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## REPORT 84-30



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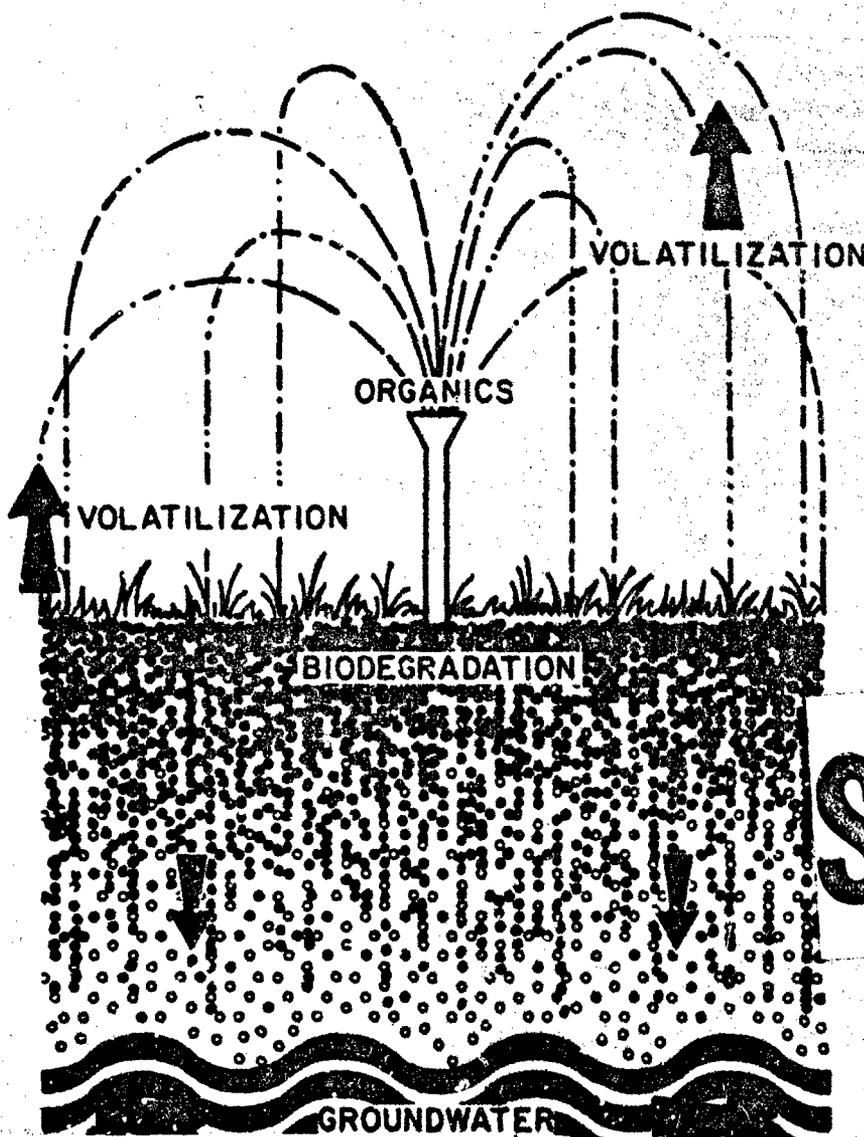
Cold Regions Research &  
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### Impact of slow-rate land treatment on groundwater quality

Toxic organics

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## **SLOW-RATE LAND TREATMENT RESEARCH REPORTS**

This is one of a series of reports on wastewater treatment by slow infiltration published by the U.S. Army Cold Regions Research and Engineering Laboratory. Other published and available reports on this topic are listed below.

**Iskandar, I.K., R.S. Sletten, D.C. Leggett and T.F. Jenkins (1976)** Wastewater renovation by a prototype slow infiltration land treatment system. CRREL Report 76-19. ADA 029744.

**Iskandar, I.K., R.E. Bates, S.T. Quarry, F. Page and J.E. Ingersoll (1979)** Changes in soil characteristics and climatology during five years of wastewater application to CRREL test cells. CRREL Report 79-23. ADA 074712.

**Jenkins, T.F. and A.J. Palazzo (1981)** Wastewater treatment by a prototype slow rate land treatment system. CRREL Report 81-14.

**Jenkins, T.F., A.J. Palazzo, P.W. Schumacher, H.E. Hare, P.L. Butler, C.J. Diener and J.M. Graham (1981)** Seven-year performance of CRREL slow-rate land treatment prototypes. CRREL Special Report 81-12.

**Palazzo, A.J. and J.M. Graham (1981)** Seasonal growth and uptake of nutrients by orchard-grass irrigated with wastewater. CRREL Report 81-8.

*For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380, Metric Practice Guide, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.*



# CRREL Report 84-30

December 1984

## *Impact of slow-rate land treatment on groundwater quality*

*Toxic organics*

L.V. Parker, T.F. Jenkins and B.T. Foley

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spring as a result of application during the colder months was also observed. The two substances that were most persistent in the soil were PCBs and diethylphthalate. PCBs were apparently slowly lost from the system, probably by volatilization. The behavior of diethylphthalate was different in the two soils tested but was more recalcitrant than expected.

## PREFACE

This report was prepared by Louis V. Parker, Physical Scientist, of the Applied Research Branch, Experimental Engineering Division; Thomas F. Jenkins, Research Chemist; and Brian T. Foley, Physical Science Technician, both of the Earth Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. This project was funded by the Environmental Protection Agency under Interagency Agreement USEPA AD96-F-2-402-1. The authors acknowledge the support and encouragement of Bert Bledsoe, Project Officer, R.S. Kerr Environmental Research Laboratory.

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## SUMMARY

Slow infiltration is one of three modes of land treatment of wastewater. In this study, wastewater was sprayed onto two outdoor, prototype test cells measuring 8.5 by 8.5 m by 1.5 m deep. The test cells were filled with either a sandy loam soil or a silty loam soil and were covered with a mixture of perennial grasses. Percolate collected at the bottom and drained into sampling manholes. The application rate was 5 cm/wk. Wastewater was applied one day a week by spray irrigation for a 7-hr period.

Because of the low application rate, the downward flow of water was by unsaturated flow. This resulted in relatively thin films of water passing through the soil and allowed a significant interaction between the solutes and the surfaces of the soil particles. Since application was only once a week, the system was maintained in an unsaturated state, and air exchange between the surface soil and the atmosphere was relatively rapid due to the relatively large pores in the soil.

In this study, municipal wastewater was given primary treatment and then spiked with a number of organic substances, including chloroform, benzene, toluene, chlorobenzene, bromoform, dibromochloromethane, *m*-dichlorobenzene, hexane, pentane, nitrobenzene, *m*-nitrotoluene, diethylphthalate, PCBs, naphthalene, phenanthrene and pentachlorophenol. Application was from June to November 1981 and from May to December 1982.

The travel time of the water was determined using a KCl tracer in the late spring and again in the late fall. This information, along with bulk density, porosity and organic carbon content of the soil and the octanol-water coefficient  $K_{ow}$  of the organic substance were used to predict the travel time of the substances applied. The predicted travel times ranged from 40 days to several hundred years in the 1.5-m soil profile.

Samples of the wastewater before and after spraying and samples of percolate from the 1.5-m soil profile were collected each week and analyzed for volatile, neutral and phenolic organic substances. On several occasions in 1982, soil cores were taken using a 1.9-cm ( $\frac{3}{4}$ -in.) corer, extracted with a hexane-acetone solution, and analyzed for neutral and phenolic substances.

The mean concentration of individual organic substances in the spiked wastewater ranged from 2 to 111  $\mu\text{g/L}$ , with typical values near 50  $\mu\text{g/L}$ . The percent removal during spraying, estimated from the liquid-phase transfer coefficient, ranged from -4.5% to 70% of the water loss for the most volatile components.

We believe that subsequent removal involved adsorption on the soil, with volatilization and biodegradation-biotransformation as the principal final removal mechanisms. Losses due to leaching were a continual problem only for chloroform, which has a very low  $K_{ow}$  and according to the literature is only biodegraded anaerobically. Leaching of other substances appears to be a problem in the colder months, when the rate of volatilization and biodegradation have been significantly reduced.

The overall performance of the slow-rate system for removal of trace-level organic substances was excellent, with greater than 98% removal in all cases.

The two substances that were most persistent in the soil were PCBs and diethylphthalate. We believe PCBs were slowly lost from the system primarily by volatilization. The behavior of diethylphthalate differed in the two soils, accumulating to a much larger degree in the sandy loam. We believe the major removal mechanism for diethylphthalate is biodegradation, which may be limited by the lower moisture-holding capacity in the sandy loam soil.

# IMPACT OF SLOW-RATE LAND TREATMENT ON GROUNDWATER QUALITY

## Toxic Organics

L.V. Parker, T.F. Jenkins and B.T. Foley

### INTRODUCTION

In recent years, vastly improved techniques for trace analysis of organic substances has led to a realization of how widespread these substances are in the environment, including groundwater. While it is unclear what concentrations of these substances in groundwater affect human health, it seems prudent to develop an understanding of the factors that control the fate of these substances in a slow-rate wastewater treatment system, since the percolate from slow-rate systems will reach the groundwater.

Groundwater in the United States has traditionally been used as a drinking water supply in rural areas. Since this water is generally consumed with little or no treatment, maintenance of the quality of this resource should have high priority. In recent years, however, more and more instances of groundwater contaminated with dissolved organic chemicals have come to light. Where the sources of the groundwater pollution have been found, they have generally been the result of improper disposal of high-level industrial wastes.

These chemicals, however, are also found in smaller quantities in a wide variety of products used in the home. As a result they become incorporated in municipal wastewater, and their fate in a wide variety of treatment processes is currently an active area of environmental research (Feiler 1979). While the concentrations of these substances in nonindustrial sewage are rather low (in the parts-per-billion or parts-per-trillion range), the tremendous volume of municipal wastewater may make this source a significant factor in the dispersal of these chemicals into the environment.

In this study we applied actual municipal wastewater, spiked with parts-per-billion levels of various toxic organics, to an operational slow-rate land treatment system. The substances were chloroform, benzene, toluene, chlorobenzene, bromoform, *m*-dichlorobenzene, dibromochloromethane, pentane, hexane, nitrobenzene, *m*-nitrotoluene, diethylphthalate, PCB 1242, naphthalene, phenanthrene and pentachlorophenol. These substances were selected because they represent a range in volatility, adsorptive properties and biodegradability. Our purpose was to determine the extent to which these organics were transported to groundwater. In addition we hoped to identify the major mechanisms responsible for the removal or attenuation of these substances and the extent of their accumulation in the soil.

### LAND TREATMENT OF WASTEWATER

Over the past ten years a tremendous amount of research has been conducted on the treatment of wastewater by application on land. One of the major products of this effort has been the joint publication of the *Process Design Manual for Land Treatment of Municipal Wastewater* by the Environmental Protection Agency, the Army Corps of Engineers and the Departments of Agriculture and Interior (EPA 1981). This manual summarizes the research results pertaining to the proper design and expected performance of the three major modes of wastewater land treatment: rapid infiltration, slow-rate infiltration and overland flow. These modes differ in a number of ways, including the types of soils best suited for their application,

the acceptable loading rate of wastewater, and the level of treatment performance.

Of these three modes the slow-rate process is the most restrictive with respect to wastewater loading rate and hence would generally be the most expensive of the three to implement. On the other hand, slow-rate infiltration produces the highest-quality water of the three, meeting or exceeding the effluent quality of any other treatment process currently in use (Jenkins and Palazzo 1981). The slow-rate mode, however, is a percolation system, and for those systems that are not underdrained, the portion of water not lost by evapotranspiration will merge with native groundwater beneath the site. A thorough understanding of the treatment efficiency of land treatment systems is desirable, then, so that the impacts on groundwater quality can be predicted. Once a groundwater aquifer is contaminated with organic chemicals, recovery may take many years because several of the terminal processes that remove these substances, such as biodegradation, photodecomposition and volatilization, are absent or minimized.

#### **Characteristics of slow-rate systems**

Slow-rate land treatment systems are generally recommended for areas with soils of moderate permeability, such as sandy loam or silty loam soils. The site is vegetated and the water percolates slowly through the plant-soil matrix. Acceptable wastewater loading rates are generally in the range of 2.5-10 cm/wk, with application by sprinkler, ridge and furrow, or border strip flooding.

Because of the fairly low application rates, downward movement of water occurs predominantly by unsaturated flow. This results in relatively thin films of water passing through the soil components, allowing a significant interaction between solutes and the surfaces of soil particles. Since wastewater is generally applied either once or twice a week, the soil is aerated most of the time. Only in relatively heavy, tighter soils would any extended period of reducing conditions be maintained. Thus, a fairly large number of soil pores are filled with air, and air exchange between the atmosphere and the surface soil should be rapid as a result of mass transfer due to changes in barometric pressure.

#### **Removal of trace organics in slow-rate systems**

In spite of the vast amount of information available on the slow-rate process, very little is known about the treatment efficiency for trace levels of organic chemicals. In studies at slow-rate systems in Roswell, New Mexico, and Dickinson,

North Dakota, the concentrations of six pesticides measured before and after treatment demonstrated significant reductions for the three substances present in highest concentrations (EPA 1981). In a study at Muskegon, Michigan, 59 trace organics were identified in the influent wastewater at concentrations as high as 2600  $\mu\text{g/L}$ . Of these substances only low levels of chloroform, trichloroethylene, benzene, acetone, dichloromethane, dichloroethane, dichloroethylene, hexadecanoic acid, dodecanoic and tetradecanol were identified in treated water that had passed through the lagoon and slow-rate land treatment sequence (Demirjian 1979).

In a third study, wastewater spiked with low levels of four pesticides was applied to two field plots and lysimeters containing five soil types (Klein et al. 1974). Soil water collected by suction lysimeters occasionally contained low levels of these pesticides, and there were very rare instances where higher concentrations were observed. The episodes of higher concentration in percolating water were attributed to the large cycling in soil water content, which created cracks in the soil surface. Klein et al. concluded that biological degradation was the most significant factor in the terminal removal of these substances.

We conducted a preliminary study at CRREL in which six volatile organic chemicals were applied by spray irrigation to two outdoor prototype slow-rate systems at mean concentrations ranging from 7 to 60  $\mu\text{g/L}$  (Jenkins and Palazzo 1981). This study, conducted over a six-month period, indicated that an average of 65% of the volatile organics were removed during the spraying process, presumably by volatilization. Analysis of percolate that passed through 150 cm of soil indicated that greater than 98% of each of these substances was removed in the overall slow-rate process.

#### **Removal of organic chemicals in other types of land treatment systems**

Several studies have been conducted to determine the removal efficiencies of organic chemicals in rapid infiltration (Bouwer et al. 1981a, Tomson et al. 1981) and overland flow (Jenkins et al. 1983). These systems are somewhat easier to study than slow-rate systems since the residence time of wastewater in the system is on the order of days or hours, rather than weeks or months, and they can be operated in a more or less steady state. As a result these studies have produced more definitive information than is currently available for slow-rate systems.

Bouwer et al. (1981a) conducted a soil column

study using soils obtained from the Flushing Meadows experimental land treatment site in Phoenix, Arizona. The soil columns were operated as rapid-infiltration systems with rates of 40, 28 and 24 cm/day of secondary wastewater from the Phoenix municipal treatment plant. The columns were operated on a two-week cycle, with nine days of inundation and five days of drying; trace organics removal was studied over a 14-day cycle.

