil Characteristics and Preparation

Soils from the 12.7-22.9 cm (5-9 in) depth were collected from a municipal sanitary landfill which had previously been used for the disposal of industrial wastes containing hexachlorobenzene (waste A). The landfill was located in the southeastern United States. The soil samples were collected directly over the portion of the landfill where HCB-containing wastes had been previously covered with soil. Samples were also taken for field bulk density measurements. The field bulk density was found to be 1.2 g/cm^3 (74.9 lb/ft^3).

All soil was pulverized to pass a 2 mm sieve and thoroughly mixed prior to use. The soil was a silty clay loam containing 1.4% organic matter, 1.7% sand, 17.4% coarse silt, 42.1% fine silt, and 38.8% clay. A soil water release curve is shown in Fig. 1.

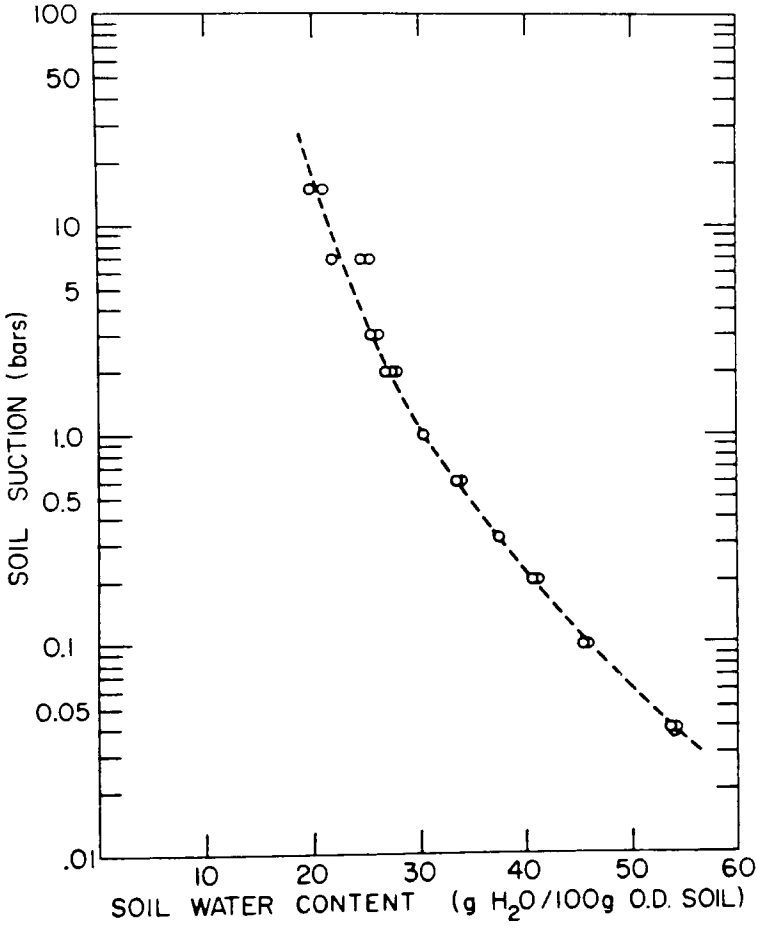


Figure 1. Soil water release curve for soil taken from municipal sanitary landfill used for the disposal of industrial wastes containing hexachlorobenzene.

For the volatilization experiments, initial soil water contents up to 17.3% (w/w) were adjusted by atomizing water onto several kilograms of soil in a 5-liter glass carboy. The soil in the carboy was turned frequently during the atomizing step to obtain uniform water content. The soil was then equilibrated in the carboy for 72 hours at 25 C in a constant temperature chamber before placing in the volatilization cell. The final soil water contents, as reported in a later section, varied from the initial values due to water uptake from or loss to humidified air which passed continuously over the soil surface during the volatilization period. An attempt was made in one of the experiments (Experiment VIII) to obtain higher soil water contents by placing the center section of the plastic volatilization cell containing a given amount of soil on a 3 atm (44.1 lb/m^2) pressure plate with excess water added to the plate. The system was equilibrated at 3 atm pressure for one week. The plastic cell with soil in place was then used in the volatilization experiment. Using this method an initial soil water content of 23.5% was attained. However, this soil lost water during the experimental period even though humidified air was used for the volatilization studies. Apparently the air was not completely saturated with water. In all cases the final soil water content which existed at the end of the volatilization period was assumed to be characteristic of the steady state HCB volatilization flux.

Hexachlorobenzene-containing Industrial Wastes

As mentioned in the Introduction, the hex waste samples were found to contain an organic liquid. This part of the Materials and Methods Section describes how the organic liquid was removed from the hex waste prior to the use of the hex waste in the volatilization experiments. In addition, some of the samples containing the organic liquid are described as some of their properties are explored in the Results and Discussion Section.

Hexachlorobenzene-containing industrial wastes (hex waste) from two different sources were used. Hex waste A from the storage lagoon of manufacturer A was mixed and a subsample filtered with suction to remove excess liquid. Most of the liquid filtered from the waste was water with a small amount of reddish-brown liquid. The reddish-brown liquid appeared to be similar to the liquid phase of the fresh hex waste which will be discussed in the later part of this section. The filtered hex waste A was spread on absorbent paper towel to remove additional liquid. The waste was considered ready for experimental use when a Kimwipe pressed against the waste with a spatula was not wetted. Hex waste B from manufacturer B was air-dried over absorbent paper towel at room temperature for 24 hours and the partially dried waste thoroughly mixed for subsampling. Both hex wastes were analyzed for their HCB content and stored in glass bottles with teflon lined screw caps for future use in the volatilization experiments. Filtered hex wastes A and B contained 54.9 and 56.9% (by weight) HCB respectively.

Portions of samples of hex waste A and B were allowed to air-dry completely and were then analyzed for HCB content. These were collected to determine the effect of extended drying on HCB content. The air-

dried hex wastes A and B contained 65.7 and 90.5% (by weight) HCB respectively. These completely air-dried hex wastes were not used in the volatilization experiments as they may not have been characteristic of hex waste deposited in a landfill site.

The fresh hex waste was the waste collected at manufacturer A from the process line before it entered the storage lagoon. A uniform subsample of fresh hex waste was filtered and the solid and liquid (reddish-brown liquid waste) phases analyzed for HCB content. The solid and liquid portions of fresh hex waste contained 74.5 and 1.4% (by weight) HCB respectively. This fresh hex waste was not used in the volatilization experiment; it was collected to assess the significance of the liquid phase to HCB movement in soils via transport processes other than volatilization.

RECRYSTALLIZED PRACTICAL GRADE HCB

Practical grade HCB was recrystallized three times from hexane and the recrystallized material used as pure HCB in the experiments as noted. The recrystallized HCB was analyzed for its HCB content using a standard from Applied Science Laboratories, College Park, Maryland, and was found to contain greater than 98% HCB.

MEASUREMENT OF HCB SOLUBILITY AND VAPOR PRESSURE

Vapor Pressure Measurement

Fig. 2 shows details of the vapor saturation cell. The saturation vapor density (vapor pressure) of HCB was measured essentially by the method previously described by Spencer and Cliath (1969). One kg of acid-washed and distilled water-washed quartz sand was coated with 3 g of recrystallized practical grade HCB by mixing the quartz sand with 1 liter of benzene containing 3 g of recrystallized practical grade HCB and evaporating the benzene. One kg of quartz sand was coated with 4 g of air-dried hex waste in the same manner. The quartz sand was placed into a vapor saturation cell. The vapor saturation cell contained a 6 cm ID x 43 cm glass column with a 10 mm OD inlet glass tube on the bottom and a glass cap with a 10 mm OD outlet glass tube on the side. The glass cap and the column were fitted together with a ground glass joint. The cell was mounted in a constant temperature chamber. Water-saturated air was passed through the vapor saturation cell from the inlet tube and air coming out the outlet tube was passed through an ethylene glycol trap. The air flow rate was varied between 2 and 7 ml/min by adjustment of a needle valve. HCB vapor densities were measured at 15, 25, 35 and 45 C.

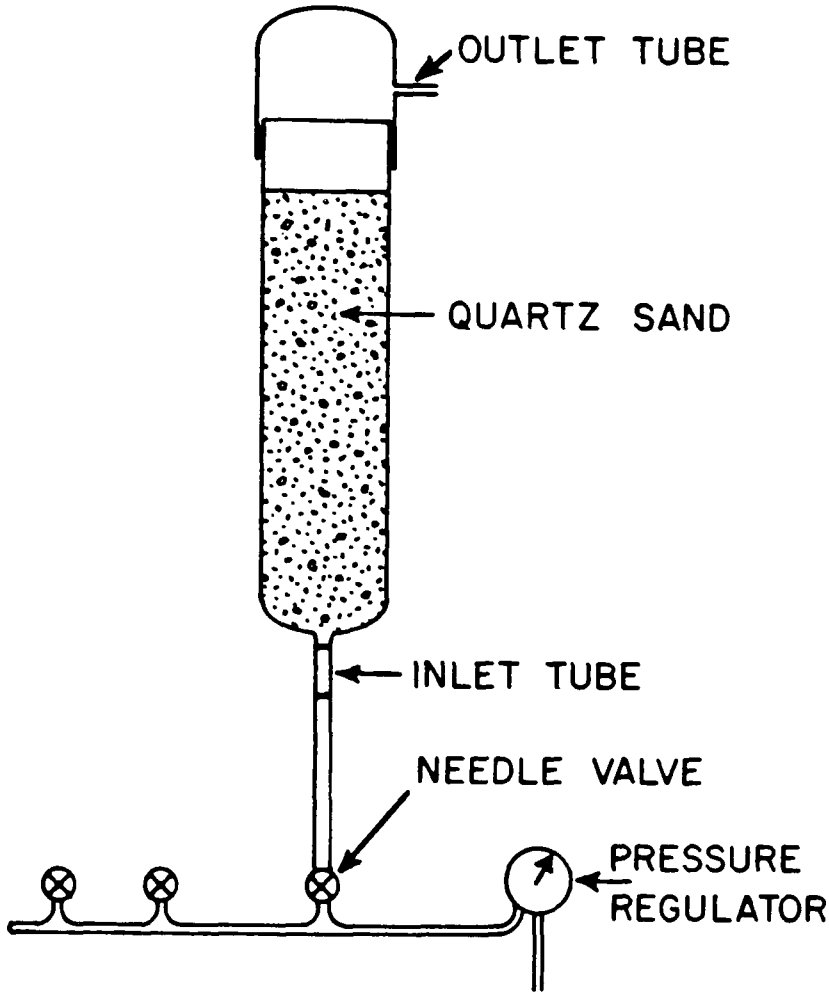


Figure 2. Schematic drawing of vapor saturation cell.

Solubility Measurement

The solubility of HCB was measured in water and in municipal landfill leachate. The sample of municipal landfill leachate was collected by the EPA project officer at the EPA Boone County Field Site near Walton, Kentucky. For the measurements 0.2 g recrystallized practical grade HCB was shaken with 2 liters of water or leachate for 24 hours at 23.5 C. The HCB-liquid suspension was filtered through a Millipore filter. The Millipore filter had a pore size of 0.22 u and was previously saturated with HCB by shaking with excess HCB in water for 24 hours. Five hundred ml increments of filtered aqueous sample were extracted twice with 50 ml of hexane by shaking in a separatory funnel

for 5 minutes. The hexane extract of the leachate formed a heavy emulsion and had to be cleaned up by washing with a 3% sodium carbonate water solution. Fifty ml increments of hexane extract from the leachate were shaken with 50 ml of a 3% sodium carbonate water solution in a separatory funnel for about 1 minute and the aqueous phase discarded. The washing was repeated (approximately 40 times) until most of the organic matter was removed and the hexane then shaken with 50 ml of saturated sodium sulfate aqueous solution to finally destroy the emulsion. The hexane extract was separated from the aqueous phase and dried through a 4" anhydrous sodium sulfate column. The hexane extract was evaporated in a Kuderna-Danish evaporative concentrator tube fitted with a Snyder distilling column and then adjusted to a suitable volume for HCB analysis.

SIMULATED LANDFILL VOLATILIZATION CELL

Figure 3 shows details of the volatilization cell which held the waste and the various coverings. The cell has been designed to accommodate HCB waste with or without a covering of soil, water or polyethylene film. The soil and polyethylene film can be used either alone or in combination with each other. The cell is constructed of Plexiglas (plastic) with a rectangular chamber 3 cm (1.2 in) wide and 10 cm (3.9 in) long. The depth of the cell is varied by stacking additional center sections to accommodate the various layers of wastes and coverings.

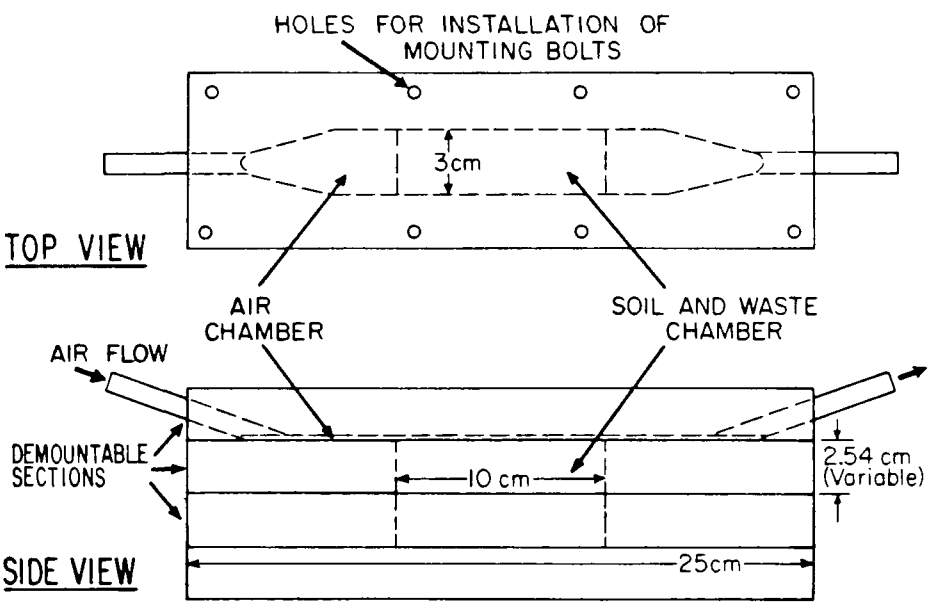


Figure 3. Details of volatilization cell used in simulated landfill.

Each section is grooved for an O-ring to provide a positive liquid and vapor seal between sections. Provisions are made to allow each section to be individually sealed in place and filled to a predetermined level before the next section is added. The upper section contains an air chamber 2 mm (0.08 in) deep and 3 cm (1.18 inch) wide matching the width of the central soil and waste chamber. The air chamber extends 7.5 cm (3 in) on either side of the sample chamber to allow air to spread out before reaching the soil surface, thus providing laminar air flow across the central chamber.

HCB VOLATILIZATION EXPERIMENT

Fig. 4 shows the schematic drawing of the volatilization measurement system for the simulated landfill. The rates of HCB volatilization from industrial wastes were measured in a closed air-flow system by collecting volatilized chemical in hexylene glycol traps in a manner similar to that used by Farmer et al. (1972).

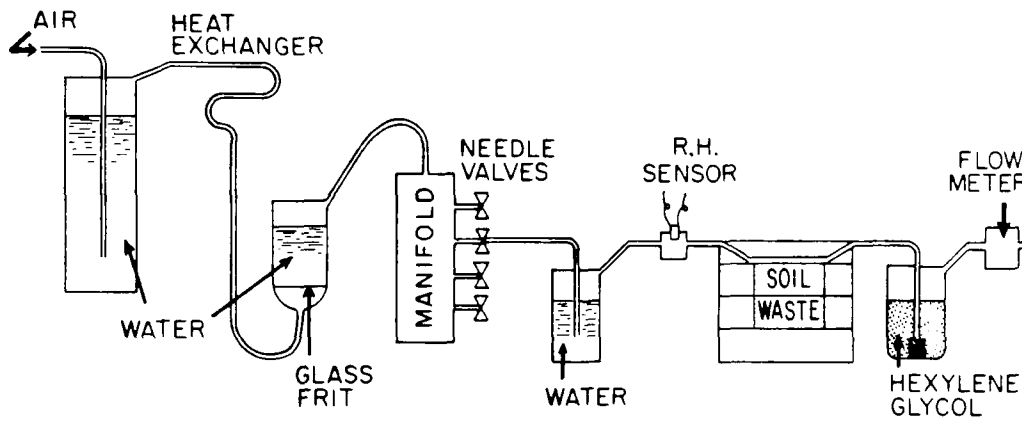


Figure 4. Schematic drawing of closed air flow system for collecting volatilized HCB from a simulated landfill operation.

The entire apparatus with the exception of the first water-bubble chamber and the flow meter were maintained inside a constant temperature chamber. The temperature was slightly elevated in the first water-bubble chamber to facilitate complete saturation of the air with water vapor. Rates of volatilization were measured from uncovered wastes, wastes covered with soil or polyethylene film alone, covered with soil plus polyethylene film, and covered with water. Rates of volatilization from recrystallized HCB covered with soil at various moisture contents and bulk densities were also measured.

The treatments used in the various HCB volatilization experiments are summarized in Table 1. Soil water contents changed slightly during the long term of the volatilization experiments from that of the initial

TABLE 1. SUMMARY OF VARIABLES USED IN THE VOLATILIZATION STUDIES

Experiment No.	Types and Thicknesses of Coverings cm	Bulk Density g/cm^3	Final Water Content % (w/w)
	Hex Waste A*, filtered		
Preliminary	soil - 0.9	1.19	--
I	polyethylene film - 0.015	--	--
II	polyethylene film - 0.025	--	--
	Hex Waste A filtered and partially dried**		
III	soil - 2.5	1.19	17-20
IV	composite soil - 1.8 and film - 0.01	1.19	--
	Hex Waste A from above after multiple soil contacts		
V	soil - 1.8	1.19	20.05
VI	composite soil - 1.8 and film - 0.01	1.19	--
	Hex Waste B†, partially air-dried		
VII	soil - 1.8	1.19	18.36
	Recrystallized practical grade HCB		
VIII	soil - 1.8	1.15	19.58
IX	soil - 1.8	1.05	19.73
X	soil - 1.8	0.96	19.75
XI	soil - 1.8	1.15	17.24
	Hex Waste A powder, air-dried		
XII	polyethylene film - 0.015	--	--
XIII	Hex Waste A, uncovered	--	--
XIV	Hex Waste A water - 1.43	--	--

* Collected from an industrial source in the southeastern United States.

