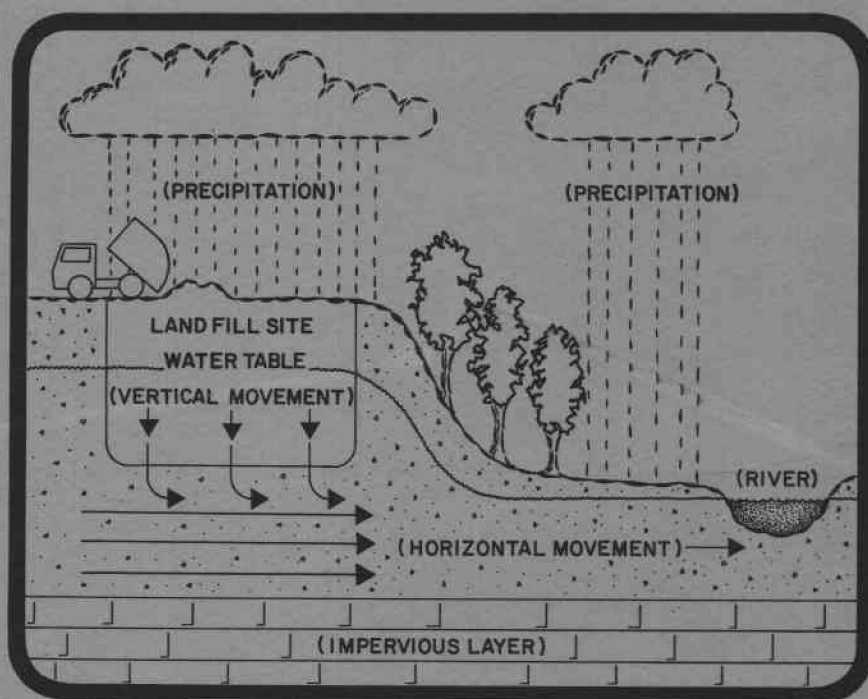


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# Analysis of the Movement of Hazardous Waste Chemicals in and from a Landfill Site via a Simple Vertical-Horizontal Routing Model



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Oregon State University, Corvallis



Analysis of the Movement of Hazardous Waste  
Chemicals in and From a Landfill Site Via  
a Simple Vertical-Horizontal Routing Model

A Report of the  
Environmentally Hazardous Waste Subcommittee\*  
To the  
Oregon State University  
Environmental Health Sciences Center  
Corvallis, Oregon 97331

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## SUMMARY

A simple mathematical model based upon a chemical mass balance at each point in time and space has been developed to allow concentration estimates inside of as well as exterior to a landfill disposal site. The model incorporates the important physical-chemical parameters: 1) hydrodynamic flow velocity based upon the porosity and hydrodynamic gradient of the porous medium; 2) variable water table; 3) variable rainfall; 4) reversible adsorption-desorption phenomena; 5) first order irreversible sorption if any; 6) first order chemical reaction; and 7) first order microbial degradation kinetics. The model system is basically an adaptation and an extension of the well-known moisture routing techniques of Remson et al. (1969) to include both vertical and horizontal mass transfer.

An easy to follow development of the principles of the model is presented by first considering only a few cells of the landfill and the surrounding porous medium structure. With the working principles in hand, the ideas are put to use in a large-scale demonstration landfill with all the above mentioned model features operating. Lastly, a simulation of a landfill site approximating that of the Brown's Island landfill site in Salem, Oregon, is made using the hydrogeologic and meteorologic data of the site itself, and a range of chemical and microbiological parameters running from nitrate type compounds to the persistent chlorinated hydrocarbon compounds. In the latter case, the data

are presented as effluent concentration (ppm) 400 feet down gradient from the lower boundary of the landfill site as a function of elapsed time in years from the initial chemical charging. Also shown in tabular form is the fraction of the total initial chemical charge which has been transferred to the environment (lost from both the landfill site and the adjoining soil [porous medium column]) as a function of time in years.

Three appendices are involved. Appendix I gives the mathematical details for the derivation of the continuous and discrete tank systems used in the validation (confidence checking) of the below water table horizontal movement portions of the general SLM-1 (sanitary landfill model - one) model. Appendix II gives the nomenclature (definition of computer terms and symbols) and the actual computer program of SLM-1 together with input-output instructions (all in Fortran 4, OS-3, OSU Computer Center language) and subroutines used in the simulations. Appendix III contains a collection of useful tables, graphs, and laboratory reports relating to physical-chemical properties of many pesticide compounds. Some common Oregon soils and hydrogeologic information is also included mainly as reference material.

## INTRODUCTION

In determining whether a specific material is environmentally hazardous under a given disposal situation, a number of factors must be considered. Important material properties or characteristics include toxicity, solubility, biodegradation rate, vapor pressure, adsorption on soil, amount, concentration, and others. Other important factors include containment and geologic or hydrologic conditions of disposal.

In only a few instances can the environmental hazard of disposal of a certain material be defined on the basis of only one or two of the factors mentioned above. In most cases it appears necessary to consider many factors and consequently hazard evaluation may become quite complicated. For example, a typical disposal situation is a sanitary landfill or other solid waste disposal site. The major threat to the environment presented by disposal of hazardous or toxic chemicals in such a disposal site is contamination of ground water or surface water with toxic material. To predict potential ground water or surface water contamination, it would be necessary to consider all important physical and chemical characteristics and environmental conditions (geologic and hydrologic) at the same time by a mathematical approach.

Accordingly, the Task Force set out to develop a simple predictive model to serve this purpose.



## Historical Resumé

A review of the literature reveals numerous papers dealing with the mathematical aspects of water and chemical movement in both unsaturated and saturated porous media. Of particular relevance to this sanitary landfill modeling project is the extensive mathematical modeling and computer simulation studies of regional groundwater flow by Freeze (1971) and by Freeze (1972). He considers the interaction between a pollutant source and the soil-moisture and groundwater flow systems, although results are given only for the hydrodynamics. The Freeze model can predict both transient and steady state subsurface flow patterns in two or three dimensions and includes consideration of both saturated and unsaturated zones. Quantitative interpretation of Freeze's results provides predictive values of rate of entry of pollutants into the flow system, lengths of flow paths, travel times of pollutants, discharge rates to surface water, water-table movements, and pressure-field development. These results do not consider dispersion or hydrochemical interactions between pollutants and soils.

Pinder et al. (1968) and Pinder et al. (1970) have also been active in the modeling and computer simulation of groundwater flow systems, including mass transport in flowing groundwater. Recently, Schwartz (1973) considered the simulation of hydrochemical patterns in regional groundwater flow.

The current status of the literature is that the general hydrodynamics of groundwater flow can be predicted quantitatively; however, much remains to be done to reach the same level of confidence in predictions for the behavior of a chemical contaminant particularly in the

case of a chemical that adsorbs onto the surface and undergoes biodegradation.

In this sanitary landfill modeling project, constraints of time and funds virtually eliminated consideration of modeling using the techniques of the above workers. For example, Freeze (1971) reported that transient two-dimensional hydrodynamic models required from 10 to 30 minutes of computer time (IBM 360/91) for 100 time step solutions. Since the current project requires a simulation of sanitary landfill behavior over a time period of years, it is obvious that computer charges would be prohibitive.

For practical reasons, a simple approach was taken using the vertical moisture routing procedure of Remson et al. (1968), Fungaroli (1971), and Bredehoeft et al. (1973), coupled with a simple model of the chemical transport in the horizontal direction. The hydrodynamics are not computed. Constant horizontal water velocities in the landfill and soil are estimated from soil or landfill permeability and porosity and local hydraulic gradients. The water table variations are entered as input data and are obtained from measurements taken near the landfill site.

While this approach of using greatly simplified hydrodynamics has obvious inadequacies, the simple model should be useful for management of chemical disposal in sanitary landfills. Comparisons of model predictions with actual sanitary landfill behavior will enable the model accuracy to be determined.

## THE SLM-1 MODEL

The objective of this project is to develop a computer model of a sanitary landfill which can be used to assess the potential environmental contamination by transport of a given undesirable chemical from a landfill through underground porous media such as rivers, lakes, or local water supplies. The model is to be as simple as possible and yet still include the principal factors affecting the underground transport of the contaminant.

At a minimum, the model must account for the following factors:

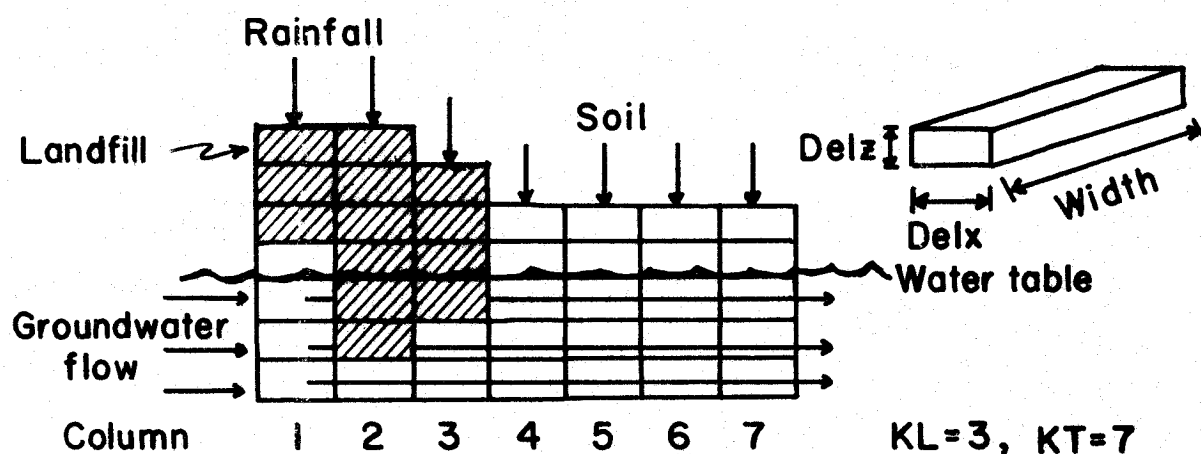
1. both vertical and horizontal movement of the contaminant (i.e. two-dimensional distribution of chemical),
2. adsorption on the porous media,
3. biodegradation of the contaminants,
4. variable water table which may rise to any height in the landfill (possibly even completely flooding the landfill) or drop to a depth below the landfill,
5. permeability, porosity, hydraulic gradient and moisture bearing characteristics of the soil and landfill.

The sanitary landfill model SLM-1, which meets these requirements, has been developed in this study. The model is based on a vertical routing of contaminant by a method similar to Remson et al. (1968) and a horizontal routing corresponding nearly to flow through a series of stirred tanks. The model is greatly simplified by performing a mass balance on the contaminant only. No water balance is performed. The horizontal velocity of the groundwater is assumed constant in the landfill and soil and is estimated from the permeability, porosity, and the hydraulic gradient of each media. Both the landfill and the

soil are assumed to be homogeneous with uniform permeability, porosity, hydraulic gradient, biodegradation, and adsorption characteristics within each porous medium.

#### Two-Dimensional Structure of SLM-1

The landfill and soil region is divided into a grid, each compartment having dimensions of length DELX, depth DELZ = 2 feet, and width WIDTH sufficient to encompass the contaminated zone of the landfill. SLM-1 is considered to be a two-dimensional model since calculations account for distribution of chemical in two directions only; i.e., vertical and horizontal. Since dispersion of chemical in a lateral direction is ignored, the model tends to calculate a higher concentration at a point downstream from the landfill than would exist if the three-dimensional dispersion character were modeled.



The elevation of the top of each landfill and soil column and the elevation of the bottom of each landfill column are specified as input data. It is assumed that columns 1 to KL are landfill columns followed by KL+1 to KT columns of soil where KL and KT are specified as input data. KI=0 means that the entire region is soil.

#### Water Movement

The horizontal groundwater flow below the water table is assumed to be unidirectional with a velocity  $V(1)$  ft/day in the landfill and  $V(2)$  ft/day in the soil. Movement of the chemical in the lateral direction is neglected.

Rainfall at an arbitrary rate  $R(J)$  falls on the landfill and soil region and a fraction XINFL is assumed to infiltrate into the porous media. This water moves downward in the columns according to the simple mechanism suggested by Remson et al. (1968).

Each two-foot layer above the water table has an initial moisture volume fraction of  $YI(1)$  for landfill and  $YI(2)$  for soil. Water entering the top layer in a column is retained until a moisture volume fraction corresponding to field capacity is reached, i.e.,  $YF(1)$  for landfill and  $YF(2)$  for soil. Additional water entering a layer at field capacity freely drains to the next layer below and so on. Eventually, all layers above the water table will reach field capacity. Additional water into the top layer will then move downward to the water table carrying the chemical contaminant into the groundwater. Each calculational time period is two days; thus, it is assumed that the porous media above the water table can drain from saturation to field capacity within this time.

### Chemical Source

At time zero, the chemical contaminant distributed in any compartment of the landfill or soil columns is specified as  $M(I,K)$  grams (entered as input data) where  $I$  is the layer number and  $K$  is the column number. An arbitrary source  $S(I,K)$  of chemical can be specified for any layer  $I,K$  as a function of time period  $J$ . Groundwater flowing below the water table into column 1 and the precipitation entering the top layer of each column are assumed to contain no chemical contaminant.

### Adsorption Characteristics

Reversible adsorption of the contaminant onto the soil and/or landfill material is assumed to be described by the Freundlich equation:

$$MA = K \cdot C \cdot \text{SOLID} \quad (1)$$

where:  $MA$  = chemical adsorbed (grams),

$C$  = concentration of chemical in free solution (mg chemical/liter or ppm),

$\text{SOLID}$  = grams of porous solid material,

$K$  = adsorption constant, may be different for soil and landfill material (liter/gm solid).

### Biodegradation of Contaminant

Biodegradation of the contaminant is assumed to be first order:

$$MC = k \cdot C \cdot W \cdot \Delta t \cdot 10^{-3} \quad (2)$$

where:  $MC$  = chemical degraded by reaction (grams),

$k$  = rate constant ( $\text{hr}^{-1}$ ), may be different for soil and landfill material,

$W$  = volume of solution under consideration (liters),

$\Delta t$  = time period (hours).

### Chemical Mass Balance

#### Layer Above the Water Table

Each layer compartment receives leachate from the layer immediately above and discharges leachate of different concentration to the layer immediately below.

The mechanism proposed for mass balance calculations for a two-day period is as follows:

The volume of leachate from above,  $Q_{in}$  liters, is added to the volume of liquid in the layer from the previous time period.

$$W = W_{old} + Q_{in}, \text{ with } W \text{ and } Q, \text{ measured in liters.} \quad (3)$$

The total grams of contaminant is computed.

$$M = M_{old} + Q_{in} \cdot C_{in} \cdot 10^{-3} + S, \quad (4)$$

where  $S$  is the source function, i.e., grams of contaminant added during this two-day time period. The total grams of chemical now is considered to adsorb on the porous surface, to degrade by reaction or to remain in free solution.

$$M = MA + MF + MC \quad (5)$$

where:  $MA$  = adsorbed chemical (grams),

MF = contaminant in the free solution (grams),

MC = chemical degraded (grams).

Since  $C = \frac{MF}{W}$  (1000), where C is the concentration in ppm, the equations can be combined to yield:

$$MF = \frac{M}{1 + \frac{K}{W} \cdot \text{SOLID} \cdot 10^3 + k\Delta t} \quad (6)$$

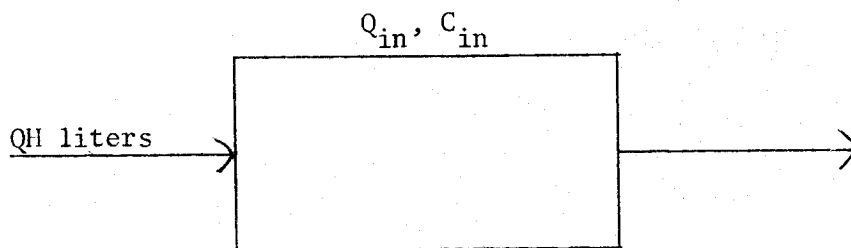
The total grams of chemical in free solution MF, the free concentration C, and the grams of chemical degraded MC can now be calculated. If the volume of liquid in the layer exceeds that corresponding to field capacity, VFC liters, the layer is drained to field capacity, i.e., if  $W > \text{VFC}$ ,  $Q_{\text{out}} = W - \text{VFC}$ , otherwise  $Q_{\text{out}} = 0$ . The loss of contaminant to the layer below  $Q_{\text{out}} \cdot C \cdot 10^{-3}$  grams, is computed next. The total liquid in the layer is now reset to  $W - Q_{\text{out}}$  and the total grams of chemical adjusted to  $M = M - MC - Q_{\text{out}} \cdot C \cdot 10^{-3}$ .

The layer collects the leachate from above, mixes, adsorbs, reacts, and then drains to field capacity to supply leachate to the layer below. Thus, the process proceeds.

#### Layer Below the Water Table

A layer below the water table has a horizontal flow input and output from groundwater flow. It is assumed that the layer immediately below the water table receives all the chemical in the leachate which is routed vertically because of rainfall infiltration. This assumption implies that the landfill is located in a groundwater discharge area. Layers further below the water table do not distribute the chemical vertically.





Where QH = volume of liquid into the layer in a two-day period.

$$QH = V \cdot DELZ \cdot WIDTH \cdot 2 \cdot 28.32 \cdot YS \quad (7)$$

where:  $V$  = groundwater velocity (ft/day),

28.32 = conversion factor ( $\text{ft}^3$  to liters),

YS = saturation volume fraction for porous media = porosity.

A layer below the water table is saturated, i.e.,  $W = \text{VSAT}$ . Horizontal routing is assumed to occur in the following way. QH liters of liquid flows from the layer at concentration C ppm, thus  $QH \cdot C \cdot 10^{-3}$  grams are transferred to the next layer downstream. Source chemical (S grams), chemical in the groundwater from the layer immediately upstream (MTX) and chemical from the layer above (only for the first layer below the water table) are added to the layer.

$$M = M_{\text{last J}} - QH \cdot C \cdot 10^{-3} + \text{MTX} + Q_{\text{in}} \cdot C_{\text{in}} \cdot 10^{-3} + S. \quad (8)$$

(downstream)    (upstream)            (above)            (Source)

The total chemical now mixes, adsorbs, and is partially degraded. The total grams of chemical  $M_{\text{this J}}$  is adjusted accordingly,  $M_{\text{this J}} = M - MC$ .

#### Variable Water Table

##### Rising Water Table

If the water table has risen since the last time period, it is assumed that the layers now saturated which were previously at field

capacity (or lower) are brought to saturation with water having no contaminant. That is, bringing these layers to saturation has resulted in no movement of chemical. Then, calculations are performed to distribute the chemical vertically by infiltration and horizontally by groundwater flow as described earlier for the constant water table case.

#### Falling Water Table

When the water table drops, the layers at saturation capacity above the new water table must drain to field capacity which causes a vertical routing of chemical in a manner similar to the usual case for layers above the water table.

For calculational simplicity, the water from rainfall infiltration and this excess water (VSAT - VFC) are routed vertically at the same time.

#### Demonstration Example for SLM-1

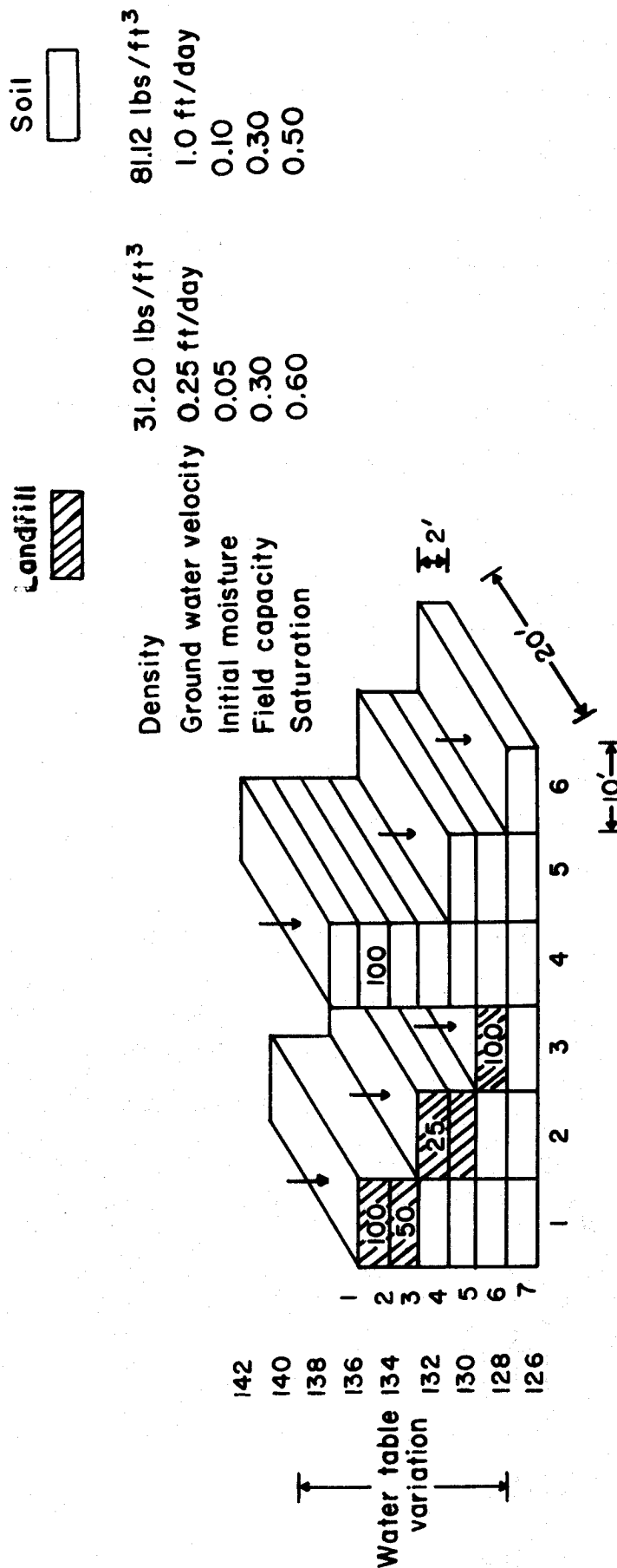
An example to illustrate the utility and flexibility of SLM-1 has been prepared. All input data are given in Figure 1. A rather arbitrary landfill-soil region was chosen with a varying water table that, at times, completely floods the landfill and soil. The high rainfall was chosen to speed the routing process for illustration purposes only.

At time  $t=0$ , 275 grams of chemical are distributed in the landfill and 100 grams in layer 2 of column 4, a soil layer. No source is added thereafter.

A data subroutine is prepared and a source function  $S(I,K)$  written. These are listed on page 14. The nomenclature given in Appendix II defines all variables.

Complete teletype instructions are given on page 15 to run this case. Logical unit number 30 is first defined as a file. All binary programs

# DEMONSTRATION EXAMPLE



WATER TABLE: Z/T = 132, 132, 128, 128, 132, 138, 138, 142, 132, 128, 128

RAINFALL: R = 2(8,4746), 0., 7(8,4746), 0.

NOTE: 8,4746 INCHES IN 2 DAYS CORRESPONDS TO 4000 LITERS

INFILTRATION = 50%

SOURCE: AT T = 0, 375 GRAMS OF CHEMICAL ARE PRESENT IN LANDFILL AND SOIL, NO ADDITIONAL

SOURCE AFTER T = 0

ELEVATION OF SURFACE: 138, 134, 130, 140, 132, 128

ELEVATION OF BOTTOM OF LANDFILL: 134, 130, 128

Figure 1 Demonstration example for SLM-1

including the compiled DATA and S subprograms are loaded and the RUN command is given. During program execution, several case parameters and data are requested by the main program. LUN = 30 indicates that all output is to be sent to logical unit 30, a defined file. NYR = 1 and NJ = 11 indicate eleven time periods per year for a run duration of one year are to be calculated for KL = 3 landfill columns and KT = 6 total columns. The output option variables KO = 1, JO = 1, IO = 0 indicate that complete output for each column is desired at each time period and a summary report for all columns is desired at the end of each time period. Output options are summarized in Appendix II, page 58. KA1 = KA2 = KR1 = KR2 = 0 indicates no adsorption or biodegradation is to be considered

After KR2 = 0 is entered as data, the SLM-1 program computes and outputs on logical unit 30. Then SLM-1 gives the user the option of continuing the run for another year.

