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THE COLLECTION AND PRESENTATION OF THE LITERATURE IN THIS REPORT WAS DONE UNDER THE CONTAMINANT LEACHING STUDY, INITIATED IN MAY, 1978. THIS REPORT IS ONE OF TWO-PART SERIES AND COVERS A REVIEW OF THE LITERATURE ON THE LEACHING BEHAVIOR OF SUBSTANCES FOUND AT RMA, COLORADO. THE ASSESSMENT OF CONTAMINANT MIGRATION IN THE SOIL OF RMA WILL BE GIVEN IN PART II.

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MIGRATION POTENTIAL OF CONTAMINANTS IN

THE SOIL OF ROCKY MOUNTAIN ARSENAL

I. OPEN LITERATURE REVIEW

DRAFT

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Prepared for the US Army Toxic and Hazardous Materials Agency

PREFACE

The collection and presentation of the literature in this report
was done under ITARMS Task 1.05.41, Contaminant Leaching Study,
initiated in May 1978.

This report is one of a two-part series and covers a review of
the literature on the leaching behavior of substances found at Rocky
Mountain Arsenal (RMA), Colorado. The assessment of contaminant
migration in the soil of RMA will be given in Part II.

The use of trade names in this report does not constitute an
official endorsement for the use of such products.

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greatly appreciated.

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I. INTRODUCTION.

With the widespread practice of industrial and municipal waste disposal on land, attention has been given to the fate of the waste material in the soil. Most solid wastes ultimately end up in landfills or settling ponds. This can present a problem if the pollutants are transported by rainfall or other water source from the disposal sites into the water table. The aquifer is then contaminated and, if pollutant concentrations exceed acceptable standards, the groundwater must be treated before use.

If treatment is needed, it then becomes a question of how long contaminants will continue to migrate into the water table. Possibilities of reducing the treatment time are to modify the leaching behavior by: (i) fixing the chemicals in the soil, (ii) enhancing their rate of degradation or (iii) increasing the migration rate.

The situation at Rocky Mountain Arsenal, Colorado is one where the soil and groundwater contain toxic industrial wastes. It is necessary to answer the question of whether the wastes in the soil pose a continuing threat to the groundwater outside the arsenal property and, if so, for what length of time and how can the situation best be modified.

II. GENERAL CONCEPTS OF POLLUTANT MIGRATION IN SOIL.

Leachate is the liquid containing dissolved foreign matter that results when water passes through a waste disposal site. The concentration of material in the leachate decreases from a maximum at the waste source as the liquid migrates through the surrounding soil. This decrease in concentration is known in the literature as "attenuation" and can occur by one or

more mechanisms which are determined by the properties of the contaminant(s) and the soil environment.

A material which is removed from the leachate and held by the soil can form new leachate if conditions are sufficiently altered. The mechanisms of attenuation are briefly described here and will be discussed for specific cases in Section III.

A. Attenuating Mechanisms.

1. Dilution: This is simply the mixing of leachate with quantities of less contaminanted soil water to reduce the concentration of the leachate components. The water solubility is the most important property of the material as regards leachate formation. With highly soluble components dilution may be the only means of attenuation as in the case of chloride ion which is commonly used as a "tracer" in soil to study movement of water. However, the high polarization or ionic charge of many soluble materials can also result in greater adsorption to the soil.

Water input and mobility are the controlling factors for dilution and are dependent on amount of rainfall, surface water runoff, evaporation in the soil, transpiration by plants and permeability of the soil.

2. Precipitation: After a contaminant is in soil water and when its solubility is exceeded, the contaminant will solidify and be mechanically filtered by the soil. Precipitation can be brought about by a number of conditions such as a change in temperature, pH of the soil water, addition of other components, or evaporation of the soil water. Many of the heavy metals which ionize when dissolving in water have solubilities which are extremely pH dependent.

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3. _Volatilization_: The major property which determines whether a material is transported through soil in either the vapor or liquid phase is its vapor pressure. This is in return dependent on temperature and soil moisture content.

4. _Degradation_: This is determined by the ability of the contaminant to be chemically or biologically changed into other substances. If the products of degradation are harmless, then this mechanism effectively eliminates the waste from posing a future hazard. Chemical breakdown most often occurs by oxidation or hydrolysis.

5. _Adsorption_: For the majority of contaminants this is the most important attenuating mechanism. Adsorption is the accumulation of a component directly onto the surface of a solid material from the solution phase and can occur in a variety of ways, depending on the chemical nature of the materials involved. Of the two major types of adsorption, physical and chemical, chemisorption is the more important in soil systems. Physical adsorption, in the form of van der Waals attraction, plays a relatively minor role.

Many organic components of leachate are able to form hydrogen bonds to the clay and organic matter fractions of soil. Hydrogen bonding is a major means of attenuation for pesticides. Heavy metals can adsorb onto some constituents of the soil organic matter by formation of chelates.

The clay, metal hydrous oxide and organic matter surfaces possess ion exchange sites and give soils an ion exchange capability. This mechanism plays a limited role in the adsorption of heavy metals and is pH dependent.

B. Influence of Soil on Leachate.

Soil, as found in nature, is a highly complex environment formed by the action of weathering, plants and microorganisms on the parent rock. The many living and non-living things which comprise the soil in a given location make it unique. An accurate prediction of the fate of a material in soil is difficult due to the many interdependent factors which must be evaluated.

Key properties that give an indication of leachate generation, persistence and migration are the soil texture, the type(s) of clay present, the type and quantity of amorphous minerals, the organic matter content, soil pH and microbial activity. These are determined by the original material from which the soil was derived, the climate, vegetation and relief of the region, and the age of the soil.

The soil depth profile or cross-section is divided into three general layers known as the A, B and C horizons. The A horizon begins at the surface and is where most of the organic residue from plants has accumulated. The B horizon, just below, contains most of the clays and amorphous minerals. This is the layer where most of the leachable materials from the A horizon end up. The C horizon contains the material from which the A and B horizons originate and this layer extends down to the impermeable bedrock.

Water infiltration rate and time of leaching are the most influential in governing the development and establishing characteristics of a soil profile. Old soils in high rainfall areas have well developed profiles,

meaning that the individual horizon is well defined and extensive in depth. In younger soils from more arid regions, the horizons are not as thick and, in some cases, may be so poorly defined as to be indistinguishable. Rainfall is a dilute acid and, as it percolates through a soil, displaces the alkali metal ions from the A and B horizons and replaces them with the hydronium ion. The displaced alkali metals then accumulate in the lower depths of the soil or are leached out completely. The same happens with salts which may be solidified in the upper levels of the soil profile.

Regions with high rainfall rates normally have thick vegetation cover which contributes to the acidity of the leaching rain water through the decaying plant tissue. In addition, the plant roots extract the alkali metal ions from soil. Thus, the pH of well-leached soils is relatively acidic and, as the C horizon is approached, becomes more alkaline due to some alkali metal accumulation in the lower depths. The amorphous metal oxides and hydroxides are dissolved by acidic rain water and then reprecipitate in the C horizon as the pH increases. In constrast, the soils found in arid regions generally have a higher alkaline, salt and amorphous mineral content throughout.

If the topography of a region changes greatly there can be many variations in the soil profile for even a small area. This is because the relief influences the amount of rainfall which effectively infiltrates the soil for a given rainfall rate. The surface runoff and internal drainage (aeration) are determined by the soil slope with hilltops having

a decreased infiltration rate and greater aeration (chemically oxidizing condition) and low spots having an enhanced infiltration and decreased aeration (chemically reducing condition).

The vegetation cover of a soil determines its organic matter content. Plant tissue degraded into a humified form is highly important in the adsorption of many organic components of leachate. In humid regions, where much vegetation exists, the soil contains a large amount of organic matter whereas soils low in organics are found in arid regions. In semi-arid regions, where grasses are the dominate species, the organic matter content is low to moderate.

The effect of particle size distribution (soil texture) on leachate results from the surface area available for adsorption of solutes along with the soil permeability to water flow. The diameter of soil particles are arranged in the following general categories.

Gravel > 2 mm

Sand $50 \, \mu m - 2$ mm

Silt $2 \, \mu m - 50 \mu m$

Clay $< 2 \, \mu m$

The US Department of Agriculture (USDA) classification system based on the fraction of sand, silt and clay content in a given soil is presented in Figure 1.

The permeability of soils is controlled by the particle size distribution and the structure of the soil matrix. As the size of the particles increase the total void volume decreases but, since the individual voids are larger, the soil will be more permeable. If the particles are arranged in some form of a structure instead of being dispersed, the soil permeability will increase.

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In addition to their large surface area, most clays have a net
negative charge which makes them among the most important adsorbents
in soil. Clays are crystalline mineral colloids and have two general
lattice formations, the 1:1 and 2:1 arrangements. The details of
these lattice arrangements and the origin of the net internal charge
have been presented elsewhere[1].

These lattice units are planar and, in the 1:1 arrangement, one
surface consists of oxygen atoms and the other hydroxyl groups. Both
outer surfaces of the 2:1 lattice unit consist of oxygen atoms. The 2:1
units of montmorillonite clay, where the outer oxygen surfaces of the
lattice have more attraction toward water than each other, increase
their separation when immersed. This explains the swelling action of
montmorillonite in water which is known as an expanding clay. The
swelling exposes a large internal surface area for adsorption. The
2:1 clay illite, however, contains monovalent cations in between the
lattices which effectively cements the units together and prevents
swelling in water resulting in a greatly reduced surface area. The 1:1
units have oxygen-facing-hydroxide groups and the resulting attraction
between the lattices prevents these clays from expanding.

