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CONCENTRATION OF PHENOLS IN WASTE WATERS
AND THEIR ADSORPTION BY SOILS

by

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SIGNED:

A handwritten signature in black ink, appearing to read "J. A. Fisher", is written over a horizontal line. The signature is cursive and somewhat stylized.

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ABSTRACT

The concentration of phenols in the soils environment and their fate was studied as a function of five different soil types, six different monohydroxyphenols, and three different municipal landfill leachates media. Concentrations of naturally occurring phenols were also followed for a period of one year in young and old leachates. Methods for analysis of phenols were reviewed for quantitative and qualitative analysis of phenols in landfill leachates.

To determine the adsorptive capabilities of the soils used in this study, the isotherm approach was used after the equilibration time of phenols in soils was determined to be five days. Concentrations of phenols varying from 5 ppm to 100 ppm were used to construct isotherm graphs. The soil-phenol isotherm curves conformed very well to the Freundlich equation, indicating multiple adsorption mechanisms and slow equilibration times in the soils-phenols reactions.

A statistical analysis of the isotherm data showed % free iron oxides to be the most important soil characteristic for the adsorption of phenols by all soils; followed by soil pH and % clay in order of significance. High

solubility and moderate polarity of phenols also were found to be favorable factors in the adsorption of phenols by soils. Naturally occurring phenols such as cresols disappeared faster from soil solutions than synthetic phenols.

The reactivities of phenols with MSW leachates increased with the age of the leachates. Very young leachates, having low pH and high TOC levels favored synthetic phenols over naturally occurring phenols to react with. All leachates studied demonstrated an ability to remove from solution one or more of the six phenols used in large quantities over a period of 15 days or less. The overall performance of the leachates used in this study seemed to be a function of the humic acid levels found in them.

Levels of naturally occurring phenols in leachates varied from several ppbs to more than 9000 ppbs for a year's period. The highest phenol levels were found in the young phenols and the lowest levels in the old phenols; indicating that pH and TOC concentration determine the amounts of phenols in solution.

In column studies of perfusion of leachates through 10 cm of soil materials packed at field densities, no soil was able to stop the migration of phenols for more than 5 to 10 pore volume displacements. Low pH and high TOC levels seemed to play a much larger role in the migration

of phenols through soils than the levels of phenols found in the leachates used.

The use of phenol enriched deionized water passed through soil columns showed the fact that there is a clear dependency of adsorption of phenol on the flow rate. Slow rates favored adsorption of phenol by all soils studied.

The TOC analysis of the effluents from the phenol enriched water-soil columns studies indicated that some mechanisms for the disappearance of phenol from soil solution may have been transformation reactions as well as adsorption reactions. Varying TOC levels with flux seemed to indicate that these reactions are much slower than the adsorption reactions.

The use of Cu^{+2} saturated soils in an attempt to correlate transformation reactions of phenol with transition metal catalytic properties failed to increase the adsorption and/or transformation of phenol in the soil media.

The 4-aminoantipyrine colorimetric method performed well in the analysis of phenols in air unstable leachates. Gas-liquid chromatography using $\text{NPGSB} + \text{H}_3\text{PO}_4$ on Anakrom A 90/100 mesh was used for the quantitative and qualitative analysis of phenols in leachates.

INTRODUCTION

Toxic Wastes

The production of larger amounts of wastes by modern society, is compelling man to study the effect of these residues in the natural environment. Liquid wastes, the byproduct of both natural and synthetic discards, contain both inorganic and organic materials. It is the organic phase of these wastes about which scientists know the least; especially its forms and interactions with the terrestrial environment.

Naturally occurring compounds, products of biodegradation of organic wastes can enter man's food chain when produced in large quantities. The effect aforementioned can also take place with synthetically produced chemicals, when not disposed of properly (Nemerow, 1978).

Increasing attention is being focused on the heterogeneity of the organic constituents of liquid wastes produced in solid waste disposal sites, whether municipal or industrial. Many inorganic compounds not only affect the migration of inorganics such as metals (Faust and Hunter, 1969) through the soil profile; but they themselves can migrate (Bolt and Bruggenwert, 1976) together or independently of other inorganic pollutants (Fuller, 1978).

Consequently, organics are also possible pollution sources of surface waters.

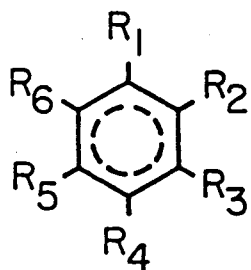
Liquid wastes found in sanitary landfills are called leachates. They are the result of decomposition and solubilization of unprocessed solid wastes (Bolt and Bruggenwert, 1976; and Chian and DeWalle, 1977). There is strong evidence that both the inorganic and organic phase of these liquid wastes, under anaerobic conditions, will be preserved for long periods of time; thus, enabling them to travel through the soil profile and underlying strata unchanged and possibly reach underground water sources (Fuller, 1978). Two types of organic compounds are present in municipal solid waste (MSW) leachates which are similar to the ones found in the soil medium. These are: (a) biochemicals which occur in living organisms; (b) complex polymers formed by secondary synthesis among the species of the first group (Mortvedt, Giordano, and Lindsay, 1972). In natural leachates, the early stages of decomposition and biodegradation are characterized by the solubilization of large amounts of organics belonging to the first groups such as organic acids (from acetic to paraffinilic and to aromatic acids). Phenolics, not necessarily acidic, also will be present. With further degradation some of these compounds become simple molecules such as CO_2 , CO , SH_2 , NO_3^- and others, and elemental as O_2 and N_2 (McLaren and Peterson, 1967). Other molecules polymerize and form complex

compounds of little known molecular composition such as compose the humic and fulvic acid fractions.

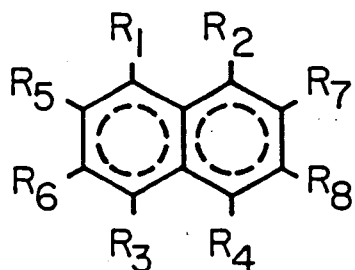
Phenolics

Of the organics which are produced during the decomposition of organic residues, phenolics are of particular interest. In general, the term "phenolics" applies to any aromatic which has a benzene ring or rings with at least one -OH group in any position in the ring or rings. Normally, if the ring contains other more acidic groups such as -CHO or -COOH, it takes the name of the aromatic, and it is no longer called a phenol but an aldehyde or an acid. Obviously the compound still has phenol characteristics. Even though, anthracene and naphthalene hydroxy derivatives qualify as phenols, they are usually, but not always, referred to as polyphenols. To define more precisely the use of the term "phenols" throughout this thesis, we shall refer to only hydroxy derivatives of benzene with other less acidic groups substituted in ortho, meta or para positions to the main -OH group (Fig. 1).

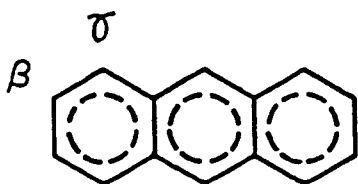
Phenols originate from the natural breakdown of organic tissues such as lignin as well as from biosynthesis during biological decomposition of organic residues (Finkle and Runeckles, 1967). The breakdown of coal and oil also produces large levels of phenols (Chian and DeWalle, 1977). According to the U. S. EPA (1979), phenol and cresols



Single benzene ring with six substitute groups; at least one of these groups must be an -OH group.

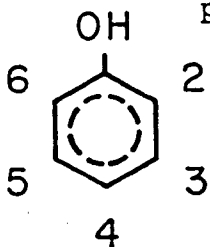
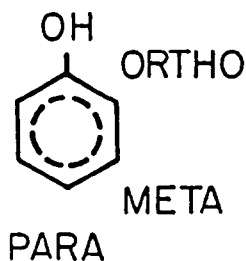


Naphthalene with eight different groups; at least one of them must be an -OH group.



Anthracene and other polycyclic hydrocarbons with up to eight benzene rings exist. The word "phenolic" usually applies to up to three benzene rings with one or more hydroxy groups substituted.

In the family of phenolics, phenols refer to only a benzene ring with one or more hydroxy groups (one -OH in simple phenols) and less acidic groups substituted in the other positions.



where positions 2-6 can be occupied by: -OH, Cl, -CH₃, -(CH₂)_n-CH₃ and unsaturated chain or cyclic hydrocarbons.

Fig. 1. Phenolics and phenols, examples.

leaching from coal tar wastes may reach concentrations of several hundred ppms. Other natural wastes when concentrated in a small area can raise the level of phenols above normal. Lakes and lagoons used by paper mill industries for disposal of large amounts of delignified wood effluents are a case in point (Keith, 1976). Other natural occurrences of phenols are responsible for some of the aromaticity of fermented beverages such as wines and whiskey (Braus and Miller, 1958).

Phenols, both of natural and synthetic origin are used in large quantities by industry. Phenols, and especially phenol (also known as carbolic acid), are used in the making of medicinals, dyes, resins, photo developers, perfumes, explosives, and disinfectants (Degering, 1957; Elias, 1972, and the Merk Index, 1960). Some chlorinated phenols are being used as pesticides or are the byproducts of pesticide hydrolysis in the soil environment (Faust and Hunter, 1969; and Muirhead-Thomson, 1971). Phenols with substituted hydrophobic groups have been used as water repellents in soils (Goring and Hamaker, 1972).

Phenols in Humic and Fulvic Acids

The fate of phenols in the soil is not very well understood. At the turn of the century, soil scientists and microbiologists began to determine the structures of

lignin and humic acids. They postulated that the aromatic structure of these compounds as consisting mostly of condensed mono, di, and polyphenolics (Ermolenko, 1966). Other theories about the structures of humic and fulvic acids included also the aromatic skeleton, but only composed of di and trihydroxy phenolics with ketone aldehyde, and acid groups, bridged by oxygen, nitrogen, and sulfur, and other molecules (Mortvedt, Giordano, and Lindsay, 1972; and Dubach and Mehta, 1963) (Fig. 2).

The humic and fulvic acids may be formed by phenolase oxidation and auto-oxidation of phenols at pH 6 and up (Haider and Martin, 1967). Through sodium amalgam reductive degradation of humic-like substances Martin, Haider, and Saiz-Jimenez (1974) obtained simple phenols yields of 4% to 32%. Haider and Martin (1967) also claimed that over 16 different phenols were separated from humic substances. Schnitzer, Ortiz, and Ivarson (1973) have played down the importance of phenolics in the skeleton of the humic and fulvic acids. According to these workers, the Na-amalgam reduction of humic-like substances yields organic substances which have aliphatic and aromatic structures, only some of which are phenolic acids and simple phenols. Schnitzer and Khan (1978) further emphasize that humic and fulvic acids contain mostly aliphatic acids, benzenecarboxylic compounds and phenolic acids. Through various degradative methods,

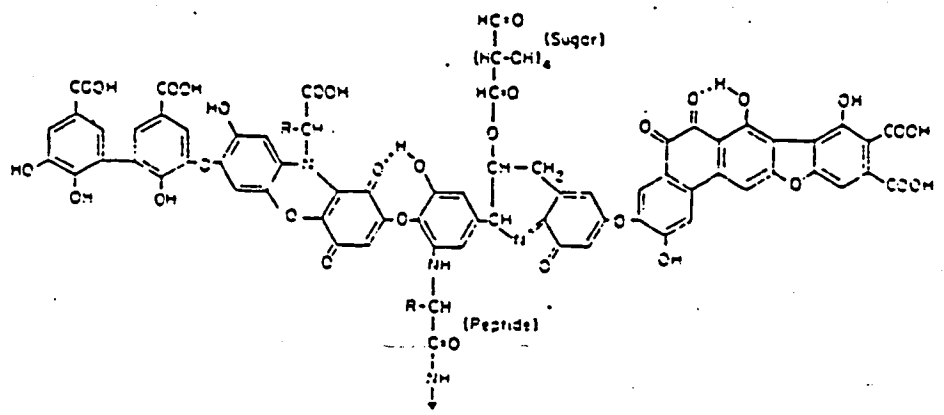


Fig. 2. Structure of humic acid according to Mortvedt, Giordano, and Lindsay (1972).

Figs. 3 and 4, Schnitzer and Khan (1978), report obtaining up to 52 different compounds from humic and fulvic acids. In their book titled Soil Organic Matter, Schnitzer and Khan (1978) conclude that no simple monohydroxyphenols are found in the structures of humic and fulvic acids. Furthermore, the structural formula of these two acids presented by these two workers, is not one of long chain polymerized aromatics, but one of mostly saturated one-ring phenolic and benzene-carboxylic acids, with some substituted aliphatics; all of which are held together by H-bonding, Van der Waals, and pi-bonding forces, Fig. 5.

From the above references it can be inferred that phenols can end up as part of the humic and fulvic acid structures, provided they increase the number of hydroxy groups from one to two or more and/or add or replace into their ring one or more acidic groups. No other recent evidence points to the possibility of the direct incorporation of monohydroxyphenols into the humic and fulvic acids structures.

Assuming that the humic and fulvic acids model presented by Schnitzer and Khan (1978) is correct, phenols in soils have only a few general choices as to their possible fate. They can undergo partial oxidation by adding =O, -OH, -CHO, and -COOH groups in the ring or oxidating the existing groups (Norman, 1968; Schnitzer and Khan,

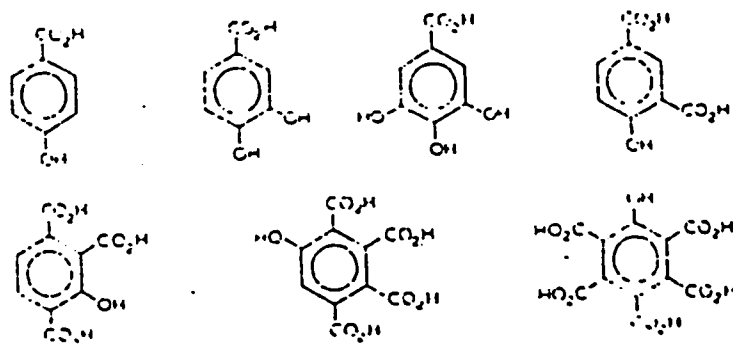


Fig. 3. Major phenolic compounds obtained by oxidative degradation of humic acids.

(Schnitzer and Khan, 1978.)

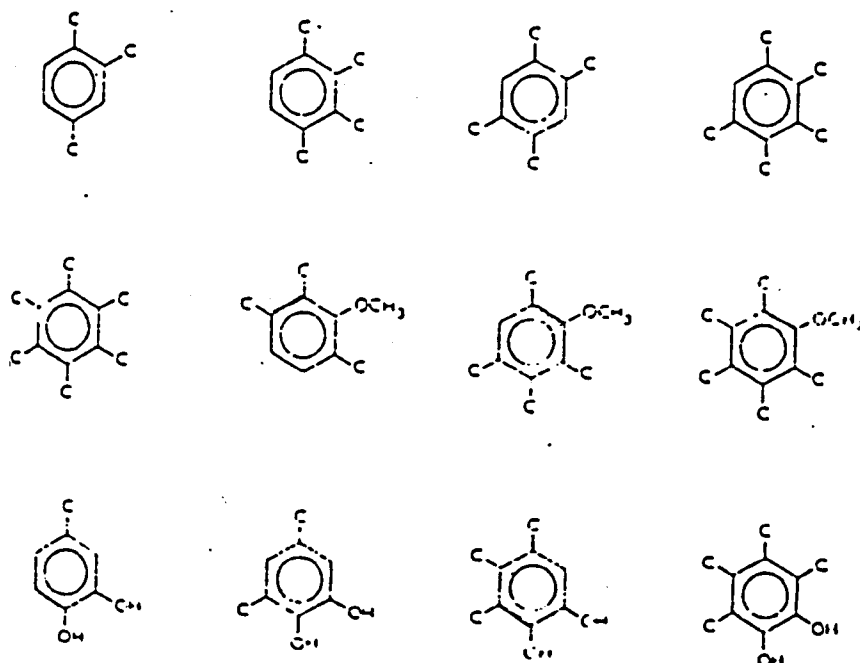


Fig. 4. Some major aromatics obtained by KMnO_4 oxidation of methylated and unmethylated humic and fulvic acids ($-\text{C} = -\text{COOH}$).

(Schnitzer and Khan, 1978.)

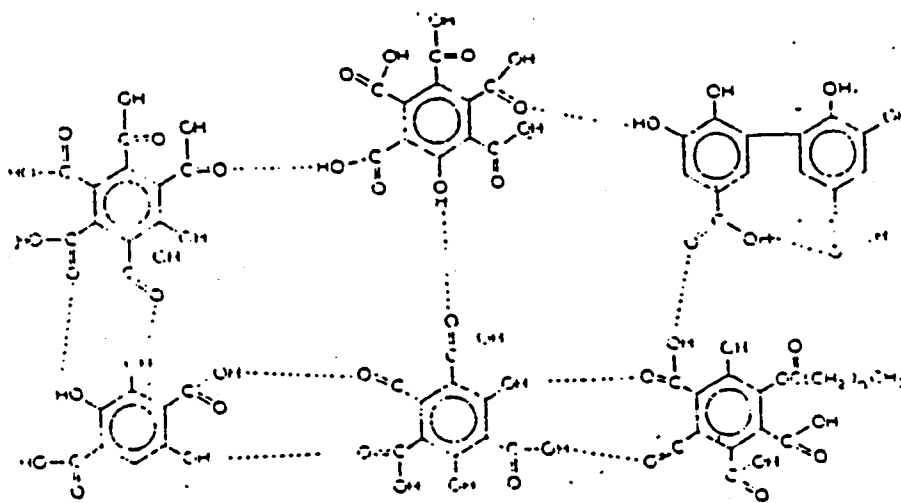


Fig. 5. Structure of humic acid, according to Schnitzer and Khan (1978).

1978; and Brewster, 1953). Phenols can dimerize via oxidative coupling microbe induced (Hendrickson, Cram, and Hammond, 1970) and via oxidants such as FeCl_3 (Ho, 1977). Phenols can undergo halogenation, especially chlorine addition, even when low concentrations of Cl^- are present in the soil (Nemerow, 1978) to give ultimately pentachlorophenol but usually di and trichlorophenols (Norman, 1958). The decomposition of aromatics in soils has been studied by several scientists, for example Evans (1963) and Dagley (1971). More recently, research studies by Haider and Martin (1975) and Martin and Haider (1979), on the decomposition of phenolic acids indicate that group losses from the benzene ring can be extensive, particularly if the groups are $-\text{COOH}$. Ring cleavage also takes place during the incubation periods, but varies with pH, types of microbes present, and the other organic environment (Haider and Martin, 1979). No studies reporting decomposition rates of simple phenols containing other groups than acids have been found in the literature. A prerequisite for the splitting of a benzene ring seems to be the presence of two or more acidic groups. This is accomplished in soils by monooxygenase enzymes (Evans, 1963).

The absorption of phenols by inorganic and organic parts of the soil appears to be a productive approach and one that has just begun to be explored by some workers

despite all the work involving the fate of pesticides in soils. Research on the adsorption of organics by soils are numerous in the literature. Montmorillonite clay has been studied extensively, relating it to the adsorption of ketones (Parfitt and Mortland, 1968), polysaccharides (Parfitt and Greenland, 1970), anilines (Swoboda and Kunze, 1968). Adsorption of pesticides by clays are many and extensive. For example, those reported by Weber and Weed (1968), Bailey, White, and Rothberg (1968), Saltzman and Yariv (1976), and Gamar and Mustafa (1975). Work also has been done on the adsorption of pesticides by natural sediments and their different particle size fractions (Karickhoff and Brown, 1978; and Khan, Hassett, and Banwart, 1979). The type and amounts of cations exchanged in clays and their influences on pesticide adsorption have been considered by Bowman and Sans (1977). Some investigators have begun to consider the effects of humic and fulvic acids on the adsorption of pesticides by clays (Bowman, 1978) and the effect of these acids themselves on the adsorption of some organic hydrophobic compounds such as pesticides (Schnitzer and Khan, 1972).

In an extensive review by Yariv (1978), interactions between different types of organic molecules and clay minerals are discussed with respect to the types of bonds and reactions that can take place between these two phases.

He presents examples of different types of organic-clay interactions which include: organic cations, anions, polar and nonpolar molecules. He specifically points to the effect of the hydrophobic and hydrophilic groups that organic molecules may have in relation to clay-surface affinity and water affinity.

Schnitzer and Khan (1978) dedicate an entire chapter to the interaction of organic matter with pesticides. These soil scientists extensively dissect and review the different, sometimes contradictory, reports of adsorption-desorption mechanisms and types of bonding that pesticides have with soil organic matter. They conclude that pesticides can bind onto soil organic matter in ways which include hydrogen bonding, Van Der Waals forces, and ion exchange. Schnitzer and Khan (1978) bring light to the fact that both the organic and clay phases of the soils have to be considered together when dealing with pesticide adsorption, and transformations in the soil environment. Bolt and Bruggenwert (1976) point out the importance of such soil parameters as pH and iron and aluminum oxides with respect to pesticide adsorption in soils. The decomposition of pesticides is clearly summarized by these scientists. They divided the subject into three main groups which are: photodecomposition, primarily in aquatic media, chemical degradation which includes oxidation,

hydrolysis and polymerization, and biodegradation which includes such micro-organism controlled reactions as beta oxidation, reduction and ring cleavage.

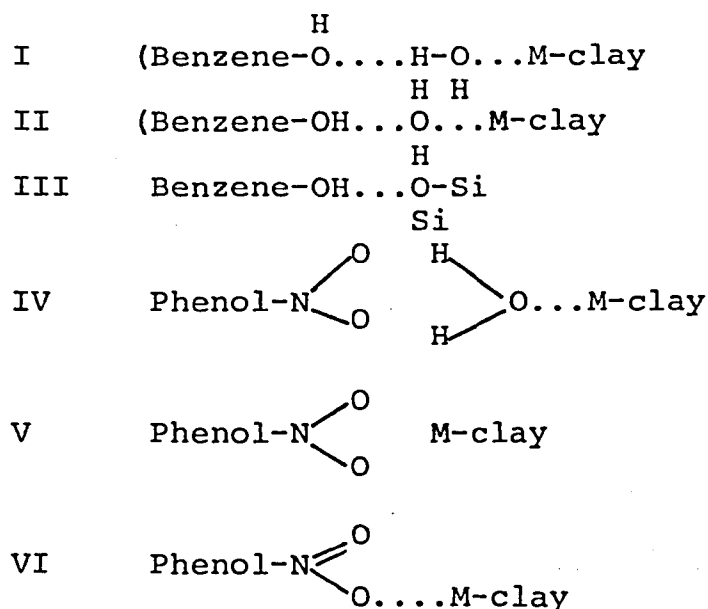
Phenols in Pesticides

As pointed out earlier, simple phenols can enter the soil medium directly via disposal sites which include municipal and industrial discards. Still, other phenols will appear in the soil through synthesis and decomposition of natural residues which are concentrated in small areas. But increasingly larger levels of simple phenols appear in the soil medium through decomposition of pesticides. Most pesticides have aromatic structures (Goring and Hamaker, 1972). Chlorinated pesticides such as DDT produce chlorinated phenols as bi-products of their degradation (Ciaccio, 1973). Parathion, one of many nitro-substituted aromatic pesticides, produces nitrophenols along its degradation pathways in the soil (Sudhakar-Barik and Sethunathan, 1978). Other pesticides like PCP (pentachlorophenol) and Dinoseb (2-sec-butyl-4,6-dinitrophenol) are simple phenols themselves (Schnitzer and Khan, 1978).

Soil-phenols Interactions

As large levels of these simple phenols are now entering soil and water sources, a closer look is being given to their direct interaction with the soil medium.

Saltzman and Yariv (1975) have looked at the adsorption mechanisms of phenol and p-nitrophenol by montmorillonite and concluded that several types of bonds between phenols and clay can take place. Phenol can act as either proton donor or a proton acceptor depending on acidity of the -OH group. Substituted electrophilic groups such as $-NO_2$ can act as electron donor to metals adsorbed in clay complexes and also can H-bond with water in the metals' hydration sphere. According to Saltzman and Yariv (1975) these are the possible bonding configurations:



Clay, saturated with metals seems to induce polymerization of phenols as reported by Mortland and Halloran (1976). Aromatic radical cation formation induced by transition metals in clays has also been reported by Pinnavia et al. (1973). Polymerization reactions of organics in soils,

usually believed to be microbially induced, now have taken a new angle in view of the fact that some scientists have reported these reactions in clays saturated with some selective transition metals only; without microbial help (Krumbein, 1978). Although most studies on phenols-clay interactions have been done under dry, carefully controlled conditions, Knickmeyer, Mayhan, and Bertrand (1973) used activated carbon to look at the adsorption desorption mechanisms of phenol in water systems.

Phenols-toxicity

The literature is very sparse concerning studies relating the disposal and fate of phenols in the soil environment. According to the 1979 publication of Dangerous Properties of Industrial Materials by Sax, phenols as, phenol, cresols, chlorophenols and nitrophenols are listed as carcinogens (section 8, Sax, 1979). OSHA's environmental standards are spelled out, in terms of exposure times and concentrations, for most of these phenols. The U. S. EPA standards for phenols and phenolics in drinking water are 1 ppb or less (Drinking Water Standards, 1962). Phenols can be adsorbed through the skin and lungs at very fast rates (Sax, 1979). Acute toxicity data vary from phenol to phenol, but in general the THR is high for most phenols in any route they enter the body.

Phenols, defined as hydroxy derivatives of benzene, are found in waste waters due to breakdown of organic matter and industrial disposal. Phenols, even at ppb levels, impart undesirable odors to drinking water and render it unfit for human consumption.

Adsorbents and Adsorbates-isotherms

The word "isotherm" refers to a mathematical relation between the amount of material adsorbed per unit weight of adsorbent and the amount of material left in solution at equilibrium (Schnitzer and Khan, 1978).

A fair amount of work exists in the literature concerned with adsorbents and adsorbates in liquid systems. Most of these works present theoretical and/or empirically derived relationships from carefully defined systems. Some examples are by Mittal (1975) who discusses a variety of adsorbents such as simple glass surfaces and a host of solvents and solutes, both inorganic and organic, with countless isotherms describing the solvent-solute-adsorbent equilibrated systems. The theory of adsorption (chemical sorption) is further discussed by Strazhesko (1973). Again, this author uses highly constrained and carefully defined systems to obtain empirical relationships.

For a long time soil scientists have been using two types of isotherms to fit empirical data of solutes adsorbed

by soils. These are, the Langmuir equation, first used by Langmuir (1918) to describe the adsorption of gases onto glass surfaces, and the Freundlich relationship, used to fit empirical data of ions in solution adsorbed onto solid surfaces (Freundlich, 1926). These two equations, defined in Table 1, have been used largely to compare properties of soils and adsorbates rather than to qualify and understand mechanisms of adsorption. Harter and Baker (1977) point out that the Langmuir equation usually is thought of to apply at low equilibrium concentrations by most workers who have used it to construct isotherms. These two scientists have modified the Langmuir equation to include desorbed ions when they can be measured. In the adsorption studies of low levels of pesticides by soils scientists have used the Langmuir equation to fit the data obtained (Gamar and Mustafa, 1975). In general, though, since most soil systems will include multiple adsorption mechanisms, the Freundlich equation has been found to fit best due to its inherent versatility. For the adsorption of organics by soil material, both the inorganic and organic phases, most workers have used the Freundlich equation (Bowman and Sans, 1977; Griffin et al., 1978; and Khan, Hassett, and Banwart, 1979). Some workers have chosen to report isotherms without attempting to fit them into any known equations; perhaps, recognizing the

Table 1. The Langmuir and Freundlich equations.

The Langmuir Isotherm
(common form)

$$x/m = \frac{K(M) b}{1+K(M)}$$

where M = ion activity (moles/l)

x/m = meq of ion M
adsorbed/100 gr.

b = maximum amount
of M adsorbed.

K = $\frac{\text{rate of adsorption}}{\text{rate of dissociation}}$

The Freundlich Isotherm

$$x/m = kC^{1/n}$$

where x/m $\frac{\text{is quantity adsorbed}}{\text{unit of adsorber}}$

k = constant

n = constant

C = equilibrium concen-
tration

complexity and variability of the soil-organic solute systems (Hoffman and Brindley, 1960).

Many pesticides are found in water in an ionic form (either a cation or an anion), but many of them also exist as neutral molecules or a mixture of both neutral and charged species, since they are weak acids and bases (Schnitzer and Khan, 1978). This fact allows many organics in the soil environment to act both as neutral and charged molecules. Thus, there will be several mechanisms of adsorption in order to accommodate one or more of the species present. These mechanisms are: cation and anion exchange, in which one species is replaced by another, sorption into double layers and on broken edges, bonded by Van Der Waal forces and pi and hydrogen interactions (Yariv, 1978), interaction of polar, uncharged molecules with clay surfaces when these have polarized water which can act as proton donors to the sorbates or proton acceptors from the sorbates (Yariv, 1978), sorption via complexation with a metal exchanged on a clay surface also can take place, especially with aromatic molecules with electron rich groups (Yariv, 1978).

Confronted with weak acids such as phenols, the soil surfaces will be exposed to neutral polar species and anions. This can be illustrated as follows: if a phenol has a K dissociation of 1×10^{-10} which represents the ratio

of products over the reactants such that $K_{diss} = \frac{[H][phO^-]}{[phOH]}$ it follows that at pH 7.0 the ratio of neutral (phOH) to charged (phO⁻) phenol species will be 1000 to 1. Thus the ratios of the amounts of neutral and charged species are both K dissociation constant and pH dependent.

The adsorption of phenols by soils probably will be a function of several factors which are: organic matter, clay and iron oxides content, a cation exchange capability and pH of the soil, solubility, dipole moment and acid-base properties of the phenol molecules involved. Some of these variables will be discussed when analyzing the results of the isotherms obtained in this study.

The fate of phenols in soil environments is not very well known. It seems obvious that the degree of mobility and adsorption/desorption of phenols is a function of both the soil medium and the liquid phase in which they are found. It is also evident that each phenol will behave in a different manner, in accordance with the types of groups it has substituted around the benzene ring.

OBJECTIVES

The objectives, therefore, are to: (a) review and test methods for determining phenols concentrations in certain liquid wastes; (b) follow the phenols concentrations in some young and old leachates for a period of one year to determine the variations associated with age; (c) to determine the phenols adsorptive capabilities of five representative soil types from throughout the United States using adsorption isotherms; (d) to determine the relative abilities of leachates to react with phenols in solution; (e) perfuse some soil columns with MSW leachates to determine the ability of soils to retain phenols; and (f) involve the use of phenol in water to evaluate the effect of flow rate and exchanged Cu ions on the ability of five different soils to adsorp and/or chemically modify phenol.

