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OVERLAND FLOW: REMOVAL OF TOXIC VOLATILE ORGANICS

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OVERLAND FLOW RESEARCH REPORTS

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Carlson, C.A., P.G. Hunt, T. B. Delaney (1974) Overland flow treatment of wastewater. *Misc. Paper Y-74-3*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi.

Chen, R.L. and W.H. Patrick, Jr. (1980) Nitrogen transformations in a simulated overland flow wastewater treatment system. *CRREL Special Report 80-16*.

Hoeppel, R.E., P.G. Hunt, T. B. Delaney. (1974) Wastewater treatment on soils of low permeability. *Misc. Paper Y-74-2*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi.

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

Lee, C.R. et al. (1976) Highlights of research on overland flow for advanced treatment of wastewater. *Misc. Paper Y-76-6*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi.

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Cover: Diagram of CRREL overland flow test site.

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PREFACE

This report was prepared by T.F. Jenkins and D.C. Leggett, Research Chemists, and H.E. Hare, Physical Sciences Technician, of the Earth Sciences Branch, Research Division and C.J. Martel, Research Environmental Engineer, Civil Engineering Research Branch, Experimental Engineering Division, U.S. Army Cold Regions Research and Engineering Laboratory.

This study was conducted as part of the U.S. Army Corps of Engineers Civil Works Research Work Unit CWIS 31299, *Evaluation of Techniques of Overland Flow in Cold Regions*.

This report was technically reviewed by Dr. C.L. Grant of the University of New Hampshire and R.E. Peters and Dr. C.R. Lee of the U.S. Army Engineer Waterways Experiment Station.

The authors would like to acknowledge the technical assistance of C.J. Diener of the Civil Engineering Research Branch for operation of the overland flow prototype and measurement of the detention times reported in this manuscript. P.L. Butler is also acknowledged for providing the biochemical oxygen demand and suspended solids analyses in this report.

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OVERLAND FLOW: REMOVAL OF TOXIC VOLATILE ORGANICS

T.F. Jenkins, D.C. Leggett, C.J. Martel and H.E. Hare

INTRODUCTION

Chlorine disinfection of water and wastewater produces a number of volatile organics (Rook 1974, Glaze and Henderson 1975) of which haloforms are the volatile organochlorine compounds produced in highest concentration. The mechanism of formation of haloforms has been discussed elsewhere (Morris 1975). Others have discussed the role of naturally occurring humic and fulvic acids as haloform precursors in natural waters (Rook 1974, 1976, 1977, Stevens et al. 1976). Because surface waters always contain some organic precursors, haloforms are always found when water derived from surface sources is chlorinated (Symons et al. 1975).

Evaluation of the human health risks associated with exposure to low concentrations of haloforms and other volatile organics has begun (Jolley 1978), but it will probably be some time before a clear understanding of the extent of risk associated with low-level exposure to these substances is developed. The environmental impact associated with introduction of these substances into the aquatic environment is also being evaluated (Jolley 1978).

The ability of primary and secondary treatment processes to remove volatile organics has not been investigated systematically. There is some indication that activated sludge processes are effective in removing volatile organics (Brown 1978). Removal of haloforms from water using activated carbon has been investigated (Rook 1976, Suffet et al. 1978), but indications are that frequent regeneration of the carbon would be required to maintain efficient removal. Air-stripping was also found to be an effective method for haloform removal (McCarty 1980). Rook (1976) found 50% removal of CHCl₃ in a cascading tower aerator at an air/water ratio of 11 m^3/m^3 (1.5 ft³/gal) and 80% removal at a ratio of 82 m^3/m^3 (11 ft³/gal). Houel et al. (1979) provide information on the costs of these methods.

Very little is known about the ability of land treatment systems to remove volatile trace organic compounds from domestic wastewater. Results from a slow rate land treatment system at Muskegon, Michigan, showed that significant reduction in several volatile organics occurred during lagoon storage and subsequent soil percolation (U.S. EPA 1977). Volatilization was suggested as the mechanism for removal during lagoon storage.

In overland flów, treatment occurs as wastewater flows at a shallow depth over the surface of a sloping, relatively impermeable soil surface. Since overland flow provides a large liquid surface area in contact with the atmosphere, volatilization could be a significant removal mechanism for substances with high vapor pressures.

OBJECTIVES

The objectives of our study were

- 1. To determine the effectiveness of overland flow in removing volatile toxic organics from wastewater.
- 2. To determine the rate of removal of volatile toxic organics by overland flow.
- 3. To determine the mechanism for removal.
- 4. To develop predictive relationships for use in design of overland flow systems.

