THE MOBILITY OF MALATHION IN A SILT LOAM SOIL AS AFFECTED BY PHOSPHATE AND NATURALLY OCCURRING ORGANIC ACIDS

by

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(ABSTRACT)

A laboratory study of the mobility of Malathion in the
soil environment was conducted. A Malathion solution was
applied to columns of a silt loam soil to investigate the
pesticide’s potential for adsorption. The effects of
solutions of phosphate and naturally occurring organic acids
on Malathion’s adsorption potential were then investigated
by coapplication of each of these solutions with the
Malathion solution. Finally, the potential for desorption
of Malathion from the soil column was studied by applying
deonized water, both alone and in series with either
phosphate or organic acid solutions, through soil columns to
which Malathion had been previously applied.

Malathion was found to be readily adsorbed on the silt
loam soil. The phosphate solution increased the mobility of
Malathion within the soil column in two ways. First, the
phosphate solution decreased Malathion’s adsorption when the
two solutions were applied simultaneously. Secondly, when
applied as a leaching solution, the phosphate increased the
desorption of Malathion over that of the deionized water leaching solution. Naturally occurring organic acid solutions similarly reduced the adsorption of Malathion, but did not appear to have a significant effect on its desorption. The observed increases in mobility were believed to be caused by competitive adsorption.
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An example of discipline, of uncompromising
adherence to high academic standards.

An educator who takes his students beyond
the numbers, beyond the equations, to
an understanding and appreciation of
the subtleties, the symmetry, and the
complex interrelationships that are
environmental engineering.

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INTRODUCTION

The quality of our groundwater supplies is a topic of ever increasing interest. As the quality of surface water supplies becomes more difficult to protect, as the staggering demand for the limited sources of fresh water continues to rise, and as the folly of not protecting our natural resources becomes all the more apparent, well deserved concern and attention are finally being focussed on groundwater quality.

The threat to groundwater supplies from agricultural practices is well recognized [52,72,83]. The heavy chemical dependence of this industry, expressed in its continued reliance on insecticides, herbicides, and fertilizers to increase production, creates one of the more significant sources of groundwater contamination [19-21,27,64]. It has been estimated that four dollars of additional income is generated for every dollar that the agricultural industry spends on pesticides [48,59]. Pesticide usage due to this incentive is compounded by the spread of some of these same agricultural practices and chemicals from rural areas to the burgeoning suburbs. With homeowners dedicating themselves
to producing perfect, ever-green, pest-free lawns, and lawn service companies employing the most timesaving and cost effective methods to achieve these results, it may be seen that the potential stresses on our groundwater supplies could reach overwhelming levels [17,39,43,53,67,70,79].

Much of the early research into this problem concentrated on the more environmentally persistent chemicals, such as the organochlorine compounds. This was due to the extensive usage of these compounds as well as the greater environmental threat they appeared to pose, with half-lives in the soil environment ranging from up to four years for Chlordane to as much as seven years for Dieldrin [48]. But as more attention is focussed on the groundwater problem and as solutions are sought, a shift to less persistent, more readily degradable chemicals is occurring.

With this shift comes the increasing use of organophosphorus pesticides. These pesticides are a group of hydrocarbon compounds that contain at least one phosphorus atom in the molecular structure. They are water soluble, relatively short lived in biological systems, and are readily hydrolyzed [48,82]. The half-lives of this group of pesticides in the soil environment range from 0.2-0.5 years [48]. Although much of the early concern about organophosphorus pesticides was mitigated by their relative instability in the environment, the dramatic rise in their usage—the sheer volume of these chemicals being produced
and distributed throughout the environment--appears to pose a new and serious threat to our groundwater supplies.

Compounding this problem is the method of application used for organophosphorus pesticides. These pesticides are usually applied directly to the ground. In the typical application procedure, the pesticide is first spread over the soil surface, then mixed into the soil column by plowing [48].

In addition, the more water soluble nature of the organophosphorus pesticides makes them more susceptible to leaching than those of the organochlorine class [72]. The organophosphorus pesticides are also one of the more toxic groups of pesticides with some of the lowest LD$_{50}$ values (the oral dose of a toxicant sufficient to kill fifty percent of a test species) of any pesticide class [52, 75, 82].

In this regard, the following study focuses on one such organophosphorus compound, 0,0-dimethyl-\(\text{S}-(1,2\)-dicarbethoxyethyl) phosphorodithioate, commercially known as Malathion. This pesticide was chosen because it is one of the more widely used of the organophosphorus pesticides and because it shares the chemical characteristics of other phosphorus esters, such as parathion, which have been studied extensively in the literature.

Malathion is a clear amber liquid, with a vapor pressure of 0.00004 mm Hg at 30 °C, a water solubility of 145 ppm at 25 °C, and an LD$_{50}$ value of 1000 mg/kg [15, 22, 48].
It is a polar, nonionic molecule [84] with the chemical formula $C_{10}H_{19}O_6PS_2$ [15]. Malathion is used as an insecticide and miticide on a wide variety of insect pests that attack field crops, vegetables, fruits, ornamentals, livestock, and stored grain. It is also used in many mosquito control and medfly eradication programs. Malathion's mode of activity is cholinesterase inhibition [23]. In 1986, approximately twenty million pounds of Malathion were applied domestically. Its usage was divided across all sectors of our economy as follows: forty per cent for industrial, commercial, and governmental uses; thirty-three per cent for private homes; and twenty-seven per cent for agricultural applications [23].

In a study by Felsot and Dahm in 1979, it was concluded that "since adsorption phenomena can influence the translocation, volatility, persistence, and bioactivity of an insecticide, it is probably the major process that affects the behavior of a soil insecticide" [28]. In this study, those adsorption phenomena, as well as the general mobility of Malathion in the soil environment, were investigated through the use of soil columns. Because pesticides are commonly applied with other agricultural chemicals, the effects of one such chemical, phosphate, on the adsorption and mobility of Malathion was examined. Finally, the influence of naturally occurring organic acids
on the adsorption and mobility of Malathion was investigated.

Through a better understanding of how this increasingly popular class of pesticides reacts in the soil environment, a better assessment of the risk they pose to groundwater supplies may be performed.
LITERATURE REVIEW

Soil Properties Affecting Adsorption of Organophosphorus Pesticides

The two soil variables that most influence the adsorption and desorption of pesticides are the clay and the organic matter content [2, 5, 28, 48, 72]. Of these two variables, the one most critical to the adsorption of organophosphorus pesticides is the organic matter content, because these pesticides have a greater affinity for organic rather than mineral surfaces [11, 16, 28, 32, 37, 45, 46, 49, 50, 60, 62, 63, 65, 78, 86].

The relative contributions of these two soil constituents have been investigated in numerous studies, usually employing one of the following three procedures: utilization of isolated soil fractions, examination of a natural soil before and after organic matter removal, or the use of several natural soils with considerably different concentrations of organic matter [63]. While the initial two procedures present the potential disadvantage of
altering the adsorptive surfaces by either the isolation or removal process, results obtained in these studies, illustrated in the following study descriptions, have been fairly consistent.

In 1979, Felsot and Dahm, employing the technique of organic matter removal by hydrogen peroxide, found that the increased adsorption of several different organophosphorus pesticides correlated to higher percentages of organic matter content. A significant correlation was found between the extent of adsorption as expressed by the log of the Freundlich adsorption constant, the log of the organic matter concentration, and the log of the cation exchange capacity (CEC) [28]. Because the CEC of most soils is derived from the organic fraction [48], these correlations are an even stronger indication of the dominant role of soil organic matter in organophosphorus pesticide adsorption.

Natural soils with significantly different concentrations of organic matter were chosen by Lichtenstein for his study of parathion mobility under nonleaching conditions [54]. His procedure involved surrounding a parathion-treated layer of soil with several nontreated layers in a large diameter column. Individual layers were separated by cheesecloth. Diffusion of the pesticide to the surrounding layers was found to be far greater in a Plainfield sand soil (low organic matter content) than in a muck soil (high organic matter content). The greater
adsorption of the organophosphorus pesticide by the soil with the higher organic matter content was concluded to be the crucial difference between the two columns [54].

Further studies indicated that it was the concentration rather than just the presence of organic matter that determined if it was the dominant factor in soil adsorption. In one such study using parathion, it was found that the inorganic soil constituents dominated pesticide adsorption in soils containing less than 2% organic matter, but that this contribution was completely masked by that of organic matter in soils containing greater than 2% organic matter [77]. A later study found similar results, but the crucial boundary was determined to be 6% organic matter content [78].

References to the effect of soil organic matter on pesticide adsorption abound in the literature. It is well established that the organic fraction of soil is primarily responsible for adsorption of organophosphorus pesticides. However, "the properties of the organic colloids relevant for adsorption have not yet been characterized" [63]. It appears that several factors may be characteristic of the adsorption potential. The first is the relative proportion of the following organic matter constituents: fulvic acid, humic acid, and humin. The second is the presence of the following functional groups: amino, carbonyl, carboxyl,
hydroxyl, and methoxy. The final factors are the cation exchange capacity and the total amount of surface area [63].