In clays the internal negative charge is balanced by the accumulation
of cations on exposed surfaces. That these cations are able to be dis-
placed by other cationic species explains the origin of the "cation
exchange capacity" (CEC) of clays. Further the monovalent cations which
are bound in between the lattices of illite neutralize much of the net

charge, partly explaining why the CEC of illite is lower than that of montmorillonite. Exchangeable amions are found only at the edges of the clay lattice and, as a result, there is little anion exchange capability. Data for representative clay minerals, along with other soil components, are reproduced in Table I[2].

A highly significant adsorption mechanism which occurs between polar organic molecules and soil is the hydrogen bond. This occurs whenever a dipole moment exists in a functional group of the solute molecule which can bond to a clay surface. Either a water molecule or hydrogen atom serves as a link. There is always competition between polar water and organic molecules for hydrogen bonding sites.

The remaining adsorbents in soil, the amorphous hydrous oxides and organic matter, are not as well characterized. Iron, aluminum and especially silicon are the most common elements in the amorphous complexes. These mineral complexes, because they are unstructured, expose a much greater specific surface area than the non-expanding clays. Metal hydrous oxides have an ion exchange capacity which is highly pH dependent and capable of anionic as well as cationic exchange. These two factors arise from the amphoteric nature of the minerals, i.e., the surface reacts with both hydrogen and hydroxide ion.

The soil organic matter which is active as an adsorbent is that which has been humified (greatly altered from the original living tissue) by soil microorganisms. These substances have phenolic and carboxyl functional groups which act as cation exchange sites. Most organic matter found in soil possesses a high degree of ion exchange capability.

In the adsorption phenomena the individual contributions of clay, amorphous mineral, and organic matter content are difficult to separate. These absorbents are known to coat one another in the soil environment making a portion of their surfaces unavailable. The net effect is a reduction of the adsorptive capacity of all three constituents.

III. CONTAMINANT - SOIL SYSTEMS INVESTIGATED IN THE LITERATURE.

A general literature review, covering journal articles and published reports, was conducted on contaminant leaching. The leaching behavior of the following major types of contaminants in soil was investigated.

     1. Organics - insecticides, DIMP, DCPD and DBCP.

     2. Inorganics - heavy metals and soluble salts.

The specific elements or compounds focused on were those which have been shown to exist in the soil, groundwater or surface water of Rocky Mountain Arsenal. Other substances were included when necessary for completeness.

A. Organics.

1. General. In the past few decades much research had been directed toward the fate of pesticides in the soil environment. Their adsorption and migration in soil has been widely studied, most of the work being concerned with applications used in agriculture. The persistence and migration of pesticides is dependent on the form they are applied to the soil (granular, emulsion, liquid powder or dust) and the initial concentration in addition to the other factors previously described.

Two of the most common and widely studied groups of pesticides are the organochlorine and organophosphorous insecticides. The former are

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practically insoluble in water and have long half lives, many in excess of 5 years. As a result, they are highly persistent and can pose a long term environmental threat if present in sufficient amounts. In addition, some yield toxic substances on degradation. For example, aldrin and heptachlor oxidize into dieldrin and heptachlor epoxide, respectively. The organophosphorous compounds are much more water soluble and have shorter half lives, under 1 year.

The compounds diisopropylmethylphosphonate (DIMP) and dicyclopentadiene (DCPD) have been closely monitored in the groundwater at RMA. DIMP is a byproduct from the manufacture of nerve agent GB and DCPD is a raw material for pesticide production. The only work found which studies the fate of these compounds in soil is the Aerojet report[3].

The physical and chemical properties of DIMP, DCPD and selected pesticides are presented in Table 2[3,4,5]. The structural formulas are shown in Figure 2.

In the laboratory, two common methods of observing leaching behavior are by means of the batch and column techniques. The soil in the column may be either extracted "undisturbed" directly from a field plot or formulated as desired. In field experiments the soil core samples and groundwater are analyzed for contaminant concentration.

Batch studies are normally used to plot the adsorption and desorption isotherms for a particular solute-substrate environment. A measured amount of the substrate is subjected to a known volume and concentration of the compound in solution until an equilibrium is reached. The decrease in concentration is then said to be due to adsorption on the substrate.

In determining desorption isotherms the contaminated substrate is immersed in a known volume of solvent and the solute concentration measured after equilibrium is reached.

Soil column studies are used to estimate the vertical migration of a contaminant in the field and to verify models of leachate transport. One method is to apply the compound in solution directly to the column followed by leaching with water. Another widely used procedure is to first adsorb the material on a top layer in a batch mixing process. The column is then rinsed with water after the treated layer is replaced. The soil is usually divided into segments and each segment is analyzed for contamination level. The column effluent is monitored throughout the experiment.

Analysis of organics in soil is done by solvent extraction followed by passing the solution through a gas chromatograph. The groundwater samples may be injected directly into the chromatograph column. Gas chromatography is a highly sensitive technique for both quantitative and qualitative analysis of organic compounds.

A rapid and versatile technique for determining pesticide mobility in soil was introduced by Helling and Turner[6]. The method, soil thin-layer chromatography (TLC), is performed by first spreading a 500-750 μm layer of soil-water slurry onto a glass plate. After drying, a spot of ^{14}C pesticide solution is applied to the soil layer. The plate is then vertically immersed in water or aqueous solution below the spot and as the water migrates upward the spot will tend to be leached in the same direction. The displacement of the pesticide is then measured by auto-radiography after the wetting front stops. This displacement divided by the distance of water movement is designated Rf.

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The mobilities of 82 pesticides were classified into 5 mobility categories based on their Rf values[7]. The "average" soil used for 40 of these was a silty clay loam of 2.50% organic matter, 39.5% clay and with a pH of 6.8 and CEC of 14.7 meg/100g[8,9]. Parathion and all the organochlorine insecticides evaluated were in the lowest mobility class (Rf = 0-0.09). Within this category the relative mobilities in decreasing order were estimated as Lindane > Parathion > Isodrin > Dieldrin > Heptachlor > Endrin > Aldrin > Chlordane > DDT[7].

Of the four soil properties, organic matter content was found to have the greatest contribution to pesticide adsorption with clay content having a lesser, but still important, influence[2]. The soil pH and cation exchange capacity made the least contribution. An inverse relationship was found to exist between adsorption and solubility. This holds for compounds within the same chemical family, i.e., with the same functional groups. Also within a family of compounds a direct relationship was observed between solubility and migration in soil. Attenuation was found to increase in soils of low moisture content. This was said to be due to the following: (a) as the amount of water decreases the compound appears to be adsorbed but in fact precipitates out of the soil solution or (b) the competition for adsorption sites is lessened with moisture content decrease. In another review the inverse relationship between water solubility and adsorption of pesticides was also stated and adsorption was said to be influenced most by the soil organic matter[10].

The adsorption of many pesticides by soil have been described in terms of the Freundlich isotherm[11]. This, the simplest and most empirical of isotherms is described by the following equation:

$$S = KC^{1/N}$$

where S = amount of species adsorbed per unit amount of substrate

C = equilibrium concentration of species in solution

K and 1/N are constants for a specific soil-solution system

Those systems exhibiting a high degree of adsorption will have $1/N > 1$ while those with a low extent of adsorption will have $1/N < 1$. Adsorption is said to be non-linear in both these cases. Most systems are assumed to exhibit linear adsorption ($1/N \approx 1$) which results in K being a partition coefficient ($K = S/C$).

The relationship between "persistence" of a pesticide and its adsorption in soil was differentiated[12]. The soil used in this study, a silt loam, had an organic matter content of 4.2% and a moisture capacity that was maintained at 20%. The persistent compounds dieldrin and DDT were removed in greater amounts by organic solvent extraction and, therefore, were less tightly bound to the soil than the nonpersistent methyl parathion. Parathion's persistence and binding strength was intermediate between methyl parathion and the two organochlorines. Conclusions drawn by the investigators relate the persistence of a compound to chemical stability rather than to its strength of adsorption.

The resistence of pesticides to leaching by water in a loam soil of similar organic matter content to the silt loam was found in the decreasing order aldrin > dieldrin > parathion[13]. The leachability of

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these pesticides in a soil column was not enhanced even after attempted desorption by the addition of anionic surfactants.

2. Organochlorine Insecticides. Principally as a result of their high resistance to degradation the chlorinated hydrocarbons and cydodiene compounds pose an environmental hazard. Most organochlorines, in both soil columns and field plots, remain near the depth of the soil to which applied. The downward mobility of these pesticides in soil occurs only to a slight extent mainly because of their extremely low water solubility.

The persistence of these compounds has been well documented and it is known that they are readily adsorbed and retained by soil and sediment alike. Volatilization is a more significant mechanism for transport in soil than leaching even though the vapor pressures are low. In many instances, soil cultivation has greatly reduced the retention of these pesticides.

In a comprehensive work on the leaching behavior of 11 insecticides[14], eight different soils were used as adsorbents in chromatographic columns. The organochlorines studied were lindane, heptachlor, DDT (p,p´ isomer), aldrin, endrin, heptachlor epoxide and dieldrin. Of these, only endrin formed degradation products during the experiment. Lindane appeared in the column effluent in highest concentrations whereas DDT was not leached from any of the soils. Migration was greatest in the soil with lowest clay content. Nothing passed through the soils above 6% in organic matter except for traces of lindane. The effect of clay on soil permeability was seen when the elution rate varied by 2 orders of magnitude as clay content ranged from 2 to 37%.