For brevity, the complete output is given only for the first column. Summary output is given for all layers at each time period.

```

00001:      SUBROUTINE DATA
00002:      INCLUDE CRIE
00003:      DATA((Z(K),K=1,12)=138,134,130,140,132,128)
00004:      DATA((ZEL(K),K=1,3)=134,130,128)
00005:      DATA((ZWL(J),J=1,11)=132,132,128,128,132,138,138,142,
00006:      * 132,128,128)
00007:      DATA((F(J),J=1,11)=2(8.4746),0.,7(8.4746),0.)
00008:C
00009:      XINFL=0.5
00010:      ZMAX=140 $ ZE=128
00011:C
00012:      DO 1 I=1,7
00013:C      INITIALIZE MTX AND M ARRAYS
00014:      MTX(I)=0
00015:      DO 1 K=1,15
00016:      1 M(I,K)=0
00017:      M(2,1)=M(2,4)=M(6,3)=100
00018:      M(3,1)=50 $ M(4,2)=25 $ TOTSIART=375
00019:C
00020:      DELX=10 $ DELZ=2 $ WIDTH=20
00021:      ICAP=0 $ DELT=48
00022:C
00023:      YI(1)=0.05 $ YI(2)=0.10
00024:      YF(1)=0.30 $ YF(2)=0.30
00025:      YS(1)=0.60 $ YS(2)=0.5
00026:      D(1)=31.2 $ D(2)=81.12
00027:      V(1)=0.25 $ V(2)=1.0
00028:C
00029:      RETURN
00030:      END

```

```

00001:      FUNCTION S(I,K)
00002:      INCLUDE CRIE
00003:      S=0
00004:      RETURN
00005:      END
00006:

```

#EQUIP,30=FILE  
#LOAD,\*SLM1,BDATAVWT1  
RUN  
RUN

SLM 1

LUN=30  
NYR=1  
NJ=11  
KL=3  
KT=6  
KO=1  
JO=1  
IO=0  
KA1=0  
KA2=0  
KR1=0  
KR2=0

CALCULATE FOR ANOTHER YEAR?  
NO

SLM 1

#LOGOFF

SANITARY LANDFILL MODEL SLM 1  
 ENVIRONMENTAL HEALTH SCIENCES CENTER  
 OREGON STATE UNIVERSITY

YEAR 1  
 TIME PERIOD 1  
 COLUMN 1

LAYER	WATER (LITERS)	CHEM ADSORB (GMS)	CHEM REACTED (GMS)	CHEM FREE (GMS)	TOTAL CHEM (GMS)	CHEM CONC (PPM)	CHEM TX HORIZ (GMS)
2	2506.41	0	0	100.00	100.00	38.97	0
3	566.40	0	0	50.00	50.00	88.28	0
4	1132.80	0	0	0	0	0	0
5	5664.00	0	0	0	0	0	0
6	5664.00	0	0	0	0	0	0
7	5664.00	0	0	0	0	0	0

YEAR 1  
 TIME PERIOD 2  
 COLUMN 1

LAYER	WATER (LITERS)	CHEM ADSORB (GMS)	CHEM REACTED (GMS)	CHEM FREE (GMS)	TOTAL CHEM (GMS)	CHEM CONC (PPM)	CHEM TX HORIZ (GMS)
2	3398.40	0	0	74.42	74.42	21.90	0
3	1734.41	0	0	75.58	75.58	43.58	0
4	1132.80	0	0	0	0	0	0
5	5664.00	0	0	0	0	0	0
6	5664.00	0	0	0	0	0	0
7	5664.00	0	0	0	0	0	0

YEAR 1  
 TIME PERIOD 3  
 COLUMN 1

LAYER	WATER (LITERS)	CHEM ADSORB (GMS)	CHEM REACTED (GMS)	CHEM FREE (GMS)	TOTAL CHEM (GMS)	CHEM CONC (PPM)	CHEM TX HORIZ (GMS)
2	3338.40	0	0	74.42	74.42	21.90	0
3	1734.41	0	0	75.58	75.58	43.58	0
4	1132.80	0	0	0	0	0	0
5	3398.40	0	0	0	0	0	0
6	3338.40	0	0	0	0	0	0
7	5664.00	0	0	0	0	0	0

YEAR 1  
TIME PERIOD 4  
COLUMN 1

LAYER	WATER (LITERS)	CHEM ADSORB (GMS)	CHEM REACTED (GMS)	CHEM FREE (GMS)	TOTAL CHEM (GMS)	CHEM CONC (PPM)	CHEM TX HORIZ (GMS)
2	3398.40	0	0	46.85	46.85	13.79	0
3	3398.40	0	0	93.87	93.87	27.62	0
4	1468.82	0	0	9.28	9.28	6.32	0
5	3398.40	0	0	0	0	0	0
6	3398.40	0	0	0	0	0	0
7	5664.00	0	0	0	0	0	0

YEAR 1  
TIME PERIOD 5  
COLUMN 1

LAYER	WATER (LITERS)	CHEM ADSORB (GMS)	CHEM REACTED (GMS)	CHEM FREE (GMS)	TOTAL CHEM (GMS)	CHEM CONC (PPM)	CHEM TX HORIZ (GMS)
2	3398.40	0	0	29.49	29.49	8.68	0
3	3398.40	0	0	70.02	70.02	20.60	0
4	3398.40	0	0	49.46	49.46	14.55	0
5	5664.00	0	0	1.02	1.02	.18	0
6	5664.00	0	0	0	0	0	0
7	5664.00	0	0	0	0	0	0

YEAR 1  
TIME PERIOD 6  
COLUMN 1

LAYER	WATER (LITERS)	CHEM ADSORB (GMS)	CHEM REACTED (GMS)	CHEM FREE (GMS)	TOTAL CHEM (GMS)	CHEM CONC (PPM)	CHEM TX HORIZ (GMS)
2	6736.80	0	0	28.02	28.02	4.12	0
3	6736.80	0	0	66.52	66.52	9.79	0
4	5664.00	0	0	39.57	39.57	6.99	9.89
5	5664.00	0	0	.82	.82	.14	.20
6	5664.00	0	0	0	0	0	0
7	5664.00	0	0	0	0	0	0

YEAR 1  
TIME PERIOD 7  
COLUMN 1

LAYER	WATER (LITERS)	CHEM ADSORB (GMS)	CHEM REACTED (GMS)	CHEM FREE (GMS)	TOTAL CHEM (GMS)	CHEM CONC (PPM)	CHEM TX HORIZ (GMS)
2	6736.80	0	0	26.62	26.62	3.92	0
3	6736.80	0	0	63.19	63.19	9.30	0
4	5664.00	0	0	31.66	31.66	5.59	7.91
5	5664.00	0	0	.66	.66	.12	.16
6	5664.00	0	0	0	0	0	0
7	5664.00	0	0	0	0	0	0



TIME PERIOD 8  
COLUMN 1

LAYER	WATER (LITERS)	CHEM ADSORB (GMS)	CHEM REACTED (GMS)	CHEM FREE (GMS)	TOTAL CHEM (GMS)	CHEM CONC (PPM)	CHEM TX HORIZ (GMS)
2	6796.80	0	0	25.29	25.29	3.72	0
3	6796.80	0	0	60.03	60.03	8.83	0
4	5664.00	0	0	25.33	25.33	4.47	6.33
5	5664.00	0	0	.52	.52	.09	.13
6	5664.00	0	0	0	0	0	0
7	5664.00	0	0	0	0	0	0

YEAR 1  
TIME PERIOD 9  
COLUMN 1

LAYER	WATER (LITERS)	CHEM ADSORB (GMS)	CHEM REACTED (GMS)	CHEM FREE (GMS)	TOTAL CHEM (GMS)	CHEM CONC (PPM)	CHEM TX HORIZ (GMS)
2	3398.40	0	0	9.77	9.77	2.87	0
3	3398.40	0	0	21.05	21.05	6.20	0
4	3398.40	0	0	18.76	18.76	5.52	0
5	5664.00	0	0	61.48	61.48	10.86	.10
6	5664.00	0	0	0	0	0	0
7	5664.00	0	0	0	0	0	0

YEAR 1  
TIME PERIOD 10  
COLUMN 1

LAYER	WATER (LITERS)	CHEM ADSORB (GMS)	CHEM REACTED (GMS)	CHEM FREE (GMS)	TOTAL CHEM (GMS)	CHEM CONC (PPM)	CHEM TX HORIZ (GMS)
2	3398.40	0	0	6.15	6.15	1.81	0
3	3398.40	0	0	15.53	15.53	4.57	0
4	3398.40	0	0	17.56	17.56	5.17	0
5	3398.40	0	0	31.85	31.85	9.37	0
6	3398.40	0	0	13.68	13.68	4.03	0
7	5664.00	0	0	26.29	26.29	4.64	0

YEAR 1  
TIME PERIOD 11  
COLUMN 1

LAYER	WATER (LITERS)	CHEM ADSORB (GMS)	CHEM REACTED (GMS)	CHEM FREE (GMS)	TOTAL CHEM (GMS)	CHEM CONC (PPM)	CHEM TX HORIZ (GMS)
2	3398.40	0	0	6.15	6.15	1.81	0
3	3398.40	0	0	15.53	15.53	4.57	0
4	3398.40	0	0	17.56	17.56	5.17	0
5	3398.40	0	0	31.85	31.85	9.37	0
6	3398.40	0	0	13.68	13.68	4.03	0
7	5664.00	0	0	21.03	21.03	3.71	5.26

SANITARY LANDFILL MODEL SLM 1  
 ENVIRONMENTAL HEALTH SCIENCES CENTER  
 OREGON STATE UNIVERSITY

YEAR 1  
 TIME PERIOD 1

TOTAL GRAMS OF CHEMICAL IN LAYER I, COLUMN K						
	1	2	3	4	5	6
1	0	0	0	0	0	0
2	100.0	0	0	100.0	0	0
3	50.0	0	0	0	0	0
4	0	25.0	0	0	0	0
5	0	0	0	0	0	0
6	0	0	95.0	5.0	0	0
7	0	0	0	0	0	0

YEAR 1  
 TIME PERIOD 2

TOTAL GRAMS OF CHEMICAL IN LAYER I, COLUMN K						
	1	2	3	4	5	6
1	0	0	0	0	0	0
2	74.4	0	0	100.0	0	0
3	75.6	0	0	0	0	0
4	0	18.6	0	0	0	0
5	0	6.4	0	0	0	0
6	0	0	90.3	8.8	1.0	0
7	0	0	0	0	0	0

YEAR 1  
 TIME PERIOD 3

TOTAL GRAMS OF CHEMICAL IN LAYER I, COLUMN K						
	1	2	3	4	5	6
1	0	0	0	0	0	0
2	74.4	0	0	100.0	0	0
3	75.6	0	0	0	0	0
4	0	18.6	0	0	0	0
5	0	3.2	0	0	0	0
6	0	1.2	45.1	3.8	.4	0
7	0	2.0	45.1	5.0	.6	0

YEAR 1  
TIME PERIOD 4

	TOTAL GRAMS OF CHEMICAL IN LAYER I, COLUMN K					
	1	2	3	4	5	6
1	0	0	0	0	0	0
2	46.8	0	0	69.8	0	0
3	93.9	0	0	30.2	0	0
4	9.3	11.7	0	0	0	0
5	0	6.4	0	0	0	0
6	0	3.1	28.4	3.8	.3	0
7	0	3.4	53.2	13.0	1.6	.1

YEAR 1  
TIME PERIOD 5

	TOTAL GRAMS OF CHEMICAL IN LAYER I, COLUMN K					
	1	2	3	4	5	6
1	0	0	0	0	0	0
2	29.5	0	0	44.0	0	0
3	70.0	0	0	41.4	0	0
4	49.5	7.4	0	14.7	0	0
5	1.0	10.4	0	0	0	0
6	0	2.5	27.6	4.4	1.0	0
7	0	2.7	43.3	21.1	3.9	.4

YEAR 1  
TIME PERIOD 6

	TOTAL GRAMS OF CHEMICAL IN LAYER I, COLUMN K					
	1	2	3	4	5	6
1	0	0	0	0	0	0
2	23.0	0	0	35.2	0	0
3	66.5	0	0	33.1	0	0
4	39.6	16.9	0	11.7	0	0
5	.8	10.1	0	0	0	0
6	0	2.0	26.7	4.9	1.7	0
7	0	2.2	35.2	25.5	7.3	1.1

YEAR 1

TIME PERIOD 7

TOTAL GRAMS OF CHEMICAL IN LAYER I, COLUMN K

	1	2	3	4	5	6
1	0	0	0	0	0	0
2	26.6	0	0	28.1	0	0
3	63.2	0	0	26.5	0	0
4	31.7	24.0	0	9.4	0	0
5	.7	9.7	0	0	0	0
6	0	1.6	25.8	5.3	2.3	0
7	0	1.8	28.6	27.4	11.0	2.4

YEAR 1

TIME PERIOD 8

TOTAL GRAMS OF CHEMICAL IN LAYER I, COLUMN K

	1	2	3	4	5	6
1	0	0	0	0	0	0
2	25.3	0	0	22.5	0	0
3	60.0	0	0	21.2	0	0
4	25.3	29.1	0	7.5	0	0
5	.5	9.4	0	0	0	0
6	0	1.3	24.8	5.5	2.9	0
7	0	1.4	23.2	27.7	14.3	4.1

YEAR 1

TIME PERIOD 9

TOTAL GRAMS OF CHEMICAL IN LAYER I, COLUMN K

	1	2	3	4	5	6
1	0	0	0	0	0	0
2	9.8	0	0	7.7	0	0
3	21.1	0	0	10.0	0	0
4	18.8	11.2	0	7.9	0	0
5	61.5	26.9	0	25.6	0	0
6	0	1.0	23.8	5.6	3.4	0
7	0	1.1	18.8	26.8	16.9	6.1

YEAR 1  
TIME PERIOD 10

TOTAL GRAMS OF CHEMICAL IN LAYER I, COLUMN K						
	1	2	3	4	5	6
1	0	0	0	0	0	0
2	6.1	0	0	4.8	0	0
3	15.5	0	0	8.1	0	0
4	17.6	7.1	0	8.0	0	0
5	31.8	12.0	0	13.4	0	0
6	13.7	6.2	9.2	7.7	1.2	0
7	26.3	14.8	29.9	40.0	21.2	8.3

SANITARY LANDFILL MODEL SLM 1  
ENVIRONMENTAL HEALTH SCIENCES CENTER  
OREGON STATE UNIVERSITY

YEAR 1  
TIME PERIOD 11

TOTAL GRAMS OF CHEMICAL IN LAYER I, COLUMN K						
	1	2	3	4	5	6
1	0	0	0	0	0	0
2	6.1	0	0	4.8	0	0
3	15.5	0	0	8.1	0	0
4	17.6	7.1	0	8.0	0	0
5	31.8	12.0	0	13.4	0	0
6	13.7	6.2	9.2	7.7	1.2	0
7	21.0	17.1	26.9	38.0	24.9	10.9

SUMMARY OF CHEMICAL DISTRIBUTION AT THE END OF THIS TIME PERIOD  
 TOTAL CHEMICAL IN LANDFILL & SOIL AT TIME ZERO = 375.000 GRAMS  
 TOTAL CHEMICAL NOW IN LANDFILL = 49.950 GRAMS  
 TOTAL CHEMICAL NOW IN SURROUNDING SOIL = 251.238 GRAMS  
 TOTAL CHEMICAL DEGRADED BY REACTION SINCE TIME ZERO = 0 GRAMS  
 TOTAL CHEMICAL TO ENVIRONMENT IN THIS TIME PERIOD = 1.656 GRAMS  
 TOTAL CHEMICAL RELEASED IN PREVIOUS TIME PERIODS = 72.156 GRAMS  
 TOTAL CHEMICAL ADDED SINCE TIME ZERO = 0 GRAMS

### Validation of SLM-1

In the SLM-1 model, there are three major calculational procedures that must be validated:

1. Vertical routing of the chemical from the landfill or soil media to the water table, an unsaturated flow mechanism,
2. Horizontal distribution of chemical by groundwater flow beneath the water table, a saturated transport mechanism,
3. And routing of the chemical near the water table interface as the water table rises or falls.

#### Vertical Routing of Chemical Above Water Table

The SLM-1 model uses the method of Remson et al. (1968) to route moisture downward in the unsaturated media to the water table. These investigators have shown that this simple procedure satisfactorily agrees with experimental results in a laboratory landfill. The SLM-1 model extends the Remson et al. (1968) procedure to chemical routing by assuming that each two-foot layer of porous media acts as a well-mixed vessel in transporting the chemical downward. Although untested with experimental data, this procedure is expected to satisfactorily predict chemical movement above the water table.

#### Horizontal Distribution of Chemical in Groundwater Flow

To determine the validity of the SLM-1 model predictions of chemical movement beneath the water table, two auxiliary models were developed in this study. The one-dimensional continuous model described in Appendix I has been generally accepted in the literature as a satisfactory description of saturated flow in porous media. The multitank model of Appendix I is a simplified model which predicts results identical to

the continuous model in the limit of infinitesimal tank size (i.e. infinite number of infinitesimally thick tanks in a given region).

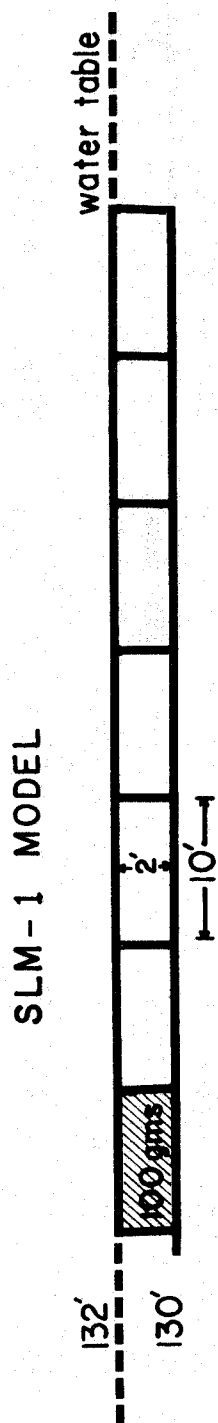
These auxiliary models were used to ascertain the validity of the method of calculating the horizontal chemical transport in the horizontally flowing groundwater of SLM-1 (Figure 2).

- a. The continuous and multitank models were compared. Figure 3 shows that the multitank results do approach the continuous model results as the tank size decreases. This agreement confirms the accuracy of these two independent models.
- b. The SLM-1 model for a single horizontal layer with each unit 10 feet long is compared to the continuous and multitank models in Figure 4, for three cases of chemical degradation and/or adsorption. SLM-1 predicts chemical concentrations between the predictions of the multitank and continuous models. The SLM-1 predictions are only slightly different from the multitank model which is to be expected. From these comparisons, it can be seen that SLM-1 with 10-foot-long compartments in the direction of flow compares well with the continuous model (the accepted standard) except near the "front" of the chemical dispersion curve. If the groundwater velocity is 1 ft/day, the "front" after 30 days is about 30 feet from the source for the case of no adsorption (Figure 4). Figure 5 shows that the position of the front decreases as the degree of adsorption increases.

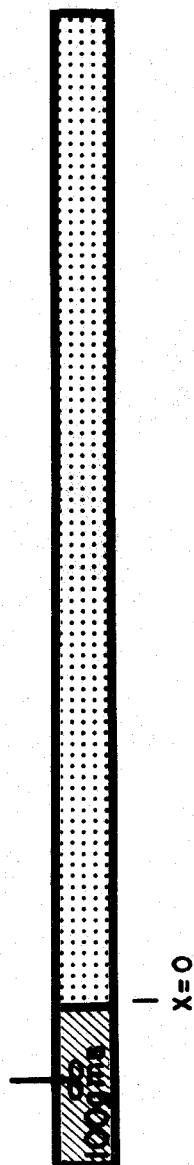
It is concluded that SLM-1 satisfactorily predicts the horizontal chemical distribution under the water table.

#### Variable Water Table Effect on Chemical Distribution

The model calculations for the case of a rising or falling water table have not been validated because of the lack of a satisfactory standard for comparison. Future studies should attempt to validate the assumed distribution mechanism.



**CONTINUOUS MODEL**  
Landfill & Soil Saturated



**TANK MODEL**  
Landfill & Soil Saturated

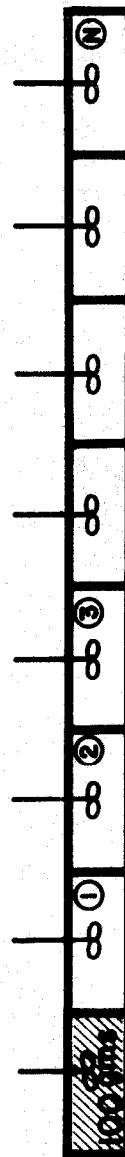
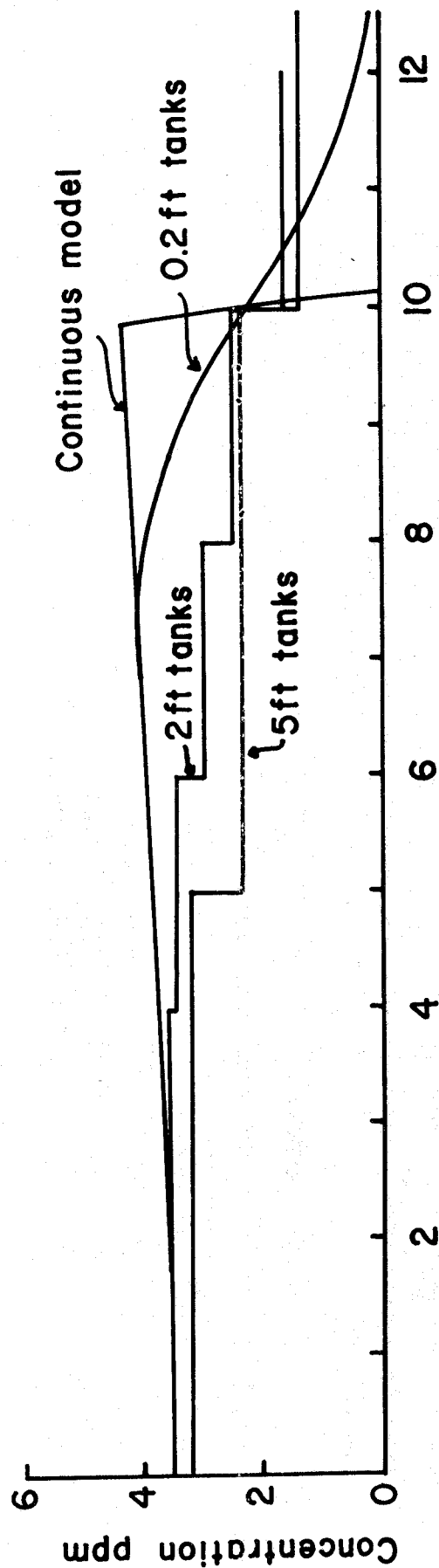
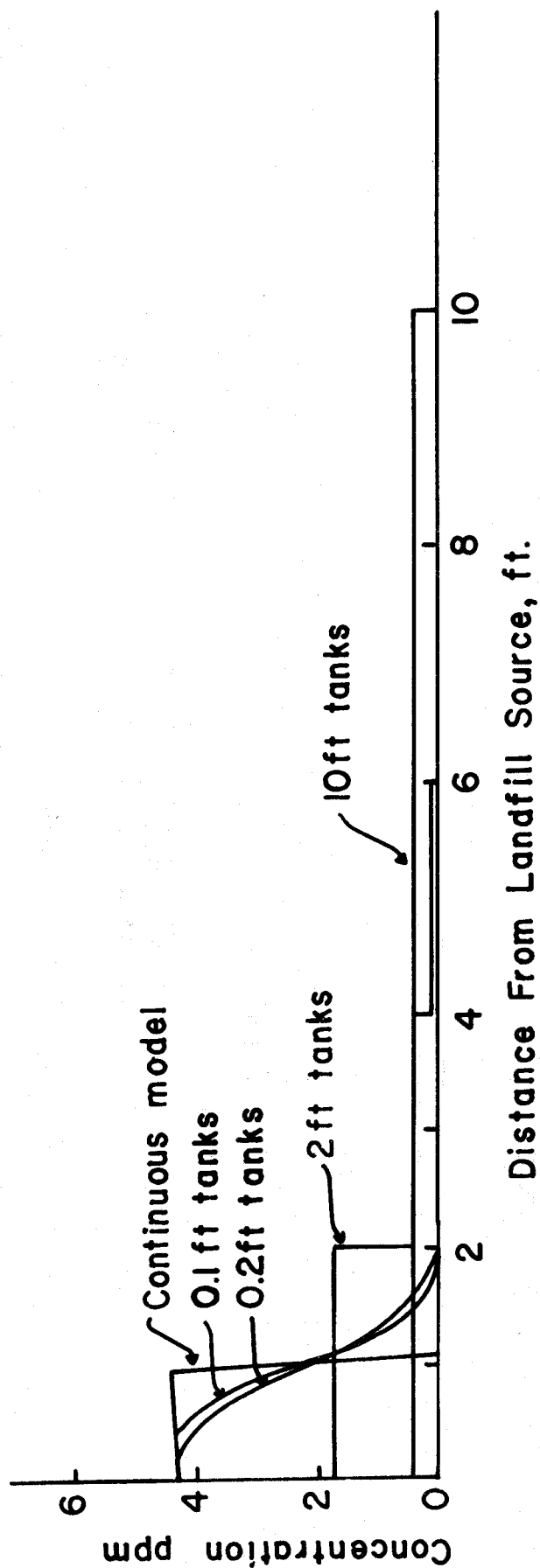


Figure 2 Comparison study of SLM-1 with continuous and multitank models





Distance From Landfill Source, ft.