METHODS OF ANALYSIS

The 4-aminoantipyrine Method (4-a)

The colorimetric test for phenolics was first attributed to Emerson, Beacham, and Beegle (1943). Thereafter, other workers such as Ettinger, Ruchhorft, and Lishka (1951) and Dannis (1951) began to use the 4-aminoantipyrine condensation with phenols as a quantitative test for phenols. This method eventually displaced such methods as the Gibbs test and the nitrosophenol test (both also colorimetric) as shown by Moher and Jacob (1957), and Gordon (1960). Although these workers, through the quantitative development and publication of the 4-a method, pointed out some of the inherent deficiencies of the condensation process; none studied and presented this method as well as Faust and Mikulewicz (1967). In their critique these workers extensively dissected the reactions and kinetics of the 4-aminoantipyrine-phenols condensations. They clarified the fact that total phenols determination was not possible with the 4-a method; since, the absorptivity coefficients of the condensates varies significantly with the types of phenols reacting with the 4-aminoantipyrine molecule. They also pointed out that para substitution on the benzene ring blocks the condensation reaction, effectively preventing

para substituted phenols from being detected via this method. In spite of all the criticisms by these two workers, the 4-a method remains the best colorimetric test available today for the "total" phenols determination. Her Majesty's Stationary Office (1972) and American Public Health Association, American Water Works Association, and Water Pollution Control Federation (1975) still list the 4-a method as the test of choice for total phenols analysis, together with gas chromatography. Some modifications have been made in the procedure which were found to best accommodate the type of aqueous municipal solid waste (MSW) landfill leachate that was analyzed during this research. The detailed procedure is provided in Appendix A. Explanations are provided along with each step modified.

The Gas-liquid Chromatography Method (GLC)

This separation technique was first introduced by Nobel prize winners James and Martin in 1952. It has since become the method of choice for qualitative and quantitative analysis of complex organic mixtures. GLC remains primarily a separation technique for qualitative analysis, but recent advances in detection and separation allow today the quantitative analysis of organics routinely with reproducibilities better than 5% (Willard, Merritt, and Dean, 1974). GLC was used during the course of the experiments reported in this work, as both a quantitative and qualitative tool

for the analysis of phenols. A review of the different stationary phases recommended for the analysis of phenols in several publications and the results obtained with them; as well as a new, better stationary phase used in this study, is provided in Appendix B.

Soil Columns

The soils were packed into 11 cm long by 5 cm in diameter PVC cylinders capped with PVC bases containing input-output fittings. The soils were packed so that their bulk densities would approximate field conditions as follows: Molokai clay, 291g/10cm; Davidson clay, 268g/10cm; Ava silty clay loam, 287g/10cm; Fanno clay, 300g/10cm; Mohave-Ca clay loam, 290g/10cm. River bottom sand 370g/10cm. All soils were placed between 0.5 cm of quartz sand of inert adsorptive properties to allow for even liquid diffusion into the soil media. The flow rates (flux) were regulated using peristaltic pumps which allow constant flow at varying pressures. All connections and most tubing to and from the columns consisted of 1/4 and 1/8 inch glass pipe, and the enriched phenol water was stored in glass containers.

All samples were stored in Vacutainers (blood tubes) and kept under anaerobic conditions in refrigeration up to the time of analysis.

MATERIALS

Soils

The soils used in these studies were obtained from typical sites throughout the United States and represent five of the ten soil orders. They are Molokai (clay), Davidson (clay), Ava (silty clay loam), Fanno (clay), Mohave-Ca (clay loam), and River bottom sand (sand). These soils were selected for their varying chemical and physical characteristics, notably clay which was suspected of being reactive in retention of phenols. All soils were air dried and sieved through a 0.50 mm sieve to allow only the smaller, more homogeneous particles of the soils to be used. Otherwise, the soils were left untouched and untreated so as to represent their field conditions as closely as possible. River bottom sand was sieved through a 2.0 mm sieve, since most of its particle sizes fall in the sand range. Table 2 lists the major properties as reported according to Fuller et al. (1976).

Phenols

The six phenols used were purchased in stock at purities of 99% or better from the Aldrich Chemical Company. To prepare stock solutions of 1000 ppm of each phenol,

Table 2. Some significant properties of the soils used.¹

<u>Soil Properties</u>	<u>Molokai clay</u>	<u>Davidson clay</u>	<u>Ava silty loam</u>	<u>Fanno Clay</u>	<u>Mohave-Ca clay loam</u>	<u>River bottom sand</u>
Soil order	oxisol	ultisol	alfisol	alfisol	aridisol	entisol
soil pH	6.2	6.2	4.5	7.0	7.8	7.2
Cation exchange (meq/100g)	14	9	19	33	12	2
clay %	52	51	31	46	40	1
Iron oxides-%	23	17	4	3.7	2.5	less than .1
Organic carbon-%	0.5	0.3	0.4	0.9	0.4	less than .1
Soil surface area-m ² /cm ³	67.3	51.3	61.5	122.1	127.5	3.6
Electrical con- ductivity-mhos/cm	1262	169	157	395	510	210
Column bulk Density-g/cm ³	1.44	1.40	1.45	1.48	1.54	1.73
Silt-%	25	23	60	19	28	2
Sand-%	23	25	10	35	32	97

¹from Fuller et al. (1975).

weighed amounts (± 0.0001 g) of each phenol were diluted in doubly deionized water (distilled water run through an organic removal deionizing column). These stock solutions were examined for total organic carbon to standardize the total levels of phenols.

The phenols used are: Phenol (phenilic acid), othocresol, para-cresol, 2,6-dimethylphenol, 2,4-dichlorophenol, and para-nitrophenol. Figure 6 shows their structures and Table 3 lists the chemical properties as given in the Handbook of Chemistry and Physics (54th Edition, 1975-76). Phenol, o-cresol and p-cresol were chosen as examples of simple phenols because they are naturally occurring phenols. Some of the most common chlorinated phenols are the dichlorophenols. Of these, 2,4-dichlorophenol was chosen because it is fairly common in chlorinated waters. Chlorinated phenols are also found in the breakdown paths of some chlorinated pesticides. P-nitrophenol, a by-product in the degradation of nitro-containing pesticides, has markedly different chemical properties from the other phenols selected making it another good choice. Dimethylphenols (xylenols) are used in industry and cover a fairly large family of low solubility, high toxicity and strong odor phenols. All phenols selected are carcinogens. See Fig. 6 for structures and some constants.

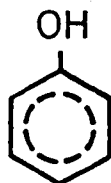
Table 3. Chemical properties of phenols.

(Handbook of Chemistry and Physics, 54th Edition, 1975-76.)

<u>Name</u>	<u>Formula Weight</u>	<u>Boiling Point</u>	<u>Melting Point</u>	<u>Solubility in Water</u>
Phenol	94.11	181.9C	40.6°C	Soluble
2,6-dimethyl-phenol	122.17	203.0C	44.-46°C	Slightly soluble*
Ortho-phenol	108.14	191.0C	32.-34°C	Soluble
Para-cresol	108.14	202.2C	32.-35°C	Slightly soluble*
2,4-dichloro-phenol	163.0	209.5C	32-34°C	Slightly soluble**
Para-nitro-phenol	139.11	279.8	112-114°C	Slightly soluble*

* At least 1000 ppm soluble in water at 20C

**At least 500 ppm soluble in water at 20C



PHENOL (Carbolic Acid, Phenic Acid, Phenilic Acid).

Colorless crystals.

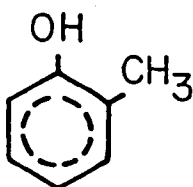
Moles per 1000 ppm solution:
.0106 moles/liter.

Percent Organic Carbon in the
molecule: 76.51%.

K_a (Dissociation Constant)

1.28×10^{-10}

Dipole Moment 1.70 in water
1.45 gas



Ortho-CRESOL (Ortho-Methyl Phenol,
Ortho-Hydroxy Toluene)

Colorless to Yellowish crystals--
very hydroscopic.

Moles per 1000 ppm solution:
.0092 moles/liter.

Percent Organic Carbon in the
Molecule: 77.68%.

K_a (Diss. Const.) 0.63×10^{-10}



Para-CRESOL (Para-methyl Phenol,
Para-Hydroxy Toluene)

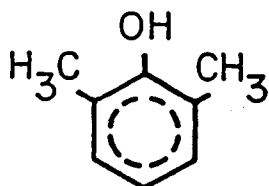
Brownish Crystals, very hydroscopic.

Moles per 1000 ppm solution:
.0092 moles/liter

Percent Organic Carbon in the
Molecule: 77.68%.

K_a (Diss. Const.) 0.67×10^{-10}

Fig. 6. Names and some constants of six phenols.



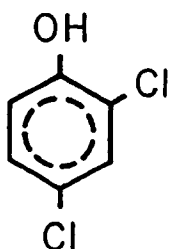
2,6-DIMETHYLPHENOL (2,6 Xylenol)

Whit, Powder-like Crystals.

Moles per 1000ppm solution:
.0082 moles/liter

Percent Organic Carbon in the
Molecule: 73.58%

Kdissociation less than 63×10^{-11}



2,4-DICHLOROPHENOL

Yellowish crystals

Moles per 1000 ppm solution:
.0061 moles/liter.

Percent Organic Carbon in the
Molecule: 44.17%

Kdissociation 3.6×10^{-8}



Para-NITROPHENOL (4-Nitrophenol)

Yellowish Crystals

Moles per 1000 ppm solution:
.0072 moles/liter

Percent Organic Carbon in the
Molecule: 51.9%

Ka(diss. Const. 7.0×10^{-8})

Fig. 6, Continued.

Leachates

The municipal liquid wastes used are produced from representative municipal solid wastes deposited in landfills. They are produced in a leachate generator as described by Fuller (1978). Table 4 gives the major characteristics of the three leachates used which are labeled I, II, IIa, and III. All leachates were transported and stored under CO₂ gas as suggested by Fuller (1978). These liquid wastes were at different stages in decomposition or maturity as can be seen from Table 4 which shows the pH, TOC, and EC ranges as being diverse. Leachate III is a young leachate (1 year old) with an acidic pH and high TOC and EC levels. This leachate was also very sensitive to air since oxidation of its major constituents had not fully taken place yet. Leachate III, thus is a prime candidate to study large levels of naturally produced phenols and their effects on soils. Leachate II is more advanced in its stage of decomposition as seen by its slightly basic pH and low TOC levels. Leachate I is similar in characteristics to Leachate II but older. These leachates provide a good chance to study the change in TOC with respect to humic and fulvic acid contents and the effects of enrichment with various phenols.

Table 4. Leachate characteristics of the three leachates used in this study.

Leachate	pH	EC mhos/cm	Fe	TOC	TIC	mg/liter			K	PO ₄	Si	Other Metals
						Ca	Na	Mg				
I(1/9/79)	6.8	3800	33	1296	-	167	116	62	612	21	25	<1
I(12/14/79)	6.8	3750	17	306	389	140	120	40	450	5.7	21	<1
II(1/9/79)	6.9	4650	43	1467	-	116	138	48	498	-	21	<1
II(11/14/79)	6.9	4500	23	422	493	130	130	31	350	30	22	<1
III(1/12/79)	4.3	8000	598	9423	-	623	380	159	1670	95	31	<10
III(11/14/79)	7.2	10000	45	890	1014	83	270	71	960	21	29	<10

Date Leachate Collected	TOC	Phenols ppb	ph	Fe	Ca	Mg	K	Na	EC µmhos/cm
March 3, 1978	1863	648	6.7	367	370	130	430	740	5250
Leachate IIa March 11, 1978	1890	730	6.7	350	324	125	444	-	5300

Batch Study

To determine the equilibrium time of the phenols with the different soils, enriched deionized water with phenols was added to 10.00 g soil samples in 250 ml flasks and capped with a stream of CO₂ gas. The containers were shaken and sampled every 24 hours for total phenols in solution via GLC analysis. The enriched water aliquots were of 200 ml per 10 of soil and varied from 5 ppm to 200 ppm of phenols. Similar setups were used for the amking of the isotherm plots once the equilibrium time for the phenols-soils system was determined. The large sample volume of enriched water per 10.00 g of soil was justified to allow hydration of the soil sample without changing significantly the concentration of the phenols in solution. This step did not prevent the soil samples from buffering the water-phenols aliquots to their own natural pH values.

All shaking was done at room temperature (22°C).

RESULTS

Equilibrium Time Determination

Figures 7 and 8 show the results obtained by shaking five soils with phenol for up to twelve days, and by shaking 10 g of Molokai clay soil with five water solutions containing five different phenols, for fourteen days. In both cases the phenols retention seems to level off considerably after five days. This study permits the construction of isotherm curves assuming that the equilibrium time is five days, and that after that time no significant adsorption or transformation of phenols by soils takes place. In the literature, the equilibrium times of pesticides in clays and soil materials vary from a few hours to days. Due to the consistency of the results obtained, a 5-day time constant was used for all phenols-soils isotherms.

Isotherms

The data on the pH ranges of the phenols-soils isotherms are given in Table 5 and indicate that the soils were able to buffer the water-phenol solutions.

Isotherms with five soil and six phenols were constructed and are shown in Figs. 9, 10, 11, 12, and 13. River bottom sand was also used but no significant adsorption was obtained of any of the six phenols, at any of the levels used.

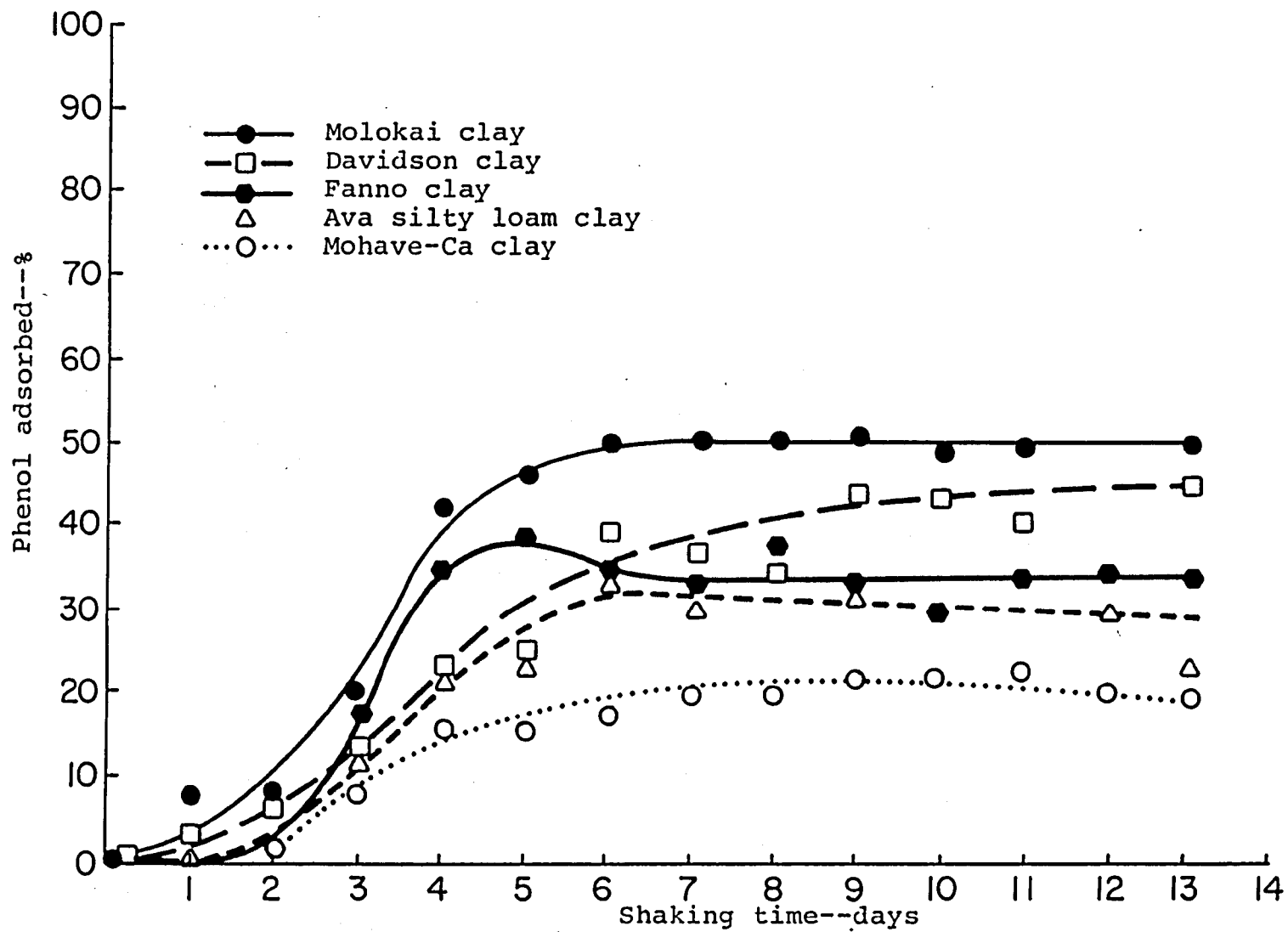


Fig. 7. Adsorption of phenol in contact with five soils 10 g each with 250 ml of 200 ppm phenol in aqueous solution.

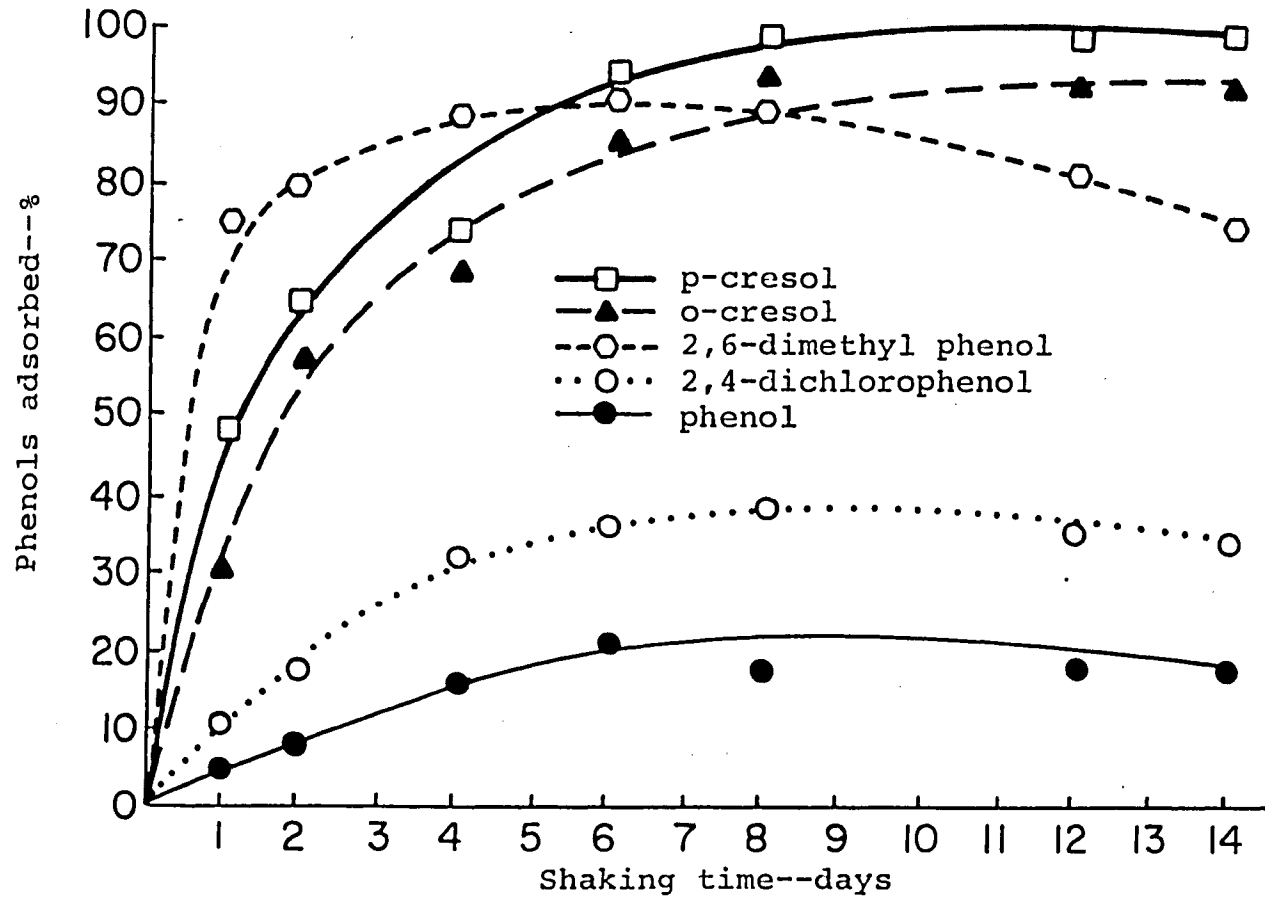


Fig. 8. Adsorption of five phenols in contact with Molokai clay for fourteen days.

Table 5. pH ranges of isotherms of soils shaken with deionized water enriched with phenols.

Phenols	Molokai c*	Davidson c	Ava si c	Soils		River bottom sand s
				Fanno c	Mohave- Ca c l	
	pH					
Phenol	6.0-6.1	5.7-5.8	5.0	-	6.8-6.9	5.4-5.5
O-Cresol	6.2	5.3-5.5	4.3-4.8	5.9-6.0	6.9	5.4
P-Cresol	6.2	5.3-5.7	4.3-4.8	5.7-6.1	6.8-6.9	5.4
2,6-dimethyl phenol	6.2-6.3	5.9-6.2	4.9-5.3	6.1-6.3	7.0-7.1	5.5
2,4-dichloro- phenol	6.0	5.7-5.9	5.0-5.3	5.4-6.1	6.9-7.1	5.4
P-nitrophenol	6.1-6.3	5.5-5.7	5.0	6.0	6.8-7.1	5.5
	6.1	5.9-6.3	5.0	6.0	6.8	5.5

*10 gr. of soil + 200 ml of phenol-enriched water.

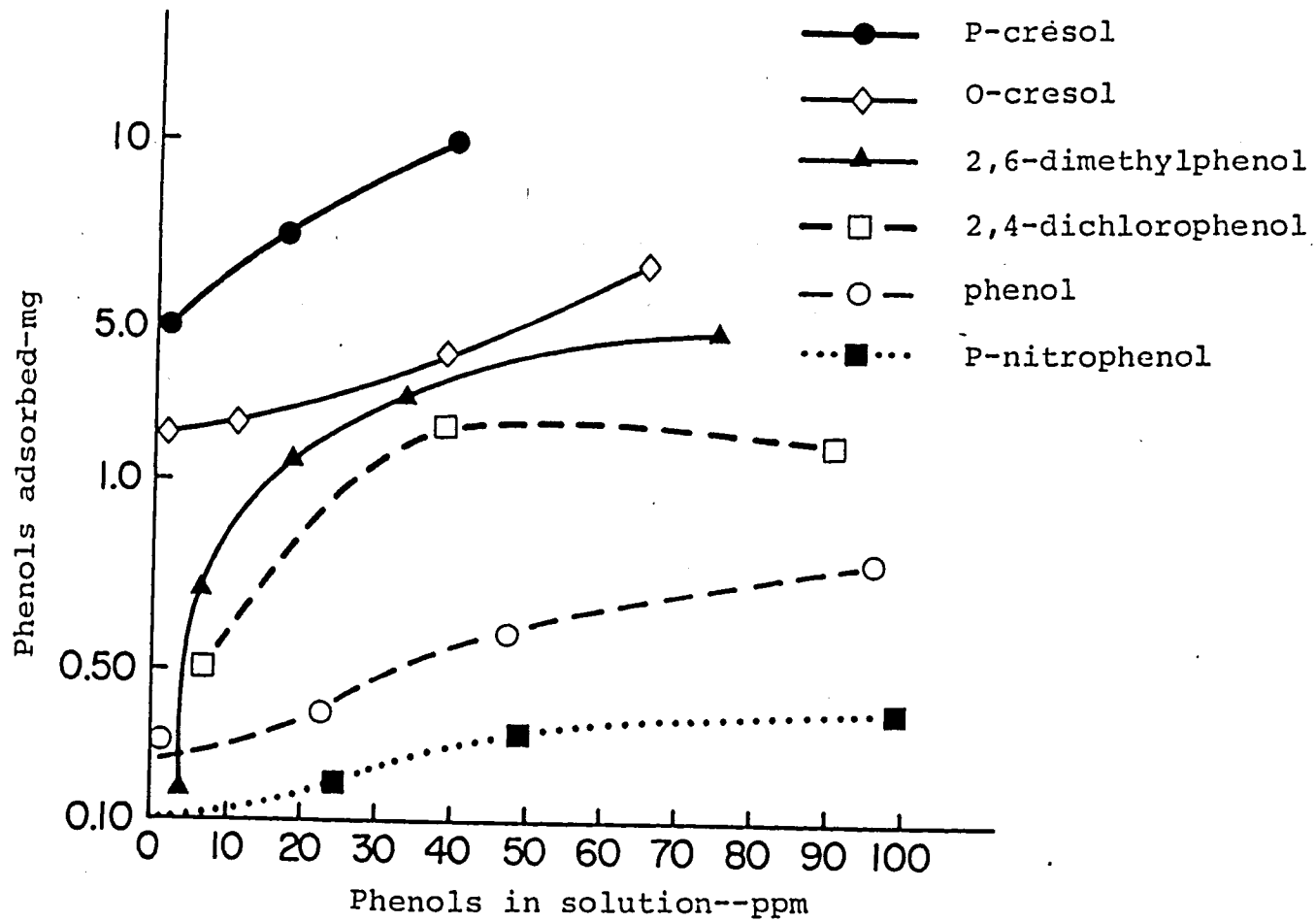


Fig. 9. Isotherms of Mohave-Ca with six phenols.

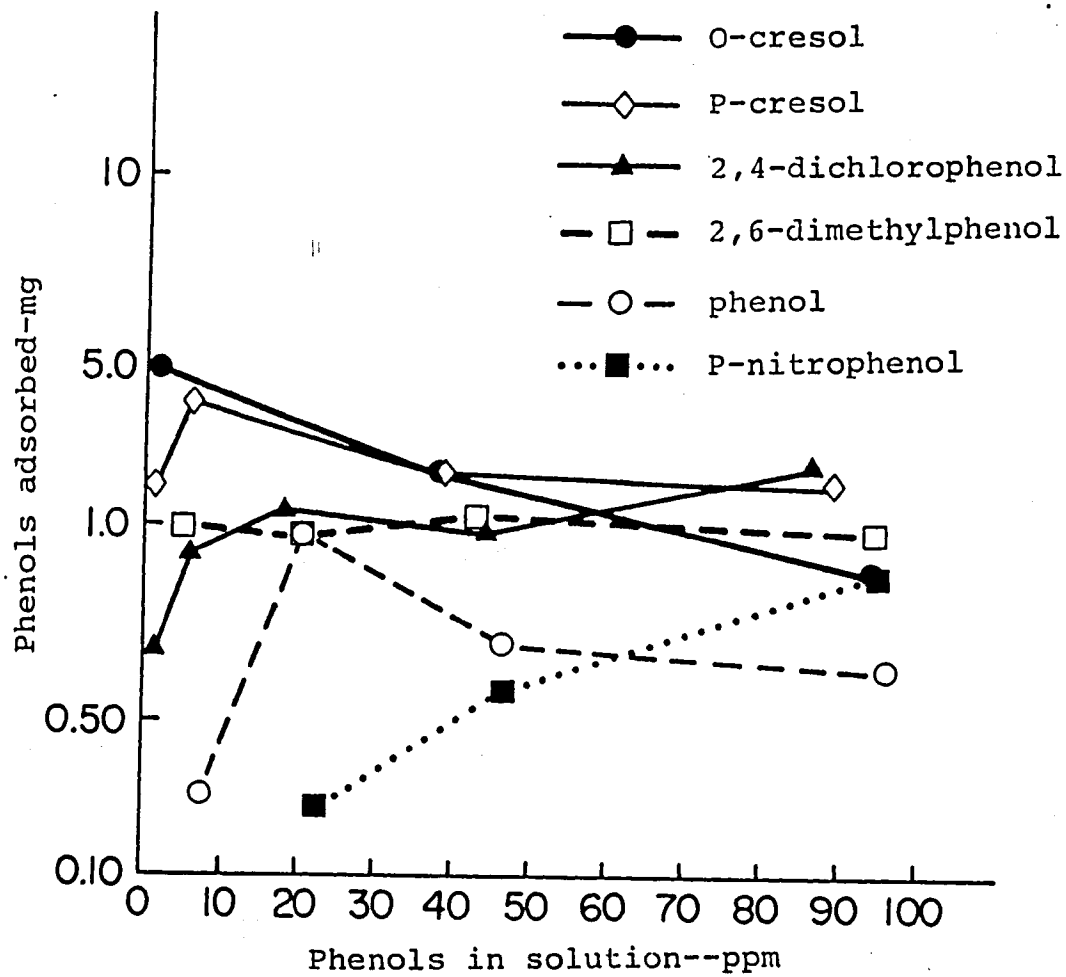


Fig. 10. Isotherms of Fanno soil with six phenols.

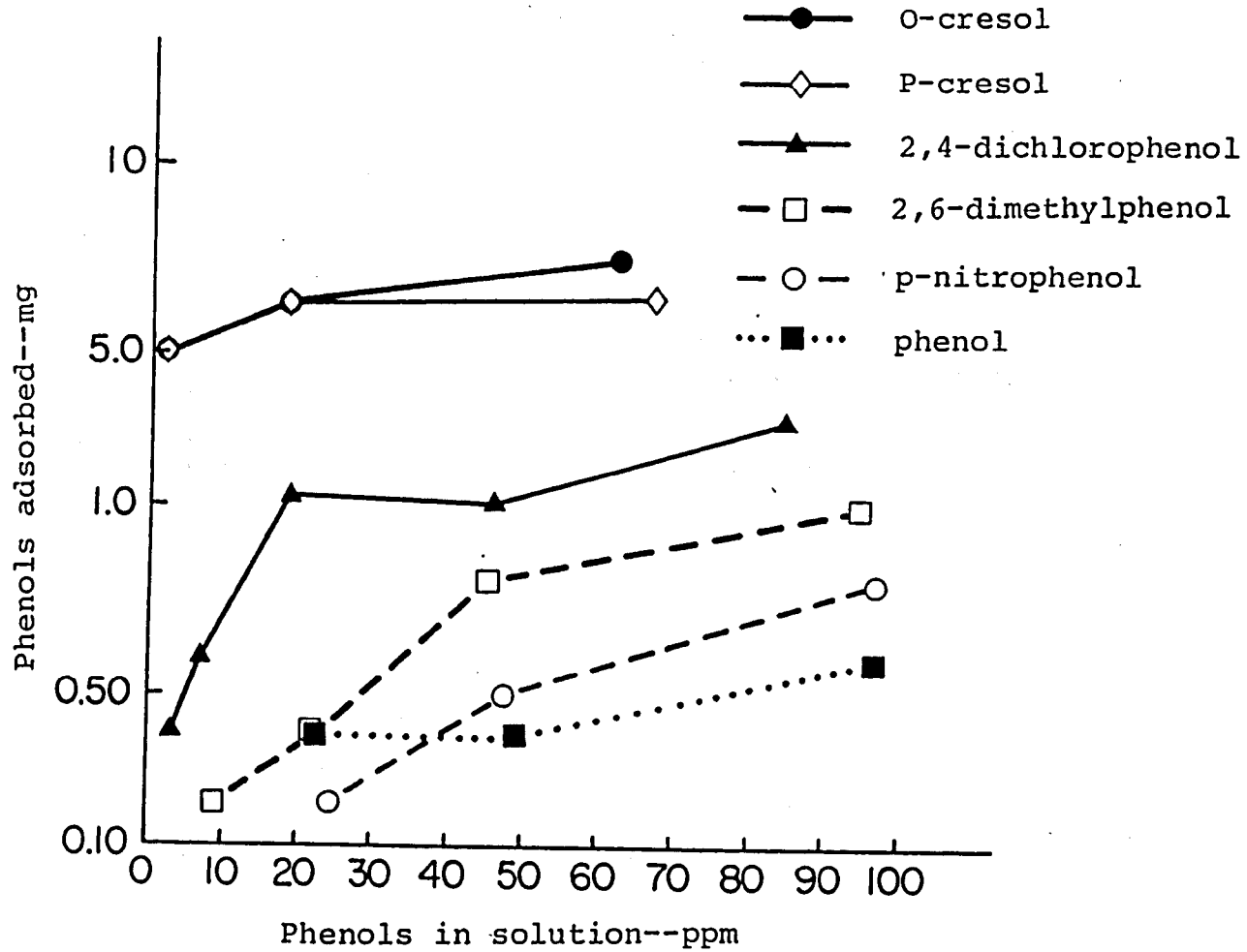


Fig. 11. Isotherms of Ava soil with six phenols.