** After filtering, sample was further dried by pressing with paper toweling (III) or with soil (IV).

† Collected from an industrial source in the midwestern United States.

soil water content. The final soil water contents are presented in Table 1 as that being most characteristic of steady state diffusion flux.

The lower 25.4 mm (one inch) section of the volatilization cell was filled with hex waste or recrystallized HCB and coverings were added above. In the experiment with recrystallized HCB, 19.05 mm (three-quarter inch) of the lower portion of the bottom chamber was filled with wetted, filtered, acid-washed quartz sand and the upper 6.35 mm (one-quarter inch) was then filled with recrystallized HCB.

Sufficient soil, previously equilibrated to the appropriate water content, was weighed to give the desired bulk density in the volatilization cell. When the soil was packed into the soil chamber, a metal plate was placed between layers of the cell to prevent compaction of the layer below. The metal plate was removed during assembly of the cell. When polyethylene film was used as a cover alone, or as part of a cover, it was inserted at a junction of two sections and the film allowed to extend beyond the O-ring seal in all horizontal directions to insure a positive seal.

Packing and assembly of the cell were performed at room temperature. The assembled cell was placed immediately in the constant temperature chamber at 25 C. The cell was connected to the closed air-flow system and air flow adjusted to 0.769 l/min (0.027 ft /min). The hexylene-glycol trap was changed at suitable time intervals to obtain a measurable concentration and the HCB trapped in the hexylene glycol was extracted into hexane to be analyzed by gas liquid chromatography. All volatilization experiments were conducted at 25 C.

EXTRACTION, CLEAN-UP, AND ANALYSIS OF HCB

HCB Extraction

The HCB trapped from air in hexylene glycol and ethylene glycol was extracted into hexane by liquid-liquid partition. Fifty ml of glycol was mixed with 100 ml of hexane-washed distilled water and the mixture shaken with 50 ml of hexane for about 10 minutes in a glass bottle on a high speed shaker. When hexylene glycol was utilized as the vapor trapping medium, the mixture contained, in addition to hexane and water, 70 ml of acetone used to wash the glycol from the trap. The hexane was separated from the aqueous phase in a separatory funnel. The aqueous phase was discarded and the hexane dried through a 4" anhydrous sodium sulfate column.

Soil samples taken from the landfill were extracted with a 2:1 (v/v) hexane-ethanol mixture. Twenty ml of distilled water was added to 100 g of air-dried soil and shaken with 200 ml of 2:1 (v/v) hexane-ethanol mixture for 1 hour. The slurry was filtered through Whatman GF/C grade glass fiber filter paper. The filtrate was washed with 100 ml of hexane-washed distilled water twice and the hexane extract dried through a 4"

anhydrous sodium sulfate column. Soil samples, spiked with known concentrations of HCB, were extracted by the same method to verify the recovery efficiency and accuracy of the analytical procedures.

Sample Clean-up

Considerable difficulty was encountered with the GC analysis of several of the volatilized samples from the industrial waste. Tailing solvent peaks, unstable base lines, overlapping peaks, and dirty detectors were common occurrences. The difficulties were assumed to be caused by the presence in the hex waste of interfering compounds which volatilized into the air in the simulated landfill and were extracted into the hexane along with HCB. Certainly, one would suspect the formation of compounds with similar chemical and physical properties to those of HCB during the industrial manufacturing process. A column cleanup procedure was developed using activated neutral alumina to remove the interferences. Anhydrous sodium sulfate was layered on top of the alumina to remove any traces of water which may have been present in the hexane extract containing the HCB. The hexane sample was first placed on the cleanup column. The column was then eluted with pure hexane followed by 10% benzene in hexane. Essentially all of the HCB minus the interfering compounds eluted with the 10% benzene in hexane fraction. This cleanup procedure was considered to be a significant development. Essentially no information exists in the literature on procedures suitable for the cleanup of industrial waste samples for analysis by GC. Details of the procedure are given in the appendix.

Gas Liquid Chromatographic Analysis of HCB

The HCB was analyzed by gas liquid chromatography (GC). A Varian Aerograph model 1520 equipped with a tritium electron capture detector and a 0.093" ID x 6 ft stainless steel column packed with 2.5% QF-1 and 2.5% DC-200 on 80/100 mesh Chromosorb W was used. The operating parameters were: injector 185 C, column 175 C, detector 220 C. Nitrogen carrier gas was adjusted to obtain a retention time of 4 to 6 minutes. All injections were made at 2 to 8 ul. The identity of HCB was confirmed using a 5% OV-17 column. All HCB standard solutions were prepared from recrystallized HCB or the HCB standard from Applied Science Laboratories, College Park, Maryland.

SECTION 5

RESULTS AND DISCUSSION

SOLUBILITY AND VAPOR PRESSURE OF HCB

HCB Solubility in Water and in Landfill Leachate

In the study of HCB solubility in distilled water and landfill leachate, recrystallized practical grade HCB was used rather than the hex waste. The recrystallized material, which contains more than 98% pure HCB, was used in order to establish the maximum solubility level and to exclude any compounds in the hex waste which may interfere with the analysis. The solubility of HCB contained in the hex waste would not be expected to be different from that of the pure material. Because HCB is a non-polar, non-reactive compound, its solubility in aqueous solution would not be influenced by the presence of other compounds.

The solubilities of HCB in distilled water and landfill leachate at 23.5 C were found to be 6.2 and 5.1 ug/l, respectively. The solubility is very low compared with many other chlorinated hydrocarbons. The Millipore filter was saturated with HCB in advance and any chance for it to adsorb HCB from the water is relatively small. However, the Millipore filter has a finite pore size of 0.22 u which may permit HCB particles smaller than 0.22 u to pass through and result in an exaggerated solubility. The actual solubilities might be smaller than the values obtained here. Although little has been published on HCB solubilities, discussions with other investigators have indicated solubilities as low as 0.4 ug/l. At this low level, these differences in solubility values are of little significance.

Any significant movement of chemicals into the deep soil strata and groundwater will have to be by mass flow. Assuming other factors being equal, the solubility of the chemical will determine the amount transported by mass flow. Since the solubilities of HCB in water and landfill leachate are extremely low, the transport of HCB by mass flow would not be significant. Results using soil thin layer chromatography have shown no movement of HCB on a silt loam soil when either water or landfill leachate was used as the leaching medium (R. A. Griffin, Illinois State Geological Survey). The lack of mobility of HCB in aqueous systems would be expected based on its low water solubility.

Work by others with the chlorinated hydrocarbons has shown essentially no leaching with compounds of comparable or even higher solubility

than HCB. Helling, Kearney and Alexander (1971) in their review on pesticide behavior in soils have ranked a number of pesticides according to their relative mobilities in soils. The chlorinated hydrocarbons were ranked as the least mobile of any group of pesticides. Many of these compounds have solubilities considerably higher than that of HCB. The chlorinated insecticide DDT [1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane] was the least mobile of all pesticides tested and it has a solubility comparable to that of HCB. In a more recent review of the theory of pesticide movement, Letey and Farmer (1974) also concluded that DDT and related compounds were among the least mobile of all pesticides in soils. Based on our knowledge of the leaching characteristics of the chlorinated hydrocarbons and on the measured solubilities of HCB in water and landfill leachate, there is no leaching hazard expected from HCB in soil.

The methods used in this study for measuring solubilities are standard methods. However, the difficulties encountered in measuring the solubility of HCB in landfill leachate suggest the need for additional work to confirm our results with landfill leachate. Numerous washings with 3% sodium sulfate in water as described in Section 4 under Materials and Methods, were required to break a heavy emulsion which had formed during the solubility measurement with landfill leachate. The action of the sodium carbonate was to remove some of the organic matter originally present in the landfill leachate and thereby reduce the emulsion in the hexane layer. The high affinity of HCB for hexane compared to its affinity for an aqueous layer would cause any HCB molecules to be retained in the hexane phase during the washing with the sodium carbonate solution. Nevertheless, there is the possibility for some HCB molecules to be carried over into the sodium carbonate aqueous phase with the organic matter of the landfill leachate. This would have the effect of causing our reported value for HCB solubility in landfill leachate to be lower than the actual value. This effect would be expected to be slight to non-existent. The highly non polar nature of the HCB molecule would cause it to have a low affinity for the organic matter of the landfill leachate. The HCB would remain in the hexane phase and thereby be counted as present in the landfill leachate.

HCB Vapor Density and Vapor Pressure

The HCB saturation vapor densities from recrystallized practical grade HCB and hex waste A at 15, 25, 35, and 45 C are shown in Table 2. In the range of air flow rates used, the vapor density is not affected by the flow rate and the air can be assumed to be saturated with HCB. Spencer and Cliath (1969) were also able to obtain saturated vapor densities with dieldrin at a similar range of air flow rates.

The vapor densities from recrystallized practical grade HCB and from hex waste A are very close to each other at all four temperatures. The differences between the vapor densities of recrystallized HCB and hex waste A are less than 3% except at 15 C where the difference is 8%. These small differences in vapor density are within experimental error and it will be assumed that the recrystallized HCB and hex waste A have

TABLE 2. HCB SATURATION VAPOR DENSITIES FROM PRACTICAL GRADE HCB AND HEX WASTE AT 15, 25, 35, and 45 C

15 C				25 C			
HCB		Hex Waste		HCB		Hex Waste	
Flow Rate ml/min	Vapor Density ug/l	Flow Rate ml/min	Vapor Density ug/l	Flow Rate ml/min	Vapor Density ug/l	Flow Rate ml/min	Vapor Density ug/l
7.53	0.0612	10.81	0.0746	5.68	0.26	6.75	0.287
5.74	0.0679	6.02	0.0625	6.02	0.325	5.86	0.273
4.06	0.0666	5.05	0.0594	6.76	0.331	5.97	0.278
3.57	0.0583	7.76	0.0794	7.14	0.264	2.86	0.304
3.93	0.0615	4.96	0.0678	6.93	0.292	2.90	0.289
3.84	0.0624	3.31	0.0677	6.74	0.293	7.95	0.282
						7.16	0.292
---------- Average ----------				---------- Average ----------			
	0.0630		0.0686		0.294		0.286

35 C				45 C			
HCB		Hex Waste		HCB		Hex Waste	
Flow Rate ml/min	Vapor Density ug/l	Flow Rate ml/min	Vapor Density ug/l	Flow Rate ml/min	Vapor Density ug/l	Flow Rate ml/min	Vapor Density ug/l
4.14	0.928	4.35	0.973	3.51	2.905	3.29	3.409
4.64	0.960	4.35	1.006	3.82	3.109	3.45	3.03
4.29	0.997	5.13	1.059			3.31	2.858
4.24	0.839	5.13	0.858			2.49	3.033
4.53	0.978	5.25	1.187			3.36	3.126
1.51	0.953	2.18	0.867			3.68	3.114
1.75	1.072	1.55	0.778				
1.33	0.976	2.07	0.820				
4.35	0.967	2.11	0.929				
4.49	0.860						
---------- Average ----------				---------- Average ----------			
	0.95		0.92		3.007		3.095

the same vapor densities within the temperature range studied. For future calculations the vapor density of the pure compound will be used and assumed to be identical to that of HCB in hex waste. Comparison of the vapor densities at different temperatures indicates that increasing the temperature ten centigrade degrees increases the vapor density by more than three times. Thus the temperature has an exponential effect on HCB vapor density.

The vapor pressure of HCB can be calculated from the following equation,

$$p = (W/V)(RT/M)$$

where p (mmHg) is vapor pressure, W/V (g/l) is vapor density, R (liter, mmHg/deg/mole) is the universal gas constant, T (^{o}K) is Kelvin temperature and M (g/mole) is molecular weight.

The average vapor pressures of HCB calculated from the experimental results are shown in Table 3. Sears and Hopke (1949) studied the vapor pressure of HCB from 96 to 124 C, and HCB vapor pressures calculated by extrapolating their empirical equation downward to our experimental temperature range are also shown in Table 3. The vapor pressures calculated from their equation are slightly greater than those obtained in this experiment, and the differences increase with decreasing temperature as also can be seen from Figure 5. However, the present data agree very well with their extrapolated values except at 15 C where the difference in vapor pressure between measured and extrapolated value amounts to 47%. For this reason, the measured HCB vapor pressure probably is much closer to the true value than the extrapolated value.

TABLE 3. VAPOR PRESSURE OF HCB AT 15, 25, 35, and 45 C

Temp. (^{o}C)	Vapor Pressure* (mm Hg)	Vapor Pressure** (mm Hg)
15	3.96×10^{-6}	5.81×10^{-6}
25	1.91×10^{-5}	2.10×10^{-5}
35	6.36×10^{-5}	6.97×10^{-5}
45	2.09×10^{-4}	2.15×10^{-4}

* From experimental data.

** Extrapolated from Sears and Hopke, 1949.

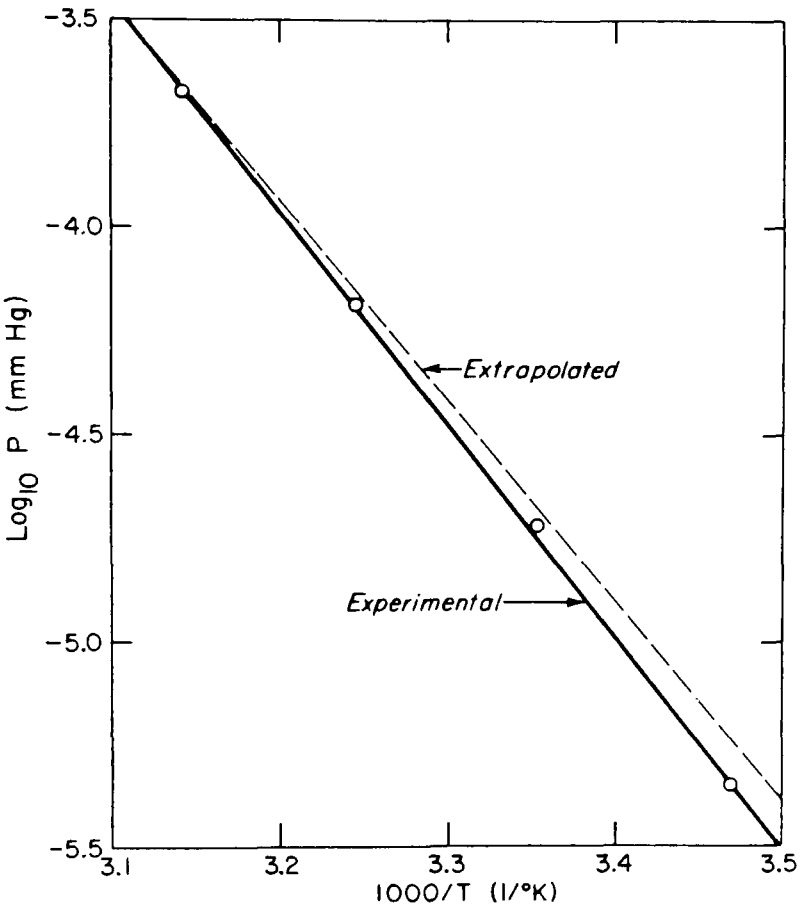


Figure 5. Effect of temperature on the vapor pressure of hexachlorobenzene. Extrapolated curve from data of Sears and Hopke, 1949.

The relation between the vapor pressure and the temperature within the range of temperatures studied can be represented in the following equation:

$$\log_{10} p = -(5217.7/T) + 12.74$$

The heat of vaporization of HCB can be calculated from the Clausius-Clapeyron equation

$$\Delta H_V = -2.303\ Rm$$

where ΔH_V is the heat of vaporization in calories per mole when R is in calories per mole per degree and m is the slope of line when $\log_{10} p$ is plotted vs. 1/T. Thus the heat of vaporization of HCB is

$$\Delta H_V = (-5217.7)(-4.58) = 23.9 \text{ kcal/mole}$$

As would be expected, this value for the heat of vaporization of HCB is close to and greater than that of 21.9 kcal/mole obtained by Sears and Hopke. This value also is close to that of 23.6 kcal/mole for dieldrin (Spencer and Cliath, 1969) and 24.17 for lindane (Spencer and Cliath, 1970a).

VOLATILIZATION OF HCB FROM SIMULATED LANDFILL

HCB Volatilization from Uncovered Hex Waste

The HCB vapor density and flux from uncovered hex waste A (Experiment XIII) are shown in Table 4. The vapor density is about 80.9% of that of the saturated vapor density even though the air flow rate is about 100 to 200 times greater than that used in the saturation vapor density experiment. This means that HCB from uncovered hex waste is highly volatile and that the volatilization rate would be much higher at higher rates of air exchange.

TABLE 4. HCB VAPOR DENSITY AND VAPOR FLUX FROM UNCOVERED HEX WASTE AT 25 C. THE DATA ARE FOR CONSECUTIVE TIME PERIODS AFTER START OF THE EXPERIMENT

Flow Rate l/min	Vapor Density ug/l	Flux $ng/cm^2/day$
.769	0.24	8861
.769	0.232	8566
	Average	
		8713

The source of the hex waste would not have any significant effect on HCB volatility from uncovered waste. This is based on the observation that quartz sand containing a concentration as little as 3 mg of HCB per gram of sand gives a saturated HCB vapor density and any solid-phase hex waste containing more than 3 mg of HCB per gram of waste would also have the potential to yield a saturated HCB vapor density at low air flow rates unless HCB were to form complexes with other components of the waste. Spencer et al. (1973) reviewed pesticide volatilization and reported that in moist Gila silt loam, saturation vapor densities of dieldrin, lindane, p,p'-DDT, and o,p'-DDT were reached at soil concen-

trations of 25, 55, 12, and 39 ug/g, respectively. This relatively low soil concentration needed for a saturated vapor in moist soil indicates that weakly adsorbed pesticides such as lindane, dieldrin and DDT will be subject to relatively high rates of loss by volatilization. HCB is a weakly polar, relatively non-reactive compound and it is conceivable that any waste containing as little as 10 to 100 ug HCB per gram waste may have the potential to produce a saturated vapor density. This would further indicate that the source of hex waste would not have any great impact on HCB volatility. Measurements of HCB volatilization flux from two different hex wastes covered with soil, which is discussed in a later part of this report, support the conclusion that there is no difference in HCB volatility from these two hex wastes.