Figure 3 Comparison of continuous and tank models at  $t = 1$  day (top) and  $t = 10$  days (bottom)

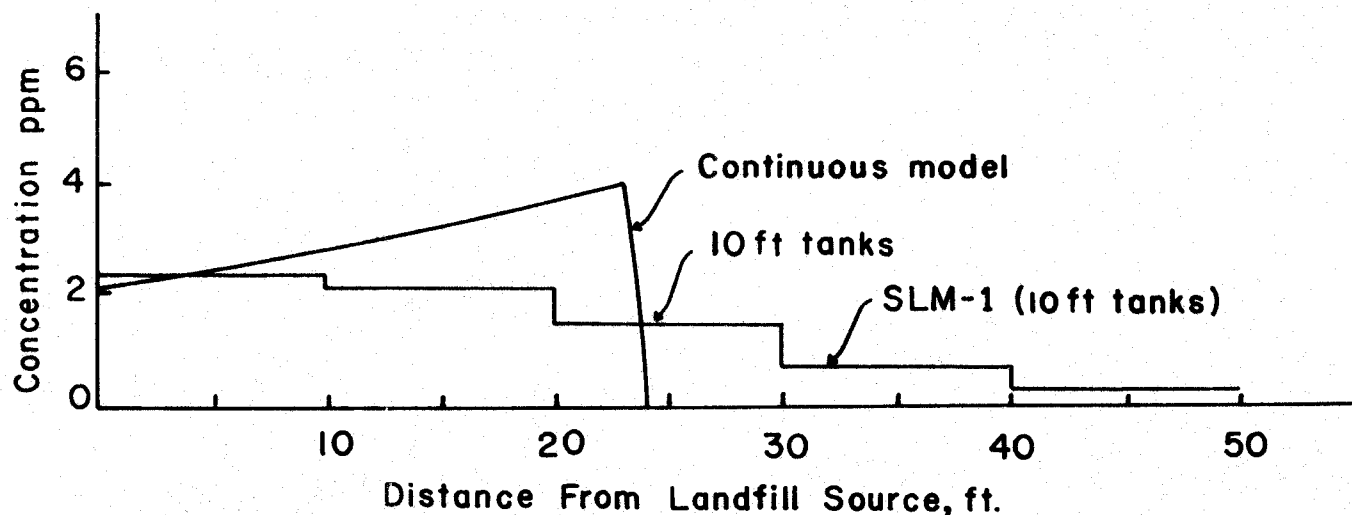
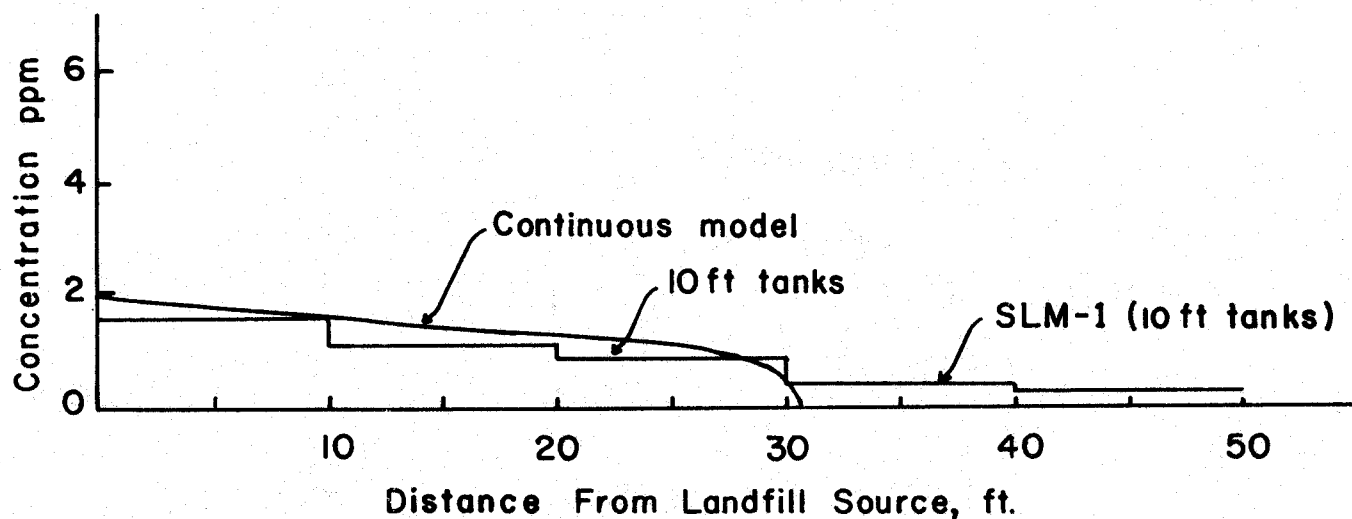
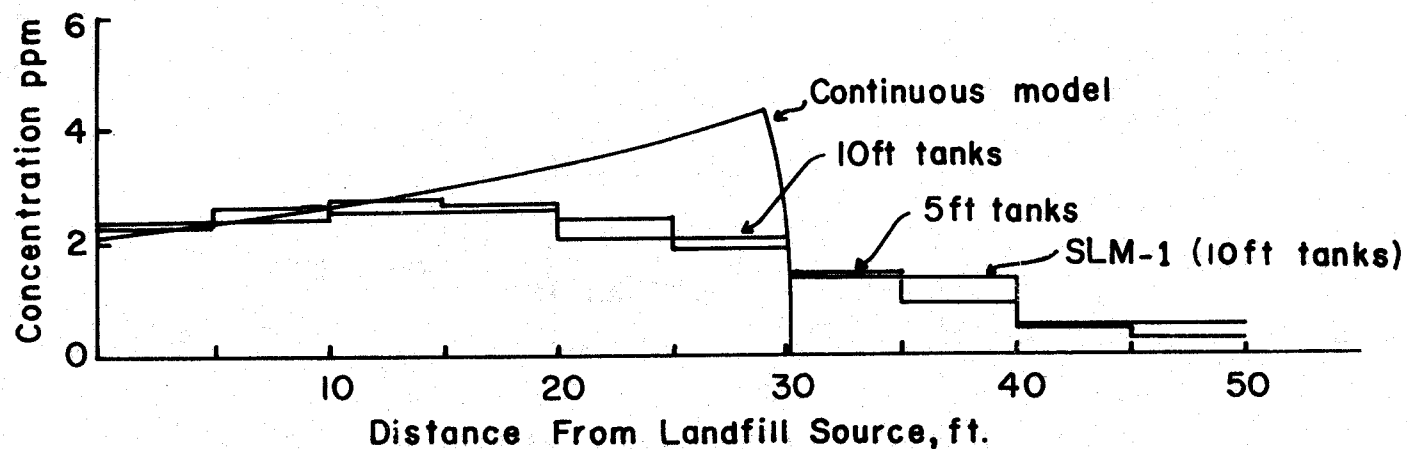


Figure 4 Comparison of SLM-1 model with continuous and tank models at  $t = 30$  days; top = no degradation, no adsorption; middle = no adsorption, mild degradation; bottom = weak adsorption, no degradation.

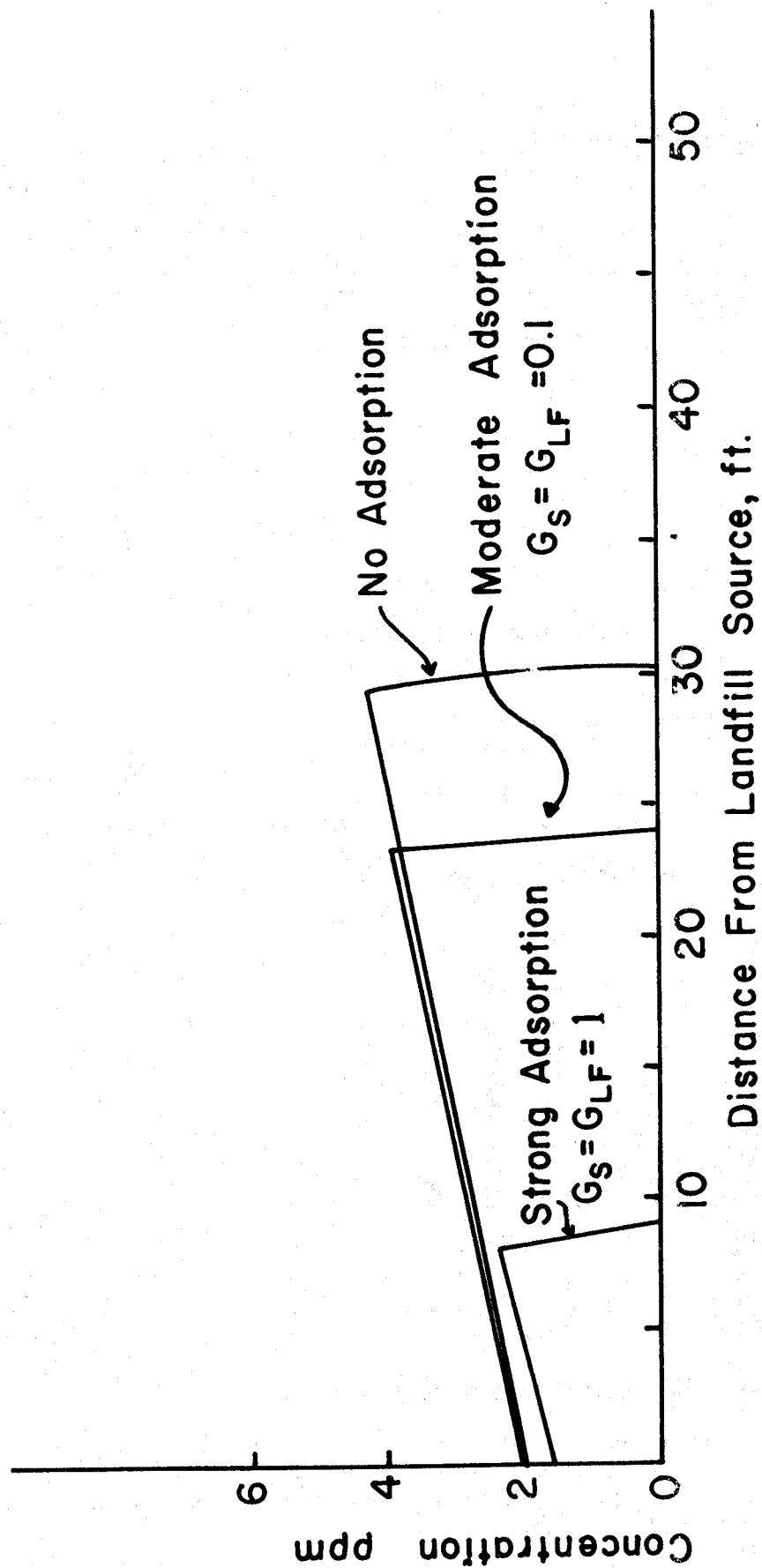


Figure 5 Effect of adsorption on chemical distribution predicted by the continuous model at  $t = 30$  days

## CASE STUDY

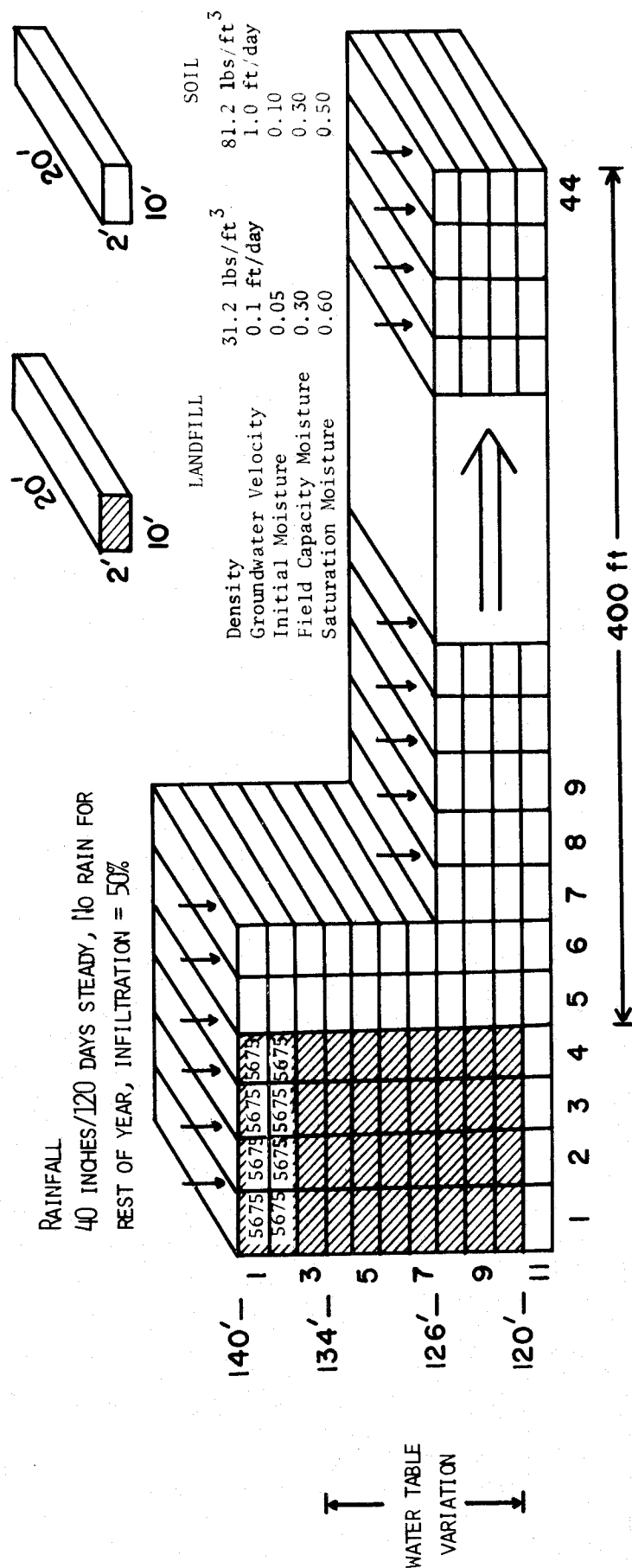
### Case Study of a Sanitary Landfill Similar to Brown's Island at Salem, Oregon

Figure 6 on page 30 gives all the input data used in this case study. Figure 6a on page 31 shows graphically the water table elevation, in feet above mean sea level, of the Brown's Island area. This one-year graph is assumed to be operative periodically (with a period of one year) over the shortly to be discussed ten-year simulation runs. It was assumed that 45,400 grams of a chemical were initially distributed in an area 4 ft by 40 ft by 20 ft at the top of the landfill with no source added thereafter. The simplified rainfall and soil characteristics correspond to conditions typical of the Brown's Island area. A brief description of Brown's Island is given on page 35.

The DATA subroutine is listed on page 37. Ten computer runs with varying parameters were obtained at a cost of \$30 each (OSU CDC 3300 Computer at non-prime rates) for runs of ten-year duration.

To demonstrate graphically the concentration distribution as a function of time at the point marked 400 feet (block 44) on Figure 6 (400 feet down the hydraulic gradient from the landfill site), Figure 6b (page 32) has been prepared. Observe that in all the cases shown in this figure that it takes at least three years before any appreciable concentration amplitude is obtained at the 400-foot distance from the landfill site. That peaks (pulses) of chemical concentration are generated and then dispersed while translating down gradient is a very real physical phenomenon and reflects, among other things, the physical interplay of a pulse type annual rainfall and the variable elevation of

# CASE STUDY OF A SANITARY LANDFILL SIMILAR TO BROWN'S ISLAND AT SALEM, OREGON



T = 0 NOVEMBER 15 2 DAY TIME PERIODS

WATER TABLE:

Z/T = 4(120), 121, 2(125), 3(124), 2(125), 126, 124, 2(122), 126, 124, 122, 3(120), 122,  
128, 126, 122, 3(120), 124, 3(126), 130, 132, 134, 132, 130, 132, 128, 2(126),  
4(124), 3(121), 5(120), 122, 126, 2(128), 124, 122, 4(120), 2(126), 3(124),  
5(120), 3(124), 105(120)

SOURCE: 45, 400 GRAMS DISTRIBUTED UNIFORMLY IN TOP 4 FT. OF LANDFILL OVER A WIDTH OF  
20 FT. AND A LENGTH OF 40 FT. AT TIME ZERO. NO ADDITIONAL SOURCE AFTER T = 0.

SURFACE ELEVATION: 6(140), 44(126)

ELEVATION OF BOTTOM OF LANDFILL: 4(120)

Figure 6 Case study of a sanitary landfill similar to Brown's Island  
at Salem, Oregon

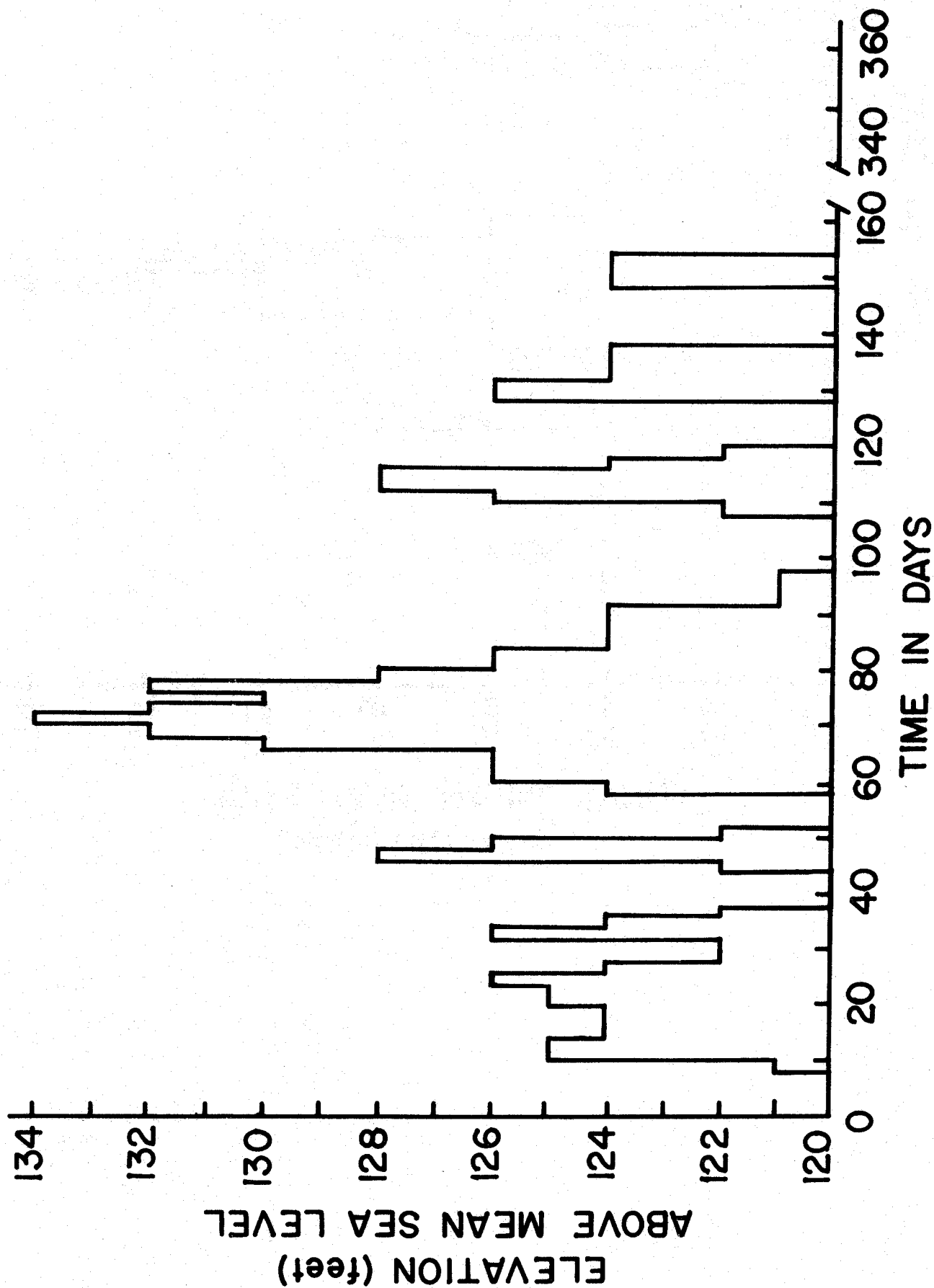


Figure 6a Yearly water table elevation record at the Salem bridge gauging station.

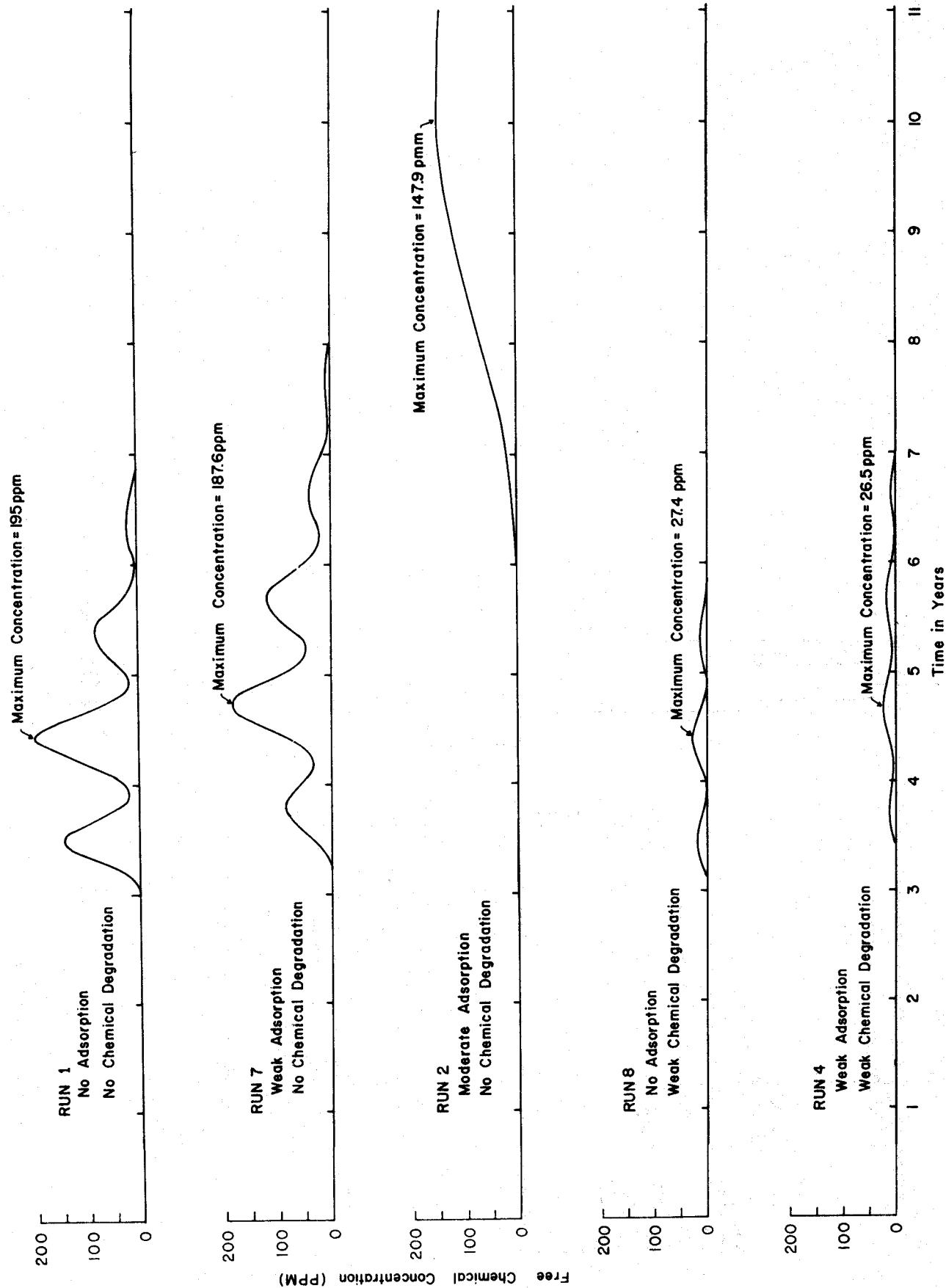


Figure 6b Typical plots of the bottom soil conduit aqueous phase chemical concentration 400 feet down gradient from the landfill.

the water table under both the landfill site (chemical source) and the soil conduit. The explanation of the peak(s) formation is as follows:

As rain falls upon the surface of the LFS (landfill site), some penetrates the LFS surface and then the potential for moving some of the chemical vertically downward (according to the rules of moisture routing previously mentioned) exists. Simultaneously, the water table is moving up and down (Figure 6a). When enough water moving downward from the top of the LFS (carrying some but not all of the chemical with it) meets the water table, then chemical is allowed to move horizontally and eventually out into the various soil conduits. Only four layers of soil conduits are shown in Figure 6. However, this is adequate to demonstrate the model.

Once the chemical pulse reaches one of the soil conduits, it can continue convecting and dispersing down gradient so long as the water table covers that conduit. When the water table drops below the level of that conduit then horizontal motion ceases and vertical motion is allowed to proceed according to the previously mentioned rules of the model. Thus, lateral mixing at any point in the system is allowed for. This further complicates the distribution analysis.

The net result, observed in a monitoring well (impervious casing) bored through the top three conduit (layers) and into the fourth at the 400-foot down gradient point, is the concentration distribution curves over time as shown in Figure 6b. The effects that reversible linear sorption and irreversible microbial degradation and/or first order chemical reaction have on the concentration distributions for this particular 400-foot down gradient monitoring well are also demonstrated in Figure 6b.

Summary tabular output similar to pages 16 to 22 for the demonstration example was obtained at the end of each year. These results



are not included in this report, however, the essence of these results (fraction of initial chemical transmitted to the environment as a function of time) is given tabularly on pages 42 through 46 and in Figures 7 through 9 on pages 38 to 40.

These results show that reversible adsorption tends to delay the transfer of the contaminants to the environment (compare runs 1, 2 and 7 on Figure 7). Moderate chemical degradation (rate constant in the range 0.001-0.01 1/hr, Table 1, page 41) in the soil essentially eliminates transfer to the environment while weak degradation (rate constant =  $0.0002 \text{ hr}^{-1}$ ) eliminates 86% of the contaminant (compare runs 1, 3, and 8 on Figure 7). Only biodegradation in the soil was considered since run 6 shows that moderate biodegradation in the landfill would essentially remove all of the contaminant. Thus, neglecting biodegradation in the landfill leads to a conservative result. Combined adsorption and biodegradation show essentially the same result as biodegradation except a slight delay in response (compare runs 4 and 8 on Figure 8). Run 5 was made with a constant water table of 120 feet, showing that by year 10 the transfer to the environment is nearly the same as for the variable water table situation (Figure 9). The groundwater velocity in the landfill was varied from 0.05 ft/day in run 10 to 0.5 ft/day in run 9 with little effect on the transfer to the environment (Figure 9).