DESCRIPTION OF EXPERIMENT

A prototype overland flow system was constructed at CRREL in Hanover, New Hampshire, in 1975. During construction, the topsoil was removed from the site and the subsoil graded to a 5% slope. An impermeable rubber membrane was placed on the surface of the subsoil and 15 cm of Hartland (Vermont) silt loam soil placed on the membrane. The soil was compacted to a bulk density of 1.4 g/cm³, creating a relatively impermeable surface. The membrane was used to ensure that downward percolation of water would not occur. The completed site was seeded with a grass mixture of K-31 tall fescue, Pennlate orchardgrass, reed canarygrass and perennial ryegrass. The prototype is 30.5 m in length x 8.8 m wide and was subdivided into three parallel test sections, separated by a raised portion of the rubber membrane. Figure 1 is a photograph of the completed site. A more detailed description can be found in Martel et al. (1980).

Primary wastewater was applied at the top of the slope to two test sections through perforated pipe. The third section was not used for this experiment. Water not lost through evapotranspiration or percolation was collected at the base of the slope in galvanized steel tanks. Applied and runoff volumes were measured to determine treatment efficiency.

Wastewater was applied at five different rates ranging from 0.40 to 1.32 cm/hr (6 to 20 L/min). The period of application was generally seven hours a day, five days per week. The average hydraulic detention time for each application rate used in this study was determined with a sodium chloride tracer (Table 1).

Five different experiments were conducted. In the first, chlorinated unspiked primary effluent was used, while in subsequent experiments the effluent was spiked with known concentrations of volatile organics.

Experiment 1

The first experiment in treatment of toxic volatile organic substances was conducted during the week of 17-21 September 1979. Wastewater was chlorinated prior to application by adding 2.0 L of 5.25% sodium hypochlorite (bleach) to approximately 5300 L of primary wastewater. A reaction period of 2 hours was allowed before onset of application. Chlorine residuals were estimated at the beginning of wastewater application and found to average 0.7 mg/L for free chlorine and 1.1 mg/L for combined forms (Hach DPD colorimetric method).



Figure 1. Photograph of overland flow site.

Table 1. Application rates and detention times of primary wastewater on the slope.

Date	Application rate (cm/hr)	Detention time (min)			
17 September	0.40	82			
18 September	0.60	50			
19 September	0.80	42			
20 September	1.05	30			
21 September	1.32	22			

Samples of applied wastewater, the runoff from the hase of the slope, and surface water samples at various distances downslope were collected after hydraulic steady state had been achieved. (Hydraulic steady state was defined as the point when the runoff rate had stabilized—usually within 90 min.) Samples were collected from the soil surface by placing screw cap test tubes (2.5 x 20 cm) on the slope and allowing them to fill directly. Samples were treated with sodium thiosulfate to destroy chlorine residuals, so that the subsequent formation of additional haloform precursors would be prevented (Leggett in prep., Nicholson et al. 1977).

All samples were analyzed on a Hewlett-Packard gas chromatograph/mass spectrometer (HP 5992 GC/MS) equipped with a purge and trap sampler (HP 7675A). Benzene was added as an internal standard just before purging. A volume of 60 mL was purged with helium at 20 mL/min for 20 minutes. Subsequently the TENAX collection tube was heated to 200°C for 5 minutes while the compounds were desorbed onto the GC column at 90°. Desorbed compounds were separated on a 45-x 0.22-cm column containing Porapak QS (Waters Assoc.), programmed from 90° to 200° at 6°/min with a helium carrier of 20 mL/min. A detection limit of about 1 μ g/L is possible using the normal scanning technique and about 10 ng/L using selective ion monitoring (SIM). The more sensitive SIM method was used to quantify the amounts of these substances present at various points on the slope. Chloroform and toluene were determined using mass 85 and 91, respectively. Due to unacceptably high levels of haloforms in both the tapwater and distilled water in the laboratory, we prepared the standards for analysis by adding reagent chemicals to water obtained from deep groundwater wells nearby.

The major trace volatile organic substances identified in the chlorinated primary wastewater were chloroform and toluene. Smaller amounts of bromodichloromethane, 1, 1, 1 trichloroethane, tetrachloroethylene, and carbon tetrachloride were also identified by comparing spectra obtained to reference mass spectra. Other substances were identified by retention times and response of selected ions.

Experiment 2

A second experiment was conducted on 25 October 1979. In this study a butanol solution of nine trace volatile chlorinated organic substances (Table 2) on the EPA Priority Pollutant List (Budde and Eichelberger 1979) was added to primary wastewater before application to the site. In this experiment the wastewater was not chlorinated prior to application. The amount of each of these substances produced concentrations in the range of 5-100 μ g/L in the wastewater. The application rate during this study was 0.60 cm/hr and the average detention time was assumed to be 50 minutes as in the previous test run at this rate (Table 1). Applied and runoff water temperatures were 16° and 10°C, respectively.