Leenheer and Ahlrichs postulated that it is not so much the type of organic matter and its specific qualities as described above, but rather, the overall magnitude of the hydrophobic nature of the organic matter surfaces that is the key determinant of organophosphorus pesticide adsorption potential [52]. They found that the source of the organic matter or the various functional groups contained on the organic matter were of negligible importance when compared to the extent of the hydrophobic nature of the soil organic matter. This view was echoed by Felsot and Dahm, who found that the adsorption of several organophosphorus pesticides occurred mainly through hydrophobic interactions with organic matter surfaces [28]. Saltzman and Yaron stated similarly that "much evidence shows that a peculiar property of soil organic matter (the presence of hydrophobic structures in addition to other adsorption sites) confers on it the almost ubiquitous character of adsorbent as far as non-ionic pesticides are concerned" [63].

A final explanation of the overriding adsorption potential of the organic matter fraction was offered by Khan. He linked this adsorption potential to the high concentration of stable free radicals found in humic substances [48].
While the organic fraction of soils is largely responsible for the adsorption of organophosphorus pesticides, Weber reported in 1972 that the amount of organophosphorus pesticides adsorbed on clay minerals was also significant [81]. Numerous studies have confirmed that organophosphorus pesticides are adsorbed by the clay fraction, and that this adsorption can be significant in isolated clay fractions and in soils of low organic matter content [12,13,16,47,57,60,61].

The solid soil volume is usually only about 50% of the actual volume of a soil sample, with the other 50% being occupied by void spaces and the thin aqueous film surrounding soil particles, the soil solution [9]. Depending on the extent of the organic matter fraction, the volume occupied by the mineral fraction may be far less than 50%. The portion of this mineral fraction that is of concern as far as pesticide adsorption is the clay fraction.

The term "clay" will be used to include clay-sized (<2um) particles of crystalline minerals as well as the crystalline and amorphous oxides and hydroxides that frequently coat their surface [48]. The main properties of clays affecting the adsorption of organophosphorus pesticides are the CEC, the hydration status, the saturating cation, the surface acidity, and the available surface area [36,61,87]. In studies using isolated clay fractions, the method of clay fraction preparation has also been shown to
affect the adsorption potential. Mechanical pretreatment of the clay, described as grinding or "the stress effect" depending on the study referred to, was found to greatly increase the adsorption potential of both kaolinite and montmorillonite clays [87].

In 1965, Greenland determined that the amorphous oxides and hydroxides of iron, aluminum, and silica can adsorb nonionic pesticides [36]. Similarly, Bowman observed substantial adsorption of the organophosphorus pesticide Dasanit onto isolated montmorillonite [10]. Numerous other studies have substantiated the ability of the clay fraction to adsorb organophosphorus pesticides [11-13,16,61].

Shortly after the study by Greenland, however, Hance suggested that in soils, clays and organic matter associate in such a configuration that little of the clay surface is actually exposed [41]. Therefore, studies employing isolated clay, oxide, or hydroxide adsorbents would overestimate the contribution of the clay fraction to adsorption. Additional studies of this time looked increasingly towards the interaction of the clay and organic matter components in pesticide adsorption [34,58]. This was illustrated by a 1972 study by Nieman and Mass, discussed in a work by Khan, which concluded that the "intimate association of organic matter and clay may cause some modification of their adsorptive properties, or they may
complement each other in the role of pesticide adsorption" [48].

These findings were later refined in a study by Saltzman, Klinger, and Yaron to determine the relative importance of organic and mineral constituents in the adsorption of parathion in the soil environment [60]. This study revealed that adsorption of organophosphorus pesticides by natural soils was greater than the adsorption by organic matter alone. It was concluded that the variation in the adsorption potential of different soils could not be explained by relative clay and organic matter content alone, but rather the "specific interactions between the organic and mineral colloids determine the nature of the adsorptive surfaces for each soil" [60]. This same finding was emphasized by Khan in his statement that the "presence of organic matter-clay complexes in most mineral soils must be considered in evaluating the importance of organic matter in pesticide adsorption" [48].

Other soil properties important in the adsorption of pesticides are the CEC, the surface area, the soil pH and eH, and the soil moisture content [48,63]. Increases in CEC and adsorption surface area, often related to increased proportions of soil organic matter, predictably lead to increased organophosphorus pesticide adsorption as cited earlier.
The effects of soil pH on organophosphorus pesticide adsorption have been fairly consistent. Generally, a pH of less than 7.0 leads to a small increase in adsorption for organophosphorus pesticides [5]. The importance of pH in adsorption potential arises from the fact that it governs the ionization of most organic molecules, as well as controlling the dissociation of functional groups contained in soil organic matter and determining the charge on the oxide coatings of clay [9,48]. A study using parathion found that significantly larger amounts of pesticide were adsorbed when $H^+$ was located on the exchange sites of organic matter [52]. The increased parathion adsorption found in acidic soils was attributed to decreased competition for the adsorption sites offered by water molecules at the lower values of pH. A 1986 study by Sharma confirmed this prediction for the adsorption of Malathion on both a silt loam and a sandy loam soil. For both types of soil, it was found that at lower pH values Malathion adsorption increased, while at higher pH values adsorption decreased [66].

The effects of soil moisture content are less well defined. Very low values of soil moisture lead to the crystallization of pesticide molecules and limited pesticide adsorption because the adsorption process usually occurs in the liquid phase. Moisture levels exceeding 30% also lead to decreases in adsorption [5]. Because pesticide transport
to the adsorption sites is usually accomplished by water, soil moisture can determine the accessibility of those sites. However, because moisture content also affects the surface properties of the adsorbent, a negative relationship between pesticide adsorption and soil moisture content is most common [63]. This result was confirmed by Yaron in 1978, who found that the adsorption of parathion by attapulgite decreased with increases in soil moisture [87].

Finally, additional studies have shown that temperature and saturation of the soil with various cation solutions affect the adsorption of organophosphorus pesticides. Because adsorption processes are exothermic, adsorption usually increases with temperature decreases [31,45]. This finding is attributed not only to thermodynamic considerations, but to the solubility of the adsorbate [88]. In a study of the adsorption of parathion by soil organic matter performed by Leenheer and Ahlrichs, it was concluded that the amount of pesticide adsorbed decreased as the temperature increased [52]. However, working with phorate in a field study, Singh found that the adsorption of this pesticide decreased in colder temperatures [69].

The effects of the saturating cation on pesticide adsorption were studied from 1970 through 1978 by Bowman. It was found that the adsorption of organophosphorus pesticides on humic materials could either be increased or decreased depending on the particular cation chosen
[10,11,13]. The same result was found by Khan in studying the effects of different saturating cations on the adsorption of fonofos by humic acid [48].

Pesticide Properties Affecting Adsorption

According to Bailey and White, the characteristics of a pesticide most applicable to its adsorption potential are the chemical character, shape, and configuration of the pesticide molecule; the acidity or basicity; the water solubility; the charge distributions on cations; the polarity of the molecule; the molecular size; and the polarizability and ionization potential of the pesticide molecule [3].

One of the factors determining the chemical character as well as the shape and configuration of a pesticide molecule is the type and configuration of its functional groups. The functional groups of particular concern are the carboxyl (−COOH), carbonyl (−C=O), hydroxyl (−OH), and the amino (−NH₂) functional groups [3]. In general, the following functional group configurations lead to increased adsorption: R₃N⁺, −CONH₂, −OH−, −NHCOR, −NH₂, −OCCR, and −NHR [3]. The P=S group, as found on both the parathion and Malathion molecules, has also been indicated in the adsorption mechanism proposed by several studies [11,13,37,61,87]. Other such factors include the nature of
substituting groups that may alter the behavior of functional groups, the position of substituting groups with respect to the functional groups, and the presence and magnitude of unsaturation [3].

The sheer weight and volume of a pesticide molecule can also affect its adsorption. Within a homologous series of nonionic pesticides, such as the organophosphorus pesticides, Bailey and White concluded that adsorption increases with an increase in molecular weight [3]. Another relationship between molecular size and adsorption was found in this same study: the greater the molecular size, the larger the van der Waals energy of adsorption. Finally, Lambert found that the parachor, a parameter proportional to the molecular volume, was useful in predicting the adsorption potential of a pesticide molecule [50]. More specifically, parachor is a "constitutive and additive function of molecular structure" that allows "comparison of molecular volumes modified to eliminate the influence of internal pressures" [50]. It was found that the larger the parachor of a pesticide molecule, the greater its adsorption potential.