A water emulsion mixture of aldrin, dieldrin and heptachlor was
applied to 7 different soils packed in columns to test for initial
migration[15]. Each soil column was arranged in layers of varying
moisture content. The penetration of all 3 pesticides was similar for
any one soil and usually, but not always, increased as soil moisture
increased. Retention was greatest in soils with high clay content and
least for the sandy soils. Migration of the pesticides increased when
more dilute formulations in greater volumes were added to the columns.

The adsorption of lindane and dieldrin on silica were compared
using both "standard" and aquifer sands with the standard sands being
free of organic matter[16]. Both pesticides obeyed the Freundlich relation.
Dieldrin was seen to adsorb to a much greater degree than lindane and the
aquifer sands adsorbed more of both pesticides. When natural lake water
(containing dissolved organic matter) instead of distilled water was
used as solvent, the adsorption of dieldrin on the aquifer sand decreased.
Dieldrin was desorbed from the standard sand in greater amounts over the
natural sand and distilled water desorbed more pesticide than the lake
water. Lindane desorbed to a much greater extent than dieldrin. These
findings were explained as the due to effect of dieldrin's epoxide ring
causing it to bond more strongly to the silica and organic matter. Also,
when other dissolved organics are present in the water, competition for
retention sites increases with the result that adsorption is lowered.

Other batch studies examined the adsorption and desorption of dieldrin,
heptachlor and DDT using 3 clay substrates[17]. The effects of pH, salt
concentration, temperature and other soluble organics (glucose, alanine
and stearic acid) were evaluated. The first three parameters had slight

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and uncertain influence on the adsorptive behavior of dieldrin. The presence of other organics showed no effect; for instance, glucose alone did not influence heptachlor or DDT uptake by montmorillonite. Desorption of heptachlor and DDT from montmorillonite was not observed under any condition.

For the adsorption of DDT, heptachlor and dieldrin on montmorillonite, illite and kaolinite, values of the exponent 1/N obtained from plots of the Freundlich isotherm are reproduced in Table 3[18]. The 1/N values seem unreasonably high in some cases but all indicate the great extent to which these compounds are adsorbed. For adsorption on illite and kaolinite, equilibrium was rapidly achieved whereas adsorption on montmorillonite was slower due to the time required for molecular diffusion into the interlamellar spaces. The extent of adsorption was found to be ordered as DDT > heptachlor > dieldrin. The interraction for DDT and heptachlor was primarily hydrogen bond formation while for dieldrin bonding between the epoxide ring and the clay surface occurred. The specific surface area and CEC of the clays did not correlate with adsorptive capacity in these cases. Little desorption of the pesticides from the clay was evident.

In a field study on DDT persistence, the technical grade pesticide (containing both p,p´ and o,p´ isomers) was cultivated into the top 15 cm of a sandy loam soil[19]. Fifteen years following the application over half of the DDT remained. A small amount was leached below 20 cm and only a trace was found beneath 30 cm. Degradation to p,p´-DDD and o,p´-DDE occurred to a slight extent.

The fate of dieldrin in the field was investigated by applying it to 4 different soils of varying slope near the shoreline of ponds[20]. The compound was in the form of an emulsifiable concentrate with the total dose being 10-20 times that used in agriculture. Little of the dieldrin migrated down into the soil and a small amount entered the ponds via surface runoff and quickly accumulated in the bottom sediment. A follow-up study using soil columns and inclined soil troughs to which dieldrin had been applied confirmed the slight extent of its leaching[21].

Endrin was applied to the silty clay loam of sugar canefields on level terrain[22]. The formulation was 2% endrin on particles of montmorillonite. The compound was detected in the groundwater for 3 months following application. The existence of cracks in the soil profile, through which soil particles containing adsorbed endrin could travel down, was given as the means of transport.

3. <u>Organophosphorous Insecticides</u>. The organophosphorous compounds have been observed by most investigators to be more leachable and migrate farther in soil than the organochlorine pesticides. This is due chiefly to the higher water solubilities of the organophosphorous group. However, the enhanced leaching is short term because of the higher degradation rate as compared to the organochlorines. Parathion and methyl parathion, the two most widely used organophosphorous pesticides, have relatively short half lives with their degradation occurring by microbial action and hydrolysis[5] .

The adsorption of parathion on soil followed the Freundlich isotherm and, unlike the organochlorines, was found to be linear with equilibrium concentration[23]. It was suggested that parathion was partitioned directly into the organic matter of the soil as a liquid phase. The compound was readily leached from a soil column with ethanol but required 6 pore volumes of water before the concentration in the column effluent reached a maximum.

Parathion adsorption was also dependent on the specific type of organic matter in soil[24]. The extent of adsorption could not be correlated to merely the total organic content itself because the organic constituents of each soil exhibited different adsorptive capacities.

In a comparison study of adsorption and leaching behavior, 6 organophosphorous pesticides (including parathion and methyl parathion) were investigated on four soils of similar organic content[25]. Parathion adsorption isotherms were measured on all soils and obeyed the Freundlich relation. The soil:water distribution ratios increased from 8:1 to 30:1 as clay content increased from 5 to 37%.

The pesticides were applied in normal agricultural doses to the soil columns followed by leaching with distilled water. Parathion displayed the greatest percent recovery as a result of its greater chemical stability. Although methyl parathion is more soluble, its leaching was less than parathion because methyl parathion was found to be the least chemically stable with a half life of only one week whereas that of parathion was calculated as being 1-2 months. Microbial degradation rather than hydrolysis was given as the chief means of decay.

4. <u>DIMP, DCPD and DBCP</u>. The Aerojet report[3] investigates the environmental fate of diisopropylmethylphosphonate (DIMP) and dicyclopentadiene (DCPD), two key contaminants of Rocky Mountain Arsenal. Plant toxicity, volatilization and soil studies were performed on DIMP. Analytical difficulties prevented an investigation of DCPD migration in soil.

Lysimeters were packed to a depth of 60 inches with 5 different field soils to observe DIMP migration. Each soil was extracted to a depth of 5 feet, in 1 foot increments, and added to the lysimeter. The soil texture ranged from a clay to a sandy loam with organic matter content varying between 0.9 and 4.1%. Table 4 includes these properties.

The soils were presaturated with water and treated with aqueous DIMP solution in two ways:

1. The solution was added directly to the top of the column, at one and two week intervals, and allowed to percolate downward. This was carried on for over 60 weeks.

2. The top 1 foot layer of soil was mixed with the DIMP solution in a batch process and put back onto the column. The soil column was then irrigated, at one and two week intervals, with distilled water for a period of 45 weeks.

The authors refer to these experiments as group I or group II depending on which of the above methods was used. Generally the group II experiments more closely relate to leaching situations in the field. Of importance is that migration of DIMP was different for the two methods of treatment.

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In the group II studies the contaminant was leached from a dry soil into a water saturated soil whereas using the first method, the DIMP was in saturated soil throughout the column.

Soil water, soil core samples and column effluent were analyzed for DIMP levels. In group I, the highest levels of soil contamination were found at the surface at the conclusion of the experiment. The soil water showed a more even distribution and higher concentration which indicates the preference of DIMP for the solution over the soil phase.

The percent recoveries of DIMP added to the column were calculated in the study and are included in Table 4. The retention of DIMP decreases in approximately the same order as organic matter for the group I results. However, the amount of DIMP in the effluent decreases as the clay content decreases. Total recovery of DIMP from each soil accounts for less than 70% of the amount initially added. The remainder is presumably in the soil solution since loss of DIMP by volatilization was found insignificant.

In group II, DIMP was completely absent in the soil water of the upper 1 foot layer of all soils after 45 weeks of irrigation. Also the distribution of contaminant was much narrower with the depth of maximum DIMP concentration ordered as shown in Table 4.

In the Brawley, Walnut and Ventura soils the DIMP contained in soil water was distributed in the mid-section with none in the top or bottom layers. In contrast, for the Chino and Fullerton soils all soil water in the lower layers contained DIMP.

The order of DIMP recovery in the soil of group II results could not be correlated with either clay or organic matter content. Curiously, no DIMP was said to be recovered in the column effluent. This is difficult to rationalize, first, because DIMP penetration to the bottom of the soil column was evident and, second, because DIMP retention in the soil was always less than half the amount originally added.

The volatility of both DIMP and DCPD on the Fullerton sandy loam soil was determined by the application of radioactive ^{14}C tracers of these two compounds to the wet and dry sandy loam. Following exposure to a stream of air for several hours, the residual radioactivity in the soil was compared to that originally present. In general, volatilization was not seen as a significant factor in loss of DIMP and DCPD from the soil. The loss through volatilization from the wet sandy loam was only 22% for DIMP and 38% for DCPD after 154 hours of airflow. From the dry soil losses for both compounds were under 5% in all but one case after 200 hours of exposure to the air stream.

The nematicide 1,2-dibromo, 3-chloropropane (DBCP), also known under the trade names Nemagon and Fumazone, was able to be leached from the surface of sandy soils low in organic matter[26,27]. The concentration-depth profile resulting when a concentrated dose was leached with water approximated a normal distribution curve[26]. Depth of penetration was found to be slightly less than half the distance which the water migrated. Adsorption of DBCP occurred to a greater extent by the soil's organic matter rather than the clay and the mobility of the compound in the same soil increased as the initial moisture content of the soil was raised[27].

B. Inorganics.

1. General. The two most common types of inorganic contaminants
in soil are the heavy metals and soluble salts. The first group is
usually defined by the literature as those elements in the periodic
table, classified as metals or transition elements, which have a specific
gravity in excess of 5.0[28]. These are composed of both the cationic and
anionic heavy metals which ionize in aqueous media. The soluble salts
are products of inorganic acids and bases which readily dissolve into
mono- and divalent ions in water.