Samples of the original wastewater, runoff, and surface samples from different points on the slope were analyzed by the GC/MS/SIM method as in experiment 1. The substances used in this study and the ion monitored for each are presented in Table 2.

Table 2. Volatile organics added towastewater, 25 October 1979.

Volatile organics	Ion monitored (m/e)*
Methylene chloride	49
Carbon tetrachloride	117
1,2-dichloroethane	49
1,1,1-trichloroethane	117
1,1,2-trichloroethane	
Trichloroethylene	130
Tetrachloroethylene	166
Bromodichloromethane	129
1,1-dichloroethane	85

* m/e is the mass to charge ratio.

Experiment 3

Since we had difficulty in separating all the substances used in experiment 2 on the analytical column, a third experiment was conducted on 1 November 1979. In this study, four trace volatile components (Table 3) were added to the wastewater as described earlier. In addition to the four substances added, chloroform and toluene were also detected. Experimental conditions were the same as described for experiment 2. Applied and runoff temperatures were 14° and 10°C, respectively.

Table 3. Volatile organics added to wastewater, 1 November 1979.

Volatile organics	Ion monitored (m/e)			
Methylene chloride	49			
1,1-dichloroethane	63			
Bromodichloromethane	85			
Tetrachloroethylene	166			

Experiment 4

In a fourth experiment, conducted on 29 November 1979, the wastewater was spiked with six volatile organic compounds including acetone, ether and ethyl acetate (Table 4). While these substances are not of concern from a health or toxicity standpoint, we selected these compounds because we expected lower rates of evaporation from water due to their higher solubility.

Chloroform and toluene were detected in this experiment as usual. The temperatures of the applied wastewater and runoff were 11° and 3° C respectively. The application rate used was 0.42 cm/hr and a detention time of 50 minutes was measured. This detention time was shorter than previously measured for this application rate (Table 1) probably due to decreased evapotranspiration. Since no internal standard was run in conjunction with this experiment, the data are only reported as relative to the initial concentration at ¼ slope (Table A4). The amounts of substances added to the wastewater were similar to those of previous experiments.

Table 4. Volatile organics added to wastewater, 29 November 1979.

Volatile organics	lon monitored (m/e)				
Acetone	43				
Benzene	78				
Carbon disulfide	7.6				
Diethyl ether	59				
Ethyl acetate	43				
Methylene chloride	85				

Experiment 5

The final experiment was conducted on 13 December 1979 to determine the effect of freezing conditions on removal of volatile substances. The wastewater was spiked with seven volatile trace organics (Table 5). Sample collection and analysis were conducted as before. The application rate was 0.40 cm/hr; however, freezing conditions caused much of the wastewater to freeze on the slope and so the actual detention time is not known. The applied and runoff water temperatures were 15° and 0°C, respectively.

Table 5. Volatile organics added to wastewater, 13 December 1979.

Volatile organics	Ion m onitored (m/e)
1,1-dichloroethane	63
Methylene chloride	47
Carbon disulfide	78
Bromodichloromethane	83
Carbon tetrachloride	47
Tetrachloroethylene	47
Chlorobenzene	112

RESULTS

The results of the first experiment are presented in Table 6. Percent removals for toluene and chloroform ranged from 96-100% and 80-99% and runoff concentrations from below detection to 0.8 μ g/L, and 0.3-1.9 μ g/L, respectively. Overall treatment efficiency for chloroform was consistently lower than that for toluene.

In order to investigate the rates of removal of these two substances, runoff samples were collected at various points on the slope. The residence time on slope for each point was estimated from downslope distance. For example, if the detention time for a slope length of 30.5 m was 60 minutes, a sample collected at 15 m downslope was assumed to have a residence time of 30 minutes.

Semilog plots of concentration (Table A1) vs residence time for chloroform and toluene are presented in Figure 2. In nearly every case, a linear relationship in the log of concentration vs residence time was found. This is the behavior expected if the removal is controlled by a process which can be dee scribed by first-order kinetics (Castellan 1964); i.e. if the rate of removal of a substance can be described by eq 1, the process is said to be first-order:

	Application	Averane detention		Concen	tration (µg/L)		Vol	ume		
	rate	time	Wast	ewater	Ru	noff	(L)	% R6	moval
Date	(cm <u>/</u> hr)	(min)	Chloroform	Toluene	Chloroform	Toluene	Applied	Runoff	Chloroform	Toluene
17 September	0.40	82	17.8	33.1	0.3	b.d.**	2568	1339	99	100
18 September	0.60	50	6.7	10.2	0.5	b.d.	3612	2679	94	100
19 September	0.80	42	13.2	28.7	0.8	b.d.	4559	3387	95	100
20 September	1.05	30	6.7	21.5	1.1	0.7	5600	4459	87	97
21 September	1.32	22	9.0	18.8	1.9	0.8	7226	6768	80	96

Table 6. Treatment efficiency* of overland flow for removal of chloroform and toluene (Experiment 1).