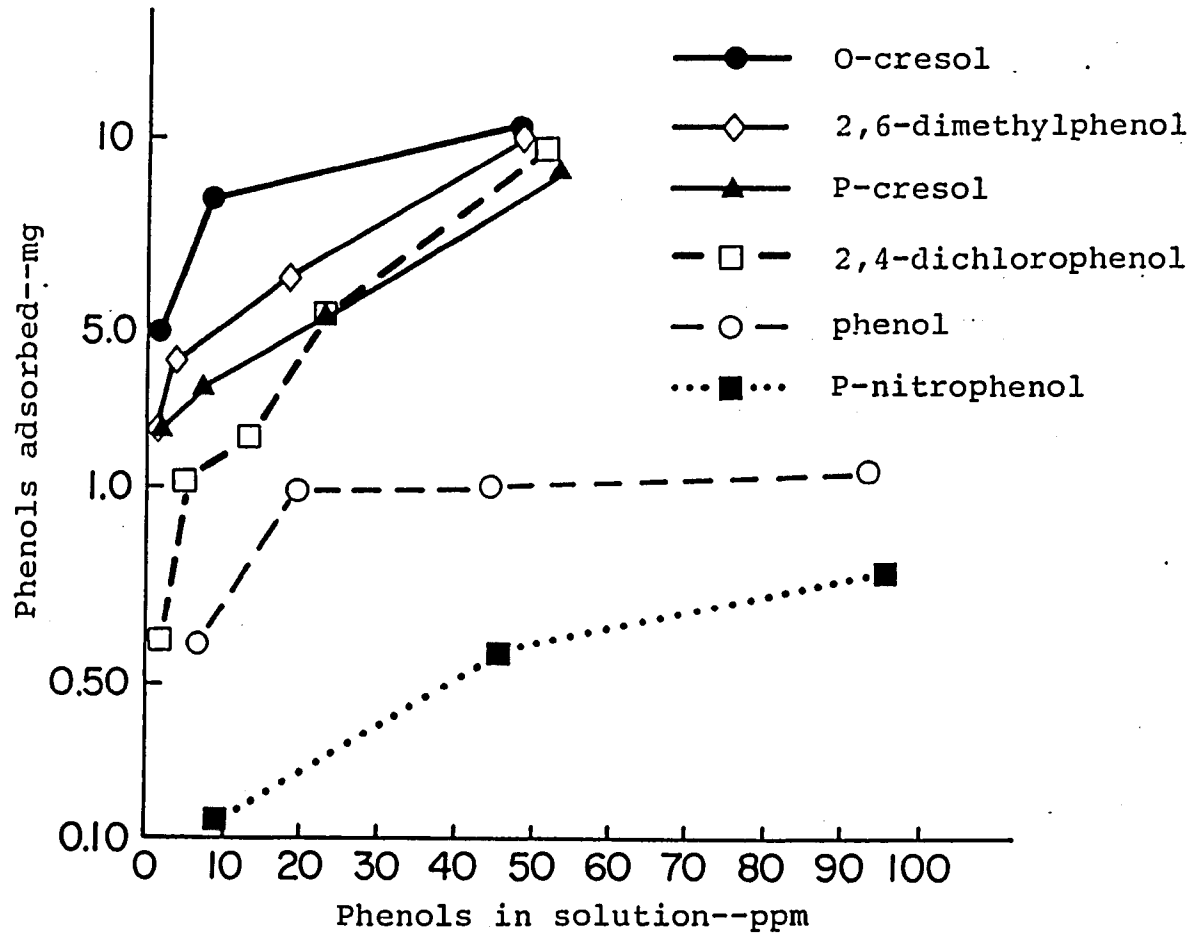


Fig. 12. Isotherms of Davidson soil with six phenols.

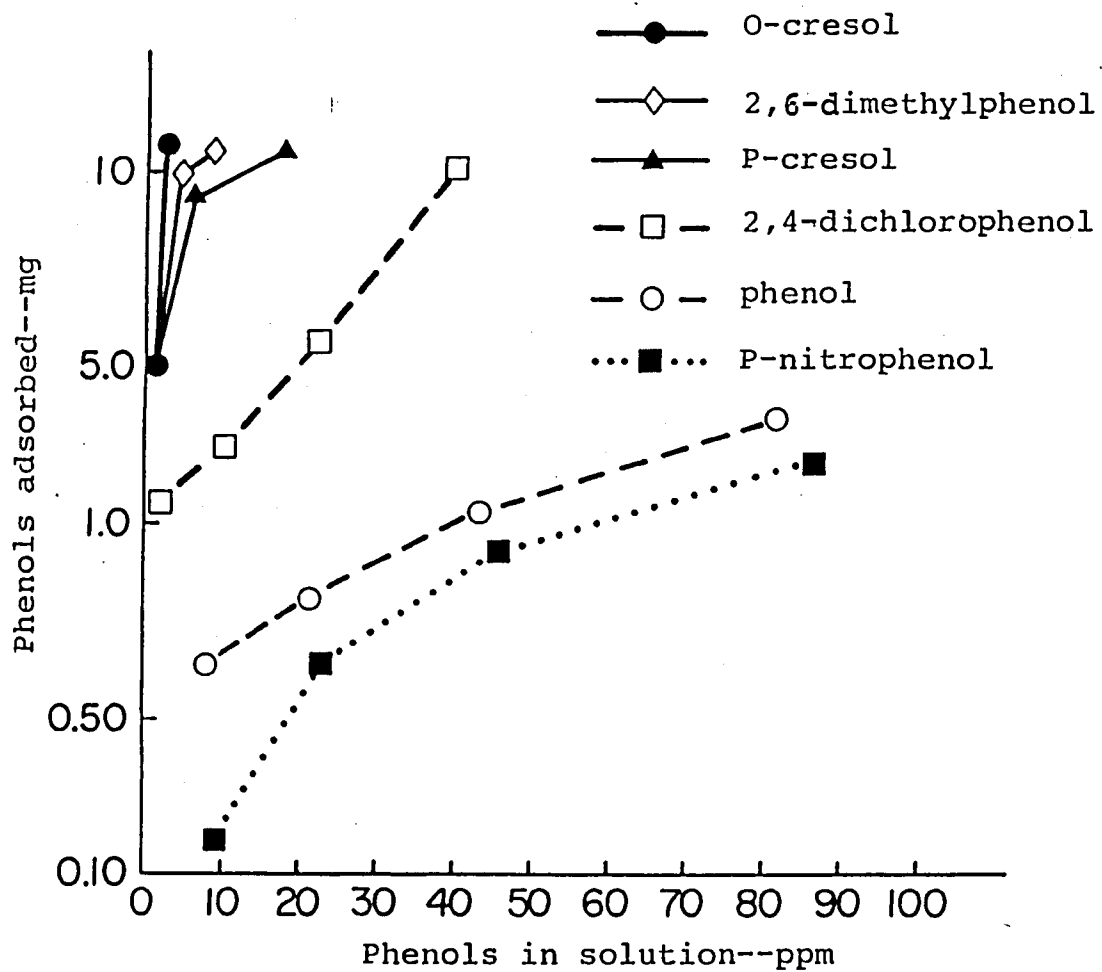


Fig. 13. Isotherms of Molokai soil with six phenols.

Both the Langmuir and the Freundlich equations were tried for a fit. As expected, the Freundlich equation gave a much better fit. The Freundlich regression R^2 are given in Table 6. As mentioned previously, this equation is more versatile, allowing for more mechanisms to be incorporated into the equation obtained. In Table 6 it can be seen that some soils fit this equation better than other soils. Molo-kai clay has an R^2 with all phenols averaging better than 0.900, followed by Davidson clay and Mohave-Ca clay loam with R^2 better than 0.800. This finding seems to indicate that for these soils, one soil property predominates over all others; thus reducing the effective multiplicity of mechanisms of adsorption of phenols by these soils. Table 6 also shows that some phenols behave more consistently in their correlation with soils. For example, p-nitrophenol has an average R^2 greater than 0.950; whereas, 2,6-dimethylphenol and 2,4-dichlorophenol have R^2 's of about 0.840. This appears to indicate that even with the varying solution pH's in which the phenols were found, other phenol properties, not related to the solution pH, are more important in controlling the adsorption of some phenols in different soils.

In an attempt to assess the effect of each soil on the phenols in terms of adsorptive capabilities, the highest amounts adsorbed from each phenol by each soil were

Table 6. Freundlich isotherm regression R^2 for five soils times six phenols.

Phenols	Soils					Average	Rankings
	Molokai c	Davidson c	Mohave-Ca c 1	Ava si c	Fanno c		
Phenol	.953	.708	.999	.392	.656	.742	4
P-nitrophenol	.970	.951	.892	.982	.992	.956	1
2,6 dimethyl-phenol	.895	.876	.758	.974	.731	.846	2
2,4-dichloro-phenol	.841	.977	.975	.689	.716	.840	3
P-cresol	.895	.754	.917	.706	.239	.702	5
O-cresol	.942	.719	.347	.739	.325	.614	6
Averaged R^2	.916	.831	.815	.748	.610		
Rankings	1	2	3	4	5		

compared, Table 7. Data were taken from the isotherm study. The values were then converted from grams to moles adsorbed to be able to compare molecular adsorption of phenols by soils. The mole values of Table 7 were submitted to an analysis of variance to determine the significance of the adsorption of each phenol by each soil. In all cases the adsorption was highly significant (<1%) for every phenol in a given soil. Having established that there were significant differences for the retention of phenols by soils, the values of Table 7 were regressed against six soil properties for each soil used in the isotherms experiments. These soil properties are: free iron oxides, clay, silt, surface area, pH, and CEC. The soil properties were regressed stepwise against each phenol. The regression program was set so that each soil property would be added into the regression equation in order of importance in predicting phenol adsorptions by soils. Free iron oxides were found to be the most important factor in soils by far, since it was the first variable to be selected by the program in the regression equation on all six phenols, Table 8. The second-most important variable was pH improving the R^2 significantly each time it was added into the regression equation and was significant each time at least at the 97% level. pH was not significant at all for the adsorption of the methylated and nitro-phenols which

Table 7. Largest amounts of phenols adsorbed by five soils, taken from the isotherm data.

Soils	Phenol Adsorption	Phenols					
		Phenol	O-cresol	P-cresol	2,6-dimethyl phenol	2,4-dichloro phenol	p-nitro phenol
Molokai c	mg (1×10^{-3})	380	204	1600	1800	1200	250
	Moles (1×10^{-5})	4.04	18.5	14.8	14.7	7.4	1.94
Davidson c	mg (1×10^{-3})	150	1000	920	1000	960	80
	Moles (1×10^{-5})	1.60	9.30	8.50	8.20	5.90	0.624
Ava si c	mg (1×10^{-3})	60	750	680	100	330	80
	Moles (1×10^{-5})	0.640	6.94	6.30	0.820	2.02	0.621
Fanno c	mg (1×10^{-3})	110	500	420	140	260	90
	Moles (1×10^{-5})	1.17	4.60	3.90	1.20	1.60	0.70
Mohave-Ca	mg (1×10^{-3})	80	700	1200	200	500	40
	Moles (1×10^{-5})	0.850	6.50	11.4	1.60	3.1	0.310

Table 8. Regression analysis of four soil properties on adsorption phenols.

<u>Phenols</u>	<u>Added Variable (Stepwise 1-4)</u>	<u>Significance*</u>	<u>R²</u>	<u>Mean² change</u>
Phenol	1- Iron oxides	.000	.6357	68.1
	2- Surface area	.056	.7348	53.7
	3- pH	.000	.9305	15.3
	4- Clay	.048	.9538	11.2
O-cresol	1- Iron oxides	.000	.8421	486.9
	2- pH	.001	.9423	192.7
	3- Surface area	.000	.9896	37.6
	4- Clay	.043	.9939	26.9
P-cresol	1- Iron oxides	.017	.3672	2026.9
	2- Surface area	.105	.4962	1748.4
	3- CEC	.000	.9144	324.0
	4- pH	.000	.9856	60.1
2,6-dimethyl-phenol	1- Iron oxides	.000	.9578	160.7
	2- Surface area	.010	.9762	98.0
	3- Clay	.000	.9974	11.8
	4- CEC	.820	.9974	12.9
2,4-dichloro-phenol	1- Iron oxides	.000	.7971	126.2
	2- pH	.029	.8660	90.3
	3- silt	.000	.9881	8.7
	4- CEC	.151	.9904	7.7
p-nitro-phenol	1- Iron oxides	.000	.6397	9.8
	2- CEC	.216	.6846	9.3
	3- Clay	.133	.7520	8.1
	4- Silt	.604	.7525	8.7

*Values .010 or smaller are significant at the 99% level.

have extremely low and extremely high K dissociation constants. The third most important variable was clay which was added to the adsorption equation of 4 phenols but only three of them were significant at the 95% level, with 4-nitrophenol being the exception significant only at the 80% level. Silt was significant only in the adsorption of 2,4-dichlorophenol. Surface area was significant in the equation of 3 phenols at the 95% level or better. These phenols, phenol, o-cresol, and 2,6-dimethylphenol were the same as the ones which had clay as being very significant, thus, indicating once again the intimate relationship between clay and surface area. Overall the R^2 was at least 0.950 after the addition of the fourth variable for all regression equations except the one for 4-nitrophenol which only had one variable significant, this being iron oxides and an overall R^2 of only 0.793. Evidently, p-nitrophenol is a case in itself due primarily to the dimerizing properties it exhibits in water which make it very unreactive to most soil fractions.

At this point it may be desirable to look at an overall view of the results by condensing them further into tables that report both the phenols and the soils. On a scale of 1 to 5 the soils were ranked with respect to the highest amounts of each phenol in moles they adsorbed. The data in Table 9 indicate that Molokai clay and Davidson clay

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 Table 9. Rankings for highest amounts of each phenol adsorbed by five soils.

	<u>Phenol</u>	<u>O-cresol</u>	<u>P-cresol</u>	<u>2,6-dimethyl-phenol</u>	<u>2,4-dichloro-phenol</u>	<u>p-nitrophenol</u>
Molckai clay	5	1	2	3	4	6
Davidson clay	5	1	2	3	4	6
Ava silty clay loam	5	1	2	4	3	6
Fanno clay	5	1	2	4	3	6
Mohave-ca clay loam	5	2	1	4	3	6

Rankings on the basis of mole concentrations.

retained the most phenols overall; results which are consistent with their large levels of free iron oxides.

Mohave-Ca clay loam was ranked third, again, in consistence with its high pH which would promote more ionic species of phenols in solution. Ranking of Ava silty clay and Fanno clay for the fourth and fifth positions is not altogether clear-cut. Ava silty clay has the pH factor going strongly against its performance, as its pH is very acidic. Furthermore, it has the lowest clay content of clay of all the soil used, but compensates with the largest silt fraction of all the soils. Fanno clay is somewhat of a puzzle since it is very high in clay (46%) and has a pH of 7.0 below the Mohave-Ca soil pH of 7.8, yet its performance was not only very erratic but perhaps also not as high as expected.

According to Stumm and Morgan (1970), hydrous iron oxides show a strong tendency to react with anions as well as cations. This fact differentiates them from clays which adsorb primarily cations. This correlates well with the high affinity that Molokai clay and Davidson clay show for phenols. On the other hand, clays may not be as important a factor as iron oxides and the data presented here support this in most instances. Phenols may react as neutral polar molecules or anions. In soils with intermediate to high pH the results here seem to indicate that anion adsorption is preferred over neutral polar molecule adsorption.

Evidently, many neutral molecules behave as anions, thanks to water proton acceptor capacity when it is attached to an active soil surface such as iron oxides.

Data in Table 10 show on a scale of 1 to 6 the ranking of phenols retained relative to each other by all soils. Again, the results shown in Table 10 were extrapolated from the isotherms study. o-cresol and p-cresol were retained to the greatest extent by soils, with o-cresol being adsorbed the most. These phenols are found naturally in the soil environment as products of organic matter decomposition. They both have similar boiling and melting points, as well as almost identical K dissociation constants. However, p-cresol is less soluble in water than o-cresol. Next in the rankings are 2,6-dimethylphenol and 2,4-dichlorophenol with the latter better adsorbed and more often than the former. No specific data on the solubilities is available on the phenols used in this study, other than the one given in Table 3. More quantitative solubilities should be correlated to phenols as they are adsorbed by soils. 2,4-dichlorophenol is a stronger weak acid than the methylated phenol is, thus making the chlorinated phenol better able to exist as an anion in solution. Phenol (carbolic acid) and p-nitrophenol ranked 5 and 6, respectively, p-nitrophenol offers a unique problem in its ability to be adsorbed by soils. According to Brewster

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Table 10. Rankings for five soils and their ability to adsorb six phenols.

	<u>Phenol</u>	<u>O-cresol</u>	<u>P-cresol</u>	<u>2,6-dimethyl-phenol</u>	<u>2,4-dichloro-phenol</u>	<u>p-nitro-phenol</u>
Molokai clay	1	1	1	1	1	1
Davidson clay	2	2	3	2	2	2
Ava silty clay loam	4	3	4	4	4	3
Fanno clay	5	5	5	5	5	5
Mohave-Ca clay loam	3	4	2	3	3	4

Rankings on the basis of moles concentrations.

(1953), this phenol has such a high dipole moment that in water it dimerizes, making it a molecule twice the size of its monomer counterpart. This property makes this phenol the strongest weak acid of all phenols in this study, a fact which does not appear to offset the dimerization problem but in fact aggravates it. p-nitrophenol is the most mobile phenol in this study; despite data by Saltzman and Yariv (1975) which indicate that under dehydrated conditions p-nitrophenol is much more strongly adsorbed by montmorillonite than phenol is. It should be pointed out that the study reported here is a more accurate model for natural water-saturated conditions than the study by Saltzman and Yariv (1975), which was conducted under very dry conditions and with excesses of phenols to allow for the otherwise impossible infrared readings. Phenol is not retained to the degree expected considering that it is more soluble than chlorinated and methylated phenols, and is a moderately strong weak acid. It should be mentioned that the lack of data on the chemical properties of all six phenols made it impossible to treat their soil retentions in a more statistical-like manner. The general trend that emerges indicates that naturally occurring phenols such as the cresols and phenol are held strongly to moderately by soils. Whereas, synthetic, low solubility phenols such as methylated, chlorinated, and nitrophenols are more mobile in soils.

Natural Phenols in MSW Leachates

For a period of one year, beginning January, 1979, and ending December 1979, three leachates were analyzed for "total" phenols. MSW leachates characteristics presented in Table 11 as I, II, and III. Leachate I is the oldest and Leachate III the youngest. Table 4 shows some chemical characteristics over a year's period. Figure 14 shows the TOC (total organic carbon) levels plotted for the three leachates over a period of one year. All three leachates underwent significant changes, particularly III, which dropped from around 8000 ppm TOC to less than 1000 in a month's time. Leachates II and I decreased from about 1100 ppm TOC to about 250 but the change was more uniform for the 12-month period. Figures 15 and 16 show the pH and "total" phenols levels for the three leachates. Evident in the pH increase is the large TOC change of leachate III reported in Fig. 14. This is to be expected as suggested by Chian and DeWalle (1977). The acidic groups keep pH down initially in young leachates but they can quickly be oxidized and lost as CO and CO₂, creating reducing conditions. This will allow the pH to rise to neutral or slightly basic values. The drop in TOC and increase in pH in Leachate III was accompanied also by a considerable drop in phenols, Fig. 14. This figure also shows that the phenols level decreased from 3800 ppb to

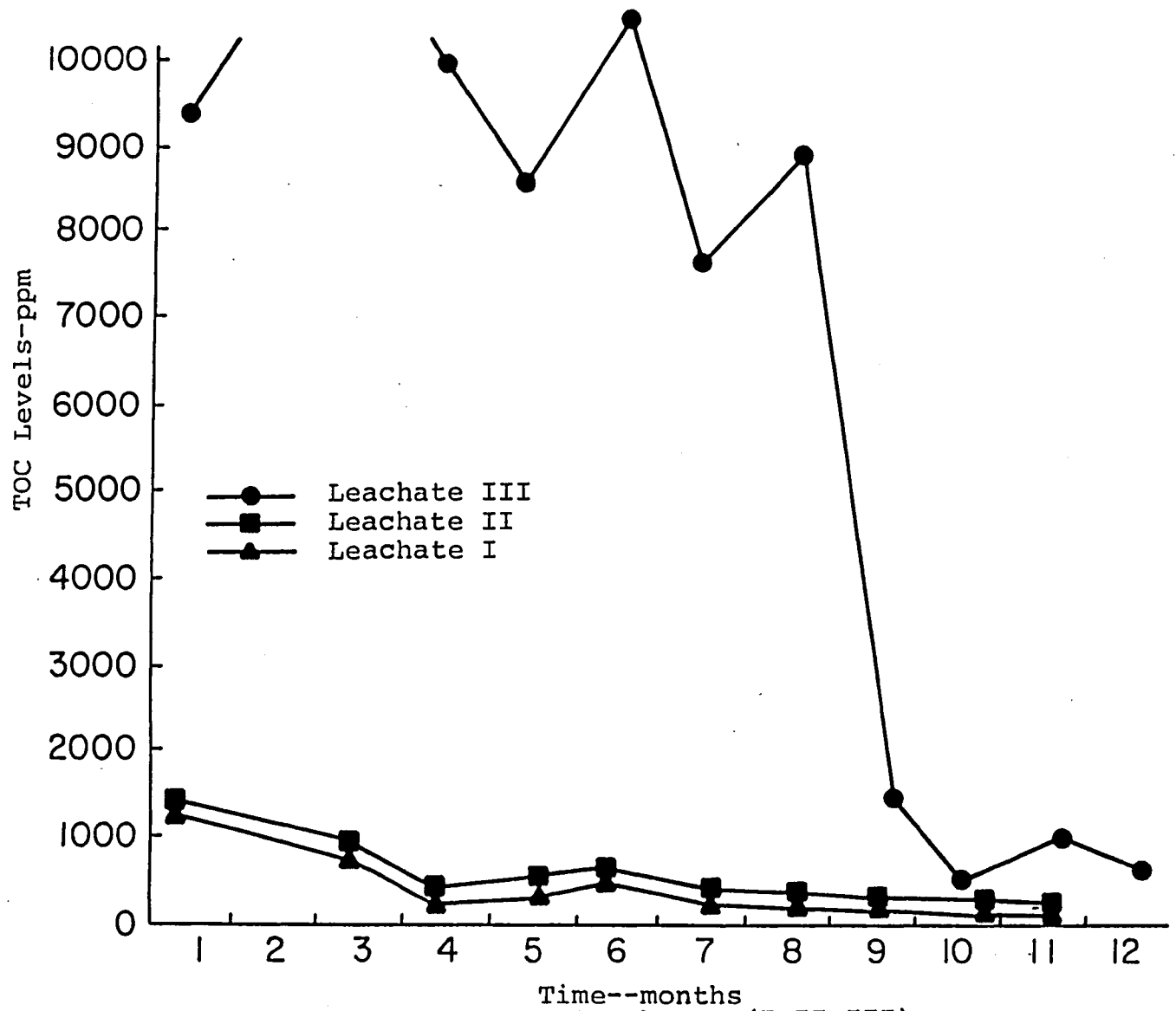


Fig. 14. TOC concentrations found in three leachates (I,II,III) over a year's time.

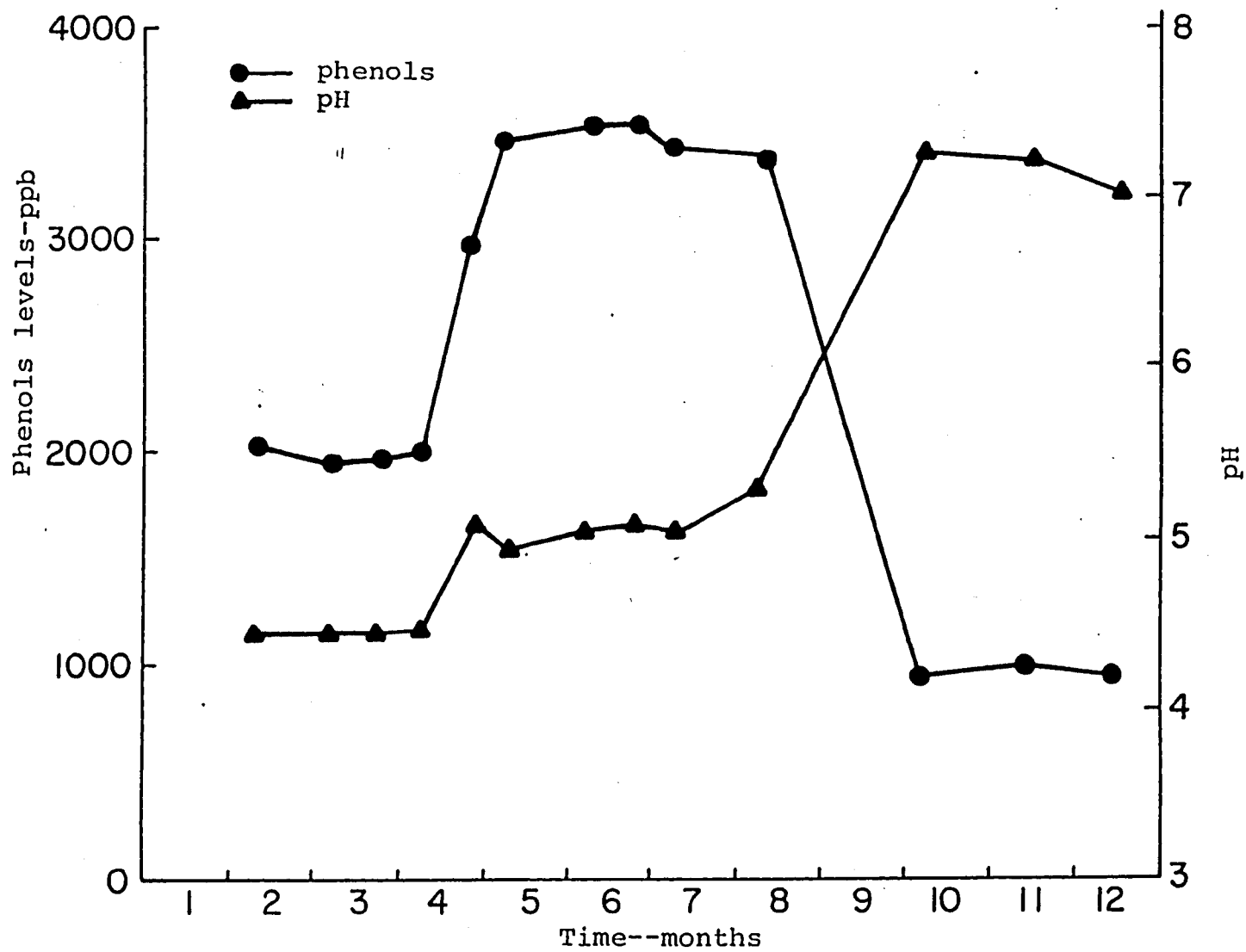


Fig. 15. "Total" phenols concentrations in Leachate III over a year's time.

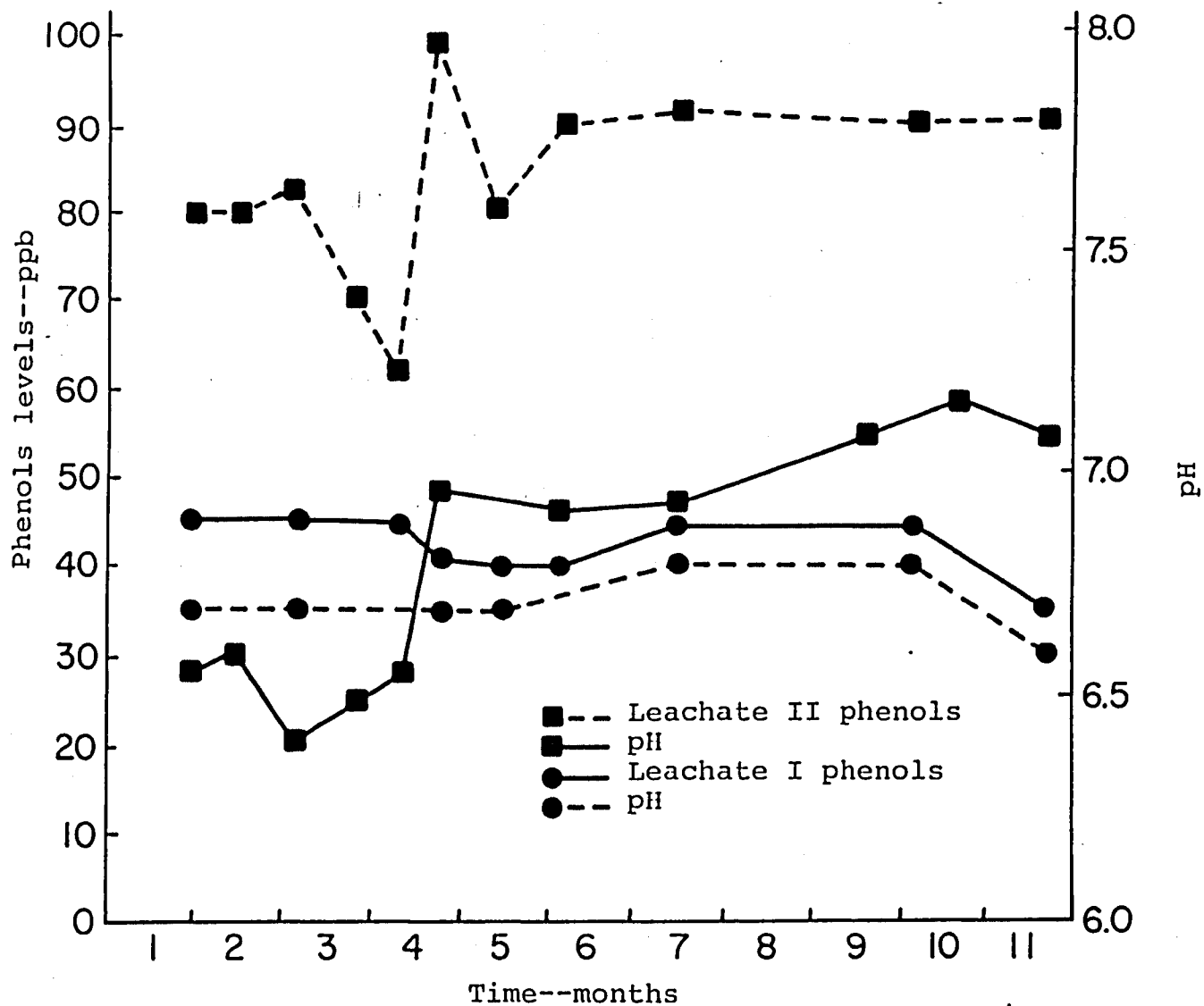


Fig. 16. "Total" phenols concentrations found in Leachates II and I over 11 months.

less than 1000 ppb in Leachate III, a considerable loss compared to the ones made by Leachates II and I. Leachate II maintained an almost steady state in "total" phenol level over the 12 month period, together with about a 0.5 pH unit rise over the same period which indicates further loss of acidic groups. Leachate I also had a fairly steady pH and "total" phenols level over the year's period, indicating a much older, weaker and stable leachate than the other two.