Many of the trace organics were largely removed during soil percolation; others, like chloroform, were not significantly attenuated. Bouwer et al. believe that volatilization, sorption and bacterial secondary metabolism are the significant mechanisms for trace organics removal.

Tomson et al. (1981) conducted a study designed to determine the short- and long-term variation in the type and amount of organic chemicals that reach groundwater below a rapid-infiltration system. A portion of their project was a column study that used soil from the Flushing Meadows system. In a second portion of the study, conducted at the 23rd Avenue Project in Phoenix, Arizona, sewage and well samples from beneath the treatment basins were collected and analyzed for trace organic chemicals by gas chromatography and mass spectroscopy. In this study an average of 92% of the amount of trace organics applied were removed by rapid-infiltration and treatment. Certain classes of organics, such as alkyl naphthalenes, alkylbenzenes, chloroaromatics, alcohols, ketones, indoles and alkoxyaromatics, were removed to a greater extent than others, such as chloroalkanes, alkanes, phthalates and amides. The type and concentration of organics detected in the well samples from beneath the rapid infiltration basins varied little with time. Tomson et al. also attributed the removals to adsorption, volatilization and biodegradation.

We studied the efficiency of overland-flow land treatment for removal of a series of organic substances by determining the rate and extent of removal at three application rates, ranging from 0.4 to 1.2 cm/hr (Jenkins et al. 1983). Greater than 94% for each substance was removed at an application rate of 0.4 cm/hr; the removal rate declined as the application rate was increased.

The rate of removal from solution was described by the sum of two mass-transport-limited first-order rate processes representing sorption and volatilization. A model was developed by nonlinear multiple regression analysis. Experimental coefficients were regressed against three properties of each substance: Henry's constant, octanol-water partition coefficient and molecular weight. The

decrease in removal rate as temperatures declined is supported by the dependence of Henry's constant and diffusivity on temperature. This model was tested on the Davis, California, municipal overland-flow system and found to describe the removal rates reasonably well (Jenkins et al. 1983). The mechanisms for ultimate removal of these organics were postulated to be biodegradation and volatilization.

Slow-rate systems have several advantages over rapid infiltration with respect to potential removal efficiency for trace organics. First, the residence time of wastewater within a 150-cm soil profile is on the order of weeks or months (Jenkins and Palazzo 1981), compared to days for rapid infiltration. Thus, much more time is available for removal by microbial degradation before the flowing solution carries the substance deeper into the soil profile and subsequently into the percolate. This would be true even for those substances that would not tend to be adsorbed by the soil. In addition the rate of microbial degradation is generally higher under aerobic conditions than under anaerobic conditions, again favoring degradation in the slow-rate system. Because slow-rate systems remain unsaturated, often even during wastewater application, mass transfer from the liquid to the gas phase should be greater than in rapid infiltration, and thus volatilization should also be more favorable. In cases where wastewater is applied with a sprinkler, volatilization for highly volatile components such as chloroform should be particularly facile (Jenkins and Palazzo 1981).

The efficiency of sorption should also be greater in slow-rate systems than in rapid infiltration. Much lower application rates result in slower water movement and thus more time for interaction with soil particles. Since the predominant mode of transport in slow-rate systems is unsaturated flow, thin films of water pass over soil particles, facilitating interaction. In overland flow the substance must be transported to the surface from a relatively deep water layer; even so, sorption was found to be quite effective from a kinetic point of view (Jenkins et al. 1983).

## REMOVAL PROCESSES

The contamination of groundwater with toxic organic chemicals from a land treatment system will occur only if the transport rate of these substances through the soil profile exceeds the sum of the terminal removal processes that act to mineralize the substance or remove it from the site in

another fashion. The major terminal removal processes applicable to slow-rate land treatment systems are thought to be microbial degradation and volatilization. Other processes, such as hydrolysis or photochemical degradation, may be important for a few substances but often lead to incomplete mineralization and the production of modified organic substances that may or may not be less environmentally significant or mobile in the soil solution.

### Adsorption

Adsorption of hydrophobic organics is not a terminal removal process because, while temporary binding occurs, the process is thought to be reversible (Schwarzenbach and Westall 1981). On the other hand, adsorption may be the most important process because it rapidly removes the substances from the mobile aqueous phase and holds them in the surface soil where the terminal processes are most active. Because sorption determines the solution concentrations of these substances, it influences the rates of the other processes (Rubin et al. 1982, Subba-Rao et al. 1982).

Theoretically adsorption of hydrophobic non-polar organics on soil surfaces is due more to weak solute-solvent interactions than to strong sorbate-sorbent interactions. Actually binding of these substances is thought to be due to weak London dispersal forces, which are proportional to molecular volume and hence molecular weight. The driving force for sorption is apparently an increase in entropy coming from two sources (Schwarzenbach and Westall 1981). First, the placement of a single, large organic molecule on a surface releases a number of water molecules bound on the surface, increasing the overall randomness. In a like manner a hydrophobic organic molecule in water apparently causes a structuring of the water molecules that surround it. When it is removed, the arrangement of these water molecules becomes more random, and entropy increases. This increase is apparently sufficient to overcome the small positive enthalpy change that often accompanies adsorption.

A number of investigators have studied the sorption of hydrophobic organics on soil and sediment particles and have found a strong correlation between the extent of sorption and the percentage of soil or sediment organic matter (Karickhoff et al. 1979, Schwarzenbach and Westall 1981). Other factors, such as the surface area and the nature of the mineral surface, apparently have a much smaller effect unless the organic carbon content is less than 0.1% (Karickhoff et al. 1979). In surface

soils the organic carbon content is generally in the percent range or higher and hence should control the extent of sorption.

The role of soil organic matter in adsorption can be viewed as similar to the partitioning that occurs for an organic chemical between water and an immiscible organic solvent. A number of workers have demonstrated excellent correlations between the soil or sediment partition coefficient and the partition coefficient for the same substance between water and octanol (Karickhoff et al. 1979, Schwarzenbach and Westall 1981):

$$\log K_p^z = A \log K_{ow}^z + \log f_{oc} + 0.49 \quad (1)$$

where  $K_p^z$  = soil or sediment partition coefficient for substance  $z$  on a mass basis

$K_{ow}^z$  = octanol-water partition coefficient on a mass basis

$f_{oc}$  = fraction of organic carbon in the soil or sediment

$A$  = coefficient established by least squares fitting of  $K_p$  and  $K_{ow}$  values for various substances.

Schwarzenbach and Westall (1981) compared partition coefficients obtained from batch experiments, where sediment or soil was shaken with the sorbate to ensure equilibration, with those obtained from column experiments with different average downward velocities of water. The results of the column studies with downward velocities of less than  $10^{-3}$  cm/s were very similar to those from batch experiments. At flow rates of less than  $10^{-3}$  cm/s, sorption kinetics were fast enough to essentially establish equilibrium as the organics moved downward through the soil, while at higher flow rates sorption was incomplete. In addition Karickhoff et al. (1975) found that the amount of sorption of each hydrophobic organic in a mixture was not affected by low concentrations of other similar substances. Thus sorption was not occurring at specific sites, as is often found for cations on soil or sediment surfaces.

Equation 2, developed by Schwarzenbach and Westall (1981), can be used to calculate the concentration of a substance in soil solution in equilibrium with an equal mass of soil material:

$$\log K_p^z = 0.72 \log K_{ow}^z + \log f_{oc} + 0.49. \quad (2)$$

The partition coefficient  $K_p^z$  is given by

$$K_p^z = S/C \quad (3)$$

where  $S$  is the concentration of sorbate on the solid on a mass per mass (dry weight) basis, and  $C$  is the soil solution concentration on a mass per volume basis. Taking logarithms of both sides of eq 3 yields

$$\log K_p = \log S - \log C \quad (4)$$

and substituting into eq 2 and solving for  $\log C$  yields

$$\log C = \log S - 0.72 \log K_{ow} - \log f_{oc} - 0.49 \quad (5)$$

If we assume that the concentration of  $z$  in the soil is 1 ppm (1 mg/kg of dry weight), the  $K_{ow}$  is  $10^4$  (a typical value for many hydrophobic organics), and the fraction of soil organic carbon is 0.02 (2%), then the equilibrium soil solution concentration is 0.021 ppm (mg/L). Of a total mass of  $z$  added to an equal mass of water and dry soil, 98% would be sorbed at equilibrium. Thus, sorption can be very significant in inhibiting downward transport of hydrophobic organics.

#### Microbial degradation

Microbial degradation may be the most important terminal removal process for many of the relatively nonvolatile trace organics in land treatment systems. Numerous investigators (Geating 1981, Wolfe et al. 1980) have related the chemical structure of a molecule with its potential to be biodegraded. A change in the structure of a molecule through incorporation of substituents can greatly affect the biodegradability of a compound. The type of substituent, the number of substituents, and the location within the molecule are important. For example, multiple halogenation or branching, the presence of two methyl groups on a single carbon, or the presence of a quaternary carbon near the end of an alkyl chain can significantly deter degradation (Alexander 1973). However, substitution does not necessarily increase the recalcitrance of the molecule. The molecule must be altered in some way so that it is no longer susceptible to enzymatic action, capable of entering the cell, or able to induce the necessary enzymes. Generally PCBs and organohalide pesticides are among the most persistent of all synthetic organic substances (Alexander 1973).

Tabak et al. (1981) tested the biodegradability in broth culture of 114 organic priority pollutants, including all the substances included in our

**Table 1. Biodegradability of organic pollutants. (After Tabak et al. 1981.)**

Substance	Type of degradation observed*
Nitrobenzene	1
Diethylphthalate	1
Toluene	1
Pentane	1
Hexane	1
Naphthalene	1
Phenanthrene	1
Benzene	2
Chloroform	2
Bromoform	2
Chlorobenzene	2†
Pentachlorophenol	2
<i>m</i> -Nitrotoluene	3
<i>m</i> -Dichlorobenzene	3
PCB 1242	4
Dibromochloromethane	4

\*1—Significant degradation with rapid adaptation.

2—Significant degradation with gradual adaptation.

3—Significant degradation with gradual adaptation followed by a deadaptative process in subsequent subcultures (toxicity).

4—Not significantly degraded under the test conditions.

†Required an adaptation period at 10 mg/L but not at 5 mg/L.

study.\* They found four types of bioresponse: significant degradation with no adaptation period required, significant degradation following an adaptation period, no significant degradation under the test conditions, and significant degradation after a gradual adaptation period followed by loss in activity in subsequent subculture, which Tabak et al. termed deadaptative (Table 1). They felt that

\* They used a static culture screening procedure with yeast-extract-supplemented water as the culture medium and domestic wastewater as the inoculum. Two concentrations of test substrate were used: 5 and 10 mg/L. Incubation was for 7 days at 25°C, followed by subculture once a week for 3 weeks (subculture is the inoculation of fresh media with a small amount of inoculum from the previous culture). Microbial activity was determined by analyzing the concentration of pollutant after incubation. Therefore, we do not know if mineralization was complete in all cases.

the loss in activity resulted either because synergistic activity on the substrate exhibited by the original heterogeneous population was lost as a result of subculture or because adaptive (induced) enzyme processes were retarded by the accumulation of toxic byproducts of metabolism. This response would probably not occur in a slow-rate land treatment system because losses by percolation and sorption would prevent metabolites from accumulating to the extent they did in static culture.

The substances that they found were rapidly degraded with no adaptation period included pentane, hexane, benzene, nitrobenzene, toluene, naphthalene, phenanthrene and diethylphthalate. Chlorobenzene required an adaptation period at 10 mg/L but not at 5 mg/L, while chloroform, bromoform and pentachlorophenol required an adaptation period at both concentrations. *m*-dichlorobenzene and *m*-nitrotoluene were both toxic, while dibromochloromethane and PCB 1242 were not degraded under these conditions.

Spain and Van Veld (1983) found that the adaptation period for aquatic microbial communities can last up to 6 weeks after exposure to similar organic compounds.

The study of Tabak et al. (1981) only indicates a potential for biodegradation. Environmental considerations such as temperature, pH, redox potential, dissolved oxygen, availability of other sources of organic carbon, presence of other compounds, salinity, particulate matter, competing organisms, concentration of compounds, and number of microorganisms will control the rate of biodegradation (Kobayashi and Rittman 1982).

The concentration of the synthetic organic substance can greatly affect biodegradation. High concentrations of these chemicals can be toxic to microorganisms. At lower concentration (ppm) microorganisms may use the substrate as a carbon source or primary energy source with complete mineralization. The rate of degradation is often linearly related to the concentration in this concentration range. Sorption of these substances on soil organic matter in our slow-rate system could affect microbial degradation by initially reducing concentrations of the organic pollutants in the soil solution.

Degradation can be cometabolic; that is, transformation of the molecule occurs but the microorganism is unable to use the substance as a source of energy or carbon. Cometabolism is especially important in the biodegradation of the more recalcitrant substances. However, because cometabolism results in incomplete mineralization, it can lead to the production of a metabolite that is po-

tentially more toxic and/or mobile in the environment.

Recently Rubin et al. (1982) studied the rates of biodegradation at lower concentrations ranging from less than 1 mg/L to more than 100 mg/L. They found, for example, that the rate of phenol mineralization is a linear function of concentration at levels below 1 mg/L, that this rate falls off between 1 and 100 mg/L, and that it is again high at levels above 100 mg/L. They and Subba-Rao et al. (1982) found, by using  $^{14}\text{C}$  labeling, that at concentrations below 1 mg/L, mineralization is complete, but the microorganisms had assimilated little or none of the organic carbon. They attributed this increased cometabolic-like activity at lower concentrations to either the activity of microorganisms capable of growing at low substrate concentrations (oligotrophs) or a reduction in thresholds due to higher levels of other degradable substances. In either case, these results may be applicable to the land treatment environment, where toxic organic chemicals are present at low concentrations (less than 1 mg/L) with higher levels of other nutrients always present.

#### Volatilization

One feature that distinguishes organic pollutants from most of their inorganic counterparts is their volatility at normal ambient temperatures. Vapor pressure varies over a wide range depending on the specific substance. Of the substances considered in this report, chloroform has the highest vapor pressure at 20°C, 139.5 torr, while pentachlorophenol has one of the lowest,  $4 \times 10^{-4}$  torr. The substances we considered as volatiles in this report were chloroform, benzene, toluene, chlorobenzene, bromoform, *m*-dichlorobenzene, dibromochloromethane, pentane and hexane.

The proportion of a volatile substance in the vapor phase at equilibrium with a water solution of that substance is a function of both its solubility and its vapor pressure. This equilibrium partition coefficient is often expressed as the Henry's law constant  $H$ . The higher the value of  $H$ , the larger the proportion of the substance in the vapor phase. For example,  $H$  values for chloroform and pentachlorophenol are  $3.14 \times 10^{-3}$  and  $2.1 \times 10^{-6}$  atm m<sup>3</sup>/mol at 20°C, respectively. Chloroform has a vapor pressure nearly six orders of magnitude greater than pentachlorophenol's, but its much higher solubility reduces the difference in Henry's constant to just over three orders of magnitude.