Most of the inorganics have a greater mobility in soil than the
pesticides previously discussed, a result of the higher solubility of
the former. The soluble salts are least attenuated whereas heavy metal
attenuation is more dependent on soil conditions, especially pH and
texture. Unlike the pesticides, the major attenuation mechanisms for
the inorganics are precipitation, adsorption via ion exchange and dis-
solution into the soil water. The soil organic matter is much less
significant.

Heavy metals and salts are common in most industrial and municipal
wastes. Several migration studies utilize actual sewage effluent and
landfill leachate for this reason. The experiments usually are performed
under anoxic, reducing conditions to duplicate the environment found at
the bottom of landfills.

Both batch and soil column techniques are used to investigate the
behavior of inorganics in soil. The concentrations are monitored by

atomic absorption spectroscopy. In soil column studies, a common practice to monitor the effluent is to plot the component "breakthrough" curves, i.e., the ratio of effluent to influent concentration plotted against the number of pore volumes of liquid passed through the column. The break-through point occurs when there is no further attenuation of the component by the soil (the effluent/influent concentration ratio is unity). Soil column experiments provide information to compare the mobilities of different contaminants under a given set of conditions. Other comparisons address the attenuating ability of different soils for any one contaminant. These relative measurements are more valid when disturbed soil samples are used because the soil is more uniform in structure compared to the undisturbed field soil.

Batch studies are used to obtain adsorption isotherm data using a procedure similar to that for organics. The Langmuir relation has been used extensively to study adsorption of ions from solution by clay minerals and is given in the linear form as:

$$C/S = \frac{1}{K'S_{max}} + \frac{C}{S_{max}}$$

where K' is a constant related to the energy of adsorption and temperature, S_{max} is the maximum extent of adsorption, and C and S are as described previously.

This expression assumes that (a) the energy of adsorption is uniform over the entire surface, (b) the adsorbed species do not interact with one another and (c) adsorption is independent of surface coverage.

At the extremes in concentration the Langmuir relation reduces to

$$S = S_{max} \text{ at high concentrations}$$

and $S \simeq K'S_{max} C$ for low concentrations. The latter equation is analogous to the linear Freundlich equation where $K'S_{max}$ becomes the partition coefficient.

2. <u>Heavy Metals</u>. Small amounts of heavy metals are naturally present in soil and for this reason they are often called "trace elements". Additional quantities of these can accumulate in the soil from waste disposal. The conditions under which attenuation of the metals occur can be found by examining their solution chemistry. The chemical species that exist in aqueous media are dependent on the solute concentration and solution pH. Hydrolysis of the cationic heavy metals (beryllium, cadmium, copper, chromium (III), iron, lead, mercury and zinc) occurs as pH increases until the hydrolyzed metal precipitates. In addition to the hydrolysis products, carbonate and sulfide precipitates of the cationic metals are common. Once attenuated, the cationic heavy metals can be released from soil if acid wastes are added to lower the soil pH enough to dissolve any precipitate or displace the metal ions from the clay minerals. Also, once the soils ion exchange capacity is reached no further retention can occur except by precipitation. The anionic heavy metals (arsenic, chromium (VI) and selenium) do not hydrolyze under the conditions found in soils. The predominant chemical species in solution determines whether attenuation will occur, and if so, whether by ion exchange or precipitation.

A comprehensive review by Fuller covers information through 1974 on migration in soil of arsenic, beryllium, cadmium, chromium, copper, iron, lead, mercury, selenium and zinc[28]. Important soil properties affecting retention were found to be texture, clay content, metal hydrous oxide content and pH. The colloidal hydrous oxides of iron, manganese and aluminum were more important than clay in retaining the heavy metals. Organic matter in the soil was a less important property and attenuated the metals by ion exchange. Migration of the heavy metals was found greater under anaerobic conditions as the presence of oxygen favored attenuation. Under anaerobic conditions CO_2 is normally present forming carbonic acid and HCO_3^- ion which tends to solubilize the metals. Methane produced by landfills had little effect on mobility. The soluble organic acids are able to form chelates with the metals by means of their carboxyl and hydroxyl functional groups resulting in enhanced migration.

The most significant work found to date on heavy metal behavior in soils was performed by the University of Arizona and the Illinois State Geological Survey. The results of these studies have been extensively reported[28-33].

In the Arizona project 11 soils from 7 major soil orders were removed from below the A horizon for a study on the attenuation of municipal leachate components under CO_2 atmosphere[28-30]. The soils ranged in texture from a clay to a sand and their pH varied from 4.2 to 7.8. The major clays represented by the soils were montmorillonite, vermiculite, kaolinite, chlorite and mica.

Overall, the chromium (VI) and mercury were least attenuated whereas lead and copper were retained most. The mobilities of arsenic, beryllium, cadmium, selenium and zinc were more sensitive to environmental conditions.

The attenuating ability of the soils increased with increasing clay and metal hydroxide content. For the heavy metals examined mercury was the only trace element whose mobility was influenced by the soil organic matter.

A follow-up study determined the relative binding strengths of the different heavy metals to the 11 soils[31]. The soil samples were contacted with water and 0.1 N HCl solution in an effort to remove the attenuated metals. Acid extraction usually achieved above 50% removal whereas water removed less than 3% of the heavy metals in most cases. The anionic elements were desorbed to a much greater degree than the others and the ease of extraction by water was in the following order:

Se > As > Cr > Zn > Cd > Hg > Cu > Pb

a. Cationic Heavy Metals. The Illinois study investigated the effectiveness of clay minerals for use as landfill liners to control contaminant migration. Commercially available montmorillonite, illite and kaolinite were mixed with quartz sand in varying amounts and made into soil columns[29,32,33]. Landfill leachate containing the trace elements cadmium, lead, mercury and zinc under argon atmosphere was used. Both natural and sterilized leachate of pH 6.9 and 7.2, respectively, was passed through the columns to observe microbial effects. The column breakthrough curves for each trace metal were plotted and the attenuation

by the sand-clay mixtures expressed as an "attenuation number" (ATN), defined as the percent difference between the area under the breakthrough curve and the total area of the graph. Retention by the soil increases with increasing attenuation number. The order of attenuating ability for the clays was found to be: montmorillonite>illite>kaolinite[32].

Lead, zinc, cadmium and mercury were highly attenuated (ATN between 95-100%) with little difference between the clay minerals (high CEC) and sand (no cation exchange capacity). High accumulations of lead and zinc were seen in the upper centimeters of the columns. Further, no lead and only trace amounts of the other metals were eluted from the pure sand. column. This indicates that precipitation rather than ion exchange is responsible for the retention. Attenuation from the natural and sterile leachate was similar.

The attenuation numbers for the elements calcium, manganese and boron were negative meaning that higher concentrations were observed in the column effluent than in the original leachate. Calcium displayed the largest negative ATN. Concentrations of calcium in the effluent were greatest for the montmorillonite columns and increased with increasing percentages of this clay. This indicates that ion exchange is occurring because Ca^{2+} is a common charge neutralizing cation found on clay minerals which can be displaced by other cationic species. The leaching of calcium from underlying soils, referred to as the "hardness halo," corresponds to the migration of landfill leachates[34].

The adsorption of the trace elements by kaolinite and montmorillonite was investigated[35,36]. Heavy metals were dissolved in deionized water and landfill leachate and, in addition, a 0.1M NaCl solution was used as solvent medium. The pH of all 3 media was independently varied. Total removal (by precipitation and ion exchange) of the trace elements from solution was plotted versus pH.

The total amount of copper, cadmium, chromium (III), lead and zinc removed from solution increased with pH, rising dramatically as precipitate was formed. With mercury, total removal steadily increased with pH. The removal of these metals was reduced in 0.1M NaCl and further suppressed in leachate. The increase in adsorption as the pH is raised, before onset of precipitation, is due to the reduction in H_3O^+ ion which competes for adsorption sites. An increase in the ionic strength of the media suppressed adsorption due to competition from Na^+ ion in the 0.1M NaCl solution and from divalent cations in the leachates.

The adsorption isotherms for any one set of conditions were plotted using data from the total removal vs pH curves. The Langmuir relation was then applied to these isotherms.

The S_{max} values for lead were found to match closely the cation exchange capacity for both montmorillonite and kaolinite. This is proof of Pb^{2+} attenuation by cation exchange.

Copper, zinc and cadmium formed precipitates between pH 4 and 6 with copper precipitating at the lowest pH. Unlike zinc and cadmium, the total attenuation of copper reached a maximum at pH 7 and then decreased

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as the pH was raised further, a behavior reportedly caused by $Cu(OH)_2$ redissolving in basic media. The S_{max} of copper, zinc and cadmium was found proportional to the cation exchange capacity of the clays.

The +3 valence state of chromium is a cationic heavy metal which forms an amorphous hydrous oxide precipitate at pH 5. Between pH 1.5 and 4, a variety of hydrolyzed chromium (III) ions undergo cation exchange.

Mercury is converted into mono- and dimethyl mercury by anaerobic microbes. After conversion, the extent of mercury adsorption by soil is diminished[37]. Unlike the other cationic heavy metals, volatilization of mercury was found significant in its total removal from solution[35,36]. The adsorption by montmorillonite was 5 times that by kaolinite which corresponds to the ratio of their cation exchange capacities, indicating adsorption by ion exchange. At pH 6, precipitation becomes the main attenuating mechanism. Also the soil organic matter plays an important role in mercury attenuation.

b. <u>Anionic Heavy Metals</u>. The anionic heavy metals arsenic, chromium (VI) and selenium did not precipitate and their adsorption by the clay minerals decreased as the pH was raised. This is the result of increased competition for anion exchange sites from the OH^- ions at higher pH. In contrast to the cationic metals, adsorption of chromium (VI) was greater from the leachate than deionized water.