It may be important to consider that the drop in phenols seen in the younger Leachate III may not have caused the pH to change but rather the opposite; that is, that the sudden pH change ionized so many molecules of phenols that they became very reactive towards other organics or even among themselves. Evidently, some microbiologically induced transformations of phenols also became much more active upon the pH rise.

In spite of weak acidic properties, Leachates II and I still had fairly large levels of phenols at the end of the year. Even though the "total" phenols amounts were in the ppb range, they were about 40 to 90 times higher than the drinking water standards permit. It is evident that phenols can either statically (without reacting) or dynamically (with loss and regeneration) maintain themselves at toxic levels over long periods of time in municipal landfill leachates, varying with pH and TOC levels.

As pointed out earlier, the "total" phenols figures obtained by the use of the 4-aminoantipyrine method are at best very conservative, since many phenols are undetected by this procedure or do not have the same absorptivity coefficient of phenol. In view of this problem and for lack of better methods to identify some of the prevalent phenol in the leachates, GLC was used to separate some phenols in these leachates. Keeping in mind that GLE is only sensitive at the ppm level, several pre-concentration techniques were employed. These included extractions with ester and ethylether, and distillation. In all cases large amounts of other low molecular weight organics were extracted which seems to have similar partition coefficient and boiling points to phenols. Thus, large background peaks were produced in the chromatograms which probably buried small phenols peaks. Chromatograms of the analysis of Leachates II, I, and III using the NPGSB+H₃PO₄ on Anakrom column were made. The separatory column is the least susceptible of the columns tried to other organics in the leachates and allows the elution of phenols after the large background peaks. Analyses of phenols in lateral Leachates II and I are shown in Figs. 17a and 17b. Other analyses at much lower attenuations were made but no possible phenols peaks were detected. Figures 18a and 18b compare the natural Leachate III and its distillate. In both cases

6'x1/8" S.S. 5% NPGSB + H₃PO₄
on Anakrom A 90/100 mesh at
135°C. N at 35 cc/min; 2 μl
sample size.

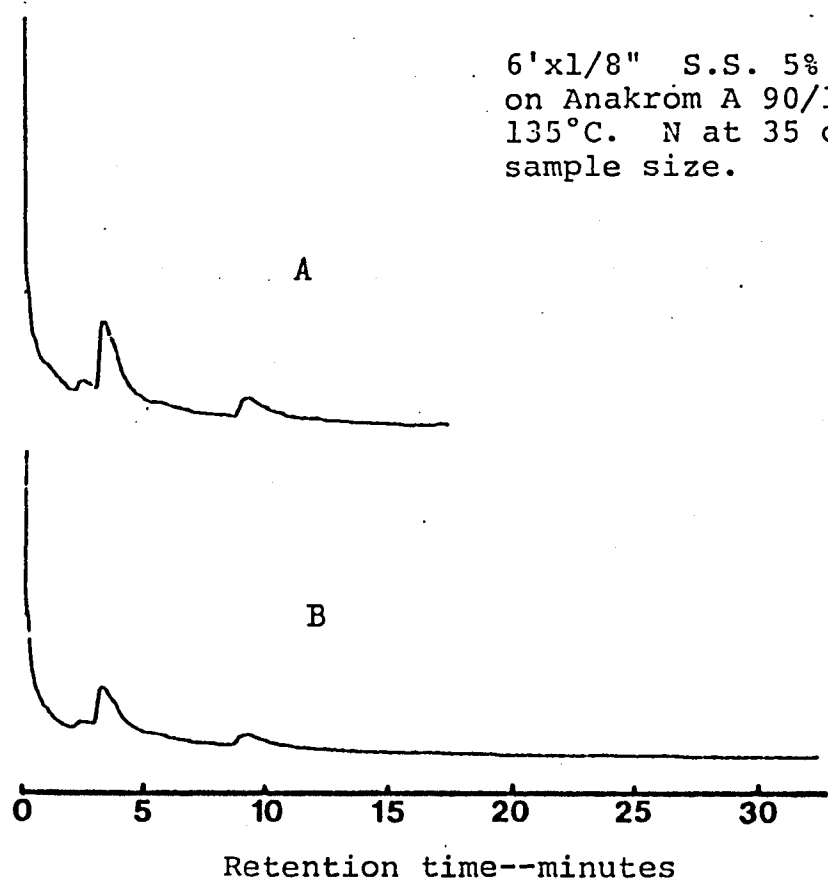


Fig. 17. Chromatograms for (A) natural Leachate II
and (B) natural Leachate I.

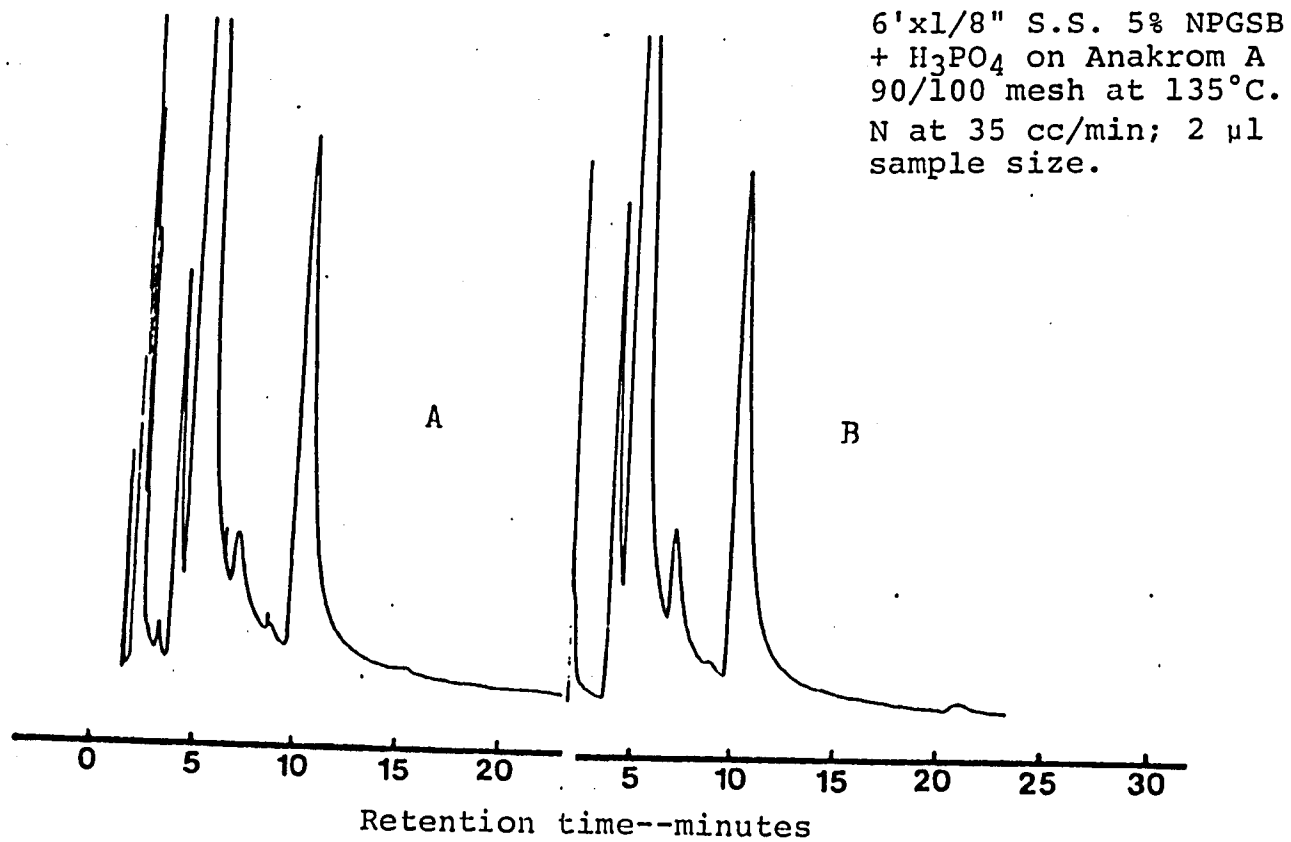


Fig. 18. Chromatograms of (A) Leachate III distillate
and (B) Leachate III straight.

large background peaks can be seen. A close look at Leachate III chromatograms shows a p-cresol peak and traces of phenol. These analyses were made on Leachate III taken on 4/30/79. These two peaks subsequently decreased from about 9 ppm for p-cresol and about 1 ppm for phenol on this date, to about 1 ppm for p-cresol and traces of phenol on Leachate III collected 11/22/79, Figs. 19, 20, and 21. The detection of p-cresol in Leachate III at such large levels indicates as thought previously that the 4-A method can give results which are very low estimates on the true phenols levels in leachates. Leachate III is a case in point with "total" phenols levels as much as four times those reported via the colorimetric 4-A method.

It is evident from the tests conducted that large levels of organics in leachates do not allow or severely hinder the concentration of extraction of phenols from these leachates. Leithe (1973) lists several extraction and concentration techniques used in air stabilized water stream effluents. No mention is made of the types of concentrations of organics allowable for these methods to work. The leachates used in this study were air unstable, and there are no data on reactivities, if any, or any reactivities with the extracting agent used. Extractions almost always produced unacceptable results in terms of lack of effectiveness in concentrating phenols and/or

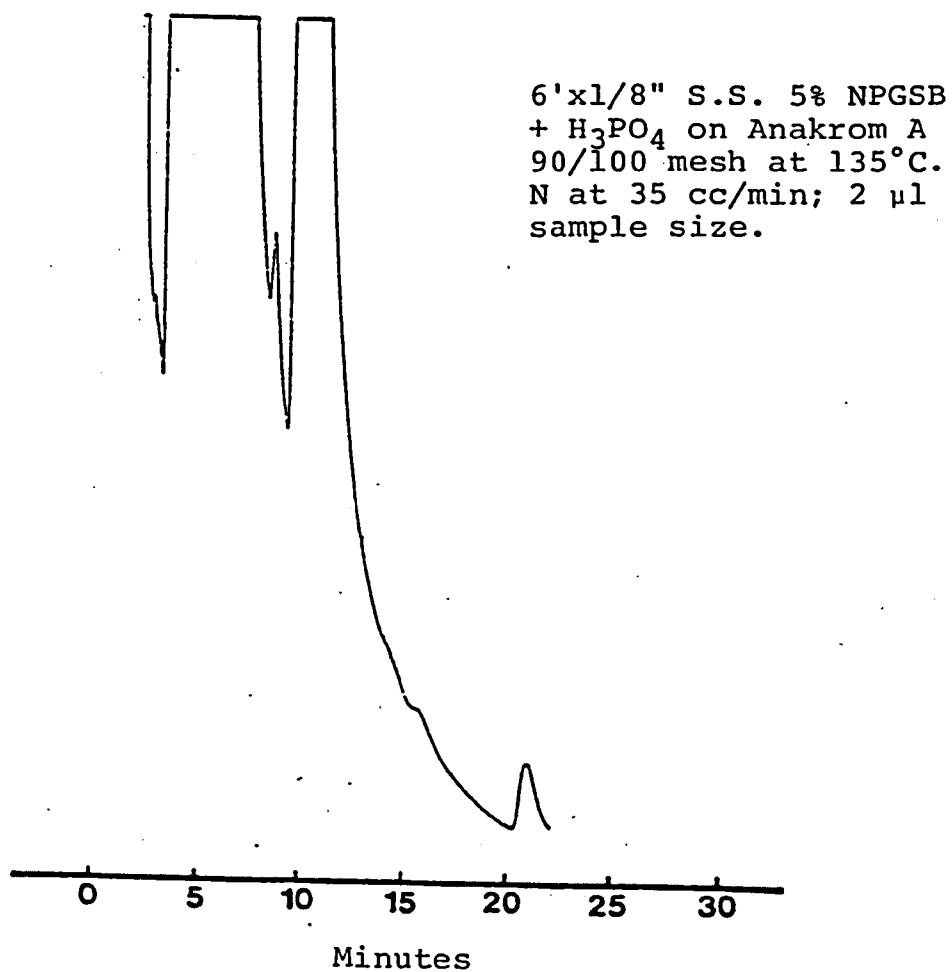


Fig. 19. Chromatogram of natural Leachate III collected 4/30/79.

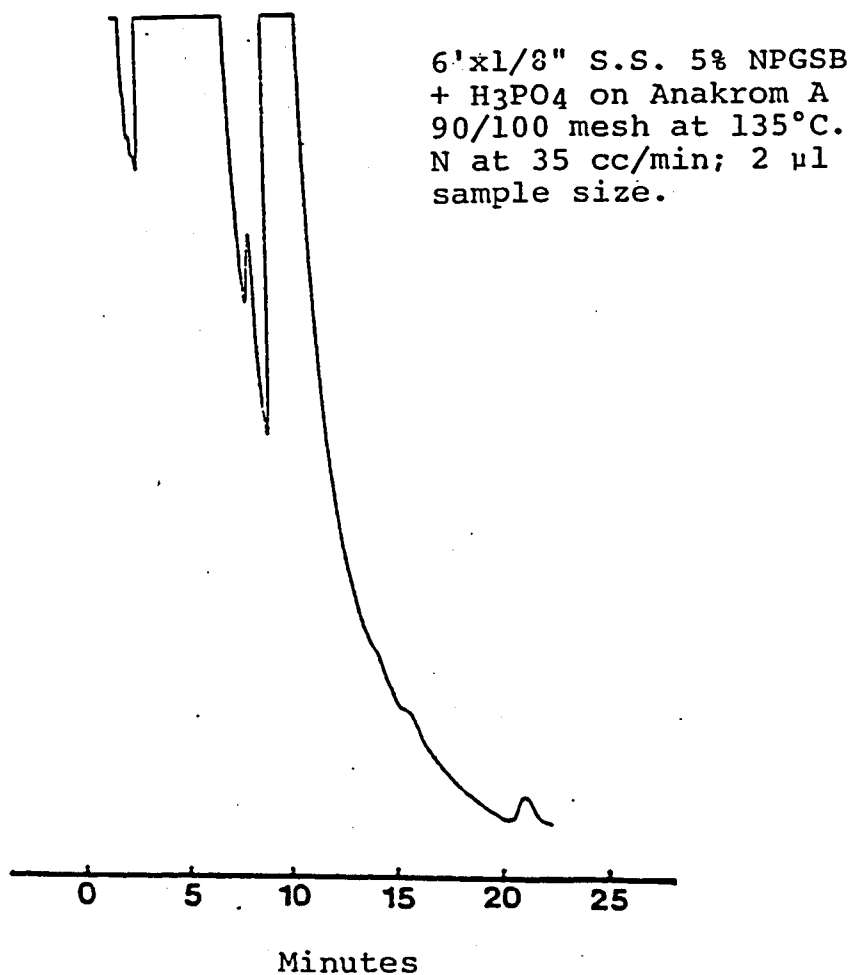


Fig. 20. Chromatogram of natural Leachate III collected 7/22/79.

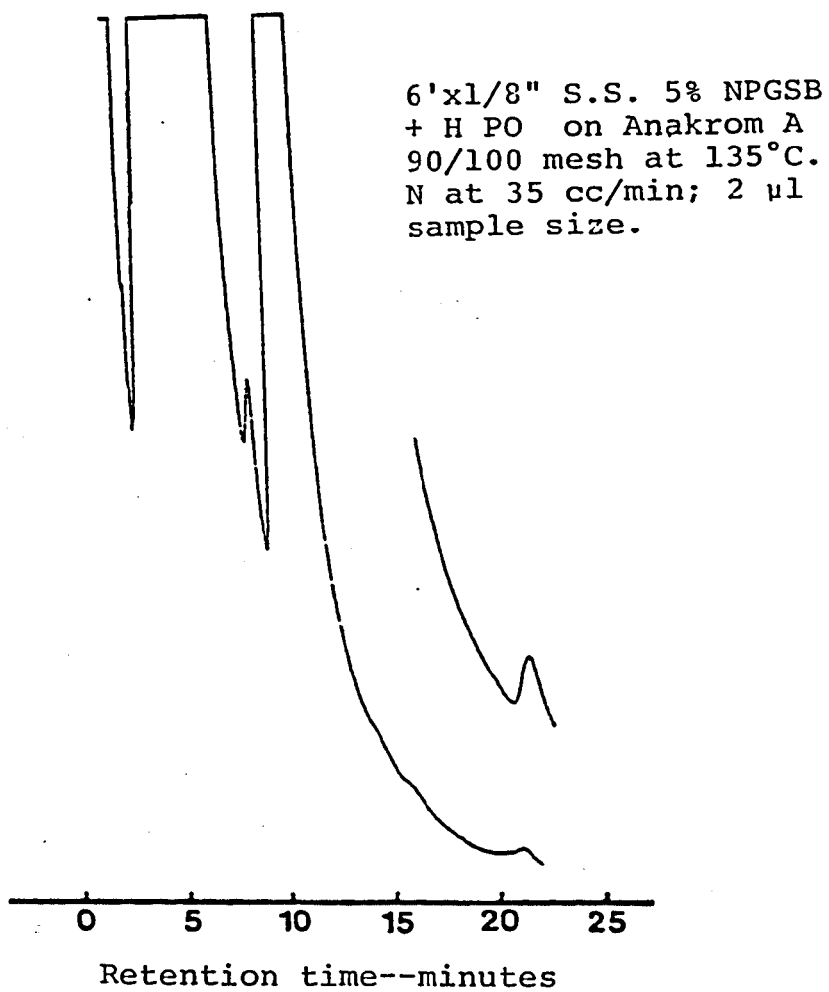


Fig. 21. Chromatogram of natural Leachate III collected 11/22/79.

producing reproducible results. Further improvement in separation-extraction techniques of phenols from anaerobic leachates are needed to understand municipal landfill leachate phenols more effectively.

Phenols-enriched Leachates

Since the natural phenols levels were so stable in all three leachates over the year's period and varied only with TOC and pH, enriching of the three leachates was done as a means of following different phenol behavior in leachates. Levels of 100 ppm were used in the leachates. The 100 ppm level was used since it was the maximum concentration to which the soils were exposed in the isotherms. After a 1:10 dilution of phenol stock solutions with leachates, six new leachates of slightly lower TOC levels by essentially the same pH values and much larger phenols levels were acquired. This fact would hopefully insure mostly chemical reaction of leachates with phenols since phenols are highly toxic to microorganisms. The new leachates in 200 ml aliquots were bubbled with air and kept under CO₂ in two separate containers for about 15 days. The leachates used for this particular study were collected 6/07/79. Figures 22, 23, 24, 25, 26, and 27 were prepared from the data of this study. Aeration worked well as expected, since Tables 11 and 12 show considerable drop in the TOC and natural phenols levels of the three leachates

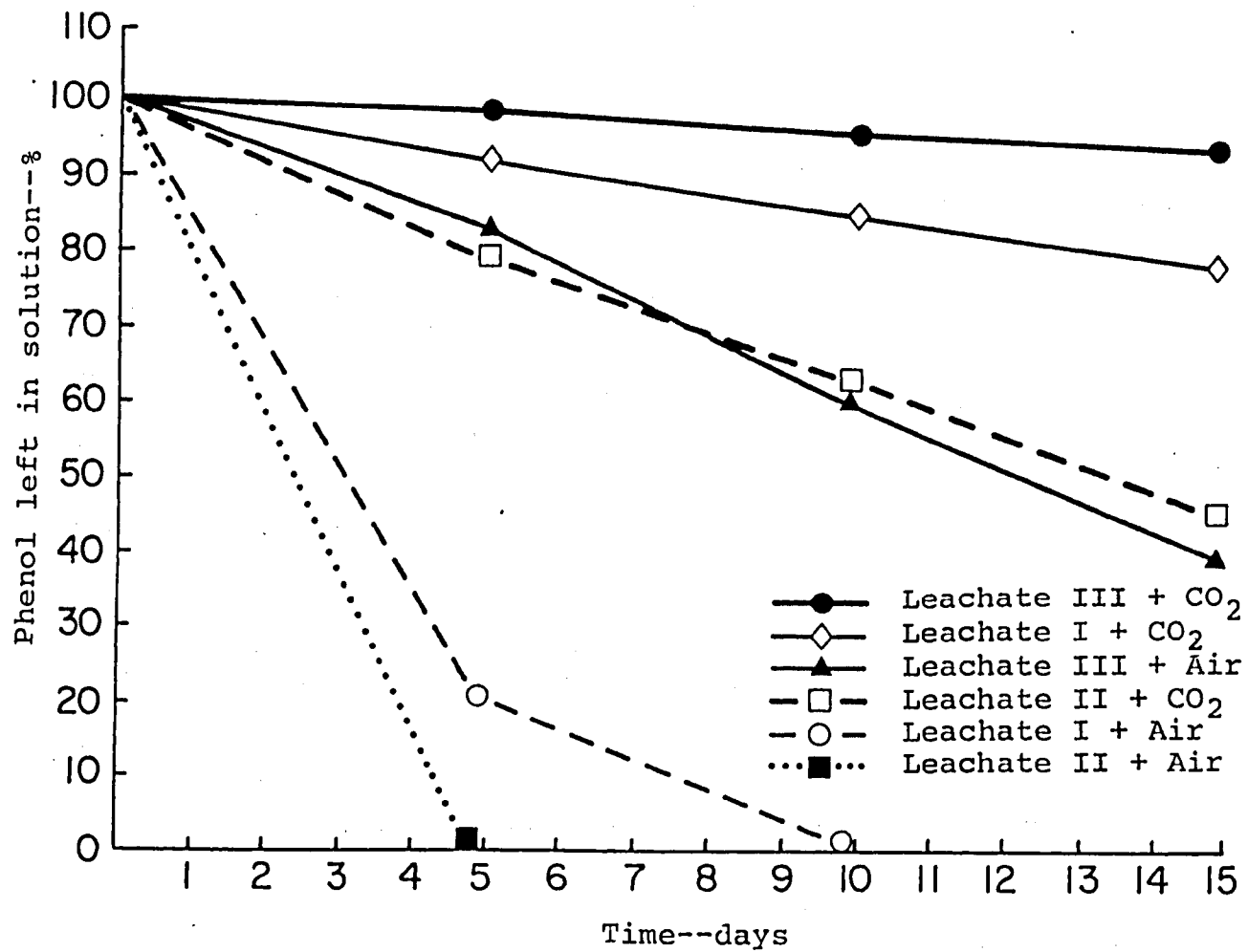


Fig. 22. Three leachates enriched with phenol (105 ppm) and bubbled under air and CO₂.

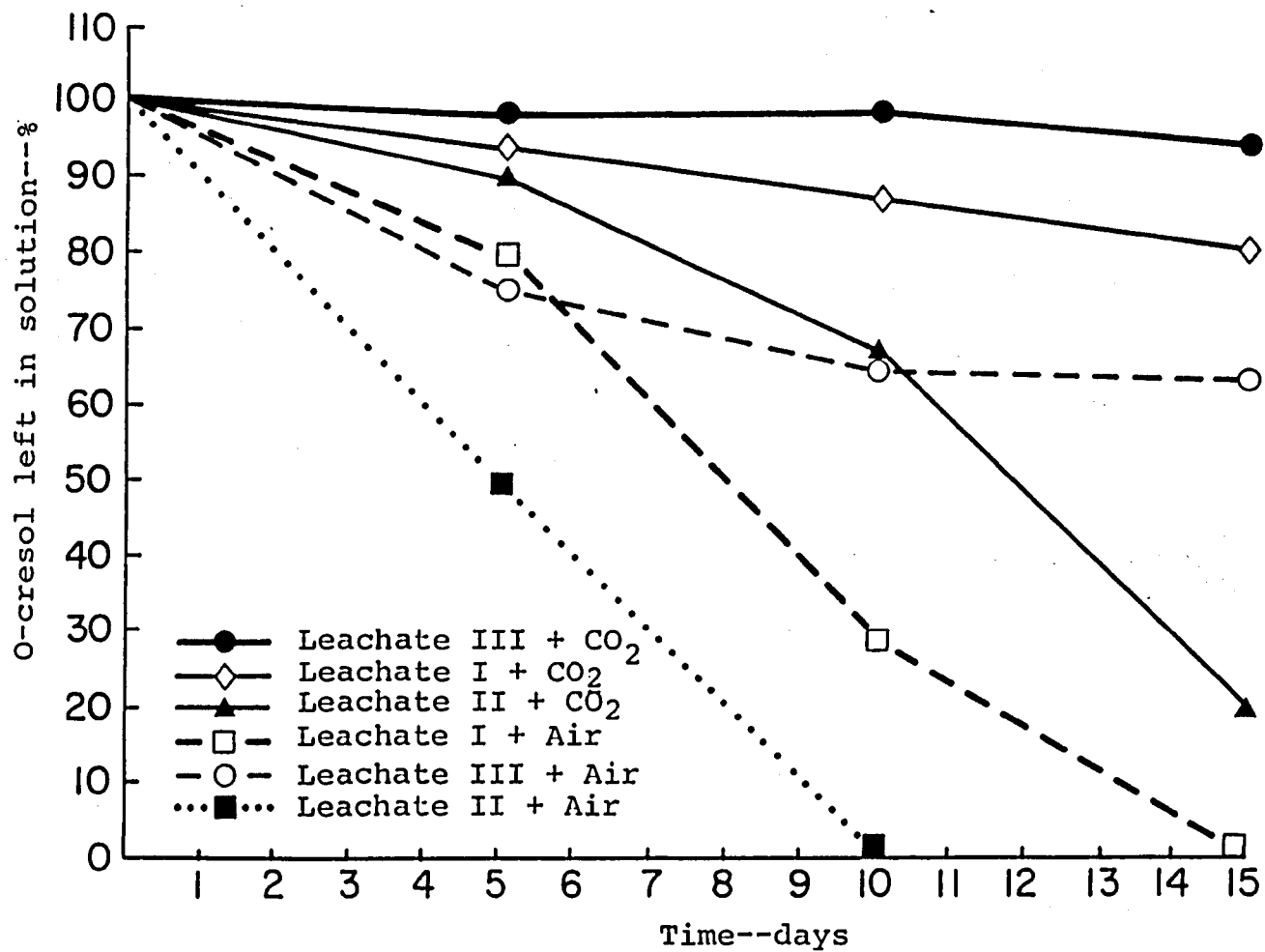


Fig. 23. Three leachates enriched with O-cresol and bubbled under CO₂ and air.

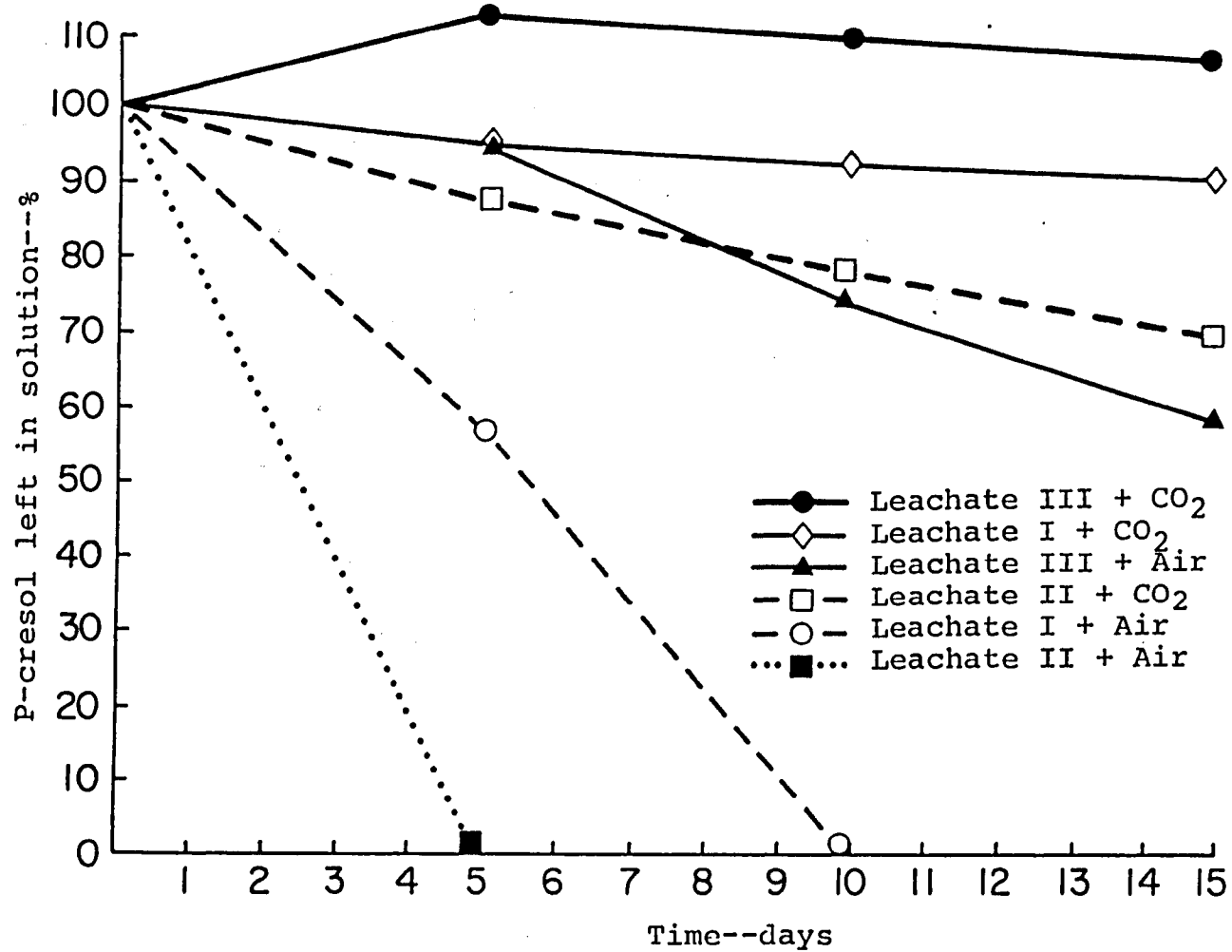


Fig. 24. Three leachates enriched with P-cresol and bubbled under CO₂ and air.