Careful observation of the model predictions for this case study shows the effects of several key parameters. Additional runs could have been made to vary other conditions if desired. These results clearly show the overwhelming importance of biodegradation and adsorption on the fate of the chemical and ultimate transfer to the environment.

### Brown's Island Landfill, Salem, Oregon

A general description of the Brown's Island area is included in Balster and Parsons (1968). The geology of the immediate and surrounding area has been mapped by Thayer (1939) and Price (1967). A complete report by Sweet (1972) concerning the hydrogeology of the landfill site is on file with the Oregon State Engineer and the Department of Environmental Quality.

The Brown's Island landfill is located between the Willamette River and a meander channel of the river. It occupies the lowest geomorphic unit in the valley, the flood plain, and is subject to surface water inundation. Both the soils and the immediate subsurface deposits at the site have relatively high hydraulic conductivity

Infiltrating precipitation and a water table which regularly saturates the putrescible material deposited at the site result in the generation of leachate at the site. The down-gradient flow of the leachate is sub-parallel to the flow direction of the adjacent surface water bodies. This results in the degradation of the shallow ground waters in the local system and the eventual drainage of some contaminants into the local surface water bodies, i.e. the sloughs, the ponds in the borrow pit bottoms, and the Willamette River.

A ground-water monitoring system has recently been installed at the site. In the future it will be possible to physically monitor the quality of the groundwater in the vicinity of the landfill and to compare the observed leachate concentrations with those predicted by the model.

The area surrounding the Brown's Island landfill site and the approximate position (marked by solid dots) of the recently installed monitoring wells in the landfill itself are shown in Figure 6c, page 36.

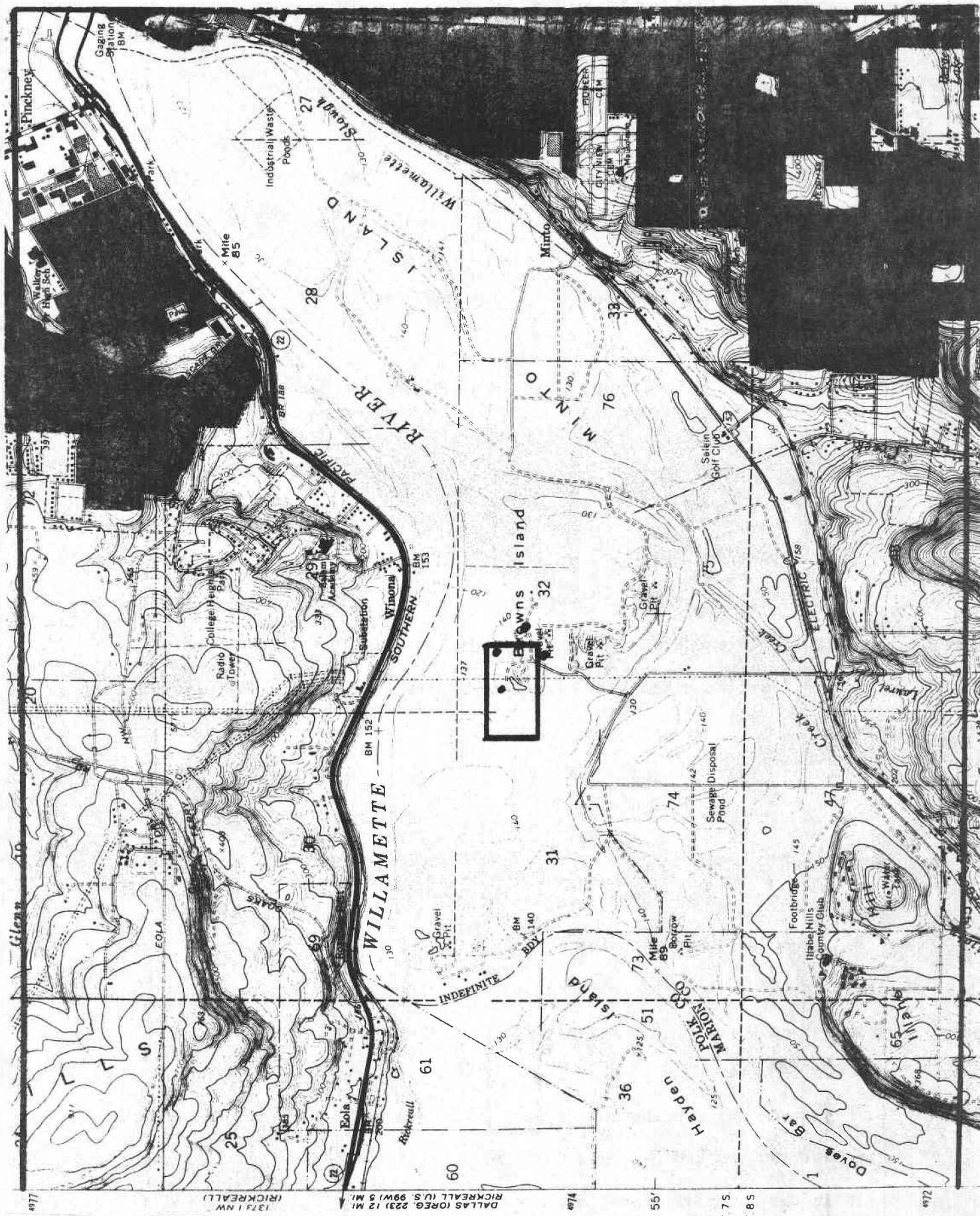


Figure 6c Brown's Island and surrounding terrain, from U.S.G.S. 15', Salem Quadrangle, topographic map

```

00001:      SUBROUTINE DATA
00002:      INCLUDE CRIB
00003:      DATA((Z(K),K=1,50)=6(140),44(126))
00004:      DATA((ZBL(K),K=1,4)=4(120))
00005:      DATA((ZWT(J),J=1,182)=4(120),121,125,125,124,124,124,
00006:      * 125,125,126,124,122,122,126,124,122,3(120),122,128,126,
00007:      * 122,3(120),124,3(126),130,132,134,132,130,132,128,
00008:      * 126,126,124,3(124),3(121),5(120),122,126,2(128),124,
00009:      * 122,4(120),2(126),3(124),5(120),3(124),105(120))
00010:      DATA((R(J),J=1,182)=60(0.667),122(0.))
00011:C
00012:      XINFL=0.5
00013:      ZMAX=140 $ ZB=120
00014:C
00015:      DO 1 I=1,12
00016:      MTX(I)=0
00017:      DO 1 K=1,50
00018:      1 M(I,K)=0
00019:      DO 2 I=1,2
00020:      DO 2 K=1,4
00021:      2 M(I,K)=5675
00022:      TOTSTART=45400
00023:C
00024:      DELX=10 $ DELZ=2 $ WIDTH=20
00025:      ICAP=0 $ DELT=48
00026:C
00027:      YI(1)=0.05 $ YI(2)=0.10
00028:      YF(1)=0.30 $ YF(2)=0.30
00029:      YS(1)=0.60 $ YS(2)=0.5
00030:      D(1)=31.2 $ D(2)=81.12
00031:      V(1)=0.1 $ V(2)=1.0
00032:C
00033:      RETURN
00034:      END

```

]

```

]
00001:      FUNCTION S(I,K)
00002:      INCLUDE CRIB
00003:      S=0
00004:      RETURN
00005:      END

```

]

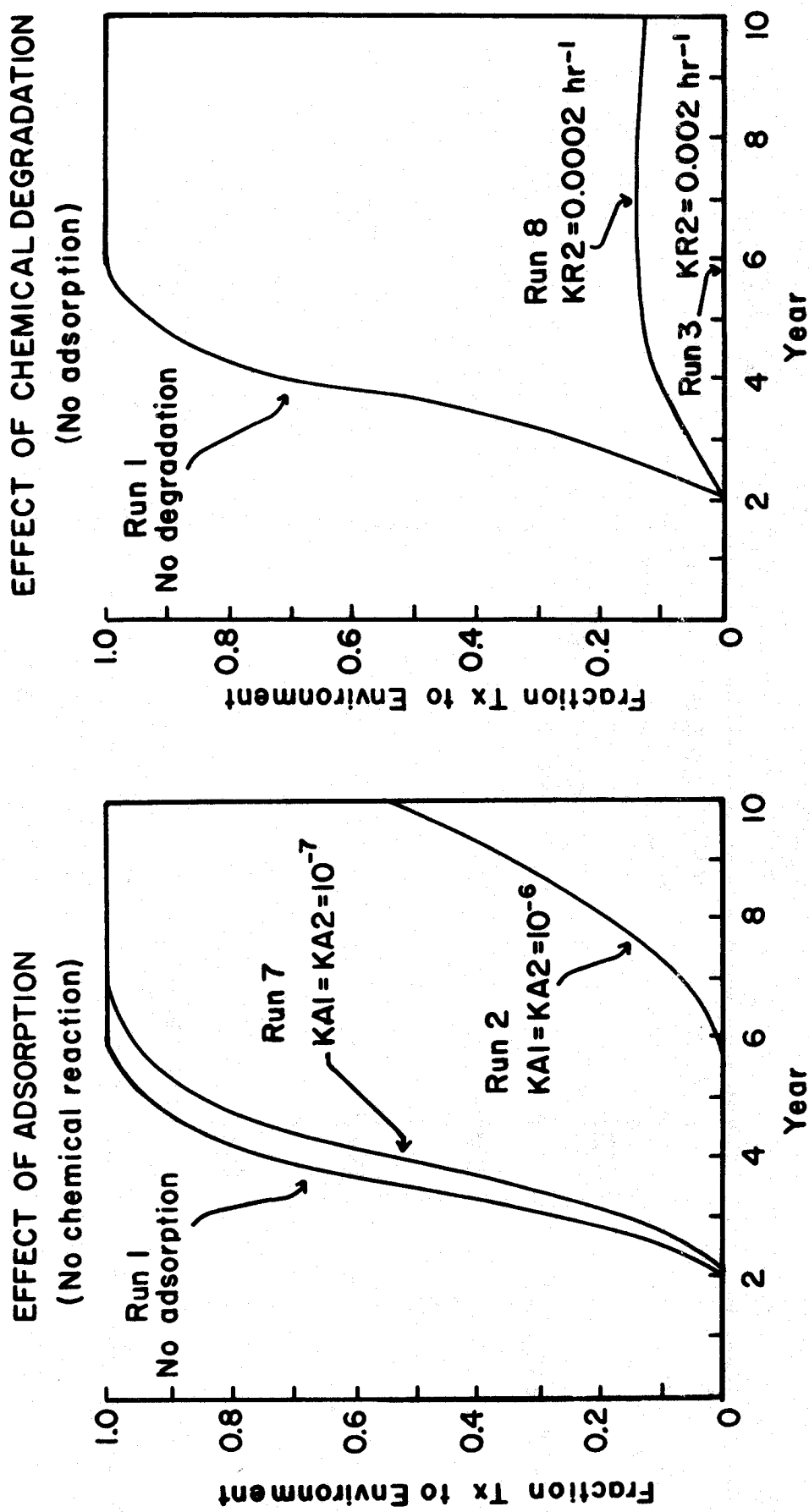
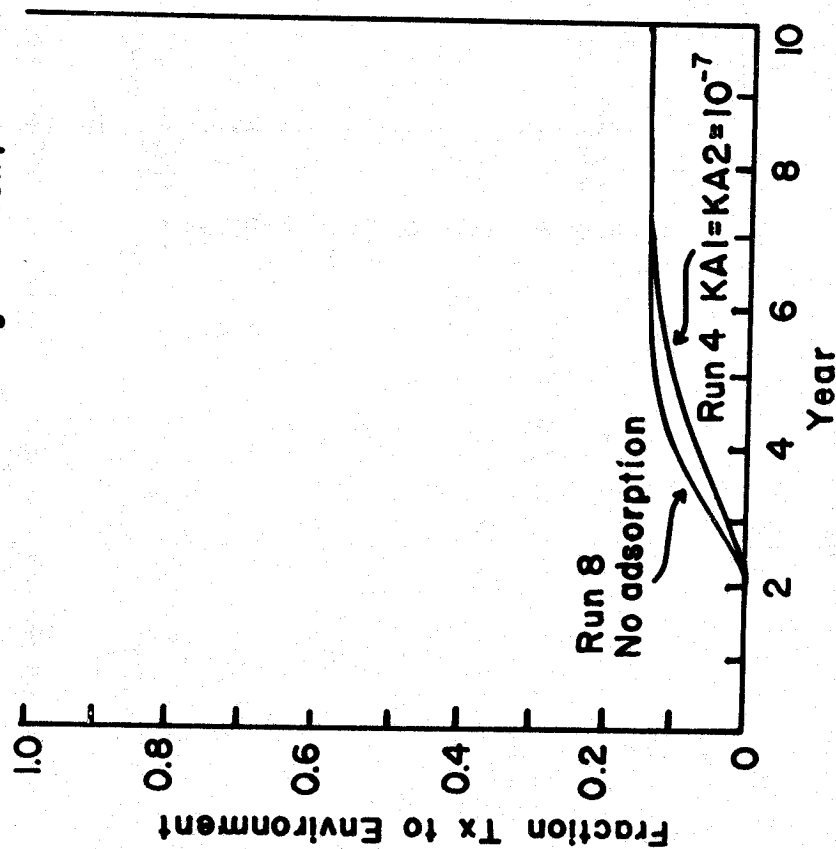


Figure 7 Effect of adsorption and chemical degradation on contaminant transferred to the environment

### EFFECT OF ADSORPTION (Mild chemical degradation)



### EFFECT OF CHEMICAL DEGRADATION (Weak adsorption)

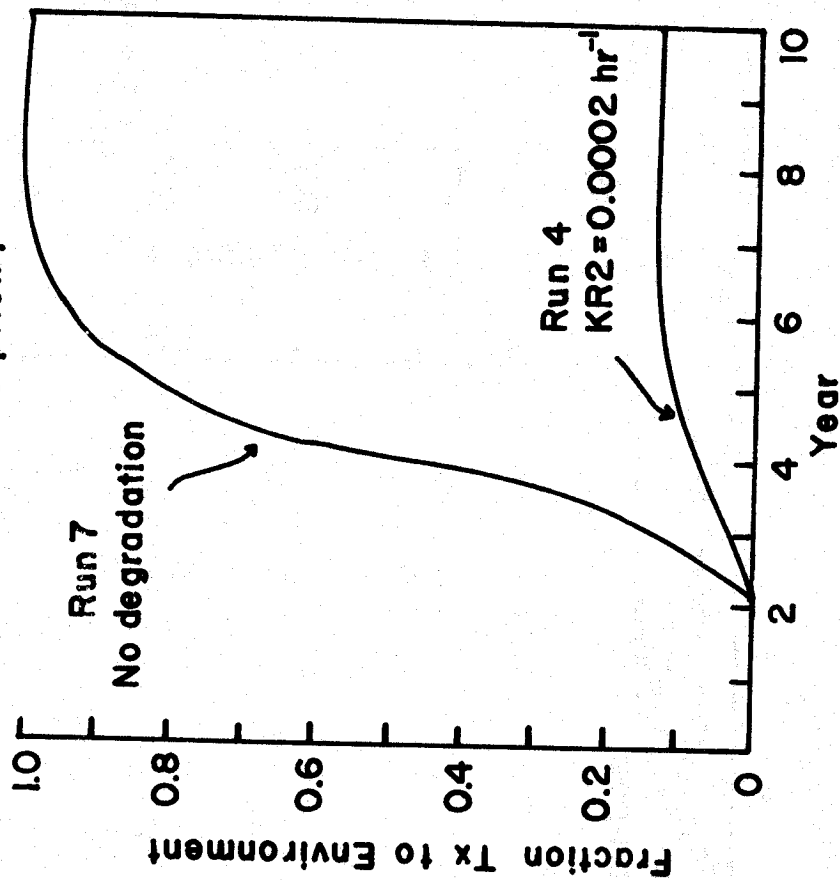
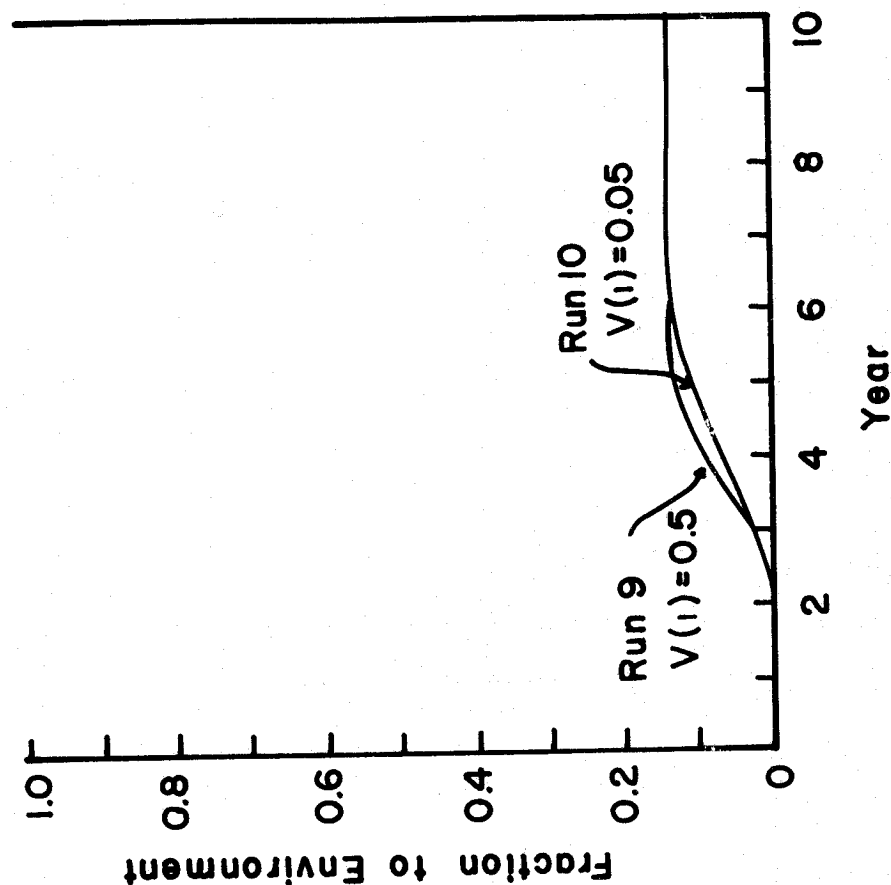


Figure 8 Effect of adsorption and chemical degradation on contaminant transferred to the environment

# EFFECT OF GROUNDWATER VELOCITY IN LANDFILL

## Weak adsorption/mild chemical degradation

Weak adsorption/mild chemical degradation



# EFFECT OF WATER TABLE

Weak adsorption/mild chemical degradation

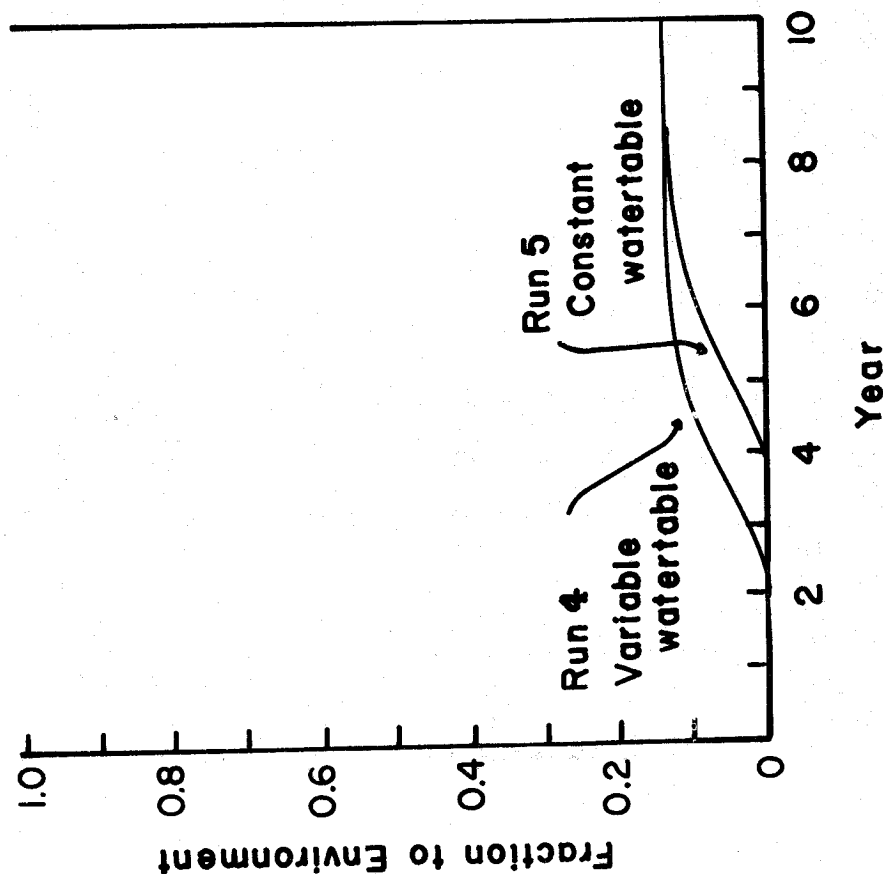


Figure 9 Effect of water table variation and groundwater velocity on contaminant transferred to the environment

Table 1 Examples of chemicals (common agricultural and industrial) covered by this report.

Biodegradation Rate Constant KR (see also Appendix II)

Sorption Coefficient KA or K (cm <sup>3</sup> /gm soil)	Biodegradation Rate Constant KR (see also Appendix II)			
	None ( $<0.0001$ 1/hr)*	Weak ( $0.0001-0.001$ 1/hr)	Moderate ( $0.001-0.01$ 1/hr)	Strong ( $>0.01$ 1/hr)
None ( $<0.01$ )**	Nitrates			
Weak ( $0.01-0.1$ )	<div> <div>Uracils</div> <div>Isocil</div> <div>Bromacil</div> <div>Terbacil</div> </div> <div>Phenol</div>	BCH (Hexachloro- cyclohexane)		
Moderate ( $0.1-1.0$ )		Carbamates IPC CIPC	Phenoxy herbicides 2,4-D 2,4,5-T	
Strong ( $>1.0$ )	Chlorinated Hydrocarbons DDT Aldrin HEOD Lindane	PCBs Aroclor 1242	Diquat (Chemical and photochemical degradation) Paraquat	Phosphates (Hydrolysis mainly) Dichlorvos Parathion Guthion

\* These values correspond to chemical half-lives in a water saturated porous soil of the Newberg silt loam type soil (50% sand, 8% organic, and 20% clay) at 25°C. E.g.; a chemical listed under the column entitled moderate biodegradation has a half-life span from 2.9 to 29 days.

\*\* These values correspond to Freundlich isotherm,  $x/m = KC_{eq}$ , K values such as those shown in Tables III-3 and III-4 in Appendix III.



RUN 1: No Adsorption, No Chemical Degradation (e.g., nitrate compounds)  
 KA1=KA2=0; KR1=KR2=0  
 V(1)=0.1 ft/day; V(2)=1.0 ft/day  
 Variable Water Table

<u>Year</u>	<u>Groundwater Concentration at 400 ft from Landfill, ppm</u>	<u>Fraction Degraded by Chemical Reaction</u>	<u>Fraction Transferred to Environment</u>
1	0	--	0
2	1.042	--	0.0013
3	26.377	--	0.2902
4	21.751	--	0.7429
5	6.532	--	0.9455
6	1.201	--	0.9916
7	0.177	--	0.9989
8	0.018	--	0.9998
9	0	--	1.0000
10	0	--	1.0000

Maximum concentration at 400 ft position is 195 ppm occurring at 4.43 years.

RUN 2: Moderate Adsorption, No Chemical Degradation (e.g., phenolated compounds)  
 KA1=KA2=10<sup>-6</sup>; KR1=KR2=0  
 V(1)=0.1 ft/day; V(2)=1.0 ft/day  
 Variable Water Table

<u>Year</u>	<u>Groundwater Concentration at 400 ft from Landfill, ppm</u>	<u>Fraction Degraded by Chemical Reaction</u>	<u>Fraction Transferred to Environment</u>
1	0	--	0
2	0	--	0
3	0	--	0
4	0.071	--	0.0006
5	2.666	--	0.0026
6	20.621	--	0.0160
7	65.907	--	0.0690
8	119.032	--	0.1875
9	146.716	--	0.3595
10	139.213	--	0.5437

Maximum concentration at 400 ft position is 147.9 ppm occurring at 10.22 years.

RUN 3: No Adsorption, Moderate Chemical Degradation in Soil  
 $KA1=KA2=0$ ;  $KR1=0$ ;  $KR2=0.002 \text{ hr}^{-1}$   
 $V(1)=0.1 \text{ ft/day}$ ;  $V(2)=1.0 \text{ ft/day}$   
 Variable Water Table

<u>Year</u>	<u>Groundwater Concentration at 400 ft from Landfill, ppm</u>	<u>Fraction Degraded by Chemical Reaction</u>	<u>Fraction Transferred to Environment</u>
1	0	0	0
2	0	0.2963	0.0005
3	0	0.7503	0.0012
4	0	0.9471	0.0014
5	0	0.9908	0.0014
6	0	0.9976	0.0014
7	0	0.9985	0.0014
8	0	0.9986	0.0014
9	0	0.9986	0.0014
10	0	0.9986	0.0014

RUN 4: Weak Adsorption, Weak Chemical Degradation in Soil (e.g., BCH compounds)  
 $KA1=KA2=10^{-7}$ ;  $KR1=0$ ;  $KR2=0.0002 \text{ hr}^{-1}$   
 $V(1)=0.1 \text{ ft/day}$ ;  $V(2)=1.0 \text{ ft/day}$   
 Variable Water Table

<u>Year</u>	<u>Groundwater Concentration at 400 ft from Landfill, ppm</u>	<u>Fraction Degraded by Chemical Reaction</u>	<u>Fraction Transferred to Environment</u>
1	0	0	0
2	0	0.1144	0.0005
3	6.550	0.4271	0.0232
4	10.593	0.7009	0.0774
5	5.614	0.8210	0.1170
6	1.695	0.8551	0.1315
7	0.371	0.8624	0.1352
8	0.071	0.8637	0.1359
9	0.018	0.8639	0.1360
10	0	0.8640	0.1360

Maximum concentration at 400 ft position is 26.5 ppm occurring at 4.68 years.