Total removal of Cr (VI) ion from leachate was explained by anion exchange which decreased sharply as the pH increased until no adsorption occurred at pH 8.5 The monovalent $HC_rO_4^-$ species was reported as the

principal ion adsorbed since the divalent CrO_4^{2-}, which predominates above pH 8.5, is repelled by the negative charge of the clay. The S_{max} values, calculated from the Langmuir isotherms, were much lower than those for the cationic Cr (III) adsorption.

Both stable valence states of arsenic, the +3 and +5, form anions in aqueous solution. As with Cr (VI) the adsorption of arsenic by anion exchange occurs via the monovalent anion. $H_2AsO_4^-$ is the key adsorbate for As (V) while As $(OH)_4^-$ is the key anion for As (III). The uptake of $H_2AsO_4^-$ was greater than As $(OH)_4^-$ and montmorillonite again adsorbed more than kaolinite. The divalent anions were repelled by the clays as in the case of CrO_4^{2-}.

Selenium exists in the +4 valence state and is one of the most mobile of the heavy metals in soil. Adsorption of Se (IV) reaches a maximum at pH 2 and then steadily declines with increasing pH. Anion exchange of $HSeO_3^-$ occurred to a lesser degree than $H_2AsO_4^-$ because of differences in their molecular structures.

3. <u>Soluble Salts</u>: The soluble salts dissolve into chloride, potassium, ammonium, sulfate, fluoride, etc. ions when in aqueous media. These are the most mobile of the soil contaminants, especially in high rainfall regions. Attenuation is normally restricted to ion exchange and dilution. Precipitation seldom occurs except in arid regions.

In the Illinois soil column study, the attenuation of K^+, NH_4^+ and Mg^{+2} from the leachate was moderate compared to the heavy metals[29,32,33]. The Na^+ and Cl^- ions were only slightly attenuated. Montmorillonite

columns gave the highest attenuation which increased further as the content of this clay was increased. Thus, cation exchange occurs as with the heavy metals. There was no difference in Cl^- ion attenuation between the clays. The attenuation of Cl^- is chiefly by dilution in the soil water with a slight degree of anion exchange. Chloride, as mentioned earlier, is commonly used as a "tracer" because it is a solute known to be least adsorbed by a soil and migrates with the soil water.

Ten different soils packed in columns were subjected to a leachate containing NH_4^+, K^+, Na^+, Mn^{2+}, Ca^{2+}, Mg^{2+} and Zn^{2+}[38]. As expected, removal of these cations from the leachate was greater by soils with higher cation exchange capacity. The concentration of Ca^{2+} and Mg^{2+} increased in the leachate, as in the case of the cationic heavy metals, indicating cation exchange. Later, deionized water was passed through the columns to affect component release. Almost no desorption of Mn^{2+} and Zn^{2+} was seen. Release of K^+ and NH_4^+ was slight while that of Na^+ was substantial.

In another study where two different soils were used as absorbents, similar breakthrough curves of Na^+, K^+ and Cl^- were in evidence[39]. Since the cation exchange capacities of both soils were low (5 meg/100 g) attenuation was reasoned to be solely the result of dilution.

Sewage effluent containing Na^+, K^+, Cl^-, Mg^{2+}, SO_4^{2-} and Ca^{2+} was put through columns of the A, B, and C horizons of a loamy sand and the A horizon of a clay[40]. The breakthrough of Cl^- and SO_4^{2-} occurred earliest followed by Na^+ after passage of 3 pore volumes. The clay retained slightly more of the ions than the loamy sand. The concentrations of

Ca^{2+} and Mg^{2+} in the sewage effluent increased slightly as the liquid was first passed through the column, indicating some cation exchange.

IV. MATHEMATICAL MODELLING OF LEACHATE TRANSPORT.

A. General.

The transport of leached chemicals through soil under intermittent water flow conditions can be described by a combination of piston displacement and hydrodynamic dispersion[41]. Movement occurs chiefly through mass transfer by the flowing water with molecular diffusion of the solute having only a limited role. Adsorption onto soil components, as stated before, will retard solute displacement. Those dissolved materials which adsorb onto soil are termed "reactive" solutes whereas those which do not are "non-reactive." Adsorption is usually assumed to be completely reversible for calculation purposes.

One-dimensional movement of solute with steady-state flow is commonly expressed as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2} - Vm \frac{\partial C}{\partial X} - \frac{\rho}{\Theta} \frac{\partial S}{\partial t} \qquad [1]$$

where X is the linear distance along the axis of flow, D is the dispersion coefficient of the system, Vm is the mean velocity of the water in the soil pores and t is the time. The soil moisture content, Θ, is defined as the volume of water per unit volume of soil and ρ is the bulk soil density. The parameters C and S are as defined in Section III.A.1. The first term on the right hand side of equation [1] represents dispersion while the second is the mass displacement term and the third, the sink or adsorption term.

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The above expression is difficult to apply in field cases partly because of the dependencies of D, Vm and θ on other variables. The dispersion coefficient, D, is a function of the mean pore water velocity and will reduce to the molecular diffusion coefficient when Vm approaches zero[42]. The mean pore water velocity can be expressed as:

$$Vm = J/\theta \qquad [2]$$

where $J = -K(\theta) \, dH/dX$

The numerator, J, is the Darcy flux, $K(\theta)$ is the hydraulic conductivity of the soil and H is the total hydraulic head. The soil moisture content, θ, is dependent on depth in the soil's zone of aeration and generally increases as the zone of saturation is approached. Often, empirical relations describing D, Vm and θ under a specific set of conditions are used in performing calculations. Equation [1] also assumes the solute is non-degradable and migrates in a homogeneous soil. For the above reasons, equation [1] is presented only to reveal the variety of factors involved in predicting leachate transport accurately.

The sink term can be expressed in an analytical form by assuming the leachate adsorbs according to the Freundlich equation, $S = KC^N$. A retardation term, R, is then derived[43]:

$$R = 1 + \frac{\rho K}{\theta} \quad \text{(linear adsorption)} \qquad [3a]$$

$$R = 1 + \frac{\rho KNC^{N-1}}{\theta} \quad \text{(non-linear adsorption)} \qquad [3b]$$

The term can then be substituted in equation [1] giving:

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2} - Vm \frac{\partial C}{\partial X} \qquad [4]$$

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As can be seen when comparing [3a] and [3b] the retardance is independent of concentration when linear Freundlich adsorption occurs and, for non-reactive solutes, the term is unity.

B. Hydrodynamic Dispersion.

When a single pulse of leachate is transported through a soil or other porous media by water the pulse will tend to disperse with increasing depth of penetration. Flow velocities in the various pores will be distributed as a normal or Gaussian density function about the mean value, V_m, as shown in Figure 3. This results in the normal concentration-depth profile given in Figure 4a where d is the depth of the maximum solute concentration, C_{max}. The standard deviation, σ, is arbitrarily defined as the half width of the pulse such that the area under the curve in Figure 4a between the limits $d-\sigma$ and $d+\sigma$ is approximately 68% of the total area.

Non-reactive solutes and those which adsorb according to the linear Freundlich isotherm have been shown to give normal concentration-depth profiles[23,41,43]. Solutes which exhibit non-linear Freundlich adsorption will have normal profiles if their initial concentrations are below 10 ppm[43]. The distribution will broaden (increasing the standard deviation) as the solute migrates downward (Figure 4b).

The normal density function was applied by Day to describe the concentration-depth profile in soils[44].

$$C(X) = \frac{C_o X_o}{(4\pi Dt)^{1/2}} \exp\left(-(X-d)^2/4Dt\right) \qquad [5]$$

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where Co is the initial concentration of leachate contained in a thin layer of topsoil the thickness of which is Xo. The standard deviation in equation [5] is $(2Dt)^{1/2}$. The above expression is presented in an alternate form as[41]:

$$C(X) = \frac{A\ U}{(4\pi DF\ d)^{1/2}}\ Exp\ (-(X-d)^2/4DFd) \qquad [6]$$

where $U = 10/(\theta + \rho K)$.

The constant A is the total amount of chemical per unit area in the soil and can be graphically represented as the area under the individual curves in Figure 4b. The parameter DF is the "dispersion distribution factor" and is related to the standard deviation by the following expression:

$$\sigma = (2\ DF\ d)^{1/2} \qquad [7]$$

The units of A are kg/ha; DF and d are both in cm while C(X) is in ppm. The factor U is required for units conversion. When X = d equation [6] reduces to:

$$C_{max} = \frac{A\ U}{(4\pi DFd)^{1/2}} \qquad [8]$$

A major weakness in applying the above expression lies in determining the value of DF.

C. Piston Displacement.

The displacement of C_{max} downward through the soil profile can be estimated by the piston-displacement model as described by Davidson, et.al.[45,46]:

$$\Delta d = \frac{1}{R} \cdot \frac{I}{\theta_{FC}} \qquad [9]$$

where $R = 1 + \frac{\rho K}{\theta_{FC}}$

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The parameter I represents the amount of water, in depth units, which enters the soil, θ_{FC} is the moisture content at field capacity (the maximum water content the soil will retain under natural conditions) and Δd is the displacement after the soil profile has drained to field capacity.