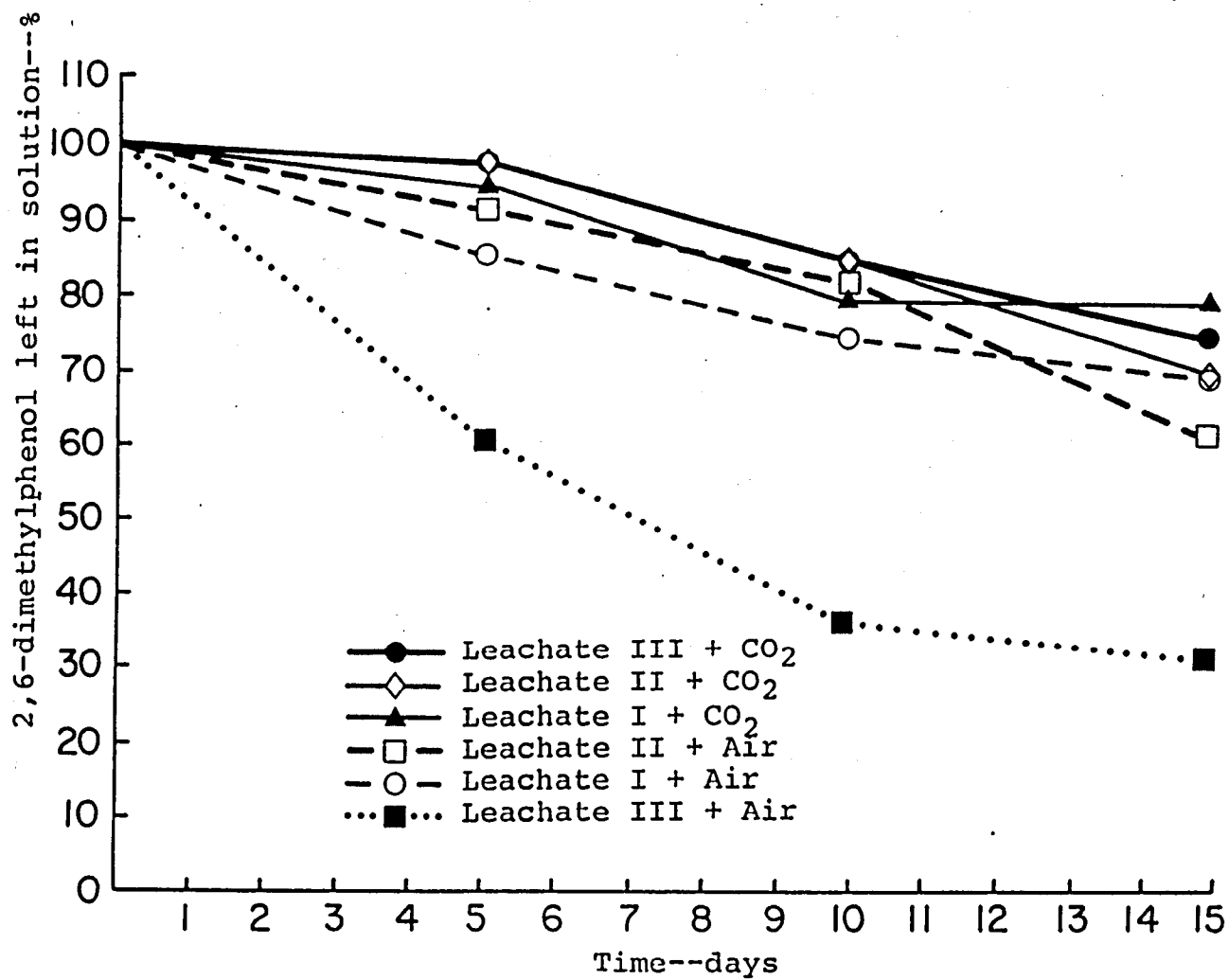


Fig. 25. Three leachates enriched with 2,6-dimethylphenol and bubbled under CO₂ and air.

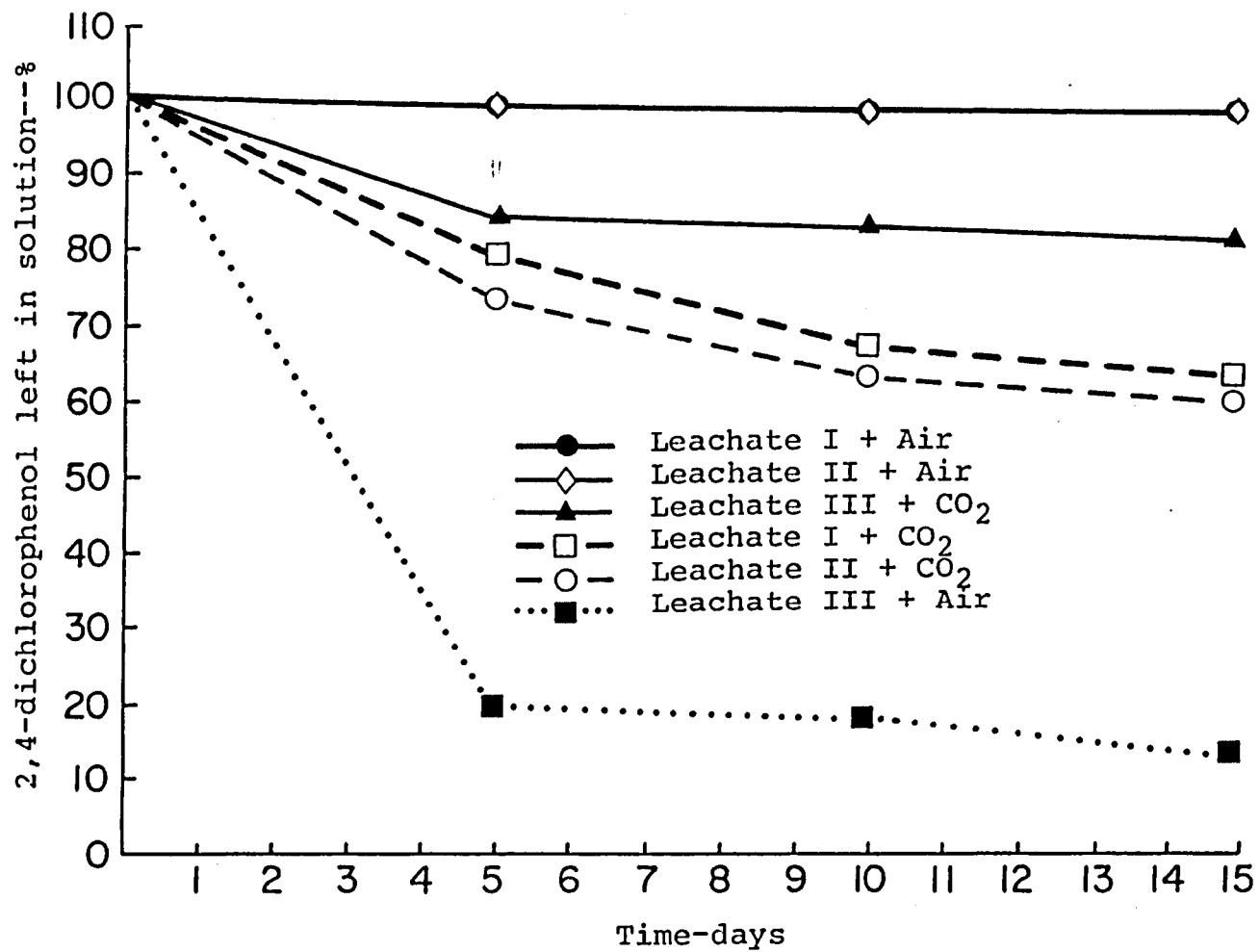


Fig. 26. Three leachates enriched with 2,4-dichlorophenol and bubbled under CO₂ and air.

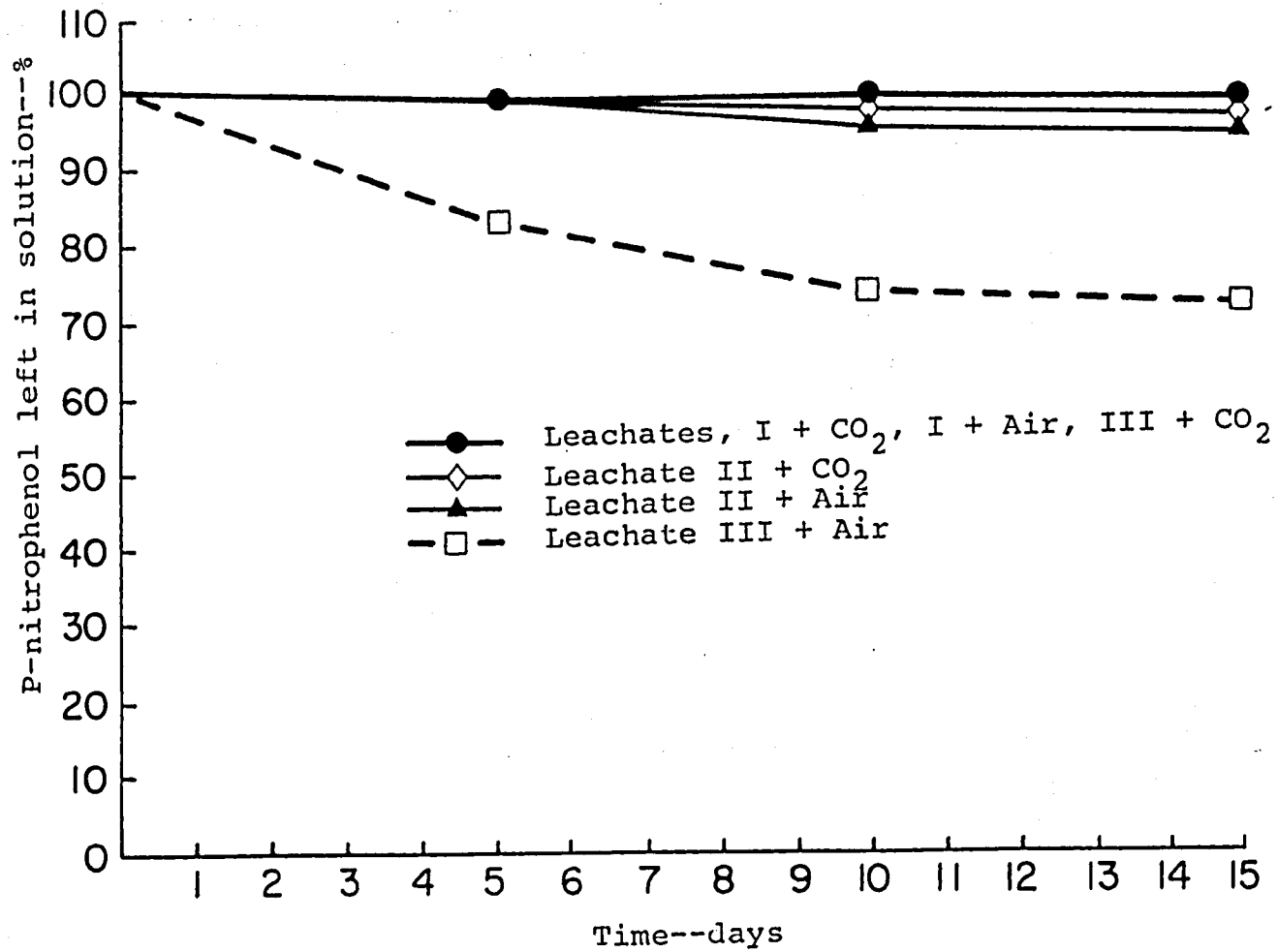


Fig. 27. Three leachates enriched with P-nitrophenol and bubbled under CO₂ and air.

Table 11. The effect of aeration with CO₂ and air on the leachates enriched with six phenols.

Leachate	Starting Values		Values after 15 Days	
	pH	TOC-ppm	pH	TOC-ppm
<u>Bubbled with CO₂</u>				
I	6.2	400	6.2	415
II	6.2	510	6.2	522
III	5.2	8431	5.1	8400
<u>Aeration with Air</u>				
I	-	-	9.3	350
II	-	-	9.3	361
III	-	-	5.2	5530

Table 12. Levels of "total" natural phenols before and after air bubbling.

Leachate	Starting Values	ppb	Values after 15 days
I	47		33
II	83		54
III	3400		540

after 15 days of aeration. Figures 22, 23, and 24 show the levels of naturally occurring phenols such as monophenol, and o-cresol and p-cresol, when added to old leachates in large levels can be reduced very quickly if aeration is initiated. However, Leachate III reacted with phenols at a slower rate than Leachates II and I. Perhaps this was due to the large levels of these phenols in equilibrium prior to enrichment. Leachate II reacted with phenols more rapidly than Leachates III and I, both when CO₂ and air bubbled systems were used. Under CO₂ Leachate III was almost completely unable to react with any of these three enriched phenols. In contrast, when air was used, phenols such as 2,6-dimethylphenol, 2,4-dichlorophenol and p-nitrophenol decreased markedly with time in this leachate. Further examination of these figures illustrates that the aerated Leachates II and I reacted poorly with all these three phenols; particularly with p-nitrophenol, with which they did not react at all over the 15-day period of exposure. The least reactive of the six phenols was p-nitrophenol. However, its unreactiveness may prove that dimerization of highly polar phenols such as p-nitrophenol does not lend itself to reactions with other organics in MSW leachates and perhaps not even with soil organic matter. Therefore this phenol is quite stable requiring more drastic measures to immobilize it. Furthermore, with p-nitrophenol

the unreactivity indicates that no apparent biological mechanisms were involved in the disappearance of phenols from leachates and soil solutions since it is one of the least toxic phenols studied and was used in lowest amounts (molewise) due to its high molecular weight. The next reactive phenols were the chlorinated and dimethyl phenols which are synthetic in origin and seem to be as relatively unreactive with leachates as they were with the soils. The simple monophenol molecule proved to be very reactive with leachates, in contrast to its behavior with soils. Ortho and para cresols were again very reactive here with Leachates II and I together with monophenol.

In an attempt to correlate the disappearance of these phenols to some leachate properties, the three leachates were analyzed for total humic and fulvic acids. The results are reported in Table 13. The values obtained for Leachate III had high variability and thus are not considered to be as reliable as the values obtained for Leachates II and I. The large humic and fulvic acid variations in Leachate III can be attributed to tank settlements and/or to a very high reactive organic phase that does not allow adequate precipitation and separation of the humic and fulvic acid fractions. Further modification from the one reported in Appendix C is needed. Extraction procedure of humic and fulvic acids from young, highly organic, air

Table 13. Concentrations of organic carbon (TOC), humic and fulvic acids in three MSW leachates collected under CO₂.

Leachate	pH	Organic Carbon					
		Total Sources		Humic Acid		Fulvic Acid	
		Average*	Range	Average*	Range	Average*	Range
I	6.3-6.4	359	320-398	136	116-156	99	52-146
II	6.3-6.4	481	440-522	210	166-264	176	122-230
III	5.2-5.4	8535	8312-8758	844	432-1256	6193	5724-6662

*Averages of at least three replicates: TOC represents 5-month averages and humic and fulvic acids 2-month averages.

unstable leachates is still under study and to date has not been reported in the literature. The large humic acid levels in the MSW leachates seem to play an important role in the phenols disappearance from solution, Table 13. Leachate III appears to have a larger humic acid value than either Leachates II or I. However, the retention effect that Leachate III had on at least three phenols indicates that the humic acids must indeed be fairly high and reactive, or that the fulvic acids, which comprise better than 70% of the TOC, are reactive enough to markedly influence interactions with methylated, chlorinated and nitro phenols. Since no finite humic and fulvic acids formulas have been identified, one may logically predict that these acids occur in a variety of forms, some of which are more reactive than others and some specifically more reactive to certain phenols than others. It is evident that organic systems such as MSW leachates have the ability to react chemically with and remove large levels of enriched phenols from leachate solutions. It may follow that large levels of organic matter in the soil will aid in phenols retention in soil profiles since humic and fulvic acids are an indigenous component of all soils. Unlike soils, leachates are fast changing, extremely dynamic systems, making them very difficult to quantify and qualify chemically. These effects may very well aid in the development of the humic

acid model presented by Schnitzer and Khan (1978) who describe these acids as being formed from one ring phenols, held together by fast-forming bonds such as H-bonding, Van Der Waal forces, and ion exchange, rather than slow forming catalyzed condensation or polymerization reactions. Even though the use of monohydroxyphenols in the humic acid structures is not generally accepted, the possibility exists that some of the simple phenols used in this study, when at large levels, could become part of the structures of these acids in the very dynamic leachate systems. This may be one way to explain the phenols disappearance from the enriched leachate solutions.

Soil Column-leachates Studies

The isotherms and leachates enrichment studies were extended in an attempt to follow the naturally occurring phenols in some leachates through soils and to evaluate phenols attenuation by soils under more natural conditions. It was feared that since municipal solid waste leachates have large levels of inorganic and organic constituents, especially TOC levels, that no significant retention or adsorption of added or natural phenols would occur due to interfering or competing molecules present in these leachates.

The first study of soil columns perfused with MSW leachates involved three soils, Molokai clay, Davidson clay,

and Fanno c. Leachate IIa, collected 3/11/78, described in Table 4 as having 730 ppb phenols and 1890 ppm of TOC was used. Figures 28, 29, and 30 were prepared from data of these experiments during which "total" phenols, and TOC of the elutants were measured each day. The "total" phenols levels from the tank which was under CO₂ constantly, stabilized at 730 ppb. From these figures it can be seen that Molokai clay, followed by Davidson clay and Fanno clay was very effective in retaining better than 60% of the phenols during the first six pore volume displacements. Davidson clay did not do as well as expected with only about 30% of the phenols retained after the sixth pore volume, and Fanno clay shows similar results. Further inspection of Figs. 28, 29, and 30 shows that the TOC levels from the Davidson clay and Fanno clay were about 50%-60% retained throughout the six pore volume displacement. But Molokai clay retained the TOC level by about 40% during the same time. These data indicate that soils act as filters for general organics but that a large portion will finally migrate. Phenols appear to migrate less rapidly than most of the other TOC constituents in leachates.

A second study was undertaken using four soils, Molokai clay, Davidson clay, Fanno clay, and Ava silty clay loam packed as previously described in 10 cm columns. Leachate III was used for this run. It is characterized

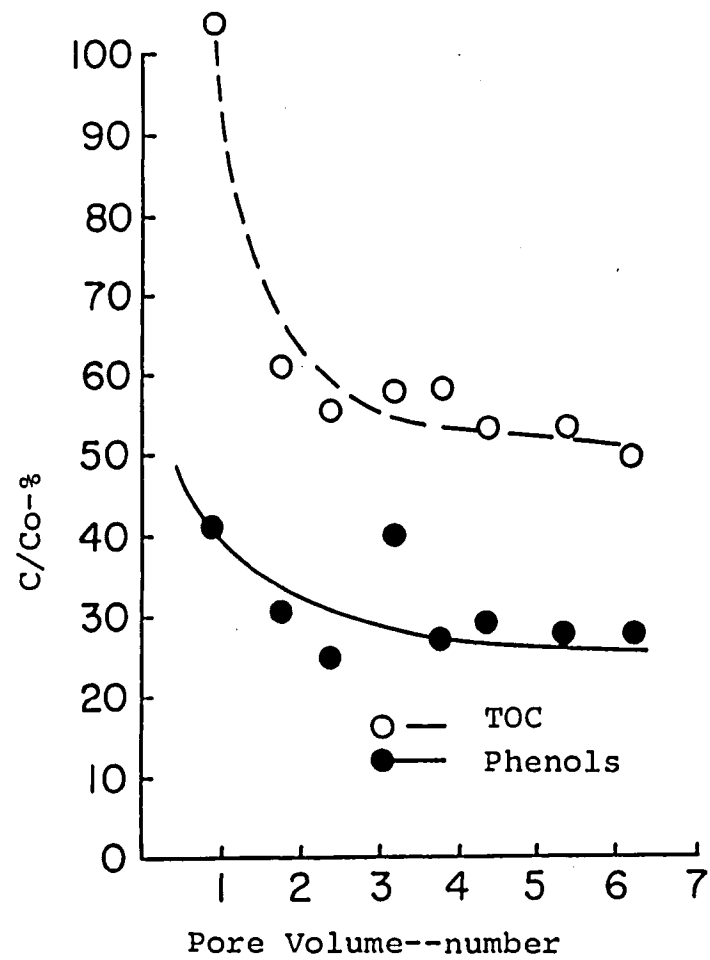


Fig. 28. Retention of phenols and TOC by Molokai clay with MSW Leachate IIa at a flux of 1 pore volume per day.

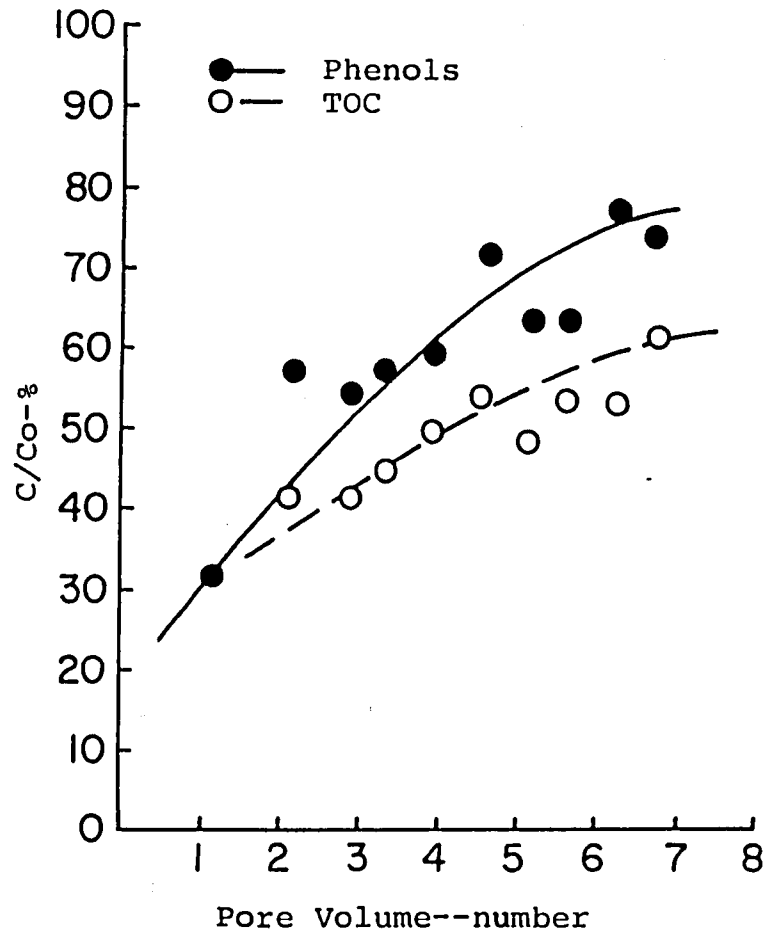


Fig. 29. Retention of phenols and TOC by Davidson clay with MSW Leachate IIa at a flux of 1 pore volume per day.

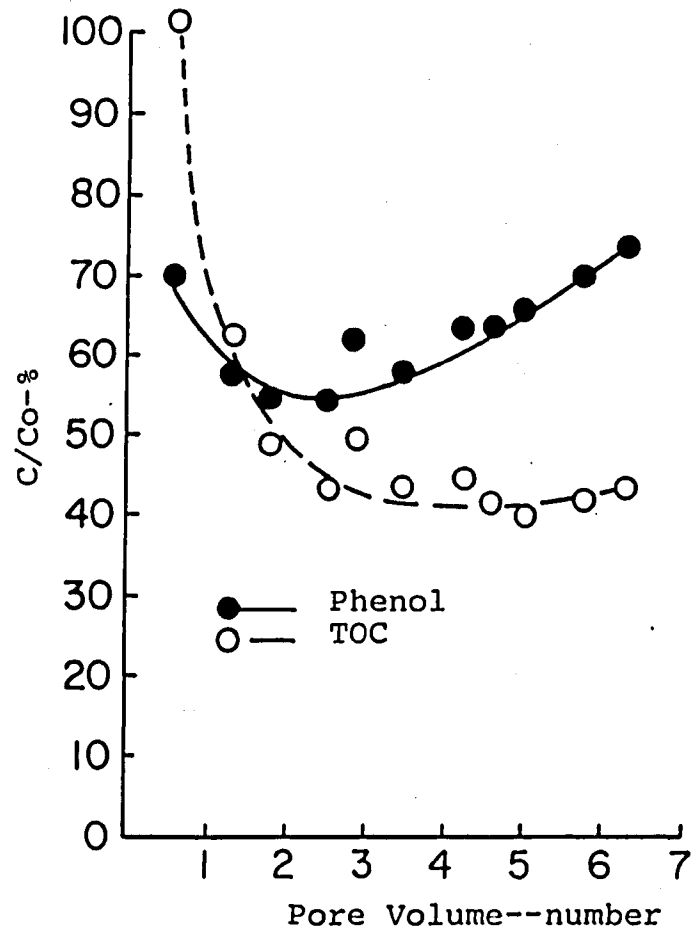


Fig. 30. Retention of phenols and TOC by Fanno clay with MSW Leachate IIa at a flux of 1 pore volume per day.

in Table 11 as having been collected on 5/02/79 and containing the highest levels of all constituents. The results of "total" phenols TOC, and pH analyses of the elutants are reported in Figs. 31, 32, and 33. These figures show that most soils reached the phenols tank levels within 7 PVD except Molokai clay soil. This is in contrast to the previous column study using Leachate IIa in which three soils had kept the phenols levels well below the tank influent levels after the same number of pore volume displacement. Molokai clay was much less able to retain the phenols from Leachate III than Leachate IIa as illustrated in Figs. 28 and 31. The soil column TOC levels of this last study were very erratic for most soils but still show a general trend to climb to the tank concentrations with time. However, like the Leachate IIa study, none of the levels from the soil columns approached that of the tank level at the end of the seven pore volume displacements. Figure 33 shows the pH of the soil column effluents decrease or increase to the pH value of Leachate III tank. The leachate pH influences the soil's buffering capacities. This effect was not as dramatic with the older Leachate IIa which presumably was less buffered, and nearer neutral pH.

At this point it is difficult to assess whether the phenol breakthrough using Leachate III was due to the high TOC level or its high "total" phenols level; since this

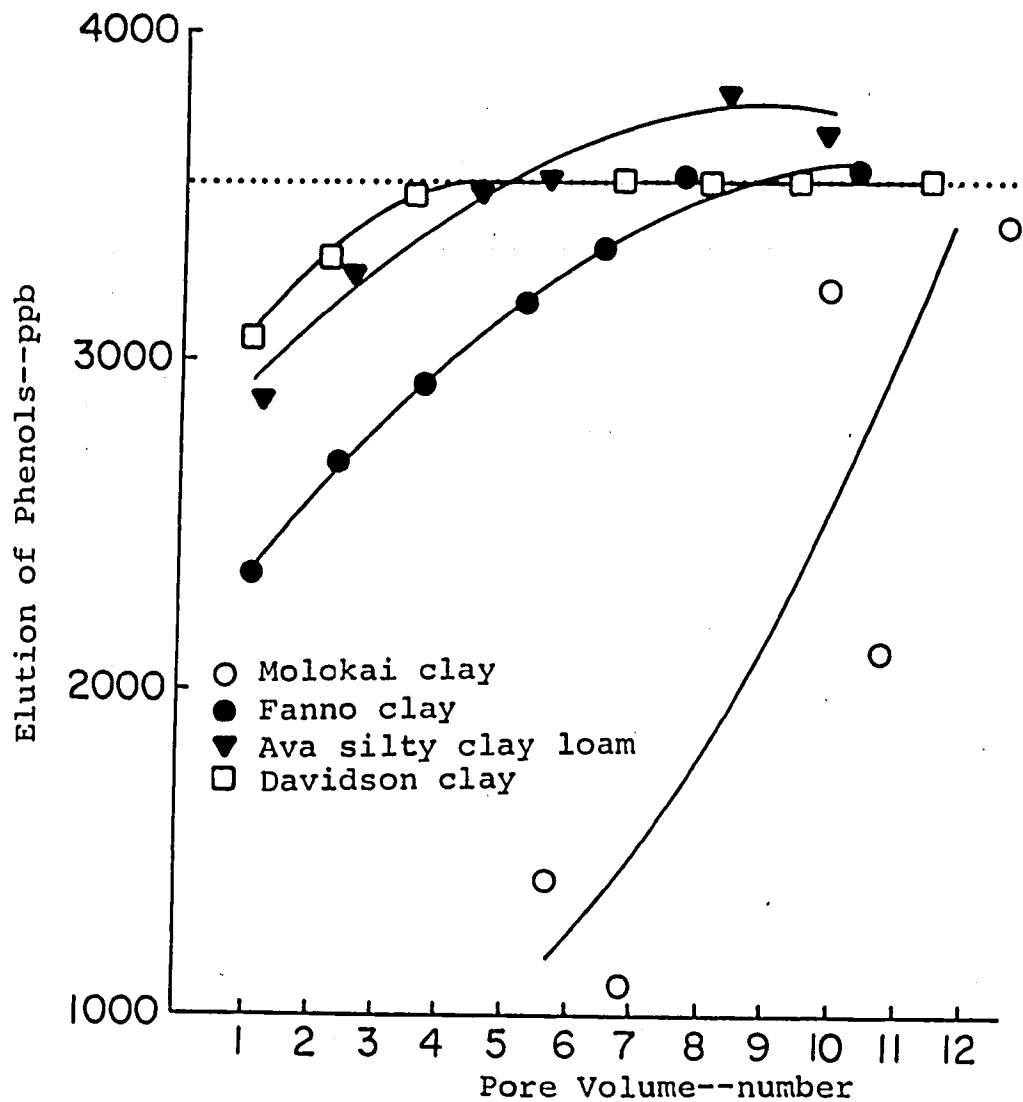


Fig. 31. Retention of phenols by five soils using Leachate III collected 5/02/79 at a flux of 1 pore volume per day.

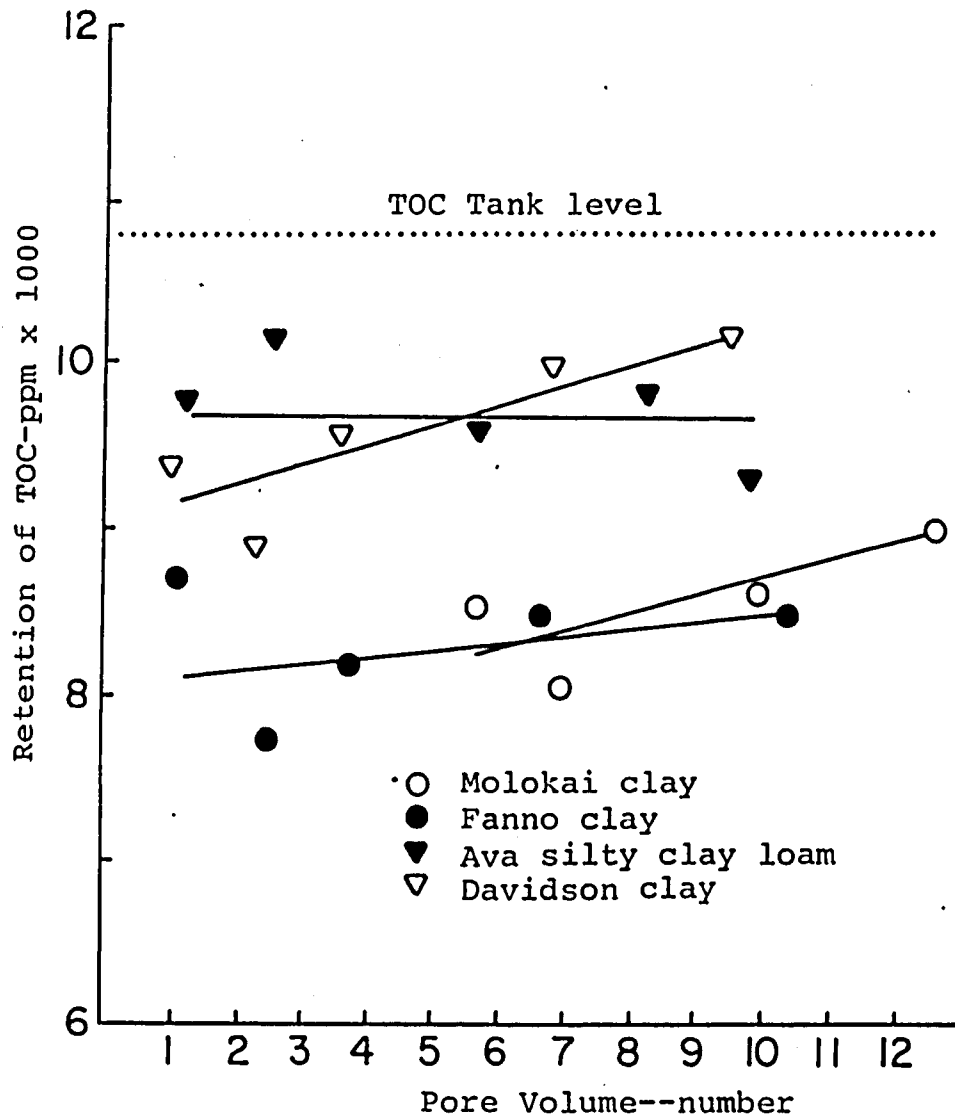


Fig. 32. Retention of TOC by five soils using Leachate III collected 5/02/79 at a flux of 1 pore volume per day.