HCB Volatilization from Hex Waste Covered with Polyethylene Film

Polyethylene film has been used in the past in conjunction with soil as a covering material in landfill sites as an aid in reducing volatilization of HCB from hex waste deposited in landfill. To evaluate the effectiveness of polyethylene film as a barrier to HCB vapor movement, HCB volatilization fluxes from filtered hex waste A covered with 0.015 cm (0.006 in) (Experiment I) and 0.025 cm (0.01 in) (Experiment II) polyethylene film alone with the film in contact with the hex waste were measured and results are shown in Figure 6 and Figure 7, respectively. In both cases the flux increases rapidly and reaches steady state in about 8 days. The steady state fluxes are about 40% and 80% of that from the uncovered hex waste A for 0.025 cm and 0.015 cm film, respectively. The flux at steady state from the 0.025 cm film cover is about one-half that from the 0.015 cm cover. This can be expected since the thickness of the film is approximately doubled. The polyethylene film when used alone in direct contact with the hex waste appears to be highly inefficient as a barrier for HCB movement.

At the end of the above studies, it was found that the reddish-brown liquid component of the waste, which is part of the original hex waste A, deposited on the film and caused the film to partially dissolve and expand. It was suspected that partial dissolution and expansion of the film might reduce its effectiveness as a vapor movement barrier. HCB volatilization fluxes from air-dried hex waste A (Experiment XII) covered with 0.015 cm polyethylene film were measured to determine the effect of the absence of the liquid component of the waste on the effectiveness of polyethylene film as a vapor movement barrier. The results together with that from Experiment I are shown in Figure 8. The steady state HCB volatilization flux from air-dried hex waste A is 5500 ng/cm^2 /day and is smaller than that of 7050 ng/cm^2 /day from filtered hex waste A. The fact that air-dried hex waste A yielded a volatilization flux smaller than that from non-air-dried hex waste A clearly indicates that the reddish-brown liquid waste component does reduce the effectiveness of the polyethylene film as a vapor barrier.

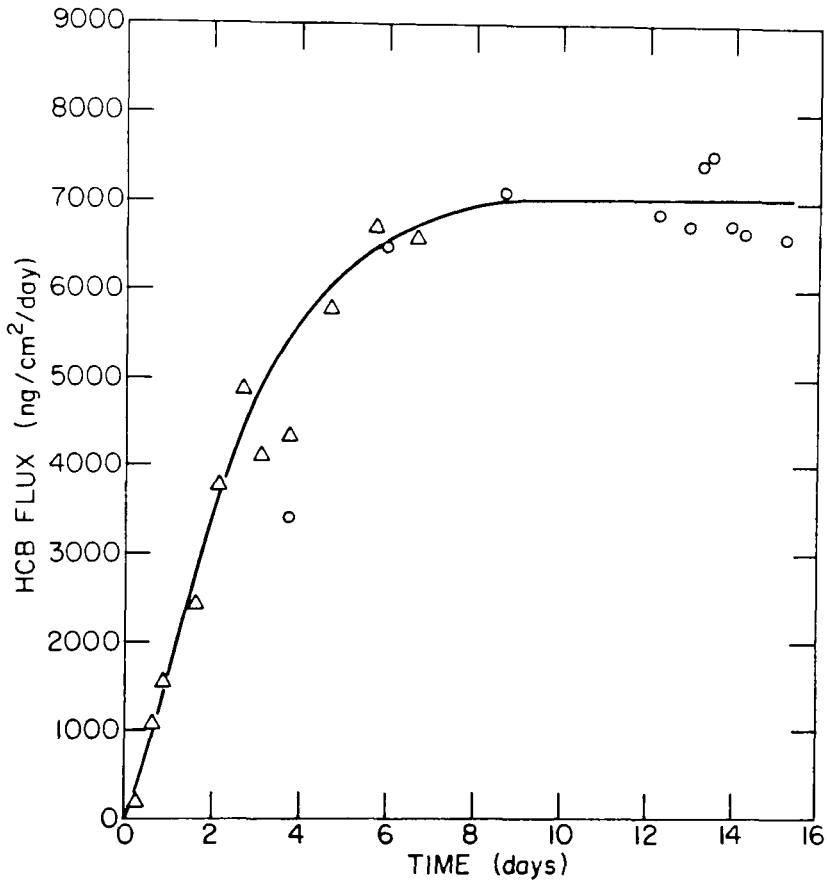


Figure 6. Volatilization vapor flux of hexachlorobenzene from hex waste A covered with 0.015 cm (0.006 in) polyethylene film in contact with waste which had been filtered only (Experiment I).

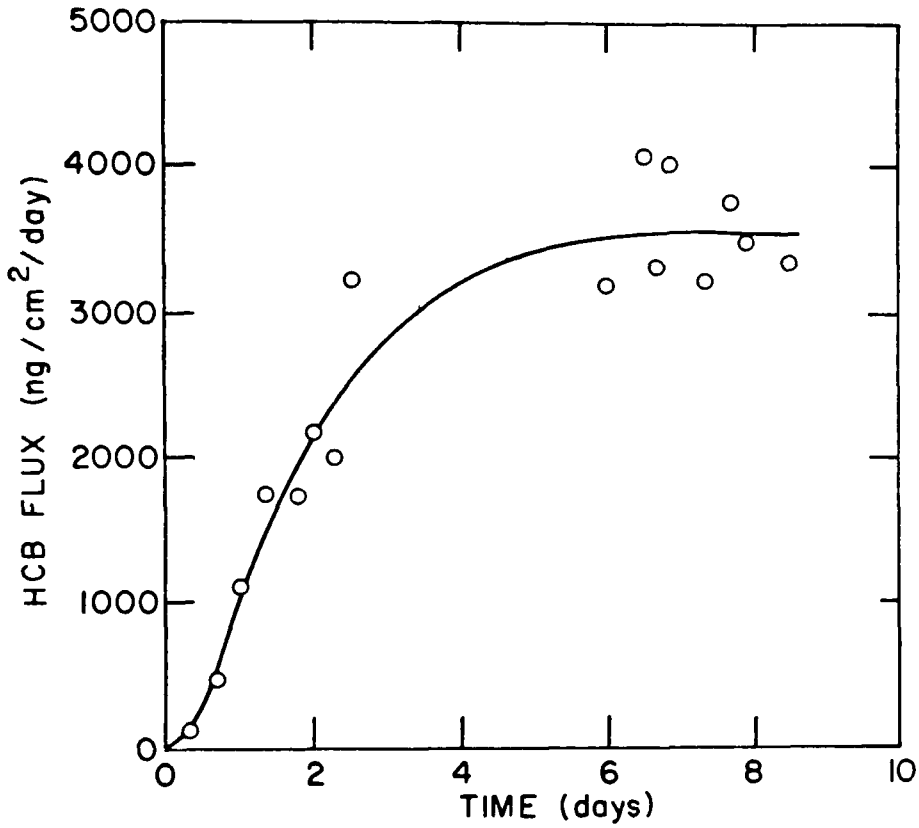


Figure 7. Volatilization flux of hexachlorobenzene from hex waste A covered with 0.025 cm (0.01 in) polyethylene film in contact with waste which had been filtered only (Experiment II).

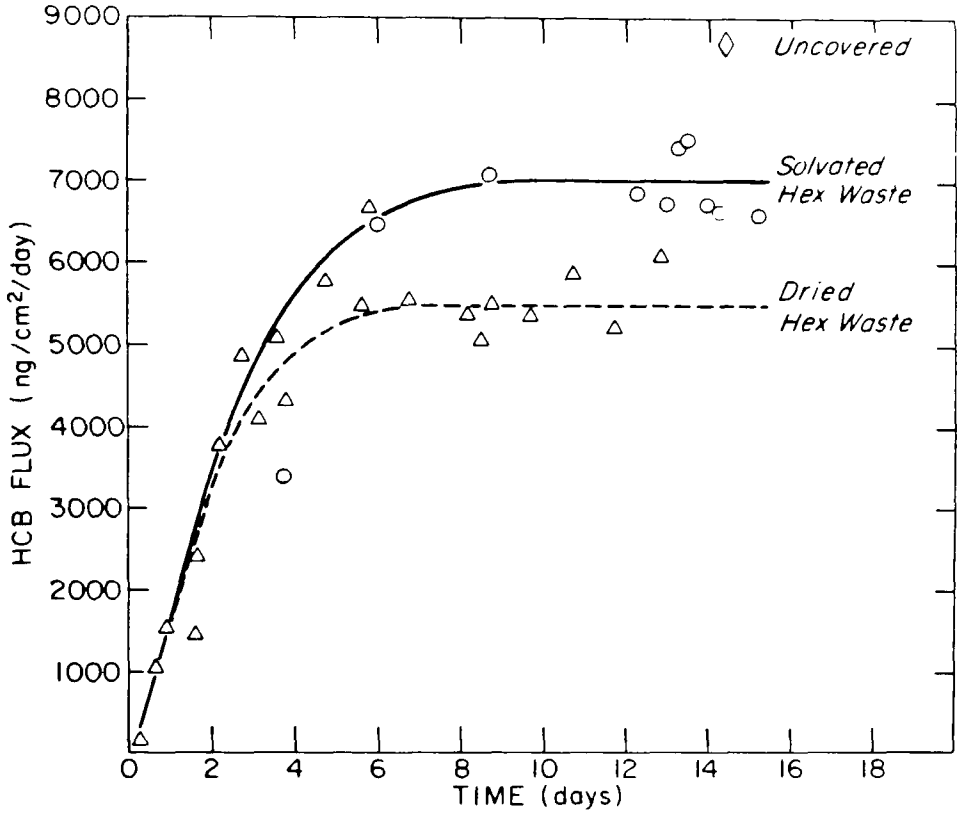


Figure 8. Effect of liquid phase in hex waste on volatilization of hexachlorobenzene from polyethylene film covered hex waste which had been filtered only (Experiment I) and film covered waste which had been air-dried (Experiment XII). The thickness of the films were each 0.015 cm (0.006 in). Volatilization from uncovered hex waste is shown for comparison.

HCB Volatilization from Hex Waste Covered With Water

Lagoon storage has been used as a temporary means for hex waste retention prior to its disposal at a landfill site. Under these circumstances, hex waste is temporarily stored under water. Therefore it is necessary to evaluate the effectiveness of a water cover in reducing volatilization. HCB volatilization fluxes from hex waste A covered with 1.4 cm (0.56 in) of water (Experiment XIV) were measured and the volatilization flux and vapor density are shown in Table 5.

TABLE 5. HCB VAPOR DENSITY AND VAPOR FLUX FROM HEX WASTE A COVERED WITH WATER AT 25 C. THE DATA ARE FOR CONSECUTIVE TIME PERIODS AFTER START OF THE EXPERIMENT

Flow Rate l/min	Vapor Density ug/l	Flux $ng/cm^2/day$
0.769	2.82×10^{-4}	10.4
0.769	2.86×10^{-4}	10.4
0.769	2.60×10^{-4}	9.6
0.769	2.97×10^{-4}	11.0
	Average	
		10.4

Comparing HCB volatilization flux from water covered hex waste A with that from uncovered hex waste A, the water cover reduces HCB volatilization flux about 870 times and is the most effective cover yet tested to reduce HCB volatilization. In the actual storage lagoon, the water cover is likely to be much deeper and would therefore be even more effective in reducing HCB volatilization.

HCB Volatilization from Hex Waste Covered With a Soil Layer

Volatilization from Untreated Soil - Vapor Phase Transport--

The soil used in the volatilization experiments as a cover for hex waste was found to contain 0.25 ppm HCB; thus it was necessary to determine the background HCB volatilization flux from this untreated soil. Since the soil was untreated, the source of the HCB had to be from hex waste at the landfill location when the soil had been collected. The HCB volatilization flux from the untreated soil is shown in Figure 9. The flux decreases rapidly with time and reaches steady state after about 4 days as HCB diffusion to the soil surface controls the flux rate. After 13 days the flux again decreases, slowly, presumably due to soil depletion of HCB.

The HCB flux in Figure 9 represents desorption of HCB from the soil. This gives an indication of how a soil which is lightly contaminated with HCB would "cleanse" itself. A heavily contaminated soil would exhibit the same type of decay curve (decreasing volatilization to the soil surface from below. This type of desorption curve from soil has been well characterized for other chlorinated compounds such as lindane, dieldrin, and DDT (Farmer et al., 1972; Spencer and Cliath,

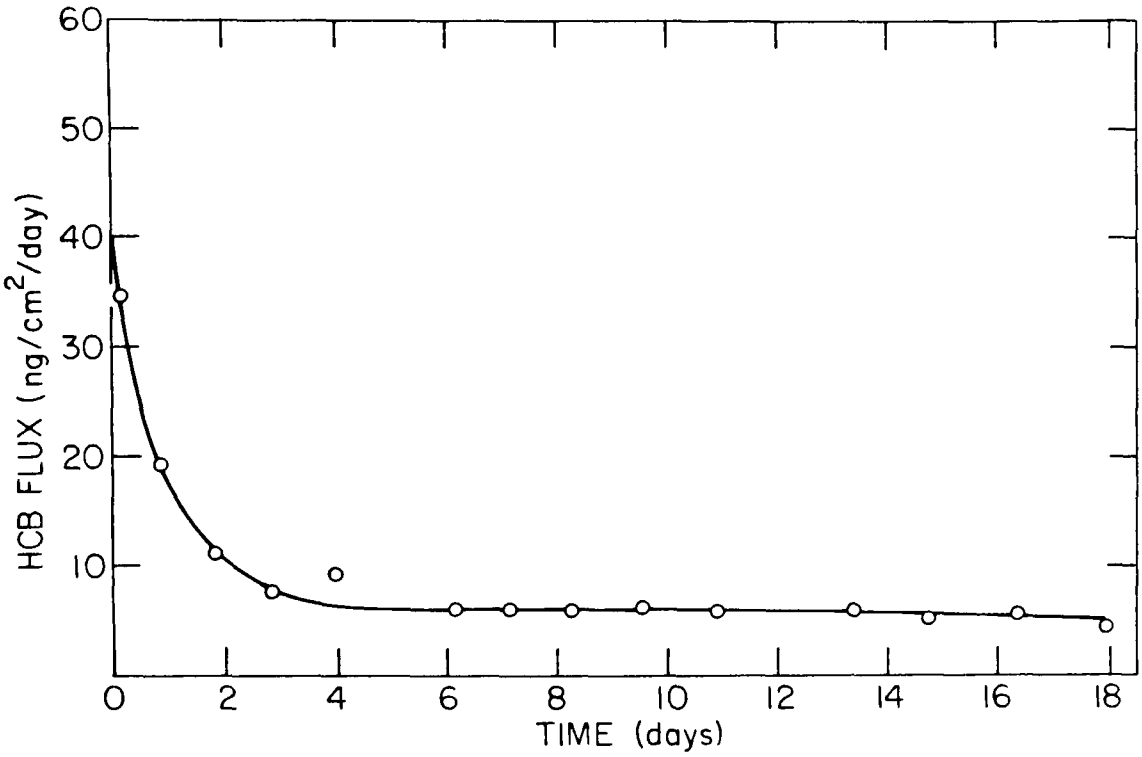


Figure 9. Volatilization vapor flux of hexachlorobenzene from untreated soil at bulk density of 1.19 g/cm^3 and 17% (w/w) soil water content. The soil was initially collected from a landfill used for the disposal of HCB containing wastes.

1973; Guenzi and Beard, 1970; Mayer, Farmer and Letey, 1973). There is a rapid initial decrease in the flux rate as surface concentrations are depleted. The lower flux rate characteristic of the later portion of the decay curve is determined by the rate at which pesticides move to the soil surface. Thus the concentration in the soil below the surface becomes the source term for surface volatilization. The rate of diffusion of HCB to the soil surface will determine the actual volatilization flux in Figure 9. Movement due to mass flow in moving water would be negligible due to low water solubility of HCB and lack of upward water movement in the soil during the experiment.

HCB may move by molecular diffusion in the vapor phase and in the solution phase. The relative importance of vapor phase and solution phase diffusion is determined by the relative magnitudes of the concentration in air (vapor density) and the concentration in solution phase.

Because the vapor phase diffusion coefficient is approximately 10^4 larger than the solution phase diffusion coefficient (Letey and Farmer, 1974), vapor phase diffusion can be important even if the chemicals have relatively low vapor densities. Hartley (1964) suggested that the partition coefficient between soil solution and soil air could be used to measure the relative importance of solution phase and vapor phase diffusion. The ratio of the concentration in saturated aqueous solution to that in saturated air may be used to calculate the partition coefficient between the soil solution and the soil air.

Since the vapor phase diffusion coefficient is approximately 10^4 larger than the solution phase diffusion coefficient, a partition coefficient of 10^4 may be considered as a transition point for determining when vapor diffusion or solution diffusion becomes dominant. Chemicals with partition coefficients much smaller than 10^4 will diffuse mainly in the vapor phase and those with partition coefficients much greater than 10^4 will diffuse primarily in the solution phase. This kind of classification principle to determine the major mode of diffusion of a chemical in a soil-water-air system has been suggested by Goring (1962). The HCB solubility in water at 23.5 C is 6.2 ug/l and the vapor density at 23.5 C can be calculated from the empirical relation $\log_{10}p = 12.94 - (5279/T)$ to be 0.224 ug/l. This gives a partition coefficient of 27 for HCB at 23.5 C and HCB would be expected to diffuse primarily in the vapor phase.

Chemicals with partition coefficients around 10^4 will have about an equal magnitude of diffusion in vapor phase and solution phase. Lindane (γ-BHC isomer) has a partition coefficient of 5.5×10^3 at 30 C and thus should have about equal magnitudes of diffusion in vapor phase and solution phase. Shearer et al. (1973) reported that the diffusion of lindane in the vapor and non-vapor phases was approximately equal at 30 C over a wide range of soil water contents. A similar distribution of vapor and solution diffusion was observed by Graham-Bryce (1969) for the diffusion of disulfoton in soil. Disulfoton has a partition coefficient of 5.5×10^3.

It is important to note that this method of classification using the partition coefficient between vapor and solution phases can be used for assessing the vapor transport potential of materials other than HCB. Those compounds with a partition coefficient less than 10^4 would diffuse primarily in the vapor phase and the procedures developed in this study for HCB would apply similarly to those compounds.

Volatilization from Hex Waste Covered with Soil--

It was during our investigations with soil-covered hex waste that the significance of the organic liquid phase as a transport medium for HCB became evident. The first few experiments described below are included because they are illustrative of how HCB can be carried in soil by liquid flow. The experiments which are useful for predicting HCB vapor transport are those performed after the organic liquid had been removed. These begin with Experiments V and VI after the hex waste had been filtered,

partially dried, and then used in several consecutive experiments so that it contacted several layers of soil.

