

1-1-1992

# Sorption of atrazine on weathered Wisconsin age glacial till in Iowa

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**Sorption of atrazine on weathered  
Wisconsin age glacial till in Iowa**

by

**Kyungseo Kim Kwon**

ISU  
1992  
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A Thesis Submitted to the  
Graduate Faculty in Partial Fulfillment of the  
Requirements for the Degree of  
**MASTER OF SCIENCE**

Department: Civil and Construction Engineering  
Interdepartmental Major: Water Resources

Approved:

Signatures have been redacted for privacy

Iowa State University  
Ames, Iowa

1992

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## INTRODUCTION

Effective management of a groundwater system requires the description and prediction of the transport and fate of contaminants in that system. The contamination of groundwater is a serious problem because groundwater supplies a large portion of drinking water supplies in the United States. Among the organic pollutants of groundwater, pesticides have received growing concern, especially in agricultural regions.

Atrazine is a heavily used herbicide in corn production and used as a selective pre- and post-emergence herbicide for the control of broad-leaf and grassy weeds in many other agricultural crops.

Atrazine was chosen as the subject material in this study because attention has been focused on it recently as the most commonly detected pesticide in groundwater, especially in Iowa (IDNR, 1990; Hallberg, 1989). Based on State-Wide Rural Well-Water Survey (SWRL) (IDNR, 1990) findings, the proportion of wells contaminated with atrazine, state-wide, lies between 6% and 10%. And the occurrence varies regionally from 4% of wells in northeastern Iowa, to over 18% in northwest Iowa. Shallow wells (< 50 ft) show a higher probability of atrazine concentration. The mean concentration of detection was  $0.90 \mu\text{g}/\ell$ . It was also detected in 0.6% of the wells state-wide at concentrations exceeding the Lifetime Health Advisory Level of  $3 \mu\text{g}/\ell$ , as established by the EPA. It has not been proven that atrazine is a carcinogen (DNR, 1990, Hallberg, 1989). But, atrazine in drinking water may increase the risk of cancer in humans. Other potential adverse health effects include tremors, changes in organ weights, and damage to the liver and heart.

The possible sources of pesticides contamination of groundwater include agricultural application, accidental spills, back-siphoning accidents, and improper

disposal of formation or rinse water. One of the most significant phenomena impacting the transport of many organic pollutants is partitioning between the solid (soil) and aqueous (groundwater) phase. The binding of pesticides and their metabolites increases the time they remain in the soil and affects various physicochemical and biological processes of their decomposition. For example, degradation of  $^{14}\text{C}$ -atrazine bound to humic acid and clay fractions was much slower than that of free  $^{14}\text{C}$ -atrazine (Kretova, 1986).

An objective of this study was to estimate the potential transport of atrazine in the groundwater in the Wisconsin age weathered till that exists at shallow depth below the soil surface in north-central Iowa, where the organic carbon content is low. Batch tests were conducted and the concentration was analyzed by gas chromatography to estimate the adsorption/desorption equilibrium isotherms of atrazine. The range of atrazine concentrations is low (original concentration ranged from  $50 \mu\text{g}/\ell$  to  $1,000 \mu\text{g}/\ell$ ) to simulate the low concentrations of atrazine typically detected in wells.

There has been developed some mathematical models and computer programs to utilize the result of laboratory experiments to simulate the field transport of organic chemicals. Based on the batch tests, an estimate of the potential velocity of atrazine in the shallow groundwater in the oxidized till is obtained.

## LITERATURE REVIEW

### Adsorption

Adsorption is a surface phenomena which is defined as the taking up of molecules by the external or internal surface (Benefield, 1982) or the interface accumulation or concentration of substances at a surface or interface (Weber, 1972). Both definitions are expressing a mass transfer process from one phase to the surface of the other phase. In the study of groundwater contamination and its remediation, it refers to the movement of solutes from water to the surface of soils.

The driving force of adsorption is classified into solvent-disliking or high affinity of the solute for the solid. The first one is the most significant factor in modeling groundwater contamination of organics because most organic contaminants are hydrophobic. In the category of the second driving force, there are three types of adsorption. The first is an exchange adsorption process in which ions of one substance concentrate at a surface as a result of electrostatic attraction to charged sites at the surface. The second is physical adsorption in which van der Waals forces play a major role. Lastly, there is chemical adsorption under which solutes react chemically with the second phase.