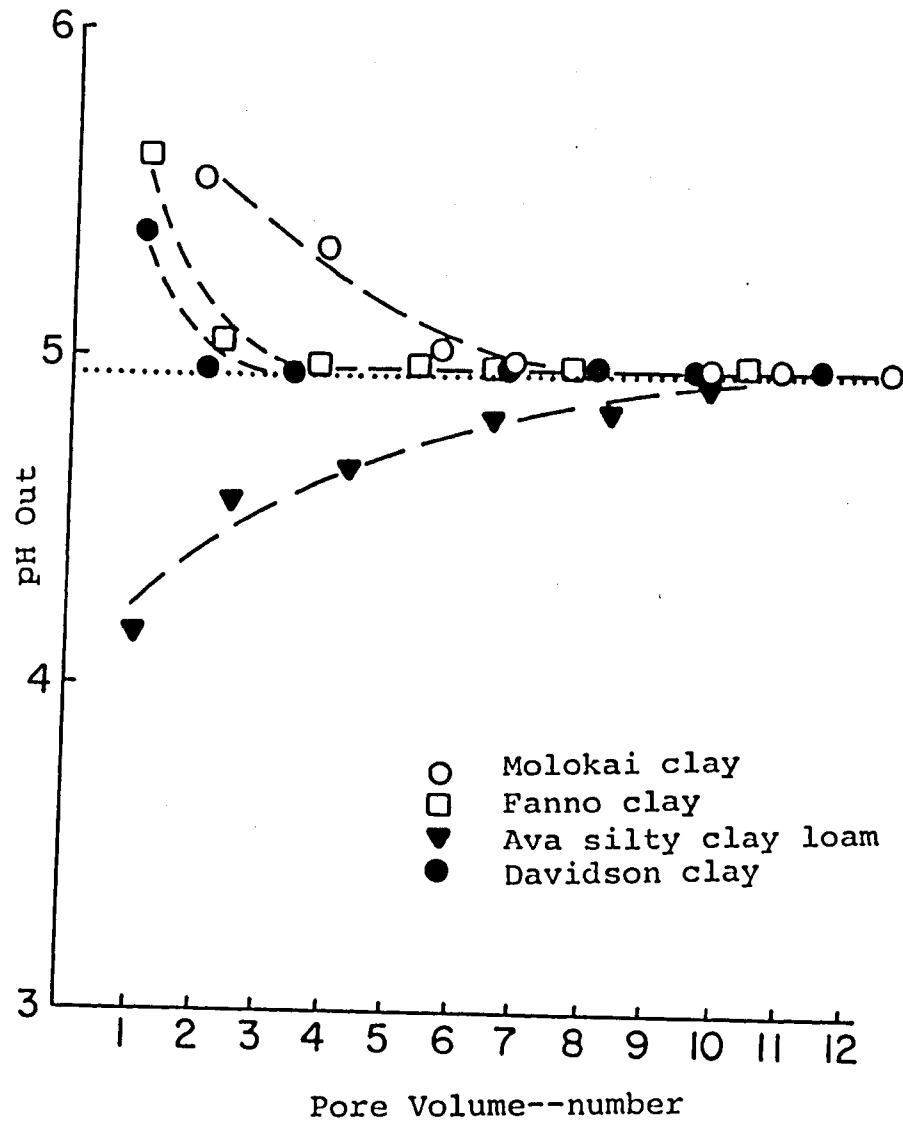


Fig. 33. pH levels of five soil elutants using Leachate III collected 5/02/79 at a flux of 1 pore volume per day.

leachate had both a TOC level 5 times higher than Leachate IIa and "total" phenols about 3 times higher. A good assessment would be that the fast breakthrough of phenols from Leachate III was due to mostly a combination of both high TOC and inorganics levels, allowing rapid saturation of exchange sites, as well as coating any active sites that may help in the chemical change of phenols by soils. In view of the large levels of phenols that soils can adsorb as in the isotherms studies, a difference of about 3 ppm in "total" phenols between the two leachates used would not have produced such large breakthrough differences had the other factors remained the same in both leachates.

Studies of older leachates like IIa enriched with large levels of phenols, in order to compare the levels found in younger leachates like III, are not possible due to the ability of older leachates to react with phenols from solution as reported previously.

Soil Column Phenol-enriched Water Studies

To remove the effect of the other leachate constituents and factors from affecting the adsorption of phenols by soils, another set of column experiments were undertaken using deionized water enriched with phenol and passed through soil columns. The same four soils were again used and the phenol-rich water was passed through the

soils at a flux of 1 pore volume per day. Even after 25 PVD none of these soils allowed the elution of phenol to exceed 0.01 ppm. These results indicate that phenol is quickly adsorbed by all soils tested. Thus, the fluid transportation system in which phenols occur plays a key role in their adsorption by soils.

Following this study another set of soil columns were prepared using the same four soils plus two additional ones, namely; Mohave-Ca clay loam and river bottom sand. This time the deionized water was enriched with 104 ppm of phenol, and the flux was again 1 PVD/day. The data for Davidson clay, Ava silty clay loam, Fanno clay, and Mohave-Ca clay loam, Figs. 34, 35, and 36, indicate that these soils behave similarly at this phenol level. However, the Davidson clay and Ava silty clay loam tended to retain phenol better than the other two soils. There was a fairly steep rise in migration in all soils to about 60%-80% C/co where they reached a plateau, maintaining a rather steady state for up to 12 PVD. At this point the study was stopped. Figure 34 shows a drop in the phenol levels in the column effluents as a result of having stopped the flow for one day before restarting it again. Overall, these four soils show the capacity to retain, change or adsorb 20%-30% of the phenol in the enriched water at a flux of

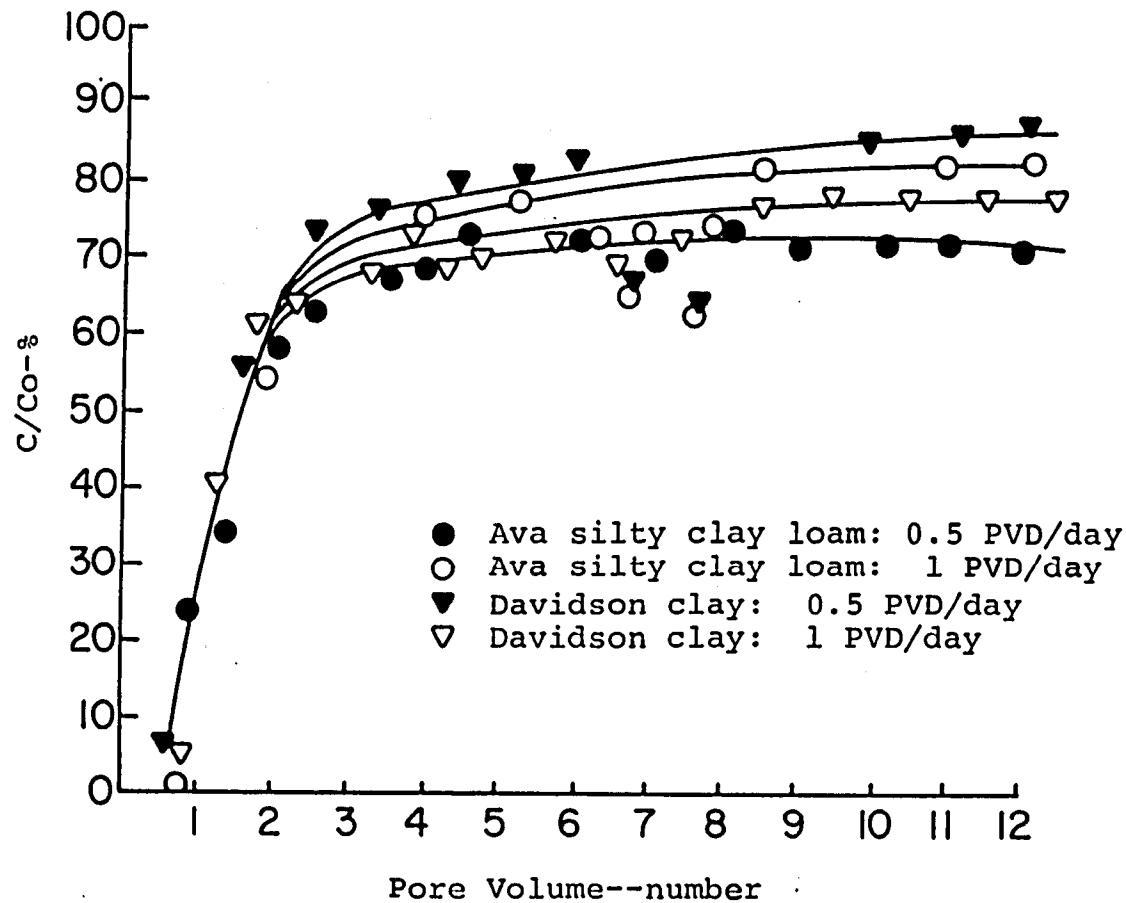


Fig. 34. The effect of Ava silty clay loam and Davidson clay on the retention of phenol in deionized water (104 ppm) at two different flow rates.

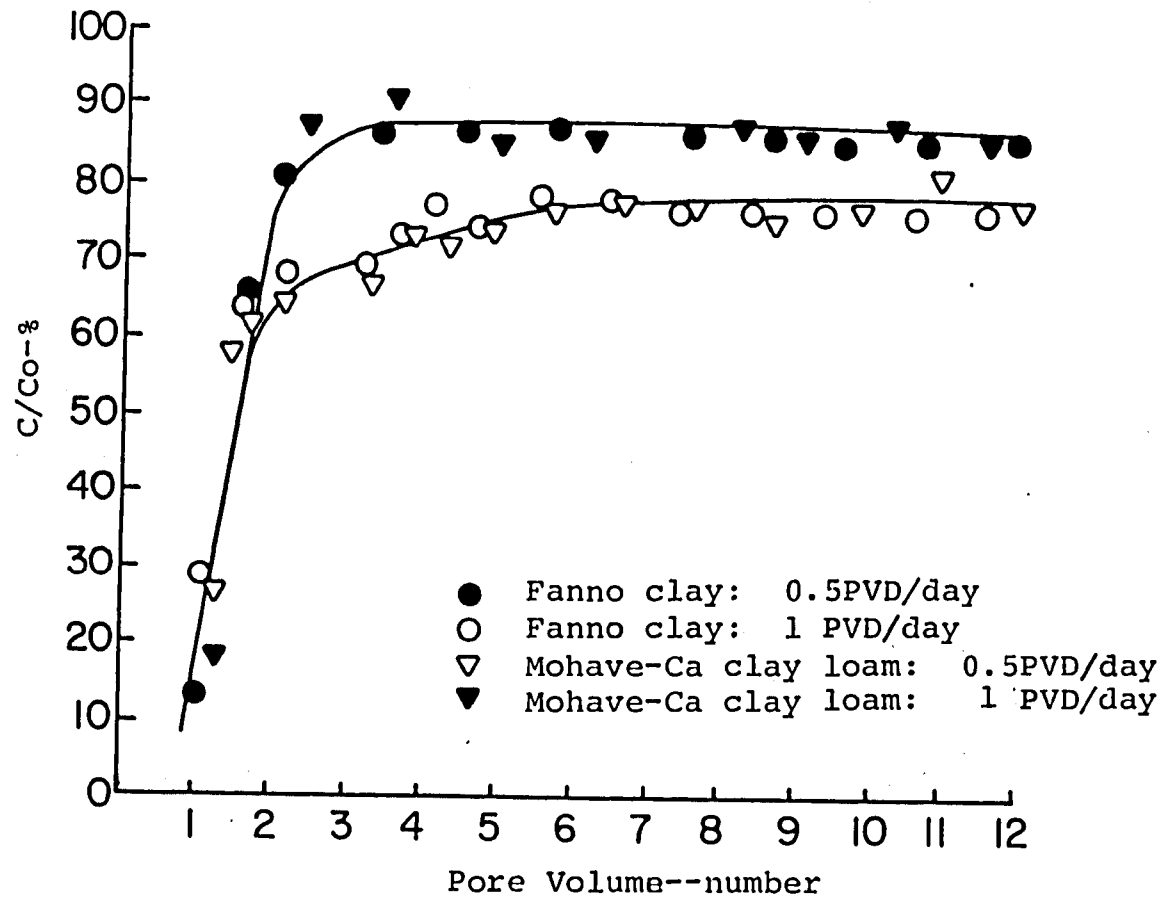


Fig. 35. The effect of Fanno clay and Mohave-Ca clay loam on the retention of phenol in deionized water (104 ppm) at two different flow rates.

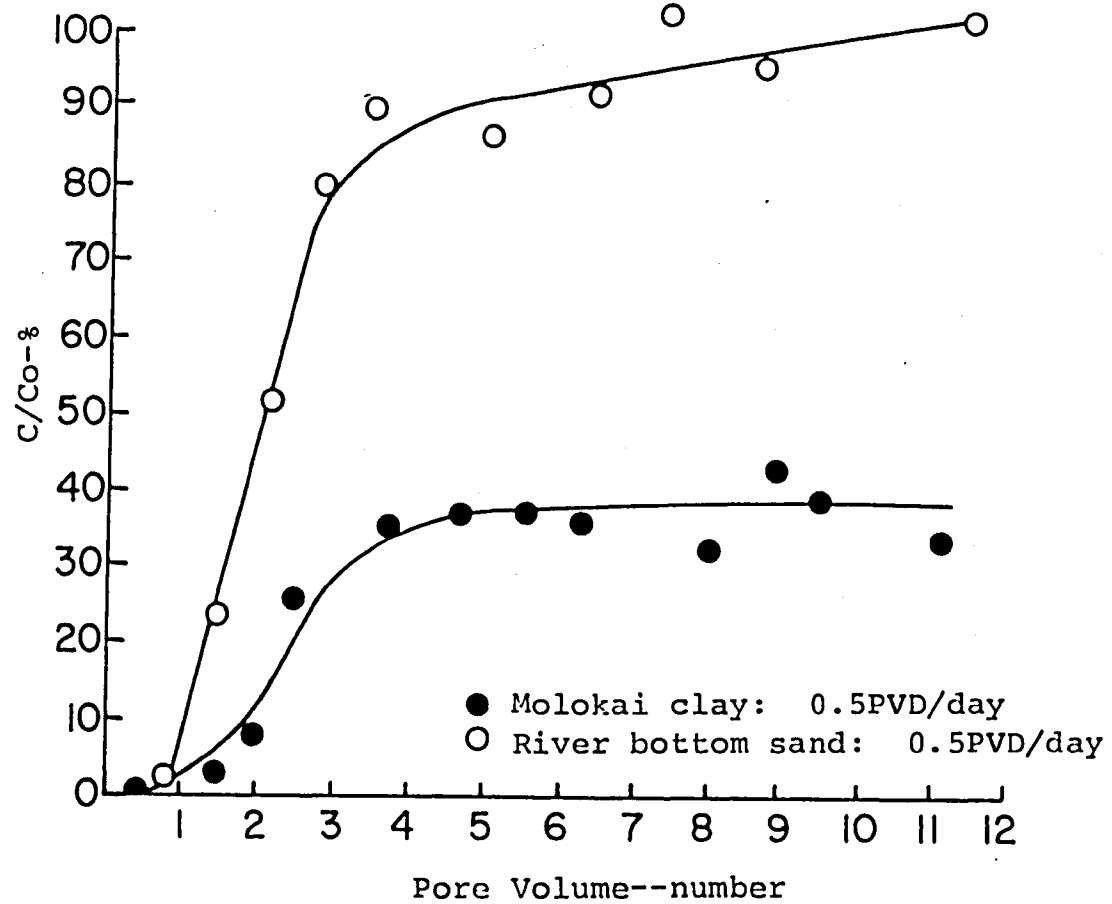


Fig. 36. The effect of two soils on the retention of phenol deionized water at a flow rate of 0.5 PVD/day

1 pore volume per day when no other interfering molecules are present in the leaching solution.

Another experiment designed to verify the effect of flow rate on the phenol retention by soil was carried out using the same soils with Molokai clay and river bottom sand at 0.5 pore volume displacements per day, Figs. 34, 35, and 36. The plotted results as pore volume number versus C/C_0 clearly indicate a greater retention (about 10 ppm more) of phenols by most soils at this lower flow rate. This indicates that the phenol disappearance from solution in soils is flow or time dependent. The Molokai soil retained phenol as well as expected in comparing its performance against the other heavy soils. River bottom sand held phenol better than expected although it reached $C/C_0 = 0.9$ rapidly and approached $C/C_0 = 1$ slowly at about 8 PVD, Fig. 36.

As a rule, all the pH values of the elutants quickly leveled off to that of the pH of each particular soil since deionized water, although slightly acidic, has no appreciable buffering capacity. The pH range agrees with that involved in the isotherm batch studies. To further determine the fate of the phenol in soils, the TOC levels were monitored at two flow rates, namely; 1 and 0.5 PVD's/day and plotted against pore volume displacement number. The phenol carbon eluting was subtracted from the TOC detected emerging from each soil column to evaluate the TOC not related to phenol.

The results shown in Figs. 37, 38, and 39 indicate that the TOC that passed through each soil column appears to be controlled significantly by flow rate (solution flux). For example, the columns maintained at a flow rate of 1 PVD/day had much lower levels of TOC than the columns with a rate of 0.5 PVD/day. The variation on TOC levels migrating at the different flow rates could be due to varying abilities of water to solubilize or remove organic matter from the inorganic phase of the soils. Another possible explanation may be that the reactions leading either to phenol polymerization and/or degradation are time dependent. Time could be a factor controlling the balance between the two reactions and adsorption mechanisms such that one or the other would gain importance depending on the length of time the phenols linger in the vicinity of soil particles. Yariv (1978) points out that organic molecules can be polymerized by the inorganic phase of soil, especially by transition metals which can aid in the formation of radicals leading to condensation reactions among organic molecules.

To explore the possibility of a differential in the solubilization of the organic matter in soils as a function of flux, a base study using the six soils and deionized water along at 0.5 PVD/day was carried out. Figures 40 and 41 illustrate the TOC output from the soil columns versus pore volume number. These curves show TOC

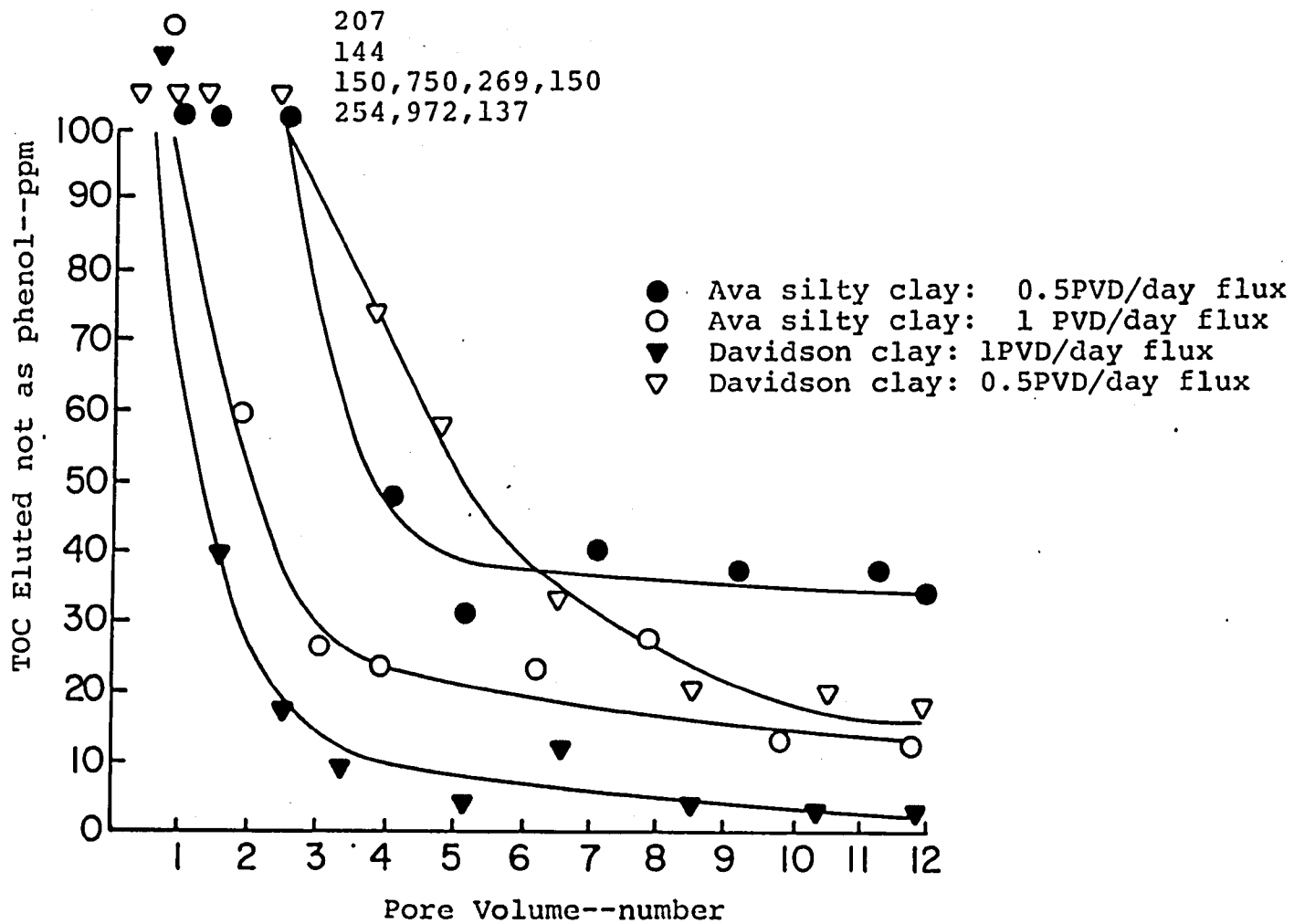


Fig. 37. The effect of flux of 1 and 0.5 PVD/day on the migration of TOC not as phenol on two soils using phenol-enriched deionized water, Ava clay and Davidson clay.

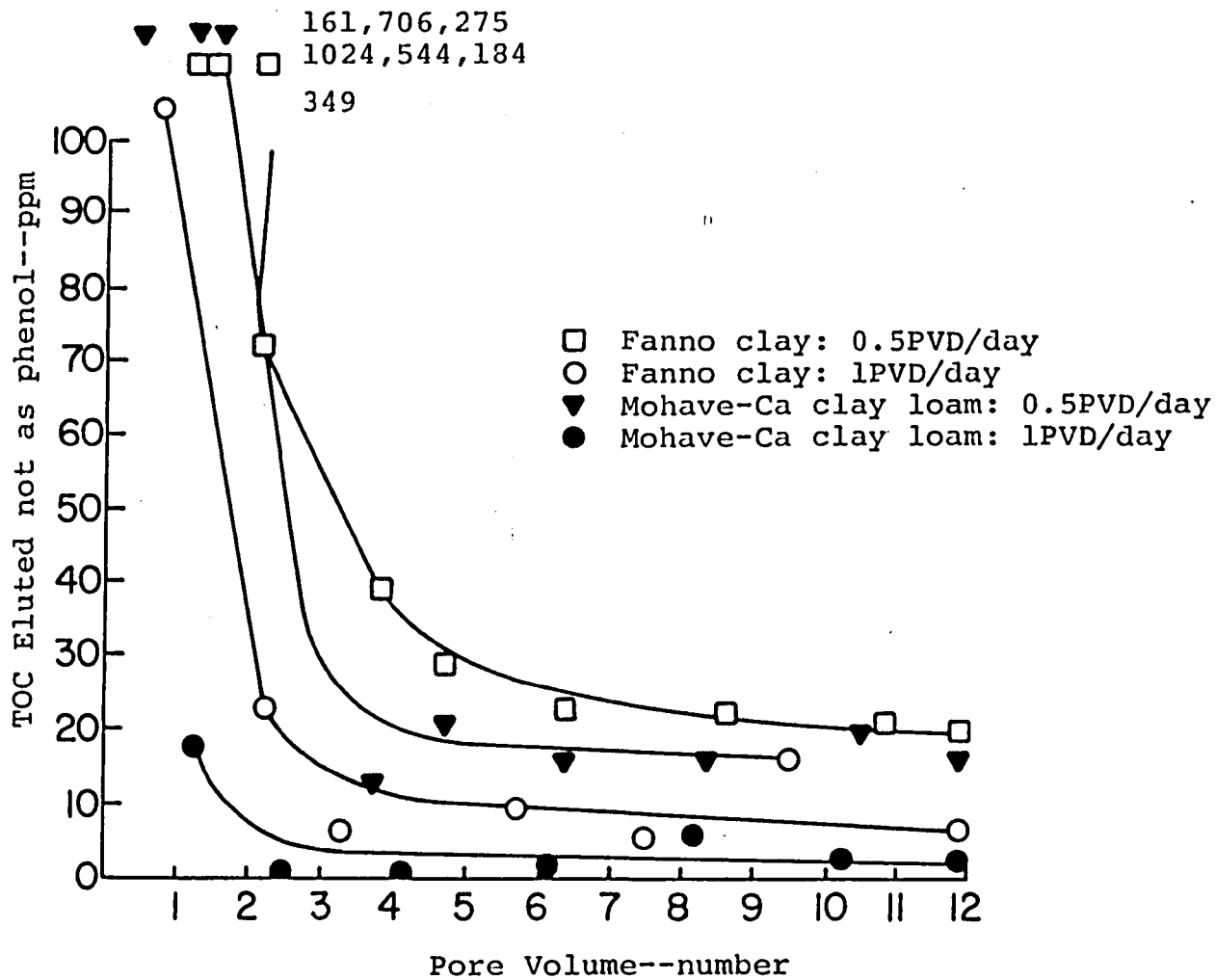


Fig. 36. The effect of flux of 1 and 0.5 PVD/day on the elution of TOC not as phenol on two soils using phenol-enriched deionized water, Fanno clay and Mohave-Ca clay loam.

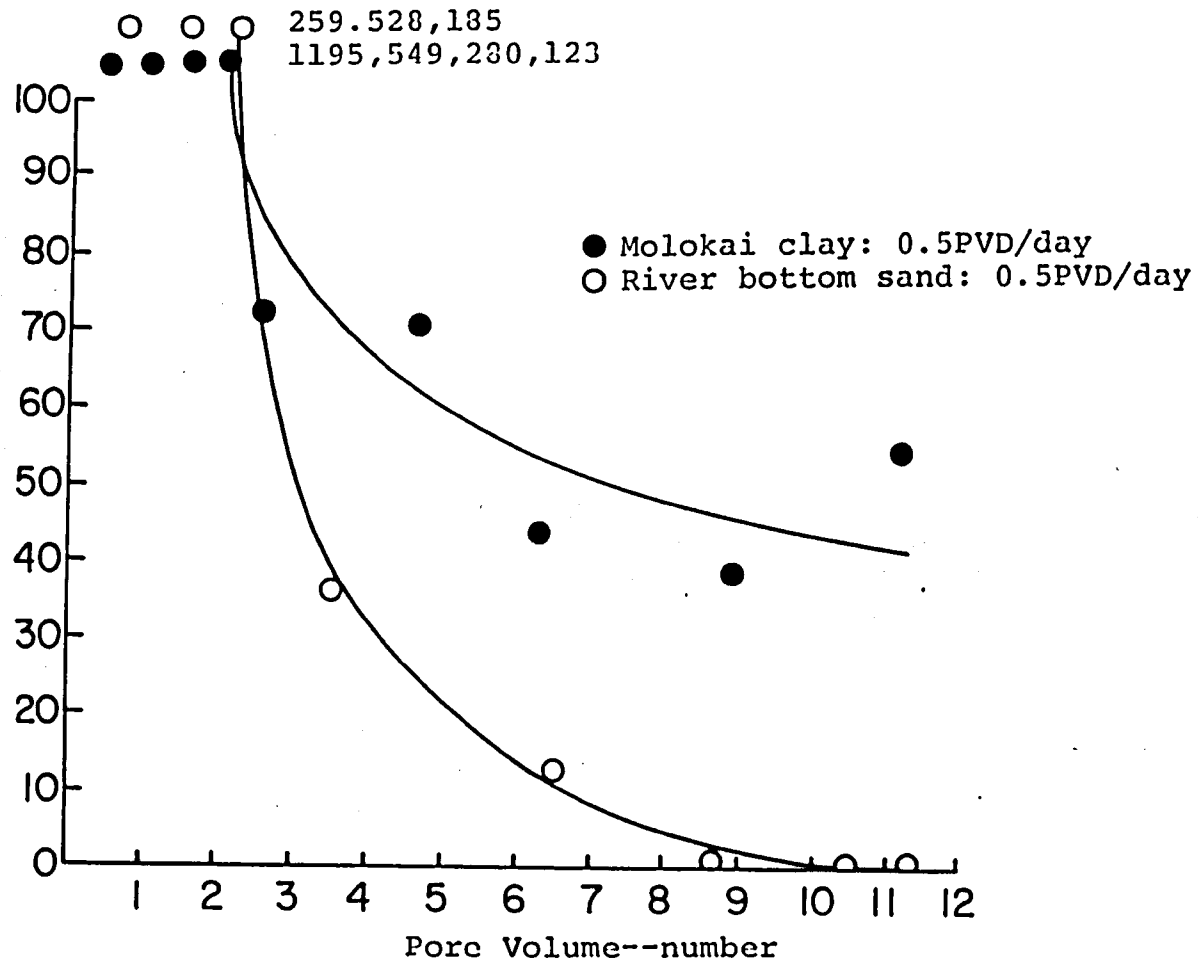


Fig. 39. The elution of TOC not as phenol from two soils using phenol-enriched deionized water at a flux of 0.5PVD/day.

