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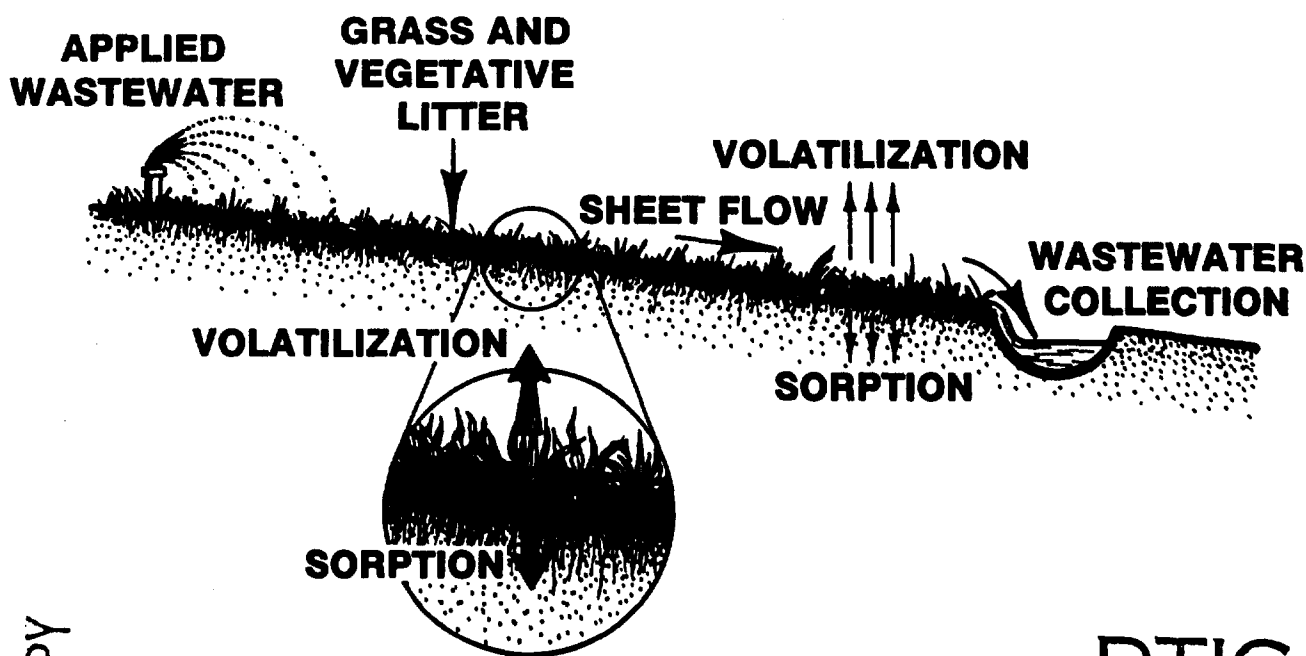


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Assessment of the treatability of toxic organics by overland flow



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Jenkins, T.F. et al. (1979) Prototype overland flow test data: June 1977-May 1978. CRREL Special Report 79-35.

Jenkins, T.F., D.C. Leggett, C.J. Martel and H.E. Hare (1981) Overland flow: Removal of toxic volatile organics. CRREL Special Report 81-1.

Martel, C.J., T.F. Jenkins and A.J. Palazzo (1980) Wastewater treatment in cold regions by overland flow. CRREL Report 80-7.

Martel, C.J., T.F. Jenkins, C.J. Diener and P.L. Butler (1982) Development of a rational design procedure for overland flow systems. CRREL Report 82-2.

Palazzo, A.J. (1982) Plant growth and management for wastewater treatment in overland flow systems. CRREL Special Report 82-5.

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 83-3

January 1983

Assessment of the treatability of toxic organics by overland flow

T.F. Jenkins, D.C. Leggett, L.V. Parker, J.L. Oliphant
C.J. Martel, B.T. Foley and C.J. Diener

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER CRREL Report 83-3	2. GOVT ACCESSION NO. AD-126387	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ASSESSMENT OF THE TREATABILITY OF TOXIC ORGANICS BY OVERLAND FLOW	5. TYPE OF REPORT & PERIOD COVERED	
	6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s) T.F. Jenkins, D.C. Leggett, L.V. Parker, J.L. Oliphant, C.J. Martel, B.T. Foley and C.J. Diener	8. CONTRACT OR GRANT NUMBER(s) Interagency Agreement USEPA AD96-F-1-402-0	
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Army Cold Regions Research and Engineering Laboratory Hanover, New Hampshire 03755	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Environmental Protection Agency R.S. Kerr Environmental Research Laboratory Ada, Oklahoma 74820	12. REPORT DATE January 1983	
	13. NUMBER OF PAGES 59	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Land treatment Organic compounds Overland flow Wastewater treatment		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The removal efficiency for 13 trace organics in wastewater was studied on an outdoor, prototype overland flow land treatment system. The removal for each of these substances was greater than 94% at an application rate of 0.4 cm/hr. (0.12 m ³ /hr-m width). The percent removals declined as application rates were increased. The rate of removal from solution was described by the sum of two mass-transport-limited, first-order rate coefficients representing volatilization and sorption. A model based on the two-film theory was developed; the observed removal rate coefficients were regressed against three properties of each substance: the Henry's constant, the octanol-water partition coefficient and the molecular weight. The dependence of the removal process on temperature was studied and is included along with		

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20. Abstract (cont'd).

average water depth in the model. The decrease in removal rate as temperature declined is supported by the known dependence of Henry's constant and diffusivity on temperature. The model was validated on a second overland flow system. The surface soil concentrations of the trace organics determined at the end of the experiment suggest that a secondary mechanism renews the surface activity rapidly enough so that contaminants do not build up on the surface, with the possible exception of PCB. Biodegradation is suggested as the predominant secondary mechanism rather than volatilization because substances less volatile than PCB were not found at the end of the experiment.

PREFACE

This report was prepared by Thomas F. Jenkins, Research Chemist; Daniel C. Leggett, Research Chemist; Louise V. Parker, Microbiologist; Dr. Joseph L. Oliphant, Research Physical Scientist; and Brian T. Foley, Physical Science Aid, of the Earth Sciences Branch, Research Division, and C. James Martel, Environmental Engineer, and Carl J. Diener, Civil Engineering Technician, of the Civil Engineering Research Branch, Experimental Engineering Division, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire.

The authors gratefully acknowledge the assistance of Patricia Butler, Stephen Mueller, Susan Ossoff and Lisa Campbell of CRREL for providing analytical assistance, Antonio J. Palazzo and John M. Graham for assistance in harvesting and vegetation sampling on the CRREL overland flow system, and Dr. Robert Smith of the Civil Engineering Department, University of California at Davis, for cooperation in the field study conducted at the Davis overland flow site.

This project was funded under Interagency Agreement USEPA AD96-F-1-402-0 by the U.S. Environmental Protection Agency, Bert Bledsoe, Project Officer, R.S. Kerr Environmental Research Laboratory (RSKERL). The authors acknowledge the support and encouragement of Mr. Bledsoe and Dr. Ray Thacker, EPA Headquarters, throughout this effort. Although the research described in this report has been funded by the EPA, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency.

This report was technically reviewed by Dr. Robert Smith, Department of Civil Engineering, University of California at Davis, Dr. Carl Enfield and Dr. William Dunlap of RSKERL, and Sherwood Reed of CRREL.

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CONTENTS

	Page
Abstract	i
Preface	iii
Summary	vi
Introduction	1
Overland flow	1
Occurrence of organics in wastewater	2
Properties of organics	3
Microbial degradation of organic chemicals	4
Organics removal by land treatment systems	4
Objectives	5
Experimental methods	5
Site description, Hanover	5
Determining average detention times	7
Addition of organics to wastewater	8
Field experiment at Davis	8
Water sampling at Hanover	9
Water analysis	9
Analytical precision	11
Soil and plant sampling and analysis	13
Results	14
Organics removal at Hanover	14
Organics removal at Davis	17
Accumulation organics in soils and plants	18
Discussion	19
Removal from solution	19
Effect of temperature on removal rates	25
Model validation using data from the Davis site	26
Final removal processes	26
Summary and conclusions	28
Literature cited	28
Appendix A. Experimental overland flow data, Hanover	31
Appendix B. Downslope removal characteristics of selected chemicals at CRREL and at Davis	45

ILLUSTRATIONS

Figure		
1.	CRREL overland flow prototype	6
2.	Diagram of CRREL overland flow system	6
3.	Example of C curve used to determine detention time	7
4.	Davis, California, overland flow system	9
5.	Division of organics studied into classes by type of analysis	10
6.	Rate coefficients vs average water temperature	16
7.	Comparison of ranked order of removal rate coefficients at CRREL and Davis ...	18
8.	Illustration of the two-film theory	20
9.	Removal rate coefficients vs K_{ow}	23

TABLES

Table		Page
1.	Occurrence of organic chemicals in household products	2
2.	Application rates of primary wastewater and average detention times of waste-water on the slopes	6
3.	Quantities of organics used to prepare stock solution	8
4.	Volatile organics studied using purge and trap GC/MS/SIM	10
5.	Neutrals analyzed by GC-ECD on OV-17 and their retention times	11
6.	Precision of neutral, less volatile organics analysis	12
7.	Precision of volatiles analysis	12
8.	Precision of phenols analysis	12
9.	Summary of water analyses for applied wastewater	14
10.	Summary of average runoff concentrations for each substance following overland flow treatment	15
11.	Water volumes applied to overland flow and volume of runoff	15
12.	Summary of average removals for each substance by overland flow	15
13.	Summary of experimental rate coefficients	17
14.	Results of water analyses for Davis field experiment	18
15.	Concentration of PCB 1242 and pentachlorophenol in soil samples	19
16.	Concentration of PCB in plant samples	19
17.	Physical properties and experimental removal rate coefficients at 20°C for the organic chemicals studied	22
18.	Experimental and predicted values for the removal rate coefficient <i>k</i> on CRREL system using eq 16	24
19.	Comparison of experimental removal rate coefficients at 20° and 2.5°C	25
20.	Experimental versus predicted removal rate coefficients for the Davis site	26

SUMMARY

Overland flow is one of the three modes of wastewater land treatment. In this mode, wastewater is applied to the top of a gently sloping, grassy terrace, flows downslope over the surface in a thin sheet, and is renovated by physical, biological and chemical processes. The remaining runoff is collected at the base of the slope for discharge. While much is now known about the performance of this type of treatment system for removing nitrogen, phosphorus, solids, oxygen demand and bacteria, little information has been reported on its ability to remove trace levels of toxic organics.

This study was conducted on an outdoor, prototype overland flow system in Hanover, New Hampshire. The overland flow system is 30.5 m long by 8.8 m wide and is divided into three test sections. During construction the site was graded to a 5% slope, and a rubber liner was emplaced and covered with 15 cm of silt loam soil. The soil was compacted and seeded with a mixture of grasses.

For this study, municipal wastewater was given primary treatment, spiked with a number of organic substances, and applied to two test sections, four days per week, seven hours per day from 2 June to 11 December 1981. Three application rates were tested, and the detention time of wastewater on the slope was determined for each rate using the centroid of the C curve obtained using a sodium chloride tracer.

About once a week, samples of the applied wastewater, runoff and surface water from a number of downslope locations were analyzed for up to 13 organics. Analysis of the most volatile components was conducted by purge and trap followed by gas chromatography mass spectrometry using selective ion monitoring. Analysis of the less volatile components was obtained by sequential extraction from solution using the microextraction method. First the neutrals were extracted using hexane after the pH was adjusted to 12. The water was then adjusted to pH 2, and the phenols were extracted using a second aliquot of hexane. The hexane extracts were analyzed using electron capture gas chromatography and high-performance liquid chromatography.

The analytical precision was estimated periodically. For the volatiles the relative precision was about $\pm 15\%$. For most of the less volatile neutrals and phenols, we estimate the precision at $\pm 10\%$ and $\pm 15\%$, respectively.

Soil and plant samples were collected several times during the study and extracted with hexane-acetone. The extracts were analyzed in a similar manner to the water solutions.

The mean concentrations of these 13 organics in the applied wastewater ranged from 11 to 113 $\mu\text{g/L}$ with an average of about 50 $\mu\text{g/L}$. At a hydraulic loading rate of 0.4 cm/hr (0.12 $\text{m}^3/\text{hr}\cdot\text{m}$ of width) in the summer, greater than 94% removal was found for all of the substances tested. At higher application rates, runoff concentrations increased and percent removals declined. Later, when the 0.4-cm/hr rate was reestablished in the fall, percent removals did not approach the values obtained in the summer, indicating that temperature affects the removal process.

The rate of removal was found to follow first-order kinetics, and the removal rate coefficients were obtained from plots of $\ln C/C_0$ vs residence time, where C_0 and C are concentrations at zero

time and other times, respectively. Removal rate constants varied somewhat from day to day, but the ranked order of the removal rate coefficients for different substances was rather consistent. Substances with the highest rate coefficients seemed to have a high octanol-water partition coefficient K_{ow} or a moderate K_{ow} and a high Henry's constant. From this result we conclude that the two major mechanisms responsible for removing organics from solution were sorption on the surface soil organic matter and volatilization.

The removal rate coefficients were determined at average water temperatures ranging from 25.7° to 2.5°C. The magnitude of the rate coefficient declined as water temperatures decreased, probably due to decreased molecular diffusivity as the viscosity of the solution increased. Since the number of individual determinations differed for each substance and the distribution of these determinations varied with water temperature, values of the rate coefficient at 20°C were obtained by linear least-squares techniques for the rate coefficient vs water temperature.

Assuming that sorption and volatilization were controlling the rate of removal from solution, we developed a relationship including both processes, using the two-film theory for each interface. This relationship describes the rate of loss for a specific substance as a function of its molecular weight M , its Henry's constant H and its octanol-water partition coefficient, the detention time of water on the slope, the average water temperature and the average depth. The magnitudes of the four coefficients for this model were obtained by multiple regression of the experimental rate coefficient at 20°C vs M , H and K_{ow} for each substance. The resulting equation predicts that sorption is more dominant than volatilization for removing organics from solution by overland flow, even for the most volatile substances tested.

The effect of temperature on these two removal mechanisms was also assessed. The major effects of decreased temperature are thought to be a reduction in the molecular diffusivity due to increased viscosity and a decrease in the Henry's constant. No information on the dependence of K_{ow} on temperature is available. An equation is given to predict the removal rates at temperatures other than 20°C.

The model seems to fit the experimental data for the CRREL system quite well. The model was tested by conducting a similar study at the overland flow system in Davis, California. The ranked order of removal rate coefficients from solution for individual substances was very similar to that found at CRREL. The rate constants obtained experimentally at Davis were compared with those predicted from the model for the water temperature and depth measured on the Davis system. In general the agreement between experimental and predicted values was good except for the most volatile substances.

The analysis of the plants and soils collected periodically on the CRREL system indicated that only PCB and, to a much smaller extent, pentachlorophenol were building up in the soil and were being taken up into the plants. Thus some additional removal mechanisms, probably microbial degradation and volatilization, must be operating once these organics are sorbed on the soil organic matter. The fact that substances less volatile than PCB were not found to build up suggests that the rate of biodegradation is fast enough so that it doesn't limit treatment efficiency. In other words, mass transport to the soil surface, not secondary removal, limits the rate.

ASSESSMENT OF THE TREATABILITY OF TOXIC ORGANICS BY OVERLAND FLOW

T.F. Jenkins, D.C. Leggett, L.V. Parker, J.L. Oliphant,
C.J. Martel, B.T. Foley and C.J. Diener

INTRODUCTION

There are three major forms of wastewater treatment by application to the land. These are rapid infiltration, slow rate and overland flow (EPA 1981). The choice of which form of land treatment is best suited for a given location is dictated by the soil characteristics, mainly its permeability. Overland flow is best suited, but not limited, to areas with gently sloping terrain having heavy soils of low permeability.

Overland flow

In overland flow, wastewater is applied to the top of vegetated, gently sloping terrain, flows downslope in a thin sheet, and is removed by physical, chemical and biological mechanisms. The runoff is collected at the base of the slope and discharged to a receiving stream in the same fashion as the effluent from a conventional wastewater treatment plant.

Overland flow has been used successfully to treat municipal wastewater in Melbourne, Australia, since 1930 (McPherson 1979). Even so, little was known about the mechanisms governing the removal of specific pollutants until the 1970s. Thomas et al. (1974) found that suspended matter and oxygen-demanding substances could be removed from raw wastewater to such a degree that secondary treatment standards could be met. The mechanisms responsible for this reduction were postulated to be sedimentation, filtration and microbial degradation. Recently Martel et al. (1980) and Peters et al. (1981) determined the temperature limits of this process.

Because of the concern over eutrophication in surface waters, these studies also investigated the ability of overland flow systems to remove nitrogen and phosphorus. Thomas et al. (1974) found that up to 90% of the applied nitrogen and 50% of the applied phosphorus could be removed. Hoepfel et al. (1974) obtained similar results and postulated that a significant portion of this removal was due to microbial nitrification and denitrification occurring in the soil, although they did not consider losses by volatilization. Jenkins et al. (1978) found that nitrogen removal remained high until the soil temperature was reduced to about 14°C. Below this point ammonia-nitrogen removal was significantly reduced. Peters et al. (1981) obtained a similar result, but the magnitude of the reduction was less because they used a lower-strength wastewater. Peters et al. also reported that 9% of the nitrogen removal was due to volatilization. Jenkins et al. (1978) also found that ammonia-nitrogen was much easier to remove than nitrate. Since many types of pretreatment result in some oxidation of ammonia to nitrate, pretreatment should be kept to a minimum. The major mechanisms for removing nitrogen appear to be plant uptake, microbial nitrification and denitrification, immobilization in soil and volatilization of ammonia, although there is some disagreement about their relative importance.

Overland flow by itself was not particularly effective in removing phosphorus. However, removal could be increased to about 90% by adding alum prior to application on the land (Thomas et al. 1976, Peters et al. 1981). There is some doubt, however,

whether overland flow should be considered for areas in which the discharge would affect a phosphorus-limited stream.

The ability of overland flow systems to remove heavy metals has also been studied. Hoepfel et al. (1974) found removal efficiencies ranging from 75% to 95% for six heavy metals on a small-scale, indoor prototype, with most of the removal occurring in the first meter of the slope. Peters et al. (1981) obtained similar results on a full-scale test system where four heavy metals were studied; the removal efficiencies ranged from 85% to 94%. These heavy metals accumulated over time in the soil biomass and were taken up in plants, particularly upslope near the point of application. While there is some concern over translocation of these metals in the food chain, Evans et al. (1979) found that this was

not observable, even when cattle were allowed to forage directly on an overland flow slope.

These studies have greatly increased our understanding of the treatability of many types of pollutants by overland flow, but little information has been provided on the ability of overland flow to remove toxic organics. In an earlier study (Jenkins et al. 1981) we found that volatile organics were removed effectively by overland flow, with treatment efficiencies ranging from 80% to 100%, depending on the application rate. It was suggested that the mechanism for this removal was volatilization.

Occurrence of organics in wastewater

The average American uses about 160 L of water per day (Hathaway 1980). This water is used for toilet flushing, bathing, cooking, laundering, washing dishes and cleaning. The wastewater generated from

Table 1. Occurrence of organic chemicals in household products. (After Hathaway 1980.)

<i>Product</i>	<i>Classes of organics</i>	<i>Product</i>	<i>Classes of organics</i>
Deodorizets	Aromatics Haloaromatics Haloaliphatics PAH Halophenols	Medicines	Aromatics Halomethanes Halophenols PAH
Disinfectants	Haloaromatics Halophenols Haloaliphatics	Preservatives	Aromatics PAH Haloaromatics Haloethers Halophenols
Pesticides	Haloaromatics Haloaliphatics Halomethanes Phthalates	Cleaners	Aromatics Haloaromatics Haloaliphatics PAH Halophenols
Laundry products and soaps	Aromatics Nitroaromatics PAH Phthalates Halophenols	Cosmetics	Haloethers Aromatics Phthalates Nitroaromatics Halomethanes Haloaliphatics PAH
Medicinal ointments	Aromatics PAH Haloethers Halophenols	Electrical appliances	PCBs
Paints	Haloethers Halophenols Aromatics		
Polishes	Nitroaromatics Phthalates Haloaliphatics Haloaromatics		

this use contains a number of types of "natural" organic matter derived from human waste, including urea, proteins, humic materials, carbohydrates, tannins, lignins and fatty acids (Rebhun and Manka 1971). These classes of organics are of little concern from a toxicity standpoint, but as a group they create a major portion of the oxygen demand on receiving streams.

Additionally, in nearly all of these uses, various synthetic organic chemicals are dissolved and become associated with the waste stream. These include a wide variety of synthetic organics that are components of cleaners, cosmetics, deodorizers, disinfectants, pesticides, soaps and detergents, paints, polishes, preservatives and medicines (Hathaway 1980). Thus, even wastewater with no industrial component contains low levels of a number of synthetic organics, many listed on the EPA Priority Pollutant List (Budde and Eichelberger 1979). Some examples of the various classes of organics and their presence in household products are given in Table 1. Wastewaters also having a significant industrial component may periodically contain nearly any of the chemicals on the EPA Priority Pollutant List. While these substances will generally be present at very low concentrations, many are difficult to degrade biologically and are thought to be rather potent carcinogens. In addition, the occurrence of these substances in wastewater can cause problems in some types of conventional treatment because of their toxicity to microorganisms (Anthony and Breimhurst 1981).

Properties of organics

The organic priority pollutants, unlike most inorganic substances, are all volatile to some degree. Vapor pressures at 20°C range from as high as 18,600 Pa (139.5 torr) for chloroform to as low as 0.05 Pa (4×10^{-4} torr) for pentachlorophenol. The solubilities of these organics in water also vary widely but in general are much lower than the inorganics of major concern from a treatment standpoint. Chloroform, for example, has a water solubility of about 9300 mg/L at 25°C, while phenanthrene's solubility at this temperature is only 1.29 mg/L. For those organics with very low solubility, a single spill could contaminate the waste stream for long periods as the substance slowly dissolves.

The proportion of a volatile substance present in the vapor phase at equilibrium with a water solution is a function of both its vapor pressure and its water solubility. Numerically this equilibrium value is often expressed as the Henry's law constant, which can be calculated in a variety of units. In any of these forms the higher the value, the higher the proportion of the substance in the vapor phase. For

example, chloroform has a Henry's law constant of 340 Pa m³/mole (3.4×10^{-3} atm m³/mole) at 20°C, while pentachlorophenol has a value of 0.21 Pa m³/mole (2.1×10^{-6} atm m³/mole). This means that at equilibrium, in solutions of equal concentration, over 1000 times as much chloroform (on a molar basis) as pentachlorophenol would be present in the vapor phase. When water solutions of these substances are exposed to the open atmosphere, as occurs in overland flow, equilibrium will never be achieved, because of removal by wind and gas diffusion. However, the removal rates of volatile substances from water solutions can be expressed as functions of the Henry's law constant (Liss and Slater 1974). Thus, in this case, chloroform should be volatilized from water solution much faster than pentachlorophenol. As a rule the higher the vapor pressure and the lower the water solubility, the higher the Henry's law constant and the higher the removal rate by volatilization.

