Simultaneous Movement of Water and Herbicides in Unsaturated Soils

Ming-shyong Yang

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SIMULTANEOUS MOVEMENT OF WATER AND HERBICIDES IN UNSATURATED SOILS

by

Ming-shyong Yang

A thesis submitted in partial fulfillment of the requirement for the degree of

MASTER OF SCIENCE

in

Soil Physics

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Ming-shyong Yang
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INTRODUCTION

Since weed killers were developed in the early part of the decade beginning in 1940, herbicides have been increasing in use until they are now widely used to control weeds. The application of herbicides has thus become a regular agricultural and ecological practice.

Some of the herbicides are applied directly to soils and accompanied by a light irrigation to wash them into the soil in order to increase their efficiency. Some of these chemicals accumulate in the soil and should be removed in order to avoid toxic effect on succeeding plants (Klingman, 1961). The toxic effect of herbicidal residues in soil and water to human subjects, livestock, and wildlife has been reported (Paynter et al., 1960; Carpenter et al., 1961). When these materials are leached out of the soil, they may pollute the water supply. The movement of water and herbicides in soils is thus closely connected to both their herbicidal and toxic effect and is becoming a serious economic problem.

It is the purpose of this investigation to study the simultaneous movement of water and herbicides in unsaturated soils by using the thermodynamic theory of irreversible processes. The adsorption of herbicides, the energy of adsorption, and the break-through curve will also be studied.

**Water flow in soils**

Darcy's Law has long been used to describe the flow of water through water-saturated porous materials including soil. It also has
become fairly commonplace to apply Darcy's proportionality to unsaturated water flow. Richards (1931) gave an expression analogous to Darcy's Law to demonstrate the relationship between flow velocity and potential gradient.

\[ v = -k(\theta) \nabla \phi \]  

[1]

where \( v \) is the volume flux per unit area, \( \nabla \phi \) is the driving force causing movement, and \( k(\theta) \) is a parameter which is called the capillary conductivity. It is based on the assumption that, at a given moisture content, volume flux of water per unit area is directly proportional to potential gradient. This expression differs from Darcy's Law in that the coefficient of proportionality \( k(\theta) \) is not constant but is a function of moisture content \( \theta \), and the driving force is considered to be a potential gradient rather than a single gradient of hydraulic head. Childs and George (1950) verified experimentally the expression, but only for sands > 0.25 mm in grain size.

From Darcy's Law and the equation of continuity, an equation for the flow of water in an unsaturated porous medium was derived by Klute (1952a). He considered that the total moisture potential was the sum of pressure and gravitational potentials and expressed the equation as

\[ \rho_0 \frac{\partial \theta_D}{\partial t} = \frac{\partial}{\partial z} (\rho k \frac{\partial \psi}{\partial z}) + \frac{\partial}{\partial z} (\rho g) \]  

[2]

where \( \rho_0 \) is the bulk density, \( \theta_D \) is moisture content in dry weight basis, \( t \) is time, \( z \) is coordinate, \( \rho \) is fluid density, \( \psi \) is the pressure of capillary potential, \( k \) is hydraulic conductivity, and \( g \) is gravitational potential. He also assumed that \( \psi \) was a single-valued function of moisture content \( \theta_D \). Youngs (1957) got a good agreement between
the above theory and experiments in which vertical infiltration was conducted with "Ballotin" grade 15 glass beads and slate dust containing particles ranging in size from 0.04 mm to 0.125 mm.

In 1964 Zaslavsky developed a theory by modifying Darcy's Law to describe the unsaturated flow of water into a non-uniform soil profile. He expressed the specific discharge \( q \) as

\[
q = \frac{H + D_1 + D_2}{\frac{D_1}{k_1} + \frac{D_2}{k_2}}
\]

where \( k_1 \) and \( k_2 \) are hydraulic conductivity through the layers of thicknesses \( D_1 \) and \( D_2 \) respectively, and \( H \) is water head over the soil surface.

In 1936 Childs (a, b) suggested that moisture movement in porous materials is a diffusion phenomenon. By combining Fisks' first law and the equation of continuity, he showed that for one dimensional flow

\[
\frac{\partial \theta_D}{\partial t} = \left( \frac{k}{\sigma} \right) \frac{\partial^2 \theta_D}{\partial x^2}
\]

where \( \theta_D \) is the moisture content in dry-weight basis, and \( k \) is the diffusion coefficient assumed to be constant, and \( \sigma \) is bulk density. Later in 1949 Kirkham and Feng pointed out that the linear diffusion equation of the type as equation [4] was not a valid mathematical model describing the movement of water in unsaturated soils. Childs and George (1948) developed a diffusion equation with concentration-dependent diffusion coefficient. Later they (1950) verified experimentally the validity of their theory, but only for sands >0.25 mm in grain size. Nakayama and Jackson (1963) also showed that the apparent diffusion coefficient of titrated water in soil was a function of water content.
By use of the equation of continuity and Darcy’s Law, Klute (1952b) developed a non-linear diffusion equation. He assumed that the conductivity (k) of Darcy’s law was a single-valued function of moisture content (θ), and the capillary potential (ψ) and the moisture content were related by a single-valued function by ignoring the hysteresis effect which was pointed out by Hubbert (1940). The equation was shown as

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial \theta}{\partial x} \right)$$

where diffusivity $D = k(\theta) \frac{\partial \psi}{\partial x}$.

Several approaches have been used to obtain a solution of the diffusion equation. Each of these approaches requires assumptions that limit the application of the solutions. The Boltzman transformation, which reduces the non-linear partial differential equations to an ordinary differential equation, has been used by several researchers (Crank and Henry, 1949; Klute, 1952a; Philip, 1955; Bruce and Klute, 1956; Gardner and Mayhugh, 1958). Numerical approaches using high-speed computers, without involvement of the Boltzman transformation, have also been used by several other researchers (Ashcroft et al., 1962; Hanks and Bowers, 1962; Klute et al., 1964), and these results appear to verify those obtained by use of Boltzman transformation. Both methods limit the solution to certain given boundary conditions of either finite or semi-finite homogeneous medium with constant or arbitrary initial moisture content. Swartzendruber (1966) also successfully employed a product form of separation of variables to solve the non-linear diffusion equation, but the problem is restricted to a special case of one dimensional water adsorption by a horizontal, semi-finite column of uniform soil initially at uniform water content.
The validity of the non-linear diffusion equation to describe the movement of water in unsaturated soils has been tested by Klute (1952b) and Gardner and Mayhugh (1958), but Nielsen et al. (1962) and Rawlins and Gardner (1963) found that diffusivity was not a function of moisture content alone. Nielsen et al. (1962) suggested that the non-uniqueness between moisture content and soil water pressure, and the heat evolved when water wet soil were attributed to the failure of the non-linear diffusion equation. Swartzendruber (1963) pointed out that the non-uniqueness of diffusivity $D(\theta)$ observed by Rawlins and Gardner (1963) was caused by neglecting the moisture gradient dependence of diffusivity. Klute et al. (1964) showed the diffusivity-water content hysteresis to be composed of crossed curve segments forming a skewed and distorted "bowtie." The hysteresis effect will make the non-linear diffusion equation more complicated and attempts to solve the equation will become unfeasible.

Swartzendruber (1966) thus used a flow velocity-gradient relationship of non-Darcy form to account for the horizontal absorption of water into air-dry soil. His equation is shown as

$$v = \beta[w - \alpha(1-e^{-\gamma w})]$$  \[6\]

where $\beta$, $\alpha$, and $\gamma$ are functions of $\theta$, $v$ is flow velocity, and $w$ is moisture gradient $w = -\frac{\partial \theta}{\partial t}$. He showed that this equation was fitted to the velocity-moisture content data for $\theta \leq 0.30$ and was a suitable formulation for expressing non-Darcy behavior, both with and without threshold gradients. For the moisture content being greater than 0.35, the equation was reduced to Darcy form, and $\alpha$ and $\gamma$ were taken as zero and $\beta$ was the diffusivity.
Transition state theory of Eyring has been applied to a study of the diffusion constant (Wang et al., 1953). Eyring's equation for diffusivity is written as

$$D_0 = k'T \exp\left(-\Delta F^+/RT\right) \quad [7]$$

where $D_0$ is the diffusivity, $k'$ is a constant involving Boltzman's constant, Plank's constant and lattice factors, and $\Delta F^+$ is the free energy of activation. Experimental evidence collected by Wang and his co-workers verified the validity of Eyring's equation.