The HCB flux from hex waste A covered with 2.5 cm (1 in) soil (Experiment III) is shown in Figure 10. The flux decreases initially but begins to increase rapidly at about 2 days and reaches steady state after 20 days. The initial HCB flux is from the HCB originally present in the soil and the upswing at 2 days represents the emergence of HCB

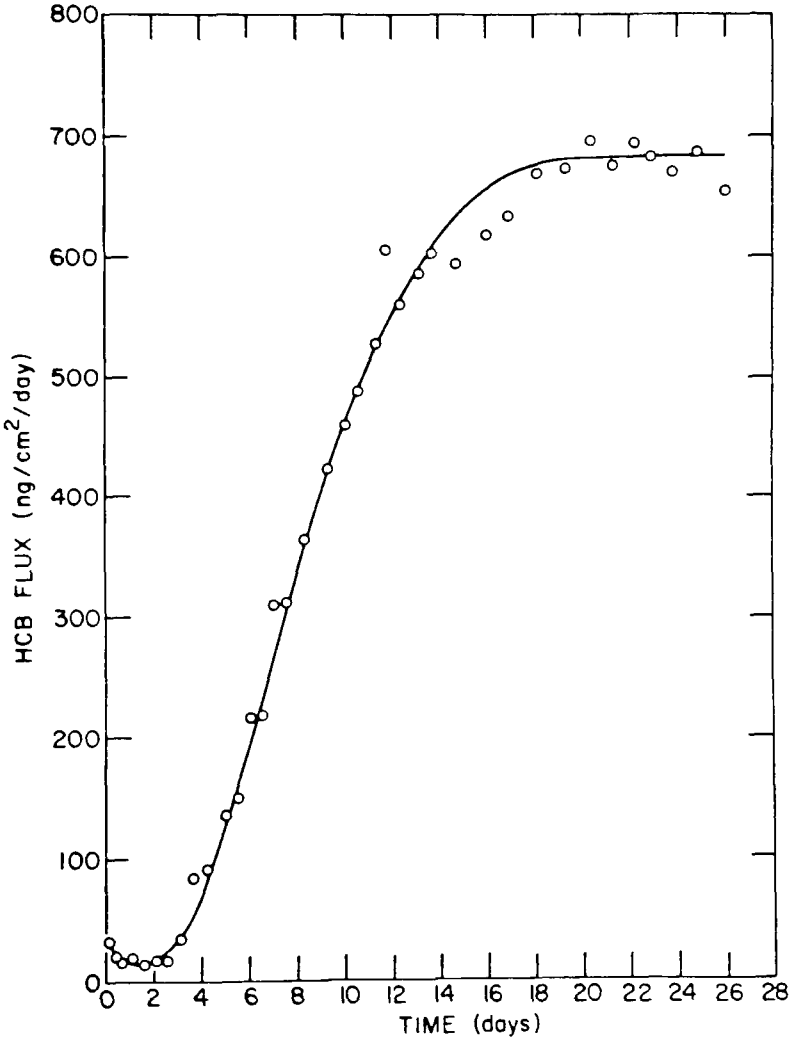


Figure 10. Volatilization vapor flux of hexachlorobenzene from hex waste A covered with 2.5 cm (1.0 in) soil at bulk density of 1.19 g/cm^3 (Experiment III). The hex waste used in this experiment had been filtered only and contained considerable quantities of the liquid waste component.

moving up from the hex waste in the chamber below the soil. The slow emergence of HCB at the soil surface indicates that adsorption of HCB by the soil matrix is very significant in determining the initial movement of HCB in soil and therefore will determine the length of time required to reach steady state. The fact that the flux reaches a steady state value of 680 ng/cm^2/day after 20 days indicates that there is no additional adsorption taking place by the soil after this time. The flux at steady state with a 2.5 cm soil cover is about 7.8% of that of uncovered hex waste. Thus soil is an effective covering material for reducing HCB volatilization. However, as shown below not all of this flux can be attributed to diffusion. With this particular hex waste sample, mass flow of HCB was taking place.

In the preliminary experiment with 0.9 cm (0.37 in) soil cover over filtered hex waste A, it was noted that part of the soil surface became wetted with the reddish-brown liquid waste shortly after placing the soil layer over hex waste A and the initial HCB volatilization flux reached as high as 200 ng/cm^2/day which is six times greater than that from Experiment III. Diffusion of HCB alone could not produce such an instantaneously high volatilization flux since diffusion is a relatively slow molecular process. Analysis of the reddish-brown liquid waste showed that the liquid waste contained 1.4% HCB. Movement of this liquid waste by capillary action into the soil cover from hex waste A would be expected to carry a large amount of HCB into the soil cover and thus result in a higher HCB volatilization flux. It was suspected that even in Experiment III a great portion of the HCB volatilization flux from the hex waste might be contributed by the mass flow of HCB carried by the reddish-brown liquid waste. The suspicion was reinforced by the fact that at the end of the experiment there was an increase of 3% in the soil "water" content, as measured by drying at 105 C, in the lower portion of the soil cover thus indicating the soil was adsorbing a significant mass from the waste that was lost on drying the soil.

To reduce the possibility of HCB mass flow caused by the liquid component of the waste, a subsample of hex waste A which had been used in earlier experiments and therefore had contacted a soil cover several times was used to measure the HCB volatilization flux from hex waste covered with 1.8 cm (0.75 in) soil (Experiment V). It was assumed that any significant amount of liquid waste contained in hex waste A had been adsorbed by soil covers in the previous experiments and the mass flow effect of liquid waste could be eliminated or reduced to a minimum. The HCB volatilization flux from Experiment V is shown in Figure 11. The steady state HCB volatilization flux reached 123 ng/cm^2/day 30 days after the start of this experiment. Comparing the steady state HCB flux from Experiments III (Figure 10) and V (Figure 11), it can be seen that the flux from the 2.5 cm soil-covered hex waste is 5 times greater than that from the 1.8 cm soil-covered hex waste. It is obvious that the capillary movement of the reddish-brown liquid waste into the soil cover does cause mass flow of HCB from hex waste into the soil cover. Volatilization experiments with recrystallized HCB to avoid any mass flow effect from liquid waste at comparable experimental conditions which are discussed in a later section of this report also yielded a steady state HCB

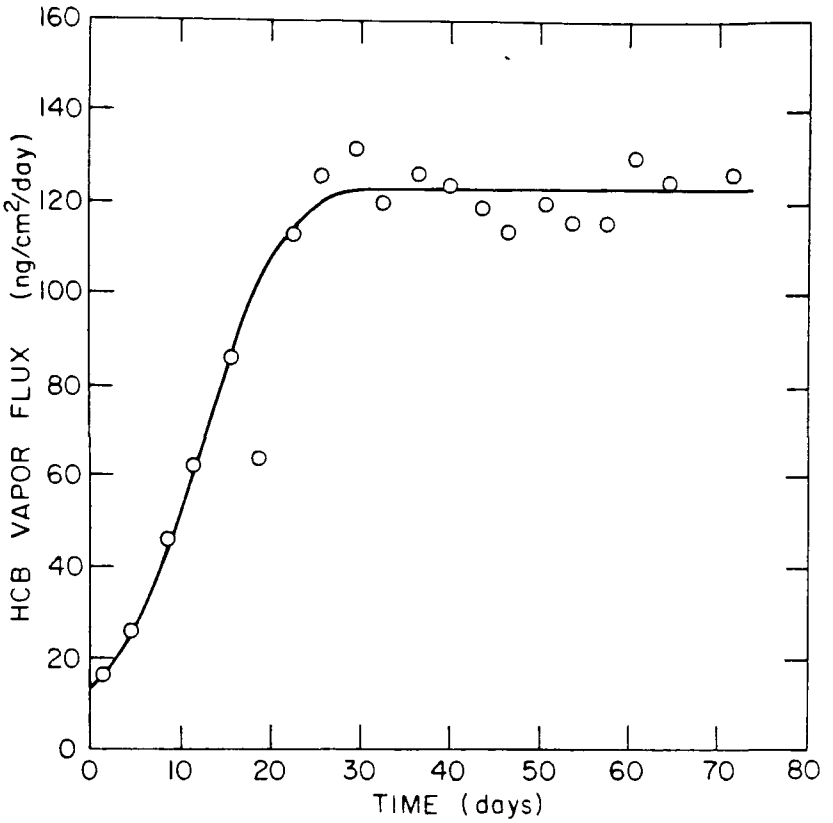


Figure 11. Volatilization vapor flux of hexachlorobenzene from hex waste A covered with 1.8 cm (0.75 in) soil at bulk density of 1.19 g/cm^3 (Experiment V). The hex waste used in this experiment had contacted several layers of soil and therefore did not contain significant amounts of the liquid waste component.

flux of 126.3 ng/cm^2/day (Experiment VIII) which is very close to that of Experiment V. This would further substantiate the mass flow effect due to the reddish-brown liquid waste. In the absence of a mass flow effect, a soil cover of 1.8 cm reduced the HCB flux from approximately 8700 ng/cm^2/day for the uncovered waste to approximately 120 ng/cm^2/day or a reduction of 98.6 percent.

Volatilization from Hex Wastes from Different Sources Covered With Soil--

Hex wastes from different industrial sources may contain different components which may affect the volatility of HCB. Hex waste B from manufacturer B was used to study HCB volatilization through a 1.8 cm soil cover (Experiment VII); the HCB volatilization flux together with that from hex waste A with a 1.8 cm soil cover (Experiment V) are shown in Figure 12. The steady state HCB volatilization flux from hex waste B is

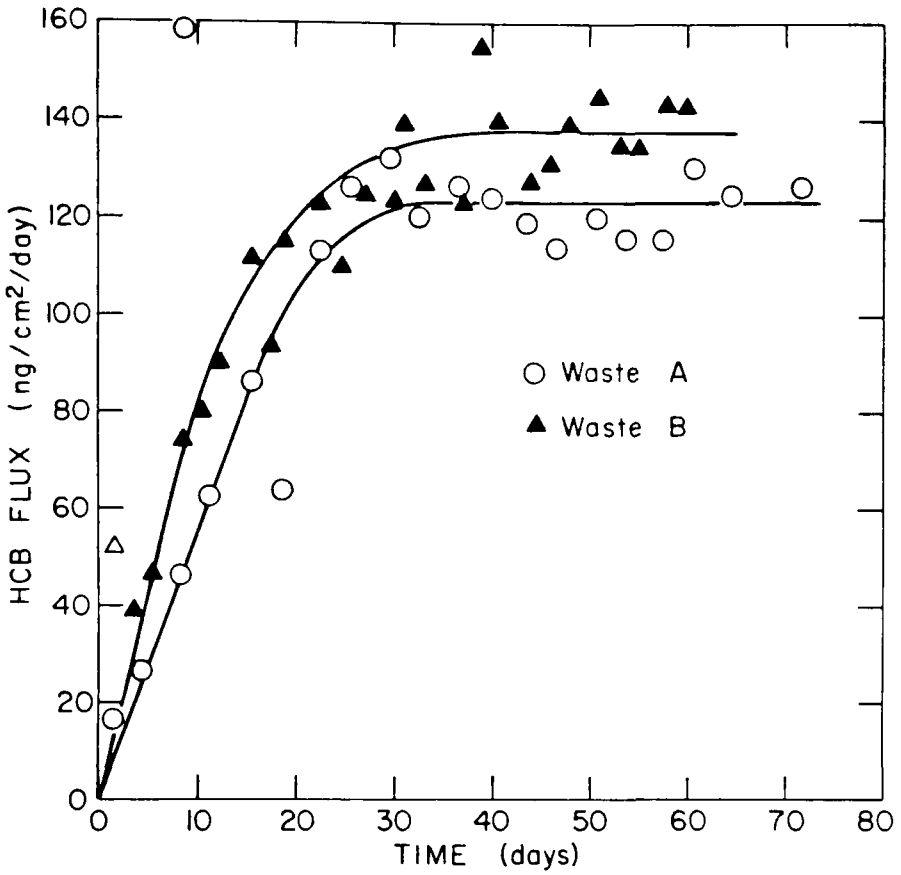


Figure 12. Volatilization of hexachlorobenzene from two hex wastes collected from separate industrial sources and covered with 1.8 cm soil (Experiments V and VII).

137 ng/cm^2/day and is slightly greater than that of 123 ng/cm^2/day from hex waste A. The slightly higher HCB volatilization flux from hex waste B can be explained by the fact that its soil cover has a slightly lower soil water content and thus has more air-filled pores through which HCB can diffuse. When the HCB flux is expressed as the flux per unit air-filled porosity, by dividing the HCB flux by air-filled porosity, the adjusted flux values are 424 ng/cm^2/day and 406 ng/cm^2/day for hex waste B and A, respectively, and the difference between these adjusted values is less than 5%. Thus the source of hex waste does not seem to have any significant effect on HCB volatilization. Previous analysis based on the concentration of HCB needed to produce a saturated vapor provided a similar conclusion.

Volatilization from Hex Waste Covered with a Composite Layer of Soil and Polyethylene Film

Soil and polyethylene film are being used together as a covering over hexachlorobenzene-containing industrial wastes in actual landfills; thus information is needed on the effectiveness of a composite layer of soil and polyethylene film in reducing HCB volatilization.

The HCB flux from hex waste A covered with a composite layer of 0.9 cm (0.35 in) soil, 0.01 cm (0.004 in) polyethylene film and 0.9 cm soil (Experiment IV) are shown in Figure 13. The flux decreases initially and begins to increase at about 2 days. After about 20 days the flux reaches a steady state value of 355 ng/cm^2/day, a flux about one-half of that from the 2.5 cm soil cover (Experiment III). The slow increase in flux and smaller steady state flux indicate that the polyethylene film does act as a barrier to reduce HCB movement toward the soil surface. Since Experiments III and IV use the same kind of hex waste A,

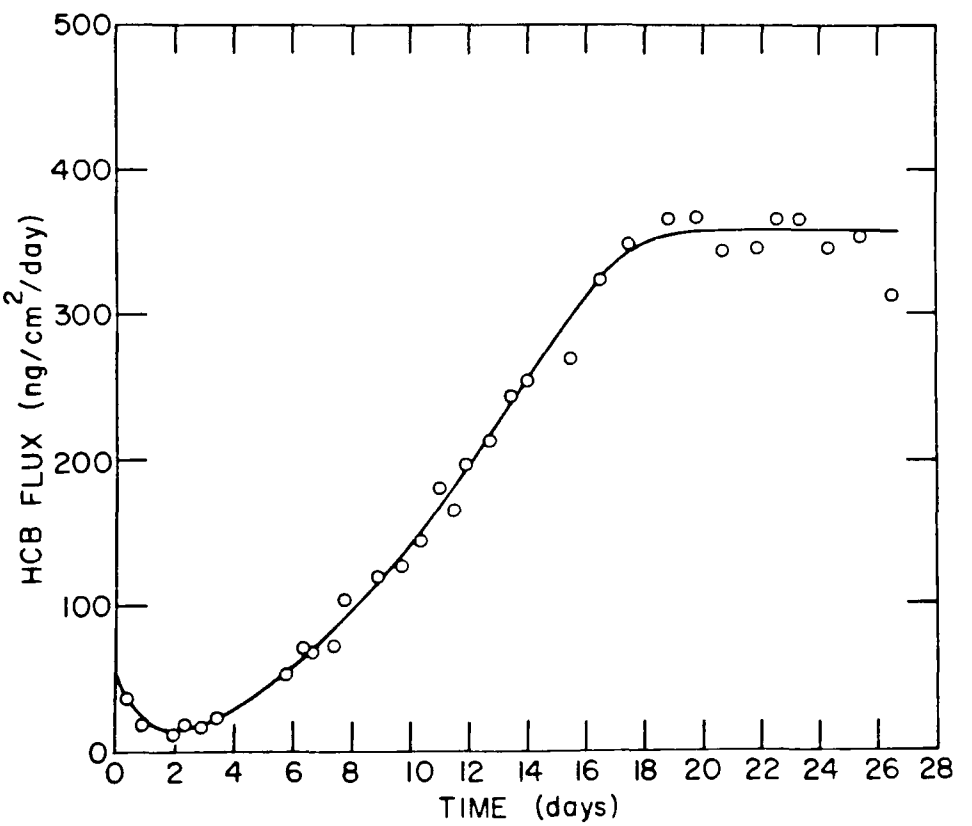


Figure 13. Volatilization vapor flux of hexachlorobenzene from hex waste A covered with a composite layer of 1.8 cm soil and 0.01 cm polyethylene film (Experiment IV). The hex waste used in this experiment had been filtered only and contained considerable quantities of the liquid waste component.

the reddish-brown liquid waste must also cause mass flow of HCB into the soil cover in Experiment IV as it did in Experiment III. At the end of Experiment IV, liquid waste was found to deposit on the polyethylene film and to cause the film to partially dissolve and expand similar to the phenomena observed in Experiments I and II using film alone. The results obtained clearly show an exaggerated HCB flux due to mass flow and cannot be used to quantitatively evaluate the effectiveness of the composite layer in reducing HCB volatilization. Additional experiments were required to evaluate the composite layer.

The hex waste A used in Experiment V does not exhibit any effect due to liquid waste, thus it was used with the composite layer in a repeat of the previous experiment. Duplicate runs (Experiment VI) were conducted and the HCB volatilization flux is shown in Figure 14. The HCB volatilization flux increases gradually with time and reaches a steady state flux of 70 $ng/cm^2/day$ after 57 days. The composite layer of 1.8 cm soil and 0.01 cm polyethylene film can reduce HCB volatilization flux approximately 125 times compared to uncovered waste and is quite effective in reducing HCB volatilization.

Comparing steady state HCB volatilization fluxes between Experiments V (Fig. 11) and VI (Figure 14), the addition of 0.01 cm polyethylene film to the 1.8 cm soil cover reduces HCB volatilization flux by 43%. Data from Experiment XII (Figure 8) showed that covering with a thicker polyethylene film (0.015 cm) over air-dried hex waste A reduces HCB volatilization flux by 37%. These results indicate that polyethylene film may tend to be more effective as an HCB vapor barrier when it is used in conjunction with the soil as a covering. The explanation for this is unknown. Perhaps the closer proximity of the film to the hex waste in the case of film alone covering the waste causes partial swelling and expansion of the film thus increasing its permeability.