Another important property of organic chemicals in water solution is their tendency to associate with organic surfaces such as are present on suspended particulates and soil organic matter. At equilibrium the relative concentration of the specific organic in water solution compared to that on the organic surface is characterized by a partition coefficient. This coefficient differs significantly from one organic chemical to another. Researchers have found it useful to simulate this value using octanol as a model for soil organic matter (Karickhoff 1981). Thus, knowing the octanol-water partition coefficient and the amount of organic carbon present, one can compare the relative sorptive properties of several organic chemicals on soils and sediments. Numerically octanol-water partition coefficients vary over a wide range and are conveniently expressed on a log basis ($\log K_{ow}$). Chloroform, for example, has a $\log K_{ow}$ of 1.96 at about 20°C, while phenanthrene has a $\log K_{ow}$ of 4.5. Thus, for equal concentrations of chloroform and phenanthrene in water solution at equilibrium, nearly 500 times as much phenanthrene as chloroform would be sorbed on a given amount of organic surface.

In overland flow systems, organic chemicals in solution are exposed to a large amount of organic surface as suspended particulates, soil organic matter and vegetation. The water flows past these surfaces rapidly, however, with linear velocities in the range of 0.1-1.0 cm/s. Schwarzenbach and Westall (1981) have used soil columns to show that equilibrium was not achieved between water and soil at linear velocities of 10^{-2} cm/s and greater. Thus, in overland flow, water flows over these surfaces much too fast for equilibrium to be achieved. Nevertheless the relative rate of removal from solution due to sorption for various organics may be a function of their

octanol-water partition coefficient. If this is true, phenanthrene should be removed much faster than chloroform by this mechanism.

Microbial degradation of organic chemicals

Organics vary in their rate of microbial degradation. Some persist in nature and may be stable indefinitely, while others are degraded to some extent under most environmental conditions. Among the most persistent are certain pesticides and PCBs (Alexander 1973). While degradation of most organics is aerobic, some are degraded both aerobically and anaerobically (Liu et al. 1981) and others only under anaerobic conditions (Bouwer et al. 1981b, McCormick et al. 1981). Where degradation occurs aerobically and anaerobically, the rate is generally faster under aerobic conditions (Delaune et al. 1980, Liu et al. 1981). Microorganisms commonly present in soils and water are capable of degrading many organics and using the organic compounds as sole sources of carbon. However, concentrations of trace organic chemicals in wastewater at land treatment systems will generally be too low to support microbial growth. In this instance the microbes may mineralize (Rubin et al. 1982, Subba-Rao et al. 1982) or alter (Herbes and Schwall 1978, Liu et al. 1981, McCormick et al. 1981) the chemicals but in such small amounts that they derive little benefit.

Incorporation of a substituent in a molecule can often have dramatic effects on its potential for and its rate of degradation. The type of substituent, the placement of the substituent in the molecule, and the number of substituents are important. Other structural features, such as multiple 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 be a significant deterrent to degradation (Alexander 1973). Polycyclic aromatic hydrocarbons with more than three rings appear to be very resistant to degradation (Herbes and Schwall 1978, Sherrill and Saylor 1980).

While a component may have the potential for degradation, it is the environmental conditions that will dictate its rate. The required types of microorganisms must be present, as well as sufficient nutrients to maintain the population. Both the concentration of organisms (Paris et al. 1981) and the concentration of the compound to be degraded (Rubin et al. 1982, Subba-Rao et al. 1982) are critical. The physical and chemical properties of a compound, such as solubility, volatility and hydrophobicity, determine its availability in solution (Kobayashi and Rittman 1982). Compounds with low water solubility degrade at slower rates than more soluble substances (Alexander 1973, Wilson et al. 1981).

Temperature is significant since microbial activity increases exponentially over the 0-20°C range.

In an overland flow system the water has a relatively short detention time on the slope, generally from a half to two hours (Martel et al. 1982). This is probably too short for significant degradation to occur in solution. We studied degradation rates of toluene and chloroform in wastewater and found that it is slow compared to the detention times for overland flow (Jenkins et al. 1981). The surface to which the water is exposed, however, is largely organic (Peters et al. 1981), and significant sorption should occur. Once this takes place and the organics are immobilized on the soil surface, degradation seems much more likely. Herbes (1981) found that organic chemicals degraded faster in soils and sediment than in water. Since wastewater is applied to many systems only eight hours per day, even if the soil temporarily becomes anaerobic, the site has sixteen hours to re-aerate between applications. During these periods the organics are exposed to a nutrient-rich environment with a high level of microbial activity.

Organics removal by land treatment systems

Except for our previous study of volatile organics (Jenkins et al. 1981) there is almost no information on the removal of organic chemicals in overland flow systems. We found excellent removal of several chlorinated aliphatics, toluene, benzene and chlorobenzene, which we tentatively attributed to volatilization. We recognize, however, that the data available do not rule out sorption followed by biodegradation. Some information is available on organic removal in other types of land treatment systems as well as for deep well injection. At the slow rate system in Muskegon, Michigan, most of the 60 or so organics detectable in the influent were removed to below detection limits in the effluent (Demirjian 1979). Of those still detectable, over 75% removal was observed. At a prototype slow rate system in Hanover, New Hampshire, Jenkins and Palazzo (1981) found greater than 98% removal of several volatile organics, some having been applied for as long as seven years. Some of this removal was shown to be due to volatilization during sprinkler application.

In some rapid infiltration tests, on the other hand, poor removals and small retardation factors were observed when organics were applied to soil columns containing a sandy soil with low organic carbon content (Wilson et al. 1981). In this study, large percentages of very volatile substances volatilized from the soil columns, but the water was not allowed to pond on the surface as it does in operating rapid infiltration systems. In another soil column experiment

with soil from the Flushing Meadows site, Bouwer et al. (1981a) found attenuation of some organics during rapid infiltration and attributed this removal to biodegradation. Other substances, such as chloroform, were not attenuated significantly. In a field experiment at the Phoenix 23rd Ave. site, Tomson et al. (1981) found 70-100% removals of organics, depending on the class, using the same wastewater as Bouwer. The depth of sampling for Tomson's field study was 18.2 m, however, compared to 2.5 m for Bouwer's column study.

Organic contaminant movement during high rate groundwater recharge was studied by Roberts et al. (1980). Some compounds, such as naphthalene, were attenuated, apparently due to biodegradation. The movement of all substances was retarded to some extent by sorption.

The transport of organic chemicals in the subsoil has been reviewed by McCarty et al. (1981) and Schwarzenbach and Westall (1981). The movement of specific chemicals was related to their octanol-water partition coefficients and the percentage of soil organic matter, conclusions similar to those reported earlier by Lambert et al. (1965).

In summary these results indicate that in the absence of biodegradation and to some extent volatilization, little attenuation of organic chemicals should occur in rapid infiltration systems, although the movement will be retarded depending on the soil organic matter content and the respective octanol-water partition coefficients. Whether or not biodegradation is significant in these systems seems to depend on the depth to groundwater and the rate of biodegradation relative to the rate of movement in the soil. The rate of biodegradation seems very hard to predict; as was stated by Wilson et al. (1981), "biodegradation studies only indicate a potential for degradation, which may or may not be realized in the field at a particular place and time."

In slow rate systems, on the other hand, the removal of organics is significantly improved. Because the rate of application is much lower and significant water loss occurs by evapotranspiration, the rate of movement to groundwater is much slower, allowing more time for degradation. Volatilization of the most volatile organics is significant during spray application and probably also from the soil surface during drying periods. Some volatilization has also been indicated in rapid infiltration systems (Bouwer et al. 1981, Wilson et al. 1981), but to a smaller extent than in slow rate systems.

Objectives

The major objectives of this research project were:

1) To determine the treatability of a number of toxic organics by overland flow land treatment as a function of detention time on the slope.

2) To determine the removal kinetics associated with each of these substances.

3) To identify the major removal mechanisms for the various substances and compare their relative importance.

4) To evaluate the effect of temperature on the treatment efficiency.

5) To determine if these substances accumulate in the soil and are incorporated into plant materials grown on the slope.

6) To develop a mathematical relationship to predict the treatability of a wide variety of organic chemicals as a function of their individual physical properties.

EXPERIMENTAL METHODS

Site description, Hanover

The major portion of this study was conducted on an outdoor prototype overland flow system at CRREL in Hanover, New Hampshire (Fig. 1). The system was constructed in 1975; wastewater has been applied since the summer of 1976.

The overland flow prototype is 30.5 m long by 8.8 m wide and is divided into three test sections, each 1.9 m wide (Fig. 2). During construction the site was graded to a 5% slope, underlain with a rubber membrane, and covered with about 15 cm of silt loam soil. The soil was compacted to a bulk density of 1.4 g/cm³ and seeded with a mixture of K-31 tall fescue, Pennlate orchardgrass, reed canarygrass and perennial ryegrass (Martel et al. 1980). When this study was begun in June 1981, the dominant plants were reed canarygrass, quackgrass and Kentucky bluegrass, with lesser amounts of tall fescue, orchardgrass and barnyardgrass (Palazzo 1982).

Municipal wastewater from a small housing area was given primary treatment and stored in a concrete, subsurface storage tank (Jenkins et al. 1981). While the wastewater composition varied considerably from day to day, typical values for total organic carbon (TOC), biochemical oxygen demand (BOD), total suspended solids, total nitrogen, pH and specific conductance were 55 µg/L, 85 mg/L, 110 mg/L, 25 mg/L, 7.2, and 500 µmhos/cm, respectively. This primary wastewater was applied to two overland flow prototypes (sections A and B) from 2 June-11 December 1981 on a four day per week, seven hour per day basis. Section C was not used for this experiment. Water not lost by evapotranspiration was collected at the base of the slope in galvanized steel tanks, its volume was

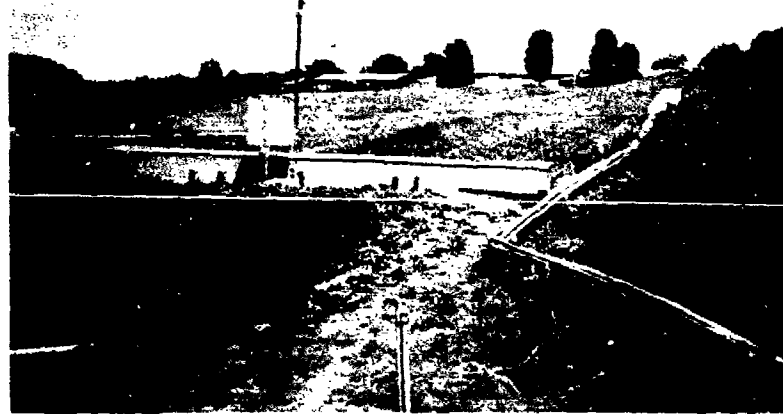


Figure 1. CRREL overland flow prototype.

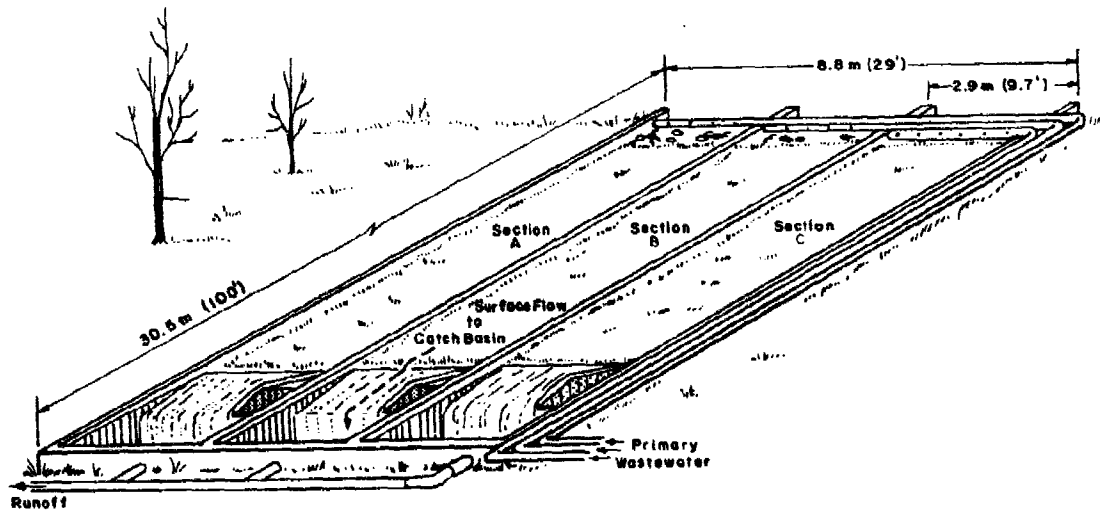


Figure 2. Diagram of CRREL overland flow system.

Table 2. Application rates of primary wastewater and average detention times of wastewater on the slopes.

Dates	Hydraulic loading rate (cm/hr)	Detention time (min)			
		Using maximum		Using centroid	
		Slope A	Slope B	Slope A	Slope B
2 June-4 August	0.40	50	85	60	119
5 August-16 October	0.80	35	50	46	67
19 October-21 October	1.20	-	30	-	36
28 October-11 December	0.40	-	85	-	108

measured by pumping through a water meter, and it was discharged to the municipal Hanover sewer. The hydraulic loading rate was varied during the experiment from 0.40 cm/hr to 1.20 cm/hr (Table 2) (0.12-0.50 m³/hr·m of width).

Determining average detention times

The average detention time of wastewater on the slope at each application rate was determined at hydraulic steady state by use of a sodium chloride tracer. A pulse of tracer was added to the wastewater as a "slug addition" to the distribution chamber in the constant head weirbox, and the tracer concentration in the runoff leaving the slope was measured as a function of time (Martel et al. 1982). The curve of tracer concentration vs time is known in a reactor engineering as the *C* curve (Levenspiel 1972). An example of this type of curve is shown in Figure 3. In a recent report Martel et al. (1982) introduced the concept of a detention time to correlate reaction rate data for overland flow systems. They assumed that the average detention time of water on the slope was at the maximum of the *C* curve. Figure 3 shows that the *C* curve is somewhat asymmetric. The average detention time \bar{t} is at the "center of gravity" of the area under the *C* curve, and because of the asymmetry, it is somewhat greater than that of the *C* curve maximum.

To measure \bar{t} accurately, the entire *C* curve would be needed and its center of gravity determined. The *C* curves obtained for the overland flow slopes had long tails, so it was impractical to obtain the entire curve. Also, there was the possibility that tracer was lost on the slope. This makes it difficult to

determine the area under the *C* curve properly, especially under the long, slowly decreasing tail. Therefore, the following expedient was used to estimate \bar{t} more realistically than by using the *C* curve maximum. It was assumed that diffusion and backmixing on the slope could be modeled as a series of well-stirred reactors. With this model an equation for the *C* curve of the form

$$C = \frac{N(Nt/\bar{t})^{N-1}}{\bar{t} \Gamma(N-1)} e^{-Nt/\bar{t}} \quad (1)$$

can be obtained (Levenspiel 1972). In this equation, *N* is the number of mixed tanks in series and *t* is time. The term $\Gamma(N-1)$ is the gamma function or generalized factorial of *N*-1. A nonlinear least-squares regression analysis was used to adjust the parameters *N* and \bar{t} in eq 1 to obtain the closest fit possible to the experimental data. The best fit for the data in Figure 3 was obtained with $\bar{t} = 35.5$ and *N* = 17.7. In this case, as well as in all the others studied, \bar{t} is longer than the *C* curve maximum shown in Figure 3. The higher the value of *N*, the less backmixing and diffusion is taking place on the slope. Figure 3 shows that while eq 1 does a reasonably good job of fitting the main part of the experimental *C* curve, it does not fit the tail of the curve well. The tail is caused by dead spaces on the slope, and a much more complex model that takes this into account would be required to fit the tail data.

Using this approach we calculated \bar{t} for each test section at each application rate (Table 2). The value of \bar{t} calculated from the peak of the *C* curve is also

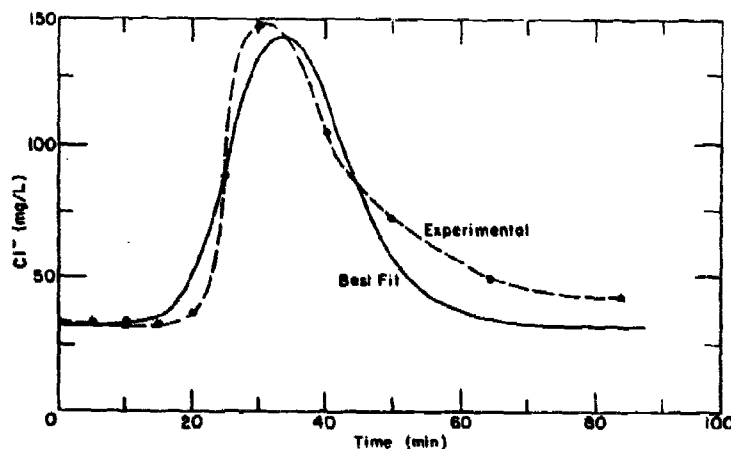


Figure 3. Example of *C* curve used to determine detention time.

given for comparison. The detention times calculated from both sets of data were always considerably shorter for section A than for section B. Winter frost action had caused channeling on slope A, resulting in a short circuit and a shorter detention time. For this reason, most of the data in this report were collected on section B.

Addition of organics to wastewater

A stock solution of trace organics was prepared by diluting the quantities of each substance given in Table 3 to 3 L with 1-butanol. Approximately 20 mL of this solution was added to the wastewater storage tank each day, and the tank was stirred for one hour prior to application. The primary wastewater was spiked with these organics with each application, whether samples were collected or not. Since the storage tank holds approximately 5000 L of wastewater, the amount of each substance added brought the concentration in the storage tank to the values shown in Table 3. From 28 October through the end of the study, 0.5 mL of nitrobenzene was also mixed with the spike solution and added on a daily basis to the storage tank, resulting in an estimated concentration of 120 µg/L. This was done to determine if the poor removal efficiencies during this period were due to the accumulation of substances applied since June or to seasonal effects.

As in an earlier study (Jenkins et al. 1981), toluene was present at detectable levels on a daily basis in the primary wastewater used in this study. The source of toluene in the waste stream is unknown. Another substance that was not intentionally added was also observed in the wastewater, but it was found to originate from our stock solution. This substance

was subsequently found to have originated as an impurity in the bromoform and was identified as dibromochloromethane.

Field experiment at Davis

To confirm the results from the CRREL experiments, a field study was conducted at the Davis, California, overland flow system on 10 December 1981. The experiment was run in the test area used by researchers of the University of California at Davis to study the performance of the system using primary wastewater. The air temperature at the time of the study was 16°C (61°F).

The experiment at Davis was conducted on one overland flow section measuring 25.6 m wide by 41.5 m long (Fig. 4). The soil at Davis is Clear Lake clay, and the site was graded to a 2% slope. The dominant plant species is tall fescue. The application rate used for the study was 64.4 L/min, or 0.16 m³/hr·m of width.

For the Davis experiment the organic stock solution described earlier was amended with nitrobenzene, benzene and toluene. Approximately 120 mL of this stock was dissolved in one gallon of methanol, and the resulting solution was pumped into the wastewater distribution line with a peristaltic pump at a rate of 10 mL/min. Wastewater spiked with these organics was applied to the system for over two hours before samples were collected. Wastewater, runoff and surface water samples were then carefully collected in a manner similar to that used at the Hanover site, except that the stainless steel tubing was not used.

The samples were immediately cooled in an ice chest and shipped cold to CRREL. The volatiles were analyzed and the other substances extracted within

Table 3. Quantities of organics used to prepare stock solution.

Substance	Class	Mass added (g)	Estimated concentration in storage tank (µg/L)
Chloroform	Haloform	30.0	40
Bromoform	Haloform	78.0	104
Chlorobenzene	Haloaromatic	75.0	100
m-Nitrotoluene	Nitroaromatic	75.5	101
Naphthalene	PAH	75.0	100
Phenanthrene	PAH	75.0	100
PCB 1242	PCB	75.0	100
2-Chloroethylvinylether	Haloether	75.0	100
Diethylphthalate	Phthalate ester	75.0	100
o-Chlorophenol	Halophenol	86.0	115
Pentachlorophenol	Halophenol	85.5	114
2,4 Dinitrophenol	Nitrophenol	78.5	105

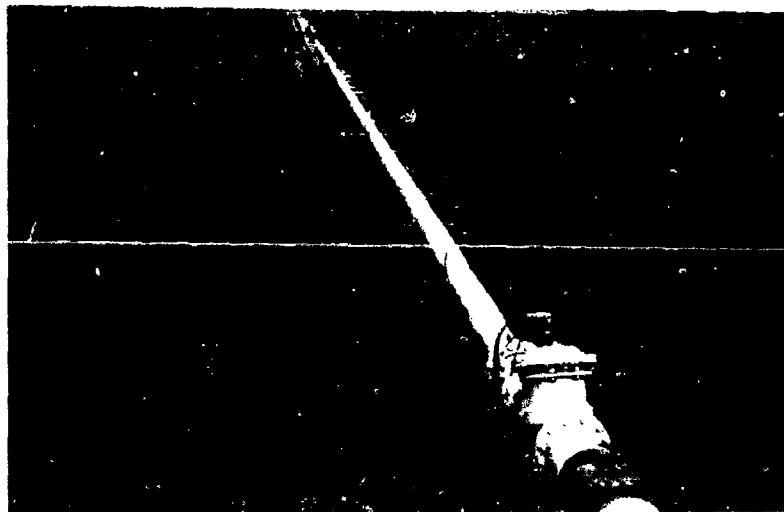


Figure 4. Davis, California, overland flow system.

26 hours after the samples were collected; the methods for doing this will be described later.

The samples were analyzed for BOD, TOC, total N and total suspended solids by Dr. Robert Smith of the University of California at Davis using standard procedures.

Water sampling at Hanover

Samples of the applied wastewater, of the runoff from the base of the slope, and from the surface at various distances downslope were collected once hydraulic steady state was achieved. Hydraulic steady state was defined as the point when the runoff rate had stabilized, usually within 90 minutes.

Three types of water samples were collected for analysis. The first was used for analyzing for volatile organics and was collected from the soil surface by placing a screw-cap test tube on the slope and allowing it to fill directly (Jenkins et al. 1981). The tube was filled to capacity, with care not to leave a headspace, and was sealed with a teflon-lined cap. The second sample was used for extraction and analysis of the remaining less-volatile organics. This sample was collected in a 300-mL all-glass BOD bottle by using the screw-cap, glass test tubes. The test tubes and BOD bottles were carefully cleaned with Baker Resi-Analyzed acetone before each sample was collected. A third sample was collected occasionally in a manner similar to the second, but the sample was stored in a 1-L Nalgene bottle. This sample was used to analyze for BOD, suspended solids, TOC and nitrogen, and was collected by placing a 0.75-m

length of 0.5-in. o.d. stainless steel tubing on the soil surface, elevating the downslope end slightly, and allowing the water to completely fill the Nalgene bottle.