The water solubility of a pesticide has been compared with its adsorption potential in many studies. As the solubility of a pesticide in water decreases, the hydrophobic character of the molecule and its adsorption potential increases [52]. In a study of four
organophosphorus pesticides, Felsot and Dahm found a significant correlation between the Freundlich adsorption constant $k$ and the inverse of the water solubility [28]. The Freundlich constant $k$ is taken from the log form of the Freundlich equation ($\log \frac{X}{M} = \log k + \frac{1}{n} \log C_0$) and is a measure of the adsorbent capacity for the adsorbate (the extent or degree of adsorption) [28]. A study of several pesticides in 1984 by Gerstl and Mingelgren found that correlations between water solubility and adsorption were significant enough to allow the prediction of a pesticide's adsorption to within one order of magnitude, based on its water solubility [30]. A study utilizing the organophosphorus pesticide Leptophos confirms the finding that the adsorption potential of a pesticide is inversely related to its solubility [16].

The same study by Felsot and Dahm examined the relationship of another pesticide property and the Freundlich constant $k$ [28]. The additional property studied was the octanol-water partition coefficient ($K_{ow}$), a measure of the pesticide molecule's tendency to favor a nonpolar milieu (octanol or organic matter) over a polar one (water or clay surfaces). The octanol-water partition coefficient had first been suggested as a predictor of a pesticide's adsorption potential by Briggs in 1973 [14]. When this theory was applied to the organophosphorus class of pesticides, a significant correlation was achieved between
\( K_{ow} \) and the Freundlich constant \( k \) [28]. Thus, large values obtained for \( K_{ow} \), predicting a tendency to favor interaction with organic matter, corresponded to a large \( k \) value, which indicates a high adsorption potential [28].

The octanol-water partition coefficient was also utilized in a study of the mobility of chlorinated and organophosphorus pesticides in the soil environment [56]. In this study, \( K_{ow} \) was incorporated into a broader measure of a pesticide's mobility potential termed the "immobilization parameters". Besides \( K_{ow} \), a pesticide's water solubility and vapor pressure, as well as the percentage of organic carbon found in the particular soil selected, were used to determine the three immobilization parameters: \( K_h \), \( K_d \), and \( K_{oc} \). \( K_h \) is the partition coefficient between air and water; \( K_d \) is the partition coefficient between soil and water; and \( K_{oc} \) is the partition coefficient relating the tendency of a pesticide to favor interaction with organic matter to the amount of organic matter found in a soil.

To interpret these parameters, a distinction must be made between the general mobility of a pesticide in the soil environment, which includes volatilization and escape to the atmosphere, and mobility that poses a threat to the groundwater. This study is concerned with the latter. Viewed in this context, the higher the values obtained for the three immobilization parameters, the lower the potential
mobility of the pesticide, and the less the potential for leaching of the pesticide through the particular soil being studied. In general, the values obtained for the organophosphorus pesticides were substantially lower than those obtained for the organochlorine pesticides, indicating that organophosphorus pesticides are potentially far more mobile in the soil environment [56].

Methods of Organophosphorus Pesticide Adsorption

The mechanisms of organophosphorus pesticide adsorption by soil constituents are van der Waals attractions, hydrophobic bonding, hydrogen bonding, charge transfer, ion transfer, and coordination through a metal ion [5,48]. Adsorption to organic matter is achieved mostly by hydrophobic bonding and by van der Waals forces [63], while the adsorption to clay minerals is largely achieved through hydrogen bonding and coordination bonds [28,48].

Adsorption of organophosphorus pesticides by clay minerals has been investigated in several studies. Through infrared and X-ray analysis, Saltzman and Yariv determined that parathion was adsorbed to montmorillonite clay through a water coordination bond between the NO₂ and P=S moieties of the parathion molecule and the metallic cations in the interlayer spaces of the clay [61]. When the system was dehydrated, parathion became directly associated with the
monovalent cations, but not with the divalent cations because water was so strongly retained in their adsorption shells. It was concluded through this study that the main adsorption sites on clays for organophosphorus pesticides are the metallic cations, and that the most important adsorption mechanism is the coordination of the organophosphorus pesticide molecule to the exchangeable cation through a water bridge, generically illustrated below:

\[
S \quad H-O \quad M
\]

\[
P \quad H
\]

[61]

It can be seen from this diagram that the water bridge is formed through the interaction of the hydration water's oxygen atom and the metallic cation, along with the coordination of the hydration water's hydrogen atom and the sulphur atom of the P=S functional group.

The importance of the water bridge was emphasized in several other studies. In examining the adsorption of Fensulfocthion on soil saturated with various cations, the three adsorption mechanisms noted were hydrogen bond formation between a functional group of the pesticide and the polarized hydration water of the exchangeable cation, protonation of one of the pesticide's functional groups by a hydrated cation, and ion-dipole interactions between the exchangeable cation and a functional group [42]. When a montmorillonite clay was saturated with Na\(^+\), Ca\(^{2+}\), Cu\(^{2+}\), Fe\(^{3+}\),
or Al$^{3+}$, Malathion was adsorbed as a double layer within the interlayer spaces by hydrogen bonding between the carbonyl oxygen atoms and the hydration water shells of the cations [12]. Saltzman and Yaron explain the water coordination bond in the following way: While the hydration of clays and the properties of the water adsorbed by these clays is not fully understood, it is generally accepted that exchangeable cations on the clay surface attract water molecules that form hydration shells. The adsorbed water is subject to increased dissociation, giving the surface a slightly acidic character and providing adsorption sites for pesticide molecules [63].

Finally, at very low moisture levels, adsorption between clay surfaces and organophosphorus pesticides is dominated by the following mechanisms: cation-dipole and coordination bonds, hydrogen bonds, and Van der Waals forces [63].

It must be remembered, however, that the adsorption of organophosphorus pesticides by clay minerals, as previously discussed, generally plays a minor role in the total adsorption spectrum. Organophosphorus pesticides are not strongly attracted to the charged surface of clays [63]. While some pesticide molecules may be adsorbed by the hydration shells forming around clay particles as discussed above, it is these same water molecules that generally prevent adsorption of the pesticide molecule on the clay
surface because the water molecules are preferentially adsorbed [38,63]. In a study conducted in 1978, Khan found that there was substantially greater adsorption of parathion on attapulgite when hexane rather than water was the carrier liquid [47]. He concluded, as did Gerstl and Yaron in 1977 [31], that while parathion could successfully compete with the nonpolar hexane molecules for the adsorption sites on the clay surface, it could not compete with the polar, strongly adsorbed water molecules [47].

Additionally, in all situations except studies with isolated clay fractions, a pesticide molecule has far less chance of coming within close proximity of a clay surface than an organic one [28]. Due to the intimate association of the organic and mineral fractions of the soil, much of the mineral fraction has an organic matter coating. This condition, along with the extensive surface area of organic matter resulting from its porous molecular structure, indicate that the probability of contact between a pesticide molecule and organic matter is very high while contact with a clay surface is much less probable [28].

The adsorption of organophosphorus pesticides occurs mainly through hydrophobic interactions with the organic matter surfaces [16,28,60]. Soil organic matter is a diverse mixture of saturated and unsaturated cyclic and heterocyclic ring structures, proteins, carbohydrate residues, carboxyls, alcohols, and many other organic
molecules. Through polymerization, molecular weights of up to 300,000 may be achieved, providing numerous hydrophobic portions where organic molecules of low water solubility are preferentially adsorbed [16]. Predictably then, the initial phase of adsorption is generally the partitioning between the organic matter and the soil solution [51,72], a partitioning into the hydrophobic sites of the organic matter [28].

Leenheer and Alrichs found that "the adsorption of parathion on soil organic matter in aqueous systems is considered to be a physical bond, involving van der Waals forces, between the hydrophobic portions of the adsorbate molecules and the adsorbent surface" [52]. They found that $H^+$ saturated organic matter had a higher adsorption capacity than $Ca^{2+}$ saturated organic matter and explained this difference by the more hydrophobic character of organic matter saturated with $H^+$. The importance of the hydrophobic nature in pesticide adsorption was concluded to be that the competitive aspects of water adsorption was minimized at these hydrophobic portions [52]. It was also found in this study that the various functional groups contained in organic matter were not directly involved in adsorption but were important in that they affected the hydrophobic or hydrophilic nature of the adsorbing surface. The adsorption was attributed to physical mechanisms due to the low heats of adsorption, the fast adsorption rates, the high
adsorptive capacities on hydrophobic surfaces, and the reversibility of the adsorption process [52].

Khan explains that parathion and other nonionic pesticides are particularly suited to such physical adsorption mechanisms because they have nonpolar regions of significant size in proportion to the polar regions of the molecule [48]. In these nonpolar regions, the functional groups bind to the nonpolar parts of humic materials through a hydrophobic interaction. Because water competition is minimal in such an interaction, adsorption of nonpolar pesticides from an aqueous solution is possible [63].