EFFECT OF SOIL PARAMETERS ON HCB VOLATILIZATION FROM SIMULATED LANDFILL

In this section the effect of soil water content, soil bulk density, and air-filled porosity on the vapor phase diffusion of HCB in soil are investigated. This discussion will be limited for the most part to results obtained using recrystallized practical grade HCB. Comparisons of vapor pressures and volatilization fluxes have shown the various industrial wastes to be similar in their HCB vapor activity to the recrystallized material.

Soil Water Content

It is a common practice to spray water over soil as a dust control measure when wastes are being covered with soil and also as an aid to obtain maximum compaction of the soil. Natural rainfall also adds water to the soil. The amount of water in a soil affects the pore space available for HCB vapor diffusion, and thus affects the HCB volatilization flux through the soil cover. Two HCB volatilization experiments

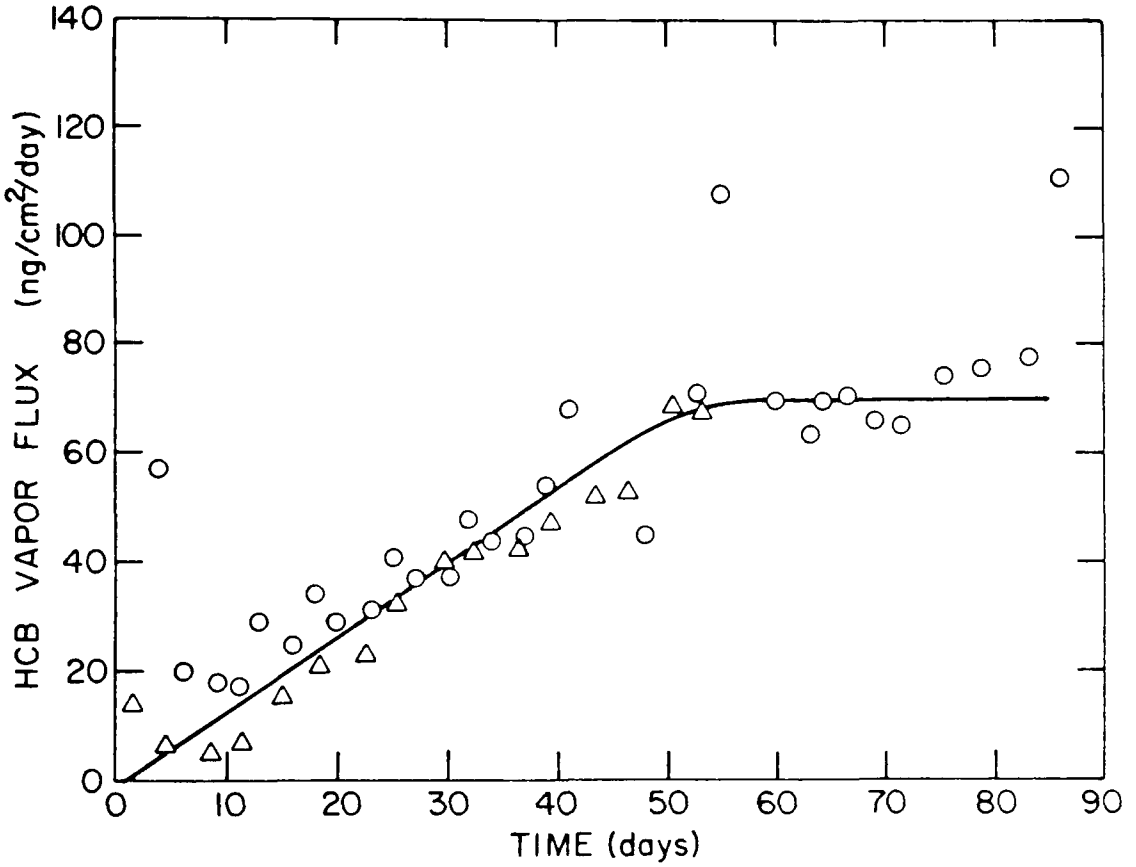


Figure 14. Volatilization vapor flux of hexachlorobenzene from hex waste A covered with a composite layer of 1.8 cm soil and 0.01 cm polyethylene film (Experiment VI). Results of duplicate experiments. The hex waste used in this experiment had contacted several layers of soil and therefore did not contain significant amounts of the liquid waste component.

were conducted with the soil cover at the same bulk density of 1.15 g/cm^3 but at different soil water contents (Experiments VIII and XI) using recrystallized HCB. The HCB fluxes are shown in Fig. 15. It is clear that steady state HCB volatilization flux through a 1.8 cm soil cover with a water content of 17.24% is higher than that through a soil cover of 19.58% water content. Since both soil covers have the same bulk density and thickness, the difference in HCB flux must be caused by the difference in water contents.

The effect of soil water content on HCB volatilization flux through a soil cover can best be seen by plotting the steady state HCB specific fluxes against the soil water contents. The specific flux is defined as the flux per unit concentration gradient. The steady state HCB specific fluxes from Experiments VIII and XI and those from Experiments V and VII

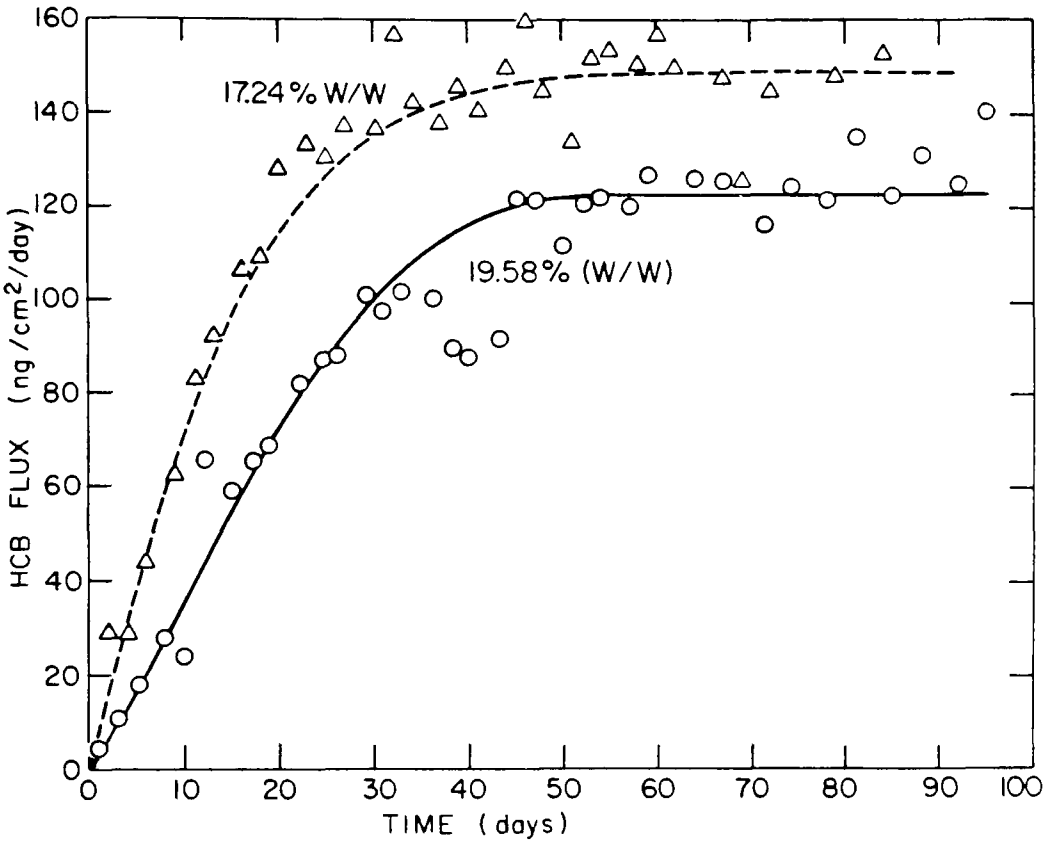


Figure 15. Effect of soil water content on the volatilization of hexachlorobenzene from recrystallized HCB covered with 1.8 cm soil at bulk density of 1.15 g/cm^3 (Experiments VIII and XI).

at a slightly higher bulk density of 1.19 g/cm^3 (74.29 lb/ft^3) are plotted against the soil water contents and are shown in Fig. 16. The steep slope of the line passing through these points indicates a marked effect of soil water content on HCB flux. Comparing the steady state HCB specific fluxes between Experiments VIII and XI shows that decreasing soil water content 2.3% increases HCB specific flux by 21.2%. Thus, the effect of soil water content on HCB volatilization flux through soil cover is exponential. Shearer et al. (1973) studied lindane diffusion in soil and observed a similar exponential effect of soil water content on vapor phase diffusion. Increasing soil water content decreases the pore space available for HCB vapor diffusion and will decrease HCB volatilization flux. When soil is saturated with water it will have the same effect as a covering of water.

In contrast, increasing soil water content has been shown to increase the volatility of pesticide in soils under certain circumstances. Gray et al. (1965) pointed out that there appeared to be a critical soil water level for each soil above which losses of EPTC were larger. Spencer

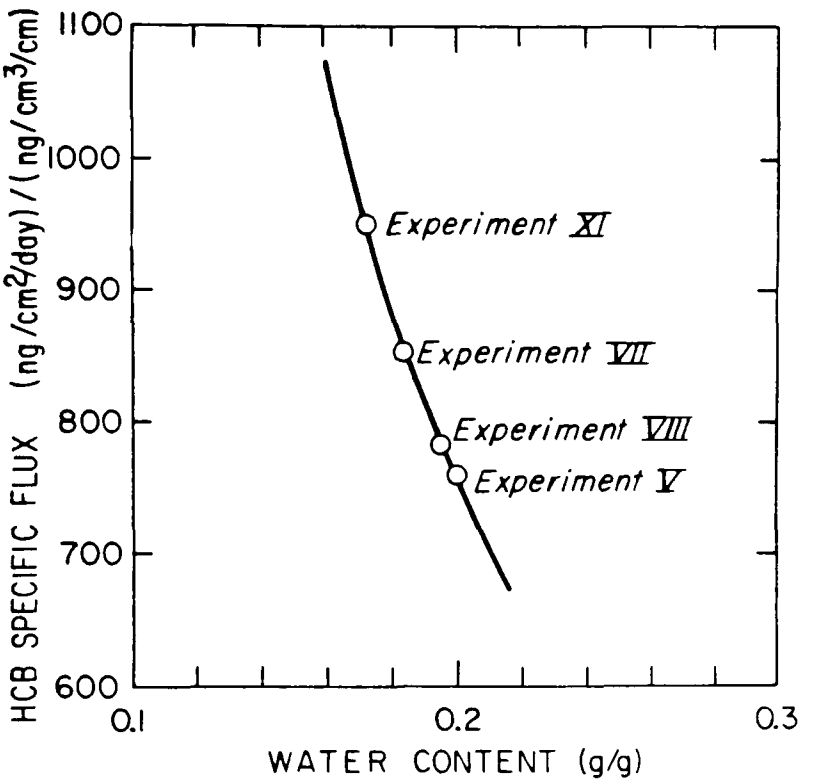


Figure 16. Effect of soil water content on the specific HCB volatilization flux through a soil cover.

and Cliath (1969, 1970) found that vapor densities of dieldrin and lindane in soil dropped to very low values when the soil water content was decreased below that equivalent to one mono-molecular layer, but vapor densities were not affected by soil water contents above one mono-molecular layer of water. Yang (1974) reported that parathion volatilization dropped rapidly when soil water content decreased below 8% and this critical soil water content was much higher than that of one mono-molecular layer of water. Spencer et al. (1973) reviewed pesticide volatilization and pointed out that the soil water content at which pesticide vapor density sharply decreased depends on the soil and the ability of the pesticide to compete with water for adsorption sites. The more strongly adsorbed the pesticide, the higher the water content at which an appreciable decrease in vapor density would occur.

In the very dry soil water content range, fewer water molecules are available to compete with the pesticide molecules for adsorption sites on the soil and more pesticide molecules are adsorbed by soil, thus having fewer available for volatilization. In essence, the soil water content affects the pesticide adsorption capacity of soil. The reduced pesticide

volatilization at a very dry soil water content can be viewed as an increased pesticide adsorption capacity of soil. The increased pesticide adsorption capacity of the soil will increase the time required to reach steady state HCB volatilization flux through the soil cover. However, the magnitude of the steady state HCB volatilization flux through soil cover at the very dry soil water content range will be much greater than that through a wet soil at the same bulk density. Such a relationship is indicated in Fig. 16.

Soil Bulk Density

When hex waste is covered with soil, the type of soil used and the amount of pressure applied to compact the soil will affect the degree of compaction of the cover soil. Soil compaction or bulk density determines the porosity of a soil and thus affects HCB vapor diffusion through the soil. HCB volatilization fluxes through a 1.8 cm soil cover (Experiments VIII, IX and X) are shown in Fig. 17. Comparing the HCB fluxes shows that HCB volatilization fluxes through a soil cover of lower bulk density are greater than those through a soil cover of higher bulk density. Since the final soil water contents are very close to one another and all of the soil covers have the same thickness, the difference in HCB volatilization must be caused by the difference in soil bulk density.

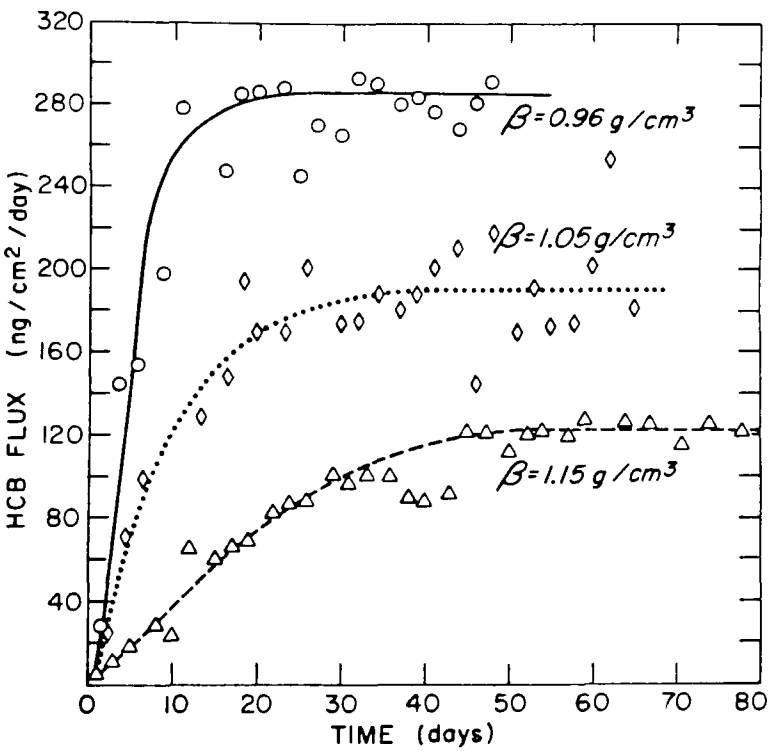


Figure 17. Effect of soil bulk density on the volatilization of hexachlorobenzene from recrystallized HCB covered with 1.8 cm soil cover (Experiments VIII, IX and X).

The quantitative effect of soil bulk densities on HCB volatilization fluxes through soil covers can be seen by plotting the steady state HCB specific flux against the soil bulk density. The results from Experiments VIII, IX and X, together with that from Experiment V are shown in Fig. 18. Comparing the steady state HCB specific fluxes from Experiments IX and X shows that decreasing the bulk density by 0.09 g/cm^3 increases the steady state HCB specific flux by 45%. Thus the soil bulk density also has an exponential effect on HCB volatilization flux through the soil cover. Similar exponential effects of soil bulk density on vapor phase diffusion flux has been shown for lindane (Ehlers et al., 1969).

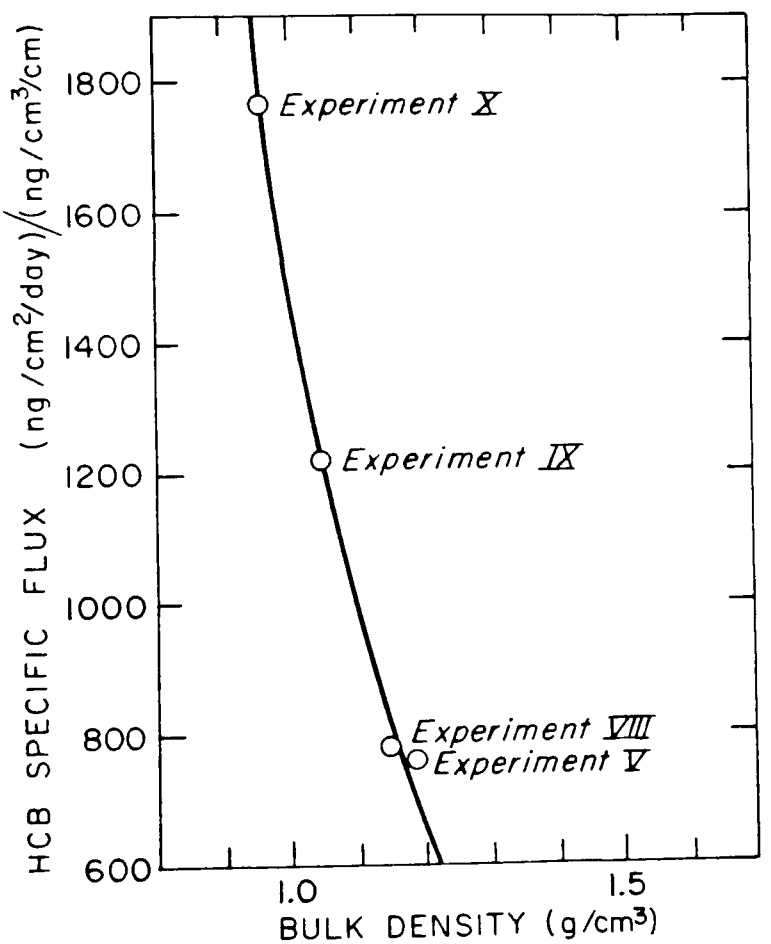


Figure 18. Effect of soil bulk density on the specific HCB volatilization flux through a soil cover.

From previous considerations of the effect of soil water content, it is obvious that a higher soil bulk density will have effects similar to that of an increased soil water content. The higher the soil bulk density, the smaller the steady state HCB flux will be. However, for any given soil there is a limit on the maximum bulk density that can be reached and there will always be a finite amount of open pore space for vapor diffusion to take place.