Solute flow through soils

The transportation of matter through unsaturated soils can be described by two types of equations, one for solute flow, and the other for flow of soil solution.

Solute usually moved from one part to another through the water in unsaturated soil as a result of diffusion. The theory of diffusion in isotropic substance is based on the assumption that the rate of movement of the diffusion substance through a unit area of a section is proportional to the concentration gradient measured normal to the section. The rate of transfer of diffusion substance $J$ for a steady state could be determined by Fick's first law as

$$J = -DA \frac{\partial C}{\partial X} \quad [8]$$

where $D$ is the coefficient of diffusion, $A$ is the cross-sectional area, $C$ is the concentration of diffusing substance, and $X$ is the space coordinate normal to the cross section (Moore, 1962, p. 340).

Equation [8] was used by Dutt and Low (1962b) to determine the apparent diffusion coefficient for the steady state diffusion of LiCl and
NaCl at intervals along the diffusion path in pastes of Li clay and Na clay. It was found that diffusion coefficient is not a constant. Husted and Low (1954) also reported that the simple theory of Fick's first law was not able to describe the diffusion of ions through bentonite gels.

A steady state diffusion experiment is usually difficult to conceive and construct. One, therefore, must determine the change of concentration with time which implies the use of transient state systems (Porter et al., 1960). By introducing Fick's first law into the law of conservation of mass, we get

\[
\frac{\partial C}{\partial t} = DA \frac{\partial^2 C}{\partial x^2} \tag{9}
\]

which is Fick's second law of diffusion. It is based on the assumption that D is constant, but if this is not the case, equation [9] can alternately be expressed as

\[
\frac{\partial C}{\partial t} = A \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) \tag{10}
\]

It is usually difficult to make use of equation [10] since the space variation of D is unknown and difficult to find.

When a solute is allowed to diffuse from a zone of high concentration into an adjacent zone of lower concentration in water medium, a plot of solution concentration against distance from the source may be represented by a smooth curve. Bouldin and Black (1954) observed large scale of irregularities in the curves relating phosphorus concentration in the soil column to the distance from the source. Heslep and Black (1954) explained that these irregularities might be a result of the interaction of phosphorus with soil through which it was moving.
When diffusion takes place through water in a porous system, the effective fraction of the total area available for flow, the macroscopic distance and the actual distance through which diffusion takes place, the fraction of the volume occupied by water, interactions between diffusing ions and the ions associated with the charged mineral particles, and the viscosity of water in the immediate vicinity of the mineral surface must be considered. Porter et al. (1960) took into account some of these geometry and interaction factors and modified Fick's first law as

$$\frac{\Delta Q}{\Delta t} = - Dr(L/Le)^2 \theta A \frac{\Delta C}{\Delta t}$$

$$= - De \theta \frac{\Delta C}{\Delta t}$$

where $Q$ is an amount, $\theta$ is volumetric moisture content, $(L/Le)^2$ is a factor accounting for the tortuosity and direction of the path, $r$ is a factor which takes into account ionic interaction and the increased viscosity of water in the porous system. The term $De = Dr (L/Le)^2$ may be called effective diffusivity.

Assuming that $De$ was independent of concentration, they applied equation [11] to study the diffusion of chloride in soils and found that chloride diffusivity obtained from soil systems were about 0.31 to 0.027 times that obtained from bulk solutions with the same concentration gradient. However, they reported that these equations should give a good estimate of the movement of nitrates, sulfates and halides in soils. This treatment should also be valid for Ca movement in Ca-saturated soils and Na movement in Na-saturated soils.

In 1966 van Schaik and Kemper considered the geometry of porous medium and relative fluidity of water a factor affecting the diffusion
of anion in clay-water system. They defined the porous system diffusivity $D_p'$ as

$$D_p' = D(L/Le)^2 \theta ae \gamma$$  \[12\]

where $D$ is the diffusivity of the anion in aqueous solution, $(L/Le)^2$ is the tortuosity factor, $ae$ is the weighted value of relative fluidity, $\theta$ is the volumetric moisture content, and $\gamma$ is the heterogeneity factor of pore size. They used $D_p'$ as the diffusion coefficient in Fick's first law to calculate the self-diffusion coefficient of chloride in sodium- and calcium-saturated bentonite. Values obtained from steady state and transient state systems agreed well.

Movement of solute through soils involves counter-exchange process. A knowledge of the self-diffusion coefficients of water in soil or mobility of cations in water will be necessary to determine the rate that ion exchange diffusion plays in cation transfer through soils. Many reports (Letey and Klute, 1959a, b; Dutt and Low, 1962 a, b) showed that ion mobility changed with increasing solution or clay concentration. Gast (1966) developed a three component model to describe the change in mobility and to predict the rates of cation movement in clays. He expressed the specific conductivity of porous medium $k_o$ as sum of three components

$$k_o = \frac{k_p k_w}{x k_p + y k_w} + \frac{k_p}{z} + \frac{k_w}{F}$$  \[13\]

where $k_p$ is specific conductance of particles, $k_w$ is specific conductance of interstitial solution, $x$, $y$, $z$ are parameters, and $F$ is formation factor. Assuming the validity of Nernst-Einstein relationship given as

$$D = \frac{1000 kRT}{CzF^2}$$  \[14\]
where $k$ is specific conductance, $D$ is diffusion coefficient, $C$ is ion concentration, $Z$ is valence, $R$ is universal gas constant, $T$ is absolute temperature, and $F$ is Faraday constant, he was able to predict rates of cation movement by calculating the diffusion coefficient from electrical conductivity measurements. Good agreement between calculated and experimental values of diffusivities were obtained by him from diffusion of Na$^+$ in Na-bentonite and Sr$^{++}$ in Sr-bentonite.

**Adsorption of solute, chromatography theory**

The adsorption of herbicides by soils plays an important role in the movement of herbicides in soils. The adsorption of herbicides was affected by temperature, the clay content and organic matter content of the soil, pH of soil solution, moisture content, and molecular structures of herbicides. The adsorption of S-Triazine herbicides was found to increase with both decreasing temperature and pH, and with increasing clay content and organic matter content (Talbert and Fletchall, 1965; Harris and Warren, 1964). By comparing the structurally related S-triazines and the large differences noted in their adsorption, Harris (1966) suggested that the -SCH$_3$ substitution of s-triazine causes strong binding forces between soil particles and the herbicide, and the chloro-substitution, conversely, appeared to lessen the attractive forces between the herbicide and soil particles. He also observed that the high adsorption of the herbicides by Chillum silt loam and the low adsorption of the herbicides in Lakeland sandy loam were in accord with their rates of movement in these soils. Thus he suggested that adsorption gave a much better indication of the resistance to movement of the herbicides in soils.
The movements of salts or chemicals in soils are also described by adsorption chromatographic theory which is based on the assumption that the profile is divided into a series of theoretical plates of finite height in each of which an equilibrium condition develops before the solution moves to the next plate. By applying this theory to study the salt leaching patterns under unsaturated soil moisture conditions, van der Molen (1956), Thomas and Coleman (1959) and Dyer (1965) showed general agreement between the theoretical curves and the data obtained from experiment. Lambert et al. (1965) also showed good agreement between the experimental distribution of herbicides caused by water percolation and the theoretical distribution curves predicted by chromatographic theory. However, chromatography theory describes distribution curves analogous to normal curves of error; this is not always the case in a complex system like soils where adsorption, desorption, and counter exchange processes occur. Berg and Thomas (1959) pointed out that the elution curves of chloride and sulfate deviated from the normal elution pattern, and they ascribed this result to the adsorption of anions. In addition, chromatography theory describes the distribution of solute only and may not be valid to predict the rate of movement of solute.