Water temperature, air temperature and prevailing weather conditions were recorded each time samples were collected. The average water depths at each sampling location were estimated by measuring and averaging the depths at three random points on the cross section.

Water analysis

The toxic organics were divided into four groups for analytical purposes (Fig. 5). These are the volatiles, the neutral electron-capturing substances, the neutral noncapturing substances and the electron-capturing phenols. The volatiles were analyzed using a Hewlett-Packard 5992 gas chromatograph-mass spectrometer (GS/MS) equipped with an HP 7675A purge-and-trap sampler (Jenkins et al. 1981). A 60-mL sample was purged with helium at 20 mL/min for 20 minutes at room temperature. The eluted volatiles were collected on a Tenax tube trap. This tube was subsequently heated to 200°C for five minutes and the desorbed compounds directed onto a Porapak Q column maintained at 90°C. The column was then programmed from 90° to 210°C at 6°/min with a helium carrier flow of 10 mL/min. Substances eluting from the GC column were analyzed using selective ion monitoring (SIM) mass spectroscopy. The substances analyzed in this manner, their retention times, and the ions used for each substance are

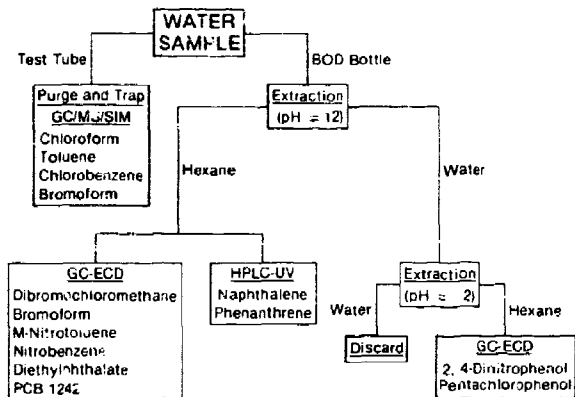


Figure 5. Division of organics studied into classes by type of analysis.

Table 4. Volatile organics studied using purge and trap GC/MS/SIM.

Volatile organic	Ion monitored (<i>m/e</i>)*	GC retention time (min)
Chloroform	85	13.7
Benzene	78	15.3
Toluene	91	19.3
Tetrachloroethylene	166	19.0
Chlorobenzene	112	21.6
Bromoform	173	24.0

*Mass to charge ratio.

given in Table 4. An internal standard of either benzene or tetrachloroethylene was added to each sample prior to analysis to allow normalization based on stripping efficiency and spectrometer performance. Quantitative data were obtained for each sample by comparing the results for each substance normalized to the internal standard with the similar result obtained when 1.0 μ L of the stock solution was added to the 60 mL of well water and analyzed in an identical manner.

The remaining classes of toxic organics were analyzed by either gas chromatography (GC) or high-performance liquid chromatography (HPLC) after solvent extraction by the microextraction technique (Rhoades and Nulton 1980). The extraction procedure was as follows. Each 300-mL BOD bottle was emptied into an acetone-rinsed, 500-ml glass separatory funnel containing 93 g of NaCl (Fisher Reagent Grade). The funnel was shaken to dissolve the salt, and the pH was adjusted to 12 with 5N

NaOH. A 10-ml portion of hexane (Baker Resi-Analyzed Grade) was then added to each BOD bottle, the bottles were swirled to rinse the glass walls, and the contents were emptied into the separatory funnel. A sample of 300 mL of well water was treated in a similar manner to serve as an analytical blank. Another 300-mL sample of well water, to which 1.0 μ L of the organic stock solution was added, was also treated in this manner to serve as the quantitative analytical standard.

The separatory funnels were then shaken on a wrist-action shaker for 30 minutes, the phases allowed to separate, and the water phases drained into acetone-washed, 400-mL breakers. The hexane solution and any emulsion present were drained into a 20-mL scintillation vial, and the vial was placed in a freezer overnight.

The separatory funnels were then rinsed with tap water and acetone and drained before returning the water solution. The pH was adjusted to 2 with a

5N H₂SO₄ solution, and 5 mL of hexane was added to each. The separatory funnels were then shaken again for 30 minutes and the phases separated. The water was discarded and the hexane solutions saved in 20-mL scintillation vials for phenols analysis and placed in a freezer overnight.

Emulsions in the hexane phases the following morning were broken by forcing the solution through acetone-washed glass wool packed in a disposable Pasteur pipette. The resulting hexane solution was dried by adding a small amount of anhydrous sodium sulfate and was saved for analysis.

The first hexane extract corresponds to the neutral fraction and was analyzed in two separate runs. The first analysis was conducted by GC-ECD on a Perkin Elmer Sigma 2 or Sigma 3 gas chromatograph. A 2- μ L subsample of the dried hexane extract was injected onto an 8% OV17 column, the column temperature programmed from 50° to 250°C at 10°/min, and the eluted components analyzed on an electron capture detector (ECD). The injector and detector temperatures were maintained at 200° and 300°C, respectively, and the column flow rate was 25 mL/min of 5% methane in argon. The substances analyzed in this manner and their GC retention times under these conditions are given in Table 5.

Quantitative results were obtained by measuring the peak height associated with each substance. Peak heights obtained from the analysis of the blank sample were subtracted on an individual basis. A measurable blank was found often for diethylphthalate and periodically for PCB. The peak height for each substance in the standard was used to obtain a response factor in units of mm per unit of concentration to enable the peak heights to be converted to concentrations in the water.

Table 5. Neutrals analyzed by GC-ECD on OV-17 and their retention times.

<i>Substance</i>	<i>GC retention time (min)</i>
Dibromochloromethane	6.6
Bromoform	8.7
Nitrobenzene	13.1
m-Nitrotoluene	14.7
Diethylphthalate	19.9
PCB #1*	22.6
PCB #2*	24.1
PCB #3*	25.7
PCB #4*	27.2
PCB #5*	29.3

*Five peaks were summed for PCB 1242 analysis.

The first hexane extract was also analyzed on a Perkin Elmer Series 3/LC-65T HPLC for naphthalene and phenanthrene by injecting a 50- μ L sample into an LC-8 reverse-phase HPLC column (Supelco) eluted with 85% methanol and 15% water. The flow rate was 2.3 mL/min, and the eluted compounds were determined on a UV detector operated at 270 nm. The retention times for naphthalene and phenanthrene under these conditions were 3.5 and 4.0 minutes, respectively. The corresponding peak heights for these substances were measured for the spiked sample for each day's samples, and a response factor was obtained in units of mm/unit of concentration. The peak heights for these two substances in each sample, minus any contribution from the blank, were converted to concentration using these response factors. The response for 2-chloroethylvinyl ether was too small to be determined accurately by either GC-ECD or HPLC, so the results for this substance are not available.

Phenols proved to be the most difficult of the various organic fractions to analyze. Initially the second hexane extract, corresponding to water extraction at pH 2, was analyzed by GC-ECD using an SP 1240 DA column (Rhoades and Nulton 1980). The conditions used for analyses were as follows: injector temperature, 235°C; detector temperature, 350°C; column temperature, 175°C; and flow rate, 20 mL/min of 5% methane in argon. Retention times of 2,4-dinitrophenol and pentachlorophenol obtained in this way were 4.6 and 7.6 minutes, respectively. *O*-chlorophenol could not be analyzed using these conditions because of its poor response on the ECD. This technique gave an excellent analysis for pentachlorophenol, but the results for 2,4-dinitrophenol were marginal because of an interfering peak that could not be separated sufficiently. For this reason and to measure *o*-chlorophenol we also tried an HPLC method for the phenols, but we were unable to separate *o*-chlorophenol and dinitrophenol; hence all data reported were obtained by GC-ECD.

The analyses of BOD, suspended solids, total nitrogen and pH were conducted according to standard methods and are described in more detail by Jenkins and Palazzo (1981). The total organic carbon analysis was performed on an Oceanography International Corporation 0524 B Total Carbon System according to the manufacturer's directions. This method is based on the persulfate oxidation method of Menzel and Vaccaro (1964).

Analytical precision

Tests were run approximately once a month to estimate the analytical precision for each substance

Table 6. Precision of neutral, less volatile organics analysis.

Date	Sample used	Number of replicates	Bromoform		m-Nitrotoluene		Nitrobenzene		Diethylphthalate		PCB 1242		Naphthalene							
			\bar{X} *	S	\bar{X}	S	\bar{X}	S	\bar{X}	S	\bar{X}	S	\bar{X}	S	RSD					
17 July†	Wastewater	5	-	-	60	10.8	18.0	-	-	75.0	7.0	9.3	40.0	4.2	10.5					
18 Aug.†	Wastewater	4	-	-	60	4.6	7.6	-	-	75.0	6.7	8.9	40.0	3.6	9.0					
9 Oct.**	Wastewater	4	121.5	4.1	3.4	78.0	0.6	0.8	-	86.2	2.1	2.4	58.0	9.0	15.5					
4 Nov.**	½ slope	5	24.5	0.15	0.6	69.6	3.1	4.5	65.5	3.3	5.1	38.7	6.1	15.8	14.3	4.2	9.2			
1 Dec.†	Runoff	5	32.7	2.3	7.0	35.1	3.2	9.1	54.9	4.0	7.3	70.0	1.1	1.6	8.4	0.6	7.1	9.2	1.0	10.8

* \bar{X} is the mean ($\mu\text{g/L}$), S is the standard deviation ($\mu\text{g/L}$), and RSD is the relative standard deviation (%).

† Replicate sample.

** Split sample.

Table 7. Precision of volatiles analysis.

Date	Sample used	Number of replicates	Chloroform		Benzene		Toluene		Chlorobenzene		Bromoform						
			\bar{X} *	S	\bar{X}	S	\bar{X}	S	\bar{X}	S	\bar{X}	S	RSD				
27 July†	Wastewater	6	29.0	2.6	9.0	-	-	10.0	1.0	9.9	72.3	10.2	14.9	58.4	10.5	18.0	
25 Aug.†	Wastewater	6	30.0	2.3	7.7	-	-	50.0	7.6	15.2	60.0	8.6	14.3	55.0	10.0	18.4	
30 Dec.**	Wastewater	4	30.0	3.5	11.7	55	4.0	7.2	50.0	3.6	7.2	65.0	4.1	6.3	60.0	4.0	6.6

* \bar{X} is the mean ($\mu\text{g/L}$), S is the standard deviation ($\mu\text{g/L}$), and RSD is the relative standard deviation (%).

† Replicate sample.

** Split sample.

Table 8. Precision of phenols analysis.

Date	Sample used	Number of replicates	2,4-Dinitrophenol		Pentachlorophenol			
			\bar{X} *	S	\bar{X}	S	RSD	
17 July†	Wastewater	5	59.0	4.3	7.3	8.31	0.96	11.5
4 Nov.**	½ slope	5	76.6	10.4	13.6	25.9	7.3	28.1
1 Dec.†	Runoff	4	49.1	6.4	13.0	8.6	0.73	8.5

* \bar{X} is the mean ($\mu\text{g/L}$), S is the standard deviation ($\mu\text{g/L}$), and RSD is the relative standard deviation (%).

† Replicate sample.

** Split sample.

using the three analytical methods. These tests were conducted on separate days than the analysis of authentic samples because of the time required to conduct both the purge-and-trap analysis for volatiles and the sequential extraction procedure for the other types of substances.

Determinations for both "split samples" and "replicate samples" were obtained for estimating the precision of the analysis alone vs the precision also reflecting sample collection and sample variability over time. The results obtained are presented in Tables 6-8. In general the estimates of precision obtained from split samples were about the same as from replicates. Thus most of the imprecision seems to be associated with the analytical methods rather than with sampling.

For the neutral, less volatile organics (Table 6), the analytical precision is estimated to be $\pm 10\%$ for all substances except PCB at all concentrations and phenanthrene at low levels. The consistent, relatively large imprecision associated with PCB was because the response was divided among five separate, rather small peaks and because of the difficulty in establishing the true baseline on a temperature-programmed ECD analysis. For low levels of PCB and phenanthrene we estimate the analytical precision to be $\pm 20\%$ and $\pm 15\%$, respectively.

For the volatiles analysis we estimate the chloroform and benzene data to be precise to $\pm 10\%$, toluene and chlorobenzene to $\pm 15\%$ and bromoform to $\pm 20\%$ (Table 7). The precision for these substances seems to be related to the retention time on the Porapak column and may be a result of peak-broadening effects for the later-eluting substances such as bromoform.

Although we had one large value for pentachlorophenol, we estimate the overall analytical precision for the two phenols to be about $\pm 15\%$ (Table 8). It is surprising that the precision is nearly as good as for the less volatile neutrals, because two sequential extracts are required while only one is required for the neutrals.

Soil and plant sampling and analysis

Grass samples from the overland flow prototypes were collected for organics analysis at the three normal harvests on 19 June, 4 August and 5 October 1981. Additional grass samples were taken for analysis on 23 July and 2 September. The grass samples were frozen in hexane- and acetone-rinsed, glass canning jars and stored for later analysis.

For analysis the grass samples were thawed, air-dried for several days at room temperature, and ground to pass through a 20-mesh sieve. After careful mixing, a 5-g subsample was removed, placed in

a screw-cap test tube, and extracted by shaking with 25 mL of 50% hexane, 50% acetone solution (Tomson et al. 1981) for 30 minutes on a wrist-action shaker. The test tubes were then centrifuged at 1000 rpm for 30 minutes, and 10 mL of solution was removed with a 10-mL pipette. The extracts were placed in 20-mL scintillation vials and dried with anhydrous sodium sulfate.

This extract was analyzed directly for electron-capturing neutrals by the same GC method described in the water analysis section. Then the remaining extract was placed in a 500-mL separatory funnel, extracted with 300 mL of distilled water containing 93 g of NaCl, and adjusted to pH 12 with aqueous 5N NaOH. A 10-mL portion of hexane was added, and the separatory funnel was shaken for 30 minutes on a wrist-action shaker. The funnels were then allowed to stand while the two phases separated. The green color due to chlorophyll remained largely in the organic phase. The water solution was removed and the organic phase retained.

The separatory funnels were washed with tap water and acetone and drained, and the water phase was returned. The pH was adjusted to 2 with 5N H_2SO_4 . 10 mL of hexane was added, and the funnels were shaken for 30 minutes as before. The funnels were then allowed to stand while the phases separated, and the organic phase was retained for phenols analysis. The phenol fraction was concentrated using a Kuderna-Danish evaporator and analyzed as described in the water analysis section. The plant extracts were analyzed using standards carefully prepared by dissolving the pure substances in hexane.

Soil samples from sections A and B of the overland flow prototypes were collected on 23 July, 2 September and 18 October. Soil samples from section C, the untreated section, were also collected to be used as an analytical blank. Soil samples were kept frozen in glass canning jars until analyzed.

For analysis the samples were thawed and air-dried for several days at room temperature. The soil was ground with a mortar and pestle and mixed carefully. A 5-g subsample of each soil was placed in a screw-cap test tube and shaken on a wrist-action shaker for 30 minutes with 25 mL of a 50% hexane, 50% acetone solution (Tomson et al. 1981). The test tubes were then placed in a centrifuge at 1000 rpm for 30 minutes. A 15-mL portion of the clear supernatant was carefully removed with a glass pipette, placed in a 20-mL scintillation vial, and dried with anhydrous sodium sulfate. A 10-mL portion of the dried extract was then placed in a Kuderna-Danish evaporator and the volume reduced to about 1.5 mL. This concentrated sample was then analyzed in a manner similar to that described for the less volatile organics in the water analysis section.

RESULTS

Organics removal at Hanover

Results of the analysis of individual water samples are presented in Appendix A. The maximum, minimum and mean values for each organic substance in the applied wastewater are presented in Table 9. These data show that the applied concentrations varied considerably from day to day, probably because of varying degrees of volatilization and because of sorption on suspended matter and on the walls of the storage tank. The extent of these processes depends on the amount of suspended matter and the length of time between when the wastewater was spiked and when it was applied. In addition, no attempt was made to ensure that the same volume of wastewater was present in the tank from day to day, and hence the volume in which these organics were diluted probably varied significantly. In general, though, the concentrations of these substances ranged from about 20 to 70 $\mu\text{g/L}$. The sum of these trace organics generally amounted to less than 1 mg/L .

Three hydraulic loading rates were tested during this study, 0.4, 0.8 and 1.2 cm/hr . Table 10 presents the average runoff concentrations for each loading rate. Two values are presented for the 0.4- cm/hr rate, one for June-August and the second for October-December. In nearly every case, runoff concentrations increased with increasing loading rate. The most striking example is diethylphthalate, where the average runoff concentrations were 4.2, 21.5 and 68.3 $\mu\text{g/L}$ at 0.4, 0.8 and 1.2 cm/hr , respectively.

In overland flow, comparing the changes in concentration alone is not sufficient for calculating the

percent removal because significant water loss occurs by evapotranspiration. Table 11 presents the total amount of water applied to section B at each application rate, the total volume of water measured in the runoff, and the percent lost by evapotranspiration. At the 0.4- cm/hr rate, about 54.6% of the water was removed by evapotranspiration during the summer. For the 0.8- cm/hr rate, only about 28.6% was lost. The 1.2- cm/hr rate was only studied over a period of three days, and a slight increase in volume was noted, mainly a result of nearly 2 cm of rain over the period. When the 0.4- cm/hr rate was reestablished in the late fall, the water loss was only 28.4%, because there was less plant transpiration and evaporation than during the July-August period.

The average applied and runoff concentrations and volumes were combined, and the mass removals were calculated (Table 12). At the 0.4- cm/hr loading rate in the summer, more than 94% of the mass was removed for each of the organics tested. Even at this loading rate, though, consistent differences from substance to substance were observed on a daily basis. When the hydraulic loading rate was increased, removal decreased significantly for many of the substances, with the worst removal for 2,4-dinitrophenol at 1.2 cm/hr . On the other hand, the removal of naphthalene was still greater than 90%, even at the highest loading rate tested.

To determine the rate of removal for each substance on a daily basis, samples collected downslope were analyzed and the concentrations plotted as $\ln C/C_0$ vs residence time (Jenkins et al. 1981). The residence time of each sample collected downslope was estimated from downslope distance. For example, at the 0.4- cm/hr rate the total residence time of

Table 9. Summary of water analyses for applied wastewater.

Substance	Applied concentration ($\mu\text{g/L}$)			N
	Maximum	Minimum	Mean	
Chloroform	58	17	33	9
Toluene	64	2	19	8
Chlorobenzene	110	23	58	9
Bromoform	125	20	68	20
Dibromochloromethane	17	7	11	11
m-Nitrotoluene	115	20	50	20
Diethylphthalate	109	29	63	19
PCB 1242	69	19	37	21
Naphthalene	148	32	63	14
Phenanthrene	89	20	45	13
Pentachlorophenol	85	13	39	15
2,4-Dinitrophenol	255	18	79	13
Nitrobenzene	315	48	113	5

Table 10. Summary of average runoff concentrations ($\mu\text{g/L}$) for each substance following overland flow treatment.

Substance	Average runoff concentration			
	0.4 cm/hr 1 June-4 Aug	0.4 cm/hr 28 Oct-11 Dec	0.8 cm/hr 5 Aug-16 Oct	1.2 cm/hr 19-21 Oct
Chloroform	2.3	2.4	2.0	-
Toluene	0.4	-	<d*	-
Chlorobenzene	0.4	1.4	0.3	-
Bromoform	2.2	7.4	10.3	20.7
Dibromochloromethane	-	0.5	1.0	1.6
m-Nitrotoluene	0.5	12.2	8.9	22.5
Diethylphthalate	4.2	24.7	21.5	68.3
PCB 1242	1.4	2.9	3.1	7.3
Naphthalene	<d	0.8	2.3	3.8
Phenanthrene	0.1	0.7	0.4	-
Pentachlorophenol	0.9	2.4	2.2	13.4
2,4-Dinitrophenol	11.0	15.6	14.5	39.0
Nitrobenzene	-	29.5	-	-

*Less than detectable level.

Table 11. Water volumes (L) applied to overland flow and volume of runoff.

Substance	Volume			
	0.4 cm/hr 1 June-4 Aug	0.4 cm/hr 28 Oct-11 Dec	0.8 cm/hr 5 Aug-16 Oct	1.2 cm/hr 19-21 Oct
Wastewater applied	82,586	36,325	124,700	15,664
Runoff (section B)	37,495	26,013	89,008	16,728
Evapotranspiration (?)	54.6	28.4	28.6	-6.8

Table 12. Summary of average removals (% by mass) for each substance by overland flow.

Substance	Average removal			
	0.4 cm/hr 1 June-4 Aug	0.4 cm/hr 28 Oct-11 Dec	0.8 cm/hr 5 Aug-16 Oct	1.2 cm/hr 19-21 Oct
Chloroform	97	95	96	-
Toluene	>99	-	>99	-
Chlorobenzene	>99	97	>99	-
Bromoform	98	94	89	73
Dibromochloromethane	>98	97	94	84
m-Nitrotoluene	>99	86	87	57
Diethylphthalate	96	77	76	15
PCB 1242	98	92	95	64
Naphthalene	>99	99	97	92
Phenanthrene	>99	98	99	-
Pentachlorophenol	99	94	97	44
2,4-Dinitrophenol	94	79	92	9
Nitrobenzene	-	81	-	-

water applied to section B was found to be about 119 min from chloride tracer experiments. For a sample collected at half slope, the residence time is therefore estimated to be 59.5 min, at quarter slope it is 29.8 min, and so on. This procedure for estimating residence times for samples collected at various points on the slope was tested by conducting a chloride tracer experiment, measuring the chloride concentration with time in both the runoff and water collected at half slope, and obtaining the residence times from the centroid of the C curves as described earlier. The values determined for full slope and half slope were 35.5 and 16.5 min, respectively, indicating that the method used for estimating residence times is valid.