Air-filled Porosity

Previous theoretical analysis of HCB water-air partition coefficients and experimental results show that vapor phase diffusion is the major mode of HCB movement through soil. HCB molecules will have to diffuse through the air-filled pore space of the soil. Thus the effects of soil water content and soil bulk density on HCB volatilization flux through a soil cover can be attributed to their effect on the air-filled porosity, which in turn is the major soil factor controlling HCB volatilization through soil.

Figure 19 shows the effect of air-filled porosity on steady state HCB volatilization flux through a soil cover (Experiments V, VII, VIII, IX, X, and XI). Comparison of Experiments IX and X shows that increasing the relative air-filled porosity 13.4% increases specific HCB volatilization flux 45%, indicating that air-filled porosity has an exponential effect on the HCB volatilization flux through soil.

CALCULATIONS OF DIFFUSION COEFFICIENT

As stated in the Introduction the steady state HCB volatilization flux through a soil cover can be expressed as

$$J = -D_s(C_2-C_s)/L \qquad (1)$$

where J is the vapor flux ($ng/cm^2/day$),

D_s is the apparent steady state diffusion coefficient (cm^2/day),

C_2 is the concentration in the air at the surface of the soil (ng/cm^3),

C_s is the concentration in the air at the bottom of the soil layer (ng/cm^3), and

L is the depth of the soil layer (cm).

Since the HCB concentration measured is the average concentration in the air above the soil surface, C_2 has to be estimated from the relationship:

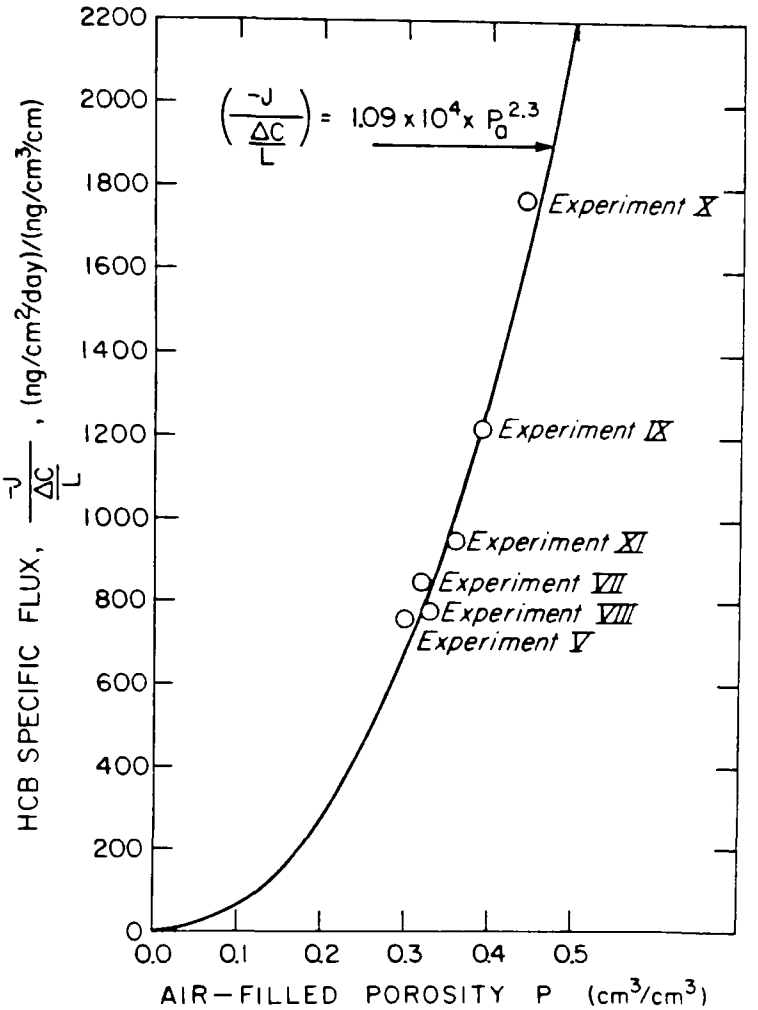


Figure 19. Effect of air-filled porosity on the specific HCB volatilization flux through a soil cover.

$$K_4 = C_{aw}/C_s = C_a/C_2$$

$$C_2 = C_a/K_4 \qquad (2)$$

where C_a is the average concentration in the air above the soil (ng/cm^3),

C_{aw} is the average concentration in the air above the uncovered hex waste (ng/cm^3), and

K_4 is the ratio.

Since C_s is the saturation vapor density and C_{aw} is known from the uncovered hex waste experiment, C_2 can be estimated.

Although air-filled porosity is found to be the major factor controlling HCB volatilization flux through the soil-water-air system, the apparent vapor diffusion coefficient does not depend only on the amount of air-filled pore space. Shearer et al. (1966) pointed out that in adding liquid to a porous system, there was a much greater reduction in the apparent gas diffusion coefficient than that found accompanying reduction in gas-filled pore volume by the addition and closer packing of the solid. The presence of liquid films on the solid surface not only reduces the porosity, but also modifies the pore geometry and the length of the gas passage. Thus the apparent gas diffusion coefficient through a porous medium is clearly a function of both internal geometry and porosity.

Millington and Quirk (1961) suggested an apparent vapor diffusion coefficient which includes the porosity term to account for the geometric effects of the soil system. Based on a theoretical derivation, they presented a formula for the apparent vapor diffusion coefficient including air-filled porosity and the total porosity of the soil system. Shearer et al. (1973) successfully used the apparent vapor diffusion coefficient formula suggested by Millington and Quirk (1961) to compute the apparent vapor phase diffusion coefficient of lindane in soil. The apparent vapor diffusion coefficient can be expressed as

$$D_s = D_o \, (P_a^{10/3} / P_T^2) \tag{3}$$

where D_o is the vapor diffusion coefficient in air (cm^2/day),

P_a is the air-filled porosity (cm^3/cm^3), and

P_T is the total porosity (cm^3/cm^3).

Substituting D_s into equation (1) and rearranging the equation to obtain the specific HCB volatilization flux $-J/(C_2-C_s)/L$ through soil cover, the equation becomes

$$-J/(C_2-C_s)/L = D_o \, (P_a^{10/3} / P_T^2) \tag{4}$$

The diffusion coefficient D_o can be determined by plotting $-J/(C_2-C_s)/L$ against $(P_a^{10/3} / P_T^2)$ and the slope of the linear regression line is the value of D_o. Figure 20 shows the experimentally determined linear regression line $-J/(C_2-C_s)/L = 20.2 + 10056.3 \, (P_a^{10/3} / P_T^2)$, and the corresponding HCB vapor diffusion coefficient in air is found to be 1×10^4 cm^2/day.

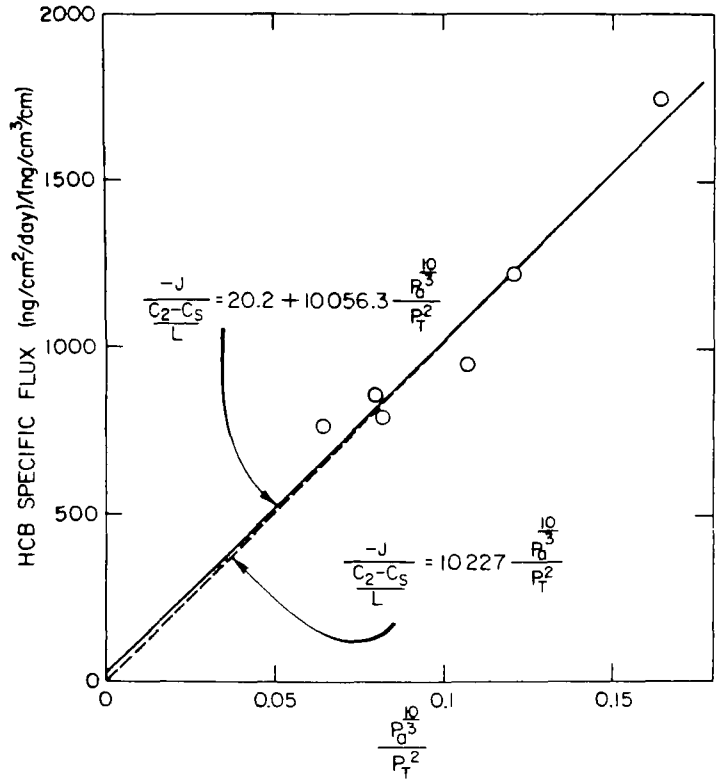


Figure 20. Linear regression line for the relationship between the specific HCB volatilization flux and the ratio $P_a^{10/3}/P_T^2$.

The linear regression line shown as the solid line in Figure 20 does not pass through "zero" as Equation (3) predicted. However, the deviation from passing through the origin is very small as can be seen by comparing it with the linear regression line that results when the constriction is added that it pass through the origin and shown as the dashed line in Figure 20.

The vapor diffusion coefficient also can be estimated from the known vapor diffusion coefficient in air of other compounds. The self-diffusion coefficient of a gaseous compound has been shown as (Moore, 1962)

$$D = 1/3 \quad \lambda \overline{C}$$

where λ is the mean free path, and

$\overline{C}$ is the average speed.

$\overline{C}$ is shown as

$$\overline{C} = (8RT/\pi M)^{\frac{1}{2}}$$

where R is the gas constant,

T is the absolute temperature, and

M is the molecular weight.

The diffusion coefficient is then expressed as

$$D = 1/3 \ \lambda (8RT/\pi M)^{\frac{1}{2}}$$

or

$$D \propto (T/M)^{\frac{1}{2}} \tag{5}$$

The vapor diffusion coefficient of compound A can be estimated from the known vapor diffusion coefficient of compound B by using the relation in Equation (5) and is expressed as

$$D_A = D_B \ (M_B/M_A)^{\frac{1}{2}} \tag{6}$$

where the subscripts A and B denote compounds A and B, respectively.

When the temperature changes from T_1 to T_2, the diffusion coefficient at temperature T_2 can be estimated by using Equation (5) and is shown as

$$D_2 = D_1 \ (T_2/T_1)^{\frac{1}{2}} \tag{7}$$

where the subscripts 1 and 2 denote the value at the temperatures T_1 and T_2, respectively.

The diffusion coefficient of oxygen in air at 0 C has been reported to be 0.178 cm^2/sec (Handbook of Chemistry and Physics, 1973). The diffusion coefficient of oxygen in air can be used to estimate the vapor diffusion coefficient of HCB in air at 25 C by using Equations (6) and (7). The HCB vapor diffusion coefficient in air is estimated to be 0.54 x 10^4 cm^2/day which is about half of the measured value of 1 x 10^4 cm^2/day. Thus the measured HCB vapor diffusion coefficient in air seems to be quite reasonable. It is important to note here that diffusion coefficients of other compounds which move mainly in the vapor phase can also be estimated by using Equations (6) and (7) and the estimated diffusion coefficient can then be used to predict vapor flux through soil.

Equation (4) can be used to show the effect of air-filled porosity on vapor phase diffusion. This is illustrated in Fig. 21 where the HCB vapor flux through a soil layer 100 cm in depth is plotted, using Equation (4), as a function of soil water content and soil bulk density. The temperature is 25 C.

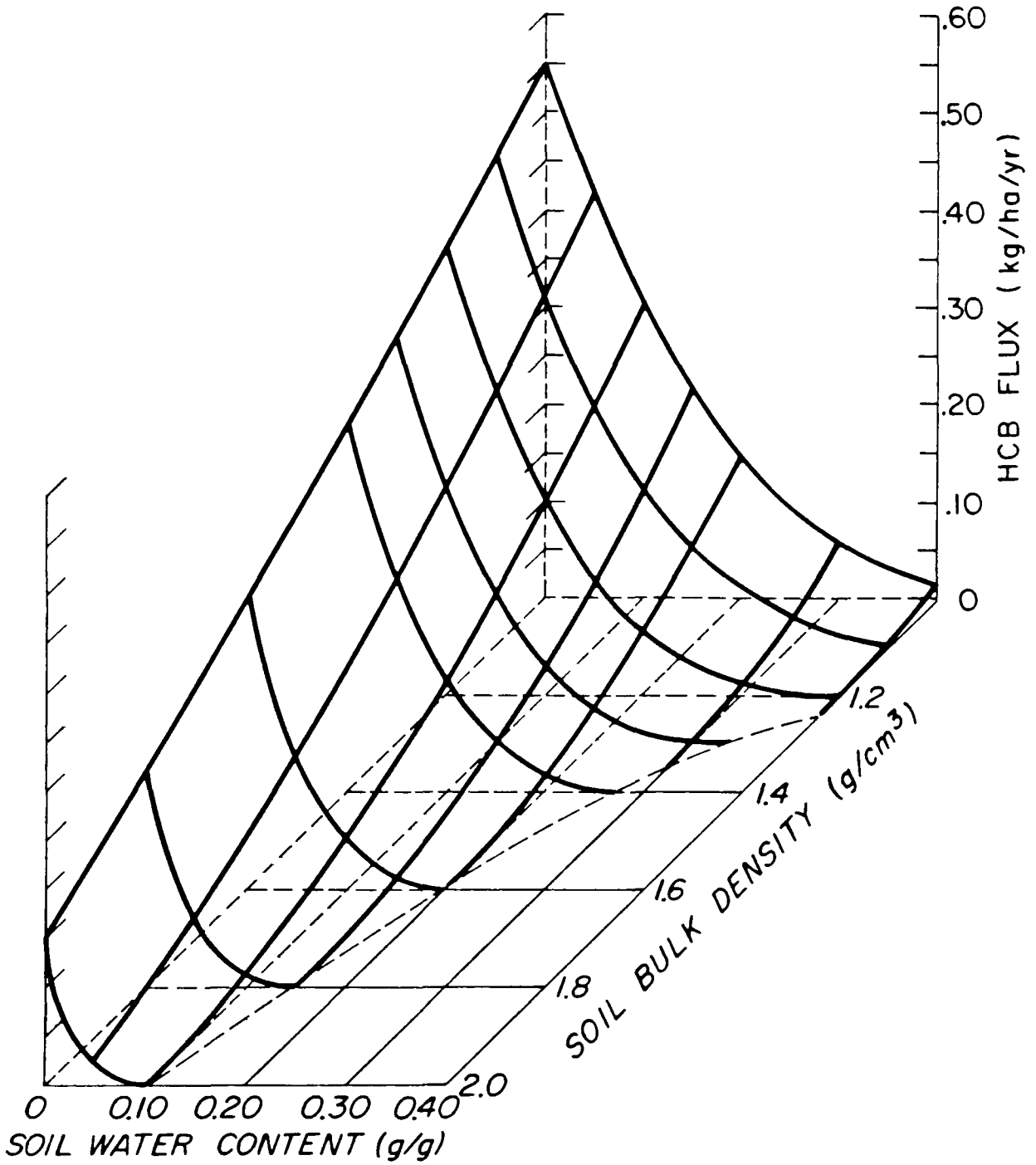


Figure 21. Predicted HCB volatilization flux through a soil cover as a function of soil water content and soil bulk density. Soil thickness is 100 cm.

SECTION 6

SIGNIFICANCE OF THE FINDINGS FOR SOME LANDFILL DISPOSAL PRACTICES

EQUIVALENT THICKNESS OF POLYETHYLENE FILM TO SOIL

Polyethylene film can be used alone or in conjunction with other covering materials to reduce the volatilization of HCB from hex wastes. The effects of polyethylene film are two-fold: the direct effect is to act as a barrier to HCB vapor, and the indirect effect is to maintain a high water content in the soil underlying the film so that the soil cover can be more effective in reducing HCB volatilization flux through the soil cover. In order to aid in the design of the thickness of the total covering and to achieve the maximum effectiveness of the covering, it is necessary to know the quantitative effectiveness of the film or the equivalent thickness of the film to soil.

When polyethylene film is used with soil, the equivalent thickness of polyethylene film to soil in reducing HCB vapor flux at steady state can be calculated when the diffusion coefficient of the polyethylene film is known. The diffusion coefficient of the polyethylene film is determined using the flux data in Experiment VI (Figure 14) using the following equation:

$$\Sigma L_i/D_A = \Sigma (L_i/D_i) \qquad (8)$$

where L_i is the depth of an individual layer in a multilayered system

D_A is the average apparent diffusion coefficient over the whole system, and

D_i is the apparent diffusion coefficient for each layer in a multilayered system.

Experiment VI is a two-layered system consisting of a 1.8 cm deep soil layer and a 0.01 cm deep polyethylene layer. The apparent diffusion coefficient of the soil layer will be the same as the soil layer in Experiment V since soil water contents and soil bulk densities were the same in both experiments. Using Equation (8) the sum is:

$$(L_{soil} + L_f)/D_A = L_{soil}/D_{soil} + L_f/D_f$$

where L_{soil} is the depth of the soil layer in a multilayered system,

L_f is the depth of the polyethylene layer,

D_{soil} is the apparent diffusion coefficient for the soil layer, and

D_f is the apparent diffusion coefficient of the polyethylene film.

The apparent diffusion coefficient of the polyethylene film was calculated to be 5.6 cm^2/day using the flux data from dry hex waste A covered with a composite layer of soil and 0.01 cm polyethylene film (Experiment VI, Fig. 14).

The effectiveness of a 0.01 cm polyethylene film for reducing HCB volatilization flux is equivalent to that of a 1.36 cm layer of soil at 1.19 (g/cm^3) bulk density and 20% dry weight soil water content. This equivalent layer was extrapolated linearly to other film thicknesses and plotted in Fig. 22. The film is not very effective in reducing HCB volatilization flux, especially when considering the cost of the material and the thickness of soil cover used.

It is valid to use Fig. 22 to estimate the equivalent film thickness of other soils that have the same bulk density and soil water content as that used in the figure. Comparisons with soils of other bulk densities and soil water contents can be made by using Equation (3) to calculate a D_s for the soil and comparing to the value of 5.6 cm^2/day diffusion coefficient of the polyethylene film.

PROBLEMS ASSOCIATED WITH LIQUID COMPONENT OF THE HCB WASTE

The sample referred to earlier as fresh hex waste was collected from the process line before being discharged into the storage lagoon and contained 76.6% liquid by volume. This liquid component has a very strong odor and a reddish brown color. It has a density of about 1.67 g/ml and contains 1.4% HCB. Because it is heavier than water, it may move downward when placed in a landfill or a storage lagoon and have a potential to leach HCB into ground water.

The liquid component of the HCB waste A was found to deposit on the polyethylene film in Experiments IV, I, and II and to cause the film to partially dissolve and expand. The HCB volatilization flux through the partially dissolved and expanded polyethylene film was found to be 28% greater than that through an unaffected film . Obviously the liquid component of HCB waste caused the polyethylene film to dissolve and expand and thus affected the HCB transmission properties of the film. It is conceivable that this liquid component may also have deleterious effects on other synthetic membranes and thereby reduce their effectiveness as barriers to liquid and gas movement when used in a landfill or storage lagoon.