Miscible displacement

Biggar and Nielsen (1963) compared three mathematical models for adsorption with data of the distribution of ions obtained from the miscible displacement involving exchange processes and found that the theories were generally inadequate. These theories describe the distribution of concentration only and are not able to describe flow processes.

Gardner and Brooks (1957) studied the leaching of soluble salt and
found the evidence that the flow process itself, rather than diffusion, was the important factor in the redistribution of salt. Day (1956) also described the spreading of a "cluster" owing to hydrodynamic dispersion without regard to spreading by diffusion. Biggar and Nielsen (1962 a, b) observed an interaction of diffusion of chloride ion and velocity of water. They also verified experimentally (1960, 1961, 1962a, b) that both diffusion and hydrodynamic dispersion must be included in the theory of solute and water transfer in soil.

Salt concentration difference can cause water flow in soils. Kemper (1961) compared experimentally a salt-induced free energy gradient with a pressure-induced free energy gradient in causing water to flow. Later Kemper and Evan (1963) pointed out that osmotic pressure and hydraulic pressure were both effective in moving water. Quayyum and Kemper (1962) studied the effect of salt concentration gradient on moisture movement and evaporation. Their results indicate a definite movement of water toward the salt-bearing side of the profile. Taylor and Cary (1960) showed that gradients of temperature, salt, electricity or pressure imposed across a soil column caused moisture movement. Abd-el-Aziz and Taylor (1965) also showed that both water and salt potential gradients could cause water and salt to move.

**Thermodynamic theory**

Classical thermodynamics is essentially a theory of equilibria or of reversible processes. It is concerned largely with closed systems that do not exchange matter with the surroundings. Soil and living organisms, on the other hand, are dynamic systems that are seldom if ever at equilibrium and are constantly exchanging matter with the surroundings.
Therefore, for the description of the dynamic processes in biological systems, a thermodynamic theory of flow is needed (Taylor, 1963).

The field of non-equilibrium thermodynamics provides us with a general framework for the macroscopic description of irreversible processes. In non-equilibrium thermodynamics the so-called balance equation for the entropy plays a central role. This equation expresses the fact that the entropy of a volume element changes with time for two reasons. First, it changes because entropy flows into the volume element; second, because there is an entropy source resulting from irreversible phenomena inside the volume element (de Groot and Mazur, 1962). The rate of change of entropy source \( \frac{dS_i}{dt} \) with respect to time \( \frac{dS_i}{dt} \) is called the entropy production \( \sigma \).

When \( T \frac{dS_i}{dt} \) is calculated for any system, it turns out to be a sum of terms each being a product of a flux characterizing an irreversible process \( J_i \), and a quantity, called thermodynamic force \( X_i \).

\[
\sigma = T \frac{dS_i}{dt} = \sum_i J_i X_i \tag{15}
\]

The entropy source strength can thus serve as a basis for the systematic description of the irreversible processes occurring in a system (de Groot and Mazur, 1962).

Since equation (15) contains the irreversible fluxes as unknown parameters and can, therefore, not be solved with given initial and boundary conditions for the state of the system, an additional set of phenomenological equations which relate the irreversible fluxes and the thermodynamic forces appearing in the entropy production must be supplemented. Fick's law of diffusion, Fourier's law of heat conduction, and
Darcy's law of water flow, for instance, belong to this class of linear phenomenological laws. When two or more of these phenomena occur simultaneously, they interfere and give rise to new effects. Such cross-phenomena are, for example, the Soret effect which results from diffusion in a temperature gradient. Many others exist such as the thermoelectric effects and electro-kinetic effects (de Groot and Mazur, 1962).

In general, if there is more than one irreversible process occurring, it is found experimentally that each flow $J_i$ is not only linearly related to its conjugate force $X_j$, but is also linearly related to all other forces found in the entropy production. If the general linear coefficient is denoted by $L_{ij}$, the general form for $J_i$ is

$$J_i = \sum_{j=1}^{n} L_{ij} X_j \quad . \quad [16]$$

In 1931 Onsager established the so-called reciprocity theorem which related the cross coefficient

$$L_{ij} = L_{ji} \quad . \quad [17]$$

Onsager's reciprocal relation of equation [17] reduces considerably the number of experimental quantities necessary to describe the irreversible flows. Thus, the experimental verification of [16] is of great interest in current literature (Aziz, 1964).

In 1960 the validity of Onsager's theory was checked by Miller for various systems, e.g. thermoelectricity, electrokinetics, etc. The experimental checks were sufficiently good that the general validity of the theorem was established.

Taylor and Cary (1960) proposed the use of thermodynamics of irreversible processes and linear rate equations containing Onsager's
reciprocal relations as a tool to analysis of the simultaneous flow of water and salt, water and heat, or water and electricity in soils. Later in 1962, they confirmed the validity of Onsager's relationship in analyzing the simultaneous flows of heat and water.

Taylor and Cary (1964) also published generalized linear equations for the simultaneous flow of matter and energy in a continuous soil system. This kind of equation was used by Abd-el-Aziz and Taylor (1965) to analyze the simultaneous movement of water and salt through unsaturated soils and their results confirmed the validity of Onsager's reciprocal relation.

In view of the previous review, there is not yet experimental verification for the application of the theory to the more complicated system of simultaneous movement of water and herbicides in porous media which is considered in this investigation.
DEVELOPMENT OF THEORY

Consider a system (Figure 1) having vessels I and II which are separated by a porous medium C(soil). The two vessels are at different pressure. A herbicide solution of given concentration is introduced into vessel I to replace the water in a porous medium, and the replaced solution flows into vessel II. The whole system is under isothermal condition. The expression for the entropy production is given by equation [15]. The two driving forces operating the system are the difference in chemical potential of water and solute. The fluxes corresponding to these two forces operating in the system are solvent flux $J_w$ and the flux of solute $J_H$. The thermodynamic driving forces on a single solute (herbicide) and water are $\Delta \mu_H$ and $\Delta \mu_w$ (de Groot, 1959). For a constant temperature, the entropy production [15] for flow of water ($J_w$) and herbicide ($J_H$) is

$$\sigma = J_w \frac{\Delta \mu_w}{T} + J_H \frac{\Delta \mu_H}{T}$$  \hspace{1cm} [18]

The corresponding phenomenological equations can be expressed as

$$J_w = -L_{ww} \frac{\Delta \mu_w}{T} - L_{wh} \frac{\Delta \mu_H}{T}$$  \hspace{1cm} [19]

$$J_H = -L_{hw} \frac{\Delta \mu_w}{T} - L_{hh} \frac{\Delta \mu_H}{T}$$  \hspace{1cm} [20]

where $L_{ww}$, $L_{hh}$, and $L_{wh}$, $L_{hw}$ are straight and linked transport coefficients.

Since the herbicide solution is extremely diluted, we can make use of the approximation that the chemical potential for ideal solution may be used, so that at constant temperature
where \( \bar{v}_i \) is the partial molar volume of the component \( i \), \( \Delta p \) is the pressure difference between the two vessels, and \( a_i \) is the relative activity of the component \( i \) at constant pressure. Thus, equation [21] for water becomes

\[
\Delta \mu_w = \mu_w^{II} - \mu_w^{I} = \bar{v}_w \Delta p + RT \Delta \ln a_w \quad [22]
\]

and the corresponding equation for herbicide is

\[
\Delta \mu_H = \mu_H^{II} - \mu_H^{I} = \bar{v}_H \Delta p + RT \Delta \ln a_H \quad . [23]
\]

According to Gibbs-Duhem equation (Moores, Physical Chemistry, 1962), these two forces are not independent and can be related as

\[
n_w d\mu_w + n_H d\mu_H = 0 \quad [24]
\]

where \( n_w \) and \( n_H \) are the number of moles of water and herbicide respectively. Under the condition of constant temperature and pressure, if we divide equation [6] with the volume \( v \) of the solution, equation [24] becomes

\[
\frac{n_w}{v} \frac{dC_w}{C_w} + \frac{n_H}{v} \frac{dC_H}{C_H} = 0 \quad [25]
\]

where \( C_w \) and \( C_H \) are the concentration of water and herbicide respectively, and the approximation,

\[
d\omega_i = RT d \ln a_i = RT d \ln C_i = RT \frac{dC_i}{C_i} ,
\]

for extremely diluted ideal solution has been used. By using the definition of concentration, \( C_w = n_w/v \), \( C_H = n_H/v \) and integrating equation [25], we get
Again using the approximation \( d \ln a_i = d \ln C_i \) and integrating the equation, we get

\[
\ln a_i = \int d \ln C_i = \int \frac{dC_i}{C_i} \quad .
\]  

For an extremely diluted solution, \( C_i \) can be replaced by \( \overline{C}_i \) which is the mean of the concentration of component \( i \) in the two vessels.