When water solutions of hydrophobic organics are exposed to the atmosphere, equilibrium is

never achieved, but the rate of transfer of a specific substance can be expressed as a function of its Henry's constant and molecular weight (Liss and Slater 1974). Differences in the rate of removal from aqueous solution, therefore, are expected to parallel differences in Henry's constant for substances of equivalent molecular weight.

In slow-rate land treatment, volatilization of hydrophobic organics can occur during application and also from the soil surface. Sprinkler application, as we have seen, can significantly reduce the amounts of the most volatile components (Jenkins and Palazzo 1981). Surface application methods are likely to be much less effective.

Volatilization from wet soil is generally assumed to occur mainly via the liquid phase. Thus, the rate of loss should have the same functional dependence on Henry's constant and molecular weight as for solutions. Sorption on surfaces and on dissolved or colloidal organics or macromolecules should reduce the effective concentrations and the rate of loss. Even so, for relatively volatile components of wastewater, such as chloroform, volatilization from soil will likely be an important removal mechanism.

#### **Other removal processes**

Several other removal processes may play some role in the fate of trace organic chemicals applied to a land treatment system. Photochemical transformations could take place for those substances sorbed at the soil surface. The rate of reaction of the sorbed molecules may be somewhat different than for the same substance in solution. However, only partial degradation is likely (Miller and Zepp 1979, Occhiucci and Patacchiola 1982).

Organic chemicals applied to soil may also become humified, that is, incorporated in the humic fraction of soil organic matter. This is known to account for a portion of pesticide residues (Stevenson 1976) and likely takes place for many other types of organic molecules as well. The rate of incorporation of organic chemicals with different types of organic functionality is unknown, but these molecules have rather long residence times in the active surface soils, and it is not unreasonable to expect that some incorporation will take place.

### **EXPERIMENTAL METHODS**

This experiment was designed to identify the major removal mechanisms and the extent to which toxic organics reach groundwater in a slow-rate land treatment system.

#### **Site description**

This study was conducted over the 18-month period from 10 June 1981 to 1 December 1982 on a prototype slow-rate land treatment system at CRREL in Hanover, New Hampshire. Primary wastewater containing trace levels of 16 toxic organic chemicals was applied over this period to two large outdoor lysimeters (test cells). Both lysimeters were constructed in 1972 and have had wastewater applications during late spring, summer and fall for 10 years.

The test cells are each 8.5 by 8.5 m with a soil profile 1.52 m deep. They were constructed with reinforced concrete walls and bottom. One was filled with Windsor sandy loam soil and the other with Charlton silty loam soil. Both soils were obtained locally and were separated into individual soil horizons, sieved to remove large stones, and carefully backfilled and compacted to simulate the undisturbed condition as closely as possible. A summary of the soil characteristics is presented in Appendix Table A1. The concrete base of each test cell was sloped to sampling manholes, which received the drainage from each cell. The volume of percolate was measured using a water meter, and the water was then exhausted to a town sewage line. Further details of the test cell design and construction are given in Iskandar et al. (1976).

The surface of the two test cells was initially seeded with a mixture of perennial grasses. However, by the time this study was conducted (8 years later), the surface was dominated by quackgrass, with lesser amounts of Kentucky bluegrass, orchardgrass and reed canarygrass (Jenkins and Palazzo 1981).

A detailed analysis of the climate at the treatment site has been presented elsewhere (Bilello and Bates 1978, Iskandar et al. 1979). The most pertinent information is presented in Appendix Table A2.

#### **Wastewater application**

The municipal wastewater used in this study came from a small housing development. It was given primary treatment and stored in a concrete, subsurface storage tank. The physical and chemical characteristics of this wastewater varied from day to day; mean values are presented in Appendix Table A3 for the 1981 and 1982 application periods.

For this study the wastewater was spiked with trace levels of a series of toxic organics by adding approximately 20 mL of a stock solution to approximately 5000 L of wastewater in the storage tank. The tank was stirred for one hour following addition before the wastewater was applied.

Different stock solutions were used in 1981 and 1982. In both cases the solution was prepared by diluting weighed quantities of each substance to 3 L using 1-butanol. The amount of each substance added should theoretically bring the concentrations in the storage tank to the values shown in Appendix Table A4. However, variation in the volume of water in the storage tank, sorption on side walls, etc., resulted in variation in concentration from day to day. The substances used in 1982 are listed in Appendix Table A5 with their  $K_{ow}$ , Henry's constant and vapor pressure.

Spiked wastewater was applied to the surface of the test cells with a sprinkler, using 1.9-cm (3/4-in.) Fulljet nozzles mounted on 66-cm (26-in.) risers. The nozzles were operated at a pressure of 105 kPa (15 psi), resulting in an instantaneous flow rate of 0.53 L/s and a spray circle about 7.6 m in diameter.

Wastewater was applied to each test cell at a rate of 5 cm/week. Application was one day per week over a seven-hour period. In 1981 wastewater was applied to the test cells from 10 June to 25 November, and in 1982, from 6 May to 1 December. This application rate and schedule has been used on these test cells since June 1973 (Jenkins and Palazzo 1981), but only since June 1981 has the wastewater been spiked with organics.

#### Soil water movement

The travel or retention time of wastewater in the soil profile is not constant but varies with application rate, temperature, and amount of precipitation and evapotranspiration. In an earlier study the travel time was determined by applying a potassium chloride tracer at the surface and measuring the chloride ion concentration in samples of percolate from the two cells over several months. The tracer was applied in late April 1977; the mean travel time was estimated to be 67 days for the Windsor sandy loam and 81 days for the Charlton silty loam (Jenkins and Palazzo 1981).

To determine if the travel time was significantly different in early fall, a similar study was conducted. Potassium chloride was applied on 28 September 1982, and percolate samples from both test cells were analyzed for chloride ions from 1 October to 2 December 1982. The travel time was estimated to be 30 days for the Windsor sandy loam and 50 days for the Charlton silty loam, a considerably shorter retention time than in the summer. This may be related to the amount of evapotranspiration, which is lower in the late fall than in early summer.

#### Water sampling

Wastewater samples were collected in two ways: grab samples representing the composition of wastewater before spraying were collected from the storage tank, and samples were collected at the surface of the test cells after spraying. For analysis of volatiles, both types of samples were collected in glass, screw-cap test tubes. The tubes were filled to capacity, with care to minimize headspace, and were sealed with a Teflon-lined cap. For analysis of other types of organics, samples were collected in 300-mL BOD bottles. All samples were kept cold with ice during sample collection and were protected from direct sunlight with aluminum foil. The glass test tubes and BOD bottles were carefully cleaned and rinsed with Baker Resi-Analyzed acetone before each sample was collected.

Percolate samples were obtained directly from the outlet pipe. Samples to be analyzed for volatiles were collected in screw-cap test tubes. Samples to be analyzed for the remaining substances were collected in either 1-L or 4-L ground-glass-stoppered bottles. Percolate was generally collected in the morning of the day after the wastewater was applied, since it took eight hours or more after spraying started before percolate emerged from the bottom of the 152-cm profile.

Samples used for volatiles analysis were analyzed the same day they were collected. Samples collected for other analyses were extracted within two hours after they were collected.

#### Water analysis

The toxic organics were divided into four groups for analytical purposes: volatiles, phenols, neutral electron-capturing substances, and neutral non-electron-capturing substances. The volatiles were analyzed by purge-and-trap GC/MS/SIM using a Hewlett-Packard 5992 GC/MS equipped with an HP 7675A purge-and-trap sampler (Olynyk et al. 1981). A 60-mL sample was purged for 20 minutes with helium (20 mL/min). The eluted volatiles were collected on a Tenax collection tube and subsequently thermally desorbed at 200°C for 5 minutes onto the head of a Porapak Q column maintained at 90°C. The column was then programmed from 90° to 210°C at 10°/min with a helium carrier gas at 30 mL/min. Substances that eluted from the GC column were analyzed using selective ion monitoring (SIM) mass spectroscopy. The retention time and the ion monitored for each volatile substance are given in Appendix Table A6. An internal standard of tetrachloroethylene, which was not found at detectable levels in our un-

spiked wastewater, was added to each sample prior to analysis to allow normalization based on differences in stripping efficiency and spectrometer performance for each sample. The results were quantified by comparing the peak areas for each substance, normalized to the internal standard, with the same result when 1.0  $\mu$ L of the stock solution was added to 60 mL of well water and analyzed as described above. The detection limits were estimated for each substance analyzed in this manner (Table A7).

The remaining classes of organics were separated from the water solution using solvent extraction. For the wastewater samples the 300-mL BOD bottles were emptied into a clean separatory funnel; 10 mL of Baker Resi-Analyzed hexane was added to the empty bottle, swirled to dissolve any organics sorbed to the walls of the container, and emptied into the separatory funnel. The solution was adjusted to pH 12 with 5 N NaOH and saturated with salt by adding 93 g of NaCl. The separatory funnels were shaken briefly by hand to dissolve the salt and then for 15 minutes using a wrist-action shaker. Once the phases had separated, the water phase was emptied into acetone-cleaned 400-mL beakers. The hexane solutions and any emulsions present were drained into a 20-mL glass scintillation vial and placed in a freezer overnight. These extracts contained the neutral capturing and noncapturing organics.

The separatory funnels were then rinsed carefully with distilled water and acetone and drained before the water phase was returned. The pH was adjusted to approximately 2 using 5 N  $H_2SO_4$ , and 5 mL of hexane was added. The funnels were shaken for 15 minutes on a wrist-action shaker, the phases were allowed to separate, and the water layer was discarded. The hexane layers were retained in 20-mL glass scintillation vials and placed in a freezer overnight. This extract contained pentachlorophenol.

Emulsions present in the hexane phases the following morning were broken by forcing the solutions through acetone-washed glass wool packed in a disposable Pasteur pipette. The resulting hexane solutions were dried over a small amount of anhydrous sodium sulfate and saved for analysis by electron-capture gas chromatography (GC-ECD) or high-performance liquid chromatography (HPLC).

A solution of 300 mL of well water was used for the analytical blank, and a solution of 300 mL of well water spiked with 5  $\mu$ L of a one-to-ten dilution of the stock solution was used for the microextraction procedure standard (Rhoades and Nul-

ton 1980). These samples were extracted in the manner described above.

The percolate samples were extracted using a slightly different procedure because of the very low concentrations present and hence the need to extract a much larger volume. For this extraction either 2100 or 4200 mL of percolate was extracted in the same all-glass container used for sampling. In this case 100 mL was poured off into a clean, glass graduated cylinder, 10 mL of hexane was added to the bottle, and the solution was adjusted to pH 12 with 5 N NaOH and saturated with salt using either 372 or 744 g of NaCl. The bottle was stoppered and stirred vigorously using a magnetic stir bar for 15 minutes. The phases were allowed to separate by adding the remaining 100 mL of sample, which pushed the hexane layer into the neck of the bottle, where it could be removed with a Pasteur pipette and placed in a 20-mL glass vial.

The solution was then adjusted to pH 2 using 5 N  $H_2SO_4$ , 100 mL was removed as described previously, 10 mL of hexane was added, the top was capped, and the solution was stirred vigorously for 15 minutes. Then the extra solution was again returned to the bottle, and the phases were allowed to separate. The hexane was removed with a Pasteur pipette and placed in a glass vial, and the water was discarded. The hexane phases from each extraction were dried over anhydrous sodium sulfate.

The first hexane extracts correspond to the neutral fractions and were analyzed by two separate methods. The first was conducted by GC-ECD on either a Perkin Elmer Sigma 2 or Sigma 3 gas chromatograph equipped with nickel 63 electron-capture detectors. A 2- $\mu$ L subsample of the dried extract was injected onto a 1.8-m  $\times$  0.32-cm (6-ft  $\times$  1/4-in.), 3% glass OV17 column. The column was programmed from 100 $^\circ$  to 220 $^\circ$ C at 10 $^\circ$ C/min, with the injector and detector temperatures set at 175 $^\circ$  and 350 $^\circ$ C, respectively. The column flow rate was 30 mL/min of 5% methane in argon, with an additional 20 mL/min of purge gas at the detector. The substances and their GC retention times are given in Appendix Table A8.

Quantitative results were obtained by measuring peak heights associated with each substance. The peak heights of blanks extracted on the same day with the same reagents were subtracted individually. Small but measurable blanks were often found for bromoform, diethylphthalate and several of the PCB peaks. The peak heights of the standard, which was extracted in the identical manner as the samples, were used to obtain a response factor in units of millimeters per unit of concentration to

allow conversion of peak heights to concentration. The detection limits estimated for each substance analyzed in this manner are presented in Appendix Table A7.

The first hexane extract was also analyzed on a Perkin Elmer Series 3/LC-65T HPLC for naphthalene and phenanthrene using a UV detector (254 nm) by injecting 10  $\mu$ L of sample onto an LC-8 reverse-phase HPLC column (Supelco) eluted with 75% methanol and 25% water. The flow rate was 1.5 mL/min, and the resulting retention times were 3.5 min for naphthalene and 6.8 min for phenanthrene. Peak heights of the standard were used to obtain response factors for each substance. Peak heights of the samples, minus any contribution from the blank, were converted to concentration using these response factors. The estimated detection limits for naphthalene and phenanthrene are presented in Appendix Table A7.

The second hexane extract (pH 2 extraction) was used to analyze for pentachlorophenol by GC-ECD. A volume of 0.2 mL of sample was injected into a 1.8-m (6-ft) SP1240 DA column programmed from 100° to 170°C at 10°C/min, with a two-minute initial hold at 100°C. The flow rate of nitrogen carrier gas was 30 mL/min. The retention times for pentachlorophenol was 13.7 min under these conditions. The detection limits are given in Appendix Table A7.

#### Soil, litter and plant sampling and analysis

Soil samples were collected on 26 April, 30 July, 17 August, 26 October and 7 December 1982. Samples were collected with a 1.9-cm (3/4-in.) corer and sectioned into the following subsamples by depth: 0-5, 5-10, 10-15, 15-30, 30-45, 45-60, 60-75, 75-90, 90-120 and 120-152 cm. For most depths the samples were split in half lengthwise; half were placed in aluminum pans and used for determining moisture content, and the other half were placed in weighed, glass, screw-cap test tubes in which they were directly extracted. For the top three depths, separate samples were collected for moisture determinations because of the small amount of soil in the 5-cm sections.

The soil was extracted by adding 25 mL of 50% acetone-50% hexane to approximately 15 g of soil in the screw-cap test tubes, shaking on a wrist-action shaker for 30 min, and allowing the suspended matter to settle out overnight in the refrigerator. The following day the tubes were centrifuged at 1000 rpm for 30 min, and the resulting clear supernatant was removed with a Pasteur pipette and placed in a glass scintillation vial. The solution was dried over anhydrous sodium sulfate. The soil

extracts were analyzed as described for neutral electron-capturing and neutral non-electron-capturing substances in water. The concentrations given in this report have had the concentration of each specific organic substance in a similar control soil sample subtracted from them.

Moisture contents were measured gravimetrically by drying the soil samples at 105°C for 24 hours and determining weight loss.

Samples of plant material were collected on 15 June and 29 July 1982. Tissue samples were air dried to a constant weight and ground to pass a 20-mesh sieve. Approximately 5 g of plant material and 25 mL of 50% acetone-50% hexane were placed in glass, screw-cap test tubes. The tubes were shaken for 30 min on a wrist-action shaker and centrifuged at 1000 rpm for 30 min to remove suspended material. The supernatant was removed with a Pasteur pipette and dried over anhydrous sodium sulfate. However, analysis of these samples indicated that there were strong interferences that degraded our GC columns. We were unable to resolve these problems within the funding constraints of this project, so the results of the plant analyses are not presented.