Water continually applied to the soil, allowing no drainage of the profile (i.e., flooding) will yield less displacement than if an equivalent amount of water was applied and the soil permitted to drain to field capacity. This is shown by the following expression[45,47]:

$$\frac{\Delta d}{\Delta d'} = 1 + \frac{\theta_f - \theta_{FC}}{\theta_{FC}} \quad , \quad \theta_f > \theta_{FC} \tag{10}$$

where $\Delta d'$ is the displacement when the soil remains at the wetting moisture content, θ_f, under continuous irrigation. This behavior has been observed in comparing the leaching of chloride by continuous and intermittent irrigation[42].

When infiltration of leachate into a dry soil (whose initial moisture content, θ_i, is zero) occurs the retardation term is equal to 1/Rf where Rf is the TLC parameter described in Section III.A.1. This can be seen by substituting θ_f for θ_{FC} in equation [9] and comparing the result to the following expression[45,47]:

$$\Delta d_f = \frac{I}{\theta_f - \theta_i} \tag{11}$$

where Δd_f is the displacement of the wetting or solvent front of the leachate.

The piston displacement model is valid if water in all the soil pores participates in the transport process and the water initially present is completely displaced ahead of any incoming water[47]. These assumptions were found to be correct for permeable soils if two conditions were satisfied, namely, any aggregates of soil particles present were less than 0.2 cm in diameter and the flow velocity of the water was below 4 cm/hr[47].

To account for depletion of water in the soil profile, such as by plant roots, the amount of water which effectively transports the solute, Ie, is given by[45]:

$$Ie = I - Id \qquad [12]$$

where $Id = \int_{o}^{d} (\theta_{FC} - \theta(X)) \, dX.$

The integral Id gives the amount of water needed to replenish the moisture deficit to field capacity before the solute can be moved. Use of Ie yields a modified form of equation [9]:

$$\Delta d = \frac{1}{R} \cdot \frac{Ie}{\theta_{FC}} \qquad [13]$$

This displacement model was successful in predicting movement of chloride through a field plot of fine sand with fully grown vegetation under natural rainfall conditions[45,47]. The difficulty in applying the model is in calculating Ie which varies with the soil depth.

D. Multilayered Soils.

In the case of a soil containing n distinct horizontal layers an average retardation term, $\overline{R}$, can be obtained by the weighted mean expression[48]:

$$\overline{R} = \frac{1}{L} \cdot \sum_{i=1}^{n} R_i L_i \qquad [14]$$

with R_i and L_i the retardation term and depth, respectively, of layer i and L the total depth of the soil profile. The term $\overline{R}$ cannot be used in cases of non-linear adsorption since it becomes dependent on solute concentration (see equation [3b]).

Soil column studies showed that the order in which the layers of soil were arranged in the profile did not influence the solute concentration in the column effluent[48]. The same results showed that the average water content of the unsaturated soil layers may be used in lieu of actual water content distribution for predicting the concentration distribution of both reactive and non-reactive solutes. Consequently, the expressions for hydrodynamic dispersion and piston displacement can also be applied to non-homogeneous or multilayered soils.

V. SUMMARY.

The extent of contaminant migration for a given rainfall rate is most dependent on the water solubility of the pollutant and the adsorptive capacity of the soil. The capability of a soil as adsorbent is determined by its clay, amorphous mineral and humified organic matter content in addition to pH. Vapor pressure and chemical stability are less important in determining mobility of most pollutants.

Humified organic matter content is the most important soil property in limiting mobility of pesticides with the clay content and type having less of an influence. Adsorption of the pesticides is mainly by hydrogen bonding to the clay and organic matter. Organochlorine insecticides are

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relatively stationary in soil due to their extremely low water solubility while the organophosphorous insecticides are able to be leached. The nematicide DBCP, the most soluble of the pesticides studied, was also the most leachable although soil organic matter adsorbed the compound to a moderate extent.

The soil pH and clay content have the most influence on mobility of heavy metals with organic matter being relatively unimportant. Cationic and anionic heavy metals exhibit different solubility and adsorptive behavior, the solubility of the former being highly sensitive to both the pH and ionic strength of the soil water. In neutral and alkaline soils the cationic heavy metals exist as immobile precipitates. Under acidic conditions these metals will ionize into solution and undergo some adsorption by clay minerals through ion exchange. This results in the release of calcium ion and other displaced cations from the clays. The anionic heavy metals are more soluble and mobile under most conditions. These trace elements will undergo less adsorption, via anion exchange, on the clay minerals with the monovalent anion being the species that adsorbs. Ion exchange from amorphous minerals in soil is not widely studied.

Mercury was unique among the heavy metals because its vapor pressure was sufficient to result in the element's loss from the soil by volatilization. Also, mercury was the only heavy metal whose mobility was greatly affected by the soil organic matter.

The soluble inorganic salts are the most mobile and are readily leached through soil. Attenuation is restricted to dilution and limited ion

exchange. Sodium and chloride ion underwent ion exchange only to a slight degree and otherwise migrated with the soil water.

The compound DIMP migrated appreciably through 5 different soils representing a wide range in texture.

Leachate migration can be estimated for both non-reactive solutes and those which undergo linear Freundlich adsorption. The penetration of leachate in a single or multilayered soil can be predicted using the piston displacement model, equation [13], if the following parameters are known:

    a. The amount of incoming water that transports the solute, Ie.

    b. The soil moisture content at field capacity, θ_{FC}.

    c. The partition coefficient of the solute, K.

    d. The bulk soil density, ρ.

Deeper penetration of solute occurs if the soil is allowed to drain to field capacity following water infiltration rather than if the same amount of water is applied by continuous irrigation.

If penetration is sufficiently deep to reach the water table, the maximum concentration of leachate flowing into the aquifer can be estimated using equation [8] with the following known parameters:

    a. The total amount of chemical initially present in the soil, A.

    b. The depth to the water table, d.

    c. The soil moisture content at field capacity, θ_{FC}.

    d. The partition coefficient, K.

    e. The bulk soil density, ρ.

    f. The dispersion factor of the distribution, DF.