By treating \( \overline{C}_i \) as a constant, equation [27] becomes

\[
\Delta \ln a_i = \frac{\Delta C_i}{\overline{C}_i} \quad .
\]  

Introducing equations [26] and [28] into equations [22] and [23], we get

\[
\Delta \mu_w = \overline{v}_w \Delta p - RT \frac{\Delta C_H}{\overline{C}_w} \quad [29]
\]

\[
\Delta \mu_H = \overline{v}_H \Delta p + RT \frac{\Delta C_H}{\overline{C}_H} \quad [30]
\]

In case of dilute solutions (in which the concentrations of herbicides are 4 ppm) used in this study, the partial molar volume \((\overline{v}_H)\) for the herbicide is very small and is assumed to be zero, while \( \overline{v}_w \) is considered to be the specific volume of pure water (Lewis and Randall, 1961, p. 208).

Introducing [29] and [30] and [19] and [20], we get

\[
TJ_w = -L_{ww} \overline{v}_w \Delta p - RT C_H \left( \frac{L_{WH}}{\overline{C}_H} - \frac{L_{WW}}{\overline{C}_w} \right) \quad [31]
\]

\[
TJ_H = -L_{WH} \overline{v}_H \Delta p - RT C_H \left( \frac{L_{HH}}{\overline{C}_H} - \frac{L_{WH}}{\overline{C}_w} \right) \quad . \quad [32]
\]

Since \( C_H/\overline{C}_H >> C_H/\overline{C}_w \), equations [31] and [32] can be reduced to

\[
TJ_w = -L_{ww} \overline{v}_w \Delta p - L_{WH} RT \frac{\Delta C_H}{\overline{C}_H} \quad [33]
\]
Equations [33] and [34] will be tested to see if they can be used to describe the simultaneous movement of water and herbicides and the interaction of these two fluxes.

Since there are two equations and four unknowns ($L_{ww}$, $L_{wh}$, $L_{hw}$, $L_{HH}$), the phenomenological coefficient $L_{ww}$, $L_{wh}$, and $L_{HH}$ could be determined by simultaneously solving equations [33] and [34] with experimental data relating herbicide fluxes to driving forces under constant pressure difference. This makes it possible to solve the equations and see if $L_{wh} = L_{hw}$ as predicted by Onsager's reciprocal theory.

If we use partial specific quantities instead of partial molar quantities, the units of the components in the rate equations [15] and [16] are as follows:

\[ J_w, J_H = \text{gm sec}^{-1} \text{cm}^{-2} \]
\[ v_w = \text{cm}^3 \text{gm}^{-1} \]
\[ \Delta p = \text{dyne cm}^{-2} = \text{gm cm}^{-1} \text{sec}^{-2} \]
\[ R = \text{erg gm}^{-1} \text{deg}^{-1} = \text{cm}^2 \text{sec}^{-2} \text{deg}^{-1} \]
\[ T = \text{deg K}^0 \]
\[ \frac{\Delta C_H}{C_H} = \text{dimensionless quantity} \]
\[ L_{ww}, L_{wh}, L_{hw}, L_{HH} = \text{gm sec deg cm}^{-4} \].
EXPERIMENTAL PROCEDURE

Apparatus and materials

Draper loam from the Farmington experimental farm and Timpanogas silt loam from experimental turkey farm near the U.S.U. campus were used. The soils were air-dried and sieved through a 2 mm round hole sieve.

Soil sample containers were constructed so that herbicide solutions and water could be brought into contact with one end of a soil column (c) as shown in Figure 1. The sample container consisted of lucite cylinders (G) 5 cm inside diameter and 10 cm long. The solution compartments (I) and (II) were 5.2 cm inside diameter and 1.5 cm deep. Fritted glass bead porous plates (B) and (B') were sealed to compartments (I) and (II) at the ends next to a porous media (soil) column (c) through which herbicide solution and water move. The porous plates have a diameter of 5 cm (area 19.6 cm²), and thickness of 0.2 cm. The pore size ranged from 2μ to 5μ. Glass beads porous plates were used because they give a more uniform pore size than plates of other materials and little or no adsorption can occur on the glass plate. The porous media (soils) was confined between compartments I and II and in lucite cylinder G. O rings were used to achieve water-tight seals and the whole system was held together with steel bolts which were inserted through corresponding holes.

Compartment I had openings at top and bottom for introducing herbicide solutions through the connected tubes from the solution reservoirs L and L'. Three-way valve joints (X) were used to maintain the contact of only one solution at any time and to remove air bubbles that
appear in the compartment from time to time. Reservoirs (L) and (L') were connected through two glass tubes with the bottles (A) and (A') which held herbicide solution and water. One of the glass tubes introduced herbicide solution into the reservoir and the other introduced air into the bottle such that the solution level of the reservoir could be kept at constant height.

Compartment II had an opening at the bottom which was connected through an on-off valve with glass funnel (J), which was held inside the vacuum chamber (v). The effluent collected in the funnel could be drained out through the valve connected at its bottom. The vacuum chamber was connected with a mercury manometer (M) and with a cartesian manostat which was used to regulate the suction produced by a vacuum pump. Bottle (H) was used to buffer the sudden change of suction.

Suctions were introduced into compartment I by hanging the solution reservoir at different height below the compartment and were introduced into compartment II by adjusting the manostat which was connected with a vacuum pump.

The apparatus was designed so that a variable pressure difference could be established across the system from compartments I to II simultaneously with the herbicide concentration difference.

**Preparation of stock solutions and calibration curves**

Radioactive C-14 ring labeled Atrazine (specific activity 7.8 μc/mg) and Ametryne (specific activity 5.6 μc/mg) were used in this investigation. Stock solutions containing 2-20 ppm of these herbicides were prepared utilizing magnetic stirrers and 0.01 M CaCl₂ solution. The presence of this small amount of CaCl₂ was to prevent soils from dispersion
when the herbicide solution or water (0.01 M CaCl₂ solution) was passed through the column.

The solutions were then subjected to scintillation counting which was done on a Packard Tri-Carb automatic liquid scintillation counter. The liquid scintillator consisted of 10 gm of 2,5 diphenyloxazole (PPO), 0.5 gm of 1,4 bis-(2-)5-phenyloxazolyl) benzene (POPOP), plus 50 gm of Naphthalene in a liter of 16.7% of Cellosolve and 83.3% of Dioxane. One-half ml of the aqueous sample was added to 19.5 ml of the liquid scintillator, dissolved by a slight shaking, and counted for three 1-minute periods. The radioactivity was usually quite high and the counting efficiency was approximately 65 percent or better. Differences in quenching between samples were corrected with a calibration curve.

The calibration curves relating the concentrations of herbicides and counts per minute were constructed by plotting the concentration of herbicide against the corresponding counts per minute.

Flux measurement

Water (0.01 M CaCl₂) held in Bottle A' was introduced into reservoir L' and compartment I under 10 cm H₂O suction. Suction was introduced into compartment II so that there was a suction difference across the porous media (soils) (C) and fluid could flow from compartment I to compartment II under unsaturated conditions.

At the appropriate time 4 ppm herbicide solution held in bottle A was introduced into reservoir L. By operating the valves (X's), the herbicide solution replaced water and began to flow through the soil column at particular time while retaining the same suction difference. At a later time this solution again was replaced by water.