In a study of the adsorption of several organophosphorus pesticides, Felsot and Dahm substantiate that the physical mechanisms of adsorption are properly indicated in the adsorption of organophosphorus pesticides [28]. The rapid equilibration of the pesticide between the soil and the soil solution witnessed in this study was determined to be characteristic of a physical adsorption mechanism. No activation energy is required in physical adsorption so that the adsorption can occur immediately when the adsorbate and adsorbent come into sufficiently close proximity of one another [28]. Because the Gibbs Free Energy values (delta G) associated with the adsorption of these organophosphorus pesticides were far too low to be associated with chemisorption, it was concluded that their adsorption onto soil surfaces must be primarily due to the
physical adsorption processes of hydrophobic bonding and van der Waals forces. The justification for choosing hydrophobic bonding as one of the physical means of adsorption stems from numerous studies reporting an inverse relationship between the water solubility of the pesticide and the adsorption by organic matter [63].

However, hydrophobic bonding and van der Waals forces, while considered to be the main mechanisms of organophosphorus pesticide adsorption to the soil organic matter, are not the only mechanisms. H-bonding and coordination to inorganic cations, as well as the interactions between the polar active sites of the organic matter and the appropriate functional groups of the pesticide molecule, could also be involved [63].

Additional adsorption mechanisms between the organophosphorus pesticides and the soil organic matter could be possible depending on the hydration status of the soil organic matter. By affecting the molecular shape of humic substances, the hydration status also affects the accessibility of pesticide molecules [63]. According to Saltzman and Yaron, "strong, sometimes irreversible retention of pesticides by hydrated humic substances could be explained by the penetration and trapping of pesticides into the internal structure of the swollen humic substances" [63]. In addition to the "trapped" pesticides, pesticide adsorption can be increased by the additional adsorption
sites resulting from the hydrated status: hydrated exchangeable cations, dissociated functional groups, and water held by polar groups within the humic substance structure [63].

The kinetics of the adsorption of organophosphorus pesticides to organic matter has also been investigated. Identical adsorption studies of parathion on soil organic matter conducted at 5, 25, and 40 °C revealed that the adsorption rate increased as the temperature was increased, even though the total amount of pesticide adsorbed was decreased [52]. It was also found that this adsorption proceeded in two distinct stages. The first and faster of the two stages involved the transference of the solutes from solution to the surface of the adsorbent. This rate was dependent on the "solute diffusion through the water film surrounding the adsorbent particle" [52]. The second stage, which proceeded more slowly, was identified as the diffusion of the pesticide molecules from the surface into the interior of the adsorbent [52].

Desorption and Mobility

In several studies, adsorption was identified as the most important factor influencing the mobility of a pesticide through a soil-water system [1,4,40,42,44,61]. Adsorption of an organophosphorus pesticide is generally
reversible, at least partially so, leading to the concept of desorption [28,52,89]. However, desorption cannot be considered as simply the reverse of adsorption, because different processes are at work.

A study conducted by Giles in 1972 identified an energy of activation for desorption that was equivalent to the heat of adsorption [33]. This seems to suggest that adsorption and desorption may simply be the reverse of one another. The results of two adsorption-desorption studies using organophosphorus pesticides, however, help to clarify the distinction [28,60]. In both studies, when the Freundlich isotherms for adsorption and desorption were plotted, the two curves did not overlap. The "noncoincidence of adsorption and desorption isotherms is called hysteresis, which indicates that a different range or spectrum of forces are involved in adsorption than in desorption" [28].

These same two studies shared another conclusion. In both studies, the desorption from natural soils with organic matter content was compared to the desorption from natural soils with lower organic matter content and to soils treated with $\text{H}_2\text{O}_2$ to remove the soil organic matter. The organophosphorus pesticides tested were found to be more mobile—more susceptible to desorption and leaching—in soils of lower organic matter content [28,60]. This result expressed itself both in the smaller differences between the adsorption and desorption isotherms for $\text{H}_2\text{O}_2$-treated soils,
and in the steep slope of the desorption isotherm obtained for these soils, showing that adsorption was easily and totally reversible [60]. The increased mobility of organophosphorus pesticides in soils of lower organic matter content was attributed to the relative strength of the pesticide organic complexes compared to the pesticide mineral complexes [60,89]. This finding was verified in the work of Wolcott, who determined that similar leaching treatments of pesticides adsorbed to different soils would result in the complete release of pesticides from clays, but only a partial release from highly organic soils [86].

In a study conducted by Swabota and Thomas, parathion was subjected to leaching by various solutions in soils of varying organic matter and clay content [72]. This study also found reduced desorption in the soils of higher organic matter content. Further, it was determined that parathion was not effectively desorbed by water or by electrolyte salt solutions. However, when subjected to leaching by ethanol, the mobility of parathion in the soil column was substantially increased [72]. From these results, several conclusions were drawn. From the low effluent concentrations of parathion obtained when the soil columns were leached with water, far less than would have been predicted by the pesticide's water solubility, it was determined that some additional factor other than water solubility was interfering with the leaching process.
Because electrolyte leaching solutions were equally ineffective, it was further determined that adsorption by ion exchange processes was not responsible for the unusually low desorption. Rather, because a 95% ethanol solution readily extracted the parathion, the obstacle to the leaching was determined to be the adsorption of parathion "as an organic constituent of the soil similar to the partitioning process in liquid-liquid extractions" [72].

In a very extensive study, Helling analyzed the mobility of eight nonionic pesticides, including the organophosphorus pesticide azinphosmethyl, in fourteen different soils [44]. The mobility of the pesticides on each of the soils was determined using soil thin-layer chromatography, a chromatographic technique employing soil as the adsorbent phase and water as the carrier. The movement of the adsorbate, the pesticide, relative to that of the water front yields an "R_f" value, which is a measure of the pesticide's mobility. The R_f values resulting from Helling's study were correlated with the following soil properties: organic matter content, clay content, moisture capacity, pH, and CEC. As in the studies discussed above, this study confirmed that high organic matter content correlated with reduced pesticide mobility. Significant correlations to reduced mobility were also found with moisture capacity, clay content, and CEC [44].
In a leaching study using phorate, it was determined that the pesticide could be more effectively desorbed and leached to greater depths depending on how the leaching solution was applied. Water applied at a constant rate led to greater desorption than water applied under variable flux conditions [68]. A leaching study using several different organophosphorus pesticides, including Malathion, found that of several different salt leachates applied, maximum mobility of all the pesticides was achieved with a potassium chloride solution [66]. A further study of Malathion and other organophosphorus pesticides revealed that additions of CaCO$_3$ and flyash decreased the mobility of the pesticides in soil columns while saline solutions achieved the maximum mobility [65].
MATERIALS AND METHODS

The soil utilized in this study was a Manor silt loam. This soil was chosen because it is the predominant type of soil found in Fairfax County. Specific chemical characteristics and constituents of the soil are listed in Table 1. A detailed soil profile description is provided in Table 2. The soil profile was described from a hand dug soil examination pit with a depth of 72 inches. After the profile description had been completed and the soil horizons carefully delineated, samples to be used in this study were removed from the midpoint of each horizon. Each soil horizon sample was then air-dried and passed through a 2 mm sieve [18,25,28,29,35]. Plexiglass columns measuring 20 cm long, with an inner diameter of 1.5 cm, were used in the study. All columns were filled with the air-dried soil using exactly the same procedure to obtain column uniformity [29,35]. Moisture was not added to the columns before applying the pesticide solutions [24-26]. The initially dry condition was chosen due to the great difficulty in achieving uniform initial moisture levels in all columns,
Table 1. Chemical Analysis of Soil\(^1\)  
(all concentrations in PPM)

<table>
<thead>
<tr>
<th>Horizon</th>
<th>pH</th>
<th>%OM</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
<th>Mn</th>
<th>NO(_3)-N</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5.0</td>
<td>2.3</td>
<td>108</td>
<td>55</td>
<td>26</td>
<td>23.9</td>
<td>5</td>
<td>1.2</td>
</tr>
<tr>
<td>B1</td>
<td>5.1</td>
<td>1.0</td>
<td>72</td>
<td>56</td>
<td>24</td>
<td>20.0</td>
<td>3</td>
<td>0.8</td>
</tr>
<tr>
<td>B2t</td>
<td>4.9</td>
<td>0.7</td>
<td>48</td>
<td>31</td>
<td>19</td>
<td>11.5</td>
<td>3</td>
<td>0.7</td>
</tr>
<tr>
<td>B3</td>
<td>4.9</td>
<td>0.5</td>
<td>48</td>
<td>15</td>
<td>25</td>
<td>6.4</td>
<td>3</td>
<td>0.4</td>
</tr>
<tr>
<td>CR</td>
<td>5.1</td>
<td>0.5</td>
<td>48</td>
<td>14</td>
<td>39</td>
<td>7.8</td>
<td>3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

\(^1\)Analyzed at the Soil Testing and Plant Analysis Laboratory; Virginia Polytechnic Institute and State University; Blacksburg, Virginia
Table 2. Soil Profile Description