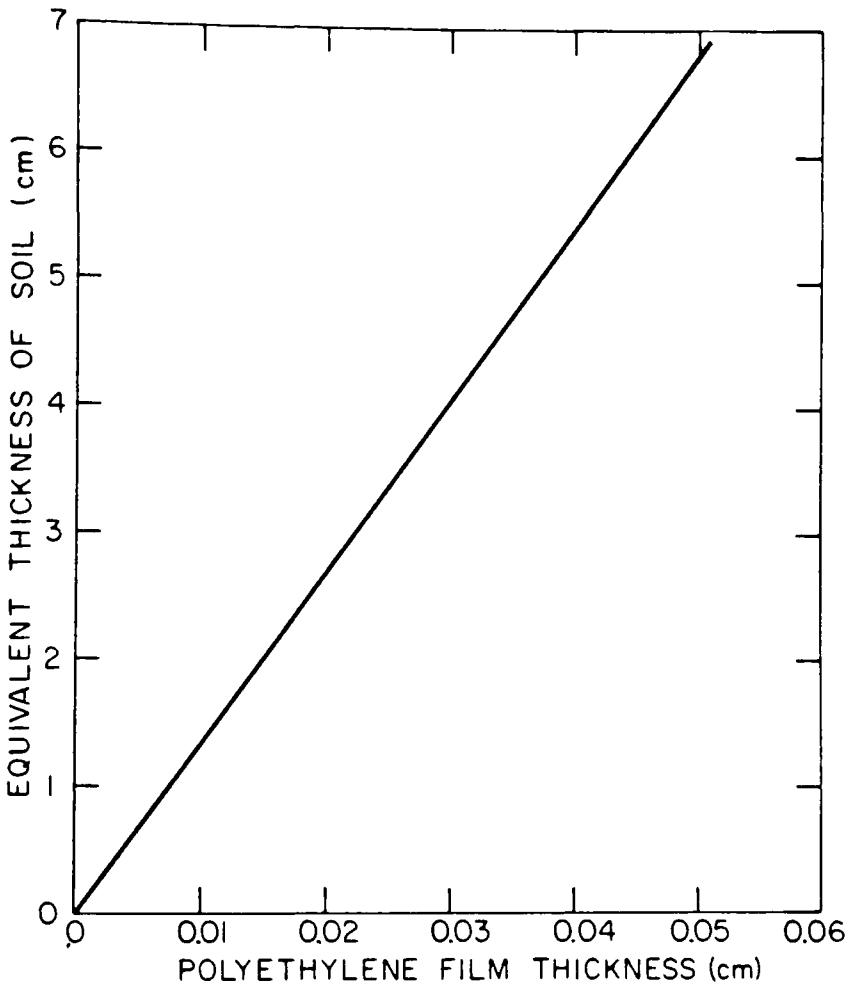


Figure 22. The equivalent thickness of polyethylene film to soil assuming a soil bulk density of 1.19 g/cm^3 and a soil water content of 20% (w/w).

SECTION 7

APPLICATION OF THE FINDINGS IN DESIGNING LANDFILL COVERS

The findings of this study may be used to assist a planner in designing a landfill cover that minimizes the escape of HCB or other vapors. Alternatively, an existing landfill may be assessed, using the results of this study, for its potential for allowing HCB vapor fluxes through the surface of the landfill.

The volatilization or vapor loss of HCB and other compounds from landfill can be treated as a diffusion controlled process. The rate at which compounds will volatilize from the soil surface and be lost to the atmosphere will be controlled by the rate at which they diffuse through the soil cover over the waste. Assuming no degradation of the compound and no transport in moving water, the volatilization can be predicted using Equation (1) of this report which is Fick's First Law for steady state diffusion:

$$J = -D_s(C_2 - C_s)/L \qquad (1)$$

where J is the vapor flux from the soil surface ($ng/cm^2/day$),

D_s is the apparent steady state diffusion coefficient (cm^2/day),

C_2 is the concentration of the volatilizing material in air or vapor density at the surface of the soil (ug/l),

C_s is the concentration of the volatilizing material in air or vapor density at the bottom of the soil layer (ug/l), and

L is the soil depth (cm).

The negative sign is present to indicate that the vapor flux is in the opposite direction from the vapor concentration gradient in the soil. Table 6 gives several conversion factors which may be useful depending on whether regulatory agencies specify flux in metric or English units.

Table 6. Conversion Factors

To convert	into	multiply by
atmospheres	mm Hg	760
centimeters	ft	3.28×10^{-2}
cm^2/day	mm^2/week	700
feet	cm	30.48
g/cm^3	lbs/ft^3	62.4
kg/ha	lbs/acre	0.89
mm Hg	atm	1.32×10^{-3}
ng/cm^2	kg/ha	10
ng/cm^2	lbs/acre	8.9×10^{-5}

In order to use Equation (1) for predicting volatilization, the apparent diffusion coefficient, D_s, must be evaluated. The investigators, Millington and Quirk (1961) have suggested an apparent diffusion coefficient which included a porosity term to account for the geometric effects of soil on diffusion. This was Equation (3) of this report and was expressed as

$$D_s = D_o(P_a^{10/3}/P_T^2) \tag{3}$$

where D_o is the vapor diffusion coefficient in air (cm^2/day),

P_a is the soil air-filled porosity (cm^3/cm^3), and

P_T is the total soil porosity (cm^3/cm^3).

Combining Equations (1) and (3) yields the following expression:

$$J = -D_o(P_a^{10/3}/P_T^2)(C_2-C_s)/L \tag{4}$$

This equation will be used in this paper as the basis for a suggested step-wise procedure intended to assist a planner in designing a landfill cover that minimizes the escape of HCB or other vapors. Alternatively, an existing landfill cover may be assessed, using Equation (4), for its potential for allowing HCB vapor flux through the surface of the landfill. The validity of Equation (4) has been experimentally verified for hexachlorobenzene in this project. The diffusion coefficient in air, D_o, for HCB was found to be 1×10^4 cm^2/day.

This procedure for assisting in the design of a landfill cover is only a suggested procedure and is not an accepted official EPA procedure. This will be an example of how research findings can be used to arrive at a suggested set of procedures that will assist planners in designing landfill covers taking advantage of the best current knowledge available for reducing vapor flux from a landfill.

DESIGN APPLICATION

In order to use the results of this study in designing a proposed landfill, the planner will normally begin with an acceptable value for HCB flux through a cover and determine the most efficient combination of soil porosity and soil depth to produce the acceptable value. The establishment of the actual values for an acceptable flux through the landfill cover is beyond the scope of this research or that of the landfill designer. Flux from the soil will be established through regulations by state or federal agencies. Alternatively the regulating agencies may establish acceptable air concentration values at some specified distance from the landfill site. In the latter case the landfill designer may have to calculate the acceptable flux at the soil surface using the specified air concentration and existing wind dispersion models (Pitter and Baum, 1975).

Once an acceptable flux value has been established either directly by a regulatory agency or indirectly by use of an air dispersion model, the following steps can be followed to determine what soil conditions would limit flux to this value. The following steps are based on Equation (4) relating vapor flux through soil to soil depth and soil porosity. Initially the soil depth necessary to produce the desired flux will be calculated assuming a dry soil and a minimum reasonable compaction of the soil at the landfill site. If this calculated soil depth is unrealistically high, then increased compaction and/or an appropriate water content will be considered. Finally a modified soil will be considered when necessary and a new flux value calculated. Equation (4) is rearranged below to allow calculation of L, the soil depth (cm).

$$L = -D_o(P_a^{10/3} / P_T^2)(C_2 - C_s)/J$$

or

$$L = -D_o P_a^{10/3} (C_2 - C_s)/JP_T^2 \qquad (9)$$

By assuming that C_2 is zero, Equation (9) simplifies as follows:

$$L = D_o C_s P_a^{10/3} / JP_T^2 \qquad (10)$$

This is a reasonable assumption since under actual landfill conditions the amount of vapor reaching the soil surface from below hopefully will be small and will be rapidly dispersed by wind currents and by diffusion in air. Additionally the assumption of C_2 equaling zero introduces a safety factor into the calculation. Any increase in C_2 will reduce the vapor flux from the soil surface.

The diffusion coefficient in air for HCB has been measured to be $1.0 \times 10^4 cm^2/day$. If soil cover is being designed for some material other than HCB, values for diffusion coefficients in air are available for a limited number of compounds. (Handbook of Chemistry and Physics, 1973.) For those compounds of interest for which no published values are available, reasonable estimates can be made using the Equations (6) and (7) which are reproduced below. The vapor diffusion coefficient of compound A can be estimated from the known vapor diffusion coefficient of compound B by using the previously given Equation (6)

$$D_A = D_B \ (M_B/M_A)^{\frac{1}{2}} \tag{6}$$

where the subscripts A and B denote the values of the diffusion coefficients for compounds with molecular weights M_A and M_B, respectively.

When the temperature changes from T_1 to T_2, where T is the absolute temperature (^oK), the diffusion coefficient at temperature T_2 can be estimated using the previously given Equation (7)

$$D_2 = D_1 \ (T_2/T_1)^{\frac{1}{2}} \tag{7}$$

where the subscripts 1 and 2 denote the values of the diffusion coefficients at the temperatures T_1 and T_2, respectively.

The value for the vapor concentration at the bottom of the soil layer, C_s, can be taken as that equivalent to the saturation vapor pressure of the pure compound. This is true because a waste need contain only a relatively small amount of a volatile material to give a saturated vapor. In the case of HCB, a saturated vapor density was obtained with only 0.3% HCB coated on sand. It is conservative to assume C_s equal to the saturation vapor density. If the actual vapor density is less than saturation, the actual vapor flux through the surface of the soil layer will be less than calculated. Saturation vapor densities are calculated from the following using vapor pressure data which are available for a number of compounds

$$C_s = pM/RT$$

where p is the vapor pressure (mm Hg),

M is the molecular weight of the compound (ug/mole),

R is the molar gas constant (1 mm Hg/deg mole), and

T is the absolute temperature (^{o}K).

The value of C_s for HCB is 0.294 ug/l at 25 C calculated from a vapor pressure of 1.91×10^{-5} mm Hg.

Based on the above considerations the following steps are to be followed in calculating the optimum combination of soil depth and soil porosity to achieve the desired vapor flux. A suggested method or sequence for working through these steps is shown in Figure 23.

1. Base all flux calculations on total soil porosity assuming a dry soil. Thus $P_a = P_T$ and Equation (10) is further simplified to

$$L = D_o C_s P_T^{4/3} / J \qquad (11)$$

This not only simplifies the calculations but introduces another safety margin. The addition of any water to the soil by irrigation or by natural rainfall will reduce the air-filled porosity and thereby reduce the vapor flux from the soil surface. The total porosity of the soil can be calculated from the soil bulk density, β , using the following equation:

$$P_T = 1-\beta/\rho \qquad (12)$$

where β = soil bulk density (g/cm^3) and

ρ = particle density (g/cm^3).

The particle density can be measured. However, the particle density for most soil mineral material is usually taken as 2.65 g/cm^3 (165 lbs/cu ft).

2. Establish a minimum and maximum soil porosity that is likely to be achieved through maximum and minimum compaction of the soil type available at the proposed landfill site. Standardized procedures such as the Procter (ASTM D-698) and modified Procter (ASTM D-1557) (American Society for Testing Materials, 1976) tests are available for estimating the densities that can be achieved for a given soil with various degrees of effort. The degree of compaction need not be limited to either minimum or maximum as intermediate values may be calculated if necessary to determine the precise limiting density.

3. Using the porosity value established in Step 2 above, Equation (11) is used to determine the depth of soil necessary to attain the acceptable vapor flux value through the soil surface.

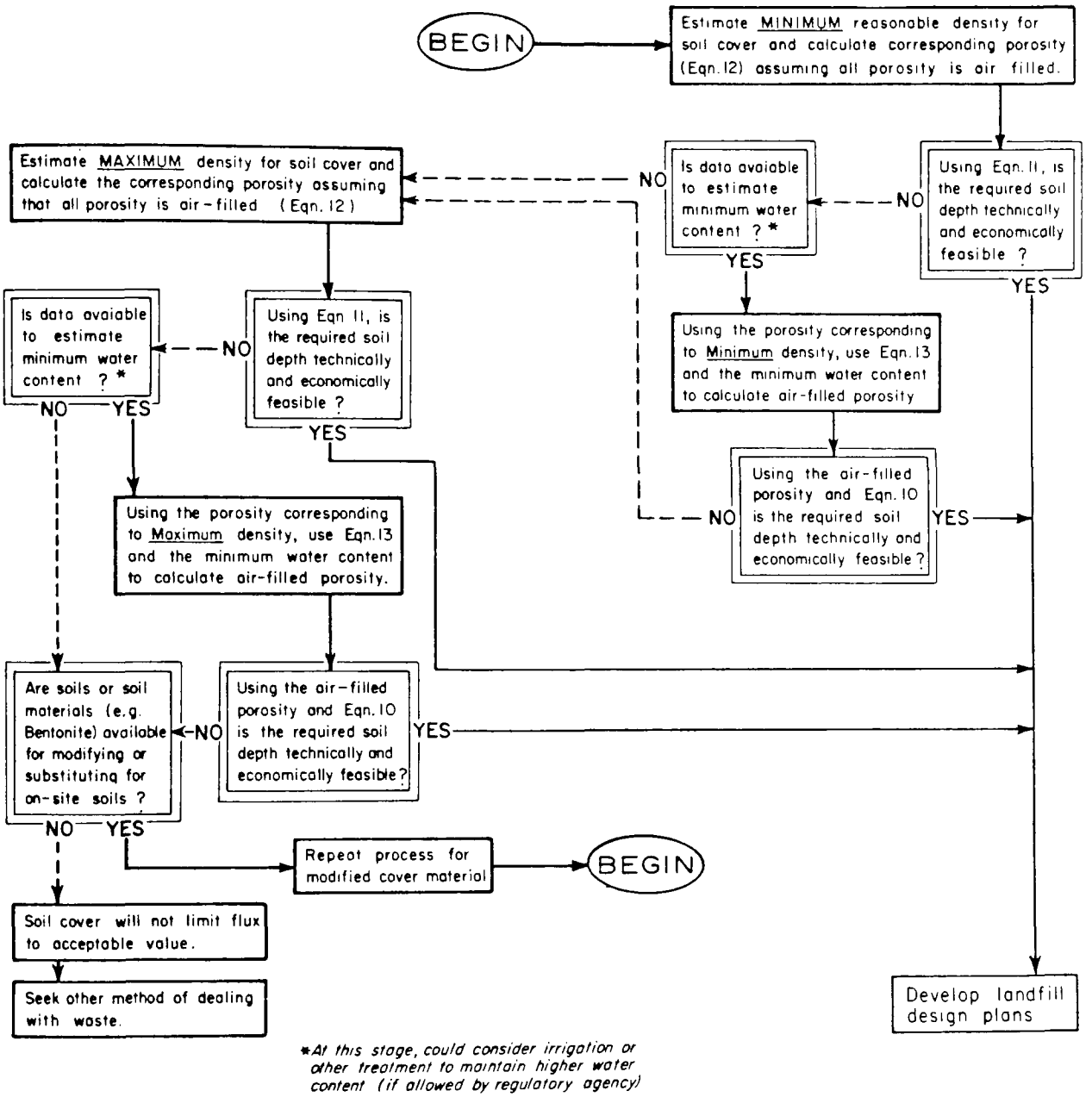


Figure 23. Flow diagram for predicting depth of soil cover required to limit vapor flux through soil cover to an acceptable value.

4. If circumstances allow an estimate of long-term soil water contents in the landfill cover, the planner can refine the flux calculations to give a reduced flux due to reduced air-filled porosity. This refinement requires the use of Equation (10), taking into account the air-filled porosity as affected by soil water content. The air-filled porosity, P_a, is calculated from the total porosity, P_T, and the volumetric soil water content, θ, by the following:

$$P_a = P_T - \theta \tag{13}$$

The volumetric water content (cm^3/cm^3) is determined from the gravimetric soil water content as follows:

$$\theta = W\beta/\rho_w \tag{14}$$

where W is the gravimetric soil water content (g/g), and ρ_w is the density of water (g/cm^3). For practical purposes the density of water can be taken as one and the volumetric water content is simply the gravimetric water content multiplied by the soil bulk density, β.

5. If the soil depths calculated in the previous steps prove to be too great to be technically or economically feasible then the planner will need to decide if it is possible to replace or modify the on-site soil with other soil materials (e.g., bentonite) to increase soil bulk density. If soil modification is feasible then it will be necessary to go back and calculate a new soil porosity term, and thus a new flux value, using the higher bulk density.

6. If none of the above procedures will produce a soil cover that will limit the vapor flux to an acceptable value, other disposal methods may have to be considered for dealing with the waste.

ASSESSMENT APPLICATION

In the case where an existing landfill site has a history of accepting and disposing of HCB-containing materials or other waste of similar concern, it may be desirable to evaluate the cover and to estimate the HCB vapor flux through the surface of the soil to determine if the landfill cover should be redesigned.

Equation (11) is rearranged as follows to calculate vapor flux through a dry soil cover of depth, L, and total porosity, P_T.

$$J = D_o C_s P_T^{4/3} / L \tag{15}$$

The same considerations apply to the use of this equation for calculating flux as applied to Equation (11) for calculating soil depth:

1. The diffusion coefficient in air for HCB is 1.0×10^4 cm^2/day. For other compounds, a value for D_o can be estimated if the actual value has not been determined.

2. The concentration in air at the soil surface, C_2, is assumed to be zero. As discussed before, this is a reasonable assumption and introduces a safety factor into the calculation of a maximum value for the vapor flux through the soil surface.

3. The concentration in air at the bottom of the soil layer, C_s, is the saturation vapor concentration of the compound calculated from its vapor pressure data.

4. In making these calculations a dry soil is assumed so that $P_a = P_T$.

5. If data is available on soil water content, Equation (4) can be used to estimate vapor flux assuming C_2 equal to zero.