By measuring the effluent in funnel (J) at some time intervals,
the fluid velocity was measured. The fluid velocity was then converted to volume flux of the solution with dimensions ml sec\(^{-1}\) cm\(^{-2}\). Since the concentration of herbicide was 4 ppm, the partial specific volume of herbicide was assumed to be zero, and the partial specific volume of water was taken as 1. The volume flux of solution was taken as volume flux of water which was then converted to mass flux with dimensions gm sec\(^{-1}\) cm\(^{-2}\). The herbicide flux with dimensions gm sec\(^{-1}\) cm\(^{-2}\) was calculated by multiplying the concentration of herbicide with its corresponding water flux.

The relative concentrations \(\frac{C}{C_0}\) of effluent were plotted against the accumulated volume to construct the break-through curves when water was displaced by herbicide solution. The desorption curves were constructed in the same manners for the displacement of herbicide solution by water.

**Adsorption isotherm experiment**

Six gm of air-dry soil was weighed into a 50 ml glass centrifuge tube and 20 ml of C-14 labeled herbicide solution was added. The tube was then stoppered with an aluminum foil-covered rubber pad. Each sample was allowed to equilibrate for 24 hours on a shaker. The samples were then centrifuged and 0.5 ml of the supernatant fluid removed for counting. Samples of the herbicide solution without soil were treated in the same manner and used as standards.

The difference between the amount of herbicide found in the appropriate standard and in the supernatant fluid from the sample was assumed to have been adsorbed. Each treatment was applied in triplicate.

The isothermal adsorption experiments were conducted at 0° C and
25° C. The empirical Freundlich equation was used to describe mathematically the relationship between the specific adsorption and the concentration of solute in equilibrium solution. The Freundlich equation is written as

\[ \frac{x}{m} = kC^{1/n} \]  \[35\]

where \( x/m \) is specific adsorption (mg herbicide/kg soil), \( C \) is concentration of solute in equilibrium solution (mg herbicide/kg solution), and \( k \) and \( 1/n \) are constants. A plot of \( \log x/m \) vs. \( \log C \) gives a straight line of slope \( 1/n \) and intercept of \( \log k \). The experimental data were plotted on log log paper and the best straight lines were drawn through the point.

The apparent heat of adsorption is related to equilibrium concentrations at two different temperatures by Clausius-Clapeyron equation which is expressed as

\[ \frac{d \ln C}{d \ln \left(\frac{1}{T}\right)} = -\frac{\lambda}{R} \]  \[36\]

where \( C \) is equilibrium concentration, \( T \) is absolute temperature, \( \lambda \) is apparent heat of adsorption, and \( R \) is universal gas constant. The apparent heat of adsorption is assumed to be constant in the range of temperature used in this investigation, and equation [36] can be integrated and expressed as

\[ \frac{\ln \frac{C_1}{C_2}}{(\frac{1}{T_1} - \frac{1}{T_2})} = -\frac{\lambda}{R} \]  \[37\]

where \( C_1 \) and \( C_2 \) are the equilibrium concentration for a given specific
adsorption at temperature $T_1$ and $T_2$ respectively. Equation [37] can be rearranged and expressed as

$$\lambda = - R \frac{\ln(C_1/C_2)}{\frac{1}{T_1} - \frac{1}{T_2}}$$  \text{[38]}$$

The apparent heat of adsorption ($\lambda$) can be calculated by inserting the equilibrium concentration $C_1$ and $C_2$ for a given specific adsorption and the corresponding temperature $T_1$ and $T_2$ into equation [38].
EXPERIMENTAL RESULTS

The calibration curves relating the concentrations of herbicides in stock solution and counts per minute are shown in Figure 2.

The adsorption isotherm curves for Atrazine and Ametryne on Draper loam at 0 and 25°C are shown in Figure 3, and those for Atrazine and Ametryne on Timpanogas silt loam are shown in Figure 4.

The apparent heats of adsorption for the adsorption of Ametryne and Atrazine on Draper loam are shown in Table 1, and those for the adsorption of Ametryne and Atrazine on Timpanogas silt loam are shown in Table 2.

The values of phenomenological coefficients for the flow of water and herbicides in Draper loam are given in Table 3.

The break-through curves and desorption curves are shown in Figures 5, 6, 7, and 8.
Table 1. The apparent heat of adsorption in k-calories/mole for Ametryne and Atrazine on Draper loam

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Specific adsorption mg hercibide/kg soil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Ametryne</td>
<td>1.628</td>
</tr>
<tr>
<td>Atrazine</td>
<td>2.732</td>
</tr>
</tbody>
</table>

Table 2. The apparent heat of adsorption (k-calories/mole) for Ametryne and Atrazine on Timpanogas silt loam

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Specific adsorption mg hercibide/kg soil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Ametryne</td>
<td>0.582</td>
</tr>
<tr>
<td>Atrazine</td>
<td>1.025</td>
</tr>
</tbody>
</table>

Table 3. The values of phenomenological coefficient for Draper loam

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>$L_{WW}$ gm sec deg cm^{-4}</th>
<th>$L_{WH}$ gm sec deg cm^{-4}</th>
<th>$L_{HW}$ gm sec deg cm^{-4}</th>
<th>$L_{HH}$ gm sec deg cm^{-4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ametryne</td>
<td>$9.4 \times 10^{-7}$</td>
<td>$3.2 \times 10^{-10}$</td>
<td>$3.54 \times 10^{-12}$</td>
<td>$-8.32 \times 10^{-16}$</td>
</tr>
<tr>
<td>Atrazine</td>
<td>$9.25 \times 10^{-7}$</td>
<td>$4.3 \times 10^{-10}$</td>
<td>$5.2 \times 10^{-12}$</td>
<td>$-7.8 \times 10^{-16}$</td>
</tr>
</tbody>
</table>
Figure 1. Schematic cross-section of apparatus. A and A' are bottles, L and L' are reservoirs, I and II are solution compartments, B and B' are fritted glass-beads porous plates, C is soil column, D and D' are O rings, G is lucite cylinder, J is funnel, V is vacuum chamber, H is buffer bottle, M is manometer, and X's are on-off valves.
Figure 2. Calibration curves for Ametryne and Atrazine
Figure 3. The adsorption isotherm curves of Atrazine and Ametryne on Farmington soil at 0°C and 25°C.
Figure 4. The adsorption isotherm curves of Atrazine and Ametryne on Turkey farm soil at 0°C and 25°C.
\[ V = 0.512 \text{ cm/hr} \]
\[ C_0 = 4 \text{ P.P.M.} \]
\[ \theta = 35.5\% \text{ by volume} \]

Figure 5. The break-through curve and desorption curve for Ametryne during displacement of water by 4 P.P.M. Ametryne solution and displacement of Ametryne solution by water in Farmington soil.
\[ V = 0.49 \text{ cm/hr} \]
\[ C_0 = 4 \text{ P.P.M.} \]
\[ \theta = 35.4\% \text{ by volume} \]

Accumulated volume of effluent ml.

Figure 6. The break-through curve and desorption curve for Atrazine during displacement of water by 4 P.P.M. Atrazine solution and displacement of Atrazine solution by water in Farmington soil.
\[ \bar{V} = 0.584 \text{ cm/hr} \]

\[ C_0 = 4 \text{ ppm} \]

\[ \theta = 39.8\% \text{ by volume} \]

Figure 7. The breakthrough curve and desorption curve for Ametryne during displacement of water by 4 ppm Ametryne solution and displacement of Ametryne solution by water in Turkey farm soil.
$V = 0.159 \text{ cm/hr}$

$C_0 = 4 \text{ P.P.M.}$

$\theta = 40.8\% \text{ by volume}$

Figure 8. The break-through curve and desorption curve for Atrazine during displacement of water by Atrazine solution and displacement of Atrazine solution by water in Turkey farm soil.
DISCUSSION

Calibration curves

Since the concentration of herbicide in samples is determined by subjecting the sample to liquid scintillation counting and by comparing the corrected counts per minute with the calibration curve, the accuracy of the calibration curve determines the precision of the results. The variation of counts per minute for a given sample can be caused by quenching effect, the errors associated with techniques for preparing stock solutions, and taking samples. The counting efficiency is higher than 65 percent and the quenching effect has been corrected for each sample. This along with the linear calibration curve indicates that there is little error associated with the technique for preparing stock solution and taking samples.