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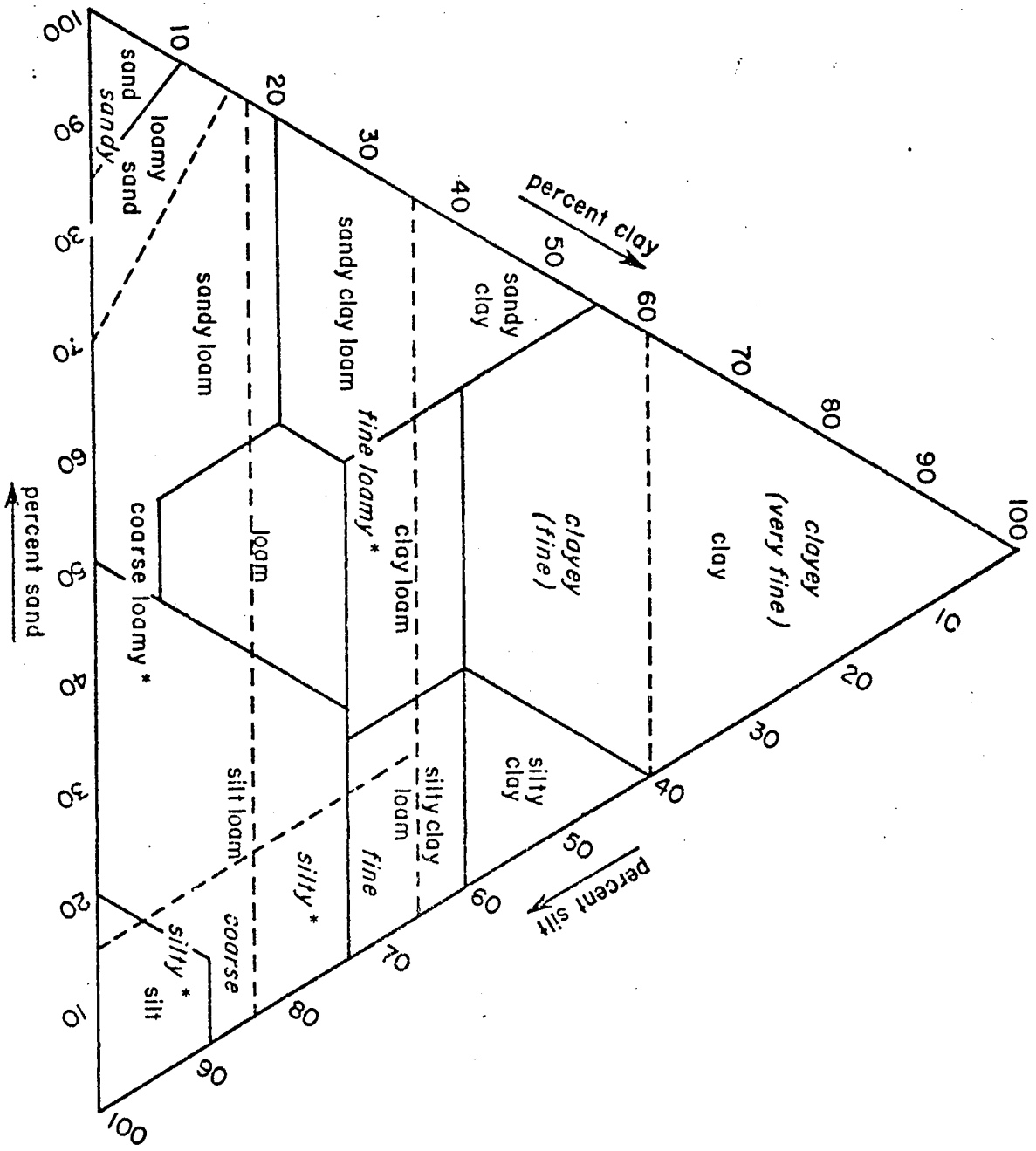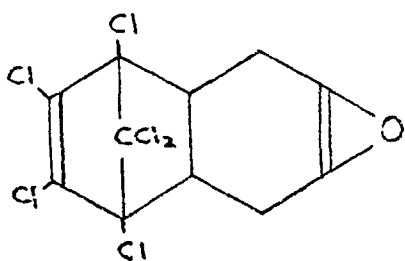
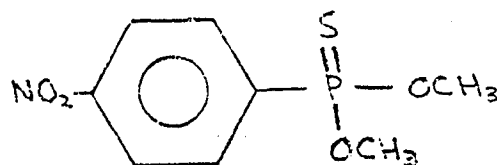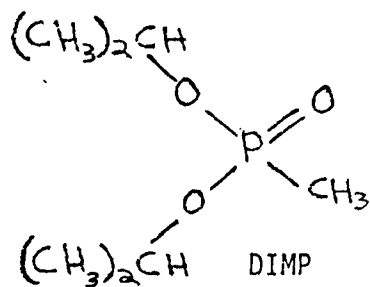FIGURE 1. Textural classification (USDA) of soil
[from reference 28]
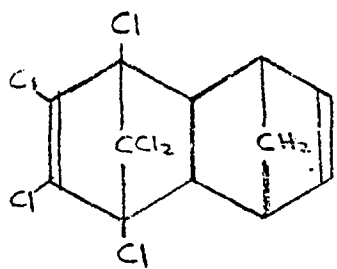
Aldrin
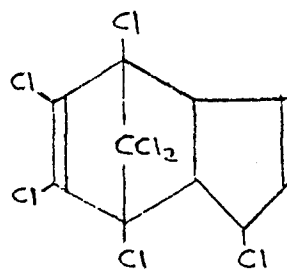
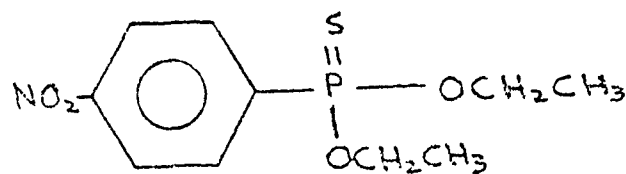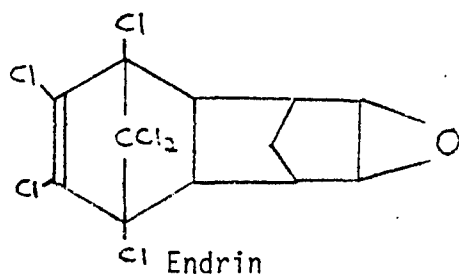Heptachlor
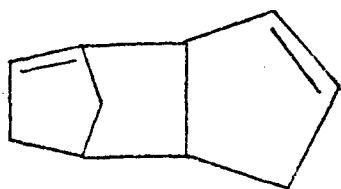
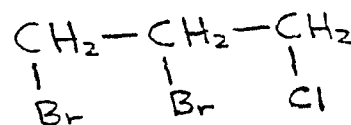DCPD
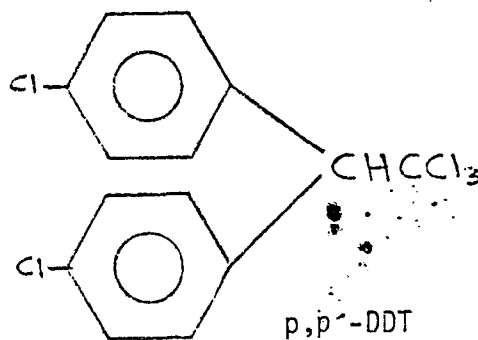
p,p'-DDT

Dieldrin

Methyl Parathion

DIMP

Parathion

Endrin

DBCP

FIGURE 2. Structural Formulas of Selected Organic Compounds

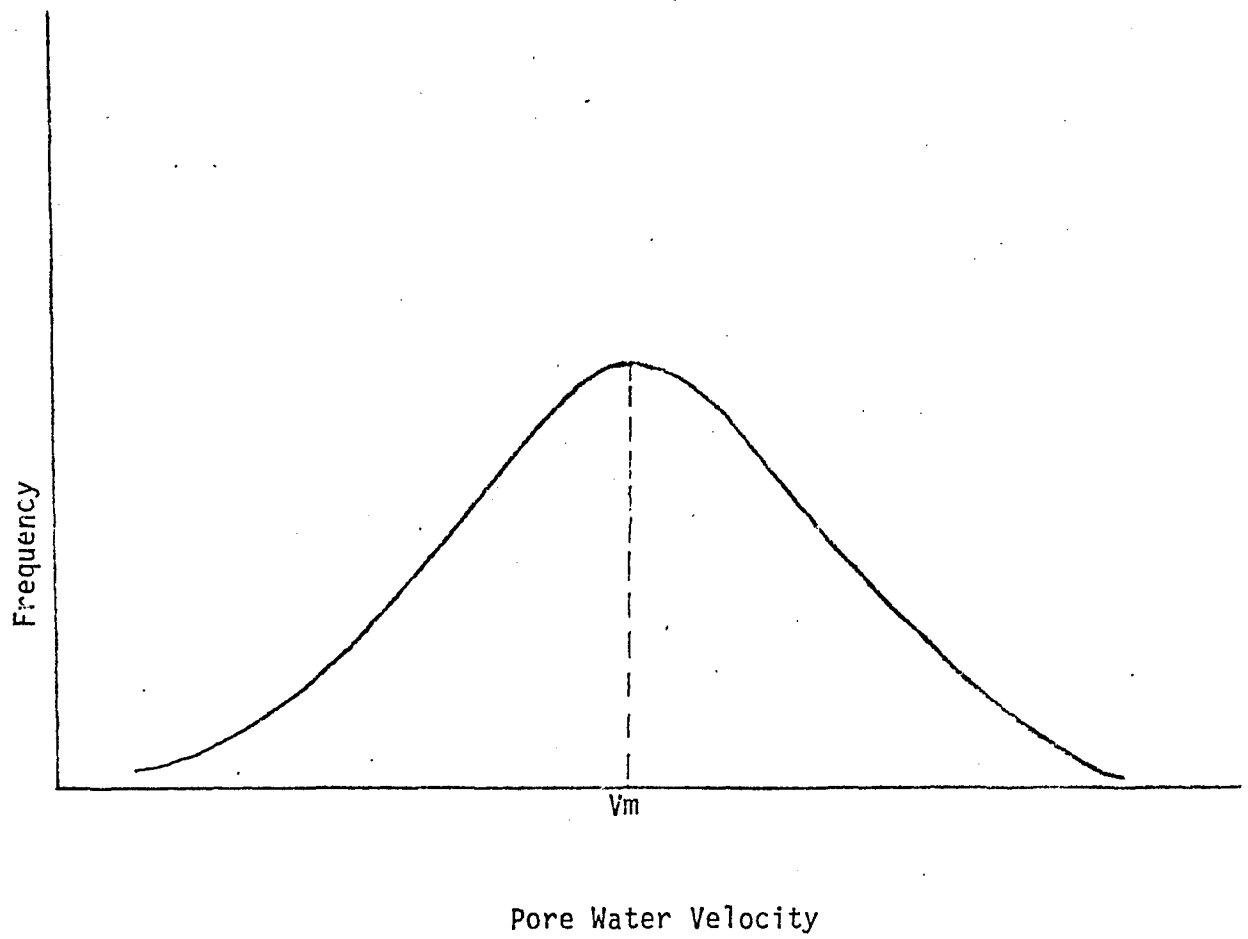FIGURE 3. Normal Distribution of Pore Water Velocities