RUN 5: Weak Adsorption, Weak Chemical Degradation in Soil (e.g., BCH compounds)  
 $KA1=KA2=10^{-7}$ ;  $KR1=0$ ;  $KR2=0.0002 \text{ hr}^{-1}$   
 $V(1)=0.1 \text{ ft/day}$ ;  $V(2)=1.0 \text{ ft/day}$   
 Water Table Constant at 120 ft

<u>Year</u>	<u>Groundwater Concentration at 400 ft from Landfill, ppm</u>	<u>Fraction Degraded by Chemical Reaction</u>	<u>Fraction Transferred to Environment</u>
1	0	0	0
2	0	0	0
3	0	0.0002	0
4	0.353	0.2078	0.0001
5	4.343	0.4971	0.0404
6	4.008	0.7040	0.0867
7	2.278	0.8067	0.1163
8	0.953	0.8462	0.1298

RUN 6: Weak Adsorption, Moderate Chemical Degradation in Landfill  
 $KA1=KA2=10^{-7}$ ;  $KR1=KR2=0.002 \text{ hr}^{-1}$   
 $V(1)=0.1 \text{ ft/day}$ ;  $V(2)=1.0 \text{ ft/day}$   
 Water Table Constant at 120 ft

<u>Year</u>	<u>Groundwater Concentration at 400 ft from Landfill, ppm</u>	<u>Fraction Degraded by Chemical Reaction</u>	<u>Fraction Transferred to Environment</u>
1	0	0.7613	0
2	0	0.9469	0
3	0	0.9883	0
4	0	0.9973	0

RUN 7: Weak Adsorption, No Chemical Degradation (e.g., Uracils)  
 $KA1=KA2=10^{-7}$ ;  $KR1=KR2=0$   
 $V(1)=0.1$  ft/day;  $V(2)=1.0$  ft/day  
 Variable Water Table

<u>Year</u>	<u>Groundwater Concentration at 400 ft from Landfill, ppm</u>	<u>Fraction Degraded by Chemical Reaction</u>	<u>Fraction Transferred to Environment</u>
1	0	--	0
2	0.018	--	0.0005
3	61.511	--	0.1463
4	103.955	--	0.5332
5	57.309	--	0.8398
6	17.832	--	0.9604
7	4.043	--	0.9921
8	0.759	--	0.9986
9	0.124	--	0.9998
10	0.018	--	1.0000

Maximum concentration at 400 ft position is 187.6 ppm occurring at 4.73 years.

RUN 8: No Adsorption, Weak Chemical Degradation in Soil  
 $KA1=KA2=0$ ;  $KR1=0$ ;  $KR2=0.0002$  hr<sup>-1</sup>  
 $V(1)=0.1$  ft/day;  $V(2)=1.0$  ft/day  
 Variable Water Table

<u>Year</u>	<u>Groundwater Concentration at 400 ft from Landfill, ppm</u>	<u>Fraction Degraded by Chemical Reaction</u>	<u>Fraction Transferred to Environment</u>
1	0	0	0
2	0.265	0.2011	0.0010
3	4.273	0.5801	0.0420
4	3.037	0.7927	0.1031
5	0.830	0.8513	0.1296
6	0.141	0.8618	0.1355
7	0.018	0.8633	0.1364
8	0	0.8635	0.1365
9	0	0.8635	0.1365
10	0	0.8635	0.1365

Maximum concentration at 400 ft position is 27.4 ppm occurring at 4.39 years.

RUN 9: Weak Adsorption, Weak Chemical Degradation in Soil (e.g., BCH compounds)  
 $KA1=KA2=10^{-7}$ ;  $KR1=0$ ;  $KR2=0.0002 \text{ hr}^{-1}$   
 $V(1)=0.5 \text{ ft/day}$ ;  $V(2)=1.0 \text{ ft/day}$   
 Variable Water Table

<u>Year</u>	<u>Groundwater Concentration at 400 ft from Landfill, ppm</u>	<u>Fraction Degraded by Chemical Reaction</u>	<u>Fraction Transferred to Environment</u>
1	0	0	0
2	0	0.1381	0.0023
3	5.491	0.4700	0.0288
4	7.786	0.7298	0.0814
5	3.672	0.8339	0.1164
6	1.024	0.8614	0.1284
7	0.212	0.8670	0.1313
8	0.035	0.8679	0.1318
9	0	0.8681	0.1319
10	0	0.8681	0.1319

RUN 10: Weak Adsorption, Weak Chemical Degradation in Soil (e.g., BCH compounds)  
 $KA1=KA2=10^{-7}$ ;  $KR1=0$ ;  $KR2=0.0002 \text{ hr}^{-1}$   
 $V(1)=0.05 \text{ ft/day}$ ;  $V(2)=1.0 \text{ ft/day}$   
 Variable Water Table

<u>Year</u>	<u>Groundwater Concentration at 400 ft from Landfill, ppm</u>	<u>Fraction Degraded by Chemical Reaction</u>	<u>Fraction Transferred to Environment</u>
1	0	0	0
2	0	0.1114	0.0002
3	6.709	0.4215	0.0225
4	11.035	0.6971	0.0768
5	5.950	0.8194	0.1168
6	1.819	0.8544	0.1317
7	0.406	0.8620	0.1354
8	0.071	0.8634	0.1362
9	0.018	0.8636	0.1363
10	0	0.8637	0.1363

## RECOMMENDATIONS

We feel confident that this rather general predictive model for the movement of hazardous waste chemicals in both landfill and the surrounding porous medium (soil and/or rocky structure), is valid enough to use as a decision-making tool. It clearly sets the upper limits on the expected concentrations for a real field situation. However, it is recommended that the complete model be given a long-term (ten-year, possibly) field test. This field test might be carried out by incorporating a sufficient number of monitoring wells together with known charges (geometric position and actual chemical mass known at the time of introduction) of certain industrially and agriculturally important chemicals, which may be disposed of by dumping them into a landfill site. The reason for this recommendation stems from the fact that, while the model is composed of generally field-tested components (vertical routing techniques worked out at Drexel University by Remson et al. (1968), and horizontal saturated flow techniques well-known in chemical engineering), it appears that this particular model (the synthesis of both vertical and horizontal techniques) has never been field tested.

## APPENDIX I

### CONTINUOUS AND DISCRETE TANK MODEL DERIVATION

In the discussion section of this report, mention of the comparison of free phase chemical concentrations in the landfill and soil columns for SLM-1, the continuous model, and the series of well-stirred chemical reactors model, was made. In this part, abridged derivations of the continuous model and the series of well-stirred chemical reaction tanks are given.

#### Continuous Model

Suppose that the landfill (or a single section of the landfill which initially contains all the chemical) and the soil column or conduit are placed as is shown in Figure I.1. The symbol used in Figure I.1 and all the equations is given in the nomenclature section of this appendix.

It is supposed that the entire system is below the water table, i.e., both the landfill portion and the soil section are saturated with water and that initially all the chemical to be dispersed resides in the landfill portion (tank).

The assumptions governing the movement of the chemical in the continuous system are:

1. The free phase chemical concentration in the landfill is assumed representable by the equation:

(Water table)

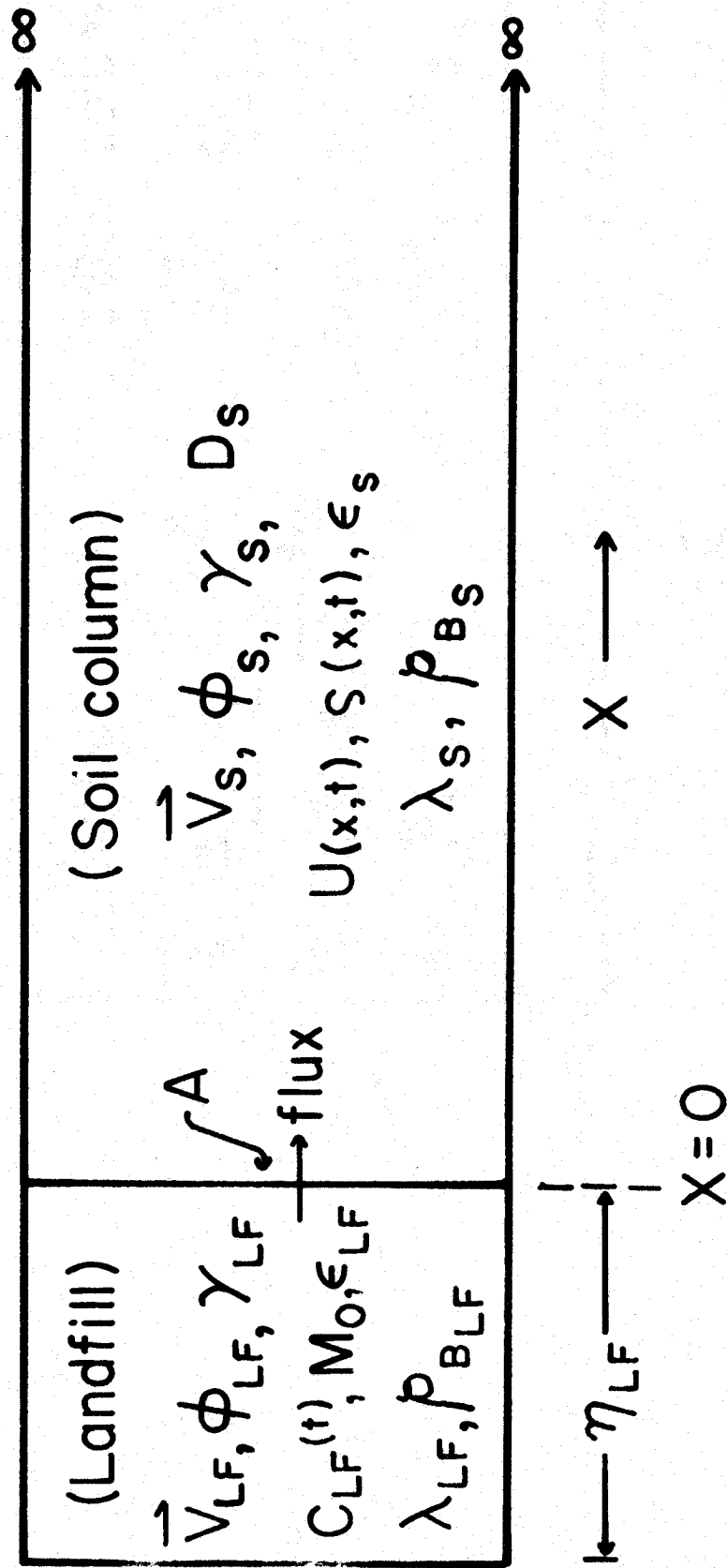


Figure I.1 Schematic of the sub water table landfill-soil conduit for the continuous model



$$C_{LF}(t) = C_0 e^{-R_{LF}t}, t \geq 0, \quad (I.1)$$

2. The mass flux of chemical from the landfill section to the soil column is representable as:

$$\text{free phase mass flux} \Big|_{x=0} = E_{LF} \cdot A \cdot V_{LF} \cdot C_{LF}(t) \quad (I.2)$$

3. The free phase chemical is distributed (transported) in the soil column via the rule:

$$E_s A (D_{os} U_{xx} - V_{os} U_x) = E_s A U_t + (1-E_s) A S_t + E_s A \lambda U, \quad (I.3)$$

which is based upon mass balance in an infinitesimal section of the soil column.

4. The initial and boundary conditions in the soil columns section are:

$$\begin{aligned} (i) \text{ I.C. } U(x,0) &= S(x,0) = 0, \\ (ii) \text{ B.C. } \lim_{x \rightarrow \infty} (D_{os} U_x - V_{os} U) &= 0, \end{aligned} \quad (I.4)$$

$$E_s A (-D_{os} U_x + V_{os} U) \Big|_{x=0} = E_{LF} \cdot A \cdot V_{LF} \cdot C_{LF}(t),$$

(conservation of mass flux).

5. The sorption rule operating in both the landfill and the soil column is that of a simple Freundlich type:

$$S(x,t) = \frac{\int_{B_s} \gamma_s U}{1-E_s}. \quad (I.5)$$

Upon substitution of  $S(x,t)$  into equation (I.3) and with subsequent simplification via the definitions:

$$\begin{aligned} (i) \quad D_s &= \frac{D_{os}}{1 + \phi_s \gamma_s} , \\ (ii) \quad V_s &= \frac{V_{os}}{1 + \phi_s \gamma_s} , \\ (iii) \quad L_s &= \frac{\lambda_s}{1 + \phi_s \gamma_s} , \end{aligned} \quad (I.6)$$

obtains for the transport equation for the free phase distribution  $U(x,t)$

$$D_s U_{xx} - V U_x = U_t + L_s U. \quad (I.7)$$

Solving for the distribution  $U(x,t)$  by the method of Laplace transforms using equations (I.4) and (I.1) yields the free phase distribution:

$$U(x,t) = C_0 \frac{G_{LF}}{\epsilon_s} \frac{V_{LF}}{1 + \phi_s \gamma_s} \frac{e^{\frac{x V_s}{2 D_s}} e^{-(L_s + \frac{V_s^2}{4 D_s})t}}{\sqrt{D_s}} \cdot \chi(x,t), \quad (I.8)$$

where

$$\chi(x,t) = \frac{1}{2\pi i} \int_{Br_1} \frac{e^{pt} e^{-x \sqrt{\frac{p}{D_s}}}}{(p - \theta) (\sqrt{p} + \frac{V_s}{2\sqrt{D_s}})} dp, \quad (I.9)$$

and

$$\theta = L_s + \frac{V_s^2}{4 D_s} - \beta_{LF}.$$

The complex inversion integral in equation (I.9) has been carried out by Lindstrom and Oberhettinger (1973). Putting all the parts together gives:

$$u(x,t) = \frac{C_0}{2} \frac{\epsilon_{LF}}{\epsilon_s} \frac{V_{LF}}{1+\phi_s \delta_s} \frac{e^{-\beta_{LF} t}}{\beta_{LF} - L_s} \cdot$$

$$\left\{ \delta_1 e^{\delta_1 x} \operatorname{erfc} \left( \frac{x+2\delta_3 t}{2\sqrt{D_s t}} \right) + \delta_2 e^{\delta_2 x} \operatorname{erfc} \left( \frac{x-2\delta_3 t}{2\sqrt{D_s t}} \right) \right. \quad (I.10)$$

$$\left. - \frac{V_s}{D_s} e^{-(L_s - \beta_{LF})t} e^{\frac{xV_s}{D_s}} \operatorname{erfc} \left( \frac{x+V_s t}{2\sqrt{D_s t}} \right) \right\},$$

where

$$\delta_1 = \frac{V_s}{2D_s} + \sqrt{\frac{L_s}{D_s} + \frac{V_s^2}{4D_s^2} - \frac{\beta_{LF}}{D_s}},$$

$$\delta_2 = \frac{V_s}{2D_s} - \sqrt{\frac{L_s}{D_s} + \frac{V_s^2}{4D_s^2} - \frac{\beta_{LF}}{D_s}},$$

$$\delta_3 = D_s (\delta_1 - \delta_2).$$

Equation (I.10) then defines the free phase chemical distribution in the soil column at any point  $x \geq 0$  at any time  $t \geq 0$  subject to the landfill chemical distribution decaying away according to equation (I.1).

The calculated constants used in the free phase distribution model are as follows:

$$(a) \quad \phi_s = \frac{\rho_{Bs}}{\epsilon_s}, \text{ (gms soil / cm}^3 \text{ soil void space),}$$

$$(b) \quad \phi_{LF} = \frac{\rho_{B_{LF}}}{\epsilon_{LF}}, \text{ (gms Land fill / cm}^3 \text{ L.F. void space),}$$

$$(c) \quad \beta_{LF} = \frac{V_{LF}}{\eta_{LF}(1 + \phi_{LF}\gamma_{LF})} + L_{LF}, \text{ (1/hrs),}$$

$$(d) \quad L_s = \frac{\lambda_s}{1 + \phi_s \gamma_s}, \text{ (1/hrs),}$$

$$(e) \quad L_{LF} = \frac{\lambda_{LF}}{1 + \phi_{LF} \gamma_{LF}}, \text{ (1/hrs),}$$

$$(f) \quad D_s = \frac{D_{os}}{1 + \phi_s \gamma_s}, \text{ (cm}^2 \text{/hr),} \quad (I.11)$$

$$(g) \quad V_s = \frac{V_{os}}{1 + \phi_s \gamma_s}, \text{ (cm/hr),}$$

$$(h) \quad \delta_1 = \frac{V_s}{2D_s} + \sqrt{\frac{L_s}{D_s} + \frac{V_s^2}{4D_s^2} - \frac{\beta_{LF}}{D_s}}, \text{ (1/cm),}$$

$$(i) \quad C_o = \frac{M_o}{\epsilon_{LF} A \eta_{LF} (1 + \phi_{LF} \gamma_{LF})}, \text{ (gm chem. / cm}^3 \text{ void).}$$

The actual method used in evaluating equation (I.10) to give the free phase distribution is that listed under section 7.1.25 in the book by Abromowitz and Stegun (1965) page 299. This method consists basically of replacing the erfc function by a high order accuracy modified inverse polynomial-exponential function approximation. This allows easy and rapid computations to be made on any high speed digital computer.

#### Series of Well-Stirred Chemical Reaction Tanks Model

All the assumptions pertaining to the landfill section (tank), mentioned previously under the continuous model, apply here. The major differences between the continuous model and this one (shown schematically in Figure I.2) are:

1. dispersion *per se* is neglected

and

2. as chemical is introduced into any one of the series tanks it is instantaneously well mixed with the contents of the tank. Simultaneously, some of the chemical is being stored, with the remainder being transported out to the next tank.

In view of the large number of common symbols, the reader is referred to the nomenclature section of this appendix and the calculated constants listed under I.11 for aid in understanding the terminology.

Assume:

1. Each tank is of the same size with  $A$  being the cross-sectional area ( $\text{cm}^2$ ) normal to the mass flux direction and  $\eta_s$  is the length of each section.

2. The mass balance equation for the  $i$ -th tank is written as

(Water table)

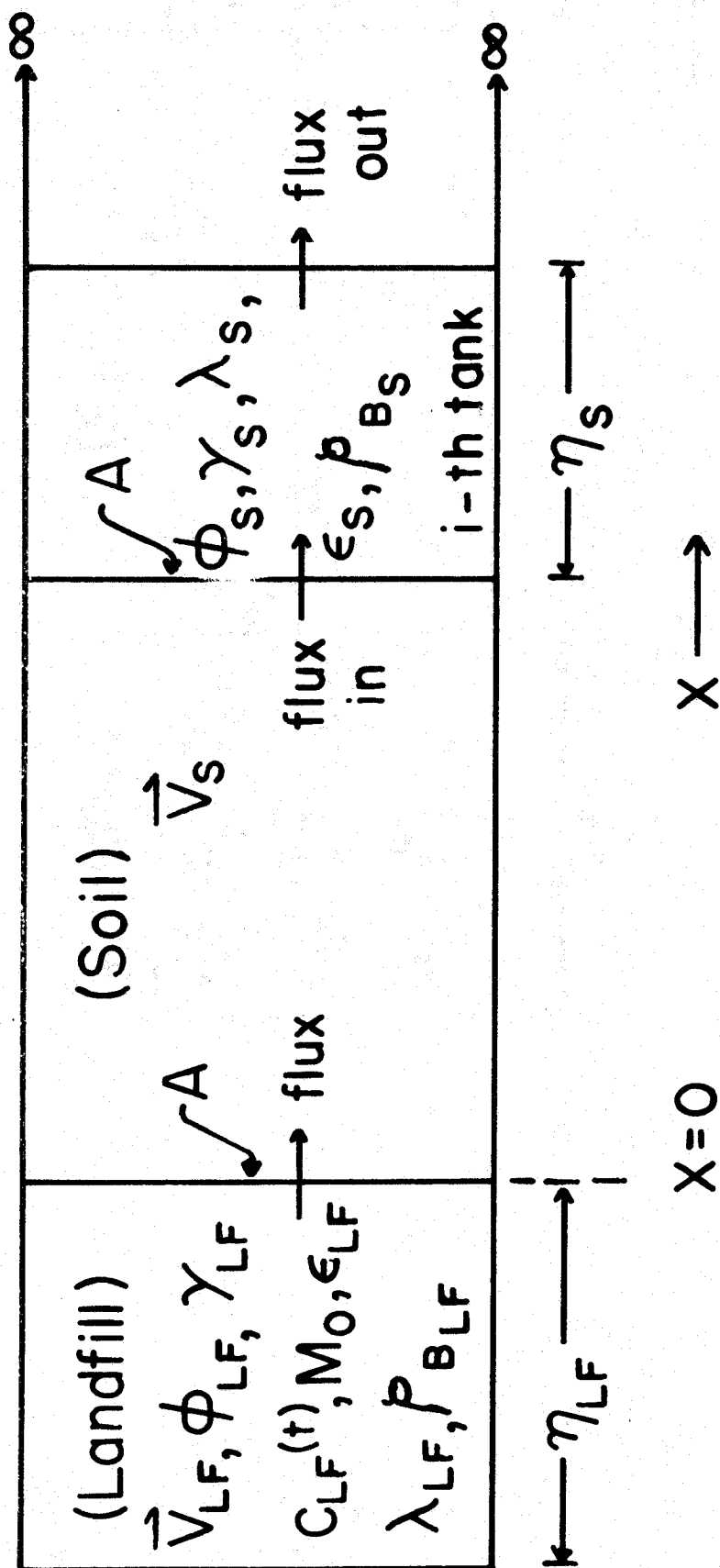


Figure I.2 Schematic of the sub water table landfill-coupled well-stirred tanks system for the series tank model

$$\epsilon_s \eta_s A \frac{dC_{i-1}}{dt} + (1-\epsilon_s) \eta_s A \frac{dS_{i-1}}{dt} + \lambda_s \epsilon_s A \eta_s C_{i-1} = \epsilon_s V_s A (C_{i-1} - C_{i-2}), \quad (I.12)$$

for  $i = 2, 3, 4 \dots$  and

3.

$$\epsilon_s \eta_s A \frac{dC_1}{dt} + (1-\epsilon_s) \eta_s A \frac{dS_1}{dt} + \lambda_s \epsilon_s A \eta_s C_1 = \epsilon_{LF} A V_{LF} C_{LF}(t) - \epsilon_s A V_s C_1, \quad (I.13)$$

for the first tank downstream from the landfill.

As in the continuous case, the sorbed phase chemical is assumed to be accounted for via the simple rule:

$$S_{i-1}(t) = \frac{\rho_{B_s} \gamma_s C_{i-1}(t)}{1-\epsilon_s}, \quad i = 1, 2, 3, \dots, \quad (I.14)$$

and the landfill free phase chemical concentration is assumed to be characterized by the rule:

$$C_{LF}(t) = C_0 e^{-\beta_{LF} t}, \quad t \geq 0.$$

By use of Laplace transform methods on the landfill distribution and the soil tanks (in an iterative manner) leads to the following distributions:

$$\begin{aligned} (a) \quad C_{LF}(t) &= C_0 e^{-\beta_{LF} t}, \\ (b) \quad C_1(t) &= C_0 B_{LF} \left\{ \frac{e^{-\beta_{LF} t} - e^{-\beta_s t}}{\beta_s - \beta_{LF}} \right\}, \\ (c) \quad C_n(t) &= \frac{C_0 B_{LF} B_s^{n-1}}{(\beta_s - \beta_{LF})^n} \left\{ e^{-\beta_{LF} t} - \sum_{j=0}^{n-1} \frac{[(\beta_s - \beta_{LF}) t]^j}{j!} e^{-\beta_s t} \right\}, \end{aligned} \quad (I.15)$$

$n = 2, 3, 4, \dots$  and

$$B_{LF} = \frac{\epsilon_{LF} V_{LF}}{\epsilon_s \eta_s (1 + \phi_s \gamma_s)}, \quad (1/\text{hrs}),$$

$$B_s = \frac{V_s}{\eta_s (1 + \phi_s \gamma_s)}, \quad (1/\text{hrs}),$$

$$\beta_{LF} = \frac{V_{LF}}{\eta_{LF} (1 + \phi_{LF} \gamma_{LF})} + L_{LF}, \quad (1/\text{hrs}),$$

$$\beta_s = \frac{V_s}{\eta_s (1 + \phi_s \gamma_s)} + L_s, \quad (1/\text{hrs}).$$

There is no theoretical limit on  $n$ , the number of series tanks.