When the concentrations for each substance were plotted in this way ($\ln C/C_0$ vs residence time), a relationship, which generally appeared to be linear,

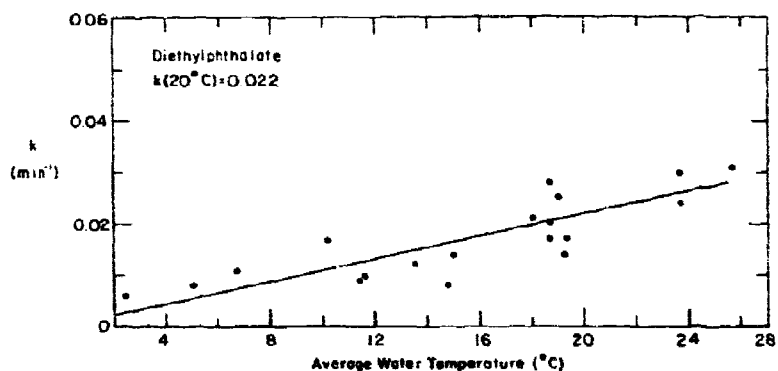
was obtained for all the substances tested in this study. Examples are shown in Appendix B. When the best-fit straight lines were obtained by least-squares techniques, an intercept very near zero was found in all cases, with correlation coefficients generally ranging from 0.94 to 0.99. Thus these empirical relationships can be described by

$$\ln \frac{C}{C_0} = -kt \quad (2)$$

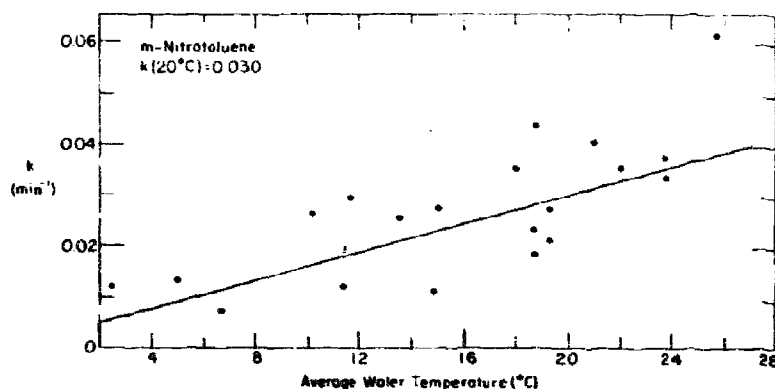
where k is the slope of the best-fit straight line and C_0 is the value of the concentration C at $t=0$; in our case C_0 is the applied concentration. Equation 2 is the integrated form of the first-order rate law

$$\frac{dC}{dt} = -kC \quad (3)$$

where k is the first-order rate coefficient (min^{-1}).



a. Diethylphthalate.



b. m-Nitrotoluene.

Figure 6. Rate coefficients vs average water temperature.

Experimental values of k were determined in this way for each substance each day samples were analyzed; the values are presented in Appendix Table A2 along with the average water temperatures for that day. Depending on the substance, between 5 and 21 individual determinations of k were obtained at average water temperatures ranging from 25.7°C on 9 July to 2.5°C on 2 December. When the experimental rate coefficients were plotted vs runoff temperature, the type of relationship shown in Figure 6 was obtained. In all cases the value of k decreased as runoff temperatures declined in the fall and early winter. Since the number of determinations for each substance differed as well as the distribution of these determinations with respect to runoff temperature, it would not be meaningful to compare the k values for each substance by simply averaging all the values obtained. Instead, for most of the substances, we obtained the best-fit straight line from the plot of the individual k values vs average water temperature and solved these equations for the k value at 20°C. These values are summarized in Table 13 along with the maximum and minimum values and the number of determinations. For a few of the volatile substances, such as chloroform, toluene and chlorobenzene, insufficient data were available to obtain the k value for 20°C in this way. For these substances the k (20°C) values were estimated by averaging the experimental values obtained for the summer months (June–September). Values of k (20°C) obtained in this way for other substances such as

m-nitrotoluene and diethylphthalate compared favorably with values obtained from the best-fit lines of k vs average temperature.

The substance with the highest k (20°C) value was phenanthrene, followed by toluene, chlorobenzene and naphthalene, with removal rate coefficients ranging from 0.077 to 0.056 min⁻¹. The substances that were removed the slowest were nitrobenzene, dinitrophenol and diethylphthalate, with k (20°C) values ranging from 0.018 to 0.022.

Organics removal at Davis

To determine if the same behavior would be found on a full-scale system, a field test was conducted at the Davis, California, overland flow system as described in the experimental section. The results of the water analyses for this test are presented in Table 14. Except for diethylphthalate the removals were greater than 90% by mass.

The relationships of $\ln C/C_0$ vs residence time for the various samples at Davis were linear for most of the substances (Appendix Figs. B9 and B10). This indicates that the removal processes at Davis are also governed by first-order kinetics, and the removal rate coefficients can be obtained from the slope of the best-fit line. (Only data obtained from samples collected as far downslope as 75 ft were used to calculate rate coefficients. Samples collected farther downslope were obtained before the full detention time on the slope was achieved.) The order of the rate coefficients at Davis (ranked from fastest to slowest) is very similar to that at CRREL (Fig. 7).

Table 13. Summary of experimental rate coefficients.

Substance	First-order rate coefficients (min ⁻¹)			N†
	Maximum	Minimum	k(20°C)*	
Chloroform**	0.047	0.017	0.030	9
Toluene**	0.127	0.024	0.070	8
Chlorobenzene**	0.105	0.030	0.064	9
Bromoform	0.045	0.017	0.032	17
Dibromochloromethane	0.062	0.021	0.053	11
<i>m</i> -Nitrotoluene	0.062	0.007	0.030	20
Diethylphthalate	0.031	0.006	0.022	19
PCB 1242	0.061	0.013	0.035	21
Naphthalene	0.084	0.029	0.056	15
Phenanthrene	0.131	0.027	0.077	14
Pentachlorophenol	0.052	0.009	0.036	15
2,4-Dinitrophenol	0.029	0.003	0.019	12
Nitrobenzene	0.019	0.003	0.018	5

* The value of k at 20°C from linear best fit of experimental k values vs average water temperature, except when indicated otherwise.

† The number of individual determinations.

**The value of k (20°C) was obtained by averaging experimental k values obtained from June–September 1981.

Table 14. Results of water analyses for Davis field experiment.*

Substance	Concentration ($\mu\text{g/L}$)		Mass (mg)		Removal rate (%) by mass	Removal rate coefficient (min^{-1})
	Applied	Runoff	Applied	Runoff		
Chloroform	51.1	1.8	592	18.8	96.8	0.012
Toluene	70.7	0.7	820	7.4	99.1	0.018
Benzene	78.6	1.5	911	15.5	98.3	0.015
Chlorobenzene	88.9	0.9	1031	8.7	99.2	0.018
Bromoform	187	4.8	2168	49.1	97.7	0.017
Dibromochloromethane	24.7	0.3	286	2.6	99.1	0.018
m-Nitrotoluene	144	8.6	1669	87.9	94.7	0.011
Diethylphthalate	107	54.2	1240	554.0	55.3	0.003
PCB 1242	98.9	3.5	1146	35.8	96.9	0.020
Naphthalene	179	2.7	2075	27.2	98.7	0.020
Phenanthrene	149	1.2	1727	12.5	99.3	0.031
Pentachlorophenol	315	6.1	3654	61.0	98.3	0.013
2,4-Dinitrophenol	238	15.6	2761	156.0	94.6	0.009
Nitrobenzene	118	13.3	1368	13.6	90.1	0.008

* The data from the Davis system were obtained only once (10 December 1981), so it is not possible to assess the statistical significance of the rate coefficient data.

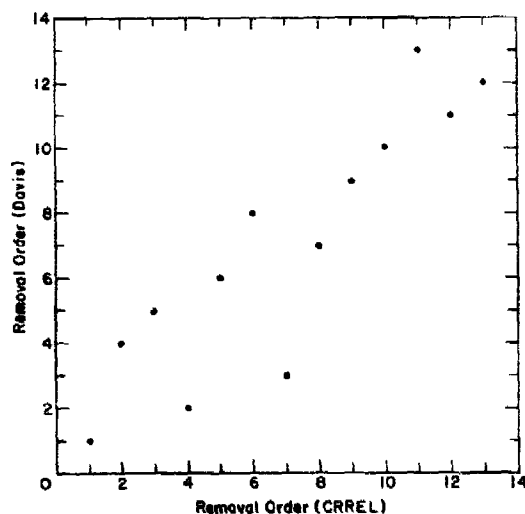


Figure 7. Comparison of ranked order of removal rate coefficients at CRREL and Davis.

At Davis we added benzene in addition to the substances tested at CRREL. The results indicated its rate of removal was lower than toluene, dibromochloromethane and naphthalene and very similar to that of pentachlorophenol.

Accumulation of organics in soils and plants

As described earlier, soil samples collected from

the Hanover site were analyzed for organics as well. Of those added, only PCB 1242 consistently accumulated in the soil at levels above the background. In a few instances pentachlorophenol (PCP) was also detected above background levels. All of the other substances were present at concentrations below a detection limit of about $0.2 \mu\text{g/g}$. The results for PCB and PCP are presented in Table 15.

The soil from sections A and B had detectable levels of PCB in all cases, with values ranging from 0.37 to $4.87 \mu\text{g/g}$. While there is little consistency from location to location, there is a clear tendency toward larger accumulations with time. Of the samples collected on or before 2 September, no values over $1.21 \mu\text{g/g}$ were found. For the samples collected on 12 October, a number of samples had values greater than $3 \mu\text{g/g}$. Soil samples from section C (the control area), on the other hand, showed no detectable PCB. No application of wastewater containing these organics was made to section C, so these analyses serve as an analytical blank.

Samples of plant tissue from the two treatment sections (A and B) and the control section (C) were analyzed to determine to what extent these substances had accumulated. Only PCB was found at measurable concentrations, although analytical difficulties prevented measurement for dinitrophenol and pentachlorophenol. For the treatment areas, concentrations of PCB ranged from <0.04 to $0.85 \mu\text{g/g}$ on an air-dried plant material basis (Table 16).

Table 15. Concentration of PCB 1242 and pentachlorophenol (PCP) in soil samples.

Sample	Date collected	Concentration ($\mu\text{g/g}$)	
		PCB	PCP
Slope B (upper)	23 July 81	0.37	<d*
Slope B (lower)	23 July 81	1.19	<d
Slope A (lower)	23 July 81	0.54	-
Slope C (upper)	23 July 81	<d	-
Slope C (lower)	23 July 81	<d	-
Slope B (lower)	2 Sept 81	1.21	-
Slope A (upper)	2 Sept 81	1.09	-
Slope B (1/8 slope)	12 Oct 81	0.58	<d
Slope B (1/4 slope)	12 Oct 81	4.24	0.73
Slope B (1/2 slope)	12 Oct 81	1.89	0.07
Slope B (3/4 slope)	12 Oct 81	3.06	<d
Slope A (1/8 slope)	12 Oct 81	1.87	<d
Slope A (1/4 slope)	12 Oct 81	4.58	<d
Slope A (1/2 slope)	12 Oct 81	4.87	<d
Slope A (3/4 slope)	12 Oct 81	0.61	<d
Slope C	12 Oct 81	<d	<d

* Less than detection limits estimated at about 0.2 $\mu\text{g/g}$ for PCB and 0.05 $\mu\text{g/g}$ for PCP.

Table 16. Concentration of PCB in plant samples.

Sample	PCB concentration ($\mu\text{g/g}$)		
	4 Aug	2 Sept	5 Oct
Section A (upper)	0.14	0.04	0.20
Section A (lower)	-	<d	0.85
Section B (upper)	0.13	0.13	0.22
Section B (lower)	0.07	0.06	0.08
Section C (upper)	<d*	<d	-
Section C (lower)	<d	-	-

* Less than a detection limit estimated at 0.03 $\mu\text{g/g}$ of air-dried plant material.

DISCUSSION

Removal from solution

The results from the water analyses at both the CRREL and the Davis overland flow systems show excellent removal of most of the organics applied. In addition, when we order the substances according to the magnitude of their experimental rate coefficients for removal from solution, the orders are nearly identical for the two sites (Fig. 7). In both cases the four substances removed at the greatest rate were phenanthrene, toluene, chlorobenzene and naphthalene, while nitrobenzene and diethylphthalate were removed the slowest. This consistent behavior at both sites seems to indicate that

the same mechanism or mechanisms are operating and that the relative removal rate depends on some property or properties of the specific substance. Since the same removal order was observed at the CRREL site, where these organics were applied every day, and at the Davis site, where they were applied only once, removal from solution does not seem to be associated with an adaptive process, as one might expect if the development of an acclimatized microbial population was a predominant mechanism.

There are a number of mechanisms that could be operating to remove these organics from solution, including volatilization; sorption on surface soils and vegetation; and sorption on suspended material followed by sedimentation, biodegradation, chemical hydrolysis or photodegradation. Earlier work (Jenkins et al. 1981) shows that volatilization seems to account for some portion of the removal, at least for the most volatile substances such as toluene, chloroform and chlorobenzene. On the other hand, sorption on surface soils was not eliminated as a significant removal process, even for these very volatile substances. While the other mechanisms probably do occur to some extent, the solution is present on the slope for only a relatively short period, 36-119 minutes on the average (depending on the application rate) for the CRREL system, and the rates associated with most of the other mechanisms are expected to be too low to account for the observed removal rates.

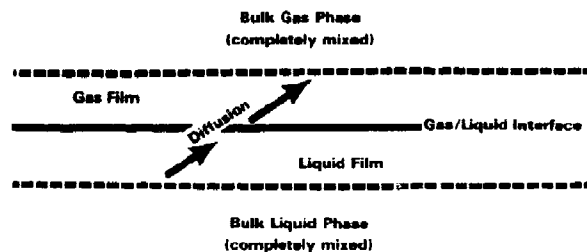


Figure 8. Illustration of the two-film theory.

Two theoretical approaches have been taken in dealing with the transfer of volatile substances across the air/water interface (volatilization). These are the two-film theory developed by Whitman (1923) and the penetration theory. Of these the two-film theory has received the greatest attention and has been the most successful in matching experimental results on transfer of gases across the air/water interface (Dilling 1977, Smith et al. 1981, Rathbun and Tai 1981). In this theory, two fictitious films are assumed to exist at the gas/liquid interface, one gas and the other liquid (Fig. 8). These films are assumed to be stagnant and to exert all the resistance to transfer across the interface. The bulk phases above and below these films are assumed to be well mixed. Equilibrium is assumed to exist at the interface, and diffusion across the liquid and gas films controls the rate of mass transport.

Since all the resistance to transfer is assumed to occur in the films, the total resistance R_T is the sum of the resistances of the liquid and gas phases:

$$R_T = R_L + R_G \quad (4)$$

where R_L is the resistance across the liquid film and R_G is the resistance across the gas film. Calculating the total mass transfer thus requires summing the two individual resistances, which can be considered to be reciprocals of their conductivities (Mackay et al. 1979):

$$R_L = \frac{1}{K_L}; \quad R_G = \frac{1}{K_G} \quad (5)$$

where K_L and K_G are the conductivity terms and are the liquid-phase and gas-phase transfer coefficients, respectively. Thus the total resistance K_T to mass transfer can be expressed as

$$R_T = \frac{1}{K_T} = \frac{1}{K_L} + \frac{1}{K_G} \quad (6)$$

Using Liss and Slater's (1974) values for air/sea exchange of CO_2 and H_2O vapor and assuming that individual phase transport coefficients are proportional to the reciprocal of the square root of the molecular weight ($M^{-1/2}$), Dilling (1977) developed a relationship for the total mass transfer coefficient for volatilization (K_{vol}) in units of cm/min:

$$K_{vol} = \frac{221.1}{\left(\frac{1.042}{H} + 100.0\right)M^{1/2}} \quad (7)$$

where H is the Henry's law constant (in dimensionless units). The half-lives for a series of volatile chlorocarbons in solution calculated with this equation matched experimental values obtained in a laboratory test quite well (Dilling 1977). But, as pointed out by Dilling, the match was rather fortuitous since the transport coefficients are a function of turbulence in both air and water phases, which were simulated only by mechanical stirring in the lab but are produced by wind and wave action in the ocean.

Experimentally determined half-lives were compared with those obtained using eq 7 for a number of volatile substances on the CRREL overland flow slope (Jenkins et al. 1981). The results did not match the calculated values but were longer by a factor of about 2-3 for most substances tested. This was explained by incomplete mixing, since the Reynolds numbers for this system ranged from 100 to 400, indicating relatively nonturbulent conditions.

Since all of the substances tested in the previous study were quite volatile (as measured by their Henry's constants), the removal rates of much less volatile substances were unknown. Experimental results

from the current study for much less volatile substances such as phenanthrene, PCB and pentachlorophenol indicate removal rate coefficients very similar to those for some of the most volatile substances such as toluene, chloroform and chlorobenzene. Since the Henry's constant for these less volatile substances are one to three orders of magnitude lower, their removal is not predictable using the volatilization model alone.

Studies conducted on other types of land treatment systems, particularly rapid infiltration, show that the movement of organics through soils is retarded by sorption on soil organic matter (Wilson et al. 1981). In rapid infiltration the transport of these substances through the soil has been found to be predictable, assuming that equilibrium is achieved with the soil organic matter. In rapid infiltration the downward velocity of water will generally be less than 10^{-3} cm/s, a value at which Schwarzenbach and Westall (1981) found excellent agreement between partition coefficients obtained from column studies and batch experiments. At velocities above 10^{-2} cm/s, however, Schwarzenbach found that transport became affected by slow sorption kinetics. For overland flow the average velocity of water across the surface and in contact with soil organic matter is on the order of 0.1-1.0 cm/s, which is 10-100 times greater than the cutoff point for equilibrium given by Schwarzenbach. Thus the movement is much too fast for equilibrium to be established.

The amount of organic matter at the surface of an overland flow system, however, is probably much greater than for the other types of land treatment. Peters et al. (1981) found the surface layer of soil at their site had a Kjeldahl-N concentration as high as 20,000 $\mu\text{g/g}$ after three years of operation. If this is mainly organic-N and there is a ratio of about 20 between organic-C and organic-N, the organic carbon content is about 20%. This large accumulation of organic matter on the surface is consistent with visual evidence from the CRREL system and other systems that have been in operation for at least several months and may be similar in character to the organic slime that develops on an operational trickling filter. Thus, while the time for sorption is rather short compared to other systems, the surface encountered by the solution in an overland flow system is largely organic in nature.

The substances studied on the CRREL system were ordered according to the magnitude of their experimental first-order rate coefficients k (20°C)_{exp} and tabulated along with literature values for the molecular weight M , the octanol-water partition coefficient K_{ow} and the Henry's constant H (Table

17). Table 17 shows that, in general, substances having low removal rate coefficients had relatively low values of both K_{ow} and H , while substances with larger rate coefficients had either a high K_{ow} , or a moderate K_{ow} and a high H . When the removal rate coefficients are plotted as a function of $\log K_{ow}$ (Fig. 9), a good linear relationship is obtained for many of the substances tested. Compared to this relationship, the experimental rate coefficients for toluene and chlorobenzene, and to a lesser extent chloroform, are too high. This result is consistent with additional removal by volatilization for these substances. The experimental rate coefficients for PCB and PCP, on the other hand, are too low, a result expected because these two substances were found to accumulate on the soil, and resolubilization should be possible. This implies that the rate of removal may be predictable using these two mechanisms: sorption on organic surfaces and volatilization. The overall removal rate coefficient k_T could therefore be expressed as the sum of two components:

$$k_T = k_{\text{sorb}} + k_{\text{vol}} \quad (8)$$

where k_{sorb} and k_{vol} are the rate coefficients for volatilization and sorption, respectively. The rate coefficient k is related to the transfer coefficient K_T by

$$k_T = \frac{K_T}{d} = \frac{K_{\text{vol}}}{d} + \frac{K_{\text{sorb}}}{d} \quad (9)$$

where d is the solution depth in cm and K_{vol} and K_{sorb} are the transfer coefficients for volatilization and sorption, respectively. In the CRREL experiment the average solution depth on the slope was about 1.2 cm.

We attempted to model the loss rate observed experimentally versus that predicted using volatilization and sorption. To do this we assumed that the total removal rate coefficient was the sum of the volatilization and sorption terms, as described in eq 8. Solving for the volatilization portion by combining eq 7 and 9, we have

$$k_{\text{vol}} = \frac{1}{d} \cdot \frac{221.1}{\left(\frac{1.042}{H} + 100.0\right) M^{1/2}} \quad (10)$$

Rearranging this equation we have

$$k_{\text{vol}} = \frac{1}{d} \cdot \frac{2.211 H}{(0.01042 + H) M^{1/2}} \quad (11)$$

Since the values of the constants 2.211 and 0.01042 are only appropriate for the well-stirred condition at the air/sea interface and the experimental system

Table 17. Physical properties and experimental removal rate coefficients at 20°C for the organic chemicals studied.

Substance	K _{ow}		H		k(20°) _{exp}
	M	Value	Source	Value (10 ⁵ atmos·m ³ /mole)	
Phenanthrene	178	2.88x10 ⁴	Hansch and Leo 1979	3.93*	Mackay et al. 1979
Toluene	92	490	Hansch and Leo 1979	515	Leighton and Calo 1981
Chlorobenzene	113	692	Hansch and Leo 1979	267	Leighton and Calo 1981
Naphthalene	128	2.34x10 ³	Hansch and Leo 1979	36	McCarty 1980
Dibromochloromethane	208	†		†	
Pentachlorophenol	266	1.32x10 ⁵	Hansch and Leo 1979	0.21	McCarty 1980
PCB 1242	261‡	3.8x10 ⁵	Veith et al. 1979	30*	Westcott et al. 1981
m-Nitrotoluene	137	282	Hansch and Leo 1979	5.3**	Dilling 1977
Bromoform	253	189††	Mackay et al. 1980	63	McCarty 1980
Chloroform	119	93.3	Hansch and Leo 1979	314	Leighton and Calo 1981
2,4-Dinitrophenol	184	34.7	Hansch and Leo 1979	0.001††	Dilling 1977
Diethylphthalate	222	162*	McDuffie 1981	0.056**	Dilling 1977
Nitrobenzene	123	70.8	Hansch and Leo 1979	1.9**	Dilling 1977
Benzene	78	135	Hansch and Leo 1979	435	Leighton and Calo 1981

* At 25°C.

† We were unable to locate values for H and K_{ow} for this substance.

‡ Average M assuming an average chlorine content of 3.2 (Safe and Hutzinger 1973).

** Calculated from H = 16.04 P·M/T·S.

†† Calculated from ln K_{ow} = 7.494 - ln S (mole/m³); Mackay et al. (1980) *Chemosphere*, 9: 701.

‡‡ Estimated from H = 16.04 P·M/T·S using S of 2,4-dinitrophenol and P of 2,4-dinitrotoluene.

*** Not studied on the CRREL system during this period.

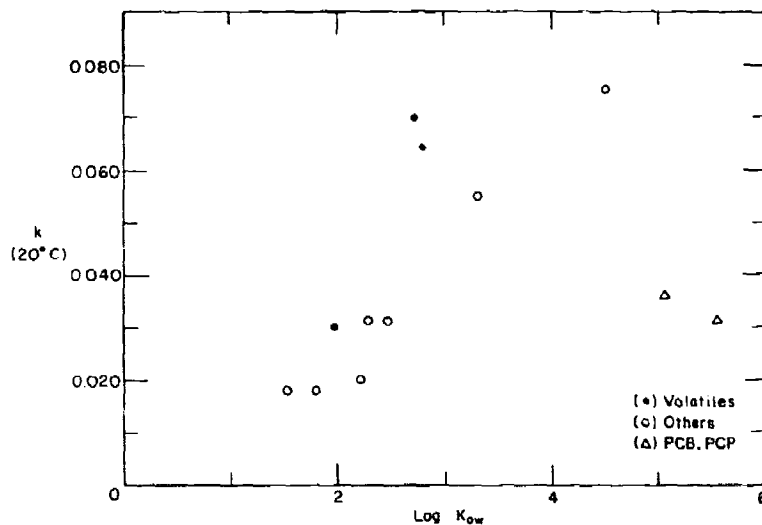


Figure 9. Removal rate coefficients (20°C) vs K_{ow} .

used by Dilling (1977), the equation was generalized as:

$$k_{vol} = \frac{B_1}{d} \cdot \frac{H}{(B_2 + H) M^{1/2}} \quad (12)$$

where B_1 and B_2 are coefficients specific to an overland flow system.