* Runoff water temperatures were about 16° C during the five-day period.

** b.d. - Concentration was below a detection limit estimated at 10 ng/L.

$$\frac{dC}{dt} = -kC \tag{1}$$

where C is concentration $(\mu g/L)$, *t* is residence time (min) and *k* is the first-order rate coefficient (min).

By separation of variables and integrating we obtain

$$\ln \frac{C}{C_0} = -kt \tag{2}$$

where C_0 is the value of C at t = 0 (initial concentration).

To obtain experimental values for k, the natural logarithm of the ratio of C/C_0 for each sample was plotted vs residence time. The rate coefficient (k) is the slope of the line, as determined by least-squares techniques. As shown in Figure 3 the experimental k values for chloroform and toluene were 0.054 and 0.11 min⁻¹, respectively.

To determine if other volatile substances were removed in a similar manner, we selected a number of volatile organic substances from the EPA list of priority pollutants for subsequent experiments on 25 October and 1 November 1979 (experiments 2 and 3). On these **two** days these substances were spiked into the wastewater and the data (Tables A2 c and A3) plotted as described earlier. In all cases, loss of these substances also seemed to occur by a first-order rate process. The first-order rate coefficients determined from these plots are presented in Table 7.

We considered several possible mechanisms to explain the removal of these substances. These include volatilization, biodegradation, sorption on suspended matter, sorption on the soil, chemical hydrolysis and photochemical degradation. Dilling et al. (1975) and (1976) reported that these types of substances are not readily removed by photochemical degradation or hydrolysis. Brown (1978) observed removal of volatile chlorinated solvents in sewage treatment plants in Great Britain and concluded that volatilization was the most likely mechanism for their loss. Recently McCarty (1980) recommended airstripping as an inexpensive process for removal of volatile organics, including most of the ones in this study, from wastewater. Volatilization has also been cited as the reason for loss of chlorinated solvents from contaminated surface waters (Giger et al. 1978, Schwartzenbach et al. 1979). Thus we felt the most likely mechanism to be volatilization.

It should be emphasized that, while we believe that volatilization is the mechanism responsible for much if not all of this removal, we do not have direct evidence for this conclusion. The extremely low amounts of the substances and the dilution occurring in the atmosphere make atmospheric analysis above the overland flow plots impractical. In the following section, we compare empirical results with those predicted from volatilization theory to see if it can account for the magnitude of removal observed.

Table 7. Experimental k values* (min^{-1}) .

	17-21	25	1
	September	October	November
Methylene chloride		0.070	0 .090
Chloroform	0.054	0.047	0,053
Carbon tetrachloride		0.073	
Tetrachloroethylene			0.087
Bromodichloromethane		0.081	0.079
1,1-dichloroethane			0.090
Toluene	0.11		0.12

* These values for the first order rate coefficients (k) were obtained from least-squares fit of $\ln C/C_0$ vs residence times.



Figure 2. Semilog plots of concentration vs residence time for chloroform and toluene, 17-21 September 1979.

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Figure 3. Natural logarithm of C/C_0 vs residence time for chloroform and toluene 17-21 September 1979.

COMPARISON WITH VOLATILIZATION MODELS

A theoretical two-film model describing the exchange of volatile substances across the gas/liquid interface was developed by Whitman (1923). This model has recently been extended to describe the flux of gases across the air/sea interface (Liss and Slater 1974) and the evaporation of volatile chlorinated organics from water (Dilling 1977).

In this approach, the interface between the two phases is assumed to consist of two layers, a gas film separating the bulk gas from the interface, and a liquid film separating the bulk liquid from the interface. Both bulk phases are assumed to be well-mixed with exchange through the interfacial layers occurring by molecular processes. The overall resistance to mass transport across the interface can therefore be separated into gas and liquid components which are assumed to be additive.

In a separate theoretical treatment, Mackay and Wolkoff (1973) developed equations to predict the transport of organic substances from water to the atmosphere. This model did not take into account the liquid phase resistance, however, and considered the evaporation process only. Predictions of flux rates based on this approach were subsequently found to be too large (Dilling et al. 1975, Dilling 1977).