Samples of litter from the soil surface were also collected on 18 October 1982 and analyzed in an identical manner as the plant samples. This litter was composed primarily of plant detritus, and the analysis was more successful than for the fresh plant material.

#### Analytical precision

Tests were run periodically during 1981 and 1982 to estimate the precision of the analyses for each substance in water. Because of the time required to complete a quality control run for the volatiles analysis, these tests were not performed along with routine samples. The analytical precision measured in 1981 has been reported elsewhere (Jenkins et al. 1983) and is summarized in Appendix Table A9.

In 1982 the precision of the analyses for the neutral, less-volatile substances was estimated on two occasions (Appendix Table A10). The precision for these two runs differed significantly, with the lower relative standard deviations agreeing quite well with those obtained in 1981 using identical methodology. The analyses with higher relative standard deviations appear anomalous based on our previous work and that reported by Rhoades and Nulton (1980). We estimate the analytical precision to be better than  $\pm 15\%$  for these substances.

For the volatiles the estimates of relative stan-

dard deviation for each substance in 1982 (Appendix Table A10) agree reasonably well with those obtained in 1981. These values also agree well with those reported by Olynyk et al. (1981).

For pentachlorophenol the two estimates of analytical precision differed somewhat (Appendix Table A10). This was also the case in earlier assessments (Jenkins et al. 1983). Because this analysis requires two extraction steps, the less-reproducible estimates are reasonable, and an overall estimate of  $\pm 20\%$  is probably appropriate.

#### Recovery of organics from soil

The ability to measure the amount of these organics extracted from a soil matrix was also tested. About 15 g of Charlton soil was spiked with 10  $\mu\text{L}$  of a 1-to-100 dilution of the stock solution. The spiked organics were allowed to interact with the soil for 30 min, and the soil was then extracted with 25 mL of 50% acetone-50% hexane in the normal manner. The percent recovery was calculated relative to direct spiking of 25 mL of solvent. Generally we recovered from 90 to 130% of the amount we put on the soil (Appendix Table A11). This was not the case for diethylphthalate, where we only recovered 38% of the sample. However, on the basis of the octanol-water partition coefficients of these substances, we believe this number is suspect.

## RESULTS AND DISCUSSION

#### Wastewater before and after spraying

The concentration of each organic substance in the wastewater storage tank is given for each application in Appendix Tables B1-B16. These data are summarized in Table 2. The concentration of each substance varied a great deal from application to application. This variation occurred because the amount of solution added to the tank was not measured precisely, and the amount of water in the tank varied with each application. However, the mean concentration of these substances was generally 40-60  $\mu\text{g/L}$  (dibromochloromethane had a mean concentration of only 2  $\mu\text{g/L}$  because it was not added to the solution but was present as a contaminant in the bromoform). These numbers are considerably lower than the 80-100  $\mu\text{g/L}$  concentration range we had previously estimated (Appendix Table A4), probably because of losses due to volatilization. The sum of these trace organics in the tank solution was approximately 1.2 mg/L. We estimate that the concentration of the solvent (butanol) used to prepare the stock solution was approximately 2 mg/L in the tank.

The mean concentrations of each organic after spraying and the percent removals due to spraying are given in Table 3. Since the major removal

Table 2. Summary of water analyses of tank samples.

Substance	Type of analysis*	Concentration ( $\mu\text{g/L}$ )		
		Max.	Min.	Mean
Chloroform	a	93	22	53
Benzene	a	63	15	43
Toluene	a	107	27	63
Chlorobenzene	a	93	15	57
Bromoform	b	121	30	62
<i>m</i> -Dichlorobenzene	a	94	10	48
Dibromochloromethane	a	3.4	0.41	1.8
Pentane	a	78	3.8	44
Hexane	a	39	5.5	14
Nitrobenzene	b	106	27	62
<i>m</i> -Nitrotoluene	b	100	21	60
Diethylphthalate	b	86	19	56
PCB 1242	b	271	47	111
Naphthalene	c	63	16	44
Phenanthrene	c	78	21	44
Pentachlorophenol	d	221	29	89

\*a Analysis by GC/MS/SIM.

b Analysis by solvent-extraction (pH 12) GC/ECD.

c Analysis by solvent-extraction (pH 12) HPLC/UV.

d Analysis by solvent-extraction (pH 2) GC/ECD.

**Table 3. Mean tank and spray concentrations and percent removal by spray irrigation.**

Substance	Concentration ( $\mu\text{g/L}$ )		Removal (%)
	Tank	Spray	
Chloroform	53	20	63
Benzene	43	13	70
Toluene	63	25	60
Chlorobenzene	57	23	60
Bromoform	62	31	50
<i>m</i> -Dichlorobenzene	48	18	63
Dibromochloromethane	1.8	0.62	66
Pentane	44	14	68
Hexane	14	6.1	66
Nitrobenzene	62	55	11
<i>m</i> -Nitrotoluene	60	53	12
Diethylphthalate	56	58	-4
PCB 1242	111	107	4
Naphthalene	44	26	41
Phenanthrene	44	46	-5
Pentachlorophenol	89	77	14

mechanism during spraying is volatilization, the degree of loss for individual substances is related to their Henry's constant. The higher the Henry's constant, the higher the proportion of substance in the vapor phase at equilibrium. In our field situation equilibrium is never achieved because the system is open to gas diffusion losses and removal by wind. However, the rate of removal can be expressed as a function of the Henry's constant and the molecular weight (Liss and Slater 1974).

The substances that were removed to the greatest extent relative to water loss (60–70%) during spraying were chloroform, benzene, toluene, chlorobenzene, dichlorobenzene, dibromochloromethane, pentane and hexane. These substances also have the highest Henry's constants, ranging from 267 to 170,000.\* Although pentane and hexane have very high Henry's constants, their percent removals were no better than for substances with Henry's constants of approximately 200–500. Bromoform and naphthalene have the next highest Henry's constants, 63 and 36, respectively, with percent removals of 50% and 40%, respectively. Nitrobenzene and *m*-nitrotoluene have still lower Henry's constants, 1.9 and 5.3, respectively, and exhibited losses of 11% and 12%. The substances with the least amount of removal were PCBs (4%), diethylphthalate (-4%) and phenan-

\* The units for Henry's constant used in this report are  $10^3 \text{ atm m}^3/\text{mole}$ .

threne (-5%). Diethylphthalate has the lowest Henry's constant of all the substances, 0.056. The Henry's constant is 30 for PCBs and 3.93 for phenanthrene. For those substances with negative percent removals, a larger proportion of water than of organics was apparently lost to evaporation.

The percent losses by volatilization given in Table 3 are relative to water. The total loss of these substances by this process should include the amount of water lost during spraying. Sprinkler evaporation losses depend on climate and operating conditions. Losses increase with temperature, wind, operating pressure and degree of breaking of spray, and decrease with increasing humidity and nozzle diameter (Frost and Schwalen 1955). We estimated the maximum losses of water due to spraying for our system to be about 2%.† This relatively low loss is due to the use of a large-diameter nozzle (6.9 cm; 25/64 in.) with low pressure (103 kPa; 15 psi). Since the water loss is expected to be quite low, the percent removals in Table 3 are probably good estimates of the total evaporative losses of these substances.

The transfer coefficient from the liquid to the gas phase may be calculated according to a procedure of Liss and Slater (1974) to give an overall liquid-phase transfer coefficient or exchange constant  $K_t$  (cm/min), which reduces to (Dilling 1977)

$$K_t = \frac{221.2}{\left(\frac{1.042}{H} + 100\right)M^{1/2}} \quad (6)$$

where  $M$  is the molecular weight and  $H$  is the Henry's constant in dimensionless units. This can be determined by dividing the Henry's constant in  $\text{kPa m}^3/\text{mole}$  by  $RT$ , which at 298 K has a value of  $2.48 \text{ kPa m}^3/\text{mole}$  (Mackay and Shiu 1981).

We regressed the percent loss due to spraying against  $K_t$  to get the following relationship

$$\% \text{ Loss} = 282 K_t + 3.34. \quad (7)$$

This relationship is highly significant (at the 0.001 level with a correlation coefficient of 0.89). There is excellent agreement between the predicted and actual percent losses for most substances (Table 4). The deviation was the highest for PCBs, phenanthrene and bromoform. The lower actual percent loss for PCB and phenanthrene may be due to strong adsorption of these substances on suspend-

† We estimated the loss using a table of Frost and Schwalen (1955).

**Table 4. Predicted vs actual losses due to spraying.**

Substance	Loss (%)	
	Predicted*	Actual
Chloroform	56	63
Benzene	70	70
Toluene	65	60
Chlorobenzene	57	60
Bromoform†	31	50
<i>m</i> -Dichlorobenzene	53	63
Dibromochloromethan:	—	66
Pentane	77	68
Hexane	71	66
Nitrobenzene	7.2	11
<i>m</i> -Nitrotoluene	12	12
Diethylphthalate	3.4	-3.5
PCB 1242†	24	3.6
Naphthalene	35	41
Phenanthrene†	9.5	-4.5
Pentachlorophenol	3.6	14

\* Predicted losses were based on liquid-phase transfer coefficients or exchange constants  $K_t$  (eq 7).

† Substances with the largest variation between the predicted and actual values.

ed particulates, as reflected by their very high  $K_{ow}$  values.

#### Percolate samples

Once the organic substances reach the soil surface, they are largely adsorbed onto the organic matter and held at the soil surface, where biodegradation and volatilization can occur. The rate these substances travel through a soil is a function of their  $K_{ow}$  and the soil's porosity, bulk density, and organic matter content (Tomson et al. 1981).

The estimated travel time through our test plots for a selected group of organics is given in Appendix Table A12. These values were determined by measuring the travel time of water and using these data to calculate the average downward velocity of water. The downward velocity of each organic substance was then calculated using the following equation of Tomson et al. (1981):

$$v/v_{pol} = 1 + (P_D/n)K_p \quad (8)$$

where  $v$  = downward velocity of water

$v_{pol}$  = downward velocity of the organic substance

$P_D$  = bulk density of soil

$n$  = porosity of soil\*

$K_p$  = partition coefficient for that substance.

$K_p$  was estimated for each soil segment using the fraction of organic carbon OC (Table A13) and the octanol-water coefficient  $K_{ow}$  [according to the relationship developed by Karickhoff (1981)]:

$$K_p = (OC)(0.63)K_{ow} \quad (9)$$

The group of organic substances selected represent a range in  $K_{ow}$ 's and are arranged in Appendix Table A12 by their  $K_{ow}$ . Substances with  $K_{ow}$ 's in the 70-160 range, such as nitrobenzene, chloroform, benzene, bromoform and diethylphthalate, have travel times of less than 200 days. Nitrobenzene has the lowest  $K_{ow}$  and has a predicted travel time of 41-95 days through sandy loam soil and 82-140 days through silty loam soil. The actual travel time depends on the amount of rainfall and the temperature. Substances with intermediate  $K_{ow}$ 's of about  $2 \times 10^3$ , such as *m*-dichlorobenzene, pentane and naphthalene, would have travel times between 2 and 5 years. Substances with very high  $K_{ow}$ 's, such as PCBs and pentachlorophenol, would essentially remain in the top few centimeters of soil, since the predicted travel time of PCBs is between 110 and 250 years for the top 10 cm.

On the basis of the predicted travel times alone (disregarding losses to volatilization and degradation), we expected to see nitrobenzene, chloroform, benzene, bromoform, diethylphthalate and *m*-nitrotoluene in the percolate within the 7-month application season in 1982. However, all of these but benzene were also applied in 1981, so they could have appeared much earlier in the 1982 season. Toluene has an estimated travel time of 5 months to 1 year. It was not added to the wastewater in 1981; however, like chloroform, it was found to be a normal component of our wastewater (Jenkins et al. 1983). Chloroform and toluene have therefore been applied to these soils for 10 years. Chlorobenzene has a calculated travel time of between 9 months and 2½ years and was applied during the 1981 season. Therefore, we expected to detect it in the 1982 leachate.

The rest of the substances (*m*-dichlorobenzene, pentane, naphthalene, hexane, phenanthrene,

\* $n = V_v/V_t$ , where  $V_v$  is the volume of voids and  $V_t$  is the total unit volume of a soil.

Table 5. Summary of water analyses of percolate samples.

Substance	Concentration ( $\mu\text{g/L}$ ) <sup>a</sup>							
	Sandy loam soil				Silty loam soil			
	Max.	Min.	Mean	Mode	Max.	Min.	Mean	Mode
Chloroform	3.1	0.02	0.76	—	1.1	0.01	0.41	—
Benzene	0.13	bd	bd	bd	0.15	bd	bd	bd
Toluene	0.12	bd	bd	bd	0.04	bd	bd	bd
Chlorobenzene	0.61	bd	$\leq 0.03$	bd	0.24	bd	$\leq 0.13$	bd
Bromoform	0.46	bd	$\leq 0.042$	bd	0.10	bd	$\leq 0.02$	bd
<i>m</i> -Dichlorobenzene	bd	bd	bd	bd	bd	bd	bd	bd
Dibromochloromethane	bd	bd	bd	bd	bd	bd	bd	bd
Pentane	bd	bd	bd	bd	bd	bd	bd	bd
Hexane	0.018	bd	$\leq 0.001$	bd	bd	bd	bd	bd
Nitrobenzene ( $d = 0.1$ )	bd	bd	bd	bd	bd	bd	bd	bd
<i>m</i> -Nitrotoluene ( $d = 0.1$ )	bd	bd	bd	bd	bd	bd	bd	bd
Diethylphthalate ( $d = 0.1$ )	0.29	bd	$\leq 0.1$	bd	0.69	bd	$\leq 0.18$	bd
PCB 1242 ( $d = 0.1$ )	bd	bd	bd	bd	bd	bd	bd	bd
Naphthalene ( $d = 0.5$ )	bd	bd	bd	bd	bd	bd	bd	bd
Phenanthrene ( $d = 0.05$ )	bd	bd	bd	bd	bd	bd	bd	bd
Pentachlorophenol	bd	bd	bd	bd	bd	bd	bd	bd

<sup>a</sup> bd = below the detection limits. The detection limit is 0.010  $\mu\text{g/L}$  except where specified.

pentachlorophenol and PCBs) have predicted travel times that exceed the length of this study, so we did not expect to detect them in the percolate samples. Of the substances in this group, *m*-dichlorobenzene would have the shortest travel time: 1.8–3.9 years in the sandy loam soil and 3.1–5.1 years in the silty loam soil.

Chloroform was the only substance detected in the percolate throughout the course of the study and was found in the highest concentrations (Table 5, Appendix Table B1). Of all the substances considered, only nitrobenzene has a lower  $K_{ow}$  and thus a more rapid predicted travel time than chloroform. Chloroform concentrations ranged from 0.02 to 3.1  $\mu\text{g/L}$  in the leachate from the sandy loam soil and 0.01 to 1.1  $\mu\text{g/L}$  in the leachate from the silty loam soil. The silty loam soil has a higher organic carbon content and therefore should have more capacity for retaining these substances. The concentration of chloroform was low in March and April before application began but started to increase one week after application in the sandy loam soil and after two weeks in the silty loam soil. This is earlier than the shortest predicted travel time of 51 days for the sandy loam soil. The concentration in the leachate dropped off after five weeks and remained lower throughout the rest of the application season. We believe this peak in concentration corresponds to the chloroform that was applied to the system late in the fall of the previous year. The chloroform had persisted in the soil through the winter because the major removal

processes, volatilization and microbial degradation, were reduced due to low temperatures; it then moved through the system during the spring melt.