**Soil Type:** Manor silt loam  
**Slope:** 2-7%  
**Landscape Position:** Upper Convex Sideslope  
**Geologic Province:** Piedmont Upland  
**Parent Material:** Weathered Sericite Schist

<table>
<thead>
<tr>
<th>Hor. Depth (in.)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 1-0</td>
<td>Very dark grayish brown; weakly decomposed and decomposed dogwood, oak, and maple leaves.</td>
</tr>
<tr>
<td>A 0 - 4</td>
<td>Dark grayish brown silt loam; granular to very weak sub-angular blocky structure; few krotovinas (up to 1/4 inch diameter), common krotovinas (up to 1/8 inch diameter); friable; clear smooth boundary.</td>
</tr>
<tr>
<td>B1 4 - 8</td>
<td>Light yellowish brown; heavy silt loam to light silty clay loam; weak subangular blocky structure; common roots up to 1/2 inch in diameter; common pores; friable; clear smooth boundary.</td>
</tr>
<tr>
<td>B2t 8 - 23</td>
<td>Light yellowish red; light silty clay loam to heavy silt loam; weak subangular blocky structure; common fine roots; few coarse roots (up to 3/4 inch in diameter); few fragments of weakly weathered schist, few fragments of quartzite (up to 1 inch in diameter), and common very fine mica flakes; thin coatings of black manganese/organic staining along old root channels; friable; clear wavy boundary.</td>
</tr>
<tr>
<td>B3 23 - 28</td>
<td>Light yellowish brown and light yellowish red silt loam; weak subangular blocky structure; few fine roots; common weakly weathered schist fragments (up to 1.5 inches in diameter) which crushes easily to expose multicolored (red to black) mineral content; friable; abrupt wavy boundary.</td>
</tr>
</tbody>
</table>
Table 2. Soil Profile Description (continued)

| CR 28-72 | Multicolored (yellowish red, olive brown, strong brown, and yellowish brown) very fine sandy loam to coarse silt loam; rock controlled structure (has appearance of platy structure which separates and crushes easily to granular); few fine roots throughout the horizon; many fine micaflakes; evidence of iron staining, manganese oxides, and thin silt and clay coatings along old fracture joints of the highly weathered schist; friable. In this horizon, a thin discontinuous seam (up to 2 inches thick) of weakly weathered to weathered schist occurs horizontally across approximately 1/3 of the pedon face, at a depth of approximately 42 inches. This seam is coated with manganese which suggests localized restriction of downward water movement. Throughout the saprolyte, there is strong evidence of eluviation of iron and manganese oxides. This, along with the thin discontinuous silt and clay coatings along old fracture joints of the parent schist materials, is indicative of good drainage. |
which would likely have caused column variability.

Soil from the A horizon was used in the investigation rather than from the B horizon, which is normally chosen for soil column investigations [29]. This selection resulted from numerous studies declaring the greater affinity of organophosphorus pesticides for adsorption by organic matter [11,16,28,32,37,45,46,49,50,60,62,63,65,78,86], which is most highly concentrated in the A horizon [29], over adsorption by the clay fraction, which is most highly concentrated in the B horizon [28,48,63]. The results of the laboratory analysis listed in Table 1 verify that the A layer contained the greatest percentage of organic matter.

Thirty-five grams of soil were slowly added to each column, tapping the column steadily during filling to allow for settling, so that a total volume of 31.6 mL was obtained. This yielded a bulk density of 1.11 g/mL [35] and a pore volume of 15.34 mL. Grade 2S filter paper was installed at both ends of the soil column to prevent erosion and channelling at the top of the column as the solution dripped in, and to prevent contamination of the effluent by escaping soil material at the bottom of the column [29].

The solution was introduced into the column by use of a peristaltic pump [29]. A Scientific Industries Model 403 pump was used. The pump withdrew the solution, which was subjected to continuous mixing by an automatic stirrer, from a beaker covered with wax sealant to prevent evaporation.
The solution was delivered to the top of the column through 2 mm (inner diameter) Tygon tubing where it then dripped onto the filter paper that covered the soil surface. Effluent leaving the column was captured by the use of a Searle Buchler Instruments Fractomette 200 Alpha automatic fraction collector [29]. A schematic of the soil column apparatus and appurtenances is provided in Figure 1. The fraction collector was set to switch collection tubes every five minutes [18]. The pump was calibrated to deliver solution at the rate of 1 mL per minute for individual and combination runs, and 1.25 mL per minute for the series runs. These flow rates were chosen during preliminary runs because they allowed substantial eluent concentrations to be reached in a reasonable time frame. Actual flow rate achieved varied slightly from run to run due to variations in flow resistance encountered in the individual columns.

Three different solutions were introduced into the columns: individually, in combination, and in series. The first solution, a 100 mg/L PO₄-P solution [7], was prepared by diluting .348 g of KH₂PO₄ [7] to a total volume of 1 L. The Malathion solution was prepared from a commercial solution manufactured by Chevron Chemical Company². This solution was chosen over pure Malathion to better approximate field use conditions. The commercial solution

² Chevron Chemical Company; Ortho Consumer Products Division; PO Box 5047; San Ramon, CA 94583-0947
Figure 1. Schematic of soil column apparatus and appurtenances
was a 50%-by-weight solution of Malathion diluted with xylene (33%) and an inert solution (17%). An approximate Malathion concentration of 100 mg/L was obtained from the commercial solution by first diluting 2 mL of the solution to a final volume of 1 L, to approximate a 1 g/L concentration. Serial dilutions then yielded the desired concentration of 100 mg/L. The exact concentration of this solution, 127.8 mg/L, was subsequently determined using gas chromatograph analysis.

As with the flow rates, the concentrations of the Malathion and phosphate solutions were arrived at through numerous preliminary runs in which concentrations were varied over a wide range, from 1 mg/L to concentrations over 100 mg/L. The final concentrations of 100 mg/L were chosen for the following reasons. As with the determination of flow rates, the concentrations of Malathion and phosphate chosen allowed substantial eluent concentrations to be reached in a reasonable time frame. In addition, pesticide and phosphate concentrations of this order of magnitude, and greater, were used in previous soil adsorption and desorption studies [7,10,44,57,61]. Finally, Malathion concentrations of 100 mg/L are far less than suggested application concentrations of the commercial solution.

The third solution used, the naturally occurring organic acid solution, was prepared by mixing 200 g of detritus from the 0 soil horizon with 2 L of water. A
chemical analysis of this solution is presented in Table 3, including values for chemical oxygen demand and pH, along with the concentrations of dissolved solids, nitrate nitrogen, and phosphates found in the solution. The mixture was stirred for 10 minutes, allowed to stand for 4 hours, and then filtered through grade 802, 24 cm filter paper. Deionized water and reagent grade chemicals were used for all solutions.

Seven different combinations of the above solutions were run through the soil columns: phosphate alone, Malathion alone, a Malathion-phosphate mixture, a Malathion-organic acid mixture, Malathion followed by water, Malathion followed by water followed by phosphate, and finally, Malathion followed by water followed by organic acid. Each of the runs was repeated at least once for verification [29]. Each of the individual and combination runs lasted 6.6 hours with 80 effluent samples collected. The duration of each series run was 10 hours with 120 effluent samples collected. For three-solution series runs, the application of the different solutions to the soil column was timed so that an equal number of samples were collected for each solution. Thus, each solution of the series contributed one third of the total number of pore volumes for the run. When only two solutions were applied in series, the first solution accounted for one third of the total number
Table 3. Chemical Analysis of the Organic Acid Solution

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Oxygen Demand</td>
<td>175.0 ppm</td>
</tr>
<tr>
<td>Dissolved Solids</td>
<td>357.0 ppm</td>
</tr>
<tr>
<td>Nitrate Nitrogen</td>
<td>29.22 ppm</td>
</tr>
<tr>
<td>Phosphates</td>
<td>3.55 ppm</td>
</tr>
<tr>
<td>pH</td>
<td>6.8</td>
</tr>
</tbody>
</table>

---

3 Analyzed at the Fairfax County Health Department Laboratory; Fairfax, Virginia
of samples; the second solution accounted for the remainder.

A separate run was made for Malathion in an attempt to obtain a breakthrough curve. Even though the run was continued for 13.5 hours with 160 samples collected, eluted Malathion concentrations never approached breakthrough concentrations. Breakthrough concentrations were approximated in the phosphate runs, however, as displayed in Figure A-2 of the Appendix.

Combination runs were achieved by premixing equal volumes of the solutions immediately prior to starting the run. Solutions of 200 mg/L were mixed to obtain a final concentration of 100 mg/L for each species. Series runs were achieved by removing the polyglass tubing from the initial solution, quickly rinsing and drying the submerged portion, then placing the tube in the subsequent solution. The resulting small air bubble, if it was not dispersed in the pump, allowed determination of the precise time of entry for each solution into the soil column.