The flow equations

From Table 3 one sees that the phenomenological coefficient \( L_{HH} \) is of the order of \( 10^{-16} \, \text{gm sec deg cm}^{-4} \) and \( L_{HW} \) is of the order of \( 10^{-12} \, \text{gm sec deg cm}^{-4} \). \( L_{HW} \) is \( 10^4 \) times larger than \( L_{HH} \); this, combined with the very small herbicide concentration difference, makes the contribution to the herbicide flux from its own driving force negligibly small compared with flux of herbicide that is carried by the water flowing under pressure (suction) difference. Hence, the flux caused by the driving force due to herbicide concentration differences can be neglected. Equations \([33]\) and \([34]\), therefore, reduce to

\[
TJ_{w} = - L_{ww} \overline{v_w} \Delta p \quad [39]
\]
\[
TJ_{H} = - L_{HW} \overline{v_w} \Delta p \quad [40]
\]
which are the correct expression for the simultaneous movement of water and herbicides in unsaturated soils under the experimental conditions used in this investigation. Thus, the linked transfer coefficient $L_{HW}$ expresses the rate of herbicide movement through the soils. 

If we eliminate $\Delta p$ from equations [39] and [40], we get

$$J_H = \frac{L_{HW}}{L_{WW}} J_W$$  \[41\]

The flux of herbicide becomes a function of the flux of water. Staverman (1951) called $-L_{HW}/L_{WW}$ the reflection coefficient describing the hold-back of solute by the membrane or soil in this case.

From Table 3 (see also Appendix A), one can see that the calculated values for the transfer coefficients, $L_{WW}$, $L_{WH}$, $L_{HW}$, and $L_{HH}$, showed inconsistencies amongst themselves. The direct transfer coefficient, $L_{HH}$, is negative, which is inconsistent with the theory which states that it must always be positive and $L_{WH} > L_{HW}$ which is contrary to the Onsager theory. The inconsistency may have been caused by the fact that the flow equations [33] and [34] are linear combinations of the pressure gradient alone and do not take into account the adsorption of the herbicide by the soil colloids as discussed below. This would give the appearance that herbicide is actually moving from low to high concentration. On the other hand, it has already been shown that both $L_{HH}$ and $L_{WH}$ are meaningless because of the extremely small concentration differences. Hence, it appears that the values of $L_{WW}$ and $L_{HW}$ calculated from [39] and [40] are both consistent and a valid representation of the true transfer of water and herbicides.

In the application of the theory of irreversible processes and Onsager's reciprocal relation for analysis of the system under study,
several assumptions and conditions should be met. The assumptions of fluctuation theory, microscopic reversibility, and regression of fluctuations have been discussed in detail by de Groot (1959).

One of the conditions obviously connecting with the adsorption phenomena is that the porous media column is inert and that no chemical reactions take place to interfere with the transference processes. This is taken account of by the Curie-Prigogine principle which states that coupling coefficients may exist relating vectorial flows to any vectorial forces in the system, but there may be no coupling coefficients relating vectorial flows to the scalar affinities of chemical reactions.

Katchalsky and Curran (1965) pointed out that there may exist indirect coupling between diffusional flows and reactions. They considered a region (porous media column in this investigation) of finite and constant volume into which an uncharged solute (herbicide) $H$ enters by diffusion at a rate $J_H$ and is then converted into a substance $y(H-y)$ at a rate $J_{ch}$. They also assumed that a third substance (water) $W$ is present and flows into the region at a rate $J_W$ without participating in chemical reaction, and the flow $J_W$ is coupled hydrodynamically to $J_H$ and there is no coupling between $J_y$ and any of the other flows. The phenomenological equations then were written (in inverted form)

$$-\Delta \mu_H = R_{HH} J_H + R_{HW} J_W$$  \hspace{1cm} [42]

$$-\Delta \mu_y = R_{yy} J_y$$  \hspace{1cm} [43]

$$-\Delta \mu_W = R_{WH} J_H + R_{WW} J_W$$  \hspace{1cm} [44]

$$-A = R_{ch} J_{ch}$$  \hspace{1cm} [45]

where $\mu_i$ is chemical potential of component $i$, $R_{ij}$ and $R_{ii}$ are linked
resistance coefficients, and $A$ is the affinity of chemical reaction.

If equations [42], [43], and [44] are converted into the usual form of phenomenological equations (Katchalsky and Curran, 1956), we get

\[ TJ_W = -L_{WW} \Delta \mu_W - L_{WH} \Delta \mu_H \]  
\[ TJ_H = -L_{HW} \Delta \mu_W - L_{HH} \Delta \mu_H \]  
\[ TJ_y = -L_{yy} \Delta \mu_t \]  

Equations [46] and [47] are identical with equations [19] and [20], but equation [48] is not included in our previous development of theory. If it could be incorporated, it would express the rate of herbicide adsorption on soil. The author was unable to make this analysis from the data at hand.

The adsorption of herbicides has been reported to be most closely related to organic matter, clay content, cation exchange capacity, and exchangeable magnesium and hydrogen (Talbert and Fletcher, 1965). Both organic matter and clay are the components of soils having the predominant exchange capacity of the soils (Bailey and White, 1964). In addition, soil colloidal components; i.e., organic matter and clay minerals, having larger specific surface area also have a high potential adsorption capacity for herbicides (Bailey and White, 1964). The adsorption of herbicides on the colloidal surface in a solution might be regarded as a competition of herbicides with some substances already adsorbed on the surface. Therefore, both chemical adsorption due to ionic exchange and physical adsorption due to exchange of herbicide molecules with the substance already adsorbed on the surface can be considered as exchange processes.
Since the flux $J_y$ is not coupled with the fluxes $J_w$ and $J_H$, equations [19] and [20] are still valid to describe the simultaneous movement of water and herbicides in unsaturated soils in accordance with the original theory.

In order to find out if the adsorption of herbicides by soils is an exchange process, the mechanism of adsorption needs further study.

**Isothermal adsorption and energy of adsorption**

The empirical Freundlich equation is often used to describe the relationship between adsorption of solutes at liquid-solid interfaces and the equilibrium concentration in solution.

From Figures 3 and 4 we can see that experimental results yielded straight lines and agreed with Freundlich equation in the concentration range used in this investigation.

High correlations between the adsorption of s-triazines and clay content have been reported by Harris (1966) and Talbert and Fletchall (1965). Since Timpanogas silt loam contains more clay than Draper loam, it will adsorb more herbicides. The experimental results confirm this expectation.

The specific adsorptions of Ametryne is found to be higher than those of Atrazine on both soils. This result agreed with those observations presented by Harris (1966) and Talbert and Fletchall (1965).

If we compare the structural formulas of Ametryne and Atrazine,
we will see that the only difference between them is the \(-\text{SCH}_3\) substitution in Ametryne and chloro-substitution in Atrazine. Harris (1966) suggested that the \(-\text{SCH}_3\) group might influence the electron density of the molecule to cause strong binding forces between the herbicide and soil particles and the chloro-substitution, conversely, appeared to decrease attractive forces between the herbicides and soil particles. In addition, Bradley (1945) studied the associations between montmorillonite and some polyfunctional organic liquids and concluded that a CH\(_2\)...O bond was being formed with the hydrogen of the methylene group (CH\(_2\)) directed to the clay surface. Thus, the hydrogen bond between \(-\text{SCH}_3\) group and the oxygen of SiO layer of clay minerals may partially contribute to the adsorption of mercapto-substituted s-triazine, therefore, has greater specific adsorption than Atrazine.

The adsorption of herbicides by soils includes two successive processes, (a) the removal of solute (herbicide) from less ordered association with solvent; and (b) the attachment of solute to a much more ordered association with adsorbent (soil). The free energy of the adsorbed molecule thus decreases and the adsorption processes are exothermic. An increase in temperature will be expected to reduce the adsorption. From figures 3 and 4 we can see that the increase in temperature did reduce the adsorption of herbicides which agreed with the report from Harris and Warren (1964) and Talbert and Fletchall (1965).