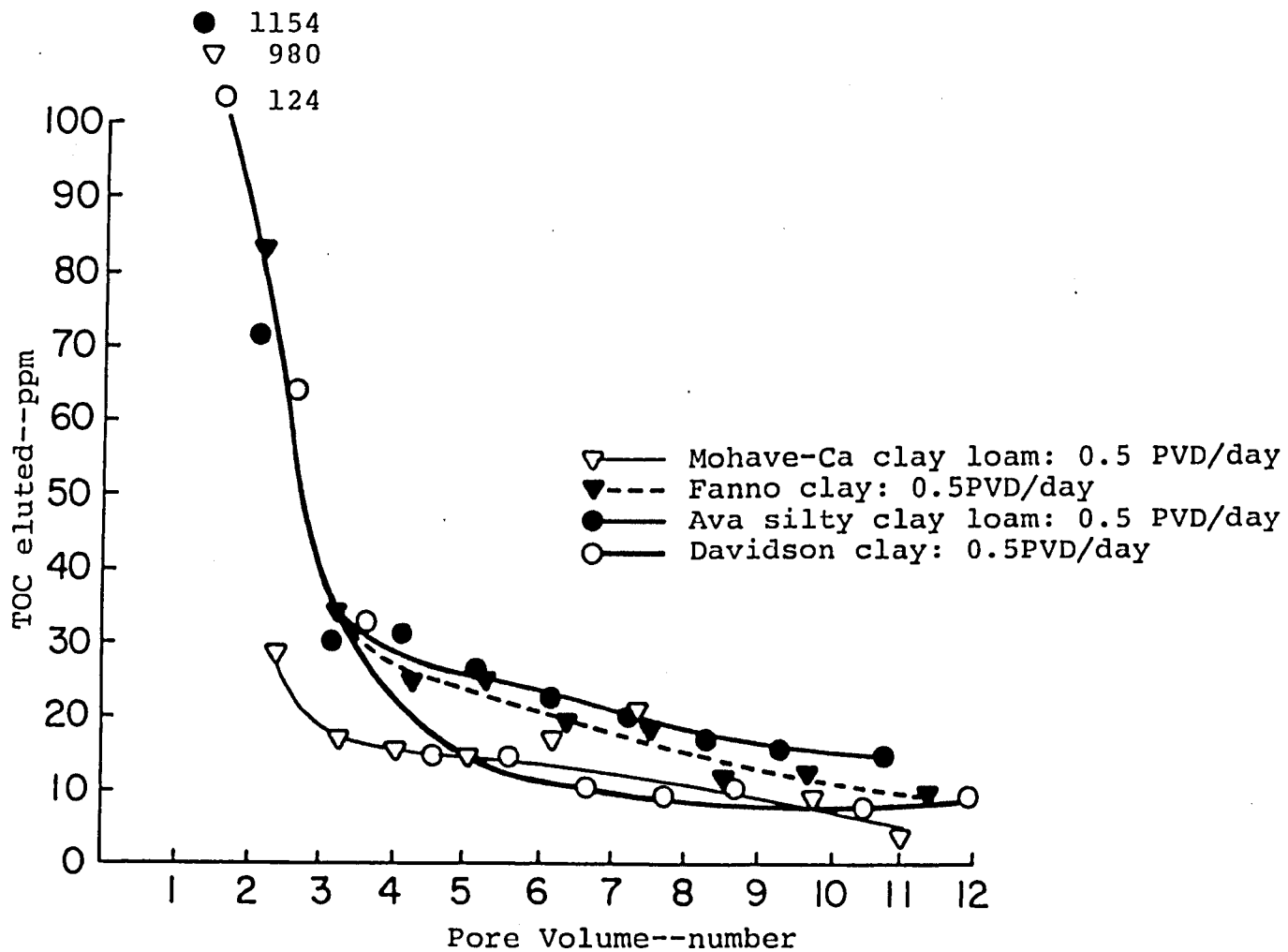


Fig. 40. Total organic carbon (TOC) solubilized by deionized water passing through four soils at a flux of 0.5 PVD/day.

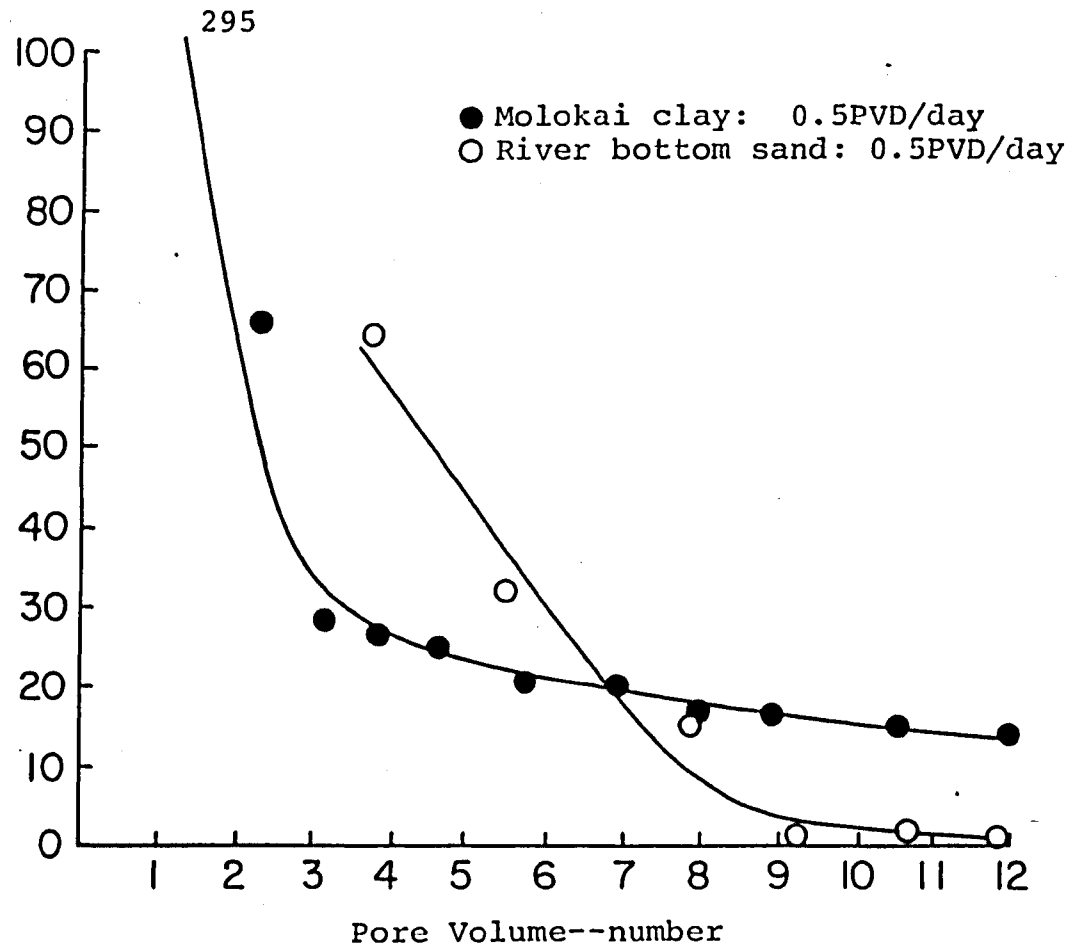


Fig. 41. Total organic carbon (TOC) solubilized by deionized water passing through two soils at a flux of 0.5 PVD/day.

levels eluting from soils which are much lower than the TOC levels in Figs. 28, 38, and 39, which correspond to the phenol-enriched water perfusion of the same soils at the same flux. It is evident that when phenol-enriched water is passed through soil, some organic matter eluted which must be the product of degradation and/or polymerization of phenol. Such phenol modification is evident in all soils except the river bottom sand which is devoid of organic matter.

Cu²⁺ Ion Saturated Soil Column Studies

The findings last reported in this research lead directly to a last test with soil columns and phenol enriched water in which the soils were previously saturated with copper ions. Copper has long been considered as a catalyst of organic reactions. Copper saturation was accomplished in a manner closely resembling field conditions by passing 1000 ppm Cu²⁺ solution through each soil column until the C/Co ratio of the copper ion was 0.9 or better. This step was followed by rinsing out the excess copper until the C/Co ratio was less than 0.05. This last step would hopefully remove all free Cu²⁺ ions not held to the soil particles by some reaction mechanisms, thus preventing chelation of phenol with copper from taking place outside the double layer of the soil surface. This was followed by

passing a solution of deionized water enriched with 103 ppm of phenol through each soil column. The TOC and phenol levels eluted were again plotted against PVD/day, Figs. 42, 43, 44, and 45. The flow rate was maintained at 0.5 PVD/day. The data failed to show any positive effect of copper on the levels of phenol in the soil column elutions. That is, phenol eluted just as fast out of the non-copper saturated columns as it did out of the copper saturated ones. Also, the TOC curves for the Cu saturated columns failed to show any significant results, with all the TOC levels being low since no apparent increase in phenol modification due to the Cu^{2+} ions took place. The failure of these soil columns to show any reactivity for phenol modification may be due to the slowness of radical formation. Lower flux rate may be required as a way to increase contact times to detect this effect in soil column experiments. Furthermore, these reactions are not very favorable under saturated conditions. Studies in the literature reporting this effect, usually involve dry conditions which in sanitary landfills are mostly saturated.

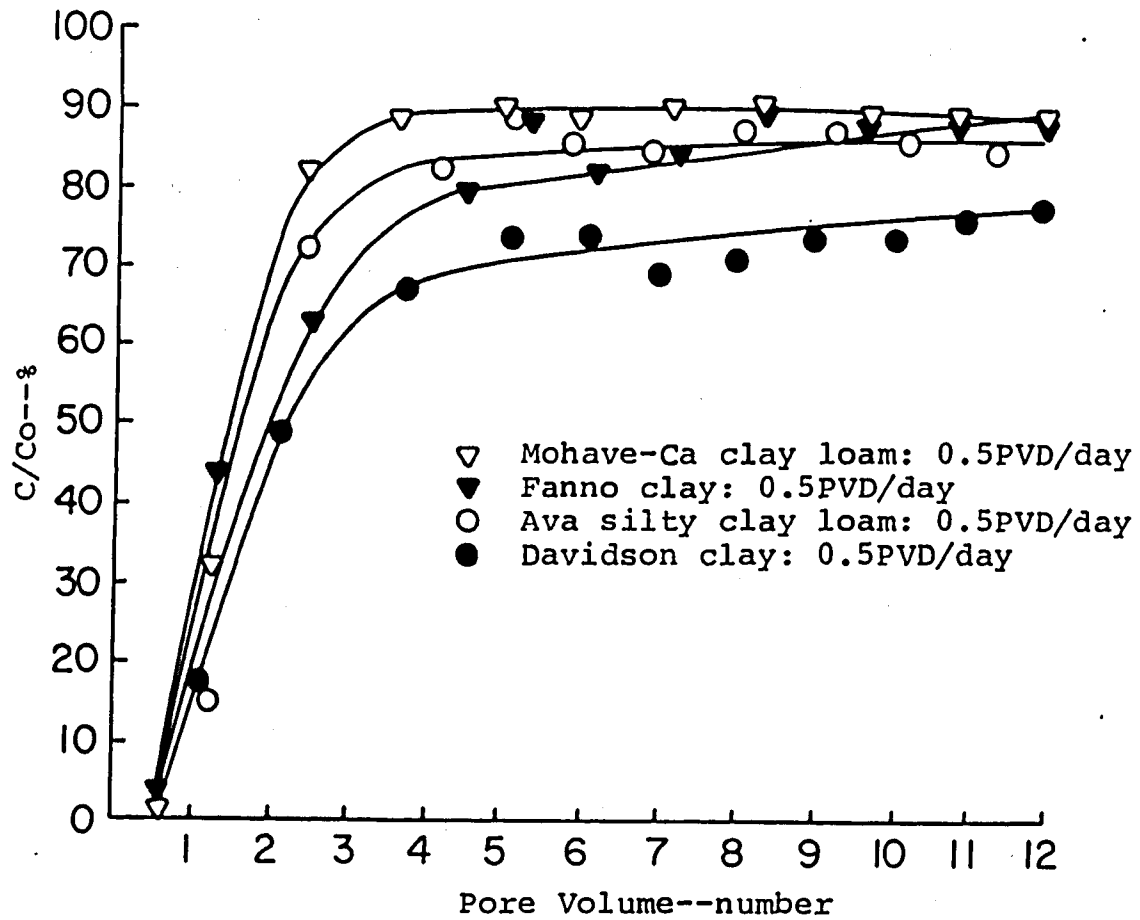


Fig. 42. The influence of Cu^{2+} saturated soil on the migration of phenol in deionized water through four soils.

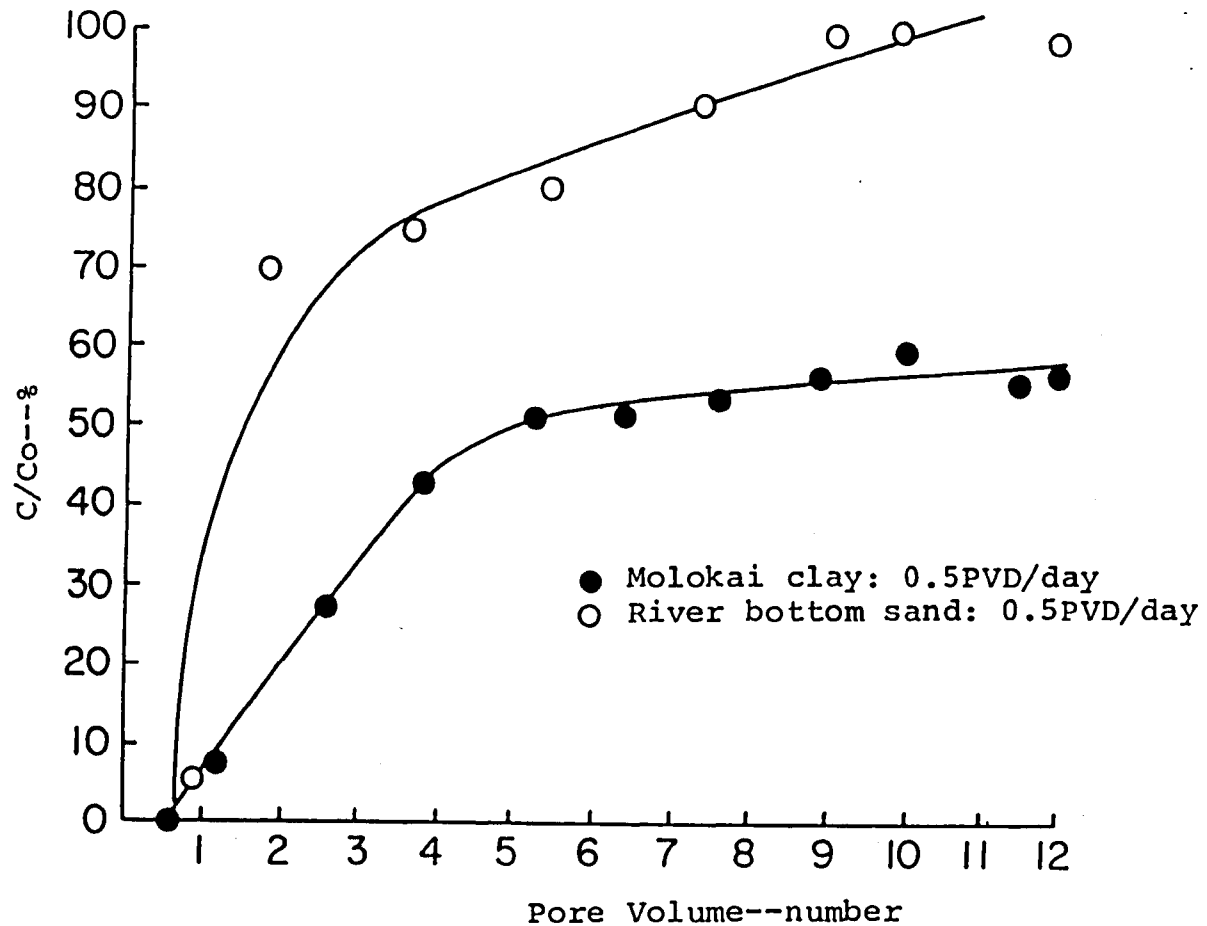


Fig. 43. The influence of Cu^{2+} saturated soil on the migration of phenol in deionized water through two soils.

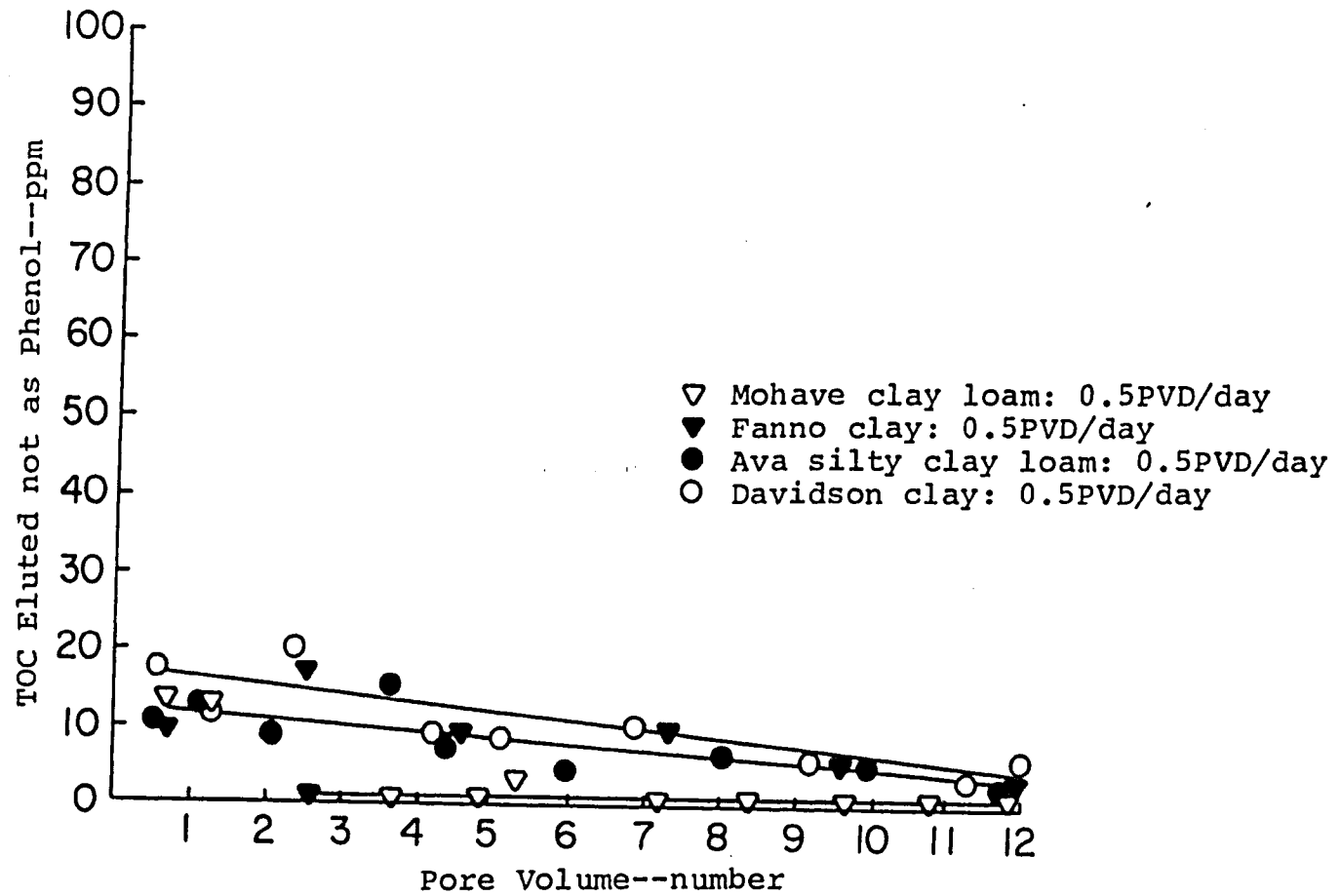


Fig. 44. The effect of Cu^{2+} saturated soil on the TOC output of four soils reacting with deionized water enriched with phenol.

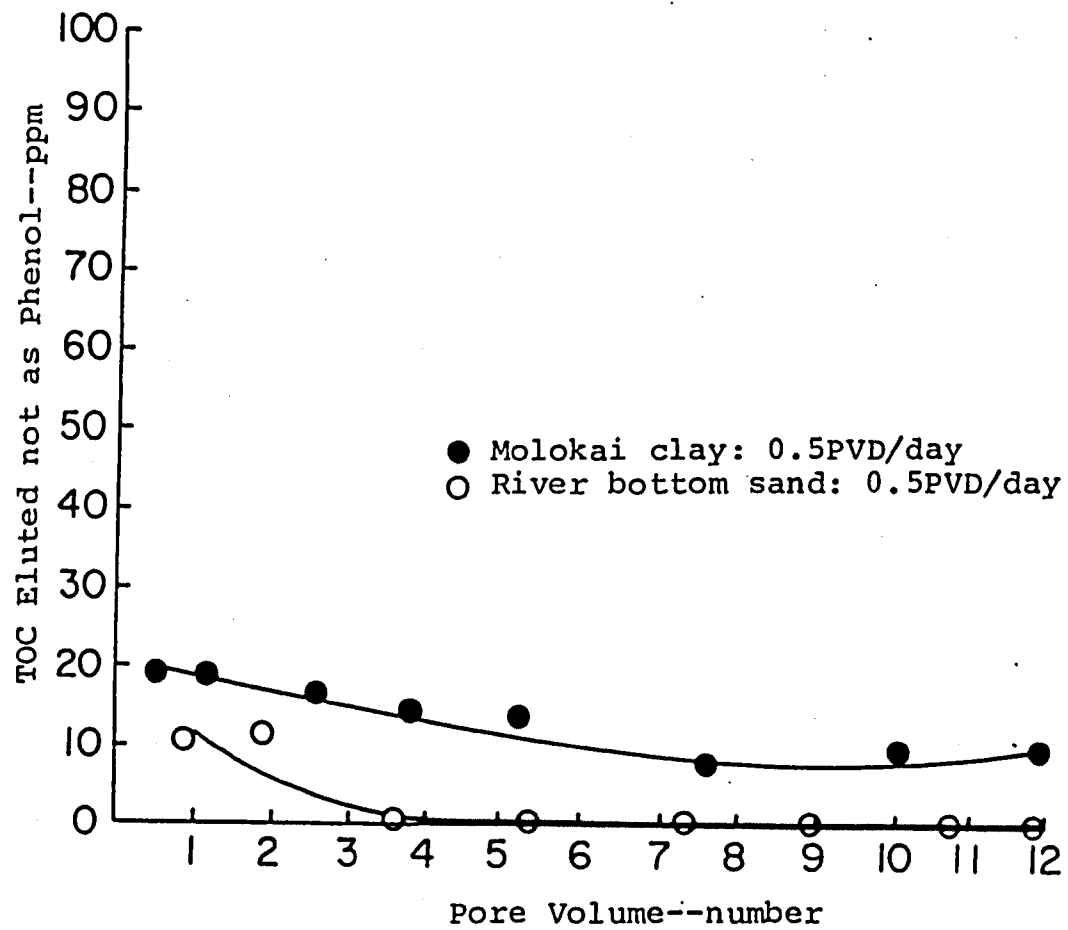


Fig. 45. The effect of Cu^{2+} saturated soil on the TOC output of two soils reacting with deionized water enriched with phenol.

SUMMARY

During the course of this study a broad view of the phenols concentration and fate in liquid wastes and soils has been presented. Through the use of isotherms it has been shown which properties in soils contribute most significantly in the removal of phenols from water solutions. Iron oxides, pH and clay are the three most important factors in order of importance influencing the adsorption of phenols by the soils used. The variability of the isotherm data not only indicated multiple mechanisms involved in the removal of phenols from soil environments but pointed to slow reaction rates due to the large equilibration times encountered. Evidently reaction times of phenols in soils vary from very fast to up to five days.

In waste disposal sites reactions involving the neutral polar phenols molecules are proposed as being involved where pH is low enough to prevent any significant ionization of phenols. Polarity, quantitized via dipole moments, is definitely important in the behavior of phenols in soils. In comparing the behavior of two phenols, o-cresol and 2,4-dichlorophenol which have K dissociation varying by a factor of 100, it becomes evident that o-cresol

was favored by soils to be adsorbed, ion exchange does not prevail in soils as this phenols is about 100 times less ionizable than chlorinated phenol. However, the chlorophenol is much less soluble in water than cresol. Also evident is the fact that strong polarity promotes dimerization of phenols such as p-nitrophenols, rendering this phenol very unreactive in both soils and leachates media. Hard data on the solubilities and dipole moments of phenols in water are needed to further analyze the results presented here.

The findings in the leachate-phenols enrichment tests seem to support Schnitzer and Khan (1978) model of these acids and the possibility of monohydroxyphenols quickly being incorporated into the structures of humic and fulvic acids due to the fast reactivities that some phenols had with leachates.

Upon inspection of naturally occurring phenols in leachates, it is apparent that levels of phenols can remain several thousand times above the desired levels for long periods of time, such as a year or more. Naturally occurring phenols, when used to enrich leachates, seem to better be able to react with these wastes (especially older leachates) as opposed to the slow reactivity of their synthetic counterparts.

The column research using packed soils shows that interactions of phenols with soils are closely related to

leachate characteristics such as TOC and pH levels. Strong, low pH leachates offer more competition and create a less desirable environment for the adsorption of phenols by soils than weak, neutral pH leachates do.

A clear dependency of the adsorption of phenol by soils on flux has been established, further reinforcing the idea that slow reaction mechanisms predominate in this system. Reactions involving polymerization or condensation of phenols via some catalysts seem to be responsible for the TOC variation with flux. However, upon saturation of soils with an active catalyst such as copper ion, phenols were not retained any more than in the non-copper saturated soils, bringing up the possibility that catalysts such as Cu^{2+} are not very active under saturated conditions.

The author of this study hopes that the broad base given and approach used here can be used as a springboard to further studies of phenols and organics in relation to the soil environment.

CONCLUSIONS

- (a) Soil-phenols isotherms conform very well with the Freundlich equation.
- (b) Multiple adsorption mechanisms, slow in nature are predicted, with equilibration times of up to five days.
- (c) Free iron oxides are the single-most important soil property controlling the adsorption of phenols.
- (d) Neutral polar phenols species seem to react with soil particles, acting as proton donors or acceptors; especially in low pH soil media.
- (e) Naturally occurring phenols are much more reactive towards soils and organic leachates than are synthetic phenols.
- (f) High polarity in the phenol molecule is an undesirable property, especially if it leads to dimerization, for its reaction with soils and MSW leachates.
- (g) Naturally occurring phenols in MSW leachates can remain several thousand times above drinking water standards for periods of up to one year, especially in young leachates, with pH and TOC being the controlling factors.

- (h) Naturally occurring phenols found in MSW leachates will promptly pass through soil columns. Leachate age and concentrations of phenols are the controlling factors.
- (i) Phenol enriched deionized water allows the adsorption and modification of phenol molecules by soils at levels which are flux dependent.
- (j) Adsorption mechanisms as well as modification mechanisms induced by natural soils constituents are responsible for the disappearance of phenol from soil solutions.
- (k) Active catalysts such as Cu^{2+} ions in the exchange sites of soils seem to be inefficient in phenol transformations under saturated conditions.

APPENDIX A

STEPWISE PROCEDURE FOR THE 4-AMINOANTIPYRINE METHOD OF ANALYSIS FOR "TOTAL" PHENOLS DETERMINATION

I. Sample preparation for strong leachates (young), air unstable (TOC more than 1000 ppm, pH less than 6.0).

- (a) Collect leachate in glass bottles and cap them under a stream of CO₂.
- (b) Immediately refrigerate sample and/or keep at room temperature under CO₂ bubbling.

Tests have shown that the phenols, TOC and pH levels will remain constant over months in these leachates as long as they are carefully kept under CO₂ at room temperature or refrigerated (Korte et al., 1975).

II. Sample preparation for weak to very weak leachates which may or may not be air unstable (TOC less than 1000 ppm, pH 6.0-7.5).

- (a) Collect leachate in glass containers and cap them, if possible under CO₂.
- (b) Store the samples in refrigerator.
- (c) (optional) Prior to storage, acidify the samples to pH 4.0 with 1:10 H₃PO₄:H₂O.

This step may be modified or omitted if the leachate is still very buffered; e.g., a lot of acid will have to be used to bring down the pH to 4.0.

(d) Add 10 ml of 0.4 molar CuSO_4 solution per liter of leachate sample.

(e) (optional) Aerate the sample for a few minutes to get rid of possible interfering sulfides.

While sulfide interferences on the 4-a analysis of phenols has been reported by Dannis (1951), and Gordon (1960) at levels as low as 10 ppm; the leachates used in this study did not exceed such sulfide levels. Omitting steps (c), (d), and (e) did not affect the results found in any of the older leachates used. Distillation together with steps (c), (d), and (e) are two tedious steps required when sulfides do interfere.

III. Sample preparation prior to phenols analysis.

At this point the American Public Health Association (1975) calls for a distillation step prior to the addition of the reagents. Distillations were carried out and the results obtained were identical, in terms of phenols levels detected, to the results obtained when the sample preparation was done as follows:

- (a) Take an aliquot of the preserved leachate and bring it to a 500 ml volume with doubly de-ionized water. The aliquot must be large enough to place the total amount of phenols within the range of the standards used.
(Aliquot sizes used in this study varied from 10 ml to 100 ml).
- (b) Place the 500 ml solution in a 600 ml beaker, and introduce a set of pH electrodes into the solution. Provide stirring.
- (c) Add 10 ml of NH_4Cl solution and adjust the pH carefully to 10.10 ± 0.05 with 30% NH_4OH .

Faust and Mikulewicz (1967) pointed out that if a buffer of pH 8.0 is used instead of 10.0, that faster and deeper coloration are obtained in the condensation steps. Tests show this to be true, but the loss in range and lack of stable, reproducible results makes the buffer at pH 8.0 not suitable for use in this study.

- (d) Add 3 ml of $\text{K}_3\text{Fe}(\text{CN})_6$ solution and mix well for one minute.
- (e) Add 3 ml of 4-aminoantipyrine solution and allow to mix well for 3 minutes. (Color development will be from light yellow to dark orange.)

It is very important that step (c) be carried out with a good working, carefully standardized pH meter for best reproducible results. Coloration is very dependent on buffer pH.

IV. Chloroform extraction.

- (a) Transfer, at the end of the 3 minutes of stirring, the contents of the beaker into a 1000 ml separary funnel.
- (b) Add 25.0 of IR grade chloroform into the funnel (use a pipette), and shake five times, times 10 shakes on the minute for five minutes.

The operator should be very consistent with this shaking step for best results.

- (c) Place up to 15 g of Na_2SO_4 granular drying agent in a fritted glass funnel (50 ml), and filter each chloroform sample promptly with vacuum suction.

V. Colorimetric analysis.

- (a) Prepare a set of standards from a stock phenol solution of 1000 ppm to contain 5, 10, 20, and 40 micrograms of phenol per 500 ml of solution plus a blank.
- (b) Proceed with sample preparation described in section III, and chloroform extractions according to section IV.

- (c) Read out Absorbance at 460 nm on a UV-VIS spectrophotometer properly calibrated.
- (d) Construct a calibration curve of grams of phenol versus absorbance.
- (e) Proceed with samples as in step (c), and extrapolate to ppbs of "total" phenol in each aliquot of leachate sample tested. Run at least duplicates of both the standards and the leachate samples.