It was later shown that most of the resistance to mass transfer for many hydrophobic organics of environmental concern was in the liquid phase (Mackay and Leinonen 1975, Dilling 1977). The liquid and gas phase transfer coefficients may be calculated according to the procedure of Liss and Slater (1974) to give an overall liquid phase transfer coefficient or exchange constant K_{ϱ} which reduces (Dilling 1977) to

$$K_{Q} = \frac{221.2}{\left(\frac{1.042}{H} + 100\right)M^{\frac{1}{2}}}$$
(3)

where H is the Henry's law constant in dimensionless units, M is the molecular weight of the evaporating compound and K_{g} is in units of cm/min. Dilling (1977) also gives a universal equation for estimating H:

$$H = \frac{C_{\text{air}}}{C_{\text{water}}} = \frac{16.04 \, PM}{TS} \tag{4}$$

where C is concentration, P is the vapor pressure (torr) of the substance at the given temperature, M is the molecular weight, T is absolute temperature in kelvins and S the solubility in mg/L. This equation is very useful since Henry's law constants are often not available, particularly at temperatures other than 25° C. The correspondence between the values calculated from this equation and experimental values appears to be quite good (Dilling 1977) and probably depends largely on the accuracy of the solubility data used. Of course, it is preferable to use measured H values where possible and a simple technique for doing this is available (McAuliffe 1971, Leggett, in prep).

It was also noted by Dilling (1977) that, for substances with an H value greater than 0.1, the overall liquid transfer coefficient (K_{g}) is insensitive to large changes in H and depends primarily on the molecular weight. Interestingly, McCarty (1980) reported that substances with H values in this range are easily removed from water by air stripping. Organics that have Henry's law constants greater than 0.1 will generally be only sparingly soluble in water and have low boiling points.

The overall liquid transfer coefficient is related to the half-life of a substance evaporating from solution (Mackay and Leinonen 1975, Dilling 1977) as

$$\tau = \frac{0.693 \ d}{K_{\varrho}} \tag{5}$$

where τ is the time (min) required for 50% loss (half-

life) and d is the depth (cm) of the liquid phase. In order to use this equation to calculate the theoretical half-lives of these substances, we measured the water depths on the slope during steady state operation and found depths ranging from 0.5 to 2.0 cm with an arithmetic mean of 1.0 cm. Using this value for d and K_{ϱ} values from Table 8, τ was calculated according to eq 5 (Tables 8 and 9). The experimental τ values were obtained from experiments conducted on 25 October, 1 November and 29 November using the experimental first-order rate constants in Table 7 (see Tables 8 and 9). The experimental half-lives were found to exceed the theoretical ones by a factor of about 2 to 3 except for acetone, ethyl acetate and diethyl ether (Table 9). This is not surprising since Liss and Slater's (1974) model is valid only for a completely mixed liquid in which transfer is controlled only by molecular processes in a microscopically thin two-film interface. As Liss and Slater indicate, the model is unrealistic for any real system. Wind speed and mixing of the liquid phase are known to be very

Table 8. Physical constants and half-lives on overland flow slope, 25 October and 1 November 1979.

					vro (cm/min)t	$\tau(min)$	τ (min) found		K _ℓ (cm/min) found	
	М	S(mg/L)*†	P(torr)**†	H†	calc.	calc.	25 Oct	1 Nov	25 Oct	1 Nov
Chloroform	119.5	8890	123	0.0921	0.182	3.8	13.0	14.8	0.053	0.047
Methylene chloride	85	20800	285	0.0649	0.207	3.3	7.7	9.9	0.090	0.070
1,1 dichloroethane	99	5780	147	0.140	0.207	3.3	7.7		0.090	
Tetrachloroethylene	166	159	10.3	0.559	0.169	4.1	8.0		0.087	
Carbon tetrachloride	154	907	72.2	0.683	0.175	4.0		9.5		0.073
Toluene	92	584	16.6	0.147	0.215	3.2	6.0		0.116	
Bromodichloromethane	163			0.0464***	* 0.141	4.9	8.7	8.6	0.080	0.081

 \dagger For water and air at 12°C

Values estimated by interpolation between 25° and 1.5°C based on CHCl₃
 (Dilling 1977 McAuliffe 1966)

** Lange's Handbook of Chemistry and Physics, 12th ed. (1979)

*** Extrapolated from experimental value at 25°C (Leggett in press)

Table 9. Physical constants and half-lives for substances applied to overland flow slope 29 November 1979.