From a kinetic point of view, sorption is analogous to volatilization in that interphase transport occurs across a water/soil interface. The same types of assumptions can be made about transport across this interface as were made for the two-film theory for transfer across the air/water interface. That is, two stagnant films can be assumed to be present on either side of the interface, with the resistance to sorption being the sum of the individual resistances of the separate films. Again equilibrium is assumed to be present only right at the interface, and transport across the interface is controlled by diffusive properties. The equilibrium at the interface can be assumed to be proportional to the octanol-water partition coefficient K_{ow} , since this constant has been shown to be proportional to the actual partition coefficient for water and soil organic matter (Karickhoff et al. 1979). For all these substances except PCB and PCP, soil analysis indicated that the substances were not accumulating with time. Thus, for these substances the back reaction, desorption, should not be important and the kinetic approach should be valid.

If we assume that the sorption term has a form similar to the volatilization term, then

$$k_{sorb} = \frac{B_3}{d} \cdot \frac{K_{ow}}{(B_4 + K_{ow}) M^{1/2}} \quad (13)$$

By combining eqs 8, 12 and 13 we can express the total rate coefficient as

$$k_T = \left[\frac{B_1}{d} \cdot \frac{H}{(B_2 + H) M^{1/2}} \right] + \left[\frac{B_3}{d} \cdot \frac{K_{ow}}{(B_4 + K_{ow}) M^{1/2}} \right] \quad (14)$$

Using a value of 1.2 cm for d and the values for M , H , K_{ow} and $k(20^\circ\text{C})_{exp}$ from Table 17 for each substance, we subjected eq 14 to a multiple regression analysis to determine the best values for the coefficients B_1 , B_2 , B_3 and B_4 . When this was done, using nine of the substances in Table 17, the following equation was obtained:

$$k_T(20^\circ) = \left[\frac{0.2563}{d} \cdot \frac{H}{(5.86 \times 10^{-4} + H) M^{1/2}} \right] + \left[\frac{0.7309}{d} \cdot \frac{K_{ow}}{(170.8 + K_{ow}) M^{1/2}} \right] \quad (15)$$

The residual root mean square for lack of fit was 3.3×10^{-3} .

The total predicted values for $k(20^\circ\text{C})$ and the volatilization and sorption components, as well as the experimental values for $k(20^\circ\text{C})$, are given in

Table 18. Experimental and predicted values for the removal rate coefficient k on CRREL system using eq 16.

Substance	k (20°C)*			
	Experimental	Predicted†		
		Total	Volatilization	Sorption
Phenanthrene	0.077	0.046	0.001	0.045
Toluene**	0.070	0.067	0.020	0.047
Chlorobenzene**	0.064	0.062	0.016	0.046
Naphthalene	0.056	0.057	0.007	0.050
Dibromochloromethane	0.053	††	††	††
Pentachlorophenol	0.036	0.037	<0.001	0.037
PCB 1242	0.035	0.042	0.004	0.038
m-Nitrotoluene	0.030	0.034	0.002	0.032
Bromoform	0.032	0.027	0.007	0.020
Chloroform**	0.030	0.036	0.016	0.020
2,4-Dinitrophenol	0.019	0.008	< 0.001	0.008
Diethylphthalate	0.022	0.020	< 0.001	0.020
Nitrobenzene	0.018	0.017	<0.001	0.016

*Values obtained from best fit line or plot of individual experimental k values for various average water temperatures.

†Predictions from eq 15 and values in Table 17.

**Experimental values for these substances were obtained by averaging k values obtained from June-September.

††Data not available for prediction.

Table 18. The four substances not used to obtain the coefficients for this model were PCB, dibromochloromethane, phenanthrene and dinitrophenol. Dibromochloromethane could not be used since we did not find values of H and K_{ow} in the literature. The experimental value for PCB was not used since it was found to accumulate in fairly large amounts on the soil with time, so the back reaction (desorption) may be reducing the rate coefficient measured. The values of phenanthrene and dinitrophenol were used initially, but most of the residual sums of squares due to lack of fit in the original tests were for these substances. For phenanthrene the predicted value was much lower than measured, possibly because an additional mechanism was operating for this substance. For example, Mill et al. (1981) found that some polynuclear aromatics undergo rapid photolysis in water. This additional mechanism could account for the larger-than-predicted experimental rate coefficient for this substance. Dinitrophenol was also found to be removed much faster than predicted. This substance, however, is a fairly strong acid with a pK_a of 4.09. Thus, in neutral solution, it will exist predominantly in the dissociated form. Removal of this type of substance is not considered in this simple model, and hence it was not used to obtain the coefficients for eq 15.

In general the fit is excellent for most of the substances (Table 18). The low experimental values obtained for PCB may be a result of accumulation on the soil organic matter. The low experimental value for chloroform may be due to some additional production of chloroform on the slope, from reaction of residual chlorine or hypochlorite with organic matter, or from degradation of larger chlorinated organics on the slope. When the total predicted value from eq 15 is divided into its two components, sorption and volatilization, sorption predominates, even for the most volatile substances (Table 18). For toluene, the substance with the highest Henry's constant tested, 70% of the total predicted removal from solution is due to sorption and only 30% due to volatilization. Equation 15 predicts that chloroform has the highest percentage of its total removal rate due to volatilization (44%) of all of the substances tested. These results are contrary to the conclusion postulated in an earlier experiment where only very volatile substances were studied (Jenkins et al. 1981). However, the values in Table 18 refer only to direct loss from the moving solution. Subsequent volatilization of substances originally sorbed probably removes a significant amount of very volatile substances such as toluene and chloroform.

From eq 15 volatilization also accounts for greater than 9% of the predicted removal rate for chlorobenzene, bromoform, naphthalene and PCB. Direct volatilization from solution is predicted to be insignificant for the remaining substances, which all have H values less than 10^{-5} atmos·m³/mole.

Equation 15 also predicts a higher rate of sorption for naphthalene than for pentachlorophenol (PCP), even though the K_{ow} for PCP is over 50 times greater. This is due to naphthalene's much lower molecular weight, which increases its molecular diffusivity relative to PCP. In fact, naphthalene had a significantly higher experimental $k(20^{\circ}\text{C})$ value than PCP (Table 18).

Effect of temperature on removal rates

The model developed in the previous section (eq 15) described the rate of removal of an organic substance from solution as a function of the Henry's law constant, the octanol-water partition coefficient and the molecular weight. Changes in water temperature can be expected to affect this removal rate in several ways. The value of H strongly depends on temperature, as illustrated by toluene, which has an H of 5.15×10^{-3} atmos·m³/mole at 20°C but only 2.02×10^{-3} atmos·m³/mole at 0°C (Leighton and Calo 1981). Thus the magnitude of volatilization is expected to decrease as temperature declines.

Information on the magnitude of K_{ow} as a function of temperature is generally not available for these substances. Some preliminary information gathered in this laboratory indicates that K_{ow} may increase by as much as 50% in going from 20° to 0°C . This is a further indication that mass transport and/or biodegradation, rather than equilibrium, controls the removal rates, since rates decreased with temperature.

Both the volatilization and sorption terms were developed using the two-film theory of interphase transport. From Fick's Law, diffusion is proportional to molecular diffusivity D . The effect of temperature on values of diffusivity can be estimated from eq 16 (Thibodeaux 1979):

$$D @ T_2 = D @ T_1 \left(\frac{T_2 \mu_1}{T_1 \mu_2} \right) \quad (16)$$

where T_1 and T_2 are the various temperatures ($^{\circ}\text{K}$) and μ_1 and μ_2 are the values of viscosity of water as these temperatures. If we assume some value for diffusivity at 20°C , we can calculate the diffusivity at 2.5°C using eq 16 and thereby determine the relative change in the magnitude of diffusion one would expect. From this effect alone, the removal rate constant at 2.5°C should be only about 57% of that at 20°C .

Experimental removal rate coefficients were obtained at an average water temperature of 2.5°C on 2 December; these values and the $k(20^{\circ}\text{C})$ values are presented in Table 19. Values of $k(2.5^{\circ})$ were lower than $k(20^{\circ}\text{C})$ values for all substances tested, with the ratio of $k(2.5^{\circ})/k(20^{\circ})$ for chloroform, toluene and chlorobenzene were 0.70, 0.31 and 0.47, respectively. The mean value of these three substances is 0.49, a value comparable to that for the less volatile substances. Based on these results, eq 15 can be modified to predict removal rates at temperatures other than 20°C :

$$k @ T_2 = \left(\frac{T_2 \cdot 1.0019}{293 \cdot \mu_2} \right) \left\{ \left[\frac{B_1}{d \cdot M^{1/2}} \cdot \frac{H_2}{(H_2 + B_2)} \right] + \left[\frac{B_3}{d \cdot M^{1/2}} \cdot \frac{K_{ow}}{(K_{ow} + B_4)} \right] \right\} \quad (17)$$

Table 19. Comparison of experimental removal rate coefficients at 20° and 2.5°C .

Substance	Rate coefficients (min^{-1})		
	$k(20^{\circ}\text{C})$	$k(2.5^{\circ}\text{C})$	$k(2.5^{\circ})/k(20^{\circ})$
Phenanthrene	0.077	0.027	0.35
Toluene	0.070	0.022	0.31
Chlorobenzene	0.064	0.030	0.47
Naphthalene	0.056	0.029	0.52
Dibromochloromethane	0.053	0.021	0.40
Pentachlorophenol	0.036	0.027	0.75
m-Nitrotoluene	0.030	0.012	0.39
PCB 1242	0.035	0.013	0.37
Bromoform	0.032	0.016	0.50
Chloroform	0.030	0.021	0.70
2,4-Dinitrophenol	0.019	0.010	0.53
Diethylphthalate	0.022	0.006	0.27
Nitrobenzene	0.018	0.007	0.39

where T_2 , μ_2 and H_2 are the runoff temperature ($^{\circ}K$), viscosity at T_2 , and Henry's law constant at T_2 , respectively, and 293 and 1.0019 are the temperature and viscosity of water at $20^{\circ}C$.

Model validation using data from the Davis site

To test the relationships developed on the CRREL system, an experiment was conducted at the Davis, California, overland flow site on 10 December 1981. The average water depth on the Davis site was estimated at 2.3 cm by making a number of measurements at various locations. The average water temperature was $16.5^{\circ}C$ on the day of the study, and the average detention time was estimated to be 240 minutes. The detention time was harder to determine than at the CRREL site because of a much longer detention time and higher background chloride concentrations.

The predicted removal rate coefficients for the 13 substances studied at CRREL plus benzene are given in Table 20, along with experimental values. The values were predicted using eq 17 for a total slope detention time of 240 minutes and an estimated water depth of 2.3 cm. The viscosity of water at $16.5^{\circ}C$ was estimated to be $1.095 \text{ N}\cdot\text{s}/\text{m}$, and the Henry's law constants for toluene, benzene, chlorobenzene and chloroform were estimated at 4.42×10^{-3} , 3.71×10^{-3} , 2.32×10^{-3} and 2.66×10^{-3} atmos-m/mole, respectively, using the best-fit relationships developed by Leighton and Calo (1981). Values of H for the other substances were estimated to be 75% of their values at $20^{\circ}C$. Values of K_{ow} were assumed to be the same at $16.5^{\circ}C$ as for $20^{\circ}C$.

The experimental rate coefficients are quite similar to those predicted using eq 17 and the coefficients for B_1 , B_2 , B_3 and B_4 obtained on the CRREL system. As found at CRREL, the experimental values for phenanthrene, bromoform and 2,4-dinitrophenol are somewhat higher than predicted. All the other values are either the same or slightly lower than predicted, with the largest deviations found for the most volatile substances.

The low results for those substances that are predicted to volatilize may be because the water is much deeper at Davis than at CRREL. The increased water depth probably decreases the surface area of the air/water interface available for gas transfer, since much of this surface area in the shallower CRREL system seems to be associated with plant debris and surface irregularities, which are mostly submerged at the Davis system. Lower rates of volatilization may also be attributed to decreased turbulence associated with the longer detention time on the Davis system. The increased depth, on the other hand, should not significantly affect the surface area of the water/soil-organic-matter interface, and the actual rate coefficients for those substances predicted to be removed predominantly by sorption are close to the predicted rate coefficients.

Final removal processes

The kinetic relationships described above only represent removal from the moving solution. Volatilization is a terminal removal process, at least with respect to the overland flow system. The proportion of removal due to direct volatilization from

Table 20. Experimental versus predicted removal rate coefficients for the Davis site.

Substance	Rate coefficient (min^{-1}) at $16.5^{\circ}C$	
	Experimental	Predicted
Phenanthrene	0.031	0.022
Toluene	0.018	0.032
Chlorobenzene	0.018	0.029
Naphthalene	0.020	0.026
Dibromochloromethane	0.018	*
Benzene	0.015	0.024
Pentachlorophenol	0.013	0.018
m-Nitrotoluene	0.011	0.015
PCB 1242	0.020	0.020
Bromoform	0.017	0.012
Chloroform	0.012	0.017
2,4-Dinitrophenol	0.009	0.004
Diethylphthalate	0.003	0.009
Nitrobenzene	0.008	0.008

*Data not available.

solution, however, appears to be small, even for the most volatile substances (Table 18). Thus, the bulk of the initial removal from solution seems to be due to sorption.

Sorption, however, is not an infinite sink for these organics. In overland flow the solution comes in contact with only a relatively small surface area, because movement occurs rapidly with little penetration into the soil. Thus, if these substances accumulate on the surface with time, desorption may reduce the net removal rate. This may have been what happened with PCB. If these substances are applied long enough, removal should cease when the rate of desorption equals the rate of sorption.

To determine if these substances would accumulate with time, soil samples were collected periodically at the CRREL site. Except for PCB, and to a lesser degree PCP, the substances did not accumulate. For most of these substances, then, some additional removal mechanism or mechanisms must be operating once the substances are sorbed; the most likely mechanisms are biodegradation and volatilization from the soil surface. Because pentachlorophenol, which has a lower *H* than PCB, accumulated to a much lesser degree than PCB, processes other than volatilization must be removing some of the previously sorbed organics from the soil. In fact, of the twelve substances tested, eight had *H* values similar to or less than that of PCB, and none were found to accumulate significantly.

Biodegradation is difficult to model at these levels of trace organics. Biofilm models have been developed for treating primary substrates of bacterial metabolism (Williamson and McCarty 1976). Rubin et al. (1982) and Subba-Rao et al. (1982) found that the kinetics of mineralization, the extent of assimilation, and the sensitivity of mineralizing populations to several organic compounds (phenol, benzene, benzylamine, aniline and 2,4-dichlorophenoxy-late) are different at trace levels than at higher concentrations, both in freshwater and sewage. They found, for example, that the rate of phenol mineralization was a linear function of concentration at levels below 1 ppm, fell off between 1 and 100 ppm, and was again high at levels above 100 ppm. They attributed this to the activity of two kinds of organisms: oligotrophs, which are active at lower concentrations, and eutrophs, which are active at higher concentrations. Oligotrophic organisms are able to live under conditions of very low carbon flux (less than 1 ppm/day) and require a lower minimum substrate concentration than eutrophs, although their maximum growth rate is also lower (Kobayashi and Rittmann 1982). Rubin and his coworkers found from ¹⁴C labeling that these oligotrophs assimilated little or none of the carbon. This co-metabolic type

of metabolism may occur because oligotrophs frequently possess several inducible enzyme systems and are able to shift metabolic pathways and use mixed substrates (Kobayashi and Rittman 1982).

Because of the low concentrations of organics added to the wastewater in this study, degradation by oligotrophs seems plausible. Rubin et al. (1982) also found that mineralization was enhanced in waters with higher nutrient status. Specifically they found greater activity in sewage than in lake water. Finally oligotrophs apparently prefer an attached rather than a free-living existence and are usually found living in biofilms (Kobayashi and Rittmann 1982). All of these factors lend credence to the idea of biodegradation by organisms associated with the nutrient-rich organic layer covering the overland flow slope following initial sorption from the moving water.

A biofilm model, similar to that of Williamson and McCarty (1976), is analogous to the two-film approach adopted here, with the rate of metabolism high enough to assure essentially no background at some distance into the film. This assumption was possibly violated only for PCB in the present case. If biodegradation accounts for all the secondary removal observed following sorption, the maximum biodegradation rate coefficient would only have to be 0.0167 min⁻¹, or one-third of the maximum observed removal rate, because wastewater was only applied 8 hours per day.

Another possible secondary removal mechanism is plant uptake. Analysis of plant tops for PCB following wastewater application yielded the results shown in Table 16. None of the other trace organics added was found, with the possible exception of pentachlorophenol, which could not be determined because of analytical interferences. This was not surprising, since no detectable residues remained in the soil either.

Uptake and translocation of PCBs have also been observed in other plant-soil systems (Mrozek et al. 1982). However, the relative amounts translocated are apparently species-specific (Strek 1980), and negative results have also been reported (Davis et al. 1981). The preferential uptake of the PCB isomers with lower molecular weights (Mrozek et al. 1982) is expected because of their higher water solubility. In this study we observed enhancement of the heavier isomers, suggesting some metabolic alteration of the lighter isomers by the plants or soil (Strek 1980). However, the low rate of accumulation in the edible plant parts suggests that there is no problem with food chain transfer, since biomagnification factors (concentrations in plant tissue compared to concentration in water) were close to 1.

SUMMARY AND CONCLUSIONS

1. Overland flow was found to be an effective process for the removal of trace levels of a variety of organic priority pollutants from municipal wastewater. The extent of removal was found to be a function of the application rate or the average detention time of a wastewater on the overland flow slope.

2. The rate of removal of these substances from the moving solution followed first-order kinetics for all the substances tested, while the first-order rate coefficients obtained varied significantly from one substance to another.

3. The magnitudes of the rate coefficients obtained for 13 substances were consistent with two transport-limited, competing, first-order processes: sorption on soil organic matter and volatilization. Equations were developed for each process at 20°C using the two-film resistance theory and the coefficients obtained by multiple regression analysis using the experimental values from the CRREL system. The resulting model allows the prediction of removal rate coefficients for a specific organic substance using its molecular weight, its octanol-water partition coefficient and its Henry's law constant.

4. Of the 13 substances tested, PCB, and to a lesser extent pentachlorophenol, accumulated on the slope. Thus, if sorption accounts for most of the removal from solution, some additional mechanisms must be operating once these substances are sorbed on the soil surface. These mechanisms are thought to be biodegradation and volatilization.

5. Except for PCB, none of these organics was detectable in the grass collected from the site.

6. The removal rate coefficients depended on temperature. The model was extended to allow predictions at water temperatures other than 20°C.

7. The model developed with data from the CRREL system was tested at the Davis, California, municipal overland flow site. The experimental rate coefficients obtained for 13 substances were very similar to those predicted.

LITERATURE CITED

Abrams, E.F., D. Derkies, C.V. Fong, D.K. Guinan and K.M. Slimak (1975) Identification of organic compounds in effluents from industrial sources. Environmental Protection Agency 560/3-75-002.
Alexander, M. (1973) Nonbiodegradable and other recalcitrant molecules. *Biotechnology and Bioengineering*, 15: 611-647.
Anthony, R.M. and L.H. Breimhurst (1981) Determining maximum influent concentrations of priority

pollutants for treatment plants. *Journal of Water Pollution Control Federation*, 53: 1457-1568.

Bouwer, E.J., P.L. McCarty and J.C. Lance (1981a) Trace organic behavior in soil columns during rapid infiltration of secondary wastewater. *Water Research*, 15: 151-159.

Bouwer, E.J., B.E. Rittmann and P.L. McCarty (1981b) Anaerobic degradation of halogenated 1- and 2-carbon organic compounds. *Environmental Science and Technology*, 15: 596-599.

Budde, W.L. and J.W. Eichelberger (1979) Organics in the environment. *Environmental Science and Technology*, 51: 567A-574A.

Davis, T.S., J.L. Pyle, J.H. Shillings and N.D.

Danielson (1981) Uptake of polychlorobiphenyls present in trace amounts from dried municipal sewage sludge through an old field ecosystem. *Bulletin of Environmental Contamination and Toxicology*, 27: 689-694.

Delaune, R.D., G.A. Hambrick III and W.H. Patrick, Jr. (1980) Degradation of hydrocarbons in oxidized and reduced sediments. *Marine Pollution Bulletin*, 11: 103-106.

Demirjian, Y.A. (1979) Muskegan County's solution of biological wastewater treatment and irrigation. In *Proceedings of International Symposium, Braunschweig Sewage Utility Association, 27-29 September*, pp. 71-94.

Dilling, W.L. (1977) Interphase transfer processes. II. Evaporation of chloro methanes, ethanes, ethylenes, propanes, and propylenes from dilute aqueous solutions. Comparisons with theoretical predictions. *Environmental Science and Technology*, 11: 405-409.

Environmental Protection Agency (1981) Process design manual for land treatment of municipal wastewater. EPA 625/1-81-013. COE EM 1110-1-501.

Evans, K.J., I.G. Mitchell and B. Salau (1979) Heavy metal accumulation in soils irrigated by sewage and effect in plant-animal system. *Progress in Water Technology*, 11: 339-352.

Hansch, C. and A. Leo (1979) *Substituent Constants for Correlation Analysis in Chemistry and Biology*. New York: John Wiley and Sons.

Hathaway, S.W. (1980) Sources of toxic components in household wastewater. Environmental Protection Agency 600/2-80-128.

Herbes, S.E. (1981) Rate of microbial transformation of polycyclic aromatic hydrocarbons in water and sediments in the vicinity of coal-coking wastewater discharge. *Applied and Environmental Microbiology*, 41: 20-28.

Herbes, S.E. and L.R. Schwall (1978) Microbial transformation of polycyclic aromatic hydrocarbons in pristine and petroleum-contaminated sediments. *Applied and Environmental Microbiology*, 35: 306-316.