Desorption is the reverse phenomena of adsorption. Desorption from the soil is not reliably predicted by the adsorption equations, i.e., the adsorption/desorption process is not reversible, especially in the case of high partition coefficient chemicals. The difference is called the "hysteresis of desorption". Usually the desorption isotherm shows a higher retention of the pesticide by the soil and the deviation of the desorption curve is greater with the lower initial concentration (Koskinen, et al., 1979).

Koskinen et al. (1979) presented several factors that could contribute to hysteresis of pesticides: nonattainment of equilibrium during desorption, changes

with time in the bonding mechanisms of the pesticide to the soil, formation of precipitates, or losses of the pesticide by volatilization, chemical decomposition, or biochemical degradation during adsorption or desorption. Another possible cause of hysteresis was reported by Savage and Wauchope (1974): physical change in the adsorptive character of the soil complex. Repeated wetting and shaking might result in an increased number of sites available for adsorption with increased dispersion or weathering of the clay-organic matter microaggregates.

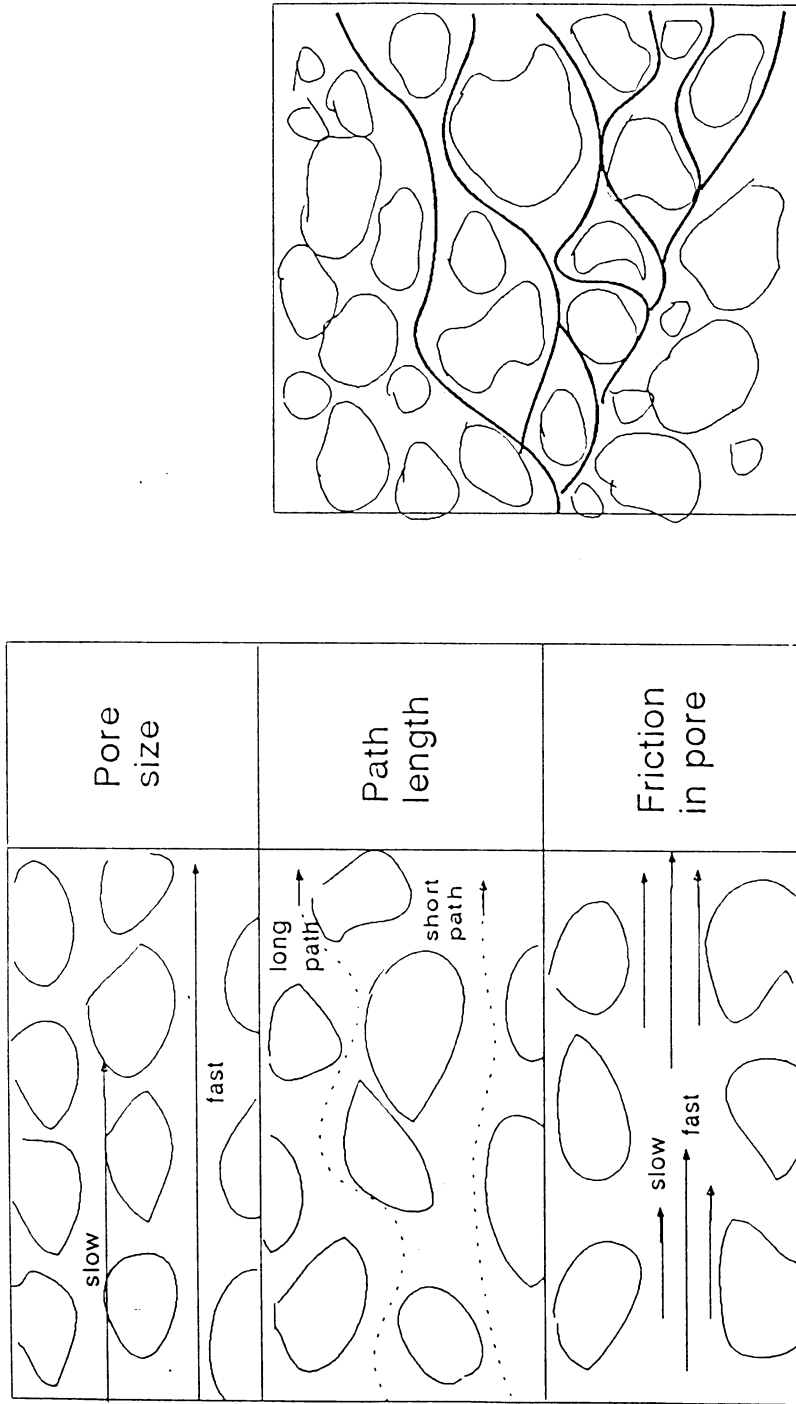
### **Transport of solutes in a groundwater system**