This procedure will not give a figure for all the phenols in the leachates; thus, the word "total" will always be written between quotes when using it to describe levels of phenols found with the 4-a method.

VI. Stock solutions.

- (a) Ammonium Chloride solution: 50 g per liter of water.
- (b) 4-aminoantipyrine solution: 2.0 g of A.R. grade chemical per 100 ml of water. Replace daily.
- (c) Potassium Ferrocyanide solution: 8.0 g (A.R.) per 100 ml of water. Replace daily.

APPENDIX B

GAS-LIQUID CHROMATOGRAPHY OF PHENOLS IN WASTE WATERS

The American Public Health Association (1975) recommends GLC as a technique for the analysis of phenols in waters. The method outlined is mostly intended for the analysis of cresols and chlorophenols at high levels. The stationary phase recommended by the American Public Health Association (1975) and Leithe (1973) is Carbowax 20M-TPA at 10-20% load on Chromosorb W.

Carbowax 20M-TPA was found to be easily bled out of the column when analyzing leachates; thus, decreasing the detection limits of phenols in them. The author feels this stationary phase is a poor choice in view of the problems encountered. The problem of bleeding due to water and some volatile polar compounds which are found in the leachates, especially young ones, is very significant with this phase. This problem is seriously aggravated at high temperatures, making the quantitative analysis of phenols very irreproducible. Reducing the loading to about 5% made the separation of phenols very poor even at low temperatures. Plain carbowax 20M has been used by Douglas (1972) for the separation of phenols in drugs and cosmetics,

but this phase is even more troublesome due to its large bleeding with water samples. Bartle et al. (1977) recommend a modified Tenax phase for the analysis of phenols in waters. The improvements described in their paper are obvious as they are able to separate quickly three phenols at the ppm level. The Tenax phase is only available in the Netherlands, and modification of it, required for the analysis of phenols, according to Bartle et al. (1977) would be beyond the scope of this work. Ma and Spiegler (1966) used a Versamid 900 as liquid phase on Chromosorb W for the separation of isomeric amino and nitrophenols. Averill and Purcell (1979) describe a host of new stationary liquid phases which are very promising for the separation of low level dimethyl, nitro, and chlorophenols.

An adequate stationary liquid phase for the quantitative and qualitative analysis of low levels of phenols in leachates was found to be 5% NPGSB + 1% H_3PO_4 on the Anakrom A 90/100 support. This phase has not been found referred to in the literature for the analysis of phenols in water samples. NPGSB, a polyester, seems to be polar enough to retain and separate phenols (see Figs. B.1 and B.2) while being stable enough at high temperatures to give a moderate bleeding peak. This fact enabled the author to analyze quickly phenols at low levels on raw leachates.

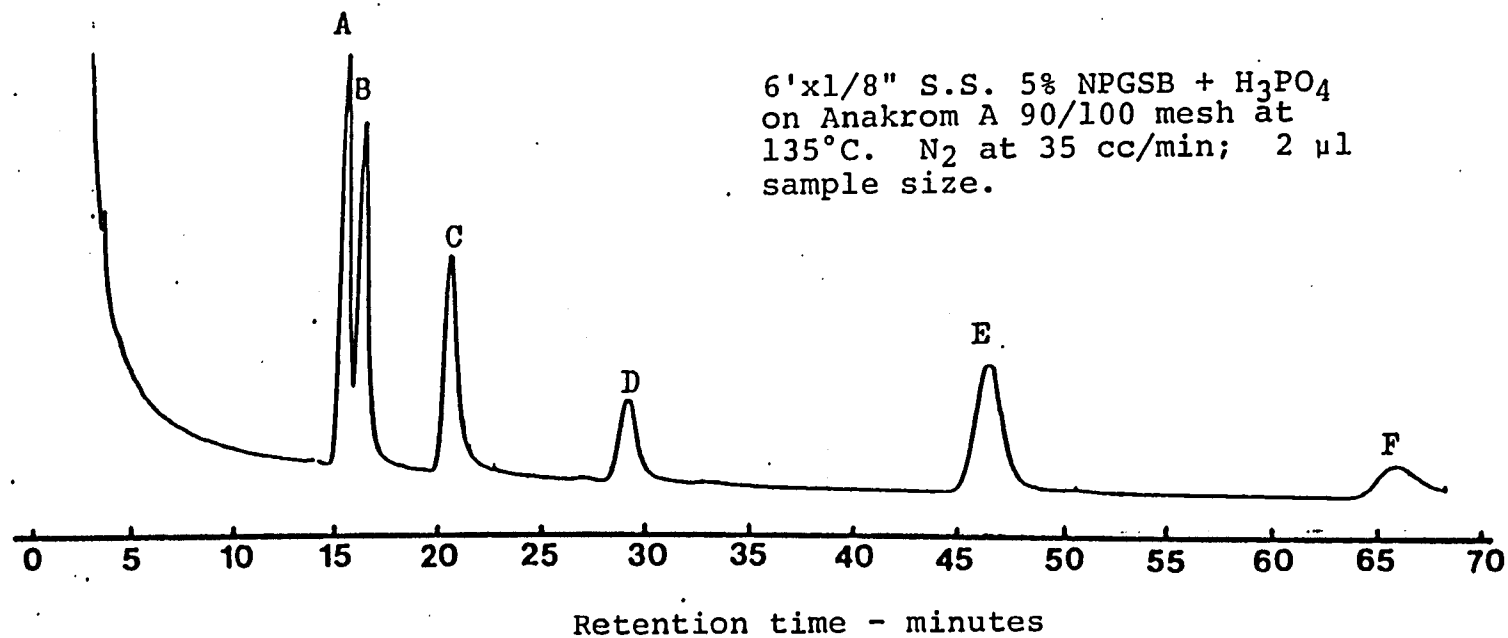


Fig. B.1 Chromatogram of (A) 2,6-xyleneol; (B) O-cresol;
(C) P-cresol; (D) 2,4-dichlorophenol; (E) 2,3,6-
trimethylphenol; and (F) P-chlorophenol.

50 ppm each.

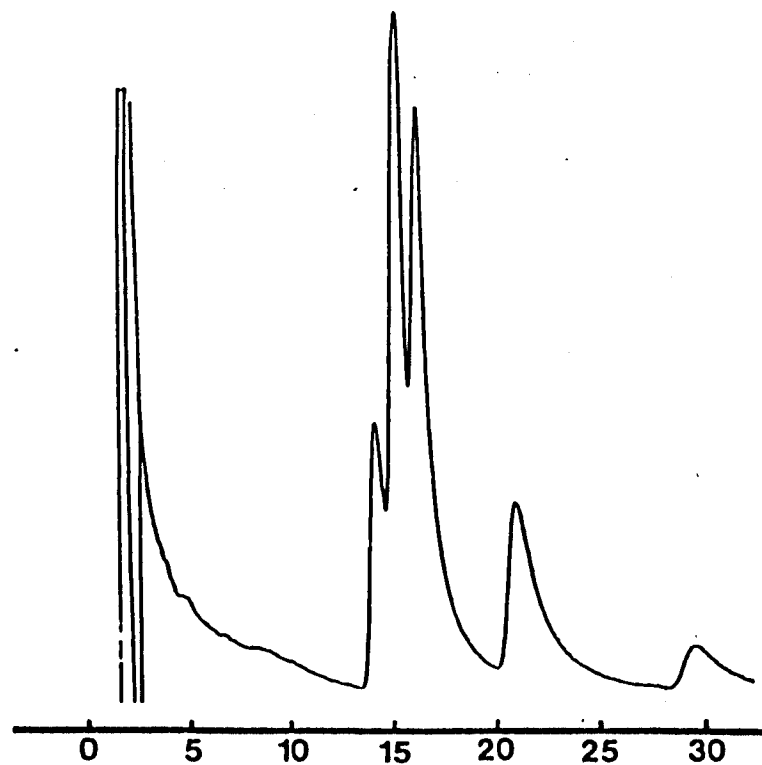


Fig. B.2. Chromatogram of five phenols.

(A) Phenol; (B) 2,6-xilenol; (C) O-cresol;
(D) P-cresol; (E) 2,4-dichlorophenol.
20 ppm each. Att. X1.

The stability and reproducibility obtained by the NPGSB phase was also a marked improvement over the Carbowaxes, Figs. B.3a and b.

The chromatograph used during this experiment was a Varian Model 3700 equipped with an FID detector, using N_2 as carrier gas. All columns were 4-6 ft. stainless steel 1/8 inch I.D. All columns used were packed and stabilized at 240 C for two days. The funnel coating method was used to apply the stationary phases onto the solid supports according to the method outlined by McNair and Bonelli (1969).

6'x1/8" S.S. 5% NPGSB + H₃PO₄
 on Anakrom A 90/100 mesh
 at 185C, N₂ at
 35 cc/min;
 2 μl sample
 size

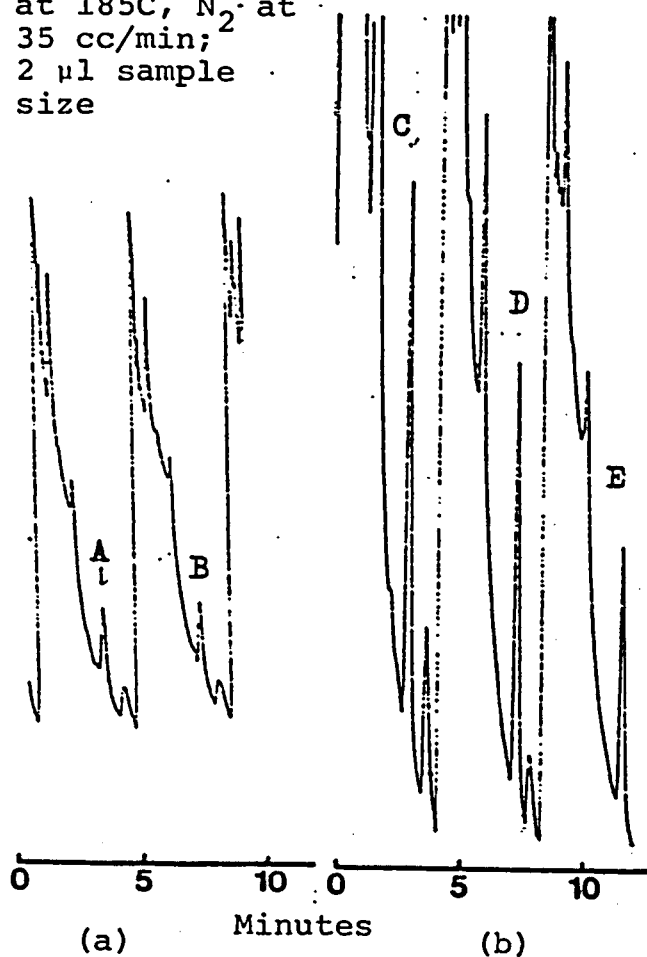


Fig. B.3. GLC Chromatographs.

(a) 5 ppm o-cresol; two consecutive injections (9a).
 (b) 40 ppm o-cresol in leachate III. (C);
 D--30 ppm of o-cresol in leachate II,
 and E--20 ppm of o-cresol in leachate I
 (9b).

APPENDIX C

HUMIC AND FULVIC ANALYSES OF MSW LEACHATES

The leachates should be collected in the field and stored under anaerobic conditions; preferably, they should be capped under a stream of CO_2 gas. Upon arrival in the laboratory, the leachate samples must be either refrigerated and/or kept under stream of CO_2 gas which should bubble the leachate solution. Analysis for humic and fulvic acids must be done as soon as possible since no leachate is completely inert or remains unchanged with time.

Stepwise Procedure:

- (a) Under an N_2 gas stream, place a 100 ml leachate aliquot in a 200 ml plastic bottle, preferably a centrifuge container. Bubble the leachate sample with an N_2 gas stream for 5 minutes to remove the CO_2 gas dissolved.
- (b) While under an N_2 gas stream, add 2.0 g of Na OH pellets A.B., and tightly seal the container under an N_2 gas stream.
- (c) Shake container overnight or at least 8 hours. If leachate is very weak, bottle should be allowed to stand overnight, provided the NaOH pellets have been fully dissolved.

- (d) Transfer the 0.5 N NaOH leachate solution while under an N₂ gas stream into a centrifuge bottle, if it was not placed in step (a) into one, and centrifuge it at 7500 RPM for about 2 hours. This step may be omitted if the leachate is very weak.
- (e) Under an N₂ stream filter the supernatant through a 0.5 micron filter, and quickly remove enough sample to analyze for Total Organic Carbon (TOC). Store the remaining supernatant in an air tight plastic or glass bottle capped under N₂ and refrigerated.
- (f) Take a 50 ml aliquot from step (e) and while under an N₂ stream add enough 6 N HCl to bring the pH down to 1.0. Note the total acid solution volume added.
- (g) Allow the acidified solution to stand for 2 hours in an air closed container (parafilm 100 ml beaker), and proceed to filter solution through a 0.5 micron filter. (No N₂ gas stream is needed for this step).

NOTE: This step is still under consideration as recent tests have shown that humic acid precipitation extends over a period of several days.

- (h) Prepare this last sample for TOC analysis and/or store in an airtight bottle and refrigerate until analysis time.

Analysis of TOC on the straight leachate sample must be carried out to be able to subtract the non-humic and fulvic acids portions from the total TOC. Analysis of TOC on sample collected in step (e) will give the total humic and fulvic acids present in the leachates. Analysis of the sample collected in step (g) will give total fulvic acids. Thus, by difference, the total humic acids will be obtained.

Automatic Carbon Analyzer

If available, this instrument (Beckman Total Carbon Analyzer) will allow the analysis of the leachate fractions as TOC in ppm of carbon. No sample preparation is needed.

Stepwise procedure

- (a) Prepare from stock solutions of 1000 ppm two sets of standards of 5, 10, 25, and 50 ppm of inorganic carbon, and 10, 25, 50, and 100 ppm of organic carbon. Must be made weekly at least.
- (b) Dilute suitable aliquots of the leachate fractions into volumetrics using deionized water, CO₂ free. Diluted samples must not exceed in carbon levels the upper range of the standards.

- (c) Proceed to construct calibration curves for total carbon (TC) using the organic carbon standards, and for total inorganic carbon (TIC) using the inorganic carbon standards.
- (d) Run at least duplicates of the various leachate fractions for TC and TIC, and obtain by difference the TOC levels in these fractions.

By performing the adequate subtractions of TOC levels from the total found in the untouched leachate, one can obtain the humic and fulvic acids fractions in the leachates.

Stock solutions.

Organic Carbon solution (1000 ppm)

Dissolve 2.125 g of oven dried (100°C for 3 hours) primary standard potassium biphthalate (primary standard) in 1000 ml of deionized water CO₂ free, and keep in cold storage.

Inorganic Carbon solution (1000 ppm)

Dissolve 4.404 g of sodium carbonate and 3.497 g of sodium bicarbonate per 1000 ml of deionized, CO₂ free water (use only A.R. grade material, and oven dry them at 80°C for ~1 hour). Store solution in cold.

All stock solution and dilutions from stock solutions must be refrigerated when not in use.

Colorimetric organic carbon analysis

This procedure, still under testing, is a modified method from the one given by Metson (1956) for the analysis of organic carbon in soils. It is assumed that the leachate samples to be analyzed contain less than 1% (10,000 ppm) TOC in solution.

Stepwise procedure.

- (a) Weigh out a set of finely ground A.R. grade sucrose standards as follows:

<u>for 10 ml leachate samples</u>	
TOC mg	Sucrose g
0	0
5.0	0.0119
10.0	0.0237
20.0	0.0474
40.0	0.0949
60.0	0.1423
80.0	0.1898
100.0	0.2372

Place sucrose standards into 250 ml volumetric flasks.

- (b) Add 100 ml of conc. H_2SO_4 A.R. slowly, and allow to stand for 20 minutes.
- (c) Add very carefully 6 ml of 10 N CrO_3 solution. Avoid splashing and/or overheating of flask.
- (d) Allow this mixture to stand for a fixed amount of time which can vary from 10 to 20 minutes but must be identical for all samples within a run.

- (e) Add enough deionized water to fill up volumetric to near volume mark, and allow solutions to cool off overnight before filling volumetrics up to the mark.
- (f) Proceed to analyze solutions with a UV-VIS spectrophotometer set at 600 nm using 10 mm cuvettes. Obtain absorbance readings for all standards including blank, and make a plot of ppm of TOC versus Absorbance.
- (g) Proceed with leachate aliquots of 10 ml through steps (b) through (e), and obtain absorbance readings to extrapolate the TOC levels using the sucrose standards plot.

Once the TOC levels in the various leachate fractions have been obtained, perform the necessary subtractions from the TOC levels in the untouched leachate to obtain the humic and fulvic acid fractions in ppm of organic carbon.

LIST OF REFERENCES

- American Public Health Association, American Water Works Association, Water Pollution Control Federation. 1975. Standard Methods for the Examination of Water and Wastewater. 14th Edition. WPCF Editor. 1015 Eighteenth St., N.W., Washington, D. C. 20036.
- Averill, W., and J. E. Purcell. 1979. The Analysis of Industrial Wastes for Priority Pollutants by Gas Chromatography. Chromatography Newsletter. 7:2: 13-17.
- Bailey, G. W., J. W. White, and T. Rothberg. 1968. Adsorption of Organic Herbicides by Montmorillonite: Role of pH and Chemical Character of Adsorbate. Soil Sci. Soc. Amer. 32:222-234.
- Bartle, A. D., J. Elstub, M. Novotny, and R. J. Robinson. 1977. Use of a modified Tenax GC Column Packing for the Direct Gas Chromatographic Analysis of Phenols in Water at the ppm Level. Journal of Chromatography. 135:351-353.
- Bolt, G. H., and M. G. M. Bruggenwert. 1976. Soil Chemistry-A. Basic Elements. Elsevier Sci. Publ. Co., New York.
- Bowman, B. F. 1978. Effect of Fulvic Acid on Adsorption of Methyl Parathion and Parathion by Ca^{2+} - and Fe^{3+} - Montmorillonite Suspensions. Soil Sci. Soc. Amer. 42:441-446.
- Bowman, B. F., and W. W. Sans. 1977. Adsorption of Parathion Fenitrothion, Methyl Parathion, Amino Parathion and Paraxon by Na^+ , Ca^{2+} , and Fe^{3+} - Montmorillonite suspensions. Soil Sci. Soc. Amer. 41:519.
- Braus, H., and F. D. Miller. 1958. Composition of Whiskey Steam-Volatile Phenols of Fusel Oil. Journal of the A.O.A.C. 41:1:141-144.
- Brewster, R. Q. 1953. Organic Chemistry. Prentice-Hall, Inc., New York.

- Chain, E.S.K., and F. B. DeWalle. 1977. Evaluation of Leachate Treatment: Volumes I and II. EPA-600/2-77/186a. U. S. Environmental Protection Agency. Cincinnati, Ohio 45268.
- Ciaccio, L. L. 1973. Water and Water Pollution Handbook, Volumes 3 and 4. Marcel Dekker, Inc., New York.
- Dagley, S. 1971. Catabolism of Aromatic Compounds by Microorganisms. *Advan. Microbial. Physiol.* 6:1-42.
- Dannis, M. 1951. Determination of Phenols by the Aminoantipyrene Method. *Sewage and Industrial Wastes.* 23:12:1516-1522.
- Degering, E. F. 1973. Organic Chemistry. Barnes and Noble, Inc., New York.
- Dibble, J. P., and R. Bartha. 1979. Leaching Aspects of Oil Sludge Biodegradation in Soil. *Soil Sci.* 187:6:365-370.
- Douglas, C. C. 1972. Gas Chromatographic Determination of Phenolic Compound: Collaborative Study. *Journal of the A.O.A.C.* 55:3:610-612.
- Drinking Water Standards. 1962. U. S. Public Health Service. Public Health Report 61, 371; (revised) U. S. Public Health Service Publication No. 956, Washington, D. C.
- Elias, H. G. 1972. Macromolecules, 2. Plenum Press, New York, Chapter 16.
- Emerson, E., H. H. Beacham, and L. C. Beegle. 1943. The Condensation of Aminoantipyrene: II. A New Color Test for Phenolic Compounds. *J. Org. Chemistry.* 8:417.
- Ermolenko, N. F. 1966. Trace Elements and Colloids in Soils. U.S.D.A. and N.C.I. Israel Program of Scientific Translations, Jerusalem.
- Ettinger, M. B., C. C. Ruchhorft, and R. J. Lishka. 1951. Sensitive 4-Aminoantipyrene Methods for Phenolic Compounds. *Anal. Chemistry* 23:1783.
- Evans, W. C. 1963. The Microbial Degradation of Aromatic Compounds. *J. Gen. Microbiol.* 32:177-185.

- Faust, S. D., and J. V. Hunter. 1963. Organic Compounds in Aquatic Environments. Marcel Dekker, Inc., New York, Chapter 16.
- Faust, S. D., and E. W. Mikulewicz. 1967a. Factors Influencing the Condensation of 4-Aminoantipyrine with Derivatives of Hydroxybenzene-I. A Critique. *Water Research* 1:405-418.
- Faust, S. D., and E. W. Mikulewicz. 1967b. Factors Influencing the Condensation of 4-aminoantipyrine with Derivatives of Hydroxybenzene-II. Influence of Hydronium ion Concentration of Absorptivity. *Water Research* 1:509-522.
- Finkle, B. J., and V. C. Runeckles. 1967. Phenolic Compounds and Metabolic Regulation. Appleton-Century-Crofts Publ. Co., New York.
- Freundlich, H. 1926. Colloid and Capillary Chemistry. Methuen and Co., Ltd., London.
- Fuller, H. F., N. H. Korte, E. E. Niebla, and B. A. Alesi. 1976. Contribution of the Soil to the Migration of Certain Common and Trace Elements, *Soil Sci.* 122:4:223-235
- Fuller, W. H. 1978. Investigation of Landfill Leachate Pollutant Attenuation by Soils. EPA-600/2-78-158. U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.
- Gamar, Y., and M. A. Mustafa. 1975. Adsorption and Desorption of Diquat and Paraquat on Arid-zone Soils. *Soil Sci.* 119:1:290-295.
- Gordon, G. E. 1960. Colorimetric Determination of Phenolic Material in Refinery Waters. *Anal. Chem* 32:10:1325-26.
- Goring, C.A., and J. W. Hamaker. 1972. Organic Chemical in the Soil Environment. Marcel Dekker, Inc., New York. Chapter 11.
- Haider, K., and J. P. Martin. 1967. Synthesis and Transformation of Phenolic Compounds by *Epicoccum Niigrum* in Relation of Humic Acid Formation. *Soil Sci. Soc. Amer. Proc.*, 31:768-771.
- Haider, K., and J. P. Martin. 1975. Decomposition of Specifically Carbon-14 Labeled Benzoic and Cinnamic Acid Derivatives in Soil. *Soil Sci. Soc. Amer. Proc.* 39:657-662.

- Harter, R. D., and D. E. Baker. 1977. Applications and Mis-applications of the Langmuir Equation to Soil Adsorption Phenomena. *Soil Sci. Soc. Am. J.* 41: 1077-1080.
- Hendrickson, J. B., D. J. Cram, and G. S. Hammond. 1970. Organic Chemistry. McGraw-Hill, New York, p. 823.
- Her Majesty's Stationary Office. 1972. Analysis of Raw and Potable Waste Waters, London, England.
- Ho, T. L. 1977. Hard and Soft Acids and Bases Principle in Organic Chemistry. Academic Press, New York, Chapter 6.
- Hoffman, R. W., and G. W. Brindley. 1960. Adsorption of Non-ionic Aliphatic Molecules from Aqueous Solutions on Montmorillonite, Clay-organic Studies-II. *Ceochimica et Cosmochimica Acta.* 20:15-29.
- Karickhoff, S. W., and D. S. Brown. 1978. Paraquat Sorption as a Function of Particle Size in Natural Sediment. *J. Environ. Qual.* 7:2:246-251.
- Keith, L. H. 1976. Identification and Analysis of Organic Pollutants in Water. Ann Arbor Science Pub. Inc., P. O. Box 1425, Ann Arbor, Michigan.
- Khan, A., J. J. Hassett, and W. L. Banwart. 1979. Sorption of Acetophenone by Sediments and Soils. *Soil Sci.* 128:5:297-301.
- Knickmeyer, W. W., K. G. Mayhan, and G. L. Bertrand. 1973. Organic Desorption from Carbon-III. The Effect of Solvent in the Desorption of Phenol from Dry Carbon. *Water Research* 7:1323-1330.
- Korte, N. E., J. Skopp, E. E. Niebla, and W. H. Fuller. 1975. A Baseline Study on Trace Metal Elution from Diverse Soil Types. *Water Air Soil Pollut.* 5:149-156.
- Krumbein, W. E. 1978. Environmental Biochemistry and Geomicrobiology. Volume 1. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan 48106.
- Langmuir, I. 1918. The Adsorption of Gasses on Plane Surfaces of Glass, Mica, and Platinum. *J. Am. Chem. Soc.* 38:2221-2295.

- Leithe, W. 1973. The Analysis of Organic Pollutants in Water and Waste Water. Ann Arbor Science Publ., Inc., P. O. Box 1425, Ann Arbor, Michigan 48106.
- Ma, T. S., and D. Spiegel. 1966. Gas Chromatography of Phenols, I. Microdetermination of Isomeric Phenolic Compounds. *Microchemical Journal* 10:61-66.
- Martin, J. P., and K. Haider. 1979. Effect of Concentration and Decomposition of Some ¹⁴C Labeled Phenolic Compounds, Benzoic Acid, Cellulose, Wheat Straw, and Chlorella Protein in Soil. *Soil Sci. Soc. Am. J.* 43:917-921.
- Martin, J. P., K. Haider, and C. Saiz-Jimenez. 1974. Sodium Amalgam Reductive Degradation of Fungal and Model Phenolic Polymers, Soil Humic Acids, and Simple Phenolic Compounds. *Soil Sci. Soc. Amer. Proc.* 38:762-765.
- McLaren, A. D., and G. H. Peterson. 1967. Soil Biochemistry. Marcel Dekker, Inc., New York, Chapter 12.
- McNair, H. M., and E. J. Bonelli. 1969. Basic Gas Chromatography. Varian Aerograph Publishing Co., 2700 Mitchell Drive, Walnut Creek, CA 94598.
- Merck Index. 1960. Merck and Co., Inc., Rahway, New Jersey, 7th Edition.
- Metson, A. J. 1956. Methods of Chemical Analysis for Soil Survey Samples. *New Zealand Soil Bureau Bulletin* 12:208.
- Mittal, K. L. 1975. Adsorption at Interfaces, ACS Symposium Series 8. Published by American Chemical Society, Washington, D. C.
- Mohler, E. F., Jr., and L. N. Jacob. 1957. Determination of Phenolic-type Compounds in Water and Industrial Waters. *Anal. Chem.* 29:9:1369-1374.
- Mortland, M. M., and L. J. Halloran. 1976. Polymerization of Aromatic Molecules on Smectite. *Soil Sci. Soc. Amer.* 40:367-370.
- Mortvedt, J. J., P. M. Giordano, and W.L.L. Lindsay. 1972. Micronutrients in Agriculture. *Soil Sci. Soc. Amer.*, Chapter 5.

- Muirhead-Thomson, R. C. 1971. Pesticides and Freshwater Fauna. Academic Press, London and New York, Appendix.
- Nemerow, N. L. 1978. Industrial Water Pollution. Addison-Wesley Publ. Co., Reading, MA, Chapter 1.
- Norman, R.O.C. 1968. Principles of Organic Synthesis. Methuen and Co., Ltd., and Science Paperbacks. Distr. by Barnes and Noble, Inc.
- Parfitt, R. L., and D. J. Greenland. 1970. Adsorption of Polysaccharides by Montmorillonite. *Soil Sci. Soc. Amer.* 34:862-866.
- Parfitt, R. L., and M. M. Mortland. 1968. Ketone Adsorption on Montmorillonite. *Soil Sci. Soc. Amer.* 32:356-363.
- Pinnavia, T. J., P. L. Hall, S. S. Cady, and M. M. Mortland. 1973. Aromatic Radical Cation Formation on the Intercrystal Surfaces of Transition Metal Layer Lattice Silicates. *The Journal of Physical Chemistry* 78:10:994-999.
- Saltzman, A., and S. Yariv. 1975. Infrared Study of Sorption of Phenol and P-nitrophenol by Montmorillonite. *Soil Sci. Soc. Amer. Proc.* 39:474-479.
- Saltzman, A., and S. Yariv. 1976. Infrared and X-ray Study of Parathion-Montmorillonite Sorption Complexes. *Soil Sci. Soc. Amer. J.* 40:34-38.
- Sax, N. I. 1979. Dangerous Properties of Industrial Materials. Van Nostrand Reinhold Co., New York.
- Schnitzer, M., and S. U. Khan. 1972. Humic Substances in the Environment. Marcel Dekker, Inc., New York Chapter 5.
- Schnitzer, M., and S. U. Khan. 1978. Soil Organic Matter. Elsevier Sci. Publ. Co., New York.
- Schnitzer, M., M. I. Ortiz, and K. Ivarson. 1973. The Chemistry of Fungal Humic-like Polymers and of Soil Humic Acids. *Soil Sci. Soc. Amer. Proc.* 37:229-236.
- Strazhesko, D. N. 1973. Adsorption and Adsorbents. John Wiley and Sons, New York, Toronto.

- Stumm, W., and J. J. Morgan. 1970. Aquatic Chemistry. Wiley Interscience Publ. Co., New York.
- Sudhakar-Barik, and N. Sethunathan. 1978. Metabolism of Nitrophenols in Flooded Soils. *J. Environ. Qual.* 7:3:349-357.
- Swoboda, A. R., and G. W. Kunze. 1968. Reactivity of Montmorillonite Surfaces with Weak Organic Bases. *Soil Sci. Soc. Amer.* 32:806-811.
- U. S. EPA. 1979. Comparison of Three Waste Leaching Tests. EPA-600/2-79-071.
- Weber, J. B., and S. B. Weed. 1968. Adsorption and Desorption of Diquat, Paraquat, and Prometone by Montmorillonitic and Kaolinitic Clays Minerals. *Soil Sci. Soc. Amer.* 32:485-485.
- Willard, H. H., L. L. Merritt, and J. A. Dean. 1974. *Instrumental Methods of Analysis*, Van Nostrand Co., New York, Chapter 8.
- Yariv, C. 1978. Geochemistry of Colloid Systems. Elsevier Scientific Publ. Co., Amsterdam, Oxford, New York.

Stone, R., and J. L. Bryan. 1970. Acoustic Chemistry. Wiley-Interscience, New York.

Holmes, R. L., and R. L. Bunch. 1974. Measurement of Nitrogen in Flooded Soils. J. Environ. Qual. 3:187-192.

Went, R. W., and R. W. Jones. 1958. Activity of Microbiological Systems with Water Organic Matter. Soil Biol. Soc. Amer. 22:100-111.

H. R. 1974. Comparison of Three Waste Treatments. Texas. 224-653/2-72-872.

Went, R. W., and R. W. Jones. 1958. Activity of Microbiological Systems with Water Organic Matter. Soil Biol. Soc. Amer. 22:100-111.

Went, R. W., R. L. Bunch, and R. W. Jones. 1974. Measurement of Nitrogen in Flooded Soils. J. Environ. Qual. 3:187-192.

Went, R. W. 1970. Acoustic Chemistry. Wiley-Interscience, New York.



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