A 1 mL portion of the each effluent sample was immediately analyzed for phosphate using the vanadomolybdophosphoric acid colorimetric method [71]. A Bausch and Lomb Spectronic 20 spectrophotometer set at a 400 um wavelength was employed in this analysis. Another 1 mL portion of the effluent was used in an extraction procedure in preparation for gas chromatograph analysis. The extraction procedure involved the mixing of the 1 mL portion
of effluent with 10 mL of pesticide-quality hexane in a 125 ml separatory funnel [52,57,71,76]. The mixture was shaken vigorously for 2 minutes [52,80]. The organic and water phases were then allowed to separate completely before draining off the water phase. The organic phase was then sealed in a test tube and stored at 0 °C until gas chromatograph analysis could be performed (never longer than 24 hours after the extraction) [52,71]. In addition to the effluent samples extracted, a 1 mL sample of the approximately 100 mg/L Malathion solution was also extracted for comparison. Due to the high concentrations of Malathion used and the purity of the solutions, both the concentration by evaporation and the "sample clean-up" by column adsorption chromatography procedures detailed in Standard Methods proved unnecessary [71].

Malathion analysis was performed using a Perkin Elmer Sigma 2 gas chromatograph and a Perkin Elmer LC1-100 computing integrator. The electron capture detector was used along with a 4 mm by 1.83 m 5% OV-210 chromatographic column [55,71,80]. The following parameters were used for the entire analysis: injection temperature of 200 °C, oven temperature of 220 °C, a detector temperature of 350 °C, and an injection volume of 15 uL [29,71]. Argon-methane (95% + 5%) was used as the carrier gas at a rate of 70 mL/min [71]. A Malathion peak was obtained after an average
retention time of 3.8 minutes. A sample gas chromatograph curve illustrating this retention time is shown in Figure A-1. The gas chromatograph was always conditioned with two injections of a 100 mg/L Malathion standard solution before starting sample injections. The injection syringe was thoroughly cleaned with hexane in between injections of samples. Freshly prepared Malathion standard solutions of 0.25, 0.5, 1.0, 2.0, 3.3, and 5.0 mg/L were run for each use of the gas chromatograph. These solutions were prepared from 0.5 g pure Malathion diluted to a total volume of 500 mL, yielding a final concentration of 1.0 g/L. This solution was then reduced to the above concentrations through serial dilutions.
RESULTS AND DISCUSSION

The results of this study are most easily analyzed and interpreted through graphical representation. Pore volume versus concentration plots for each type of run are presented in Figures 2-8. Plots of verification runs are displayed in Figures A-8 through A-16 of the Appendix. The plots are presented in the pore volume versus concentration format rather than the breakthrough curve format of pore volume versus $C/C_0$. This format proved more useful in this study because breakthrough concentrations of Malathion could not be achieved in the specified run times.

Adsorption Study

Comparison of the plots representing the phosphate analysis of the phosphate-only run and the combined phosphate-Malathion solution run, displayed in Figure 2, revealed great similarity. The presence of Malathion appeared to have little effect on the adsorption of phosphate to the soil. For clarity, these two runs are
Figure 2: Comparison of phosphate elution curves for phosphate-only solution vs. combined Malathion and phosphate solution.
Figure 3: Comparison of Malathion elution curves for malathion-only solution vs. combined Malathion and phosphate solution.
Figure 4: Comparison of Malathion elution curves for malathion-only solution vs. combined Malathion and organic acid solution.
Figure 5. Malathion elution curve for application of solutions in series: Malathion solution followed by deionized water.
Figure 6. Malathion elution curve for application of solutions in series: Malathion solution / deionized water / phosphate solution.
Figure 7: Phosphate elution curve for application of solutions in series: Malathion / deionized water / phosphate solution.
Figure 8. Malathion elution curve for application of solutions in series: Malathion solution / deionized water / organic acid solution.
presented as individual plots in Figures A-3 and A-4.

Figure 3, a comparison of the plots representing the Malathion analysis of these same two runs however, showed a substantial difference. Again, individual plots for these runs are provided in Figures A-5 and A-6. Malathion, when introduced into the column along with the phosphate solution, showed far greater mobility than Malathion alone. The reduced travel time through the column in the presence of phosphate may suggest that the Malathion and phosphate molecules were in competition for the same adsorption sites on the clay and soil organic matter, and that the phosphate molecule was preferentially adsorbed over the Malathion molecule. This conclusion appears to be compatible with the phosphate analysis for these runs. Finding almost no change between the curves obtained for the phosphate solution alone and for phosphate in combination with Malathion seems to suggest that phosphate is so preferentially adsorbed that the Malathion molecules provide little to no interference.

That phosphate and Malathion could actually be competing for the same adsorption sites can be postulated from a study by Evans of phosphorus mobility in coarse-textured soils [26]. It was determined in that study that neither the clay fraction nor the hydrous oxide coating, but rather, the organic matter coating was primarily responsible for phosphate adsorption. Numerous studies cited in the literature search indicate that organophosphorus pesticides
seek adsorption sites on the organic matter fraction as well. Whether both the phosphate and Malathion molecules are actually competing for identical adsorption sites, or whether the adsorption of the phosphate molecule blocks or somehow alters the adsorption sites that would normally be occupied by Malathion could not be determined from this study.

These results are also displayed in Table 4, where the total amount of Malathion introduced into the soil columns is compared with the total amount eluting from the column and the total amount adsorbed within the column. In the Malathion-only run, a total of 55.397 mg of Malathion entered the soil column, slightly more than the total amount of Malathion introduced during the Malathion-phosphate run. This difference may be attributed to the small variations in flow resistance resulting from varied soil particle and pore space arrangements within a packed column, as well as tortuous flow. But even though slightly less Malathion was introduced into the soil column during the Malathion-phosphate run, more Malathion eluted from the column, emphasizing the phosphate solution's ability to increase the mobility of the Malathion molecule. The final row of entries in Table 4 corrects for the effects of varying flow resistance and tortuosity by presenting the amount of Malathion adsorbed in relation to the total volume of solution applied to the column.
Table 4. Comparison of the Mass of Malathion Introduced to, Adsorbed in, and Eluted from the Soil Column

<table>
<thead>
<tr>
<th>Name of Run</th>
<th>Malathion Only</th>
<th>Malathion and Phosphate</th>
<th>Malathion and Organic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Volume of Malathion Solution</td>
<td>0.433</td>
<td>0.432</td>
<td>0.408</td>
</tr>
<tr>
<td>Added to the Column (L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Mass of Malathion Added to</td>
<td>55.397</td>
<td>55.167</td>
<td>52.208</td>
</tr>
<tr>
<td>the Column (mg)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cumulative Eluted Malathion (mg)</td>
<td>6.397</td>
<td>9.826</td>
<td>9.711</td>
</tr>
<tr>
<td>% of Total</td>
<td>11.55%</td>
<td>17.81%</td>
<td>18.60%</td>
</tr>
<tr>
<td>Mass of Malathion Adsorbed in Column</td>
<td>49.000</td>
<td>45.341</td>
<td>42.494</td>
</tr>
<tr>
<td>(mg)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% of Total</td>
<td>88.45%</td>
<td>82.19%</td>
<td>81.39%</td>
</tr>
<tr>
<td>Mass Malathion Adsorbed per Liter</td>
<td>113.039</td>
<td>105.036</td>
<td>104.939</td>
</tr>
<tr>
<td>of Solution Applied (mg/L)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Similarly, a comparison of the plots representing the Malathion analysis of the Malathion-only run and the combined Malathion-organic acid solution run, displayed in Figure 4, showed substantial differences in time of transport through the soil column. The mobility of the Malathion was increased in the presence of the organic acid solution, indicating that either the adsorptive qualities of the various adsorption sites on the organic and mineral portions of the soil were reduced by the organic acid solution or that the organic molecules were in direct competition with phosphate for the same adsorption sites. The Malathion-organic acid solution run is also presented individually in Figure A-7.

Again, the data presented in Table 4 help to clarify these results. In comparing the total volume of Malathion solution applied to each column, a greater difference is found between the Malathion-only and Malathion-organic acid runs than was found between the Malathion-only and the Malathion-phosphate runs, far greater than could reasonably be explained by varying flow resistances or tortuosity alone. It was observed that the organic acid solution, or the organic acid solution in combination with Malathion, appeared to have a negative impact on the porosity of the soil column. To determine whether this was caused by an occlusion of the soil pore spaces, by a change in the
viscosity of the solution, or by some additional effect would require further investigation.

No matter what the cause, however, the finding that less Malathion solution was applied during the Malathion-organic acid run highlights the effect of the organic acid solution on the mobility of Malathion. As with the Malathion-phosphate run, more Malathion eluted from the column even though less Malathion solution was applied. In addition, the Malathion solution traversed the soil column at a slower rate during the Malathion-organic acid run than during the Malathion-only run. A reduced rate of flow through a soil column has been found to correlate with increased adsorption \([18,68]\), because a longer reaction time is provided. That adsorption was found to decrease during the Malathion-organic acid run, despite the slower flow rates, dramatizes the "mobility increasing" effect of the organic acid solution.