When contaminants are transported by fluid flow through a porous media the rate of mass transport is determined by two basic processes; advection and dispersion. By the process of advection, the fluid carries with it dissolved solutes as if it is piston flow. On the other hand, dispersion acts to lower the concentration by mixing with noncontaminated water. The three basic causes of longitudinal dispersion (along the stream lines of fluid flow) and lateral dispersion (normal to the pathway of fluid flow) are well conceptualized in Figure 1.

When the solutes are conservative, they do not react with the groundwater or soil matrix. However, in the case of reactive substances which undergo chemical, biological, and radioactive reactions in the system, considerable retardation effects will exist, in which contaminate movement is slower than that predicted from advection and dispersion alone.

Adsorption/desorption is one of the most important processes retarding contaminant movement by groundwater flow.

Several mathematical relationships have been developed to describe the equilibrium distribution of solutes between the solid and liquid phases when the tests are conducted at constant temperature, and the relationship is called an isotherm.



**Figure 1.** Factors causing longitudinal dispersion (left) and lateral dynamic dispersion (right) (Fetter, 1988, p. 392, 393)



Both Langmuir and Brumauer, Emmett, Teller (BET) isotherms are deduced from kinetic considerations or the thermodynamics of adsorption. The Langmuir model is built on the assumptions that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface.

On the other hand, the BET model is more sophisticated and assumes a number of layers of adsorbate molecules form at the surface and that the Langmuir equation applies to each layer. A further assumption of the BET model is that a given layer need not complete formation prior to initiation of subsequent layers; the equilibrium condition will therefore several types of surfaces in the sense of layers of molecules on each surface site. Figure 2 represents typical isotherms for Langmuir and BET adsorption.

The other isotherm relationship which is the most commonly used for systems which exhibit nonlinear partitioning behavior is the Freundlich isotherm. This model is an empirical equation. The assumption is that the adsorbent has a heterogeneous surface composed of different classes of adsorption sites, with adsorption on each class of site following the Langmuir isotherm. The Freundlich isotherm is given by

$$q_e = K_F C_e^{1/n} \quad (1)$$

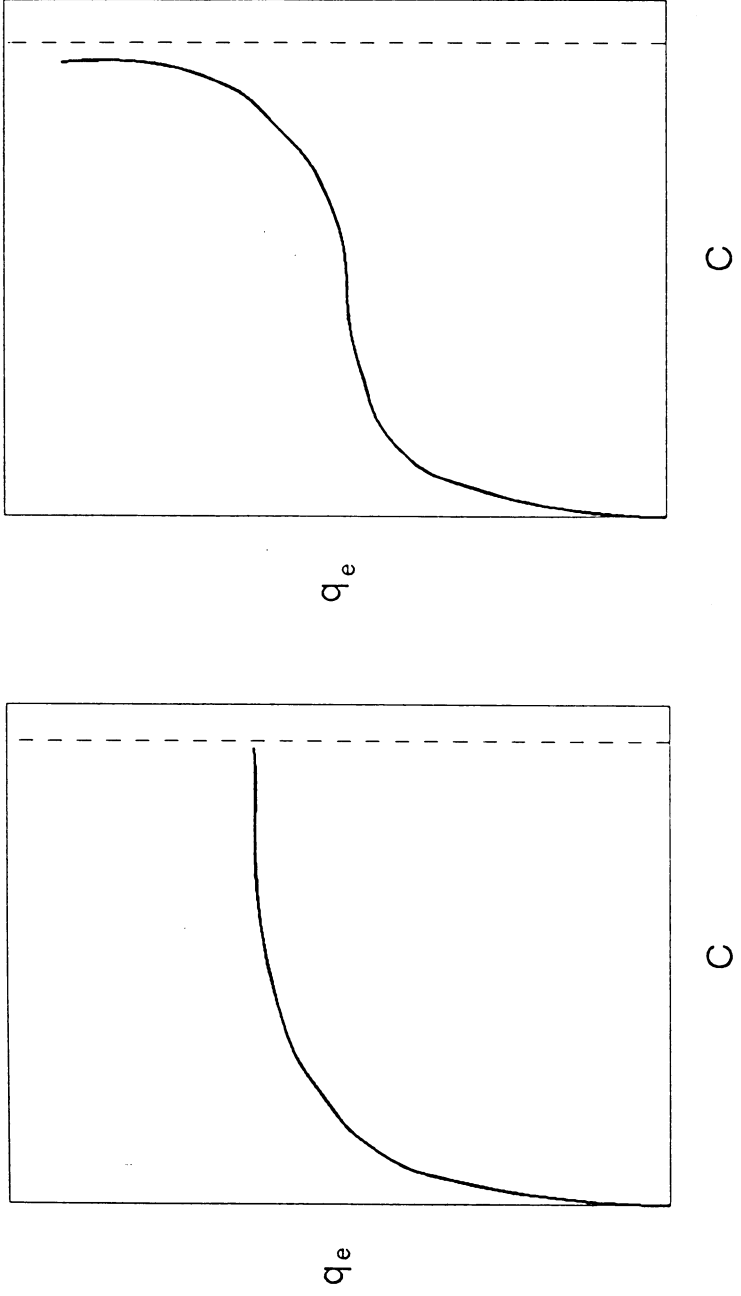
where  $q_e$  = solid phase concentration (M/M)