The compound that occurred in the next highest concentrations and frequency was bromoform. The concentration ranged from below the detection limit to 0.46  $\mu\text{g/L}$  in May and June and then fell below the detection limit and remained there (Table 5, Appendix Table B5). We believe that bromoform also had persisted in the soil over the winter and traveled through the soil profile with the spring melt. Once again the concentrations were higher in the leachate from the sandy loam soil. The concentration remained below the detection limit into December, strongly suggesting that there is significant volatilization and microbial degradation, as predicted by Tabak et al. (1981).

Benzene appeared in the leachate at concentrations ranging from below the detection limit to 0.15  $\mu\text{g/L}$  in March and April and then fell below detection limits for the remainder of the year (Table 5, Appendix Table B2). Although benzene was not added to the wastewater the previous year, it may have been initially present in wastewater; it could have accumulated during the late fall and early winter and then traveled through the profile with the spring melt. It is difficult to explain its early appearance in any other way. Once again there appears to be significant losses to biodegradation.

Other substances that have relatively rapid pre-

dicted travel times are nitrobenzene, diethylphthalate and *m*-nitrotoluene. Nitrobenzene and diethylphthalate can be readily degraded, according to Tabak et al. (1981). They found that degradation of *m*-nitrotoluene resulted in toxicity in the broth culture. However, as mentioned previously we do not expect metabolites to accumulate to the same extent in a soil system, and therefore we expect that degradation could be significant. Nitrobenzene and *m*-nitrotoluene were not detected in the leachate, while diethylphthalate was detected only one time for each soil in the late fall (Table 5, Appendix Tables B10-B12).

Toluene has a predicted travel time of 5 months to 1 year, but has been applied to our site for many years as a common component of the wastewater. While toluene may be readily degraded (Tabak et al. 1981), we saw low levels in the percolate during April (0.01-0.12  $\mu\text{g/L}$ ). It then fell below the detection limit and remained there (Appendix Table B3). Again we believe the breakthrough in the early spring is the result of the substance's persistence during the preceding winter.

Chlorobenzene has a predicted travel time of 9 months to 2½ years and was applied both seasons. It can be readily degraded once an active microbial population is established (Tabak et al. 1981). We did detect very low levels on one occasion in early May, but the concentrations returned to below detection limits very quickly (Appendix Table B4).

Pentane, *m*-dichlorobenzene, naphthalene, hexane, phenanthrene, pentachlorophenol and PCBs have predicted retention times from several years to several centuries. We did not detect them in the percolate (Table 5, Appendix Tables B6, B8, B9, B13-B16). There were single exceptions for phenanthrene, *m*-dichlorobenzene and hexane, but we believe these determinations to be suspect.

Among all the substances with travel times of less than an application season (nitrobenzene, chloroform, benzene, bromoform, diethylphthalate and *m*-nitrotoluene), only chloroform was consistently detected in the percolate. The rest were retained by the soil and showed significant losses, probably due to microbial degradation and volatilization. Chloroform and nitrobenzene have the lowest  $K_{ow}$ 's of any of these substances and should be retained the least. Chloroform has a higher Henry's constant (314) than nitrobenzene (1.9), so we would expect chloroform to be lost to volatilization more rapidly than nitrobenzene. During spraying we did observe significantly more loss of chloroform than nitrobenzene; removal was 63% for chloroform and only 11% for nitrobenzene. Therefore, nitrobenzene must be more

rapidly degraded, since it was never detected in the percolate, while chloroform was consistently detected.

In a rapid-infiltration study Wilson et al. (1981) also found that nitrobenzene is apparently more rapidly degraded in soil than chloroform. They determined the fate of several organic pollutants in a sandy soil (organic carbon content of 0.087%) using 140-cm columns. They studied chloroform, toluene, chlorobenzene and nitrobenzene at concentrations of 1.0 or 0.2 mg/L. They found the travel times (or retardation factors) of these organics to be roughly equivalent. However, they found that only 5-8% of the chloroform was degraded, while 21-60% of the nitrobenzene was degraded.

The apparent recalcitrance of chloroform may be best explained by the work of Bouwer and McCarty (1983a,b) and Bouwer et al. (1981b). They reported that one- and two-carbon halogenated aliphatic compounds such as chloroform, 1,1,1-trichloroethane and tetrachloroethylene are quite persistent in the environment, are transported easily by groundwater, and do not appear to be degraded under aerobic conditions. They found that trihalomethanes were degraded under anaerobic conditions at concentrations of 10-200  $\mu\text{g/L}$  (Bouwer and McCarty 1983a). They also found that chloroaliphatic compounds are transformed as a result of biological action, whereas a combination of chemical and biological processes were involved in the transformation of bromoaliphatic compounds under reducing conditions.

While Tabak et al. (1981) made no mention of the dissolved oxygen or redox potential during their tests, we do know that the tests for volatile substances were performed in glass-stoppered BOD bottles, where oxygen would become limiting. This may explain why chloroform disappeared in their tests. Nonvolatiles were tested in cotton-stoppered bottles, which allowed oxygen diffusion; in these cases, then, the systems should have remained aerobic.

#### Soils

The organic carbon content for the two soil profiles is given in Appendix Table A13. The silty loam soil had a higher organic carbon content throughout the profile. The organic carbon content ranged from 0.04% at 45-60 cm to 3.73% at 0-7.5 cm in the sandy loam soil, and from 0.83% at 30-45 cm to 4.4% at 0-7.5 cm in the silty loam soil.

We were unable to analyze all the soil samples for all substances. Therefore, we will discuss a few

of the substances that represent a range in volatility, octanol-water partition coefficients and biodegradability.

PCBs are a group of substances that are very persistent in soils. They have the highest  $K_{ow}$  ( $3.8 \times 10^3$ ) of all the substances studied and should therefore be the most strongly adsorbed on soil organic matter (Karickhoff 1981). PCBs should remain in the uppermost layers of soil; we estimated their travel time for the first 10 cm to be between 110 and 250 years. As a group they have a  $K_f$  constant of 0.0734 and hence would be slowly removed by volatilization. They are among the most recalcitrant organic substances, although they are slowly degraded cometabolically. Therefore, we expected the PCB concentration in the soil to increase during the study. This was not the case, although there is a lot of variation in the data due to the heterogeneity of the soil. We attribute the apparent loss primarily to volatilization. Appendix Tables C1 and C2 give the PCB levels in the sandy loam and silty loam soils, respectively. The concentration is consistently higher in the sandy loam soil (except for the April soil cores). This was true for all the organic substances we measured. During the 1982 season the PCB concentrations ranged from 1600 to 6500 ng/g in the top 5 cm for both soils. As expected, the concentration dropped rapidly below the first 5 cm. The concentration between 5 and 10 cm ranged from below the detection limits ( $<200$  ng/g) to 990 ng/g in the sandy loam soil and from below the detection limits to 370 ng/g in the silty loam soil. The concentrations in the layers below 15 cm were mostly below the detection limit.

Pentachlorophenol has a similar  $K_{ow}$  ( $1.3 \times 10^3$ ) and predicted travel time to the PCBs, but it has a lower  $K_f$  ( $1.10 \times 10^{-3}$ ) and can be readily degraded after an adaptation period (Tabak et al. 1981). Therefore, when compared with the PCBs, pentachlorophenol should have slower losses to volatilization but much more rapid losses to biodegradation. While we don't have any early soils data, we did find that pentachlorophenol was considerably less persistent than the PCBs in October and December (Appendix Tables C3 and C4). The concentration in the top 5 cm ranged from 240 to 500 ng/g in the sandy loam soil and from 40 to 310 ng/g in the silty loam soil. These values are approximately 10% of those found for PCBs. As expected, pentachlorophenol remained in the surface layers, with concentrations below 15 cm ranging from below the detection limits to 15 ng/g.

Dichlorobenzene has a  $K_{ow}$  that is intermediate for the substances studied ( $2.4 \times 10^3$ ) and a predict-

ed travel time of 1.8-5.1 years. We did not expect to see dichlorobenzene in the percolate since it was only applied during the 1982 season. It has a relatively high  $K_f$  (0.175) and thus should be lost by volatilization to a greater extent than either PCBs or pentachlorophenol. We expected that it could be readily biodegraded in soils. The concentration in the top 5 cm ranged from 220 to 580 ng/g in the sandy loam soil and from 15 to 410 ng/g in the silty loam soil (Appendix Tables C5 and C6). Although the concentrations are not high, they appear to remain somewhat elevated in the intermediate depths, so there had been some loss of dichlorobenzene to leaching.

Diethylphthalate has a relatively low  $K_{ow}$  (162), resulting in a predicted travel time of 2-7 months, and it can be readily biodegraded. However, it has the lowest  $K_f$  of all the substances studied ( $3.20 \times 10^{-4}$ ), so we expected the losses to volatilization to be minimal, with most of the losses due to biodegradation. Losses during spraying were insignificant. Diethylphthalate was also applied during the 1981 season, which would allow adequate time for it to travel through the soil profile prior to the 1982 application season. In 1982 the concentrations of this substance in the soil were relatively high, ranging from 1000 to 6700 ng/g in the sandy loam soil and from below the detection limit to 2200 ng/g in the silty loam soil in the top 5 cm (Appendix Tables C7 and C8). All the cores indicated there were significant levels of diethylphthalate throughout the soil profile, except in December, when the concentrations were below the detection limit (1 ng/g) at the lowest levels.

Mass balance estimates using the December cores (Tables C7 and C8) indicated that more diethylphthalate was recovered from the sandy loam soil than could be accounted for in the wastewater applications. These mass balance determinations are at best only estimates because of the variation in concentration of any of these organics in the same soil; the differences between the mass balances are due to the considerably higher levels of diethylphthalate in the sandy loam soil. An apparent increase in diethylphthalate concentration was also found in a rapid-infiltration study (Hutchins et al. 1983), and its rate of removal was low in overland flow as well (Jenkins et al. 1983). Mass balance estimates for the silty loam soil, however, indicated that significant loss of diethylphthalate occurred in this soil. This difference in loss between the two soils may be due to their water-holding capacities. The percent moisture is considerably higher in the silty loam soil: the range for the top 5 cm following an applica-

tion in August was 13-30% for the sandy loam soil and 21-51% for the silty loam silt (for the 32-hour period following spraying).<sup>\*</sup> This could result in a greater potential for biodegradation in the silty loam soil. As discussed earlier, losses due to volatilization for diethylphthalate are expected to be insignificant.

Bromoform has a  $K_{ow}$  (189) very similar to diethylphthalate's (162) and thus a similar predicted travel time (approximately 3-8 months). It also has a much higher  $K_f$  (0.0987 vs  $3.20 \times 10^{-4}$  for diethylphthalate), so removal of bromoform by volatilization should be considerably more significant. During spraying we observed a 52% loss of bromoform and a -3.5% loss for diethylphthalate. Since bromoform requires an adaptation period before biodegradation can begin, we expected significant losses to biodegradation once the adaptation period had passed. Therefore, the total losses of bromoform should have been considerably larger than those for diethylphthalate. For the 1982 application season the concentration of bromoform ranged from below the detection limit to 44 ng/g in the silty loam soil and from below the detection limit to 340 ng/g in the sandy loam soil in the top 5 cm (Appendix Tables C9 and C10). Only very small concentrations were detected at greater depths. These values are considerably lower than those for diethylphthalate. The rate of loss is apparently rapid, at least in the sandy loam soil. For example, in the sandy loam soil the concentration of bromoform, which was 110-120 ng/g on 20 and 21 October, had decreased to 49 ng/g by the 22nd and to 25 ng/g by the 25th. The concentration does appear to increase in the colder months, probably because of decreased rates of biodegradation and volatilization.

Nitrobenzene has the lowest  $K_{ow}$  (70.8) and therefore the shortest predicted travel time. It also has a relatively low  $K_f$  (0.0136) and was thus not expected to be removed significantly by volatilization. It can, however, be easily degraded micro-biologically. We saw an 11% loss of this substance during spraying. In spite of its predicted rapid travel time, we did not detect it in the percolate nor did we detect it in the silty loam soil on any occasion at any depth (Appendix Table C12). We did, however, detect it twice in the top 5 cm of the sandy loam soil at concentrations of 22 and 400 ng/g (Appendix Table C11). It appears that nitrobenzene is rapidly degraded; however, biodegra-

tion slows down in the colder months, allowing for the accumulation we observed in the final cores from the sandy loam soil.

#### Litter

In mid-October we looked at the concentration of a number of these organics in the leaf litter. We tried to sample only the leaf litter without taking any of the mineral soil. Table 6 gives the results of these analyses. We did not detect any bromoform, *m*-dichlorobenzene, nitrobenzene or *m*-nitrotoluene. We detected significant concentrations of diethylphthalate and PCBs from both soil plots; the levels were equivalent for the two soil types. The substances detected in the litter appear to be those with the lowest vapor pressures. These results seem reasonable since the litter would dry out readily, and loss would then be a function of the vapor pressure rather than the  $K_f$  constant.

**Table 6. Concentration of selected organics in leaf litter.**

Substance	Concentration (ng/g) <sup>*</sup>	
	Sandy loam	Silty loam
Bromoform	bd	bd
<i>m</i> -Dichlorobenzene	bd	bd
Nitrobenzene	bd	bd
<i>m</i> -Nitrotoluene	bd	bd
Diethylphthalate	750	740
PCB 1242	2300	2400

<sup>\*</sup> bd = below the detection limits.

#### Removal efficiency

We calculated the total efficiency of this spray irrigation system for removing these toxic organic substances (Table 7). The percent removal was determined by subtracting the percent accounted for in the percolate from 100% and is reported on a mass basis. Chloroform was the only substance that was consistently present in measurable quantities in the leachate. The removal of chloroform was 98.1% in the sandy loam soil and 99.0% in the silty loam soils. The removal of bromoform was 99.9% for both soils. For the remaining substances the percent removals are based on the analytical detection limits since these substances were not detected in the percolate. The removals of these substances all exceeded 99.0% for both soils, with the exception of naphthalene (98.5%), where a higher detection limit resulted in a slightly lower

<sup>\*</sup>Personal communication with B. Brockett and H. McKim, CRREL.

**Table 7. Total percent removal of organics in the effluent of a slow-rate system.**

Substance	Sandy loam	Silty loam
Chloroform	98.1	99.0
Benzene	>99.9	>99.9
Toluene	>99.9	>99.9
Chlorobenzene	>99.9	>99.9
Bromoform	99.9	99.9
<i>m</i> -Dichlorobenzene	>99.9	>99.9
Dibromochloromethane	>99.3	>99.3
Pentane	>99.9	>99.9
Hexane	>99.9	>99.9
Nitrobenzene	>99.9	>99.9
<i>m</i> -Nitrotoluene	>99.9	>99.9
Diethylphthalate	>99.8	>99.8
PCB 1242	>99.9	>99.9
Naphthalene	>98.5	>98.6
Phenanthrene	>99.9	>99.9
Pentachlorophenol	>99.9	>99.6

% Removal = 100 - % accounted for in percolate,  
where % accounted for in percolate =

$$100 \times \frac{(\bar{C}_{\text{percolate}})(V_{\text{percolate}})}{(\bar{C}_{\text{tank}})(V_{\text{applied}})}$$

where  $\bar{C}$  = mean concentration ( $\mu\text{g/L}$ )  
 $V$  = volume (L).

percent removal. The removal efficiency was slightly higher for the silty loam soil, reflecting its slightly higher organic carbon content and better moisture-holding capacity.