	S (mg/L)†	P (mm)†	Н	Kg(cm/min) calc.	τ (min) calc.	τ (min) found	K _Q (cm/min) found
	0,3						
Chloroform	10,300 (1.5_)"	63.1	0.0427	0.163	4.3	12.8	0.054
Methylene chloride	22,700 (1.5 [°]) ^a	159.0 ⁰	0.0347	0.184	3.8	7.4	0.094
Benzene	2,000	14.0 ^b	0.0318	0.188	3.7	8.8	0.079
Toluene	600	7.63	0.0682	0.200	3.5	9.2	0.075
Diethyl ether	<u>`</u> 85,000	204.0 ^b	0.0104	0.128	5.4	6.9	0.100
Ethyi acetate	95,000	27.5	0.00149	0.0295	23.5	13.2	0.053
Acetone	œ	77.9 ⁰	0.0005 ^c	0.0133	52.1	10.8	0.064

[†] For air and water at 2° C estimated by extrapolation of data from various sources except where indicated

a Dilling 1977

Lange's Handbook, 12 ed.

Extrapolated from loffe and Vittenberg (1978)

important factors affecting K_{ℓ} (Liss and Slater 1974, Mackay 1978). The Liss and Slater model is only appropriate for gas exchange under the turbulent conditions prevailing at the sea surface.

The Reynolds number is an index of turbulence. We can estimate Reynolds numbers R_e for the flow rates used in this study using eq 6 for flow in shallow rectangular systems (Thibodeaux 1979):

$$R_{\rm e} = \frac{4Vd}{v} \tag{6}$$

where V is the downslope velocity (Q/A), d is our average measured depth of 1.0 cm, and ν is the kinematic viscosity $(1.12 \times 10^{-6} \text{ m}^2/\text{s} \text{ at } 15.5^{\circ}\text{C})$. For these experiments the Reynolds numbers ranged from 100-400, which normally indicates non-turbulent conditions. However, it must be remembered that the calculated velocity underestimates the true value because it assumes the entire width of slope is wetted and does not include tortuosity of the flow. Consideration of these factors may increase R_{p} significantly, However, since most of our experiments were conducted at the 0.6-cm/hr application rate, for which the calculated R_{p} is 158, we feel that, despite the uncertainty in our estimates, flow is not fully turbulent and mass transfer of these volatile organics is limited by mixing of the water as it flows over the surface.

Experimental K_{ϱ} values have been determined under hydrodynamic conditions similar to those found on our overland flow slope. Cohen et al. (1978) measured the evaporation rates of benzene and toluene in a windwave tank over a range of conditions created by wind and stirring. At wind speeds below about 3 m/s (6.7 miles/hr) K_{ϱ} was nearly constant for a gently stirred solution. K_{ϱ} values of 0.03 - 0.05 cm/min were obtained for both solutes. The K_{ϱ} values obtained for the overland flow experiments (Table 8) agree well with those reported by Cohen for similar conditions (the average wind speed on the days of the experiments ranged from 0.4 - 1.8 m/s). Also Schwarzenbach et al. (1979) found an annual average K_0 for dichlorobenzene in Lake Zurich of 0.017 cm/min using a mass balance model. Thus the rates of removal found in our experiments are consistent with experimental results from similar systems.

The results obtained from the experiment conducted on 29 November (Table 9) were interesting from several points of view. The observed K_0 values are similar to those for the earlier experiments, and any effect due to decreased temperature does not seem apparent. This is not surprising since, as pointed out by Dilling (1977), there is very little change in calculated K_0 values for compounds with H > 0.1 (eq 3). On the other hand, ethyl acetate and acetone were expected to have most of their resistance to mass transfer in the gas phase, 87% for ethyl acetate and 95% for acetone, as calculated according to Liss and Slater (1974) and Dilling (1977) using the Henry's law constants in Table 9. The experimental transfer coefficient for diethyl ether was much closer to the theoretical value than that for the other compounds tested, which is reasonable for a substance with significant gas phase resistance to mass transfer.

While the rates of removal of these volatile substances are of the correct order of magnitude to be explained by volatilization models, biodegradation could not be ruled out. To test this possibility, a set of sealed, undisinfected wastewater samples spiked with the chlorinated hydrocarbons and toluene were allowed to stand for a period up to 8 days. Individual samples were analyzed periodically over this period and the results are presented in Table 10.

These results indicate that most of these substances are stable for long periods even in nutrient-rich wastewater solution. The concentration of toluene did decline with time although at a much slower rate than would be required by the detention time of wastewater on the overland flow slope. The surprisingly rapid disappearance of bromodichloromethane is not understood and probably indicates a chemical mechanism. The evidence seems to indicate that biodegradation

 Table 10. Concentration of volatile substances in wastewater with time.