$K_F$  = partition coefficient ( $L^3/M$ )

$n$  = constant  $> 1$ .

For coefficient determination, the parabolic Freundlich equation may be logarithmically linearized to give

$$\log q_e = \log K_F + 1/n \log C_e. \quad (2)$$



in which  $q_e$  : solid phase concentration  
 $C_e$ : liquid phase concentration

Figure 2. Typical isotherms of Langmuir (left) and B.E.T. (right) adsorption (Weber, 1972, p. 207)

Equation (2) plotted on log-log paper will give a straight line. The value of  $K_F$  can be determined by the intercept (when  $C_e$  is 1) and  $n$  comes from the slope of the line.

The linear isotherm is the simplest modeling approach, in which the distribution of solute between the soil and water is expressed as linear

$$q_e = K_p C_e \quad (3)$$

where  $K_p$  is the partition coefficient.

The linear isotherm has been applied to a number of soil/solute/ water systems because of its simplicity and the potential of correlation with other constitutive properties, such as octanol-water partition coefficient ( $K_{ow}$ ) and/or chemical solubilities. The other power of this model lies in the easy comparison of the sorption responses for various solute-solid systems by the sediment sorption coefficient (Sabljić, 1987). Another advantage of this approach is that it simplifies computer simulation modeling (Rao and Davidson, 1979).

Actually, much research has shown that the adsorption behavior of a broad range of organic compounds exhibit the linear isothermal relationship (Means et al., 1980; Chiou et al. 1983, Crittenden et al., 1986; Clay et al., 1988, Davidson and Chang, 1972). Among those studies, Davidson and Chang (1972) started with a Freundlich model to get  $1/n$  as 0.97, almost unity, and then assumed unity.

On the other hand, it has been strongly suggested that organic compounds, including pesticides, follow Freundlich type isotherms (Rao and Davidson, 1979; Weber and Miller 1988). Examination of the experimental concentration ranges gives the idea that the research papers which revealed linearity worked on the ranges below  $1,000 \mu\text{g}/\ell$ , or at most  $2,000 \mu\text{g}/\ell$  as in the Davidson's (1972), and they could be compared with those of Rao and Davidson (1979,  $< 50,000 \mu\text{g}/\ell$ ). But, even in the Rao and Davidson's (1972) isotherm it is apparent that there exists linearity below concentrations of  $1,000 \mu\text{g}/\ell$ .

For both linear and Freundlich isotherms, it is clear that extrapolation can lead to large errors in adsorption estimates.

For low concentrations, the linear isotherm is used for its convenience. Karickhoff (1984) presented the theoretical basis thermodynamically for using linear isotherms in low concentration organic carbon adsorption.

The general form of the transport equation for conservative contaminants which do not undergo reaction in solution phase in its one-dimensional (z) form is presented in Equation (4) (Miller and Weber, 1984).