## CONCLUSIONS AND RECOMMENDATIONS

Slow-rate land treatment of wastewater using spray irrigation is very effective at removing low concentrations of toxic organic substances (more than 98% removal). The more-volatile components are significantly reduced during spraying (60–70% losses). Once the organic substances reach the soil surface, most are readily adsorbed by the soil. Once the organics are adsorbed, terminal removal mechanisms, such as volatilization and biodegradation-biotransformation, can operate; the rate is a function of soil temperature. Only substances that have low  $K_{ow}$ 's and that are not readily biodegradable aerobically (e.g. chloroform) appear to leach throughout the year at low concentrations. If wastewater is applied at a very low temperature, other substances with relatively low  $K_{ow}$ 's may also percolate and affect groundwater.

The concentration of the organic substances in the spiked wastewater generally ranged from 40 to 60  $\mu\text{g/L}$ . The percent losses due to spraying correlate with the liquid-phase transfer coefficients. For the substances with the highest  $K_L$ 's (chloroform, benzene, toluene, chlorobenzene, *m*-dichlorobenzene, pentane and hexane), 60–70% losses were found during spray application alone. The substances that showed the least removal in the spraying process (relative to water) were PCBs (4%), diethylphthalate (–3.5%) and phenanthrene (–4.5%). Diethylphthalate and phenanthrene actually appeared to be slightly concentrated during spraying due to a slightly greater loss of water than of organic substance.

We predicted that nitrobenzene, chloroform, benzene, bromoform, diethylphthalate and *m*-nitrotoluene could all travel through the 150-cm soil profile in less than one application season (7 months). Of these substances all but benzene had been applied for two seasons, and chloroform had actually been applied for 10 years, since it is a normal component of wastewater. Chloroform was the only substance that was consistently detected in the percolate throughout the entire season; it ranged in concentration from 0.01 to 3.1  $\text{mg/L}$ . Chloroform has the second lowest  $K_{ow}$ ; nitrobenzene has the lowest  $K_{ow}$  but was never detected in the percolate. Nitrobenzene is apparently biodegraded more readily than chloroform. Chloroform has been found to be persistent in other land treatment systems. In our system we believe it may persist because anaerobic conditions did not exist to a significant extent and therefore anaerobic biodegradation could not occur. There appeared to be one period of breakthrough of low concentrations of bromoform, benzene, toluene and chlorobenzene in the spring from applications late in the previous fall.

The soils were analyzed to determine soil concentrations of PCBs, pentachlorophenol, *m*-dichlorobenzene, diethylphthalate, bromoform and nitrobenzene. PCBs and diethylphthalate were the most persistent, with concentrations in the  $10^1$ - $\text{ng/g}$  range in the top 5 cm. Pentachlorophenol and *m*-dichlorobenzene were intermediate in their persistence, with concentrations in the  $10^1$ - to  $10^2$ - $\text{ng/g}$  range, and bromoform and nitrobenzene were the least persistent, with concentrations between the limits of detection and  $10^1$   $\text{ng/g}$ .

PCBs were the most persistent substances measured. The accumulation of PCBs in the soil would be expected on the basis of its  $K_{ow}$  and recalcitrance to biodegradation. There was apparently

some loss of PCBs on a mass basis; we believe this is primarily due to volatilization (the  $K_f$  is relatively low but not among the lowest).

While we expected PCBs to persist in the soil, we did not expect to see such high concentrations of diethylphthalate. Diethylphthalate has the lowest  $K_f$  of all the substances considered in this report, so losses due to volatilization would not be expected to be significant. According to the literature this substance is readily biodegradable, so we expected significant biodegradation. However, biodegradation of diethylphthalate appears to be significant only for the silty loam soil, which had a greater water-holding capacity. Diethylphthalate also leached deep in the soil profile but was only detected once in the percolate during two years of application.

Concentrations of pentachlorophenol and dichlorobenzene in the soil were considerably lower than those seen for PCBs and diethylphthalate. There was no apparent leaching of pentachlorophenol, which is consistent with its  $K_{ow}$ . Losses were apparently due to significant biodegradation and slow volatilization.

Losses of dichlorobenzene were primarily due to volatilization and biodegradation. Although this substance has a relatively high  $K_f$  and can be easily biodegraded, there appeared to be a slight loss due to leaching to the intermediate soil layers.

Bromoform and nitrobenzene did not persist in the soil, and concentrations were often below the detection limit. Apparently the rate of volatilization and biodegradation of these substances exceeded the rate of loss due to leaching, except possibly for bromoform in the late fall.

Of the substances considered in this report, only chloroform was continually detected in the leachate and could then affect groundwater. While transport of chloroform to groundwater is not desirable, the levels of chloroform detected are significantly lower than what is often found in chlorinated drinking water (Bellar et al. 1974, Deinzer et al. 1978).

Breakthrough of bromoform, benzene and toluene, which occurred for a short period in the early spring, could be eliminated by discontinuing application early enough in the fall so that there is adequate time for terminal removal by volatilization and biodegradation. There is also some indication that breakthrough might also be a problem with some of the slower-moving substances, such as *m*-dichlorobenzene, if this practice isn't followed.

Finally, when selecting a soil for a land treat-

ment system for the removal of organic substances, consideration should be given to the organic carbon content, bulk density and porosity. The difference in percent removal of chloroform, the most troublesome component, was considerably greater for the silty loam soil than for the sandy loam soil.

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## APPENDIX A: CHARACTERISTICS OF THE SITE AND THE ORGANIC CHEMICALS.

Table A1. Summary of soil characteristics. (From Iskandar et al. 1979.)

Horizon	Depth (cm)	Bulk density (g/cm <sup>3</sup> )	Specific gravity	Void ratio*	Permeability (cm/s)
<b>Windsor sand loam</b>					
A	0-15	1.34	2.63	0.969	3.82 × 10 <sup>-6</sup>
B	15-45	1.51	2.69	0.783	21.28 × 10 <sup>-6</sup>
C	45-150	1.66	2.69	0.623	8.22 × 10 <sup>-6</sup>
<b>Charlton silt loam</b>					
A	0-15	1.05	2.63	1.506	3.00 × 10 <sup>-6</sup>
B	15-45	1.42	2.69	0.894	1.18 × 10 <sup>-6</sup>
C	45-150	1.70	2.70	0.592	0.16 × 10 <sup>-6</sup>

\* Void ratio is volume of voids per volume of solids.

Table A2. Climatic characteristics of the Hanover, New Hampshire, treatment site. (From Iskandar et al. 1979.)

Latitude	43°43'N
Prevailing winds	Northwest and south
Mean annual temperature	6.4 °C
Total annual precipitation	95 cm/yr
Mean annual snowfall	185 cm/yr
Mean annual wind speed	6 km/hr

Table A3. Mean wastewater characteristics.

Parameter	1981	1982
BOD <sub>5</sub> (mg/L)	85	120
Total organic carbon (mg/L)	55	—
Total suspended solids (mg/L)	110	60
Total nitrogen (mg/L)	25	50
pH	7.2*	7.2*
Specific conductance (μmhos/cm)	500	—

\* Median values.

Table A4. Quantities of organics used to prepare stock solutions.

Substance	1981		1982	
	Mass added* (g)	Est. conc. in storage tank† (μg/L)	Mass added* (g)	Est. conc. in storage tank† (μg/L)
Chloroform	30.0	40	54.6	73
Benzene	—	—	75.6	101
Toluene	—	—	61.5	82
Chlorobenzene	75.0	100	72.6	97
Bromoform	78.0	104	63.0	84
<i>m</i> -Dichlorobenzene	—	—	70.2	83
Pentane	—	—	71.4	95
Hexane	—	—	78.0	104
Nitrobenzene	—	—	81.0	108
<i>m</i> -Nitrotoluene	75.5	101	79.5	106
Diethylphthalate	75.0	100	66.0	88
PCB 1242	75.0	100	101.4	135
Naphthalene	75.0	100	69.9	93
Phenanthrene	75.0	100	63.0	84
Pentachlorophenol	85.5	114	46.5	62

\* Mass added and volume brought to 3 L with 1-butanol.

† Assuming 20 mL of solution added to 5000 L of wastewater.

**Table A5. Physical constants for organic substances.**

Substance	$K_{ow}^1$ at 20°C	Henry's constant at 20°C		Vapor pressure at 25°C	
		( $10^5$ atm m <sup>3</sup> /mole)	Source*	(torr)	Source*
Chloroform	93.3	314	2	194	8
Benzene	135	435	2	95.2	8
Toluene	490	515	2	28.4	8
Chlorobenzene	692	267	2	12.0	4
Bromoform	189	63	3	5.68	4
<i>m</i> -Dichlorobenzene	$2.4 \times 10^3$	360	4	2.33	4
Dibromochloromethane	—	—	—	—	—
Pentane	$1.7 \times 10^3$	125,000	4	520	4
Hexane	$7.1 \times 10^3$	170,000	4	154	4
Nitrobenzene	70.8	1.9	5	0.23	9
<i>m</i> -Nitrotoluene	282	5.3	6	0.23	9
Diethylphthalate	162†	0.056	6	$7 \times 10^{-4}$	10
PCB 1242	$3.8 \times 10^3$	30†	7	$4.0 \times 10^{-4}$	7
Naphthalene	$2.3 \times 10^3$	36	2	$8.28 \times 10^{-2}$	4
Phenanthrene	$2.2 \times 10^3$	3.93†	2	$2.03 \times 10^{-4}$	4
Pentachlorophenol	$1.3 \times 10^3$	0.21	3		

- \*1-Hansch and Leo (1979)  
 2-Leighton and Calo (1981)  
 3-McCarty (1980)  
 4-MacKay and Shiu (1981)  
 5-Jenkins et al. (1983)  
 6-Dilling (1977)  
 7-Westcott et al. (1981)  
 8-Dean (1979)  
 9-Weber et al. (1981)  
 10-Tomlinson and Samuel (1980)  
 † At 25 °C.

**Table A6. GC retention times and ions monitored for GC/MS/SIM analysis of volatiles.**

Volatile organic	GC retention time (min)	Ion monitored (m/e)*
Chloroform	6.1	85
Benzene	7.4	78
Toluene	9.7	91
Chlorobenzene	11.2	112
<i>m</i> -Dichlorobenzene	14.5	146
Dibromochloromethane	10.2	127
Pentane	3.1	43,72
Hexane	5.9	57,86
Tetrachloroethylene†	9.5	166

- \* m/e is the mass to charge ratio.  
 † Internal standard.

**Table A7. Limits of detection in the percolate analysis.**

Substance	Method*	Est. detection limit (µg/L)
Chloroform	a	0.01C
Benzene	a	0.010
Toluene	a	0.010
Chlorobenzene	a	0.010
Bromoform	b	0.010
<i>m</i> -Dichlorobenzene	a	0.010
Dibromochloromethane	a	0.010
Pentane	a	0.010
Hexane	a	0.010
Nitrobenzene	b	0.010
<i>m</i> -Nitrotoluene	b	0.1
Diethylphthalate	b	0.1
PCB 1242	b	0.1
Naphthalene	c	0.50
Penanthrene	c	0.05
Pentachlorophenol	d	0.3

- a Analysis by GC/MS/SIM.  
 b Analysis by solvent-extraction (pH 12) GC/ECD.  
 c Analysis by solvent-extraction (pH 12) HPLC/UV.  
 d Analysis by solvent-extraction (pH 2) GC/ECD.

**Table A8. Retention times of neutrals analyzed by GC-ECD on OV17.**

Substance	GC retention time (min)
Bromoform	1.5
<i>m</i> -Dichlorobenzene	2.0
Nitrobenzene	3.7
<i>m</i> -Nitrotoluene	4.9
Diethylphthalate	10.5
PCB #1*	11.3
PCB #2	12.4
PCB #3	13.4
PCB #4	14.7
PCB #5	15.7
PCB #6	16.2
PCB #7	17.4
PCB #8	18.8

\* Eight peaks were summed to quantify PCB 1242.

**Table A9. Summary of analytical precision during 1981. (From Jenkins et al. 1983.)**

Substance	Mean concentration (µg/L)	Relative standard deviation (%)
Chloroform*	30	10
Benzene	55	7
Toluene*	50	11
Chlorobenzene*	65	12
Bromoform†	121	3
Nitrobenzene†	60	6
<i>m</i> -Nitrotoluene†	70	8
Diethylphthalate†	75	6
PCB 1242†	45	12
Naphthalene**	75	5
Phenanthrene**	65	8
Pentachlorophenol†	14	16

\* Analysis by purge-and-trap GC/MS/SIM.

† Analysis by solvent-extraction GC-ECD.

\*\* Analysis by solvent-extraction HPLC.

**Table A10. Summary of analytical precision during 1982.**

Substance	22 April*			14 July			26 August		
	Mean conc. (µg/L)	Standard deviation	Relative std. dev. (%)	Mean conc. (µg/L)	Standard deviation	Relative std. dev. (%)	Mean conc. (µg/L)	Standard deviation	Relative std. dev. (%)
Chloroform†	1750	68	3.9	92.5	4.7	5.0			
Benzene†	988	37	3.7	59.5	3.1	5.2			
Toluene†	840	39	4.6	107	8.2	7.7			
Chlorobenzene†	1300	51	3.9	83.3	6.2	7.4			
Bromoform**				56.5	13.4	23.8	29.5	0.6	2.0
<i>m</i> -Dichlorobenzene†				63.5	5.0	7.9			
Dibromochlorobenzene†				1.97	0.2	10.0			
Pentane†				—	—	—			
Hexane†				14.5	1.0	6.9			
Nitrobenzene**				91.3	12.7	13.9	35.5	1.7	4.9
<i>m</i> -Nitrotoluene**				87.5	27.9	31.9	40.8	1.9	4.6
Diethylphthalate**				213	47.9	22.4	47.5	0.6	1.2
PBC 1242**				255	96.9	38.0	116	7.2	6.2
Naphthalene††				62.8	3.4	5.4	47.0	5.9	12.6
Phenanthrene††				63.8	4.1	6.5	81.8	10.4	12.8
Pentachlorophenol**				150	33	23.7	53	3.3	6.2

\* Analysis of standard samples.

† Analysis by purge-and-trap GC/MS/SIM.

\*\* Analysis by solvent-extraction GC-ECD.

†† Analysis of solvent-extraction HPLC.

**Table A11. Recovery of organics from spiked soil.**

<i>Substance</i>	<i>Recovery* (%)</i>
Bromoform	92
Nitrobenzene	119
<i>m</i> -Nitrotoluene	133
Diethylphthalate	38
PCB 1242	126

\* By solvent extraction method.