This effect may be partially explained by an earlier study of phosphate mobility by Evans in which "changes in the distribution of extractable phosphate with depth were attributed to increased competition for phosphate adsorption sites by various organic molecules which were released into the bulk solution when the organic matter coatings underwent a transition" \([25]\). Because naturally occurring organic molecules were found to compete with phosphate molecules for soil adsorption sites in that study, and because it appears
from the data presented in this study that phosphate and Malathion also compete for the same adsorption sites, preferential adsorption of the naturally occurring organic acids may have led to the increased mobility of Malathion.

In a study of the adsorption of several organophosphorus pesticides on montmorillonite suspensions, high levels of fulvic acid, a naturally occurring organic acid, were found to decrease adsorption [11]. While it has already been emphasized that the organic fraction of the soil is primarily responsible for pesticide adsorption, the conclusions drawn from that study may still be helpful in this analysis. The decreased adsorption was ultimately attributed to the competitive effects of the fulvic acid molecule. If the fulvic acid and the organophosphorus molecules compete for the same adsorption sites on the mineral fraction, it is possible that the chemical similarity between these molecules that allows such competition may lead to an affinity for like adsorption sites on the soil organic matter as well. The resulting competitive adsorption would help to explain the large difference in pesticide adsorption found in this study when naturally occurring organic acids were present, larger than could reasonably be attributed to variations in the mineral fraction's adsorption potential alone.

Wernshaw had a different explanation for the reduced pesticide adsorption experienced in the presence of a humic
acid solution. Rather than competitive adsorption, this reduction was linked to the decrease in surface water tension caused by the presence of the humic acid solution, and the resulting increase in the solubility of the pesticide [85]. Similarly, both humic and fulvic acids have been found to increase the mobility of cations and inorganic phosphates in the soil by either creating complexes, with greater solubility than the cation or phosphate alone, or by chelation [73]. It has been suggested that similar processes could increase the mobility of organic molecules [74]. However, the specific mechanism by which the organic acid solution reduces the adsorption of Malathion--be it competitive adsorption, decrease in surface water tension, complex formation, or some additional mechanism--cannot be predicted from the results of the current study.

In analyzing the data from runs utilizing the organic acid solution, it must be remembered that naturally occurring organic acids are not the sole constituent of this solution, as is evident from the results of the chemical analysis displayed in Table 3. That naturally occurring organic acids were present in the solution was confirmed by its characteristic brownish-black color. Additionally, naturally occurring organic acids are a known byproduct of the decomposition of non-humic substances in the soil [9]. However, the actual percentage of the chemical oxygen demand attributable to the organic acids was not determined.
Because other compounds were present in the solution, it cannot be conclusively stated that the naturally occurring organic acids were solely responsible for the changes in adsorption that were observed. However, the results of the laboratory analysis of the solution, as well as a review of the applicable literature, suggest that the naturally occurring organic acids are the most probable cause. Phosphates were found in the solution which have already been linked by this study with reduced adsorption of Malathion. The concentration of phosphate, however, was very low when compared to the 100 mg/L levels necessary to achieve the adsorption changes that were observed. So it would appear that the phosphate contained in the organic acid solution was likely not the primary cause of the reduced adsorption.

The pH of the solution approximated neutrality, as did the Malathion and phosphate solutions, so that its effect on adsorption should be minimal. Substantial nitrate levels were found in the solution, but because nitrate is only weakly retained by soil colloids [9], preferential adsorption of the nitrate molecule over the Malathion molecule seems unlikely. Finally, naturally occurring organic acids have already been indicated in the reduced adsorption of eluted substances by several studies in the literature [8,11,73].
Descrition Study

The above combination of solutions sought to determine if the mobility of Malathion in soil could be affected through competitive adsorption, or some other adsorption reducing mechanism, with phosphate and naturally occurring organic acids. The following combination of solutions attempted to show a different result; that is, if the Malathion, once adsorbed on the soil, could be leached by subsequent introduction of the same solutions. The curves in this section cannot be directly compared with the curves in the prior section because a slightly higher flow rate (1.25 mL/min) was chosen to facilitate movement of the various solutions through the soil column. The increased flow rate delivered by the peristaltic pump led to higher concentrations of all solutions in the eluted samples, per unit pore volume, than in the previous section.

Figure 5 represents the series run in which Malathion solution was initially introduced to the column, followed by a water leaching solution. It can be observed that the eluted Malathion concentration steadily increased as the Malathion solution was pumped through the column. Application of the solutions to the column was timed so that Malathion accounted for one third of the samples collected, and water accounted for two thirds of the samples. Thus, if the total number of pore volumes shown on the X axis of
Figure 5 is divided into thirds, the first one third marking signifies the approximate point at which water would have begun exiting the soil column, if no mixing had occurred with the Malathion solution preceding it. However, because the actual decrease in Malathion concentration occurred prior to the hydraulically predicted exit time of the water, it appears that the advancing water front did mix with and dilute the Malathion solution that preceded it. After the passing of this "mixed front", the eluted Malathion concentration continued to drop off sharply, then gradually reached a plateau.

Figure 6, the plot representing the Malathion/water/phosphate series run, showed similar initial results: the steady increase of eluted Malathion concentration followed by the sharp drop in concentration as the water was added. However, rather than settling into a plateau of constant eluted Malathion concentration, there was a slight but steady increase in eluted Malathion concentration after the phosphate solution traversed the column. This event corresponded to the point at which phosphate from the phosphate solution actually began to elute from the column, evidenced by comparison of Figure 6 with the phosphate analysis of the same run shown in Figure 7. This increase in Malathion concentration seems to indicate that the phosphate solution is more effective at leaching Malathion from the soil column than is water alone.
The Malathion/water/organic acid solution series runs were all plagued by pump malfunction so that the expected concentrations of the various effluent samples per pore volume were not achieved. Thus, these runs cannot be quantitatively compared to any of the other runs. However, when Figure 8, the plot representing this run, is viewed strictly qualitatively, it can be seen that a pattern similar to that achieved in the Malathion/water/phosphate run may have been repeated: the increase in eluted Malathion concentrations, followed by the sharp decrease upon the addition of water, followed by the steady increase as the organic acid solution was pumped through the column. As with the Malathion/water/phosphate run, application of the solution to the columns was timed so that each solution accounted for approximately one third of the total number of samples collected during the run.

Because of the pump malfunction that occurred during this run, these results are less conclusive than those obtained in the Malathion/water/phosphate run. The sharp drop in eluted Malathion concentration evident at approximately 16 pore volumes coincided with an approximately 25 minute time period in which no solution was pumped into the column. The first samples collected after pumping was restored consisted of solution that had been in contact with the soil far longer than any other samples collected during the run. The increased contact time
afforded this solution, before pumping was reestablished finally forcing the solution out of the column, may have allowed adsorptive reactions could to come closer to equilibrium.

The importance of the relationship between contact time and adsorption was emphasized by Saltzman and Yaron [62] in their discussion of a 1972 study conducted by Davidson and Chang. In that study, increased mobility of a pesticide was linked to solution flow rates through soil columns that did not allow sufficient time for adsorptive reactions to come to equilibrium. This effect was particularly evident in larger soil aggregates because of "the longer diffusion time required for a solute in the liquid phase to reach equilibrium with the internal portion of the larger aggregates."[62] The numerous studies conducting preliminary trials to determine the contact time required for adsorption and desorption reactions to come to equilibrium further emphasize the importance of this relationship [10,13,45,46,52,72].

Thus, as expected, the first samples collected immediately after pumping was restored showed a substantial decrease in Malathion concentration compared to those collected immediately prior to the pump malfunction.

Because the pump malfunction occurred at approximately the same time the organic acid solution was applied to the column, the steady increase in eluted Malathion
concentrations experienced after pumping was restored could be attributed to the greater leaching potential of the organic acid solution compared to deionized water. However, it could just as reasonably be concluded that the apparent increase in eluted Malathion concentration was primarily due to the artificially low eluted Malathion concentrations found in the samples collected immediately following the pump malfunction. As explained above, the solution collected in these samples was subjected to a longer contact time with the soil, allowing adsorptive reactions to come closer to equilibrium. In addition, during this increased contact time, the Malathion previously leached from the upper portions of the soil column may have been partially readsorbed. Because the solution collected in later samples did not experience an increased reaction time to allow more complete adsorption, and possibly readsorption, of Malathion to occur, the eluted Malathion concentrations were higher. These higher concentrations approximated the concentration of samples collected immediately prior to the pump malfunction which similarly lacked the increased contact time.