Substance	nitial	1 day	5 days	7 d a ys	8 d gys	
Chloroform	10.6	12.7	5.96	9.25	6.48	
Methylene chloride	6.15	7.66	5.55	5.53	4.05	
Tetrachloroethylene	19.1	19.5	11.9	12.1	10.4	
1, 1-dichloroethane	65.8	61.9	42.8	44.9	31.2	
Bromodichloromethane	9.04	b.d.	b.d.	0.11	b.d	
Toluene	159.	141.	90.5	`b.d	b.d	

b.d. - below detection limit of 10 ng/&



Figure 4. Natural logarithm of C/C_0 vs downslope distance for chloroform and toluene, 13 December 1979.

is not a likely mechanism to explain the observed removal of these volatile substances during overland flow.

This question was examined further on 13 December when wastewater spiked with several organic substances was again applied to the overland flow slope. The runoff water temperature on this day was measured at 0° C and ice was forming on the slope during the study. It seems unlikely that microbial degradation was occurring to any extent under these conditions. Results of the analyses for these samples are presented in Table A5. The natural logarithm of the relative concentration (C/C_0) is plotted vs downslope distance in Figure 4.

The results shown in Figure 4 clearly indicate that the removal of volatile organics is very significant even at 0° C, ranging from 99 to 100%. It should be emphasized that the actual detention time on the slope for this study is unknown due to ice formation, but it is thought to be somewhat greater than the 82 min observed in September for this application rate.

In another study, Martel et al. (in press) determined the rate constant for BOD reduction on our overland flow slope and found a maximum rate of 0.03 min⁻¹ a value somewhat lower than the rate of removal of the volatile organics studied here (Table 7), even though these were observed at lower than optimum temperatures. We confirmed this value of 0.03 in a study conducted on 12 June 1980 (Fig. 5)*. Since the volatile organics studied are thought to be much less degradable than the major organic fraction in human waste (as measured by BOD), it is likely that the high rate of removal found for these substances is due to microbial degradation.

* BOD measurements were made by Winkler titration.

From these several experiments we conclude that microbiological degradation cannot account for the observed removals of these volatile trace organics. During review of this manuscript, the suggestion was made that the observed removal of these volatile substances could be occurring due to sorption on suspended matter and sedimentation or filtration of this material. In order to assess this possibility, a study was conducted on 12 June 1980 in which samples were collected from the initial wastewater, from the surface at several points downslope, and from the runoff. Total and volatile suspended solids were



Figure 5. BOD removal downslope, 12 June 1980.



Figure 6. Suspended solids removal downslope, 12 June 1980.

measured * on these samples and the results tabulated in Table A6. A plot of the natural logarithm of C/C_0 for these measurements is given in Figure 6. Clearly the removal of suspended solids is quite different from any of the volatile organic substances tested (Fig. 2 and 3) and sorption and removal with suspended solids does not explain the behavior observed for volatile organics. Removal by sorption on the soil surface followed by a slow degradation or evaporation has not been eliminated, however, and more work is needed in this area. In future studies, analysis of surface soils would give some evidence one way or the other regarding this possibility.

DESIGN CONSIDERATIONS

If additional studies confirm these rates of removal, a simple model based on the detention time of the water on the slope could be used for design purposes. A model in the form of eq 8 could be used to obtain the amount of time required:

$$C_{\rm p} = C_0 e^{-kt} \tag{8}$$

where C_p is the permitted concentration of the substance in the runoff. If k is found to be consistent by studying a number of existing overland flow systems, eq 8 will give an estimate of the detention time required to achieve the desired treatment. This caution combined with the method outlined by Martel et al. (in press) will enable the designer to calculate the application rate of wastewater necessary to achieve the desired level of treatment.

CONCLUSIONS

Volatile_trace organics were removed efficiently by overland flow land treatment at temperatures down to 0 $^{\circ}$ C.

Volatilization is the most likely major removal process with rates in reasonable agreement with other published experimental and theoretical work.

The removal of volatile organic substances was found to be described by first-order kinetics.

Removal of volatile organics by sorption on suspended matter and sedimentation was studied and the results indicate that it is not a significant removal process for volatile organics.

Sorption on soil and sorption combined with slow microbial degradation should be assessed before the mechanism for removal of volatile organics is accepted unequivocally.

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^{*} Membrane filtration method.

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APPENDIX A. LISTING OF EXPERIMENTAL DATA.

Table Al.	Concentrations	of c	hlorofor	m and	toluene at	: various
locatio	ons on overland	flow	/ slope,	17-21	September	1979.