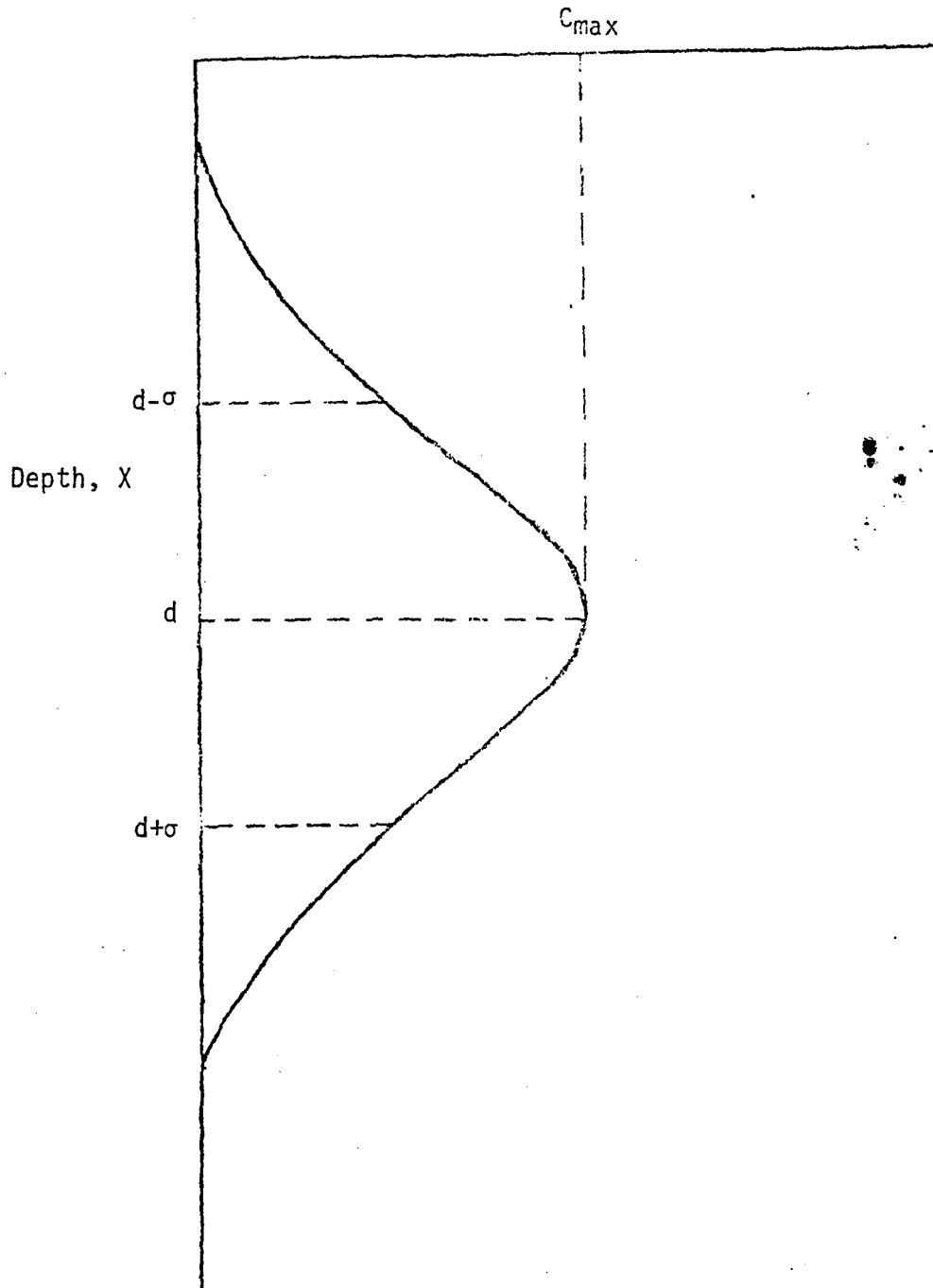Leachate Concentration, C

C_{max}

Depth, X

d-σ

d

d+σ

FIGURE 4a. Normal Concentration-Depth Profile

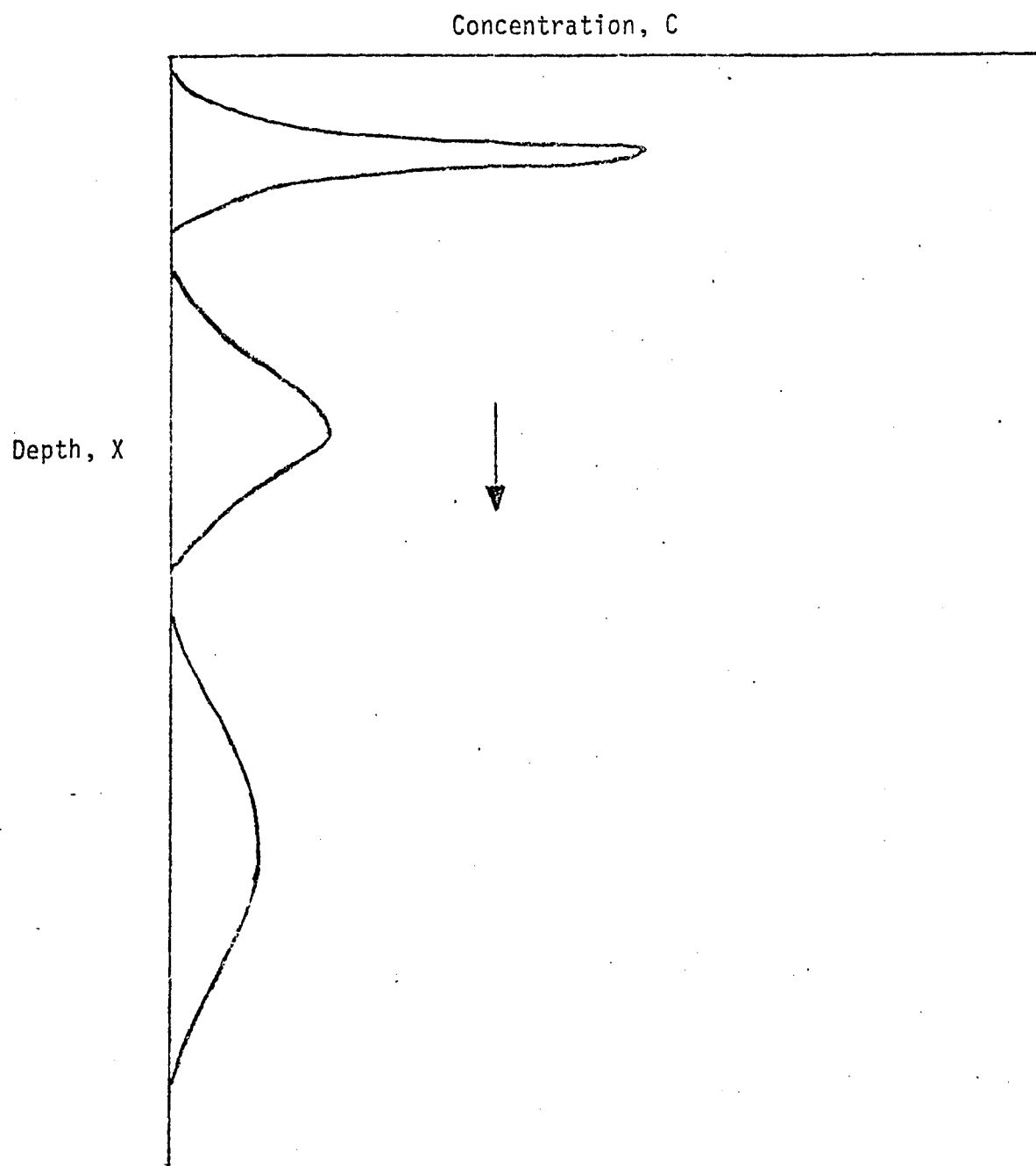Concentration, C

Depth, X

FIGURE 4b. Broadening of Normal Concentration-Depth Profile as
            Solute is Displaced Downward

TABLE 1

CATION EXCHANGE PROPERTIES OF COMMON SOIL COMPONENTS

Soil Component	Cation Exchange Capacity, meq/100 g	Specific Surface Area m²/g
Organic Matter	200-400	500-800
Montmorillonite	80-150	600-800
Illite	10-40	65-100
Kaolinite	3-5	7-30
Oxides and Hydroxides	2-6	100-800

[Data from reference 2]

TABLE 2. CHEMICAL AND PHYSICAL DATA OF SELECTED ORGANIC COMPOUNDS

Compound	m.p. (°C)	Vapor Pressure (mm Hg at 25°C)	Water Solubility (ppm at 25°C)	Half Life
Aldrin	104-104.5	$0.6 - 2.3 \times 10^{-5}$	0.01 - 0.03	>5 yr.
DCPD	33	2.2	Insoluble	6-12 mo.
DDT	108.5	1.9×10^{-7}	0.0012	>5 yr.
Dieldrin	175-6	1.8×10^{-7}	0.1 - 0.25	>5 yr.
DIMP	-	-	1,000 - 2,000	-
Endrin	235 (decomposes)	2×10^{-7}	0.1 - 0.23	>5 yr.
Heptachlor	95-6	3×10^{-4}	0.06 - 0.20	1-5 yr.
Lindane	-	9.4×10^{-6}	10	-
Methyl parathion	35-6	9.7×10^{-6}	50-60	<1 mo.
DBCP	5	0.8	≈1000	6-12 mo.
Parathion	0	3.8×10^{-5}	0.2 - 24	6-12 mo.

[Data from references 4-6]

TABLE 3

EXPERIMENTALLY DETERMINED EXPONENTS

FOR FREUNDLICH ADSORPTION ISOTHERM EQUATION

Pesticide - Clay System	1/N
DDT - Montmorillonite	5.97
DDT - Illite	3.28
DDT - Kaolinite	5.08
Heptachlor - Montmorillonite	3.52
Heptachlor - Illite	6.07
Heptachlor - Kaolinite	4.51
Dieldrin - Montmorillonite	9.24
Dieldrin - Illite	8.82
Dieldrin - Kaolinite	11.63

[Data from reference 18]

TABLE 4

RANKING OF SOILS USED IN DIMP MIGRATION STUDY
ACCORDING TO EXPERIMENTAL PARAMETERS

(VALUES GIVEN IN PARENTHESES)

Clay (%)	Organic Matter (%)	Location of Max DIMP Conc. (Group II) (inches depth)		DIMP Retention in Soil (%)		DIMP in Effluent (%)
		Soil	Soil Water	Group I	Group II	Group I
Brawley (59)	Walnut (4.1)	Fullerton (54-60)	Fullerton (60)	Walnut (32)	Brawley (46)	Brawley (32)
Walnut (34)	Chino (3.7)	Walnut (54-60)	Walnut (54)	Chino (30)	Ventura (42)	Walnut (27)
Ventura (28)	Fullerton (2.2)	Ventura (48-54)	Ventura (42)	Fullerton (27)	Fullerton (38)	Ventura (25)
Chino (25)	Ventura (1.9)	Chino (42-48)	Chino (30)	Brawley (21)	Chino (37)	Chino (37)
Fullerton (18)	Brawley (0.9)	Brawley (36-42)	Brawley (30)	Ventura (18)	Walnut (15)	Fullerton (9)

[Data from reference 4]