The apparent heats of adsorption calculated from the adsorption isotherms by the Clausius-Clapeyron equation remain almost constant in each case over a considerable wide measurable range of the isotherms (Tables 1 and 2). This also can be seen from the almost parallel isotherm curves in Figures 3 and 4.
The apparent heats of adsorption for Atrazine on both soils as shown in Tables 1 and 2 seem to be larger than those for Ametryne, but the variations of adsorption with temperature have inverse relations; i.e., the variations of adsorption with temperature for Ametryne on both soils are larger than those for Atrazine. Harris and Warren (1964) pointed out that the greater the difference in adsorption due to the change in temperature, the larger the heats of adsorption. Thus, the calculated apparent heats of adsorption seem to be contrary to the variation of adsorption of herbicide due to change in temperature. This contrary relationship may be clarified by examining the interactions between water and herbicide molecules and interactions between herbicide molecules and soils.

The magnitude of the apparent heat of adsorption is not a direct indication of the binding forces formed between adsorbent (soils) and adsorbate (herbicide), because the heat of adsorption represents the algebraic sum of the heat changes taking place in two successive processes: (a) the removal of solute from association with solvent; and (b) the attachment of solute to substrate (Giles et al., 1954). If all other factors are the same, Ametryne has hydrogen from -SCH₂ group to form hydrogen bond with water, but Atrazine with its Cl-group may not have this kind of interaction at the Cl-group. Consequently, the Ametryne molecule may be transferred from a much more ordered solvent-solute association than the Atrazine molecule. Consequently, the apparent heat of adsorption for Ametryne may be smaller than for Atrazine.

The break-through curves are shown in Figures 5, 6, 7, and 8. Nielsen and Biggar (1961; 1962; 1963) and Biggar and Nielsen (1960; 1962, a, b) studied the simultaneous transfer of water and dissolved
constituents through soils and other porous materials and concluded that the mixing of a penetrating liquid occurred by both microscopic velocity distribution and molecular or ionic diffusion. The breakthrough curve should pass through $C/C_0 = 0.5$ at one pore volume, and the area under the breakthrough curve up to one pore volume should equal the area above the curve for all times greater than one pore volume regardless of the shape of the curve.

If adsorption or exchange occurred, the point of $C/C_0 = 0.5$ of the breakthrough curve would shift to right of the one pore volume and the areas described before were not equal. All the breakthrough curves obtained in this investigation showed both the displacement of $C/C_0 = 0.5$ to the right of one pore volume a skewed sigmoid nature. Further, the area under the breakthrough curve up to one pore volume was very much less than the area above the curve. Thus, we can conclude that in addition to the adsorption of herbicides, the dispersion of penetrating solution and molecular diffusion occurred in the experiment. In addition, if we compare the shape of the breakthrough curves obtained in this investigation with the theoretical curves given by Nielsen and Biggar (1962), we can see that there is an extremely wide distribution of pore velocity in the experiment.

The breakthrough curves for Ametryne in both soils reached $C/C_0 = 0.5$ much later than those for Atrazine in the corresponding soil, thus indicating that Ametryne is adsorbed in greater amounts than Atrazine which is in agreement with the adsorption data of Figures 3 and 4.

The initial breakthrough of Ametryne in Timpanogas silt loam is much later than in Draper loam. The breakthrough curves for Atrazine
show a similar relationship. These results, again, reflect the fact that fine-textured adsorbs more herbicides than coarser textured soil.

By comparing the desorption curve with the corresponding break-through curve, we can see that some of the herbicides are retained in the soil. For the same soil, much more Ametryne is retained than Atrazine.

In Figure 6 there is a concave variation of the break-through curve between 1000 ml and 1500 ml. This was caused by the loss of suction resulting from a broken rubber tubing which allowed diffusion of the herbicide from the pore having higher concentration into the smaller pores through which the water did not normally flow; this caused $C/C_0$ to decrease and begin at a lower concentration when the pressure was again restored.
SUMMARY AND CONCLUSIONS

An experiment has been conducted to study the simultaneous movement of water and herbicides in unsaturated soils. The thermodynamics of irreversible processes and Onsager's reciprocal relation theorem are used to develop the rate equations, which are used to describe the relations between the fluxes of water and herbicide and the corresponding forces.

To gather the water and herbicide flux data, the experimental apparatus was designed so that a pressure difference could be established simultaneous with herbicide concentration difference across the soil column. Draper loam from the Farmington experimental farm and Timpanogas silt loam from the experimental turkey farm were used. The experiment was carried out under room temperature. The adsorption isotherm and the energy of adsorption were also studied.

The experimental results showed that the linked phenomenological coefficient $L_{HW}$ is $10^4$ times as large as $L_{HH}$ and the driving force resulting from concentration differences of herbicides are very small. Thus, the flow of herbicides resulting from its own concentration difference can be neglected. Consequently, the rate equations for the flow of herbicide is simply linked to the flow of water through soil. The adsorption of herbicides can be treated as an exchange process so that the rate equations developed are valid to describe the flow processes that occurred in this investigation.

The adsorption of Ametryne and Atrazine increased with decreasing temperature; thus the heat of adsorption is positive and the adsorption
of herbicides to soil occurs simultaneous and in amounts depending upon the concentrations in solution and the temperature. The adsorption of herbicide by soils explains why the linked transfer coefficient for herbicides and water is less than the water transfer coefficient above.
LITERATURE CITED


APPENDIXES
### Appendix A

#### Table 4. The calculated values of phenomenological coefficient for Draper loam

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>$L_{ww} \times 10^{-6}$ gm sec deg cm$^{-4}$</th>
<th>$L_{wh} \times 10^{-10}$ gm sec deg cm$^{-4}$</th>
<th>$L_{Hw} \times 10^{-12}$ gm sec deg cm$^{-4}$</th>
<th>$L_{HH} \times 10^{-15}$ gm sec deg cm$^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ametryne</td>
<td>1.34</td>
<td>-2.22</td>
<td>3.9</td>
<td>-1.20</td>
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</table>

#### Table 5. The calculated values of phenomenological coefficient for Timpanogas silt loam

<table>
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<tr>
<th>Herbicide</th>
<th>$L_{ww} \times 10^{-7}$ gm sec deg cm$^{-4}$</th>
<th>$L_{wh} \times 10^{-10}$ gm sec deg cm$^{-4}$</th>
<th>$L_{Hw} \times 10^{-12}$ gm sec deg cm$^{-4}$</th>
<th>$L_{HH} \times 10^{-16}$ gm sec deg cm$^{-4}$</th>
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<td>1.035</td>
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</tr>
<tr>
<td>Atrazine</td>
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<td>-2.5</td>
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<td>1.98</td>
<td>0.163</td>
<td>0.767</td>
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<td>1.21</td>
<td>1.71</td>
<td>0.529</td>
<td>-1.84</td>
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</table>
Appendix B

Table 6. The experimental data for the movement of Ametryne and water through Draper loam

<table>
<thead>
<tr>
<th>C/C₀</th>
<th>C' x 10^-6</th>
<th>Δt x 10^4</th>
<th>Δv of effluent</th>
<th>Jw x 10^-4</th>
<th>JH x 10^-10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm^-3 sec</td>
<td>cm^-3</td>
<td></td>
<td>gm sec~-1 cm^-2</td>
<td>gm sec~-1 cm^-1</td>
</tr>
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<td>40.2</td>
<td>1.367</td>
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<td>1.17</td>
<td>31.7</td>
<td>1.38</td>
<td>2.445</td>
</tr>
<tr>
<td>0.565</td>
<td>2.08</td>
<td>1.2</td>
<td>35.5</td>
<td>1.509</td>
<td>3.139</td>
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</table>

Table 7. The experimental data for the movement of Atrazine and water through Draper loam