		Chlorof	form (µg/L)		
Location	17 Sept	18 Sept	19 Sept	20 Sept	21 Sept
······································					
Wastewater	17.8	6.7	13.2	6.7	9.0
1/8 slope	12.4	5.7	6.4		7.8
1/4 slope	6.9	3.8	5.9	5.9	6.8
1/2 slope	3.1	2.1	3.7	4.1	6.1
3/4 slope		0.9	1.5		1.4
Runoff	0.3	0.5	0.8	1.1	1.9
					,
		Toluene (µg/	'L)		
Wastewater	33.1	10.2	28.7	21.5	18.8
1/8 slope	20.7	6.0	10.0		9.9
1/4 slope	4.9	2.4	7.8	9.8	7.7
1/2 slope	b.d.	0.5	3.9	7.4	6.3
3/4 slope	·	b.d.	b.d.		1.4
Runoff	b.d.	b.d.	b.d.	0.7	0.8
		Application	rate (cm/hr)	
	0.40	0.60	0.80	1.05	1.32
		Detention t	ime (min)		
	82	50	42	30	22
				•	

Table A2. Results of experiment conducted 25 October 1979 at 0.60 cm/hr application rate.

	Со	ncentration (
Component	Wastewater	1/4 slope	1/2 slope	3/4 slope	Runoff
Methylene chloride Chloroform Carbon tetrachloride Bromodichloromethane	5.24 7.05 41.8 12.3	1.27 2.99 8.62 2.52	0.78 5.37 1.63	0.32 1.72 1.95 0.58	0.22 0.56 1.83 0.25

Table A3. Results of experiment conducted 1 November 1979 at 0.60 cm/hr application rate.

Component		Concentration $(\mu g/L)$				
	Wastewater	1/8 slope	1/4 slope	1/2 slope	3/4 slope	Runoff
Methylene chlorid	le 6.15	3.11	1.97	0.78	0.19	0.47
Chloroform	10.6	7.62	5.21	3.04	1.50	0.68
Tetrachloroethyle	ene 19.1	13.2	8.51	3.60	0.69	0.18
Bromodichlorometh	nane 9.04	5.25	3.71	1.87	0.34	b.d.
1,1 dichloroethar	ne 65.4	41.2	24.8	11.2	2.11	0.59
Toluene	159	82.5	61.4	18.2	1.46	0.28

b.d. - The level was below a detection limit of about 10 ng/L

Component	Relative	concentration*	
	1/4 slope	1/2 slope	3/4 slope
Toluene	1	0.482	0.137
Benzene	1	0.405	0.134
Chloroform	1	0.499	0.262
Methylene chloride	1	0.225	0.115
Diethyl ether	1	0.238	0.087
Ethyl acetate	1	0.500	0.275
Acetone	1	0.574	0.178

Table A4. Results of experiment conducted 29 November 1979 at 0.42 cm/hr application rate.

* All concentrations are relative to the concentration of that substance at 1/4 slope.

Table A5. Results of experiment conducted 13 Demember 1979* at 0.40 cm/hr application rate.

Component	Concentration (µg/L)							
-	Waste-	1/8	1/4	1/2	3/4	Runoff	%	
	water	slope	slope	slope	slope		Removal	
Chloroform	20.4	12.6	6.55	2.18	0.43	0.19	99	
Methylene chloride	21.3	14.4	9.43	2.79	0.45	b.d.	100	
Carbon disulfide	11.3	6.85	1.55	b.d.	b.d.	b.d.	100	
Bromodichloromethane	13.4	9.03	2.41	0.77	b.d.	b.d.	100	
Carbon tetrachloride	5.95	2.16	0.97	0.28	b.d.	b.d.	100	
Tetrachloroethylene	7.88	3.96	1.85	0.29	b.d.	b.d.	100	
Toluene	125.0	68.7	27.6	3.57	b.d.	b.d.	100	
Chlorobenzene	10.6	8.01	1.67	0.25	b.d.	b.d.	100	
1,1-dichloroethane	14.8	7.39	3.77	0.90	0.10	0.03	>99	

* Runoff temperature was 0°C during this study

Table A6. Concentrations of BOD and suspended solids on two test plots, 12 June 1980.

	Tes	t Sectio	on B	1	est	Sectio	on C
	BÓD	TSS*	VSS**	Ē	BOD	TSS	VSS
Wastewater	72	77	62		72	77	62
1/8 Slope	45	27	24		40	13	12
1/4 Slope	32	14	13		32	8	8
1/2 Slope	22	11	10		23	6	6
3/4 Slope	14	8	7		16	7	6
Runoff	10	5	5		7	4	4

* TSS - Total suspended solids

** VSS - Volatile suspended solids

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