#### Nomenclature for Both Models

$C_{LF}(t)$  = free phase chemical concentration in landfill (gm chem/  
 $\text{cm}^3_{LF}$  void solution)

$C_i$  = free phase chemical concentration in soil column (i-th section)

$i = 1, 2, 3, 4, \dots$  (gm chem/  $\text{cm}^3_{\text{soil}}$  void solution)

$U(x, t)$  = free phase chemical concentration in the soil column (gms  
chemical free/  $\text{cm}^3$  soil particles)

$M_0$  = initial chemical mass in landfill section (gms)

$\epsilon_{LF}$  = landfill porosity ( $\text{cm}^3$  voids/ $\text{cm}^3_{LF}$ )

$\epsilon_s$  = soil porosity ( $\text{cm}^3$  voids/ $\text{cm}^3$  soil column)

$V_{LF}$  = average water flow velocity in  $LF$ , (cm/day)



$V_s$  = average water flow velocity in soil (cm/day)

$\eta$  = length of each cell (tank) (cm)

$\rho_{LF}$  = bulk density of L.F. (gms/cm<sup>3</sup>)

$\rho_s$  = bulk density of soil (gms/cm<sup>3</sup>)

$\lambda_{LF}$  = microbial decay const. L.F. (1/day)

$\lambda_s$  = microbial decay const. LF soil (1/day)

$\gamma_{LF}$  = Freundlich sorption coef. L.F. ( $\frac{\text{gm void solution}}{\text{gm LF}}$ )

$\gamma_s$  = Freundlich sorption coef. soil ( $\frac{\text{gm void solution}}{\text{gm soil}}$ )

$A$  = cross-sectional area of each tank or transport column normal to the average mass flux direction (cm<sup>2</sup>)

### Position of Maximum Concentration

It is not possible to arrive at any easy formula to predict the point along the soil column ( $x_p > 0$ ) at which the free phase chemical concentration has its maximum value for time  $t$  ( $t > 0$ ), for either case. However, the series of well-stirred tanks model admit an equation (transcendental in nature) which can be programmed on the computer and the position of the peak (value of  $t_{\max}$  in the  $n$ -th tank,  $n=1,2,3,\dots$ ) can be estimated.

By differentiating equation (I.15-c) with respect to time and setting the derivative equal to zero obtains the formula (after some algebra)

$$e^{(\beta_s - \beta_{LF}) t_{\max}^{(n)}} = \frac{\beta_s}{\beta_{LF}} \frac{[(\beta_s - \beta_{LF}) t_{\max}^{(n)}]^{n-1}}{(n-1)!} + \sum_{j=0}^{n-2} \frac{[(\beta_s - \beta_{LF}) t_{\max}^{(n)}]^j}{j!}, \quad (I.16)$$

$$n = 2, 3, 4, \dots$$

Many methods (e.g., direct search, Newton, divided differences, etc.) exist for finding  $t_{\max}^{(n)}$  for each  $n$  value. Thus, the maximum times for each tank can be estimated by solving the transcendental equation, (I.16).

## APPENDIX II

### THE SLM-1 COMPUTER PROGRAM

The computer program for SLM-1 consists of a main program SLM 1, subroutines COLROUTE (K,J), DISTRIB (LOS,I,K), LAYER (LOS,I,K) and OUTPUT (IOPTION,K,J,NY,LUN) and the function subprogram S(I,K).

Subroutine COLROUTE (K,J) performs all routing calculations for a single column K during time period J. The main program calls COLROUTE (K,J) for each column from 1 to KT during each time period. Subroutine COLROUTE (K,J) performs calculations for all layers in column K every time it is called, beginning with the top layer. Logic programmed into COLROUTE (K,J) determines whether it is above or below the water table. Once this information is determined, subroutine LAYER (LOS,I,K) is called which performs the actual material balance calculations for the chemical contaminant for the layer. In making these calculations, subroutine DISTRIB (LOS,I,K) is used to compute the amount of chemical adsorbed, in free solution and degraded by reaction given M total grams initially in W liters of solution and a two-day time period.

Function S (I,K) defines the source of contaminant as a function of time for a given layer. See the program listings for two examples of function S (I,K). Subroutine OUTPUT (IOPTION,K,J,NY,LUN) has several options for obtaining complete or summary results for each layer in the two-dimensional grid at each time period.

Input data, option variables, and case parameters are entered either in the data file called DATA or at the teletype during program execution.

### Nomenclature for Computer Programs of SLM-1 Model

All underlined variables are entered as data.

#### General Topology of Landfill-Soil Region

<u>I</u>	refers to the layer as measured from the top of a column
<u>K</u>	refers to the column number
<u>KL</u>	number of landfill columns
<u>KT</u>	total number of columns
<u>Z(K)</u>	top elevation of the Kth column, ft
<u>ZB</u>	lowest elevation of water table, ft
<u>ZBL(K)</u>	elevation of the bottom of columns in the landfill, ft
<u>ZMAX</u>	maximum elevation of any column, ft.

The Ith layer of all columns is on a horizontal line.

#### Calculated Variables Denoting Layer Numbers

IAWT =	$\frac{ZMAX - ZWT(J)}{2}$	= layer number just above the water table in time period J
ILLF =	$\frac{ZMAX - ZBL(K)}{2}$	= layer number of last layer in landfill column K
IMAX =	$\frac{ZMAX - ZB}{2} + 1$	= maximum layer number which is the last layer of every column
ISTART =	$\frac{ZMAX - Z(K)}{2} + 1$	= layer number of first layer in column K

NOTE: Each layer is 2 ft thick so all elevations are in increments of two feet.

### Layer Characteristics

<u>DELX</u>	length of a unit compartment, ft
<u>DELZ</u>	depth of a unit compartment, always 2 ft
<u>WIDTH</u>	width of two-dimensional section of landfill for consideration, ft

	<u>Landfill</u>	<u>Soil</u>
Density of dry material $\frac{\text{lbs}}{\text{ft}^3}$	<u>D(1)</u>	<u>D(2)</u>
Adsorption Coefficient K $\frac{x}{m} = KC$ C, ppm x,m same units	<u>KAD(1)</u>	<u>KAD(2)</u>
Reaction coefficient, $\text{hr}^{-1}$	<u>KRX(1)</u>	<u>KRX(2)</u>
Horizontal Flow, liters/time period	<u>QH(1)</u>	<u>QH(2)</u>
Grams of dry material in a compartment	<u>SOLID(1)</u>	<u>SOLID(2)</u>
Velocity of groundwater flow, ft/day	<u>V(1)</u>	<u>V(2)</u>
LOS=Landfill or Soil Indicator	<u>= 1</u>	<u>= 2</u>
Volume of water if at field capacity conditions, liters	<u>VFC(1)</u>	<u>VFC(2)</u>
Volume of water if at saturated conditions, liters	<u>VSAT(1)</u>	<u>VSAT(2)</u>
Initial moisture content, vol. fraction	<u>YI(1)</u>	<u>YI(2)</u>
Field capacity, vol. fraction	<u>YF(1)</u>	<u>YF(2)</u>
Saturation capacity, vol. fraction	<u>YS(1)</u>	<u>YS(2)</u>

### Infiltration and Water Table

J	refers to time period under consideration
<u>R(J)</u>	rainfall in Jth time period, inches $\text{H}_2\text{O}$
<u>XINFL</u>	fraction of rainfall that infiltrates soil and landfill

ZWT(J) height of water table in Jth time period

ICAP layers above water table in the landfill which are considered saturated by capillary action (these layers have no horizontal velocity component). ICAP not used in September, 1973, version of SLM-1.

Variables Relating to Chemical Mass Balance

C(I) concentration of chemical in layer I, ppm or mg/l

CHEMRX total grams disappearing by biodegradation since time = 0

DELT hours per time period = 48

JSTAR time period number since time = 0. At the start of each year J is reset to 1; JSTAR continues.

M(I,K) total chemical in layer I of column K, grams (initial)

MA(I) chemical adsorbed in layer I, grams

MC(I) chemical reacted in layer I in current two-day time period, grams

MF(I) free chemical in solution in layer I, grams

MTX(I) chemical transferred horizontally in groundwater flow for layer I, grams

Q volume of leachate transferred vertically to or from a layer, liters

SOURCE total chemical added to landfill-soil region since time = 0, grams

SUMLF total chemical in landfill, grams

SUMSOIL total chemical in soil, grams

TOTAL total chemical transferred to environment, grams

TOTJ total chemical transferred to environment in current time period, grams

TOTSTART total chemical in landfill-soil region at time = 0, grams

W(I,K) volume of water in layer I of column K, liters

<u>Output</u>	<u>Options</u>
IO $\neq$ 0	get writing of certain intermediate calculations for debugging purposes
KO $\neq$ 0	get complete output for each column after every call to COLROUTE
JO > 0	get summary output at the end of every time period
JO < 0	if KO = 0, then get column output for last time period, last year only
KO = 0, JO = 0	only get summary output at end of each year

#### Other Run Parameters

<u>LUN</u> =	logical unit number to be used for writing computed results
<u>NJ</u> =	number of time periods per year
<u>NYR</u> =	number of years desired for computations

```

00001:      PROGRAM SLM 1
00002:      INCLUDE CRIE
00003:C
00004:      4 WRITE(61,101)
00005: 101 FORMAT(1H1'SLM 1'//)
00006:C
00007:      CALL DATA
00008:C
00009:      LUN=TTYIN(4HLUN=)
00010:      NYR=TTYIN(4HNYR=)
00011:      NJ=TTYIN(4H NJ=)
00012:      KL=TTYIN(4H KL=)
00013:      KT=TTYIN(4H KT=)
00014:      KO=TTYIN(4H KO=)
00015:      JO=TTYIN(4H JO=)
00016:      IO=TTYIN(4H IO=)
00017:      KAD(1)=TTYIN(4HKA1=)
00018:      KAD(2)=TTYIN(4HKA2=)
00019:      KRX(1)=TTYIN(4HKR1=)
00020:      KRX(2)=TTYIN(4HKR2=)
00021:C
00022:C      INITIALIZING CALCULATIONS
00023:      TOTJ=TOTAL=CHEMRX=0
00024:      SOURCE=0
00025:      IMAX=(ZMAX-ZB)/2+1
00026:      VOL=DELX*DELZ*WIDTH*28.32
00027:      DO 10 LOS=1,2
00028:      VFC(LOS)=VOL*YF(LOS)
00029:      VSAT(LOS)=VOL*YS(LOS)
00030:      QH(LOS)=V(LOS)*DELZ*WIDTH*2.*28.32*YS(LOS)
00031: 10 SOLID(LOS)=DELX*DELZ*WIDTH*D(LOS)*454.
00032:C
00033:C      INITIAL WATER VOLUME IN EACH COMPARTMENT,LITERS
00034:      DO 20 K=1,KT
00035:      ISTART=(ZMAX-Z(K))/2+1
00036:      IF(K.LE.KL)ILLF=(ZMAX-ZBL(K))/2
00037:      IAWT=(ZMAX-ZWT(1))/2
00038:      LOS=1
00039:      DO 20 I=ISTART,IMAX
00040:      IF(I.GT.ILLF.OR.K.GT.KL)LOS=2
00041:      AID=YI(LOS) $ IF(I.GT.IAWT)AID=YS(LOS)
00042: 20 W(I,K)=VOL*AID
00043:C
00044:C      INITIAL OUTPUT FOR DEBUGGING PURPOSES
00045:      IF(IO.EQ.0)GO TO 22
00046:      WRITE(LUN,100)VFC,VSAT,QH,SOLID
00047: 100 FORMAT(//' VFC ='2F15.2/' VSAT ='2F15.2/' QH ='2F15.2/
00048:      * ' SOLID ='2F15.2)
00049:      CALL OUTPUT(2,K,0,1,LUN)
00050: 22 CONTINUE
00051:C

```

J



```

00052:C      ROUTING SECTION
00053:      N1=1
00054:      5 INDEX=0
00055:      DO 3 NY=N1,NYR
00056:      DO 2 J=1,NJ
00057:      TOTAL=TOTAL+TOTJ $ TOTJ=0
00058:C      JSTAR = TIME PERIOD NUMBER SINCE THE START OF THE RUN
00059:      JSTAR=(NY-1)*NJ+J
00060:      DO 1 K=1,KT
00061:      CALL COLROUTE(K,J)
00062:      IF(JO.LT.0.AND.J.EQ.NJ)INDEX=1
00063:      IF(INDEX.EQ.1.AND.NY.EQ.NYR)30,31
00064:      30 CALL OUTPUT(1,K,J,NY,LUN)
00065:      GO TO 1
00066:      31 IF(KO.NE.0)CALL OUTPUT(1,K,J,NY,LUN)
00067:      INDEX=0
00068:      1 CONTINUE
00069:      IF(JO.GT.0)CALL OUTPUT(2,K,J,NY,LUN)
00070:      2 CONTINUE
00071:      IF(JO.LE.0)CALL OUTPUT(2,K,NJ,NY,LUN)
00072:      3 CONTINUE
00073:C
00074:      WRITE(61,103)
00075:      103 FORMAT(// ' CALCULATE FOR ANOTHER YEAR?  ')
00076:      READ(60,102)IANS
00077:      102 FORMAT(A4)
00078:      IF(IANS.NE.3HYES)GO TO 4
00079:      N1=NYR+1 $ NYR=NYR+1
00080:      JO=0
00081:      GO TO 5
00082:      END

```

]

```

00001:      DEFINE CRIF
00002:      COMMON M(15,100),W(15,100),MF(15),MA(15),MC(15),MTX(15),
00003:      * X1,C(15),KAD(2),KRX(2),SOLID(2),CHEMRX,DELT,Q,
00004:      * QH(2),VFC(2),VSAT(2),TOTAL,TOTJ,IMAX,ZMAX,
00005:      * ZWT(182),ZBL(50),Z(100)
00006:      COMMON XINFL,R(182),ZB,TOTSTART,DELX,DELZ,WIDTH,
00007:      * ICAP,YI(2),YF(2),YS(2),D(2),V(2),KL,KT
00008:      COMMON JSTAR,SOURCE
00009:      REAL KAD,KRX,M,MF,MA,MC,MTX
00010:      INTEGER ZMAX,Z,ZWT,ZBL,ZB
00011:      END

```

]

```

00001:      SUBROUTINE COLROUTE(K,J)
00002:      INCLUDE CRIB
00003:      ISTART=(ZMAX-Z(K))/2+1
00004:      IAWT=(ZMAX-ZWT(J))/2 $ C(ISTART-1)=0
00005:      IF(K.GT.KL)GO TO 2
00006:C      LANDFILL COLUMN
00007:      ILLF=(ZMAX-ZBL(K))/2 $ LOS=1
00008:      IF(Z(K).LE.ZWT(J))GO TO 10
00009:      Q=R(J)*XINFL/12.*DELX*WIDTH*28.32
00010:      IF(ILLF.GT.IAWT)GO TO 100
00011:      DO 40 I=ISTART,ILLF
00012: 40 CALL UNSAT(LOS,I,K)
00013:      I1=ILLF+1
00014:      LOS=2
00015:      DO 41 I=I1,IAWT
00016: 41 CALL UNSAT(LOS,I,K)
00017:      I2=IAWT+1
00018:      DO 42 I=I2,IMAX
00019:      IF(I.GT.I2)Q=0
00020: 42 CALL SAT(LOS,I,K)
00021:      GO TO 200
00022: 100 DO 50 I=ISTART,IAWT
00023: 50 CALL UNSAT(LOS,I,K)
00024:      I1=IAWT+1
00025:      DO 51 I=I1,ILLF
00026:      IF(I.GT.I1)Q=0
00027: 51 CALL SAT(LOS,I,K)
00028:      I2=ILLF+1 $ LOS=2
00029:      DO 52 I=I2,IMAX
00030:      IF(I.GT.IAWT+1)Q=0
00031: 52 CALL SAT(LOS,I,K)
00032:      GO TO 200
00033:C      LANDFILL COLUMN TOTALLY SUBMERGED
00034: 10 Q=0
00035:      DO 11 I=ISTART,IMAX
00036:      IF(I.GT.ILLF)LOS=2
00037: 11 CALL SAT(LOS,I,K)
00038:      GO TO 200
00039:C      SOIL COLUMN
00040: 2 LOS=2
00041:      IF(Z(K).LE.ZWT(J))GO TO 20
00042:      Q=R(J)*XINFL/12.*DELX*WIDTH*28.32
00043:      DO 4 I=ISTART,IAWT
00044: 4 CALL UNSAT(LOS,I,K)
00045:      I1=IAWT+1
00046:      DO 6 I=I1,IMAX
00047:      IF(I.GT.I1)Q=0
00048: 6 CALL SAT(LOS,I,K)
00049:      GO TO 200
00050:C      SOIL COLUMN TOTALLY SUBMERGED
00051: 20 Q=0
00052:      DO 21 I=ISTART,IMAX
00053: 21 CALL SAT(LOS,I,K)
00054:C

```

```

00055: 200 IF(K.GE.KT)GO TO 201
00056: IF(Z(K+1).LT.Z(K).AND.Z(K+1).LT.ZWT(J))GO TO 205
00057: RETURN
00058: 205 ITX2=(ZMAX-Z(K+1))/2
00059: ITX1=IAWT+1
00060: IF(Z(K).LE.ZWT(J))ITX1=ISTART
00061: GO TO 202
00062:C K IS THE LAST COLUMN
00063: 201 ITX1=IAWT+1 $ ITX2=IMAX
00064: IF(Z(K).LE.ZWT(J))ITX1=ISTART
00065: 202 DO 203 I=ITX1,ITX2
00066: TOTJ=TOTJ+MTX(I)
00067: 203 MTX(I)=0
00068: RETURN
00069: END

```

J

```

00001: SUBROUTINE LAYER(LOS,I,K)
00002: INCLUDE CRIE
00003: ENTRY UNSAT
00004:C UNSATURATED CALCULATION: ADD LEACHATE FROM ABOVE,
00005:C MIX,REACT,ADSORB,DRAIN TO FIELD CAPACITY
00006:C THE LANDFILL AND SOIL ARE ASSUMED TO DRAIN FREELY
00007: W(I,K)=W(I,K)+Q
00008: ADD=S(I,K) $ SOURCE=SOURCE+ADD
00009: M(I,K)=M(I,K)+Q*C(I-1)*0.001+ADD
00010: CALL DISTRIB(LOS,I,K)
00011: Q=0
00012: IF(W(I,K).LE.VFC(LOS))RETURN
00013: Q=W(I,K)-VFC(LOS)
00014: W(I,K)=W(I,K)-Q
00015: MF(I)=MF(I)-Q*C(I)*0.001
00016: M(I,K)=M(I,K)-Q*C(I)*0.001
00017: RETURN
00018: ENTRY SAT
00019:C SATURATED CALCULATION: SEND GH LITERS OF EQUILIBRATED
00020:C LEACHATE DOWNSTREAM HORIZONTALLY, CALCULATE TOTAL CHEMICAL
00021:C NOW IN LAYER CONSIDERING INPUT FROM UPSTREAM AND FROM
00022:C ABOVE LAYER,MIX,REACT,ADSORB
00023: W(I,K)=VSAT(LOS)
00024: C(I)=M(I,K)/(W(I,K)*0.001+KAD(LOS)*SOLID(LOS))
00025: TX=QH(LOS)*C(I)*0.001
00026: ADD=S(I,K) $ SOURCE=SOURCE+ADD
00027: M(I,K)=M(I,K)-TX+MTX(I)+Q*C(I-1)*0.001+ADD
00028: MTX(I)=TX
00029: CALL DISTRIB(LOS,I,K)
00030: RETURN
00031: END

```

J

```

00001:      SUBROUTINE OUTPUT(IOPTION,K,J,NY,LUN)
00002:      INCLUDE CRIB
00003:      WRITE(LUN,100)NY,J
00004: 100 FORMAT(//////////IX'SANITARY LANDFILL MODEL SLM 1'/
00005:      * ' ENVIRONMENTAL HEALTH SCIENCES CENTER'/
00006:      * ' OREGON STATE UNIVERSITY'///' YEAR'15/' TIME PERIOD'15)
00007:      GO TO (1,2,3)IOPTION
00008:      1 WRITE(LUN,101)K
00009: 101 FORMAT(' COLUMN'15//' LAYER'4X'WATER'5X'CHEM'5X'CHEM'
00010:      * 5X'CHEM'4X'TOTAL'5X'CHEM'2X'CHEM TX'/18X'ADSORB'2X
00011:      * 'REACTED'5X'FREE'5X'CHEM'5X'CONC'4X'HORIZ'/7X'(LITERS)'
00012:      * 4X'(GMS)'4X'(GMS)'4X'(GMS)'4X'(GMS)'4X'(PPM)'
00013:      * 4X'(GMS)'/)
00014:      ISTART=(ZMAX-Z(K))/2+1
00015:      WRITE(LUN,102)(I,W(I,K),MA(I),MC(I),MF(I),M(I,K),
00016:      * C(I),MTX(I),I=ISTART,IMAX)
00017: 102 FORMAT(I6,7F9.2)
00018:      RETURN
00019:C      LANDFILL - SOIL TOTAL CHEMICAL REPORT
00020:      2 K1=KT/9+1 $ KSTART=1 $ KEND=9
00021:      DO 30 KK=1,K1
00022:      IF(KK.EQ.K1)KEND=KT
00023:      IF(KSTART.GT.KEND)GO TO 30
00024:      WRITE(LUN,103)((K),K=KSTART,KEND)
00025: 103 FORMAT(//10X'TOTAL GRAMS OF CHEMICAL IN LAYER 1,COLUMN K'/
00026:      * 3X,9(5X,12))
00027:      DO 4 I=1,IMAX
00028:      4 WRITE(LUN,104)I,(M(I,K),K=KSTART,KEND)
00029: 104 FORMAT(I3,9F7.1)
00030:      KSTART=KSTART+9
00031:      30 KEND=KEND+9
00032:C
00033:C      ADD CHEMICAL IN LANDFILL AND SURROUNDING SOIL
00034:      3 SUMLF=SUMSOIL=0
00035:      DO 10 K=1,KL
00036:      ISTART=(ZMAX-Z(K))/2+1 $ ILLF=(ZMAX-ZBL(K))/2
00037:      DO 11 I=ISTART,ILLF
00038:      11 SUMLF=SUMLF+M(I,K)
00039:      I1=ILLF+1
00040:      DO 10 I=I1,IMAX
00041:      10 SUMSOIL=SUMSOIL+M(I,K)
00042:      K1=KL+1
00043:      DO 12 K=K1,KT
00044:      ISTART=(ZMAX-Z(K))/2+1
00045:      DO 12 I=ISTART,IMAX
00046:      12 SUMSOIL=SUMSOIL+M(I,K)
00047:      WRITE(LUN,107)TOTSTART,SUMLF
00048: 107 FORMAT(//' SUMMARY OF CHEMICAL DISTRIBUTION AT THE'
00049:      * , ' END OF THIS TIME PERIOD'/
00050:      * ' TOTAL CHEMICAL IN LANDFILL & SOIL AT TIME ZERO ='F10.3
00051:      * ' GRAMS'/' TOTAL CHEMICAL NOW IN LANDFILL ='
00052:      * F10.3' GRAMS')

```

```

00053:      WRITE(LUN,105)SUMSOIL,CHEMRX
00054: 105 FORMAT('    TOTAL CHEMICAL NOW IN SURROUNDING SOIL ='F10.3
00055:      * ' GRAMS'/'    TOTAL CHEMICAL DEGRADED BY REACTION'
00056:      * ' SINCE TIME ZERO ='F10.3' GRAMS')
00057:      WRITE(LUN,106)TOTJ,TOTAL
00058: 106 FORMAT('    TOTAL CHEMICAL TO ENVIRONMENT IN'
00059:      * ' THIS TIME PERIOD ='F10.3' GRAMS'/'    TOTAL CHEMICAL'
00060:      * ' RELEASED IN PREVIOUS TIME PERIODS ='F10.3' GRAMS')
00061:      WRITE(LUN,108)SOURCE
00062: 108 FORMAT('    TOTAL CHEMICAL ADDED SINCE TIME ZERO ='
00063:      * ' F10.3' GRAMS')
00064:      RETURN
00065:      END

```

]

```

00001:      SUBROUTINE DISTRIE(LOS,I,K)
00002:      INCLUDE CRIB
00003:      MF(I)=M(I,K)/(1.+KAD(LOS)/W(I,K)*SOLID(LOS)*1000.
00004:      * +KRX(LOS)*DELT)
00005:      C(I)=MF(I)/W(I,K)*1000.
00006:      MC(I)=KRX(LOS)*C(I)*W(I,K)*DELT*0.001
00007:      MA(I)=M(I,K)-MF(I)-MC(I)
00008:      M(I,K)=M(I,K)-MC(I)
00009:      CHEMRX=CHEMRX+MC(I)
00010:      RETURN
00011:      END

```

]

```

00001:      FUNCTION S(I,K)
00002:      INCLUDE CRIB
00003:      S=0
00004:      IF(K.EQ.1 .AND. I.LE.3) 1,2
00005: 1 S=5.0 $ RETURN
00006: 2 IF(K.EQ.2 .AND. I.EQ.4) S=2.0+1.0*FLOAT(JSTAR)
00007:      RETURN
00008:      END

```

]

## THE WELL-STIRRED TANK MODEL COMPUTER PROGRAM

The Fortran listing of the computer program to calculate distribution of chemical through a series of well-stirred vessels as described in Appendix I is given on pages 74 to 75. The program will calculate the concentration (ppm) in each tank as a function of time and has an option which will calculate the time (TMAX) for tank N to reach maximum concentration and the corresponding maximum concentration at this time.

Nomenclature used in the Fortran listings closely follows that given in Appendix I. All data and case parameters are entered at the teletype during program execution. This input is given below for reference.

Function FACTJ(J) included in the listing calculates J!. Function TMAX (A,B,N,X) calculates TMAX for N=NTANK by the method of successive substitutions using equation I.16 of Appendix I.

The utility of program TANKLF and the output obtained is illustrated in the example below.