**Table A12. Calculated travel time of selected organics through the soil profile.**

<i>Substance</i>	<i>K<sub>ow</sub></i>	<i>Travel time in days (years)*</i>			
		<i>Windsor sandy loam</i>		<i>Charlton silty loam</i>	
		<i>Spring</i>	<i>Fall†</i>	<i>Spring</i>	<i>Fall†</i>
Nitrobenzene	70.8	95	41	130	82
Chloroform	93.3	117	51	147	94
Diethylphthalate	162	157	71	196	124
<i>m</i> -Dichlorobenzene	$2.4 \times 10^1$	1424 (3.9)	642 (1.8)	1810	1145
PCB	$3.8 \times 10^1$	214,845	96,900	275,185	174,355
PCB (0-10 cm only)		91,740 (251)	41,375 (113)	87,110 (238)	55,170 (151)

\* Calculated according to Tomson et al. (1981).

† Travel time is faster in the fall since evapotranspiration losses have been reduced.

**Table A13. Organic carbon content of soils.**

<i>Depth (cm)</i>	<i>Organic carbon (%)</i>	
	<i>Sandy loam</i>	<i>Silty loam</i>
0-7.5	3.73	4.40
7.5-15	1.33	2.01
15-22.5	—	2.05
22.5-30	1.18	1.23
30-45	0.34	0.83
45-60	0.04	—

**APPENDIX B: CONCENTRATIONS OF THE ORGANICS IN TANK, SPRAY AND PERCOLATE SAMPLES.**

**Table B1. Concentration of chloroform in tank, spray and percolate samples, 1981 and 1982.**

Date	Concentration ( $\mu\text{g/L}$ ) <sup>*</sup>			
	Tank	Spray	Sandy loam	Silty loam
<b>1981</b>				
23 July	—	—	2.3	1.4
2 Sept	22	30	0.4	0.74
4 Dec	45	9	0.47	—
<b>1982</b>				
24 Mar	—	—	0.02	0.01
12 Apr	—	—	0.22	0.31
14 Apr	—	—	0.05	0.15
6 May	—	—	0.38	0.63
13 May	69	35	0.85	0.45
19 May	75	31	3.14	0.98
26 May	44	23	1.55	0.38
8 Jun	64	25	2.71	0.67
17 Jun	155	73†	2.76	1.11
1 Jul	87	—	0.46	0.34
7 Jul	71	19	0.49	0.53
14 Jul	93	21	—	0.14
22 Jul	23	9	0.08	0.12
19 Aug	31	10	0.06	0.06
26 Aug	40	22	0.06	0.07
7 Oct	53	19	—	—
3 Nov	58	6	0.14	0.18
23 Nov	49	14	0.09	0.13
1 Dec	—	—	0.12	0.23
2 Dec	—	—	0.24	0.18
3 Dec	—	—	0.13	0.17

\* Detection limit is 0.010  $\mu\text{g/L}$ .

† Sample diluted by rain.

**Table B2. Concentration of benzene in tank, spray and percolate samples, 1982.**

Date	Concentration ( $\mu\text{g/L}$ ) <sup>*</sup>			
	Tank	Spray	Sandy loam	Silty loam
24 Mar	—	—	bd†	bd
12 Apr	—	—	0.13	0.07
14 Apr	—	—	0.02	0.15
13 May	—	—	bd	bd
19 May	—	—	bd	bd
26 May	—	—	bd	bd
8 Jun	—	—	bd	bd
16 Jun	125	59**	bd	bd
1 Jul	64	—	bd	bd
7 Jul	63	17	bd	bd
14 Jul	60	13	—	—
22 Jul	15	3	—	—
19 Aug	2	0.75	bd	bd
26 Aug	28	15	bd	bd
7 Oct	58	21	bd	bd
3 Nov	36	5	bd	bd
23 Nov	41	12	bd	bd
1 Dec	—	—	bd	bd
2 Dec	—	—	bd	bd
3 Dec	—	—	bd	bd

\* Detection limit is 0.010  $\mu\text{g/L}$ .

† Below detection limit.

\*\* Sample diluted by rain.

Table B3. Concentration of toluene in tank, spray and percolate samples, 1981 and 1982.

Date	Tank	Spray	Concentration ( $\mu\text{g/L}$ ) <sup>*</sup>	
			Sandy loam	Silty loam
1981				
23 Jul	—	—	bd†	bd
2 Sept	1.0	0.6	bd	bd
4 Dec	—	0.11	bd	bd
1982				
24 Mar	—	—	bd	bd
12 Apr	—	—	0.12	0.04
14 Apr	—	—	0.01	0.03
13 May	75	43	bd	bd
19 May	81	35	bd	bd
26 May	48	27	bd	bd
8 Jun	1.3	0.28	bd	bd
16 Jun	207	107**	bd	bd
1 Jul	130	—	bd	bd
7 Jul	106	33	bd	bd
14 Jul	107	26	—	—
22 Jul	42	16	bd	bd
19 Aug	37	14	bd	bd
26 Aug	64	36	bd	bd
7 Oct	76	30	bd	bd
3 Nov	27	5	bd	bd
23 Nov	34	9	bd	bd
1 Dec	—	—	bd	bd
2 Dec	—	—	bd	bd
3 Dec	—	—	bd	bd

\* Detection limit is 0.010  $\mu\text{g/L}$ .  
 † Below detection limit.  
 \*\* Sample diluted by rain.

Table B4. Concentration of chlorobenzene in tank, spray and percolate samples, 1981 and 1982.

Date	Tank	Spray	Concentration ( $\mu\text{g/L}$ ) <sup>*</sup>	
			Sandy loam	Silty loam
1981				
23 Jul	—	—	0.61	0.24
2 Sept	63	38	bd†	bd
9 Oct	93	32	bd	bd
4 Dec	42	13	bd	—
1982				
24 Mar	—	—	bd	bd
12 Apr	—	—	bd	bd
14 Apr	—	—	bd	bd
6 May	—	—	0.10	0.07
13 May	59	35	bd	bd
19 May	70	32	bd	bd
26 May	50	30	bd	bd
8 Jun	15	4	bd	bd
16 Jun	170	91**	bd	bd
1 Jul	110	—	bd	bd
7 Jul	77	24	bd	bd
14 Jul	83	22	—	—
22 Jul	23	9	bd	bd
19 Aug	52	19	bd	bd
26 Aug	46	25	bd	bd
7 Oct	68	29	bd	bd
3 Nov	53	9	bd	bd
23 Nov	64	18	bd	bd
1 Dec	—	—	bd	bd
2 Dec	—	—	bd	bd
3 Dec	—	—	bd	bd

\* Detection limit is 0.010  $\mu\text{g/L}$ .  
 † Below detection limit.  
 \*\* Sample diluted by rain.

Table B5. Concentration of bromoform in tank, spray and percolate samples, 1981 and 1982.

Date	Tank	Spray	Concentration ( $\mu\text{g/L}$ ) <sup>*</sup>	
			Sandy loam	Silty loam
1981				
9 Oct	121	60	—	—
5 Nov	85	40	bd†**	0.10
1982				
13 May	43	24	—	—
19 May	55	52	0.03	0.03
26 May	47	31	0.04	bd
8 Jun	58	18	0.02	0.01
16 Jun	90	38††	0.46	0.09
1 Jul	66	43	bd	bd
7 Jul	45	20	bd	bd
14 Jul	60	33	—	—
22 Jul	24	11	bd	bd
11 Aug	50	27	bd	bd
18 Aug	45	30	bd	bd
26 Aug	30	11	bd	bd
7 Oct	59	28	bd	bd
3 Nov	104	23	bd	bd
23 Nov	70	32	bd	bd
1 Dec	—	—	bd	bd
2 Dec	—	—	bd	bd
3 Dec	—	—	bd	bd

\* Detection limit for percolate samples is 0.010  $\mu\text{g/L}$  unless otherwise specified.  
 † d = 0.05  $\mu\text{g/L}$ .  
 \*\* Below detection limit.  
 †† Sample diluted by rain.

Table B6. Concentration of *m*-dichlorobenzene in tank, spray and percolate samples, 1982.

Date	Tank	Concentration ( $\mu\text{g/L}$ ) <sup>*</sup>		
		Spray	Sandy loam	Silty loam
13 May	—	—	bd†	bd
19 May	46	24	bd	bd
26 May	43	28	bd	bd
8 Jun	—	30	bd	0.28
16 Jun	132	74**	bd	bd
1 Jul	89	—	bd	bd
7 Jul	54	18	bd	bd
14 Jul	64	18	—	—
22 Jul	18	8	—	bd
19 Aug	10	4	bd	bd
26 Aug	36	21	bd	bd
7 Oct	57	26	bd	bd
3 Nov	55	8	bd	bd
23 Nov	94	19	bd	bd
1 Dec	—	—	bd	bd
2 Dec	—	—	bd	bd
3 Dec	—	—	bd	bd

\* Detection limit is 0.010  $\mu\text{g/L}$ .  
 † Below detection limit.  
 \*\* Sample diluted by rain.

Table B7. Concentration of dibromochloromethane in tank, spray and percolate samples, 1982.

Date	Tank	Concentration ( $\mu\text{g/L}$ ) <sup>*</sup>		
		Spray	Sandy loam	Silty loam
13 May	0.4	0.22	bd†	bd
19 May	1.0	0.96	bd	bd
26 May	1.06	0.77	bd	bd
8 Jun	—	—	bd	bd
16 Jun	5.0	3.0**	bd	bd
1 Jul	3.1	—	bd	bd
7 Jul	2.5	0.61	bd	bd
14 Jul	2.0	—	—	—
22 Jul	0.6	bd	—	—
19 Aug	1.7	bd	bd	bd
26 Aug	1.2	0.64	bd	bd
7 Oct	2.7	0.56	bd	bd
3 Nov	3.4	0.45	bd	bd
23 Nov	1.9	0.73	bd	bd
1 Dec	—	—	bd	bd
2 Dec	—	—	bd	bd
3 Dec	—	—	bd	bd

\* Detection limit is 0.010  $\mu\text{g/L}$ .  
 † Below detection limit.  
 \*\* Sample diluted by rain.

Table B8. Concentration of pentane in tank, spray and percolate samples, 1982.

Date	Tank	Concentration ( $\mu\text{g/L}$ ) <sup>*</sup>		
		Spray	Sandy loam	Silty loam
13 May	125	59	bd†	bd
19 May	285	52	bd	bd
26 May	3.8	2.1	bd	bd
8 Jun	—	—	bd	bd
16 Jun	76	27**	bd	bd
1 Jul	31	—	bd	bd
7 Jul	20	6.4	bd	bd
14 Jul	49	3.8	—	—
22 Jul	67	12	bd	bd
19 Aug	bd	bd	bd	bd
26 Aug	78	43	bd	bd
7 Oct	bd	bd	bd	bd
3 Nov	bd	bd	bd	bd
23 Nov	bd	bd	bd	bd
1 Dec	—	—	bd	bd
2 Dec	—	—	bd	bd
3 Dec	—	—	bd	bd

\* Detection limit is 0.010  $\mu\text{g/L}$ .  
 † Below detection limit.  
 \*\* Sample diluted by rain.

**Table B9. Concentration of hexane in tank, spray and percolate samples, 1982.**

Date	Concentration ( $\mu\text{g/L}$ )*		
	Tank	Spray	Sandy loam Silty loam
13 May	21	10	—
19 May	—	—	bd
26 May	6.6	4.6	0.018
8 Jun	—	1.0	bd
16 Jun	19.1	8.6**	bd
1 Jul	7.4	—	bd
7 Jul	8.1	2.2	bd
14 Jul	15	6.4	—
22 Jul	11	4.3	bd
19 Aug	0.01	bd	bd
26 Aug	7.1	4.8	bd
7 Oct	39	15.4	bd
3 Nov	0.3	bd	—
23 Nov	5.5	1.2	bd
1 Dec	—	—	bd
2 Dec	—	—	bd
3 Dec	—	—	bd

\* Detection limit is 0.010  $\mu\text{g/L}$ .

† Below detection limit.

\*\* Sample diluted by rain.

**Table B10. Concentration of nitrobenzene in tank, spray and percolate samples, 1981 and 1982.**

Date	Concentration ( $\mu\text{g/L}$ )*		
	Tank	Spray	Sandy loam Silty loam
1981			
9 Oct	—	—	bd†
5 Nov	61	55	bd
1982			
13 May	—	—	—
19 May	34	52	bd**
26 May	92	79	bd**
8 Jun	68	56	bd**
16 Jun	220	120††	bd
1 Jul	60	62	bd
7 Jul	41	39	bd
14 Jul	98	75	bd
22 Jul	27	19	bd
11 Aug	73	58	bd
19 Aug	63	54	bd
26 Aug	36	25	bd
7 Oct	45	42	bd
3 Nov	285	45	bd
23 Nov	106	102	bd
1 Dec	—	—	bd
2 Dec	—	—	bd
3 Dec	—	—	bd

\* Detection limit for percolate samples is 0.1  $\mu\text{g/L}$  unless otherwise specified.

† Below detection limit.

\*\* d = 0.05  $\mu\text{g/L}$ .

†† Sample diluted by rain.

**Table B11. Concentration of m-nitrotoluene in tank, spray and percolate samples, 1981 and 1982.**

Date	Concentration ( $\mu\text{g/L}$ )*		
	Tank	Spray	Sandy loam Silty loam
1981			
9 Oct	78	59	bd†
5 Nov	59	50	bd
1982			
13 May	—	—	—
19 May	32	49	bd**
26 May	76	78	bd**
8 Jun	73	56	bd**
16 Jun	160	91††	bd
1 Jul	62	69	bd
7 Jul	26	18	bd
14 Jul	100	56	bd
22 Jul	21	21	bd
11 Aug	66	57	bd
19 Aug	63	60	bd
26 Aug	41	23	bd
7 Oct	47	47	bd
3 Nov	228	48	bd
23 Nov	93	95	bd
1 Dec	—	—	bd
2 Dec	—	—	bd
3 Dec	—	—	bd

\* Detection limit for percolate samples is 0.1  $\mu\text{g/L}$  unless otherwise specified.

† Below detection limit.

\*\* d = 0.05  $\mu\text{g/L}$ .

†† Sample diluted by rain.

Table B12. Concentration of diethyl-phthalate in tank, spray and percolate samples, 1981 and 1982.

Date	Tank	Concentration ( $\mu\text{g/L}$ ) <sup>*</sup>	
		Sandy loam	Silty loam
1981			
9 Oct	86	bd†	bd
15 Nov	80	bd	bd
1982			
13 May	34	—	—
19 May	19	bd**	bd**
26 May	200	bd**	bd**
8 Jun	60	bd**	bd**
16 Jun	121	bd	bd
1 Jul	65	bd	bd
7 Jul	142	bd	bd
14 Jul	62	77	bd
22 Jul	42	37	bd
11 Aug	54	59	bd
19 Aug	64	67	bd
26 Aug	48	48	bd
7 Oct	63	51	bd
3 Nov	56	42	0.29
23 Nov	48	50	bd
1 Dec	—	—	bd
2 Dec	—	—	bd
3 Dec	—	—	bd

\* Detection limit for percolate samples is 0.1  $\mu\text{g/L}$  unless otherwise specified.  
 † Below detection limit.  
 \*\* d = 0.05  $\mu\text{g/L}$ .  
 †† Sample diluted by rain.

Table B13. Concentration of PCB 1242 in tank, spray and percolate samples, 1981 and 1982.