- Hoeppel, R.E., P.G. Hunt and T.B. Delaney** (1974) Wastewater treatment on soils of low permeability. Miscellaneous Paper Y-74-2, U.S. Army Corps of Engineers Waterways Experiment Station, Vicksburg, Mississippi.
- 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., C.J. Martel, D.A. Gaskin, D.J. Fisk and H.L. McKim** (1978) Performance of overland flow land treatment in cold climates. In *Proceedings of the International Symposium on State of Knowledge in Land Treatment of Wastewater, August 1978, Hanover, New Hampshire*, Vol. 2. CRREL, pp. 61-70.
- Jenkins, T.F., D.C. Leggett, C.J. Martel and H.E. Hare** (1981) Overland flow: Removal of toxic volatile organics. CRREL Special Report 81-1.
- Karickhoff, S.W.** (1981) Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere*, **10**: 833-846.
- Karickhoff, S.W., D.S. Brown and T.A. Scott** (1979) Sorption of hydrophobic pollutants on natural sediments. *Water Research*, **13**: 241-248.
- Kobayashi, H. and B.E. Rittmann** (1982) Microbial removal of hazardous organic compounds. *Environmental Science and Technology*, **16**: 170A-183A.
- Lambert, S.M., P.E. Porter and R.H. Schieferstein** (1965) Movement and sorption of chemicals applied to the soil. *Weeds*, **13**: 185-190.
- Leighton, D.T. and J.M. Calo** (1981) Distribution constants of chlorinated hydrocarbons in dilute air-water systems for groundwater contamination applications. *Journal of Chemical and Engineering Data*, **26**: 382-385.
- Levenspiel, O.** (1972) *Chemical Reaction Engineering*. New York: John Wiley and Sons.
- Liss, P.S. and P.G. Slater** (1974) Flux of gases across the air-sea interface. *Nature*, **274**: 181-184.
- Liu, D., K. Thomson and W.M.J. Strachan** (1981) Biodegradation of pentachlorophenol in a simulated aquatic environment. *Bulletin of Environmental Contamination and Toxicology*, **26**: 85-90.
- Mackay, D., W.Y. Shiu and R.P. Sutherland** (1979) Determination of air-water Henry's law constants for hydrophobic pollutants. *Environmental Science and Technology*, **13**(3): 333-337.
- Martel, C.J., T.F. Jenkins and A.J. Palazzo** (1980) Wastewater treatment in cold regions by overland flow. CRREL Report 80-7.
- Martel, C.J., T.F. Jenkins, C.J. Diener and P.L. Butler** (1982) Development of a rational design procedure for overland flow systems. CRREL Report 82-2.
- McCarty, P.L.** (1980) Organics in water - An engineering challenge. *Journal of the Environmental Engineering Division, ASCE*, **106**(EE1): 1-17.
- McCarty, P.L., M. Reinhard and B.E. Rittmann** (1981) Trace organics in groundwater. *Journal of Environmental Science and Technology*, **15**: 40-51.
- McCormick, N.G., J.H. Cornell and A.M. Kaplan** (1981) Biodegradation of hexahydro-1,3,5-trimethyl-1,3,5-triazine. *Applied and Environmental Microbiology*, **42**: 817-823.
- McDuffie, B.** (1981) Estimation of octanol/water partition coefficients for organic pollutants using reverse-phase HPLC. *Chemosphere*, **10**(1): 73-83.
- McPherson, J.B.** (1979) Land treatment of wastewater at Werrabee: Past, Present and Future. *Progress in Water Technology*, **11**: 15-32.
- Menzel, D.W. and R.F. Vaccaro** (1964) The measurement of dissolved organic and particulate carbon in seawater. *Limnology and Oceanography*, **9**: 138-142.
- Mil, T., W.R. Makey, B.Y. Lan and A. Barze** (1981) Photolysis of polycyclic aromatic hydrocarbons in water. *Chemosphere*, **10**: 1281-1290.
- Mrozek, E., E.D. Seneca and L.L. Hobbs** (1982) Polychlorinated biphenyl uptake and translocation by *Spartina alterniflora* Loisel. *Water, Air and Soil Pollution*, **17**: 3-15.
- Palazzo, A.J.** (1982) Vegetation selection and management for overland flow systems. CRREL Report 82-5.
- Paris, D.F., W.C. Steen, G.L. Baughman and J.T. Barnett** (1981) Second-order model to predict microbial degradation of organic compounds in natural waters. *Applied and Environmental Microbiology*, **41**: 603-609.
- Peters, R.E., C.R. Lee and D.J. Bates** (1981) Field investigations of overland flow treatment of municipal lagoon effluent. Technical Report EL-81-9, U.S. Army Corps of Engineers Waterways Experiment Station, Vicksburg, Mississippi.
- Rathbun, R.E. and D.Y. Tai** (1981) Technique for determining the volatilization coefficients of priority pollutants in streams. *Water Research*, **15**: 243-250.
- Rebhun, M. and J. Manka** (1971) Classification of organics in secondary effluents. *Journal of Environmental Science and Technology*, **5**: 606-609.
- Rhodes, J.W. and C.P. Nulton** (1980) Priority pollutant analyses of industrial wastewaters using a micro extraction approach. *Journal of Environmental Science and Health*, **A15**: 467-484.
- Roberts, P.B., P.L. McCarty, M. Reinhard and J. Schriener** (1980) Organic contaminant behavior during groundwater recharge. *Journal of Water Pollution Control Federation*, **53**: 161-172.

- Rubin, H.E., R.V. Subba-Rao and M. Alexander** (1982) Rates of mineralization of trace concentrations of aromatic compounds in lake water and sewage samples. *Applied and Environmental Microbiology*, 43: 1133-1138.
- Safe, S. and O. Hutzinger** (1973) *Mass Spectrometry of Pesticides and Pollutants*. Boca Raton, Florida: CRC Press.
- Schwarzenbach, R.P. and J. Westall** (1981) Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. *Environmental Science and Technology*, 15: 1360-1367.
- Sherrill, T.W. and G.S. Saylor** (1980) Phenanthrene biodegradation in fresh water environments. *Applied and Environmental Microbiology*, 39: 172-178.
- Smith, J.H., D.C. Bomberger and D.L. Haynes** (1981) Volatilization rates of intermediate and low volatility chemicals from water. *Chemosphere*, 10: 281-289.
- Strek, H.J.** (1980) Factors affecting the bioavailability of polychlorinated biphenyls in soils. M.S. thesis, North Carolina State University, Raleigh. Office of Water Research and Technology Report No. OWRT-B-122-NC.
- Subba-Rao, R.V., H.E. Rubin and M. Alexander** (1982) Kinetics and extent of mineralization of organic chemicals at trace levels in freshwater and sewage. *Applied and Environmental Microbiology*, 43: 1139-1150.
- Thibodeaux, L.J.** (1979) *Chemodynamics*. New York: John Wiley and Sons.
- Thomas, R.E., K. Jackson and L. Penrod** (1974) Feasibility of overland flow for treatment of raw domestic wastewater. EPA 660/2-74-087. R.S. Kerr, Environmental Research Center, Ada, Oklahoma.
- Thomas, R.E., B. Bedsoe and K. Jackson** (1976) Overland flow treatment of raw wastewater with enhanced phosphorus removal. EPA 600/2-76-131. R.S. Kerr Environmental Research Laboratory, Ada, Oklahoma.
- Tomson, M.B., J. Dauchy, S. Hutchins, C. Curran, C.J. Cook and C.H. Ward** (1981) Groundwater contamination by trace level organics from a rapid infiltration site. *Water Research*, 15: 1109-1115.
- Veith, G.D., N.M. Austin and R.T. Morris** (1974) A rapid method for estimating log P for organic chemicals. *Water Research*, 13: 43.
- Westcott, J.W., C.G. Simon and T.F. Bidleman** (1981) Determination of polychlorinated biphenyl vapor pressure by a semimicro gas saturation method. *Environmental Science and Technology*, 15: 1375.
- Whitman, W.G.** (1923) A preliminary experimental confirmation of the two-film theory of gas absorption. *Chemical and Metallurgical Engineering*, 29: 146-148.
- Williamson, K. and P.L. McCarty** (1976) A model of substrate utilization by bacterial films. *Journal of the Water Pollution Control Federation*, 48: 9-24.
- Wilson, J.T., C.G. Enfield, W.J. Dunlap, R.L. Crosby, D.A. Foster and L.B. Baskin** (1981) Transport and fate of selected organic pollutants in a sandy soil. *Journal of Environmental Quality*, 10: 501-506.

APPENDIX A. EXPERIMENTAL OVERLAND FLOW DATA, HANOVER.

Table A1. Results for 23 June 1981 through 10 December 1981.

The types of analysis are: a) purge and trap GC/MS/SIM, b) solvent extraction (pH 12) GC/ECD, c) solvent extraction (pH 12) HPLC/UV, d) solvent extraction (pH 2) GC/ECD. The concentration data are for the indicated fractions of the distance down the slope.

EXPERIMENT: OVERLAND FLOW - SLOPE B
 DATE: 23 JUNE 1981
 APPLICATION RATE: 6 (L/min) 0.4 (cm/hr) 0.124 (cm³/hr-c of width)
 AIR TEMPERATURE:
 WEATHER: Partly sunny breezy; rain night before

SUBSTANCE	TYPE OF ANAL	APP	CONCENTRATION			RUNOFF
			1/8	1/2	3/4	
Chloroform (ng/L)	a					
Toluene (ng/L)	a					
Chlorobenzene (ng/L)	a					
Benzene (ng/L)	a					
Tricloro (ng/L)	a					
Hexachloro (ng/L)	a					
2-Chloroethylvinyl ether (ng/L)	b					
Unknown (ng/L)	b					
Dibromochloroethane (ng/L)	b					
Nitrobenzene (ng/L)	b					
m-Nitrotoluene (ng/L)	b	27.7	16.6	9.6	2.6	<d
Dibethylphthalate (ng/L)	b					
PCB 1262 (ng/L)	b	39.5	20.9	14.1	4.1	<d
Naphthalene (ng/L)	c	52.2	28.6	18.5	4.8	<d
Phenanthrene (ng/L)	c	43.5	16.9	8.8	0.0	<d
Fluorophenol (ng/L)	d					
Pentachlorophenol (ng/L)	d					
Total-N (ug/L)		26.5		19.7		
400 (ug/L)						
TCC (ug/L)						
F ¹⁵ (ug/L)		111		29		2
V ¹⁸ (ug/L)		95		14		2
OH (pm units)						
Time (minutes)		7	10.6	21.2	42.5	89
Temperature (C)		16	20.0	22	20	22
Depth (Ave-cm)			0.7	0.6	0.5	
Volume (L)		107				107
Steady State Rate (L/min)						

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EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 25 JUNE 1981

APPLICATION RATE: 6 (l/min) 0.4 (cm/hr) 0.124 (cm³/hr-c of width)

AIR TEMPERATURE: 22 C

WEATHER: Cloudy, no wind, drizzle

SUBSTANCE	TYPE OF ANAL	APP	1/8	CONCENTRATION			RUNOFF
				1/4	1/2	3/4	
Chloroform (ng/l)	a						
Toluene (ng/l)	a						
Chlorobenzene (ng/l)	a						
Benzene (ng/l)	a						
Bromoform (ng/l)	a						
Bromoform (ng/l)	b						
2-Chloroethylvinyl ether (ng/l)	b						
Unknown (ng/l)	b						
Dibromochloroethane (ng/l)	b						
Nitrobenzene (ng/l)	b						
m-Nitrotoluene (ng/l)	b		57.3	43.2	33.0	16.1	
Diethylphthalate (ng/l)	b		50.8	52.9	41.1	35.5	7.1
PCB 1242 (ng/l)	b		56.7	52.5	33.2	15.5	2.8
Naphthalene (ng/l)	c		61.1	40.3	19.7		cd
Phenanthrene (ng/l)	c		51.8	44.1	18.8		0.3
Dinitrophenol (ng/l)	d						
Pentachlorophenol (ng/l)	d						
Total-N (ng/l)			27.5	26.6	24.5	15.7	4.1
TSS (mg/l)							
FOC (mg/l)							
VSS (mg/l)		100	88	21	8		3
VSS (mg/l)		40	72	10	4		3
pH (pH units)							
Time (minutes)		0.1	10.6	21.2	42.5		8 ^h
Temperature (C)		18	18	17	16		25
Depth (ave-cm)			1.1	1.5	2.4		
Volume (l)		25.7					10.3
Steady State Rate (l/min)							

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 30 JUNE 1981

APPLICATION RATE: 6 (l/min) 0.4 (cm/hr) 0.124 (cm³/hr-c of width)

AIR TEMPERATURE: 25 C

WEATHER: Sunny, light breeze, no rain for several days

SUBSTANCE	TYPE OF ANAL	APP	1/8	CONCENTRATION			RUNOFF
				1/4	1/2	3/4	
Chloroform (ng/l)	a						
Toluene (ng/l)	a						
Chlorobenzene (ng/l)	a						
Benzene (ng/l)	a						
Bromoform (ng/l)	a						
Bromoform (ng/l)	b						
Dibromochloroethane (ng/l)	b		6.7	5.4	1.9	0.34	cd
Nitrobenzene (ng/l)	b						
m-Nitrotoluene (ng/l)	b		51.3	31.8	35.7	5.2	1.0
Diethylphthalate (ng/l)	b						
PCB 1242 (ng/l)	b		48.9	37.6	24.9	4.5	0.4
Naphthalene (ng/l)	c		76.8	52.8	24.8		cd
Phenanthrene (ng/l)	c		58.7	38.5	19.8	0.4	
Dinitrophenol (ng/l)	d		105	71.2	71.2	23.7	7.7
Pentachlorophenol (ng/l)	d		42.2	32.4	30.7	5.0	1.5
Total-N (ng/l)			26.9	20.9	21.4	14.1	4.5
TSS (mg/l)							
FOC (mg/l)							
VSS (mg/l)		92	30	23	5		7
VSS (mg/l)		79	27	20	5		7
pH (pH units)							
Time (minutes)		0.0	14.3	29.4	54.5		11 ^h
Temperature (C)		17	19	22	25		24
Depth (ave-cm)			1.3	1.6	2.4		
Volume (l)		25.7					10.3
Steady State Rate (l/min)							

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 2 July 1981

APPLICATION RATE: 6 (L/min) 0.4 (cm/hr) 0.12% (area/hr-m of width)

AIR TEMPERATURE: 27 C

WEATHER: Partly sunny, breezy

SUBSTANCE	TYPE OF ANAL	APP	CONCENTRATION				RUNOFF
			1/A	1/B	1/C	1/D	
Chloroform (ng/L)	a						
Toluene (ng/L)	a						
Chlorobenzene (ng/L)	a						
Benzene (ng/L)	a						
Bromoform (ng/L)	a						
Bromoform (ng/L)	b		24.7	15.0	15.6	2.5	0.57
Dibromochloroethane (ng/L)	b						
Nitrobenzene (ng/L)	b						
m-Nitrotoluene (ng/L)	b		21.4	13.1	11.9	2.2	0.5
Diethylphthalate (ng/L)	b		28.7	24.4	21.9	5.7	2.1
PCB 1242 (ng/L)	b		28.1	18.9	14.0	6.7	CD
Naphthalene (ng/L)	c						
Phenanthrene (ng/L)	c						
Dinitrophenol (ng/L)	d		60.5	45.6		17.6	3.8
Pentachlorophenol (ng/L)	d		33.1	30.3		1.6	1.5
Total-N (ng/L)							
BOD (mg/L)							
TOC (mg/L)							
TSS (mg/L)			86	42	32	9	5
VSS (mg/L)			75	36	29	8	3
VSS (mg/L)			7.3	7.2	7.2	7.0	7.0
pH (pH units)			8.0	14.9	29.8	59.5	119
Time (minutes)			18	20	23	26	27
Temperature (C)				1.7	1.6	1.0	
Depth (Ave-cm)							1245
Volume (L)			2835				
Steady State Rate (L/min)							

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 7 July 1981

APPLICATION RATE: 6 (L/min) 0.4 (cm/hr) 0.12% (area/hr-m of width)

AIR TEMPERATURE: 29 C

WEATHER: Sunny, breezy

SUBSTANCE	TYPE OF ANAL	APP	CONCENTRATION				RUNOFF
			1/A	1/B	1/C	1/D	
Chloroform (ng/L)	a						
Toluene (ng/L)	a						
Chlorobenzene (ng/L)	a						
Benzene (ng/L)	a						
Bromoform (ng/L)	a						
Bromoform (ng/L)	b		26.3		9.2	0.69	2.43
Dibromochloroethane (ng/L)	b						
Nitrobenzene (ng/L)	b						
m-Nitrotoluene (ng/L)	b		24.0	12.7	9.1	0.7	0.4
Diethylphthalate (ng/L)	b		37.1	40.3	28.3	5.3	1.5
PCB 1242 (ng/L)	b		29.9	25.9	12.9	5.3	CD
Naphthalene (ng/L)	a		36.7	21.2	8.6	0.6	CD
Phenanthrene (ng/L)	c		34.0	15.8	6.4	0.3	CD
Dinitrophenol (ng/L)	d						
Pentachlorophenol (ng/L)	d						
Total-N (ng/L)			24.8	19.1	18.8	10.8	3.4
BOD (mg/L)							
TOC (mg/L)							
TSS (mg/L)			108	41	26	10	2
VSS (mg/L)			91	37	24	9	
VSS (mg/L)			7.3	7.5	7.5	7.3	7.7
pH (pH units)			8.0	14.9	29.8	59.5	119
Time (minutes)			19	21	23	26	26
Temperature (C)				1.2	2.0	1.2	
Depth (Ave-cm)							1846
Volume (L)			2340				
Steady State Rate (L/min)			6				3.5

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 9 July 1981

APPLICATION RATE: 6 (l/min) 0.4 (cm/hr) 0.124 (cm³/hr-cm of width)

AIR TEMPERATURE: 32 C

WEATHER: Sunny slight breeze

SUBSTANCE	TYPE OF ANAL	APP	1/A	CONCENTRATION		3/A	RUNOFF
				1/A	1/2		
Chloroform (ng/L)	a						
Toluene (ng/L)	a						
Chlorobenzene (ng/L)	a						
Benzene (ng/L)	a						
Bromoform (ng/L)	a						
Bromoform (ng/L)	b	26.0	32.3	29.9	1.0		0.47
Bromochloroethane (ng/L)	b						
Nitrobenzene (ng/L)	b						
m-Nitrotoluene (ng/L)	b	43.2	16.4	15.1	1.0		<d
Methylparathion (ng/L)	b	12.0	41.9	41.2	9.4		<d
PCN 1242 (ng/L)	b	47.7	15.0	11.7	2.5		<d
Naphthalene (ng/L)	c	149.4	67.0	50.3	6.7		<d
Phenanthrene (ng/L)	c	11.4	22.9	14.7	1.6		<d
1-Nitrophenol (ng/L)	c	11.8	44.7	51.5	17.3		6.4
Pentachlorophenol (ng/L)	c	10.0	44.0	27.0	3.0		0.5
Total-N (ng/L)		17.0	19.7	20.6			4.0
TCF (ng/L)							
TSC (ng/L)							
TSS (ng/L)			41	23	11		3
TDS (ng/L)			34	35	21		3
PM (µm units)			7.5	7.3	7.3		7.4
Time (minutes)			6.0	14.3	29.8	59.5	119
Temperature (C)			21	23	24	27	29
Depth (Ave-cm)				1.0	1.2	1.1	
Volume (l)			2700				819
Steady State Rate (l/min)							

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 14 July 1981

APPLICATION RATE: 6 (l/min) 0.4 (cm/hr) 0.124 (cm³/hr-cm of width)

AIR TEMPERATURE: 18 C

WEATHER: Cloudy very windy; rain yesterday and today

SUBSTANCE	TYPE OF ANAL	APP	1/A	CONCENTRATION		3/A	RUNOFF
				1/A	1/2		
Chloroform (ng/L)	a	32.7	15.0	13.5	7.5		2.0
Toluene (ng/L)	a	16.9	12.0	10.6	<d		<d
Chlorobenzene (ng/L)	a	26.5	10.8	8.8	3.0		<d
Benzene (ng/L)	a						
Bromoform (ng/L)	a						
Bromoform (ng/L)	b	5016	21.3	14.0			0.53
Bromochloroethane (ng/L)	b						
Nitrobenzene (ng/L)	b						
m-Nitrotoluene (ng/L)	b	50.9	21.4	14.0			<d
Methylparathion (ng/L)	b	40.6	29.3	26.1			1.6
PCN 1242 (ng/L)	b	35.3	19.3	14.7			<d
Naphthalene (ng/L)	c						
Phenanthrene (ng/L)	c						
1-Nitrophenol (ng/L)	c						
Pentachlorophenol (ng/L)	c	17.1	24.7	23.2	8.5		0.5
Total-N (ng/L)		24.1	21.5	21.6	10.9		4.4
TCF (ng/L)							
TSC (ng/L)							
TSS (ng/L)			107	67	58	6	2
TDS (ng/L)			85	58	52	6	2
PM (µm units)			7.4	7.5	7.4	7.4	7.3
Time (minutes)			6.0	14.3	29.8	59.5	119
Temperature (C)			18	18	18	19	19
Depth (Ave-cm)				2.1	1.2	0.3	
Volume (l)			2881				1801
Steady State Rate (l/min)			6				4.5

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 16 July 1981

APPLICATION RATE: 6 (l/min) 0.4 (cm/hr) 0.124 (cm³/hr-m of width)

AIR TEMPERATURE: 26 C

WEATHER: Sunny, breeze dry

SUBSTANCE	TYPE OF ANAL	APP	1/8	CONCENTRATION		3/8	RUNOFF
				1/8	1/2		
Chloroform (ng/L)	a		41.6	30.0	29.5	11.0	2.9
Toluene (ng/L)	a		63.5	51.8	35.4	11.4	1.5
Chlorobenzene (ng/L)	a		55.9	35.2	26.8	11.4	1.2
Benzene (ng/L)	a						
Bromoform (ng/L)	a		57.5	39.6	31.1	17.1	2.5
Bromoform (ng/L)	u						
Dibromochloromethane (ng/L)	b						
Nitrobenzene (ng/L)	b						
m-Nitrotoluene (ng/L)	b						
Diethylphthalate (ng/L)	b						
PCB 1242 (ng/L)	b						
Naphthalene (ng/L)	c						
Phenanthrene (ng/L)	c						
Dinitrophenol (ng/L)	d						
Pentachlorophenol (ng/L)	d						
Total-N (mg/L)							
BOD (mg/L)							
TOC (mg/L)							
TSS (mg/L)			247				4
VSS (mg/L)			162				7
pH (pH units)							
Time (minutes)			0.0	14.9	29.4	54.5	111
Temperature (C)				19	19	21	21
Depth (Ave-cm)				1.2	1.3	1.5	
Volume (L)			1520				429
Steady State Rate (l/min)			6				5.0

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 21 July 1981

APPLICATION RATE: 6 (l/min) 0.4 (cm/hr) 0.124 (cm³/hr-m of width)