<u>Symbols Printed on Teletype During Execution</u>	<u>Fortran Variable</u>	<u>Corresponding Variables in Appendix I</u>	<u>Definition</u>
LUN	LUN	---	logical unit number for program output
RS	RHOS	$\rho_{B_s}$	bulk density of soil, gms/cm <sup>3</sup>
RLF	RHOLF	$\rho_{B_{LF}}$	bulk density of landfill, gms/cm <sup>3</sup>
ES	EPSS	$\epsilon_s$	soil porosity
ELF	EPSLF	$\epsilon_{LF}$	landfill porosity
MO	MO	$M_o$	initial chemical mass in landfill section, gms

LS	LAMS	$\lambda_s$	microbial decay constant for soil, day <sup>-1</sup>
LLF	LAMLF	$\lambda_{LF}$	microbial decay constant for landfill, day <sup>-1</sup>
GS	GAMMAS	$\gamma_s$	Freundlich sorption coef- ficient in soil (gm solu- tion/gm soil)
GLF	GAMMALF	$\gamma_{LF}$	Freundlich sorption coef- ficient in landfill (gm solu/gm landfill)
AS	ETAS	$\eta_s$	length of soil compartment, cm
ALF	ETALF	$\eta_{LF}$	length of landfill compart- ment, cm
VLF	VLF	$v_{LF}$	average water velocity in landfill, cm/day
VS	VS	$v_s$	average water velocity in soil, cm/day
NT	NT	---	number of soil tanks in the calculation
ND	ND	---	number of days in the run
IO	IO	---	if IO $\neq$ 0, get intermediate output for debugging pur- poses
ITM	ITM	---	ITM = 0, do not perform TMAX calculations; ITM = 1, do only the TMAX calculation for a specified tank, NTANK; ITM = 2, do TMAX calculation, then NT tank calculations for ND days
N	NTANK	---	tank number for TMAX cal- culations
TG	TG	---	initial guess of TMAX for tank NTANK



```

00001:      PROGRAM TANKLF
00002:      COMMON A(100),C(100,100),CL(100)
00003:      REAL LS,LLF,MO,LAMS,LAMLF
00004:C      DATA SECTION
00005:      10 WRITE(61,100)
00006:      100 FORMAT(/////' TANK LANDFILL MODEL'//)
00007:      LUN=TTYIN(4HLUN=)
00008:      RHOS=TTYIN(4H RS=)
00009:      RHOLF=TTYIN(4HRLF=)
00010:      EPSS=TTYIN(4H ES=)
00011:      EPSLF=TTYIN(4HELFF=)
00012:      MO=TTYIN(4H MO=)
00013:      LAMS=TTYIN(4H LS=)
00014:      LAMLF=TTYIN(4HLLF=)
00015:      GAMMAS=TTYIN(4H GS=)
00016:      GAMMALF=TTYIN(4HGRLF=)
00017:      ETAS=TTYIN(4H AS=)
00018:      ETALF=TTYIN(4HALF=)
00019:      VLF=TTYIN(4HVLF=)
00020:      VS=TTYIN(4H VS=)
00021:      NT=TTYIN(4H NT=)
00022:      ND=TTYIN(4H ND=)
00023:      IO=TTYIN(4H IO=)
00024:      35 ITM=TTYIN(4HITM=)
00025:      IF(ITM.NE.0)NTANK=TTYIN(4H N=)
00026:      IF(ITM.NE.0)TG=TTYIN(4H TG=)
00027:C
00028:      V=37161.216*ETALF
00029:      PHIS=RHOS/EPSS $ PHILF=RHOLF/EPSLF
00030:      LS=LAMS/(1.+PHIS*GAMMAS) $ LLF=LAMLF/(1.+PHILF*GAMMALF)
00031:      DENOM=ETAS*(1.+PHIS*GAMMAS)
00032:      BLF=EPSLF/EPSS*VLF/DENOM $ ES=VS/DENOM
00033:      BETALF=VLF/ETALF/(1.+PHILF*GAMMALF)+LLF
00034:      BETAS=BS+LS
00035:      C(0,0)=MO/(EPSLF*V)/(1.+PHILF*GAMMALF)*1.E6
00036:      IF(ITM.EQ.0)GO TO 31
00037:C
00038:      XJ=TMAX(BETAS-BETALF,BETAS/BETALF,NTANK,TG)
00039:      IF(XJ.LT.0.)GO TO 35
00040:      E1=EXP(-BETALF*XJ) $ E2=EXP(-BETAS*XJ)
00041:      NM1=NTANK-1
00042:      SUM=0
00043:      DO 30 J=0,NM1
00044:      30 SUM=SUM+((BETAS-BETALF)*XJ)**J/FACTJ(J)*E2
00045:      CMAXTN=C(0,0)*BLF*BS**NM1*(E1-SUM)/(BETAS-BETALF)**NTANK
00046:      WRITE(61,400)NTANK,XJ,CMAXTN
00047:      400 FORMAT('/' TANK'I5,5X,' TMAX='F8.2,5X,' CONC PPM='F9.3/)
00048:C
00049:      IF(ITM.EQ.1)GO TO 35
00050:      31 CONTINUE
00051:      IF(IO.NE.0)WRITE(61,101)PHIS,PHILF,LS,LLF,ELF,BS,BETALF,
00052:      * BETAS,C(0,0)
00053:      101 FORMAT('//' PHIS,PHILF='2F15.8/' LS,LLF='2F15.8/
00054:      * ' BLF,BS='2F15.8/' BETALF,BETAS='2F15.8/
00055:      * ' C(0,0)='F15.8)

```

```

00056:      DO 1 N=1,NT
00057:      1 C(N,0)=0
00058:      DO 2 J=1,ND
00059:      XJ=J $ E1=EXP(-BETALF*XJ) $ E2=EXP(-BETAS*XJ)
00060:      D1=BETAS-BETALF
00061:      CL(J)=C(0,0)*E1
00062:      C(1,J)=C(0,0)*BLF*(E1-E2)/D1
00063:      IF(I0.NE.0)WRITE(61,200)C(0,J),C(1,J)
00064: 200 FORMAT(' C(0,J),C(1,J)='2F15.8)
00065:      DO 2 N=2,NT
00066:      N1=N-1 $ SUM=0
00067:      DO 3 JJ=0,N1
00068:      SUM=SUM+((BETAS-BETALF)*XJ)**JJ/FACTJ(JJ)*E2
00069:      3 CONTINUE
00070:      2 C(N,J)=C(0,0)*BLF*BS**N1*(E1-SUM)/D1**N
00071: C
00072:      WRITE(LUN,104)
00073: 104 FORMAT(' DAY LANDFILL'10X'SOIL COMPARTMENTS -- PPM')
00074:      J=0 $ WRITE(LUN,105)J,C(0,0)
00075:      DO 5 J=1,ND
00076:      5 WRITE(LUN,105)J,CL(J),(C(N,J),N=1,NT)
00077: 105 FORMAT(/I4,F9.3,5F9.3/(13X,5F9.3))
00078:      GO TO 10
00079:      END
00080:      FUNCTION FACTJ(J)
00081:      FACTJ=1.0
00082:      DO 1 I=2,J
00083:      XI=I
00084:      1 FACTJ=FACTJ*XI
00085:      RETURN
00086:      END
00087:      FUNCTION TMAX(A,B,N,X)
00088:      ITERMAX=100 $ TOL=0.5 $ ITER=1
00089:      3 SUM1=SUM2=0 $ N1=N-1
00090:      DO 20 K=1,N1
00091:      AID=(A*X)**(K-1)/FACTJ(K-1)
00092:      SUM1=SUM1+AID
00093:      20 CONTINUE
00094:      TMAX=LOGF(SUM1+B/FACTJ(N-1)*(A*X)**(N-1))/A
00095:      XTMAX=IMAX
00096:      WRITE(61,101)ITER,X,XTMAX,SUM1
00097: 101 FORMAT(/I5,2F10.5,E15.8)
00098:      IF(ABS(TMAX-X).GT.TOL)1,2
00099:      1 X=TMAX $ ITER=ITER+1
00100:      IF(ITER.LE.ITERMAX)GO TO 3
00101:      TMAX=-1.
00102:      2 RETURN
00103:      END

```

]

LOAD, BTANKLFS  
RUN  
RUN

# TANK LANDFILL MODEL

LUN=61  
RS=1.3  
RLF=.5  
ES=.5  
ELF=.6  
MO=100  
LS=0  
LLF=0  
GS=0  
GLF=0  
AS=6.096  
ALF=304.8  
VLF=7.62  
VS=30.48  
NT=10  
ND=2  
IO=0  
ITM=1  
N=5  
TG=5

1	5.00000	3.01038	2.90055697E 03
2	3.01038	2.60259	6.88000727E 02

TANK	5	TMAX=	2.60	CONC	PPM=	4.225
------	---	-------	------	------	------	-------

ITM=2  
N=10  
TG=5

1	5.00000	4.30630	5.23218522E 06
2	4.30630	4.03623	1.69426315E 06

TANK	10	TMAX=	4.04	CONC	PPM=	4.176
------	----	-------	------	------	------	-------

## DAY LANDFILL SOIL COMPARTMENTS -- PPM

0	14.714					
1	14.351	4.297	4.169	3.817	3.213	2.451
		1.684	1.044	.586	.299	.140
2	13.997	4.220	4.239	4.250	4.238	4.176
		4.029	3.769	3.388	2.906	2.365

## THE CONTINUOUS MODEL COMPUTER PROGRAM

The Fortran listing of the computer program to calculate the distribution of a chemical in a one-dimensional porous media as derived in Appendix I is given on pages 78 to 79. For a specified distance in the soil media as measured from the edge of the landfill, the program computes the variation in chemical concentration (ppm) with time.

Nomenclature used in program development is similar to that used in the derivation of the model as given in Appendix I. During program execution, values must be entered at the teletype for LUN, RS, RLF, ES, ELF, MO, LS, LLF, GS, GLF, ALF, VLF, VS, DS, and IO. All symbols except DS are defined on pages 72 to 73. DS is the longitudinal dispersion coefficient with units  $\text{cm}^2/\text{day}$ .

The utility of program CONTINLF and typical output is on page 78.

```

00001:      PROGRAM CONTINLF
00002:      REAL IVP1,IVP2,IVP3
00003:      REAL LS,LLF,MO,LAMS,LAMLF
00004:C      DATA SECTION
00005:      10 WRITE(61,100)
00006:      100 FORMAT(////' CONTINUOUS LANDFILL MODEL'/)
00007:      LUN=TTYIN(4HLUN=)
00008:      RHOS=TTYIN(4H RS=)
00009:      RHOLF=TTYIN(4HRLF=)
00010:      EPSS=TTYIN(4H ES=)
00011:      EPSLF=TTYIN(4HELFF=)
00012:      MO=TTYIN(4H MO=)
00013:      LAMS=TTYIN(4H LS=)
00014:      LAMLF=TTYIN(4HLLF=)
00015:      GAMMAS=TTYIN(4H GS=)
00016:      GAMMALF=TTYIN(4HGLF=)
00017:      ETA=TTYIN(4HALF=)
00018:      VLF=TTYIN(4HVLF=)
00019:      VS=TTYIN(4H VS=)
00020:      DS=TTYIN(4H DS=)
00021:      IO=TTYIN(4H IO=)
00022:C
00023:      PHIS=RHOS/EPSS $ PHILF=RHOLF/EPSLF
00024:      AID1=1.+PHIS*GAMMAS $ AID2=1.+PHILF*GAMMALF
00025:      D=DS/AID1 $ V=VS/AID1 $ LS=LAMS/AID1 $ LLF=LAMLF/AID2
00026:      BETALF=VLF/ETA/AID2+LLF
00027:      VOL=37161.216*ETA
00028:      CO=MO/(EPSLF*VOL)/(1.+PHILF*GAMMALF)*1.E6
00029:C
00030:      P=0.47047
00031:      A1=0.3480242 $ A2=-0.0958798 $ A3=0.7478556
00032:      AID3=SQRT(D*LS+V**2/4.-BETALF*D)
00033:      20 WRITE(LUN,201)
00034:      201 FORMAT(1H1)
00035:      X=TTYIN(4H X=)
00036:      IF(X.LT.0..OR.T.LT.0.)GO TO 10
00037:      IT1=TTYIN(4H T1=)
00038:      IT2=TTYIN(4H T2=)
00039:      IDELT=TTYIN(4H DT=)
00040:      WRITE(61,110)
00041:      110 FORMAT(1H1'          X CM', '          T DAYS' , '          U PFM'
/)
```

```

00042:      DO 1 I=IT1,IT2,IDELT
00043:      T=I
00044:      D1=(X+2.*T*AID3)/2./SQRT(D*T)
00045:      D2=(X+V*T)/2./SQRT(D*T)
00046:      D3=(X-2.*T*AID3)/2./SQRT(D*T)
00047:      TH1=1./(1.+P*D1)
00048:      TH2=1./(1.+P*D2)
00049:      TH3=1./(1.+P*ABS(D3))
00050:      IVP1=A1*TH1+A2*TH1**2+A3*TH1**3
00051:      IVP2=A1*TH2+A2*TH2**2+A3*TH2**3
00052:      IVP3=A1*TH3+A2*TH3**2+A3*TH3**3
00053:      COEF=EPSLF*VLF*CO/EPSS/AID1/SQRT(D)/(BETALF-LS)
00054:      H1=V/4./SQRT(D)+0.5/SQRT(D)*AID3
00055:      H2=V/4./SQRT(D)-0.5/SQRT(D)*AID3
00056:      H3=EXP(-LS*T)*EXP(-(X-V*T)**2/4./D/T)
00057:      IF(10.NE.0)WRITE(61,111)D1,D2,D3,TH1,TH2,TH3
00058: 111  FORMAT(' D1,D2,D3='3F15.8/' TH1,TH2,TH3='3F15.8)
00059:      IF(10.NE.0)WRITE(61,112)IVP1,IVP2,IVP3,COEF,H1,H2,H3
00060: 112  FORMAT(' IVP1,IVP2,IVP3='3F15.8/' COEF='F15.8/
00061:      * ' H1,H2,H3='3F15.8)
00062:      IF(D3.GT.0.)GO TO 2
00063:      U=COEF*((H1*IVP1-V/2./SQRT(D)*IVP2-H2*IVP3)*H3
00064:      * +2.*H2*EXP(-BETALF*T)*EXP(X*(V/2./D-AID3/D)))
00065:      GO TO 1
00066: 2  U=COEF*((H1*IVP1-V/2./SQRT(D)*IVP2+H2*IVP3)*H3)
00067: 1  WRITE(61,200)X,T,U
00068: 200  FORMAT(3X,3F12.4)
00069:      GO TO 20
00070:      END

```

# CONTINUOUS LANDFILL MODEL

LUN=61  
 RS=1.3  
 RLF=.5  
 ES=.5  
 ELF=.6  
 MO=100  
 LS=0  
 LLF=0  
 GS=0  
 GLF=0  
 ALF=304.8  
 VLF=7.62  
 VS=30.48  
 DS=.1  
 IO=0

X=12192  
 T1=400  
 T2=500  
 DT=5

X CM	T DAYS	U PPM
12192.0000	400.0000	2.1943
12192.0000	405.0000	3.8958
12192.0000	410.0000	3.4380
12192.0000	415.0000	3.0340
12192.0000	420.0000	2.6775
12192.0000	425.0000	2.3629
12192.0000	430.0000	2.0852
12192.0000	435.0000	1.8402
12192.0000	440.0000	1.6240
12192.0000	445.0000	1.4332
12192.0000	450.0000	1.2648
12192.0000	455.0000	1.1162
12192.0000	460.0000	.9850
12192.0000	465.0000	.8693
12192.0000	470.0000	.7671
12192.0000	475.0000	.6770
12192.0000	480.0000	.5974
12192.0000	485.0000	.5272
12192.0000	490.0000	.4653
12192.0000	495.0000	.4106
12192.0000	500.0000	.3624

### APPENDIX III

#### TABLES OF PHYSICO-CHEMICAL PROPERTIES OF SELECTED PESTICIDES, HERBICIDES, ETC., AND SOME SOILS PROPERTIES

In this section of the report the reader will find numerous tables listing many of the known physical-chemical properties of representative Oregon soils and classes of pesticides and industrial organic compounds. These physical-chemical properties (e.g., heats of solution, partition coefficients, adsorption coefficients, etc.) are listed here mainly as an aid in making judgments or guestimates on the extent of chemical binding to selected porous medium surfaces together with any microbial degradation. The extent of chemical binding to the numerous and varied surfaces together with microbial degradation in the landfill-soil conduit system forms an integral and most important part of all chemical dispersion in porous media models.



Table III-1. Chemical and Physical Properties of Eight Selected Oregon Soils

Soil Series	Horizon Depth Inches	Fe <sub>2</sub> O <sub>3</sub> %	CEC meq/100g	Exchangeable		Extractable Al meq/100g	pH (1:1,H <sub>2</sub> O)	Organic Matter %	Clay %
				Al meq/100g	Al meq/100g				
Dayton sil	0-9	1.1	7.7	.35		2.1	5.1	2.6	14.0
Jory (Aiken) sic	0-16	7.9	11.9	0		6.3	5.9	6.9	33.3
Nyssa sil	0-11	.7	18.8	0		.6	7.5	1.1	17.0
Zumwalt sil	0-7	.9	27.4	0		.4	6.2	6.0	26.1
Woodburn sil	0-9	2.1	10.5	.02		2.1	6.6	3.1	16.2
Hembre 1	0-7	3.5	18.3	3.3		16.8	5.0	29.0	12.6
Kenutchen c	0-4	1.0	45.2	0		1.9	6.9	4.7	63.7
Deschutes sl	0-4	.9	10.9	0		.7	6.7	.9	7.2

Table III-2. Cultural and Natural Features of Eight Selected Oregon Soils

Soil Series	Location in Oregon	Land Use	Parent Material	Landscape	Typical County	Extent
Dayton sil	Willamette and southern Oregon valleys, foothills and mountains	Gen. farm	Water-laid silts	Basin terrace	Linn	Extensive
Jory (Aiken) sic	Willamette and southern Oregon valleys, foothills and mountains	Gen. farm-horticulture	Basic volcanic rocks	Foothills	Marion	Extensive
Nyssa sil	Snake River Plains	Irrigation	Alluv.-loess?	Terrace	Malheur	Extensive locally
Zumwalt sil	Palouse and Nez Perce Prairies	Range	Thin loess/basalt	Dissected plateau	Wallowa	Extensive locally
Woodburn sil	Willamette and southern Oregon valleys, foothills and mountains	Gen. farm-horticulture	Water-laid silts	Basin terrace	Marion	Extensive
Hembre 1	Northern coast range and valleys	Forest	Sedimentary rocks	Mountain slopes	Tillamook	Inextensive
Kenutchen c	Willamette and southern Oregon valleys, foothills and mountains	Irrigation horticulture	Clayey alluv.	Basin terrace	Jackson	Extensive locally
Deschutes sl	Central and Eastern Oregon lava plains and hills	Irrigation	Pumice	Smooth plateau	Deschutes	Extensive

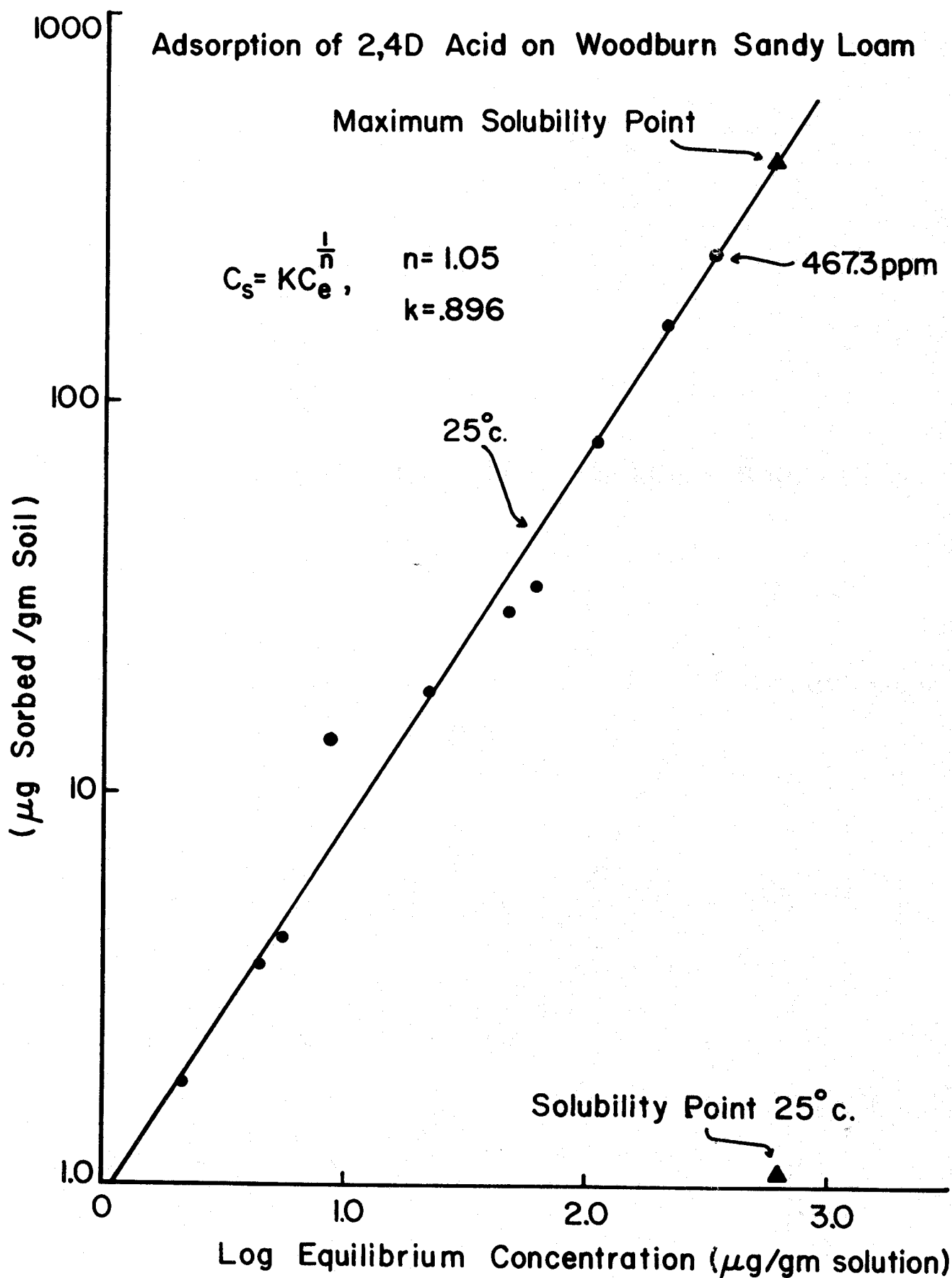


Figure III.1 Adsorption of 2,4-D acid on Woodburn silt loam. Temperature at 25°C. In vitro, water saturated conditions.

# Sorption Curves

(Illite clay)  
 $\Delta G = -1.51 \frac{\text{Kcal}}{\text{mole}}$

(Newberg silt loam)  
 $\Delta G = +.532 \frac{\text{Kcal}}{\text{mole}}$

(20-30 Mesh silica sand) (ottowa)  
 $\Delta G = +1.67 \frac{\text{Kcal}}{\text{mole}}$

$\mu\text{g 2,4-D Sorbed/gm Soil}$

Equilibrium Concentration ppm

Figure III.2 Adsorption of 2,4-D acid on three soil types (almost pure clay, Newberg silt loam, and Ottawa sand). Free energies are shown. These are in vitro experimental results under water saturated conditions. Temperature at 25°C.