DISCUSSION

Figures 24 and 25 illustrate the use of Equations (4) and (15) for predicting vapor flux at different depths of soil cover. Figure 24 shows the HCB volatilization fluxes through soil cover with dry soil at various bulk densities and thicknesses calculated with Equation (15). Soil temperature was taken as 25 C. The vapor fluxes shown in Figure 24 are the maximum to be expected through the soil cover because the addition of water would reduce the air-filled porosity and thus reduce the vapor flux through the soil. Figure 25 shows the predicted HCB vapor flux through a soil cover at various soil water contents and soil depths with the soil bulk density held constant at 1.2 g/cm^3 (74.9 lbs/cu ft) calculated with Equation (4) assuming C_2 equal to zero.

Figure 26 illustrates how changes in soil temperature would be expected to influence HCB volatilization flux through a soil cover. HCB flux is predicted as a function of soil thickness at three temperatures. A bulk density of 1.2 g/cm^3 and a water content of 17% (w/w) is assumed in Figure 26. The increase in flux with increase in temperature is due primarily to the effect of temperature upon the vapor pressure of the compound causing an increase in the vapor concentration gradient across the soil layer. The diffusion coefficient is also affected by temperature and Equation (7) was used to calculate the diffusion coefficient at the different temperatures in Figure 26. The location of a waste disposal site and seasonal changes in climate will affect the temperature of a soil cover over wastes containing HCB. In addition, heat generated inside the landfill due to the aerobic decomposition of organic wastes will have a short term effect on the temperature of the soil cover. From Figure 26 we can see that increasing temperature 10 degrees centigrade increases the HCB volatilization flux approximately three times. Thus a disposal site located in an area where the soil temperature was 10 degrees centigrade warmer than another site would have to use a soil cover at least

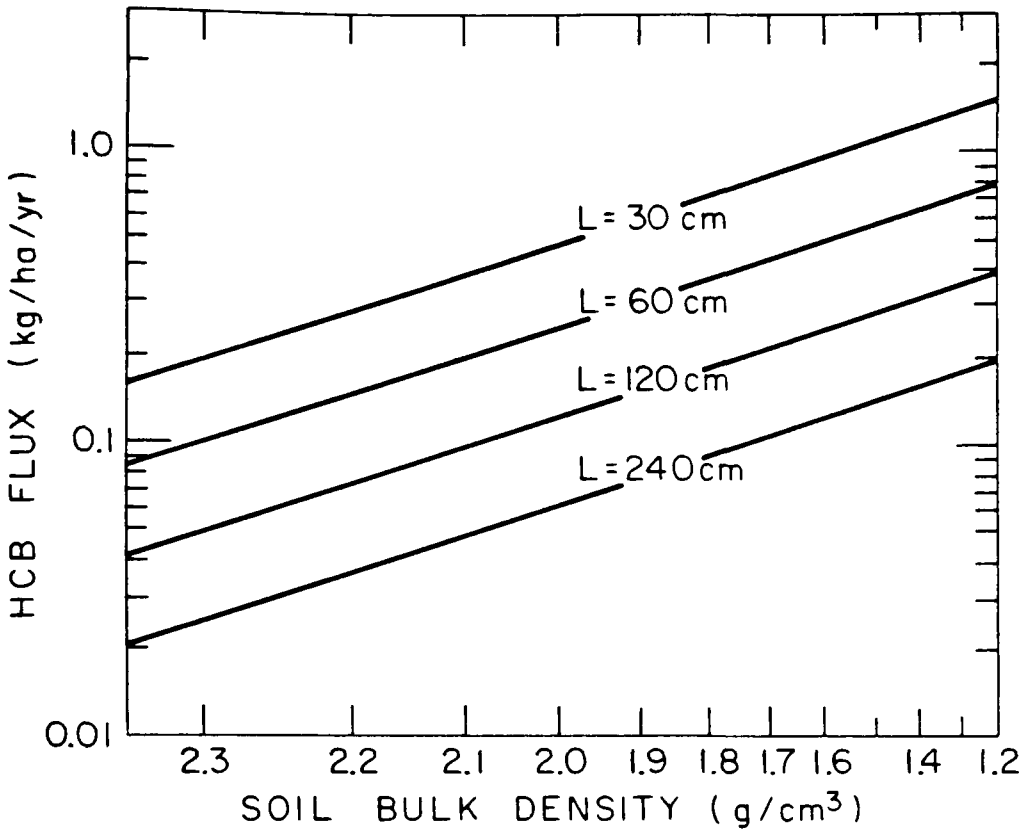


Figure 24. Predicted HCB volatilization fluxes through a soil cover of various soil bulk densities and soil thicknesses at 25 C. The soil was assumed to be dry (zero soil water content) in order to yield a maximum flux.

three times thicker to achieve the same degree of reduction in HCB volatilization flux assuming the temperature is uniform throughout the depth of soil cover and throughout the HCB waste deposit at both sites. Heat generation within the landfill due to decomposing organic wastes will eventually cease and soil temperatures along with volatilization fluxes will, in the long run, be determined by local climates. In this dicussion of temperature effects, we have been assuming a uniform soil temperature throughout the soil profile. In actual fact temperature gradients will exist across the soil cover due primarily to seasonal variations in temperature. Vapor diffusion, of course, is influenced by temperature gradients. The vapor will condense in cooler zones of the soil profile only to be vaporized later when the soil heats up. This will take place, for example, at the soil surface as day and night time temperatures fluctuate. These effects of fluctuating soil temperature gradients will tend to cancel one another and the overall effect of temperature on volatilization flux can be approximated by using an average soil temperature value.

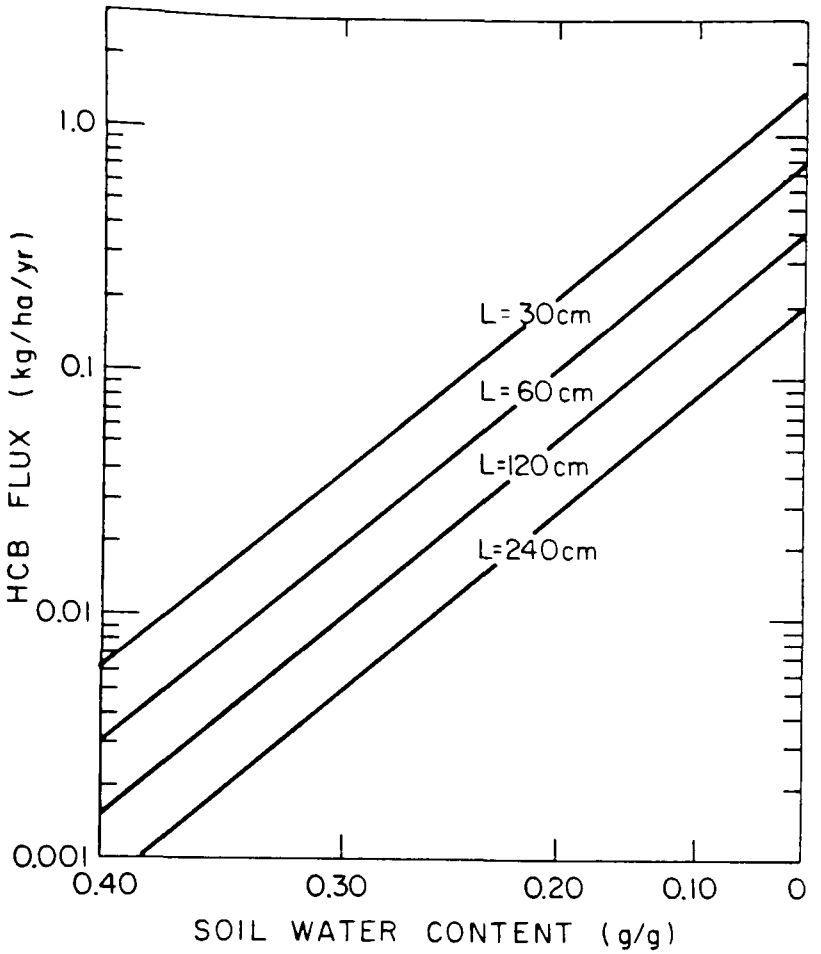


Figure 25. Predicted HCB volatilization fluxes through a soil cover of various soil water contents and soil thicknesses at 25 C. Soil bulk density is 1.2 g/cm^3.

The presence of decomposable organic wastes, such as municipal waste, in a landfill often results in gas production, particularly methane gas. This gas production may be accompanied by a positive flow of gases through the soil cover which would carry HCB vapor by mass flow from any hex wastes located near the decomposing wastes. The HCB flux from this type of mass flow would be analogous to volatilization from uncovered hex waste as depicted in Figure 8 of Section 5 of this report. This flux can be quite high compared to diffusion controlled flux through a soil cover. Again, this flux due to mass flow would be short-term in nature and the long-term volatilization flux will be determined by diffusion.

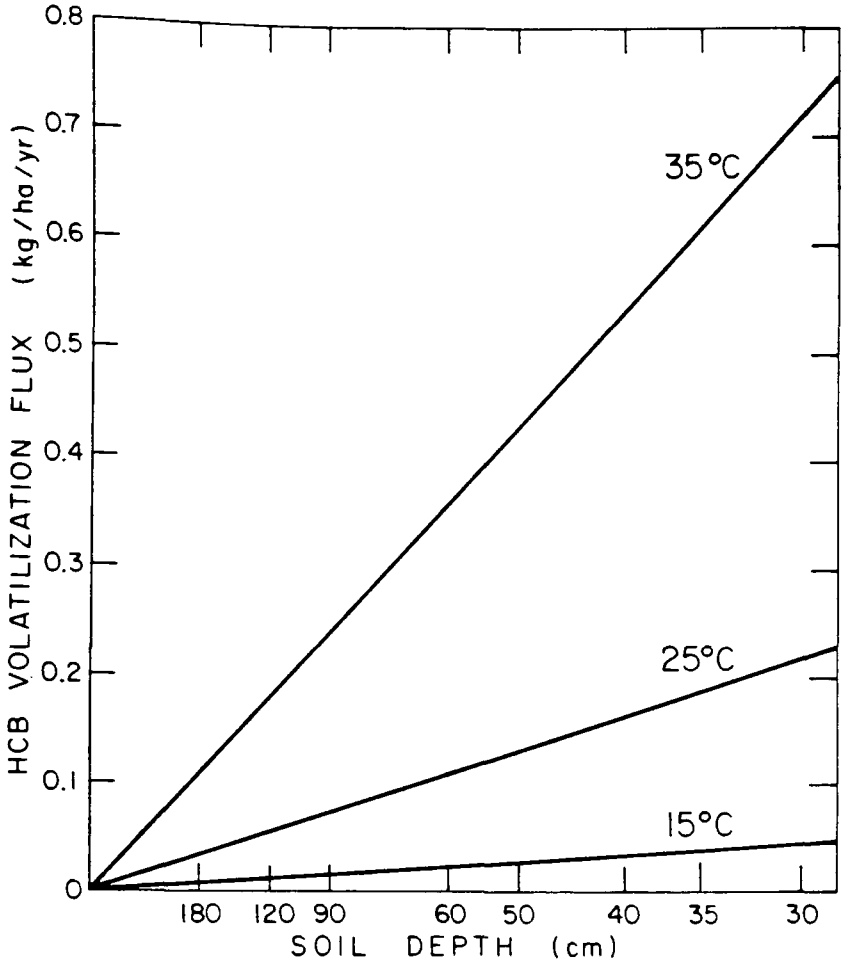


Figure 26. Predicted HCB volatilization fluxes through a soil cover as a function of soil thickness and temperature. A bulk density of 1.2 g/cm^3 and a water content of 17% (w/w) is assumed.

These procedures detailed in Section 7 are written for application to disposal of HCB-containing wastes. However, these same methods can be used to aid in designing landfill covers for other compounds as well, subject to the following qualifications. Hexachlorobenzene degrades very slowly, if at all. Since HCB is very slightly soluble (6.2 ug/l) its transport by moving water is negligible. For compounds which degrade more readily or are more mobile in moving water than HCB, these procedures will tend to overestimate the actual flux through the soil cover. These procedures assume no movement of the compound in water which may be percolating through the soil profile. If a compound is more soluble in water than HCB, it may eventually move with the water; its actual mobility being dependent upon the extent to which it is adsorbed by the soil materials. Assuming that net water flow will be downward in soil,

mobility in water will move the compound away from the surface of the soil cover. These procedures assume no decomposition of the material. Any decomposition which may occur will serve as a sink for the compound and will decrease the amount escaping as a vapor. The procedures presented here, therefore, will not account for any reduction in vapor flux due to decomposition of the compound or due to transport of the compound in water.

If hex wastes are to be placed on land, our work has shown the importance of minimizing the air-filled porosity of soil covers. However, our contribution to the design of a landfill assumes an intact soil cover is maintained. If any cracks or other small openings develop in the soil cover, they will result in an appreciable increase in HCB flux through the soil cover. The placement of hex waste with any material, such as municipal solid waste, that is subject to settlement could cause such cracking and flux increase.

If hex wastes are placed on land, consideration should be given to the need for long-term arrangements for ensuring the integrity of soil covers. Calculations assuming no degradation indicate that HCB placed on land could continue to volatilize at a maximum rate for several centuries. The integrity of the soil cover must be maintained for this period by preventing such things as erosion or digging.

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APPENDIX

COLUMN CLEANUP PROCEDURE FOR VOLATILIZATION PRODUCTS FROM HEX WASTE

The following procedure was developed because of a serious analytical problem which existed while attempting to analyze for HCB in samples collected from the volatilization cell when it contained hex waste. As discussed in Section 4, Materials and Methods, when hex waste volatilization products were injected into the GC following extraction from hexylene glycol or ethylene glycol, the GC trace was often impossible to quantify. The problem was corrected with the clean-up procedure described below using activated alumina. Although activated alumina has proved invaluable in this study for sample cleanup, the material must be used with caution to insure it remains dry and activated. Frequent checks using standards should be run to ensure that a given method is operating as intended. Reproducibility of results from the same bottle of alumina was improved by shaking the alumina bottle thoroughly each time before opening. A common practice with florisil to ensure constant activity is to keep it in a 200 C oven until it is used. This method does not work with alumina since its activation temperature is 500-600 C and heating at a lower temperature only serves to deactivate it.

The samples to be cleaned-up are contained in 100 ml volumetrics in hexane after extraction from the hexylene glycol or ethylene glycol traps. If any acetone had been used during the extraction of the samples from the traps, three water washes are added to the extraction procedure. This greatly improved sample uniformity and reproducibility. Acetone can serve to deactivate the alumina in a manner similar to water. The columns were 1.5 cm ID with 2.54 cm (1 in) Na_2SO_4 on top of 10 cm (4 in) Al_2O_3. Prepare cleanup columns as follows:

1. Put glass columns in oven (110-120 C) for 5-10 minutes. They must be <u>completely</u> dry so that they do not deactivate the aluminum oxide.

2. When the columns are cool enough to handle, clamp them in a verticle position on stand or rack. Plug them with a little glass wool. (Push glass wool down with 5 ml pipette or something else suitable.)

3. Mark columns on the outside at 4 and 5 inches above the glass wool.

4. Through powder funnel, <u>carefully</u> pour Al_2O_3 W 200 neutral (Woelm) into column up to the 4 inch mark; tap it a little at the end. (If you overfill, <u>don't</u> just pour out excess; this distorts the even layering of the alumina and later causes streaking of the sample. Start completely

over with a new column.) Close Al_2O_3 bottle immediately when you are finished; never let moist air get into it. (It is important that the Al_2O_3 is in its most active state. Any deactivation will cause the HCB to partially elute with the first hexane fraction.)

5. Add one inch of anhydrous Na_2SO_4 on top (up to the 5 inch mark).

6. Open stopcocks and wet the columns with nanograde hexane, 15-20 ml. Let hexane drain into columns until 3 mm above the Na_2SO_4, then close stopcocks.

7. Measure 40 ml of hexane for each column into graduated cylinders.

8. Make sample volumetrics up to volume - be sure to note subtracted aliquots! Add exactly 10 ml of sample onto each column. Label columns and/or receiving Erlenmeyer flasks.

9. Open stopcocks and adjust to a flow of approximately 2 drops per second.

10. Let samples completely drain into column, but don't let surface dry.

11. Immediately wash with 3 ml of hexane; rinse the inner walls of the column. Let hexane drain in and repeat washing twice more with 3 ml hexane each.

12. Add remaining hexane onto column and readjust flow (2 drops per second).

13. Prepare 10% analytical grade benzene in nanograde hexane. (Each time a new bottle of benzene is opened, inject some of it into GC to make sure that it does not contain interferences.) Measure 100 ml of the mixture for each column into graduated cylinders.

14. When all hexane has drained into the column, immediately add 100 ml of 10% benzene in hexane and readjust flow if necessary.

15. Change receiving containers. Discard eluted hexane (it contains the GC-interfering substances) and collect the 10% benzene-in-hexane fraction in a clean 125 ml Erlenmeyer flask. Wrap some aluminum foil around end of column and neck of flask and place flask so that the drops will not splash. (Now you can go for a coffee break. Never stop the column flow once the sample is on!)

16. When column has run dry, take benzene-hexane eluate, transfer quantitatively into Kuderna-Danish with hexane and evaporate to less than 10 ml.

17. Transfer cooled concentrate quantitatively into a 10 ml volumetric flask with hexane and make up to volume with hexane.

18. Sample is ready for injection into GC.

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(Please read Instructions on the reverse before completing)

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15. SUPPLEMENTARY NOTES

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16. ABSTRACT

Hexachlorobenzene (HCB) is a persistent, fat-soluble organic compound of low aqueous solubility (6.2 μg/l) present in some industrial wastes. Transport in water moving through soil will be negligible but its long term persistence and appreciable vapor pressure (1.91×10^{-5} mm Hg at 25 C) allows significant volatilization to occur. Conditions for soil covers that would control the movement of HCB out of landfills and other disposal/storage facilities into the surrounding atmosphere were studied. The volatilization fluxes of HCB from industrial wastes (hex wastes) were determined in a simulated landfill under controlled laboratory conditions. Coverings of water and soil were found to be highly efficient in reducing volatilization. Polyethylene film was less efficient when compared on a cost basis. Volatilization flux through a soil cover was directly related to soil air-filled porosity and was greatly reduced by increased soil compaction and water content. An organic liquid phase associated with the hex waste was heavier than water and contained 1.4% HCB by weight. The presence of HCB in this liquid phase creates the potential for rapid transport of HCB in porous media. A procedure is proposed for using the results of this study to design a landfill cover that will limit the volatilization flux of HCB and other compounds.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Volatilization Diffusion Polyethelene Vapor Pressure Soil Chemistry Extraction Hexachlorobenzene	HCB Volatilization Pollutant Migration	13B

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