<table>
<thead>
<tr>
<th>C/C₀</th>
<th>C' x 10^-6</th>
<th>Δt x 10^4</th>
<th>Δv of effluent</th>
<th>Jw x 10^-4</th>
<th>JH x 10^-10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm^-3 sec</td>
<td>cm^-3</td>
<td></td>
<td>gm sec~-1 cm^-2</td>
<td>gm sec~-1 cm^-1</td>
</tr>
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<td>0.031</td>
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Table 8. The experimental data for the movement of Ametryne and water through Timpanogas silt loam

<table>
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<tr>
<th>C/C₀</th>
<th>C'H x 10^-6</th>
<th>Δt x 10^4</th>
<th>Δv of effluent</th>
<th>J_w x 10^-4</th>
<th>J_H x 10^-10</th>
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<td>cm³</td>
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<td>gm sec⁻¹ cm⁻²</td>
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</table>

Table 9. The experimental data for the movement of Atrazine and water through Timpanogas silt loam

<table>
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<tr>
<th>C/C₀</th>
<th>C'H x 10^-6</th>
<th>Δt x 10^4</th>
<th>Δv of effluent</th>
<th>J_w x 10^-4</th>
<th>J_H x 10^-10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gm cm⁻³</td>
<td>sec cm³</td>
<td>cm³</td>
<td>gm sec⁻¹ cm⁻²</td>
<td>gm sec⁻¹ cm⁻²</td>
</tr>
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<td>0.432</td>
<td>1.388</td>
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</table>
Appendix C - Example of calculation

I. Calculation of the concentration of the effluent solution.

A. The prepared Ametryne sample was subjected to scintillation counting. The counts per minute for the Blue tube and Green tube were $6.685 \times 10^3$ and $7.512 \times 10^3$ respectively. The ratio of the counts per minute for Blue tube over Green tube was 0.89. From Figure 9 we can find that the efficiency of Green tube is 68.2 percent. The corrected counts per minute for Green tube will be $7.512 \times 10^3/0.89 = 8.515$ counts per minute.

B. By comparing $11.015 \times 10^3$ counts per minute with the calibration curve for Ametryne in Figure 2, one can find the concentration ($C_H$) of Ametryne for this sample to be 2.08 ppm.

II. Calculation of water flux $J_W$.

A. The volume ($\Delta v$) of the above sample was 35.5 cm$^3$, and the time interval ($\Delta t$) was $1.2 \times 10^4$ sec. The cross sectional area ($A$) of the porous plate was 19.6 cm$^2$. Since the concentration of Ametryne is 2.08 ppm, we can neglect the weight of Ametryne in the sample and take the density of water as 1 gm/cm$^3$. The flux of water $J_W$ can be calculated as

$$J_W = \frac{1 \times \Delta v}{A \times \Delta t} = \frac{35.5}{19.6 \times 1.2 \times 10^4} = 1.509 \times 10^{-4} \text{ gm sec}^{-1}\text{cm}^{-2}.$$  

III. Calculation of the flux of herbicide.

A. The concentration of Ametryne for above sample was 2.08 ppm. The flux of Ametryne ($J_H$) can be calculated as

$$J_H = \frac{C_H \times \Delta v}{A \times \Delta t} = \frac{2.08 \times 10^{-6} \times 35.5}{19.6 \times 1.2 \times 10^4} = 3.14 \times 10^{-10} \text{ gm sec}^{-1}\text{cm}^{-2}.$$
IV. Calculation of relative concentration $C/C_0$.

The concentration $(C'_H)$ of Ametryne for the above sample was 2.08 ppm, and the original concentration $C_0$ was 4 ppm. The relative concentration can be calculated as

$$C/C_0 = 2.08/4 = 0.52$$

V. Calculation of the transfer coefficient $L_{ww}$, $L_{wh}$, $L_{hw}$, and $L_{hh}$.

A. From Table 6, we can find the following information:

<table>
<thead>
<tr>
<th>$C/C_0$</th>
<th>$C'_H \times 10^{-6}$</th>
<th>$\Delta t \times 10^4$</th>
<th>$\Delta v$</th>
<th>$J_w \times 10^{-4}$</th>
<th>$J_H \times 10^{-10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gm cm$^{-3}$</td>
<td>sec</td>
<td>cm$^3$</td>
<td>gm sec$^{-1}$ cm$^{-2}$</td>
<td>gm sec$^{-1}$ cm$^{-2}$</td>
</tr>
<tr>
<td>0.443</td>
<td>1.772</td>
<td>1.17</td>
<td>31.7</td>
<td>1.38</td>
<td>2.445</td>
</tr>
<tr>
<td>0.52</td>
<td>2.08</td>
<td>1.2</td>
<td>35.5</td>
<td>1.509</td>
<td>3.139</td>
</tr>
</tbody>
</table>

The temperature $T$ is 298° K, $R$ for Ametryne is $3.66 \times 10^5$ erg gm$^{-1}$, and $\Delta p$ is $44884$ dyne cm$^{-2}$.

B. Equations [33] and [34] can be rearranged as

$$J_w = -L_{ww} \frac{\overline{v}_w \Delta p}{T} - L_{wh} \frac{\Delta C_H}{C_H}$$  \[49\]

$$J_H = -L_{hw} \frac{\overline{v}_w \Delta p}{T} - L_{hh} \frac{\Delta C_H}{C_H}$$  \[50\]

where $\Delta C_H = C_0 - C'_H$ and $\overline{C}_H = (C_0 + C'_H)/2$, and $\overline{v}_w$ is taken as 1 cm$^3$gm$^{-1}$.

C. The transfer coefficient $L_{ww}$ and $L_{wh}$ can be solved by plugging the values of $J_w$, $\Delta p$, $T$, $\overline{v}_w$, $R$, $\Delta C_H$, and $\overline{C}_H$ into equation [49] and we get

$$1.38 \times 10^{-4} = L_{ww} \frac{44884 \times 1}{298} + L_{wh} \times 3.66 \times 10^5 \times \frac{2.23 \times 10^{-6}}{2.89 \times 10^{-6}}$$
1.509 \times 10^{-4} = L_{WW} \frac{44884 \times 1}{298} + L_{WH} \times 3.66 \times 10^5 \frac{1.92 \times 10^{-6}}{3.04 \times 10^{-6}} \\

By simultaneously solving above two equations, we get

\[ L_{WW} = 1.34 \times 10^{-6} \text{ gm sec deg cm}^{-4} \]
\[ L_{WH} = -2.22 \times 10^{-10} \text{ gm sec deg cm}^{-4} \]

By neglecting the flux attributable to herbicide concentration gradient, we get \( L_{WW} = 0.92 \times 10^{-6} \) and \( 1.00 \times 10^{-6} \text{ gm sec deg cm}^{-4} \) for the left-hand member of the two equations given above.

D. The transfer coefficient \( L_{HW} \) and \( L_{HH} \) can be obtained by plugging the values of \( J_H, \Delta p, T, \bar{v}_W, R, \Delta C_H, \) and \( \bar{C}_H \) into equation [50], and we get

\[ 2.445 \times 10^{-10} = L_{HW} \frac{44884 \times 1}{298} + L_{HH} \times 3.66 \times 10^5 \frac{2.23 \times 10^{-6}}{2.89 \times 10^{-6}} \]
\[ 3.139 \times 10^{-10} = L_{HW} \frac{44884 \times 1}{298} + L_{HH} \times 3.66 \times 10^5 \frac{1.92 \times 10^{-6}}{3.04 \times 10^{-6}} \]

By solving the above equations for \( L_{HW} \) and \( L_{HH} \), we get

\[ L_{HH} = -1.20 \times 10^{-15} \text{ gm sec deg cm}^{-4} \]
\[ L_{HW} = 3.9 \times 10^{-12} \text{ gm sec deg cm}^{-4} \]

If we again neglect the contribution of the herbicide concentration gradient, we get a separate value of \( L_{HW} \) for each set of data given above as \( 1.62 \times 10^{-12} \) and \( 2.08 \times 10^{-12} \text{ gm sec deg cm}^{-4} \) both of which are smaller than the single value found from the simultaneous solution.
Figure 9. The calibration curve for quenching effect.