The fact that the increase in eluted Malathion concentrations proceeded to a level in excess of the concentrations prior to the malfunction seem to support the first conclusion, that the leaching potential of the organic acid solution is greater than that of the deionized water
alone. However, the absence of any sustained eluted Malathion concentration increases observed in the Malathion/water/organic acid verification run displayed in Figure A-16 appears to support the latter conclusion.

Calculation of Immobility Parameters

A relatively high level of Malathion adsorption was achieved in all of the soil column runs. For example, during the three runs described in Table 4, an average of 84.01% of the Malathion introduced to the column was adsorbed. Because the organophosphorus pesticides are generally considered one of the more mobile pesticide groups due to their relatively high water solubility, an explanation for the high degree of adsorption experienced in this study was sought.

In this regard, the immobilization parameters for Malathion on the Manor silt loam soil were calculated as described in the study by McLean et al.[56]. These parameters are presented in Table 5. For comparison, these same parameters that were calculated for the four organophosphorus pesticides in the referenced study are also provided. The data presented on the four additional pesticides have been revised so they are applicable to the Manor silt loam soil used in this study.
### Table 5. Immobilization Parameters for Several Organophosphorus Pesticides

<table>
<thead>
<tr>
<th>PESTICIDE</th>
<th>$K_d^5$</th>
<th>$K_h^6$</th>
<th>$K_{oc}^7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disulfoton</td>
<td>0.0138</td>
<td>.00011</td>
<td>0.5</td>
</tr>
<tr>
<td>Malathion</td>
<td>14.565</td>
<td>.00000418</td>
<td>633.28</td>
</tr>
<tr>
<td>Methylparathion</td>
<td>0.92</td>
<td>.0000024</td>
<td>39.00</td>
</tr>
<tr>
<td>Parathion</td>
<td>71.76</td>
<td>.000025</td>
<td>3112.00</td>
</tr>
<tr>
<td>Phorate</td>
<td>0.2024</td>
<td>.00024</td>
<td>8.8</td>
</tr>
</tbody>
</table>

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*Modified from [56]*

$^5K_d = (K_{oc}) \ [\text{%OC}/100]$  
$^6K = \text{g/m}^3 \text{ vapor pressure} / \text{g/m}^3 \text{ water solubility}$  
$^7\log K_{oc} = \log K_{ow} - 0.317$
As described in the literature search, $K_d$ is a partition coefficient between soil and water; $K_h$ is a partition coefficient between air and water; and $K_{oc}$ is a partition coefficient relating the tendency of a pesticide to favor interaction with organic matter to the amount of organic matter found in a particular soil. Two of these three parameters were used in the referenced study [56] as input variables for a mathematical model that attempts to predict the mass transport potential of pesticides in the soil environment. While the model is not applicable to this study because it includes pesticide degradation variables, the immobility parameters provide a useful basis for comparison of the potential mobility of different pesticides.

The higher the values of the three immobility parameters, the less a pesticide's predicted mobility due to leaching in the particular soil under study. The $K_h$ values for all of the organophosphorus pesticides listed in Table 5 are very low. Because $K_h$ is calculated as vapor pressure in $g/m^3$ divided by water solubility in $g/m^3$, low $K_h$ values are an indication "that the pesticide has a relatively strong affinity for the water phase" [56], suggesting that the pesticide would tend to stay in solution rather than volatilize into the atmosphere. In the referenced study, this parameter was meant to account for the potential for pesticide loss to the atmosphere.
But as far as a soil column study in which the solution in the column is not open to the atmosphere, the $K_h$ term may have little direct application. The applicability may be limited to a questionable extrapolation: The mobility of a pesticide with high $K_h$ values may be slightly reduced because of a tendency to volatilize into unsaturated void spaces or trapped air pockets within the soil column. Whether or not this extrapolation is valid, when the meaning of the $K_h$ parameter is viewed in the context of actual field conditions, where a highly volatile pesticide can escape to the atmosphere, there exists a very reasonable connection between high $K_h$ values and reduced mobility due to leaching.

The above discussion becomes academic, however, when the other immobility parameters are considered. For both Malathion and parathion, the low $K_h$ values are overshadowed by relatively high values for $K_d$ and $K_{oc}$. Such values indicate a preference for a soil medium over a water medium, and so suggest a reduced mobility potential for both of these pesticides, particularly for a soil with significant levels of organic matter.

Thus, the immobility parameters suggest that while there is a preference for Malathion to partition to water rather than air, the tendency to partition to the soil is greater still. So despite the high mobility generally expected of organophosphorus pesticides, the substantial levels of adsorption achieved in this study are consistent
with the potential mobility predicted by the immobilization parameters.

Table 5 illustrates one final point that should be considered. While the grouping of pesticides into various pesticide classes is an accepted practice and proves useful in many applications, substantial variation in any particular parameter may exist within a specific class. Generalizations about the performance of any designated class of pesticides under a certain set of conditions can be a useful predictor of a particular pesticide's performance, but only by subjecting that pesticide to a particular set of conditions can conclusive results be obtained.
CONCLUSIONS

The results of this study indicate that both the phosphate and the naturally occurring organic acid solutions increase the mobility of Malathion in the soil environment. The following more specific conclusions also resulted from this study:

1) The contribution of phosphate to this increased mobility expressed itself in two separate and distinct ways:

1A) First, phosphate applied to a soil column in combination with Malathion was found to reduce the adsorption of the pesticide below levels experienced when the Malathion solution traversed the soil column alone. It appears that this reduction in adsorption was accomplished through a competitive adsorption for similar, available adsorption sites on the clay fraction, and especially, the organic fraction of the soil.

1B) Secondly, when a phosphate solution was leached through a soil column to which Malathion had been previously applied and adsorbed, the phosphate was found to
increase the mobility of Malathion by increasing the rate of desorption when compared to leaching by water alone.

2) Similarly, a solution of naturally occurring organic acids was found to increase the mobility of Malathion in the soil column by decreasing adsorption. The mechanism responsible for the reduced adsorption may also have been the competition between the Malathion and organic acid molecules for adsorption sites, with the organic acid molecules being preferentially adsorbed. However, several other possible mechanisms were considered. The investigation of the desorption capability of an organic acid solution, however, produced inconclusive results. Additional study in this area would be required before the desorptive potential of an organic acid solution could be postulated.

3) The findings of this study may have application to both the agricultural and the domestic use of pesticides. Malathion was found to have a great affinity for the soil used in this study, as evidenced by the large values obtained for the applicable immobilization parameters. These high levels of adsorption seem to indicate that the mobility of this pesticide in a silt loam soil of moderate-to-high organic matter content would be limited. Thus, given this set of conditions, substantial leaching of this pesticide into any but the shallowest of water tables seems unlikely.
However, the changes in the mobility of a pesticide—the increased leaching potential observed when the pesticide interacted with the soil in the presence of another commonly applied agricultural chemical—still seems to justify cautious and carefully planned application of this and similar pesticides. The frequency, spacing, and order of application of the many and varied agricultural chemicals that are routinely applied to a single acre every growing season, or to a single lawn every spring and fall, may play an important role in their potential for contamination of the groundwater supply.

In addition, the concentration of various naturally occurring soil constituents found in a particular soil may also play an important role in the transport of these agricultural chemicals through the soil profile, and so contribute to their potential for groundwater contamination.
REFERENCES


APPENDIX OF ADDITIONAL FIGURES

Figures A-1 through A-16
Note: Numbers printed over curve refer to column retention time in minutes

0.368 minutes = Hexane Peak 3.81 minutes = Malathion Peak

Figure A-1. Sample gas chromatograph curve
Figure A-2: Phosphate elution curve approximating "breakthrough".
Figure A-3. Phosphate elution curve for phosphate-only solution.
Figure A-4. Phosphate elution curve for combined Malathion and phosphate solution.
Figure A-5. Malathion elution curve for Malathion-only solution.
Figure A-6. Malathion elution curve for Malathion and combined phosphate solution.
Figure A-7. Malathion elution curve for combined Malathion and organic acid solution.
Figure A-8. Phosphate elution curve for phosphate-only solution (secondary run).
Figure A-9. Phosphate elution curve for combined Malathion and phosphate solution (secondary run).
Figure A-10. Malathion elution curve for Malathion-only solution (secondary run).
Figure A-11. Malathion elution curve for combined Malathion and phosphate solution (secondary run).
Figure A-12. Malathion elution curve for combined Malathion and organic acid solution (secondary run).
Figure A-13. Malathion elution curve for application of solutions in series: Malathion solution followed by deionized water (secondary run).
Figure A-14. Malathion elution curve for application of solutions in series: Malathion solution / deionized water / phosphate solution (secondary run).
Figure A-15. Phosphate elution curve for application of solutions in series: Malathion solution /deionized water /phosphate solution (secondary run).
Figure A-16. Malathion elution curve for application of solutions in series: solution / deionized water / organic acid solution (secondary run).
Vita

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