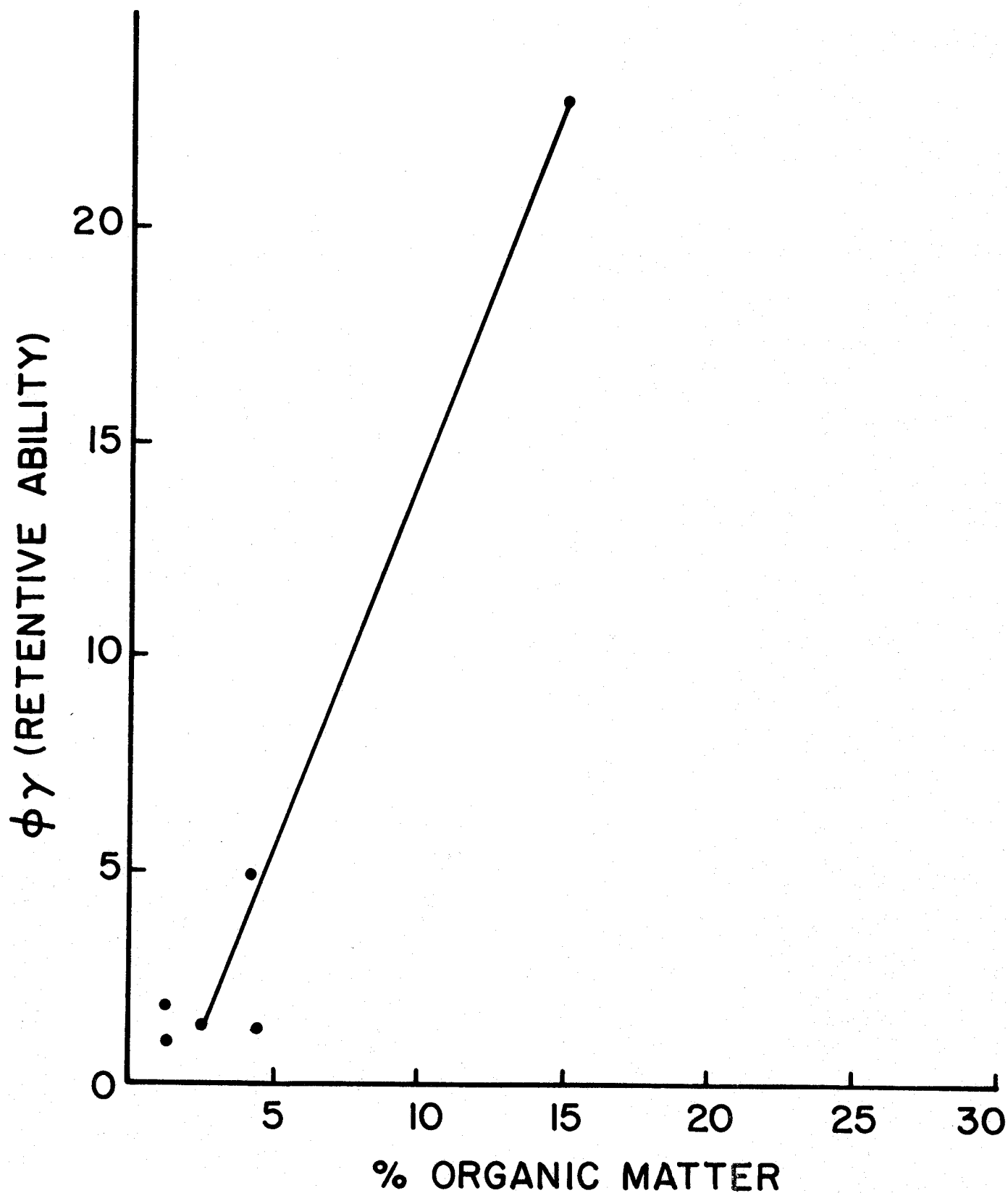


Figure III.3 Retentive ability  $\phi\gamma$  as a function of the percentage of organic matter in certain selected Oregon soils (Table III.1) (Lindstrom et al., 1967)

Table III-3. Freundlich Proportionality Coefficients\* for a 2,4-D Acid, Water, and Soil Surface at 25°C

Surface	$K \left( \frac{\text{cm}^3}{\text{gm soil}} \right)$	
	$C_{eq}$ in ( $\mu\text{g}/\text{cm}^3$ )	$C_{eq}$ in (ppm)
Ottawa sand (very high silicate)	0.04 (weak adsorbtion)	0.00000004
Newberg silt loam (50% sand, 8% organic 20% clay)	0.4 (moderate adsorbtion)	0.00000004
Illite clay	15.0 (very strong adsorbtion)	0.000015

\*Freundlich isotherm:  $x/m = K C_{eq}^n$ , K and n are temperature, moisture, surface dependent parameters.  $x$  = gms chemical sorbed; m = mass of soil onto which x is sorbed;  $C_{eq}$  = free phase chemical concentration ( $\mu\text{g}/\text{cm}^3$ ) or (ppm).

Table III-4. Freundlich Proportionality Coefficients for a PCB  
(Aroclor 1254), Water, Soil Surface at 25°C

Surface	K ( $\frac{\text{cm}^3}{\text{gm soil}}$ )	
	$C_{eq}$ in ( $\mu\text{g}/\text{cm}^3$ )	$C_{eq}$ in (ppm)
Willamette Silt Loam (from Brown's Island site)	50.0	0.00005
Shredded newsprint	160.0	0.00016

Table III-5. Solubility and Biodegradation Data on Some Selected Agricultural and Industrial Chemicals

Class	Compound	H <sub>2</sub> O Solubility	Oil Solubility	Biodegradation
Insecticides	Aldrin	0.2 ppm, 25°C	0.25 g/cm <sup>3</sup> diesel 25°C	half-life about 4 years under moist soil conditions
	DDT	0.04 ppm, 25°C	0.11 g/cm <sup>3</sup> diesel 25°C	half-life about 4 years under moist soil conditions
	BCH (Hexachloro- cyclohexane)	All 3 isomers about 8 ppm 20°C	0.02 g/cm <sup>3</sup> , cotton seed, 20°C	half-life about 1 year under moist soil conditions
Herbicides	2,4-D (phenoxyacetic acid)r	620 ppm, 25°C	0.1 ppm, 25°C (CCl <sub>4</sub> )	half-life about 2 weeks under water saturated soil conditions
	Diuron (urea)	42 ppm, 25°C	900 ppm, 25°C (cotton seed)	half-life about 6 months under moist soil conditions
	Propanil (Amide)	268 ppm, 22°C	0.25 gm/cm <sup>3</sup> , 20°C, (xylene)	(n.f.)*
	PCP (phenol)	14 ppm, 20°C	<10 ppm, 25°C (cotton seed)	(n.f.)
	Diquat (heterocyclic)	0.67 gm/cm <sup>3</sup> , 20°C	(essentially insoluble)	(n.f.)
	Atrazine (heterocyclic)	70 ppm, 27°C	360 ppm, 27°C (N-pentone)	half-life about 2 months under moist soil conditions



Table III-5 (cont)

Class	Compound	H <sub>2</sub> O Solubility	Oil Solubility	Biodegradation
Industrial	IPC (carbamate)	254 ppm, 25°C	<10 ppm, 25°C (cotton seed)	
	PCB (1242 Aroclor)	200 ppb, 25°C	>10,000 ppm, (cotton seed)	(n.f.)

\* n.f. = values not found in literature.

NOTE: The above data was obtained from the following sources:

- <sup>1</sup>Freed and Haque (1973).
- <sup>2</sup>Nelson (1972).
- <sup>3</sup>Barrier (1970).
- <sup>4</sup>Spencer (1968).
- <sup>5</sup>Freed (1969).

Table III-6. Partition Coefficients for Pesticides and Herbicides  
in Equivolumes of Non-Polar:Polar Binary Solvent Systems

$$K_p = \left( \frac{C_{np}}{C_p} \right)_{eq}$$

<u>Name</u>	<u>Temp</u>	<u>Hexane/ Acetonitrile</u>	<u>Isoctane/ 80% Acetone</u>
DDT (Beroza et al. 1969)	25°C	0.59	13.3
2,4-D (Beroza et al. 1969)	25°C	0.02	0.19
Aldrin (Voerman, 1969)	25°C	Hexane/H <sub>2</sub> O 100,000	
DDT (Voerman, 1969)	25°C	(Same) 91,000	
Lindane (Voerman, 1969)	(25°C)	(Same) 1,760	

## Direct Laboratory Reports on Pertinent Adsorption Experiments

### III - R.1

#### Adsorption of 2,4-D Onto Soil and Soil Organic Matter\*

by Lewis G. McLaren

#### Purpose

The interaction between soil and soil organic matter and its effect on the adsorption of 2,4-D is being studied by comparison of the adsorption of the herbicide on three systems: 1) soil; 2) soil with organic matter removed; and 3) extracted soil organic matter. To date, the adsorption of 2,4-D on systems 1 and 2 has been made at pH levels of 6, 7, and 8, and at concentrations of  $1.2 \times 10^{-4}$  to  $1.2 \times 10^{-3}$  molar. Adsorption on extracted soil organic matter was reported on a previous progress report.

#### Procedure

In this report the procedure is given for the study of adsorption on soil and soil without organic matter. The procedure for the study of extracted organic matter was given in a previous progress report.

The soil used was a Willamette loam, a typical Willamette Valley soil. It was pre-washed with dilute HCl followed by water washings to remove excess  $\text{Cl}^-$  from soil. The soil was then dried and pulverized. A portion was treated with hydrogen peroxide to oxidize the organic matter and remove it from the soil as water and  $\text{CO}_2$ . This portion was then dried and ground to one mm or less particle size.

---

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Four grams of the soil (or soil without organic matter) was weighed into a fifty ml centrifuge tube. The centrifuge tube plus soil was then weighed. Twenty five ml of the appropriate buffer was added to each tube and shaken for one minute. The tubes were then centrifuged and the supernatant discarded. The tubes were then reweighed. The amount of buffer remaining was determined by difference. The volume of the buffer was calculated by the relation

$$V = \frac{m}{\rho} \quad \text{where } \rho = \text{density and } m = \text{mass}$$

The density of the buffer was found to be very close to one gram per ml and was so taken. Thus, the volume of the buffer in mls is taken to be equal to the mass of the buffer found by weighing.

Ten ml of the appropriate 2,4-D solution (pH, Conc.) was added to each centrifuge tube (three replications). The tubes were shaken and placed in a constant temperature water bath for 48 hours. The tubes were shaken several times during this period.

After the 48-hour equilibration period, a two ml aliquot of the solution was removed and filtered through Whatman #42 filter paper. A 0.1 ml aliquot of the filtrate was measured into a scintillation vial for counting.

The activity of the sample must be corrected for the amount of buffer that was added to the soil. The corrected activity is determined by the relation

$$\text{corrected activity} = (\text{observed activity}) \left( \frac{\text{corr. volume}}{\text{initial volume}} \right)$$

$$\text{corrected volume} = (\text{initial volume}) + (\text{buffer volume}).$$

The 2,4-D adsorbed is determined by subtracting the corrected activity from the initial activity. Percent adsorbed is given by

$$\% \text{ ads.} = \frac{(\text{Initial activity}) - (\text{corr. activity})}{(\text{Initial activity})} \times 100\%$$

The millimoles of 2,4-D adsorbed is given by

$$\text{mM ads.} = (\% \text{ ads.}) (\text{Initial molarity}) (10^{-3} \text{ mM/mole}).$$

DATA:

1. Adsorption of 2,4-D by soil (in mmoles/gram soil).

<u>Concentration</u>	<u>Adsorption (mM x 10<sup>5</sup>)</u>		
	<u>pH 6.4</u>	<u>pH 7.1</u>	<u>pH 8.0</u>
1.2 x 10 <sup>-4</sup>	4.45	5.50	3.65
2.4 x 10 <sup>-4</sup>	12.15	9.75	12.80
6.0 x 10 <sup>-4</sup>	23.15	14.50	30.00
1.2 x 10 <sup>-3</sup>	63.75	34.25	41.25

2. Adsorption of 2,4-D by soil without organic matter (in mMoles/gram soil).

<u>Concentration</u>	<u>Adsorption (mM x 10<sup>5</sup>)</u>		
	<u>pH 6.4</u>	<u>pH 7.1</u>	<u>pH 8.0</u>
1.2 x 10 <sup>-4</sup>	4.00	3.75	4.58
2.4 x 10 <sup>-4</sup>	10.75	8.25	6.50
6.0 x 10 <sup>-4</sup>	26.25	11.00	17.75
1.2 x 10 <sup>-3</sup>	38.25	25.00	19.50

3. Adsorption: Soil vs. soil without organic matter  
(in mMoles  $\times 10^5$  adsorbed/gram soil).

<u>pH</u>	<u>Concentration</u>	<u>Soil</u>	<u>Soil Without Organic Matter</u>
6.4	$1.2 \times 10^{-4}$	4.45	4.00
	$2.4 \times 10^{-4}$	12.15	10.75
	$6.0 \times 10^{-4}$	23.15	26.25
	$1.2 \times 10^{-3}$	63.75	38.25
7.1	$1.2 \times 10^{-4}$	5.50	3.75
	$2.4 \times 10^{-4}$	9.75	8.25
	$6.0 \times 10^{-4}$	14.50	11.00
	$1.2 \times 10^{-3}$	34.25	25.00
8.0	$1.2 \times 10^{-4}$	3.65	4.58
	$2.4 \times 10^{-4}$	12.80	6.50
	$6.0 \times 10^{-4}$	30.00	17.75
	$1.2 \times 10^{-3}$	41.25	19.50

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The Adsorption of Phenol and Chlorinated Phenols on Soil\*

by Lewis G. McLaren

Purpose

The purpose of this study was to compare the adsorption of phenol and various chlorinated phenols on soil with their solubilities.

Procedure

Forty grams of soil was equilibrated on a shaker bath at 30°C with aqueous solutions of 10 ppm, 15 ppm, 20 ppm, and 30 ppm of the phenols.

The phenols used were

1. Phenol
2. o-chlorophenol
3. p-chlorophenol
4. 2,4-dichlorophenol
5. 2,6-dichlorophenol
6. 2,4,6-trichlorophenol

Time-rate studies were made to determine the time necessary for the system to come to equilibrium. Twenty ppm solutions were used for this study.

In the adsorption studies, 40 g of soil was weighed into a 250 ml Erlenmeyer flask. One hundred ml of the phenol solution was added to the soil. The flask was then stoppered and placed in a shaker bath at 30° for one hour. A two ml aliquot was removed and centrifuged at 2,500 rpms for 10 minutes. The supernatant solution was then analyzed by gas chromatography with hydrogen flame detector.

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Solubility determinations were made at 30° and at 3°C. An excess of the pure phenol was placed in an Erlenmeyer flask. Distilled water was added and the system was allowed to come to equilibrium in a constant temperature water bath. Aliquots were removed and the solubility measured by gas chromatography.

## Data and Results

### 1. Solubility

<u>Sample</u>	<u>Solubility g/ml at 29.0°</u>	<u>Solubility g/ml at 3.3°</u>
Phenol	4.63	2.6
o-chlorophenol	2.0+	2.0
p-chlorophenol	3.7	3.2
2,4-dichlorophenol	0.6	0.3
2,6-dichlorophenol	0.23	0.14
2,4,6-trichlorophenol	0.08	0.04

### 2. Time-Rate Study

<u>Sample</u>	<u>Percent Adsorbed</u>				
	<u>5 min</u>	<u>10 min</u>	<u>15 min</u>	<u>60 min</u>	<u>120 min</u>
Phenol	3.9	5.6	4.4	7.7	9.0
o-chlorophenol	32.3	29.2	28.2	28.3	37.5
p-chlorophenol	17.2	21.3	21.3	21.3	22.0
2,4-dichlorophenol	44.9	45.2	45.2	45.2	45.2
2,6-dichlorophenol	20.4	21.9	23.5	24.0	24.0
2,4,6-trichlorophenol	--	--	--	--	--

### 3. Adsorption

<u>Sample</u>	<u>µl Adsorbed Per Gram of Soil</u>			
	<u>10 ppm</u>	<u>15 ppm</u>	<u>20 ppm</u>	<u>30 ppm</u>
Phenol	2.2	2.8	4.5	4.6
o-chlorophenol	5.3	12.5	18.3	19.2
p-chlorophenol	4.4	7.7	11.1	13.1
2,4-dichlorophenol	11.0	15.2	22.6	29.0
2,6-dichlorophenol	7.2	11.6	12.0	19.5
2,4,6-trichlorophenol	9.9	15.0	--	25.8

### 4. pK, pH of 30 ppm soln, and Adsorption x Solubility= AxS

<u>Sample</u>	<u>pK</u>	<u>pH</u>	<u>AxS</u>
Phenol	9.1	5.54	841.8
o-chlorophenol	8.15	5.35	1534.0
p-chlorophenol	9.1	5.63	1931.4
2,4-dichlorophenol	7.4	5.44	696.0
2,6-dichlorophenol	6.4	5.45	179.4
2,4,6-trichlorophenol	5.95	5.19	82.4

### III - R.3 (Lab report)

#### Adsorption and Desorption Studies of 2,4-D and a Polychlorinated Biphenyl 2,4,2',5' Tetrachloro Biphenyl (PCB) on Soils and Newsprints\*

by Rizwanul Haque

These studies were carried out to determine the adsorption and desorption of the two chemicals on soil and newsprint surface. The soil samples selected were from Willamette silt-loam from Brown's Island Site. The two chemicals represent a contrast. The 2,4-D is a common herbicide; PCB is a common industrial chemical. 2,4-D is fairly soluble in water whereas PCB is very slightly soluble in water. Thus, adsorption-desorption of these two chemicals on the soil and newsprint may represent the characteristics of a large number of chemicals.

#### 2,4-D Adsorption-Desorption

SOIL (Willamette Silt Loam from Brown's Island Site)

Both soil samples were screened to collect the 40/60 mesh particles. For the UV study 1.00 g of soil was shaken in 30 ml of 2,4-D solutions ranging from 0, 1, 10, 100, 250, and 500 ppm for 48 hours. The samples were spun down and the supernate liquid spectroanalyzed for 2,4-D at 284 Å. The results showed no significant amount of 2,4-D adsorbed on the soil within  $\pm 2\%$  of the total amount for any concentration.

The adsorption was also monitored by  $^{14}\text{C}$  radioassay. This consisted of .500 g soil shaken in 10 ml of 1, 10, 100, and 200 solutions for 48 hours. The samples were spun down and two .2 ml aliquots drawn for analysis. Three 50-minute counts were done on each sample using liquid scintillation counting technique. The result again showed no significant adsorption of 2,4-D within  $\pm 1\%$ .

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It is the author's belief that the soil is almost totally sandy in nature and thus provides only poor binding sites for any organic material.

#### NEWSPRINT

1.000gr of newsprint was shaken with 30 ml of 1, 10, 100, 250, and 500 ppm 2,4-D solution for 48 hours. The samples were spun down and the supernate liquid was analyzed by uv. 2,4-D in low concentrations, i.e., 1 and 10 ppm did not show any adsorption within an experimental error of  $\pm 5\%$ . The 100 ppm solution also has no apparent adsorption within  $\pm 2\%$ . The 250 and 500 ppm solutions showed a significant adsorption of 2,4-D.

250 ppm	$510 \pm 10 \times 10^{-6}$ gr 2,4-D/gr newsprint
500 ppm	$2.93 \pm .06 \times 10^{-3}$

Desorption was done by leaving 10 ml of liquid with the paper pulp and adding 20 ml of distilled water. The samples were again shaken for 48 hours and spun down. The 1, 10, and 100 ppm solutions showed the amount of 2,4-D due to the dilution of the 10 ml retained in the paper pulp. Desorption for 250 and 500 ppm are:

250 ppm	$520 \pm 10 \times 10^{-6}$ gr 2,4-D/gr newsprint
500 ppm	$2.78 \pm .06 \times 10^{-3}$

#### 2,4,2',5',PCB Adsorption-Desorption

##### SOIL (Willamette Silt Loam from Brown's Island Site)

Both soil samples were screened to collect 40/60 mesh particles. One gm and five-tenths gm samples were used from each soil. To these samples of soil, 30 mls of 27 ppb PCB were added. The samples were shaken for at least 24 hours and up to 40 hours. They were then

centrifuged. 25 mls of the supernatant were withdrawn and the PCB was extracted from this with three, three ml portions of hexane. The extracted PCB was diluted to ten mls, and then analyzed by gas chromatography.

The sandy soil adsorbed 89% and 79% of the PCB, respectively, in one gm and five-tenths gm samples. This corresponds to 602.5 ng of PCB per gram of soil and 1061 ng/gm soil. The rocky soil adsorbed 86% and 78% of the PCB in the one gm and five tenths gm samples, respectively. This corresponds to 576 ng/gm soil and 1048 ng/gm soil. The adsorption of the different soils did not differ appreciably, 4% and 1%, respectively, for the one gm samples and five-tenths gm samples.

In the desorption study, as much of the remaining moisture (the remaining five mls) as possible was withdrawn from the soils before adding 30 mls of fresh water. Then the samples were treated in the same manner as for the adsorption study.

The desorption was small in all samples. In the sandy samples, there was about 10% and 13% desorption. In the rocky soil the desorption was about 7% and 13%.

#### NEWSPRINT

Similar studies when carried out on shredded paper showed that almost all the PCB was adsorbed on the surface.

TABLE III - R.3.1  
PCB  
ADSORPTION

<u>Sample</u>	<u>Aqueous Concentration</u>	<u>% Adsorbed</u>	<u>Soil Concentration</u>
SL			
1 gm	2.92 ppb	89%	602.5 ng/gm
.5 gm	5.75 ppb	79%	1061 ng/gm
R			
1 gm	3.90 ppb	86%	576 ng/gm
.5 gm	6.02 ppb	78%	1048 ng/gm

TABLE III - R.3.2  
DESORPTION

<u>Sample</u>	<u>Aqueous Concentration</u>	<u>% Desorbed</u>	<u>Soil Concentration</u>
SL			
1 gm	2.33 ppb	9.7%	599.7 ng/gm
.5 gm	2.79 ppb	13 %	921.9 ng/gm
R			
1 gm	1.66 ppb	7.2%	535.0 ng/gm
.5 gm	2.75 ppb	13 %	910.0 ng/gm

TABLE III - 7

PERMEABILITY DATA OF SELECTED POROUS MEDIA  
(From Peters, 1968)

Material	Permeability (gpd per sq ft @ 60°F)	
Granite	0.0000009	- 0.000005
Slate	0.000001	- 0.000003
Dolomite	0.00009	- 0.0002
Hematite	0.000002	- 0.009
Limestone	0.00001	- 0.002
Gneiss	0.0005	- 0.05
Basalt	0.00004	- 1
Tuff	0.0003	- 10
Sandstone	0.003	- 30
Till	0.003	- 0.5
Loess	1	- 30
Beach sand	100	- 400
Dune sand	200	- 600
Alluvium	(see individual materials below)	
Clay	0.001	- 1
Silt	1	- 10
Very fine sand	10	- 100
Fine sand	100	- 1000
Medium sand	1000	- 4500
Coarse sand	4500	- 6500
Very coarse sand	6500	- 8000
Very fine gravel	8000	- 11000
Fine gravel	11000	- 16000
Medium gravel	16000	- 22000
Coarse gravel	22000	- 30000
Very coarse gravel	30000	- 40000
Cobbles	Over 40000	

TABLE III - 8

## Definitions of Selected Groundwater Terms

## Relation of Units

[Equivalent values shown in same horizontal lines, † indicates abandoned term]

## A. Hydraulic Conductivity

Hydraulic conductivity (K)		†Field coefficient of permeability ( $P_1$ )
Feet per day (ft day <sup>-1</sup> )	Meters per day (m day <sup>-1</sup> )	†Gallons per day per square foot (gal day <sup>-1</sup> ft <sup>-2</sup> )
One	0.305	7.48
3.28	One	24.5
.134	.041	One

## B. Transmissivity (T)

Square feet per day (ft <sup>2</sup> day <sup>-1</sup> )	Square meters per day (m <sup>2</sup> day <sup>-1</sup> )	†Gallons per day per foot (gal day <sup>-1</sup> ft <sup>-1</sup> )
One	0.0929	7.48
10.76	One	80.5
.134	.0124	One



# C. Permeability

Intrinsic permeability

†Coefficient of permeability

$$K = - \frac{\gamma V}{d\phi/dL}$$

$$\text{Darcy} = - \frac{\gamma \mu}{d\rho/dL + \rho g dz/dL}$$

$$P \text{ or } P_M = - \frac{\gamma (\text{at } 60^\circ \text{F})}{dh/dL}$$

$$[(\mu m)^2 = 10^{-6} \text{ cm}^2]$$

$$[.987 \times 10^{-8} \text{ cm}^2]$$

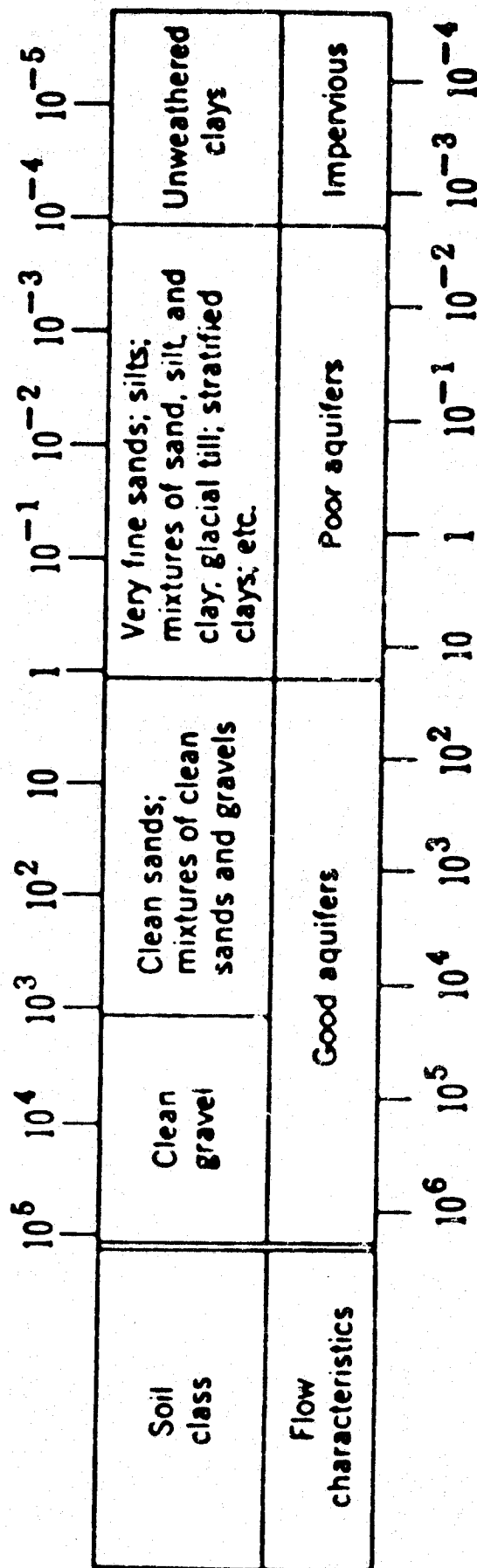
$$^\dagger [\text{gal/day/ft}^2 \text{ at } 60^\circ \text{F.}]$$

One  
0.987  
.054

1.01  
One  
.055

18.4  
18.2  
One

Specific permeability,  $k$ , darcys



Laboratory coefficient of permeability,  $K_s$ , gal/day/ft<sup>2</sup>

Figure III.4 Some useful hydrogeological data

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