Date	Tank	Concentration ( $\mu\text{g/L}$ ) <sup>*</sup>	
		Sandy loam	Silty loam
1981			
9 Oct	58	bd†	bd
15 Nov	50	bd	bd
1982			
13 May	81	114	—
19 May	47	63	bd**
26 May	95	112	bd**
8 Jun	52	36	bd**
16 Jun	190	167††	bd
1 Jul	122	148	bd
7 Jul	92	113	bd
14 Jul	271	311	bd
22 Jul	61	11	bd
11 Aug	116	107	bd
19 Aug	97	112	bd
26 Aug	116	74	bd
7 Oct	106	110	bd
3 Nov	179	107	bd
23 Nov	148	152	bd
1 Dec	—	—	bd
2 Dec	—	—	bd
3 Dec	—	—	bd

\* Detection limit for percolate samples is 0.1  $\mu\text{g/L}$  unless otherwise specified.  
 † Below detection limit.  
 \*\* d = 0.05  $\mu\text{g/L}$ .  
 †† Sample diluted by rain.

Table B14. Concentration of naphthalene in tank, spray and percolate samples, 1982.

Date	Tank	Concentration ( $\mu\text{g/L}$ ) <sup>*</sup>	
		Sandy loam	Silty loam
24 Mar	—	—	bd†
14 Apr	—	—	bd††
6 May	—	37	bd†
13 May	16	8	bd†
19 May	38	19	bd***
26 May	51	36	bd***
8 Jun	39	17	bd***
16 Jun	87	38†††	bd
1 Jul	55	33	bd
7 Jul	40	19	bd
14 Jul	63	25	bd
22 Jul	18	11	bd
19 Aug	52	61	bd
26 Aug	48	—	bd
7 Oct	53	30	bd
3 Nov	30	—	—

\* Detection limit for percolate samples is 0.5  $\mu\text{g/L}$  unless otherwise specified.  
 † d = 1  $\mu\text{g/L}$ .  
 †† Below detection limit.  
 ††† d = 1.5  $\mu\text{g/L}$ .  
 \*\*\* d = 0.3  $\mu\text{g/L}$ .  
 ††† Sample diluted by rain.

**Table B15. Concentration of phenanthrene in tank, spray and percolate samples, 1982.**

Date	Concentration ( $\mu\text{g/L}$ ) <sup>*</sup>			
	Tank	Spray	Sandy loam	Silty loam
24 Mar	—	—	bd†**	bd†
14 Apr	—	—	bd††	bd††
6 May	—	122	bd†	bd†
13 May	28	51	0.12	bd†
19 May	30	39	bd***	bd***
26 May	55	67	bd***	bd***
8 Jun	25	17	bd***	bd***
16 Jun	76	56††	bd	bd
1 Jul	67	69	bd	bd
7 Jul	49	41	bd	bd
14 Jul	62	54	—	bd
22 Jul	21	22	bd	bd
19 Aug	47	84	bd	bd
26 Aug	78	61	bd	bd
7 Oct	60	63	bd	bd
3 Nov	33	20	—	—

\* Detection limit for percolate samples is 0.3  $\mu\text{g/L}$  unless otherwise specified.

† d = 0.08  $\mu\text{g/L}$ .

\*\* Below detection limit.

†† d = 1.15  $\mu\text{g/L}$ .

\*\*\* d = 0.3  $\mu\text{g/L}$ .

††† Sample diluted by rain.

**Table B16. Concentration of pentachlorophenol in tank, spray and percolate samples, 1981 and 1982.**

Date	Concentration ( $\mu\text{g/L}$ ) <sup>*</sup>			
	Tank	Spray	Sandy loam	Silty loam
<b>1981</b>				
9 Oct	—	—	—	—
15 Nov	—	—	—	—
<b>1982</b>				
13 May	—	—	—	—
19 May	—	—	—	—
25 May	—	—	—	—
8 Jun	—	—	—	—
16 Jun	—	—	—	—
1 Jul	—	—	—	—
7 Jul	83	79	—	—
14 Jul	150	134	—	—
22 Jul	29	33	—	—
11 Aug	47	44	—	—
19 Aug	116	96	bd†	bd
26 Aug	53	42	bd	bd
7 Oct	46	42	bd	bd
3 Nov	221	98	bd	bd
23 Nov	56	122	bd	bd
1 Dec	—	—	bd	bd
2 Dec	—	—	bd	bd
3 Dec	—	—	bd	bd

\* Detection limit for percolate samples is 0.3  $\mu\text{g/L}$ .

† Below detection limit.

**APPENDIX C: CONCENTRATIONS OF SIX OF THE ORGANICS IN SOIL SAMPLES.**

**Table C1. Concentration of PCBs in sandy loam soil, 1981 and 1982.**

Date	Concentration (ng/g dry soil)* at depths (cm) of									
	0-5	5-10	10-15	15-30	30-45	45-60	60-75	75-90	90-120	120-150
<b>1981</b>										
12 Oct†	1660		500	340	30					
<b>1982</b>										
26 Apr	2100	260	140	280	bd**	bd	bd	bd	d	bd
30 Jul	3400	180	0	180	211	bd	bd	—	d	bd
20 Oct	4900	410	—	—	—	—	—	—	—	—
21 Oct	6500	460	210	—	—	—	—	—	—	—
22 Oct	5100	990	580	—	—	—	—	—	—	—
25 Oct	3200	180	bd	—	—	—	—	—	—	—
7 Dec	4800	680	430	bd	149	bd	d	d	bd	bd
9 Dec	1600††	—	bd††	—	—	—	—	—	—	—

\* Detection limit is 100 ng/g dry soil.

† Values of air-dried samples at depths of 0-7.5, 7.5-15, 15-22.5 and 22.5-25 cm, respectively.

\*\* Below detection limit.

†† Mean value of three separate core analyses.

**Table C2. Concentration of PCBs in silty loam soil, 1981 and 1982.**

Date	Concentration (ng/g dry soil)* at depths (cm) of									
	0-5	5-10	10-15	15-30	30-45	45-60	60-75	75-90	90-120	120-150
<b>1981</b>										
12 Oct†	2560		220	40						
<b>1982</b>										
26 Apr	6500	150	bd	140	bd**	bd	bd	bd	bd	bd
30 Jul	1700	130	110	140	bd	bd	bd	—	bd	bd
20 Oct	2700	370	—	—	—	—	—	—	—	—
21 Oct	3700	300	bd	—	—	—	—	—	—	—
22 Oct	4000	310	bd	—	—	—	—	—	—	—
25 Oct	3900	290	270	—	—	—	—	—	—	—
7 Dec	1600	240	bd	bd	140	bd	bd	bd	bd	bd

\* Detection limit is 100 ng/g dry soil.

† Values of air-dried samples at depths of 0-7.5, 7.5-15 and 15-22.5 cm, respectively.

\*\* Below detection limit.

**Table C3. Concentration of pentachlorophenol in sandy loam soil, 1982.**

Date	Concentration (ng/g dry soil)* at depths (cm) of									
	0-5	5-10	10-15	15-30	30-45	45-60	60-75	75-90	90-120	120-150
20 Oct	400	14	—	—	—	—	—	—	—	—
21 Oct	500	15	1	—	—	—	—	—	—	—
22 Oct	380	130	15	—	—	—	—	—	—	—
25 Oct	240	7	2	—	—	—	—	—	—	—
7 Dec	—	75	bd†	2	bd	bd	bd	2	bd	3

\* Detection limit is 1 ng/g dry soil.

† Below detection limit.

**Table C4. Concentration of pentachlorophenol in silty loam soil, 1982.**

Date	Concentration (ng/g dry soil)* at depths (cm) of									
	0-5	5-10	10-15	15-30	30-45	45-60	60-75	75-90	90-120	120-150
20 Oct	210	2	—	—	—	—	—	—	—	—
21 Oct	40	31	10	—	—	—	—	—	—	—
22 Oct	290	10	11	—	—	—	—	—	—	—
25 Oct	310	16	6	—	—	—	—	—	—	—
7 Dec	88	5	bd†	bd	bd	bd	bd	1	1	bd

\* Detection limit is 1 ng/g dry soil.

† Below detection limit.

**Table C5. Concentration of *m*-dichlorobenzene in sandy loam soil, 1982.**

Date	Concentration (ng/g dry soil)* at depths (cm) of									
	0-5	5-10	10-15	15-30	30-45	45-60	60-75	75-90	90-120	120-150
20 Oct	220	280	—	—	—	—	—	—	—	—
21 Oct	360	200	220	—	—	—	—	—	—	—
22 Oct	290	230	310	—	—	—	—	—	—	—
25 Oct	250	310	300	—	—	—	—	—	—	—
7 Dec	580	250	260	120	83	70	60	47	31	39
8 Dec	300†	—	160†	—	—	—	—	—	—	—

\* Detection limit is 1 ng/g dry soil.

† Mean value of three separate core analyses.

**Table C6. Concentration of *m*-dichlorobenzene in silty loam soil, 1982.**

Date	Concentration (ng/g dry soil)* at depths (cm) of									
	0-5	5-10	10-15	15-30	30-45	45-60	60-75	75-90	90-120	120-150
20 Oct	17	bd†	—	—	—	—	—	—	—	—
21 Oct	25	9	16	—	—	—	—	—	—	—
22 Oct	15	31	24	—	—	—	—	—	—	—
25 Oct	26	45	23	—	—	—	—	—	—	—
7 Dec	410	280	300	290	180	310	33	47	95	68

\* Detection limit is 1 ng/g dry soil.

† Below detection limit.

**Table C7. Concentration of diethylphthalate in sandy loam soil, 1981 and 1982.**

Date	Concentration (ng/g dry soil)* at depths (cm) of									
	0-5	5-10	10-15	15-30	30-45	45-60	60-75	75-90	90-120	120-150
<b>1981</b>										
12 Oct†	1200	1400	940	480	—	—	—	—	—	—
<b>1982</b>										
26 Apr	4200	3600	640	400	56	54	68	48	120	120
30 Jul	6700	690	360	830	750	160	120	—	170	81
20 Oct	3300	1800	—	—	—	—	—	—	—	—
21 Oct	3700	1700	2100	—	—	—	—	—	—	—
22 Oct	1500	2000	2100	—	—	—	—	—	—	—
25 Oct	1400	370	900	—	—	—	—	—	—	—
7 Dec	1200	820	900	79	160	64	48	24	10	bd**
9 Dec	1000††	—	1200††	—	—	—	—	—	—	—

\* Detection limit is 1 ng/g dry soil.

† Values of air-dried samples at depths of 0-7.5, 7.5-15, 15-22.5 and 22.5-25 cm, respectively.

\*\* Below detection limit.

†† Mean value of three separate core analyses.

**Table C8. Concentration of diethylphthalate in silty loam soil, 1981 and 1982.**

Date	Concentration (ng/g dry soil)* at depths (cm) of									
	0-5	5-10	10-15	15-30	30-45	45-60	60-75	75-90	90-120	120-150
<b>1981</b>										
12 Oct†	2500	570	420							
<b>1982</b>										
26 Apr	2200	480	260	430	16	26	—	200	53	53
30 Jul	1100	89	100	56	130	150	130	190	29	23
20 Oct	580	450	—	—	—	—	—	—	—	—
21 Oct	860	290	210	—	—	—	—	—	—	—
22 Oct	520	350	320	—	—	—	—	—	—	—
25 Oct	bd**	500	bd	—	—	—	—	—	—	—
7 Dec	270	160	160	55	92	90	7	13	bd	bd

\* Detection limit is 1 ng/g dry soil.

† Values of air-dried samples at depths of 0-7.5, 7.5-15, and 15-22.5 cm, respectively.

\*\* Below detection limit.

**Table C9. Concentration of bromoform in sandy loam soil, 1981 and 1982.**

Date	Concentration (ng/g dry soil)* at depths (cm) of									
	0-5	5-10	10-15	15-30	30-45	45-60	60-75	75-90	90-120	120-150
<b>1981</b>										
12 Oct†	bd**	bd	bd	bd						
<b>1982</b>										
26 Apr	4	9	31	7	bd	1	3	bd	1	bd
30 Jul	6	1	1	1	bd	bd	bd	—	bd	bd
20 Oct	110	19	—	—	—	—	—	—	—	—
21 Oct	120	19	13	—	—	—	—	—	—	—
22 Oct	49	11	18	—	—	—	—	—	—	—
25 Oct	25	30	27	—	—	—	—	—	—	—
7 Dec	340	13	14	5	4	5	4	3	3	5
8 Dec	56††	—	15††	—	—	—	—	—	—	—

\* Detection limit is 1 ng/g dry soil.

† Values of air-dried samples at depths of 0-7.5, 7.5-15, 15-22.5 and 22.5-25 cm, respectively.

\*\* Below detection limit.

†† Mean value of three separate core analyses.

**Table C10. Concentration of bromoform in silty loam soil, 1981 and 1982.**

Date	Concentration (ng/g dry soil)* at depths (cm) of									
	0-5	5-10	10-15	15-30	30-45	45-60	60-75	75-90	90-120	120-150
<b>1981</b>										
12 Oct†	bd**	bd	bd	bd						
<b>1982</b>										
26 Apr	2	bd	bd	bd	bd	bd	bd	bd	bd	bd
30 Jul	6	1	1	1	1	bd	bd	bd	bd	bd
20 Oct	17	11	—	—	—	—	—	—	—	—
21 Oct	25	3	7	—	—	—	—	—	—	—
22 Oct	24	14	11	—	—	—	—	—	—	—
25 Oct	31	12	6	—	—	—	—	—	—	—
26 Oct	bd	—	—	—	—	—	—	—	—	—
7 Dec	44	16	13	12	7	10	2	2	7	5

\* Detection limit is 100 ng/g dry soil.

† Values of air-dried samples at depths of 0-7.5, 7.5-15, 15-22.5 and 22.5-25 cm, respectively.

\*\* Below detection limit.

**Table C11. Concentration of nitrobenzene in sandy loam soil, 1982.**

Date	Concentration (ng/g dry soil)* at depths (cm) of									
	0-5	5-10	10-15	15-30	30-45	45-60	60-75	75-90	90-120	120-150
20 Oct	bd†	bd	—	—	—	—	—	—	—	—
21 Oct	22	bd	bd	—	—	—	—	—	—	—
22 Oct	bd	26	bd	—	—	—	—	—	—	—
25 Oct	bd	bd	bd	—	—	—	—	—	—	—
7 Dec	400	20	10	bd	bd	bd	bd	bd	bd	bd
8 Dec	bd**	—	bd**	—	—	—	—	—	—	—

\* Detection limit is 1 ng/g dry soil.

† Below detection limit.

\*\* Mean value of three separate analyses.

**Table C12. Concentration of nitrobenzene in silty loam soil, 1982.**

Date	Concentration (ng/g dry soil)* at depths (cm) of									
	0-5	5-10	10-15	15-30	30-45	45-60	60-75	75-90	90-120	120-150
20 Oct	bd†	bd	—	—	—	—	—	—	—	—
21 Oct	bd	bd	bd	—	—	—	—	—	—	—
22 Oct	bd	bd	bd	—	—	—	—	—	—	—
25 Oct	bd	bd	bd	—	—	—	—	—	—	—
7 Dec	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd

\* Detection limit is 1 ng/g dry soil.

† Below detection limit.

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