AIR TEMPERATURE: 29 C

WEATHER: Humid, breezy, partly sunny, rain yesterday

SUBSTANCE	TYPE OF ANAL	APP	1/8	CONCENTRATION		3/8	RUNOFF
				1/8	1/2		
Chloroform (ng/L)	a		58.1	22.8	16.3	3.9	3.9
Toluene (ng/L)	a						
Chlorobenzene (ng/L)	a		109.5	23.0	16.4	2.2	0.5
Benzene (ng/L)	a						
Bromoform (ng/L)	a		98.7	34.7	29.1	8.2	3.8
Bromoform (ng/L)	b						
Dibromochloromethane (ng/L)	b						
Nitrobenzene (ng/L)	b						
m-Nitrotoluene (ng/L)	b						
Diethylphthalate (ng/L)	b						
PCB 1242 (ng/L)	b						
Naphthalene (ng/L)	c						
Phenanthrene (ng/L)	c						
Dinitrophenol (ng/L)	d						
Pentachlorophenol (ng/L)	d						
Total-N (mg/L)							
BOD (mg/L)							
TOC (mg/L)							
TSS (mg/L)							
VSS (mg/L)							
pH (pH units)							
Time (minutes)			0.0	14.9	29.8	59.5	119
Temperature (C)				19	20	21	21
Depth (Ave-cm)				1.7	1.5	1.3	
Volume (L)			2340				1986
Steady State Rate (l/min)			6				3.7

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 23 July 1981

APPLICATION RATE: 6 (l/min) 0.4 (cm/hr)

0.124 (mm³/hr-cm of width)

AIR TEMPERATURE: 23 C

WEATHER: Dry, partly sunny, very windy

SUBSTANCE	TYPE OF ANAL	APP	1/8	CONCENTRATION		3/4	RUNOFF
				1/4	1/2		
Chloroform (ng/L)	a	17.1	9.5	6.8	1.6		1.2
Toluene (ng/L)	a	9.9	3.3	2.4	<d		<d
Chlorobenzene (ng/L)	a	22.7	12.2	9.4	0.2		<d
Benzene (ng/L)	a						
Bromoform (ng/L)	a						
Bromoform (ng/L)	b	49.8	27.5	27.3	11.3		
Dibromochloromethane (ng/L)	b						
Nitrobenzene (ng/L)	b						
m-Nitrotoluene (ng/L)	b	49.2	27.2	27.0	11.2		<d
Diethylphthalate (ng/L)	b	46.1	41.2	36.1	17.4		
PCB 1242 (ng/L)	b	36.4	25.3	24.3	14.4		
Naphthalene (ng/L)	c						
Phenanthrene (ng/L)	c						
Dinitrophenol (ng/L)	d	128	102		57.9		39.9
Pentachlorophenol (ng/L)	d	13.4	11.8		1.6		0.5
Total-N (ng/L)		26.3	17.3	20.0	11.7	6.4	5.4
BOD (mg/L)							
TOC (mg/L)		81.7	56.1	50.7	50.1	22.1	20.5
TSS (mg/L)		263	85		12		3
VSS (mg/L)		130	62		11		3
pH (pH units)							
Time (minutes)		0+0	14.9	29.8	59.5	89.3	119
Temperature (C)		18	18	18	18		20
Depth (Ave-cm)			2.0	0.7	0.8		
Volume (l)		2520					972
Steady State Rate (l/min)							

EXPERIMENT: OVERLAND FLOW - SLOPE A

DATE: 28 July 1981

APPLICATION RATE: 6 (l/min) 0.4 (cm/hr)

0.124 (mm³/hr-cm of width)

AIR TEMPERATURE:

WEATHER:

SUBSTANCE	TYPE OF ANAL	APP	1/8	CONCENTRATION		3/4	RUNOFF
				1/4	1/2		
Chloroform (ng/L)	a	20.3	6.8	5.8	3.9		1.5
Toluene (ng/L)	a	13.9	4.1	2.6	0.4		<d
Chlorobenzene (ng/L)	a	50.2	11.4	6.3	3.1		2.12
Benzene (ng/L)	a						
Bromoform (ng/L)	a	62.8	20.0	11.7	19.1		4.5
Bromoform (ng/L)	b						
Dibromochloromethane (ng/L)	b						
Nitrobenzene (ng/L)	b						
m-Nitrotoluene (ng/L)	b						
Diethylphthalate (ng/L)	b	68.0	61.2	49.3	38.3		15.2
PCB 1242 (ng/L)	b	48.8	24.4	21.9	22.4		5.5
Naphthalene (ng/L)	c		27.1	14.4	6.7		<d
Phenanthrene (ng/L)	c		10.7	5.5	2.6		<d
Dinitrophenol (ng/L)	d						
Pentachlorophenol (ng/L)	d						
Total-N (ng/L)		19.3	16.1	17.2	12.1	11.8	
BOD (mg/L)							
TOC (mg/L)		73.7	44.8	43.9	46.0	42.8	25.0
TSS (mg/L)		70	38	38			8
VSS (mg/L)							
pH (pH units)		6.9	7.1	6.9	7.0	7.3	6.9
Time (minutes)		8.8	7.5	15.8	38.0	45.0	60
Temperature (C)		18	18	18	19	19	20
Depth (Ave-cm)							
Volume (l)		2520					1848
Steady State Rate (l/min)		6					6.1

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 13 August 1981

APPLICATION RATE: 12 (l/min) 0.6 (cm/hr) 0.248 (m³/hr-m of width)

AIR TEMPERATURE: 20 C

WEATHER: Cloudy, slight breeze from south

SUBSTANCE	TYPE OF ANAL	APP	1/8	CONCENTRATION			RUNOFF
				1/4	1/2	3/4	
Chloroform (ng/L)	a						
Toluene (ng/L)	a						
Chlorobenzene (ng/L)	a						
Benzene (ng/L)	a						
Bromoform (ng/L)	a						
Bromoform (ng/L)	b	43.3	26.8	24.5	12.8		5.9
Dibromochloroethane (ng/L)	b						
Nitrobenzene (ng/L)	b						
m-Nitrotoluene (ng/L)	b	42.8	26.4	24.3	12.6		6.4
Diethylphthalate (ng/L)	b	40.7	33.7	29.5	14.6		15.6
PCB 1242 (ng/L)	b	68.8	47.0	34.4	15.2		7.1
Naphthalene (ng/L)	c	23.9	20.2	5.8	<0		<0
Phenanthrene (ng/L)	c	29.3	17.0	7.7	0.4		<0
Dinitrophenol (ng/L)	d						
Pentachlorophenol (ng/L)	d						
Total-N (mg/L)			21.3	21.0	18.5	10.3	10.5
BOD (mg/L)		113	81	70	42	29	17
TOC (mg/L)		82	66	48	39	37	28
TSS (mg/L)		79	35	26	12	4	6
VSS (mg/L)		60	32	23	11	7	5
pH (pH units)							
Time (minutes)		0.0	8.4	16.8	33.5	50.3	67
Temperature (C)		18	19	19	20	19	20
Depth (Ave-cm)			1.9	1.4	1.4	0.6	
Volume (l)		5213					3453
Steady State Rate (l/min)							

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 18 August 1981

APPLICATION RATE: 12 (l/min) 0.6 (cm/hr) 0.248 (m³/hr-m of width)

AIR TEMPERATURE:

WEATHER: Sunny, windy, dry

SUBSTANCE	TYPE OF ANAL	APP	1/8	CONCENTRATION			RUNOFF
				1/4	1/2	3/4	
Chloroform (ng/L)	b						
Toluene (ng/L)	a						
Chlorobenzene (ng/L)	a						
Benzene (ng/L)	a						
Bromoform (ng/L)	a						
Bromoform (ng/L)	b	28.4	12.3	15.1	9.2	7.7	5.5
Dibromochloroethane (ng/L)	b						
Nitrobenzene (ng/L)	b						
m-Nitrotoluene (ng/L)	b	28.2	12.1	14.9	9.1	7.6	5.4
Diethylphthalate (ng/L)	b	31.4	19.2	21.6	13.9	9.7	7.5
PCB 1242 (ng/L)	b	18.8	13.6	18.9	5.8	2.5	1.8
Naphthalene (ng/L)	c						
Phenanthrene (ng/L)	c						
Dinitrophenol (ng/L)	d						
Pentachlorophenol (ng/L)	d						
Total-N (mg/L)							
BOD (mg/L)							
TOC (mg/L)							
TSS (mg/L)		61	46	38	4		2
VSS (mg/L)		58	42	27	5		2
pH (pH units)							
Time (minutes)		0.0	8.4	16.8	33.5	50.3	67
Temperature (C)		17	18	18	19	19	20
Depth (Ave-cm)			2.2	1.4	0.8	1.1	
Volume (l)		5128					3076
Steady State Rate (l/min)		22					8.5

EXPERIMENT: OVERLAND FLOW - SLOPE F

DATE: 3 September 1981

APPLICATION RATE: 12 (L/min)

0.8 (cm/hr)

0.248 (cm³/hr-cm of width)

AIR TEMPERATURE: 20 C

WEATHER: Cloudy, slight breeze

SUBSTANCE	TYPE OF ANAL	APP	1/H	CONCENTRATION		3/A	RUNOFF
				1/A	1/B		
Chloroform (ng/L)	a	22.6		30.1	7.7		1.3
Toluene (ng/L)	a	4.4		1.5	<0		<0
Chlorobenzene (ng/L)	a	37.0		28.9	1.6 ²		0.15
Benzene (ng/L)	a						
Bromoform (ng/L)	a						
Bromoform (ng/L)	b	77.1	48.8	35.9	12.4		3.3
Dibromochloroethane (ng/L)	b	10.3	4.3	3.0	0.7 ²		0.3
Nitrobenzene (ng/L)	b						
m-Nitrotoluene (ng/L)	b	40.5	24.7	15.5	4.0		4.6
Diethylphthalate (ng/L)	b	80.5	58.5	55.5	11.2		7.1
PCB 1242 (ng/L)	b	58.0	63.5	16.7	8.4		1.2
Naphthalene (ng/L)	c	60.1	35.3	19.0	<0		<0
Phenanthrene (ng/L)	c	41.5	33.5	8.8	<0		<0
Dinitrophenol (ng/L)	d	101.6	71.0	30.0			15.5
Pentachlorophenol (ng/L)	d	55.3	26.2	7.4			1.4
Total-N (ng/L)							
BOD (ng/L)							
DOC (ng/L)							
TSS (ng/L)							
VSS (ng/L)							
pH (pH units)							
Time (minutes)		0.0	8.4	16.8	33.5	50.3	67
Temperature (C)		18	18	18	18	18	18
Depth (Ave-cm)			1.3	1.5	1.6	0.9	
Volume (L)		3600					3244
Steady State Rate (L/min)		12					8.7

EXPERIMENT: OVERLAND FLOW - SLOPE D

DATE: 24 September 1981

APPLICATION RATE: 12 (L/min)

1.8 (cm/hr)

0.298 (cm³/hr-cm of width)

AIR TEMPERATURE: 19 C

WEATHER: Cloudy, cool breeze, rain earlier

SUBSTANCE	TYPE OF ANAL	APP	1/B	CONCENTRATION		3/A	RUNOFF
				1/A	1/B		
Chloroform (ng/L)	a						
Toluene (ng/L)	a						
Chlorobenzene (ng/L)	a						
Benzene (ng/L)	a						
Bromoform (ng/L)	a						
Bromoform (ng/L)	b	63.7	49.5	38.3	17.2	9.2	7.2
2-Chloroethylvinyl ether (ng/L)	b						
Unknown (ng/L)	b						
Dibromochloroethane (ng/L)	b	8.5	6.8	6.3	1.4	0.67	0.42
Nitrobenzene (ng/L)	b						
m-Nitrotoluene (ng/L)	b	59.8	44.9	37.9	24.6	18.5	18.8
Diethylphthalate (ng/L)	b	74.9	78.4	78.1	53.9	37.7	33.7
PCB 1242 (ng/L)	b	45.3	48.4	28.5	19.8	7.7	7.5
Naphthalene (ng/L)	c	78.6	73.9	41.4	17.4	6.7	6.7
Phenanthrene (ng/L)	c	62.1	59.1	28.3	6.3	2.8	1.8
Dinitrophenol (ng/L)	d						
Pentachlorophenol (ng/L)	d						
Total-N (ng/L)							
BOD (ng/L)							
DOC (ng/L)							
TSS (ng/L)							
VSS (ng/L)							
pH (pH units)							
Time (minutes)		0.0	6.9	13.7	27.5	41.2	55
Temperature (C)		17	14.5	14	14	14	14
Depth (Ave-cm)			0.8	1.0	0.5	0.4	
Volume (L)		3600					2498
Steady State Rate (L/min)							

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EXPERIMENT: OVERLAND FLOW - SLOPE A

DATE: 29 September 1981

APPLICATION RATE: 6 (l/min) 2.7 (cm/hr) 0.248 (m³/hr-m of width)

AIR TEMPERATURE: 10 C

WEATHER: Breezy, windy, rain last night

SUBSTANCE	TYPE OF ANAL	APP	CONCENTRATION				RJVDF
			1/B	1/4	1/2	3/4	
Chloroform (ng/L)	a	24.1	14.2	10.1	4.9	4.2	2.7
Toluene (ng/L)	a	1.7	0.6	0.5	0.4	0.4	0.4
Chlorobenzene (ng/L)	a	74.5	32.0	19.9	5.5	1.4	0.53
Benzene (ng/L)	a						
Bromoform (ng/L)	a	101.7	61.1	44.8	21.5	15.5	12.5
Bromoform (ng/L)	b						
Dibromochloromethane (ng/L)	b	15.1	8.3	5.7	2.8	1.5	
Nitrobenzene (ng/L)	b						
m-Nitrotoluene (ng/L)	b	104	106	45.0	63.9	48.1	
Diethylphthalate (ng/L)	b	109	113	112	89.1	75.7	
PCB 1242 (ng/L)	b	50.2	56.0	28.8	20.0	16.8	
Naphthalene (ng/L)	c						
Phenanthrene (ng/L)	c						
Dinitrophenol (ng/L)	d						
Pentachlorophenol (ng/L)	d						
Total-N (ng/L)							
BOD (ng/L)							
TOC (ng/L)							
TSS (ng/L)							
VSS (ng/L)							
pH (pH units)							
Time (minutes)		0.3	5.75	11.5	23.0	34.5	46
Temperature (C)		16	14.5	14	12.5	12	12
Depth (Ave-cm)			1.8	0.7	1.0	0.6	
Volume (L)							
Steady State Rate (l/min)							

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 7 October 1981

APPLICATION RATE: 12 (l/min) 0.6 (cm/hr) 0.248 (m³/hr-m of width)

AIR TEMPERATURE: 13 C

WEATHER:

SUBSTANCE	TYPE OF ANAL	APP	CONCENTRATION				RJVDF
			1/B	1/4	1/2	3/4	
Chloroform (ng/L)	a						
Toluene (ng/L)	a						
Chlorobenzene (ng/L)	a						
Benzene (ng/L)	a						
Bromoform (ng/L)	a						
Bromoform (ng/L)	b						
Dibromochloromethane (ng/L)	b						
Nitrobenzene (ng/L)	b						
m-Nitrotoluene (ng/L)	b						
Diethylphthalate (ng/L)	b						
PCB 1242 (ng/L)	b						
Naphthalene (ng/L)	c						
Phenanthrene (ng/L)	c						
3-Nitrophenol (ng/L)	d						
Pentachlorophenol (ng/L)	d						
Total-N (ng/L)							
BOD (ng/L)							
TOC (ng/L)							
TSS (ng/L)							
VSS (ng/L)							
pH (pH units)							
Time (minutes)		0.0	8.4	16.8	33.5	50.2	67
Temperature (C)		14	15	14	14	12	12
Depth (Ave-cm)			2.5	1.2	1.1	1.2	
Volume (L)		2700					1841
Steady State Rate (l/min)		12					9.5

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 14 October 1991

APPLICATION RATE: 12 (l/min) 0.6 (cm/hr) 0.243 (cm³/hr-cm of width)

AIR TEMPERATURE: 13 C

WEATHER: Sunny cool

SUBSTANCE	TYPE OF ANAL	APP	CONCENTRATION			RUNOFF
			1/8	1/2	3/4	
Chloroform (ng/L)	a	51.5	62.1	44.4	32.3	
Toluene (ng/L)	a	19.0	11.4	6.1	2.1	
Chlorobenzene (ng/L)	a	102.5	76.3	57.9	26.5	
Benzene (ng/L)	a					
Bromoform (ng/L)	a					
Bromoform (ng/L)	a					
Bromoform (ng/L)	a					
Bromoform (ng/L)	a					
1,1-Dichloroethane (ng/L)	b	15.2	10.8	6.3	3.2	2.2
Nitrobenzene (ng/L)	b					
m-Nitrotoluene (ng/L)	b	42.2	40.7	43.3	36.5	32.0
Diethylthalate (ng/L)	b	52.9	48.6	47.7	43.5	33.8
PCB 1242 (ng/L)	b	20.6	14.7	17.6	14.5	4.5
Naphthalene (ng/L)	c					
Phenanthrene (ng/L)	c					
2-Nitrophenol (ng/L)	d	82.6		66.1	14.8	
Pentachlorophenol (ng/L)	d	15.9	10.5	9.9	4.4	1.4
Total-N (ug/L)						
TOD (ug/L)						
TSS (ug/L)						
VSS (ug/L)						
pH (pH units)						
Time (minutes)		0.0	8.4	16.8	33.5	50.3
Temperature (C)		15	15	15.5	14.5	14.5
Depth (Aver-age)			1.5	1.3	1.5	1.2
Volume (l)		2880				2307
Steady State Rate (l/min)		12				9.9

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 21 October 1991

APPLICATION RATE: 18 (l/min) 1.2 (cm/hr) 0.372 (cm³/hr-cm of width)

AIR TEMPERATURE: 9.4 C

WEATHER: Cloudy, cool, breeze from south

SUBSTANCE	TYPE OF ANAL	APP	CONCENTRATION			RUNOFF
			1/8	1/2	3/4	
Chloroform (ng/L)	a					
Toluene (ng/L)	a					
Chlorobenzene (ng/L)	a					
Benzene (ng/L)	a					
Bromoform (ng/L)	a					
Bromoform (ng/L)	a					
Bromoform (ng/L)	a					
1,1-Dichloroethane (ng/L)	b	61.6	41.3	45.7	29.1	20.7
2-Chloroethylvinyl ether (ng/L)	b	53.6	55.2	76.6	18.3	8.7
Unknown (ng/L)	b	1088	832	576	499	397
Dibromochloroethane (ng/L)	b	18.9	7.5	4.8	2.8	1.6
Nitrobenzene (ng/L)	b					
m-Nitrotoluene (ng/L)	b	56.0	59.2	38.2	26.3	22.5
Diethylthalate (ng/L)	b	86.3	183.1	79.8	69.3	68.3
PCB 1242 (ng/L)	b	21.4	24.7	13.6	8.2	7.3
Naphthalene (ng/L)	c	51.1	33.9	21.3	18.7	3.8
Phenanthrene (ng/L)	c	61.8	21.3	26.9	25.8	24.6
2-Nitrophenol (ng/L)	d					
Pentachlorophenol (ng/L)	d					
Total-N (ug/L)		9.4	8.4	7.8	7.5	6.4
TOD (ug/L)		76	69	43	33	19
TSS (ug/L)		28.6	28.1	21.5	21.6	18.6
VSS (ug/L)		66	49	17	17	7
VSS (ug/L)		57	42	15	15	7
pH (pH units)						
Time (minutes)		0.0	3.8	7.5	15.0	22.4
Temperature (C)		12.6	12.0	12.0	11.8	10.7
Depth (Aver-age)			1.5	1.4	1.4	1.4
Volume (l)		2251				9071
Steady State Rate (l/min)		18				38.7

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 21 October 1981

APPLICATION RATE: 6 (l/min) 1.4 (cm/hr) 0-124 (cm³/hr-m of width)

AIR TEMPERATURE: 11 C

WEATHER: Cloudy, rained last several days

SUBSTANCE	TYPE OF ANAL	APP	CONCENTRATION			RUNOFF
			1/A	1/B	1/C	
Chloroform (ng/L)	a					
Toluene (ng/L)	a					
Chlorobenzene (ng/L)	a					
Benzene (ng/L)	a					
Bromoform (ng/L)	a					
Bromoform (ng/L)	b	124.4	54.6	45.4	17.0	6.7
Dibromochloromethane (ng/L)	b	16.4	5.6	4.5	1.2	2.4
Nitrobenzene (ng/L)	b	31.0	2.4	2.2	1.7	75.1
m-Nitrotoluene (ng/L)	b	114.2	50.2	40.7	17.6	17.6
Diethylphthalate (ng/L)	b	35.1	22.4	25.3	1.2	40.1
PCB 1242 (ng/L)	b	15.0	35.1	31.5	1.0	5.0
Naphthalene (ng/L)	c	43.4	43.9	10.0		4.0
Phenanthrene (ng/L)	c	48.7	24.5	17.5		2.0
3-Nitrophenol (ng/L)	d	78.6	40.8		44.6	8.2
Pentachlorophenol (ng/L)	d	47.3	20.4		1.4	1.5
Total-N (ng/L)						
BOD (ng/L)						
TOC (ng/L)						
TSS (ng/L)						
VSS (ng/L)						
pH (pH units)						
Time (minutes)		0.0	13.5	27.0	54.0	108
Temperature (C)		13	11.6	11.2	9.6	8.2
Depth (Ave-cm)			1.3	1.1	1.0	0.8
Volume (l)		2550				1617
Steady State Rate (l/min)		6				4.9

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 3 November 1981

APPLICATION RATE: 6 (l/min) 0.6 (cm/hr) 0-124 (cm³/hr-m of width)

AIR TEMPERATURE: 11 C

WEATHER: Sunny

SUBSTANCE	TYPE OF ANAL	APP	CONCENTRATION			RUNOFF
			1/A	1/B	1/C	
Chloroform (ng/L)	a					
Toluene (ng/L)	a					
Chlorobenzene (ng/L)	a					
Benzene (ng/L)	a					
Bromoform (ng/L)	a					
Bromoform (ng/L)	b	63.8	34.6	21.6	12.3	6.1
Dibromochloromethane (ng/L)	b	8.5	3.9	2.8	0.87	0.44
Nitrobenzene (ng/L)	b	75	60.6	51.8	47.5	36.9
m-Nitrotoluene (ng/L)	b	49.4	40.5	30.9	26.8	17.5
Diethylphthalate (ng/L)	b	73.5	60.1	51.5	51.1	32.8
PCB 1242 (ng/L)	b	10.9	12.7	10.0	7.9	9.8
Naphthalene (ng/L)	c	32.1	14.8	11.9	3.8	1.4
Phenanthrene (ng/L)	c	29.2	9.6	4.8	1.7	0.8
3-Nitrophenol (ng/L)	d	47.9		37.5	23.9	22.4
Pentachlorophenol (ng/L)	d	14.0	14.1	7.6	4.8	2.2
Total-N (ng/L)						
BOD (ng/L)						
TOC (ng/L)						
TSS (ng/L)						
VSS (ng/L)						
pH (pH units)						
Time (minutes)		0.0	14.8	29.6	59.2	118
Temperature (C)		13	13	11.8	11	10.2
Depth (Ave-cm)			1.8	0.9	0.8	1.1
Volume (l)		2648				1379
Steady State Rate (l/min)		6				4.8

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 13 November 1981

APPLICATION RATE: 6 (l/min) 0.4 (cm/hr) 0.124 (cm³/hr-m of width)

AIR TEMPERATURE: 4 C

WEATHER:

SUBSTANCE	TYPE OF ANAL	APP	1/8	CONCENTRATION			RUNOFF
				1/4	1/2	3/4	
Chloroform (ng/L)	a						
Toluene (ng/L)	a						
Chlorobenzene (ng/L)	a						
Benzene (ng/L)	a						
Bromoform (ng/L)	a						
Bromoform (ng/L)	b	56.2	40.7	33.8	23.1	13.9	7.1
Dibromochloromethane (ng/L)	b	7.5	4.9	3.5	1.9	0.91	0.33
Nitrobenzene (ng/L)	b	98.3	48.2	44.3	44.5	41.2	33.0
o-Nitrotoluene (ng/L)	b	39.8	39.4	32.6	31.0	25.9	17.4
Diethylphthalate (ng/L)	b	75.6	61.4	54.9	41.8	31.4	22.4
PCB 1262 (ng/L)	b	19.6	18.4	6.2	3.4	3.0	2.4
Naphthalene (ng/L)	c	32.6	17.2	10.4	4.4	<d	<d
Phenanthrene (ng/L)	c	19.6	8.2	2.9	<d	<d	<d
Dinitrophenol (ng/L)	d						
Pentachlorophenol (ng/L)	d	36.1	23.4	21.0	21.0	14.3	
Total-H (ng/L)							
BOD (ng/L)		73	20	19	12	11	24
TOC (ng/L)		26.1	17.1	16.4	13.6	13.4	
TSS (ng/L)		4.9	13	11	7	7	4
VSS (ng/L)		41	11	10	6	6	7
pH (pH units)							
Time (minutes)		0.0	13.5	27.0	54.0	81.0	108
Temperature (C)		1	9	9	6	2.5	4
Depth (Ave-cm)			1.2	1.5	0.9	0.7	
Volume (L)		2279					1631
Steady State Rate (l/min)		6					5.0

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 24 November 1981

APPLICATION RATE: 6 (l/min) 0.4 (cm/hr) 0.124 (cm³/hr-m of width)

AIR TEMPERATURE: -1 C

WEATHER: Sunny, breezy

SUBSTANCE	TYPE OF ANAL	APP	1/8	CONCENTRATION			RUNOFF
				1/4	1/2	3/4	
Chloroform (ng/L)	a						
Toluene (ng/L)	a						
Chlorobenzene (ng/L)	a						
Benzene (ng/L)	a						
Bromoform (ng/L)	a						
Bromoform (ng/L)	b	99.6	58.2	52.9	22.2	28.3	9.7
Dibromochloromethane (ng/L)	b	13.2	6.8	5.9	2.8	1.7	0.62
Nitrobenzene (ng/L)	b	68.3	52.2	49.5	39.3	35.8	24.2
o-Nitrotoluene (ng/L)	b	48.3	38.5	34.5	23.5	20.0	10.3
Diethylphthalate (ng/L)	b	69.3	61.4	57.7	46.7	41.2	27.9
PCB 1262 (ng/L)	b	25.4	14.7	6.9	5.8	4.6	7.2
Naphthalene (ng/L)	c	64.1	24.2	19.8	5.7	<d	<d
Phenanthrene (ng/L)	c	28.3	5.5	3.8	1.2	<d	<d
Dinitrophenol (ng/L)	d	17.5	14.2	18.3	17.8		8.4
Pentachlorophenol (ng/L)	d	18.5	10.0	18.7	4.9		1.4
Total-H (ng/L)							
BOD (ng/L)							
TOC (ng/L)							
TSS (ng/L)							
VSS (ng/L)							
pH (pH units)							
Time (minutes)		0.0	13.5	27.0	54.0	81.0	108
Temperature (C)		9	7	7	4	2	2
Depth (Ave-cm)			1.6	1.4	0.9	1.0	
Volume (L)		2528					1717
Steady State Rate (l/min)		6					6.1

EXPERIMENT: OVERLAND FLOW - SLOPE B

DATE: 2 December 1981

APPLICATION RATES: 6 (l/min) 0.4 (cm/hr) 0.12% (w=3/hr-m of width)

AIR TEMPERATURE: 3 C

WEATHER: Cold, no wind, misty, freezing rain last night

SUBSTANCE	TYPE OF ANAL	APP	1/8	CONCENTRATION			3/4	RUNOFF
				1/4	1/2	3/4		
Chloroform (mg/L)	a	11.5	16.0	11.6	8.91	4.75	2.42	
Toluene (mg/L)	a	2.0	0.93	0.67	0.32	0.27		
Chlorobenzene (mg/L)	a	40.0	17.8	11.1	4.76	2.49	1.55	
Benzene (mg/L)	a							
Bromoform (mg/L)	a							
Bromoform (mg/L)	b	105	52.7	37.0	27.4	19.8	14.0	
Dibromochloromethane (mg/L)	b	14.1	6.4	5.1	3.1	2.1	1.1	
Nitrobenzene (mg/L)	b	54.4	53.2	50.2	44.8	29.6	31.2	
m-Nitrotoluene (mg/L)	b	14.2	44.9	38.8	30.4	17.6	18.1	
Methylparathate (mg/L)	b	78.7	68.4	67.3	56.1	38.7	45.2	
PCB 1242 (mg/L)	b	37.1	15.0	6.6	9.7	5.3	6.3	
Naphthalene (mg/L)	c	72.8	24.1	14.3	4.72	3.79	2.37	
Phenanthrene (mg/L)	c	37.3	7.0	2.34	1.66	1.26	1.09	
2-Nitrophenol (mg/L)	d	48.8	86.1	45.8	29.7	35.5	25.1	
Pentachlorophenol (mg/L)	d	37.7	32.4	27.7	15.6	12.0	5.6	
Total-N (mg/L)								
TSS (mg/L)		60	37	29	24	21	14	
TDC (mg/L)		99.0	31.2	25.4	23.2	20.2	20.1	
END (mg/L)		43	23	12	13	9	7	
VSS (mg/L)		47	23	10	11	7	7	
DN (mg/L)		64.6	6.2	6.9	6.9	6.7	6.2	
Time (minutes)		6.0	15.5	27.0	54.0	31.0	133	
Temperature (C)		7	5.5	4.5	0.5	0	0	
Depth (Ave-cm)			1.2	1.0	1.7	0.2		
Volume (L)		170					2149	
Steady State Rate (l/min)		6					6.2	

EXPERIMENT: OVERLAND FLOW - SLOPE DA

DATE: 10 December 1981

APPLICATION RATES: 64 (l/min) (cm/hr) 0.16 (w=3/hr-m of width)

AIR TEMPERATURE: 16 C

WEATHER: Cool, breezy, partly sunny

SUBSTANCE	TYPE OF ANAL	APP	1/8	CONCENTRATION			3/4	RUNOFF
				1/4	1/2	3/4		
Chloroform (mg/L)	a	51.1	32.8	29.7	18.1		1.84	
Toluene (mg/L)	a	78.7	23.5	18.1	5.59		0.72	
Chlorobenzene (mg/L)	a	88.9	31.6	25.7	7.74		0.85	
Benzene (mg/L)	a	78.6	36.8	39.3	19.3		1.32	
Bromoform (mg/L)	a	134	55.5	48.1	21.5		3.5	
Bromoform (mg/L)	b	187	34.4	34.1	18.1	11.4	4.8	
2-Chloroethylvinyl ether (mg/L)	b							
Unknown (mg/L)	b							
Dibromochloromethane (mg/L)	b	24.7	6.1	5.0	2.0	1.2	0.25	
Nitrobenzene (mg/L)	b	120	33.5	41.2	34.7	20.3	13.3	
m-Nitrotoluene (mg/L)	b	144	38.1	45.1	31.0	19.3	8.6	
Diethylphthalate (mg/L)	b	107	88	85.9	74.7	69.0	54.2	
PCB 1242 (mg/L)	b	98.9	14.5	21.6	3.4	5.5	3.5	
Naphthalene (mg/L)	c	179	49.6	38.6	18.7	6.1	2.44	
Phenanthrene (mg/L)	c	149	23.5	15.2	2.0	1.4	1.22	
2-Nitrophenol (mg/L)	d							
Pentachlorophenol (mg/L)	d							
Total-N (mg/L)								
NOB (mg/L)								
TDC (mg/L)								
VSS (mg/L)								
VSS (mg/L)								
DN (mg/L)								
Time (minutes)								
Temperature (C)		21.3	16.4	15.6	13.7	13.5	12.4	
Depth (Ave-cm)			2.6	2.5	2.5	1.5		
Volume (L)								
Steady State Rate (l/min)								

Table A2. Experimental first-order rate coefficients, CRREL site.

Date	Average water temp. (°C)	k_{exp} (min ⁻¹)											
		Chloro- form	Toluene	Chloro- benzene	Bromo- form	Dibromo- chloro- methane	Nitro- benzene	m-Nitro toluene	Diethyl- phthalate	PCB	Naph- thalene	Phenan- threne	2,4-Dinitro- phenol
23 June	21	-	-	-	-	-	-	-	-	0.030	0.054	0.014	0.028
25 June	19.3	-	-	-	-	-	-	-	-	0.026	0.038	-	-
30 June	22	-	-	-	-	0.050	-	-	-	0.042	0.039	0.023	0.034
2 July	23.7	-	-	-	-	-	-	-	-	0.024	-	0.023	0.029
7 July	23.7	-	-	-	-	-	-	-	-	0.037	0.071	-	-
9 July	25.7	-	-	-	-	-	-	-	-	0.030	0.051	0.017	0.043
14 July	18.7	0.022	0.042	0.030	0.036	-	-	-	-	0.045	0.073	-	0.038
16 July	19.7	0.023	0.032	0.032	0.026	-	-	-	-	0.034	-	-	-
21 July	20.3	0.022	-	0.043	0.024	-	-	-	-	-	-	-	-
23 July	18.7	0.023	0.047	0.080	0.023	-	-	-	-	-	-	-	-
28 July	19.0	0.038	0.114	0.093	0.035	-	-	-	-	-	-	-	-
13 Aug	19.3	-	-	-	0.029	-	-	-	-	-	-	-	-
18 Aug	18.7	-	-	-	0.018	-	-	-	-	-	-	-	-
3 Sept	18	0.047	0.064	0.091	0.045	0.051	-	-	-	0.015	-	0.010	0.029
24 Sept	15	-	-	-	0.035	0.048	-	-	-	0.030	0.061	-	-
29 Sept	13.5	0.045	0.127	0.105	0.045	0.062	-	-	-	0.052	0.084	-	-
14 Oct	14.8	0.017	0.066	0.041	0.022	0.029	-	-	-	0.044	-	-	-
21 Oct	11.6	-	-	-	0.039	0.054	-	-	-	0.061	0.124	0.028	0.052
29 Oct	10.2	-	-	-	0.030	0.039	-	-	-	0.031	0.043	-	0.046
3 Nov	11.4	-	-	-	0.027	0.035	-	-	-	0.036	-	-	-
13 Nov	6.7	-	-	-	0.018	0.028	-	-	-	0.026	-	0.029	0.039
24 Nov	5	-	-	-	0.020	0.027	-	-	-	0.037	0.071	0.003	0.015
2 Dec	2.5	0.021	0.024	0.030	0.017	0.021	0.008	0.012	0.006	0.020	0.042	0.005	0.023
K(20°C)		0.030	0.070	0.064	0.032	0.053	0.018	0.030	0.022	0.035	0.056	0.019	0.036

APPENDIX B. DOWNSLOPE REMOVAL CHARACTERISTICS OF SELECTED CHEMICALS AT CRREL AND AT DAVIS.

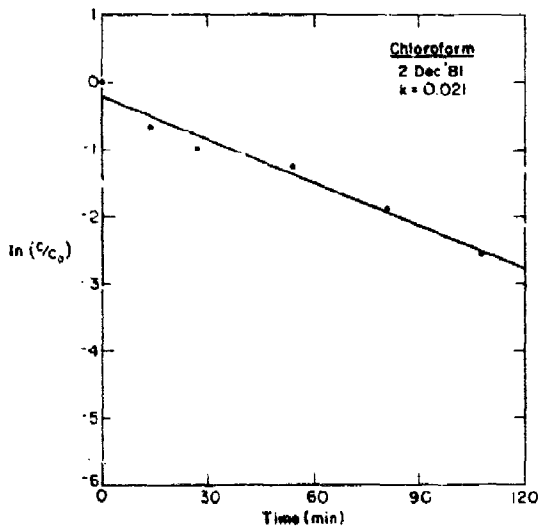


Figure B1. Downslope removal characteristics for chloroform at CRREL.

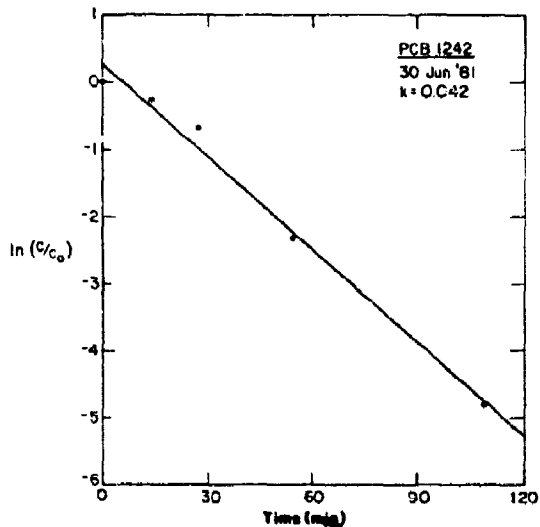


Figure B2. Downslope removal characteristics for PCB 1242 at CRREL.

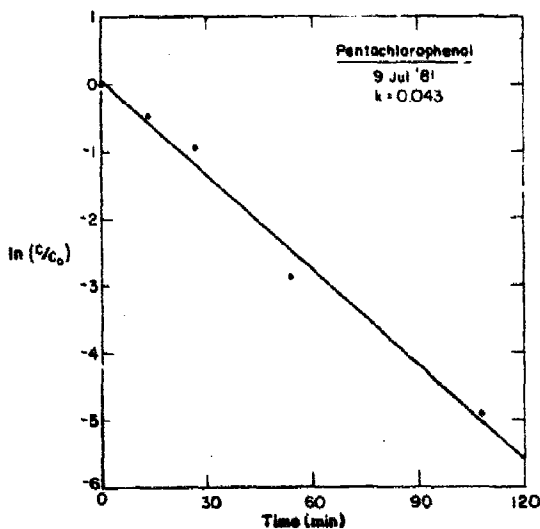


Figure B3. Downslope removal characteristics for pentachlorophenol at CRREL.

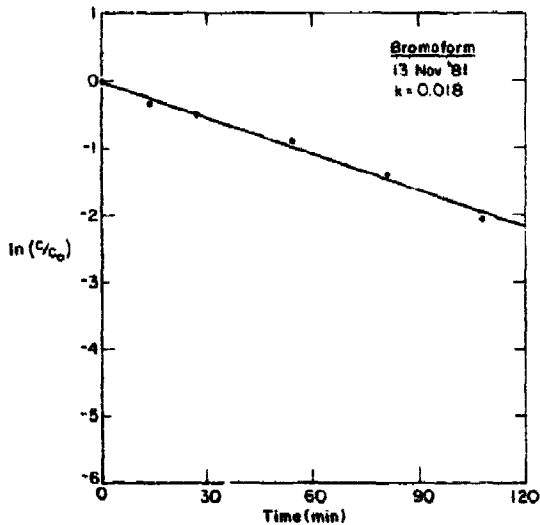


Figure B4. Downslope removal characteristics for bromoform at CRREL.

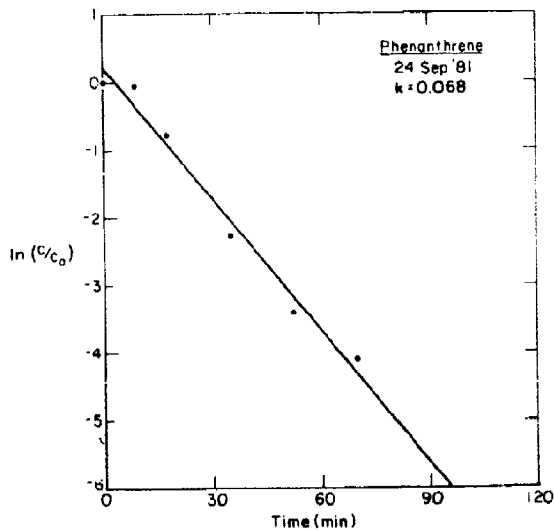


Figure B5. Downslope removal characteristics for phenanthrene at CRREL.

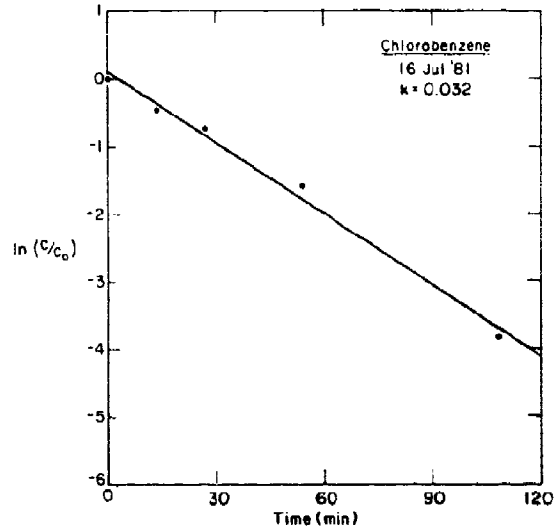


Figure B6. Downslope removal characteristics for chlorobenzene at CRREL.

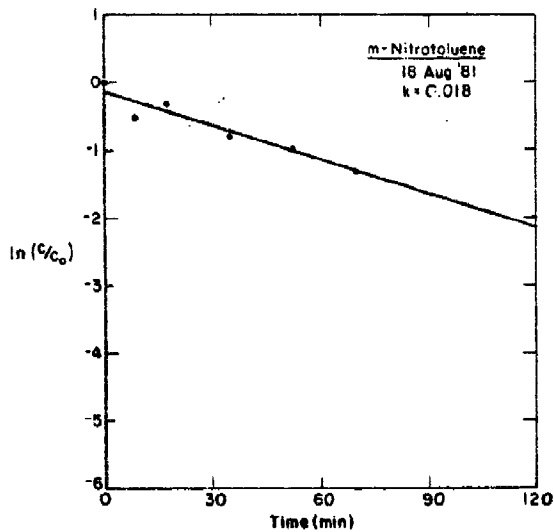


Figure B7. Downslope removal characteristics for m-nitrotoluene at CRREL.

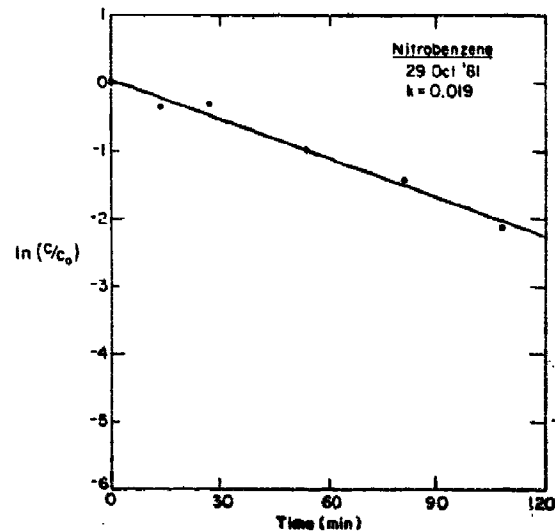


Figure B8. Downslope removal characteristics for nitrobenzene at CRREL.

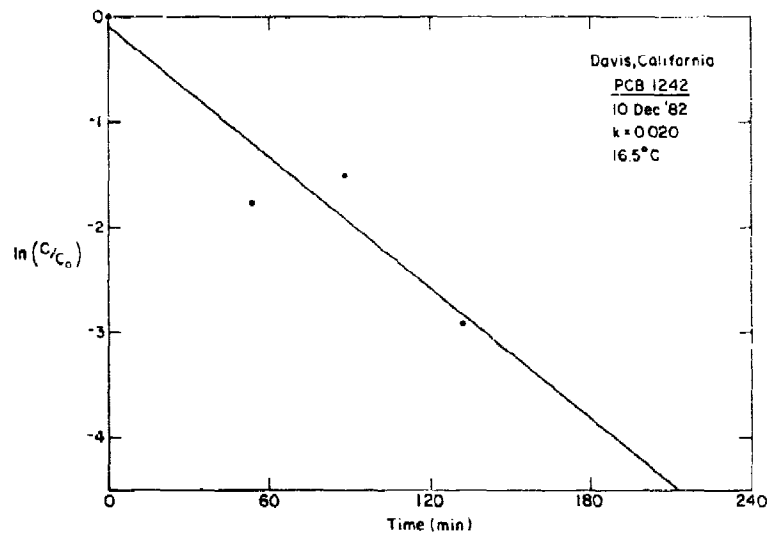


Figure B9. Downslope removal characteristics for PCB 1242 at Davis.

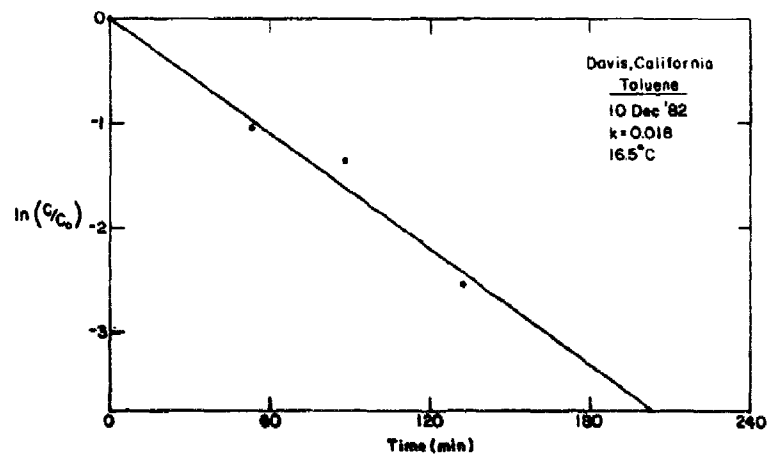


Figure B10. Downslope removal characteristics for toluene at Davis.

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Jenkins, T.F.

Assessment of the treatability of toxic organics by overland flow / by T.F. Jenkins, D.C. Leggett, L.V. Parker, J.L. Oliphant, C.J. Martel, B.T. Foley and C.J. Diener. Hanover, N.H.: Cold Regions Research and Engineering Laboratory; Springfield, Va.: available from National Technical Information Service, 1983.

vii, 59 p., illus.; 28 cm. (CRREL Report 83-3.)

Bibliography: p. 28.

1. Land treatment. 2. Organic compounds.
3. Overland flow. 4. Wastewater treatment.
I. Leggett, D.C. II. Parker, L.V. III. Oliphant, J.L. IV. Martel, C.J. V. Foley, B.T. VI. Diener, C.J. VII. United States. Army. Corps of Engineers. VIII. Cold Regions Research and Engineering Laboratory, Hanover, N.H. IX. Series: CRREL Report 83-3.