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial z} - \frac{\rho(1-\theta)}{\theta} \frac{\partial q}{\partial t} \quad (4)$$

where

- C = liquid phase concentration of solute (M/L<sup>3</sup>).
- t = time (t)
- D<sub>h</sub> = hydrodynamic dispersion coefficient (L<sup>2</sup>/t)
- V = average linear velocity (L/t)
- ρ = solid phase particle density (M/L<sup>3</sup>)
- θ = volumetric fraction represented by the liquid phase (L<sup>3</sup>/L<sup>3</sup>)
- q = normalized solid phase concentration of sorbed solute species (M/M)

Under the assumption of instantaneous equilibrium and a linear isotherm, it is reduced to

$$r_f \frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial z} \quad (5)$$

where the retardation factor  $r_f = 1 + \frac{\rho(1-\theta)}{\theta} K_p$ . (6)

When contaminants undergo adsorption to the soils, they move at a slower rate than that of the average linear groundwater velocity. Then, the rate of solute

movement is determined by the retardation equation using the retardation factor calculated from equation (6).

Fetter (1988) simplifies the calculation of velocity of the solute front to

$$V_c = V_x / r_f \quad (7)$$

where  $V_x$  = average linear velocity

$V_c$  = velocity of the solute front where the solute concentration is one-half of the original value ( $C/C_0 = 0.5$ )

### Factors affecting adsorption-desorption

There have been many efforts to predict the environmental fate of organic compounds by correlating the sorption with the chemical or physical properties of chemicals and soils.

It is currently understood that the fraction of organic carbon ( $f_{oc}$ ) of the soil or sediment is the dominant characteristic that influences the sorption of a given organic compound from an aqueous solution (Means et al., 1980; Huang et al., 1984). And if the adsorption process depends only on  $f_{oc}$ , the relationship between the organic carbon partition coefficient ( $K_{oc}$ ) and the fraction of organic carbon ( $f_{oc}$ ) is

$$K_{oc} = K_p / f_{oc} \quad (8)$$

This is the reason why so many researchers have worked to find the factors of chemicals which affect  $K_{oc}$  values to correlate those factors of chemicals with  $K_{oc}$ . Octanol-water partition coefficient ( $K_{ow}$ ) is the primary subject in this study (Brown and Flagg, 1981; Karickhoff and Brown, 1979). The researchers tried to get models to predict  $K_{oc}$ 's from  $K_{ow}$ 's. The results were different from system to system depending on what kind of soil and what kind of organic compounds they used for modeling. The same thing happened when they tried to figure out the

relationship between organic carbon partition coefficient ( $K_{oc}$ ) and solubility of chemicals (S) (Karickhoff and Brown, 1979, Chiou et al., 1983).

Banerjee et al. (1980) criticized  $K_{oc}$  – S correlations because these two parameters may be invalid for high melting point. Therefore, he suggested an alternative relationship between  $K_{oc}$  and S by adding another factor of melting point.

Miller and Weber (1984) still resisted to use the rough approximations of  $K_{oc}$ 's with  $K_{ow}$ 's because there are quantitative systems in which the approximations are not adequate. They insisted that more accurate simulation of solute transport required incorporation of kinetic parameters and/or a nonlinear isotherm relationship.

Even with criticisms, organic carbon of the solid phase and the solubility of solutes play a significant role in predicting the behavior of contaminants in soil system. Karickhoff (1984) presented a good review about the relationship of these factors. He estimated equations for  $K_{oc}$  from water solubility, and  $K_{oc}$  from  $K_{ow}$  as

$$\log K_{oc} = 0.83 \log X_s - 0.01 (mp - 25) - 0.93 \quad (r^2 = 0.93). \quad (9)$$

where

$X_s$  = mole fraction solubility

mp = melting point in °C

and

$$\log K_{oc} = \alpha \log K_{ow} + \beta \quad (10)$$

in which  $\alpha$  and  $\beta$  are data fitted coefficients.

Molecular topology has been shown to be a very useful structural parameter for describing and predicting the soil sorption coefficients (Sabljić, 1987). A linear relationship was established between  $^1X$  and  $\log K_{oc}$ :

$$\log K_{oc} = 0.55 \ ^1X + 0.45 \quad (11)$$

with  $n = 37$ ,  $r = 0.973$ ,  $S = 0.338$ ,  $F^{1,35} = 613$

where  $^1X$  is molecular connectivity index which can be calculated by the computer program GRAPH III written in FORTRAN for the IBM PC/XT personal computer. The ability of the molecular connectivity model was tested for 72 compounds from a broad range of organics. Sabljic (1987) asserted that the model outperformed the traditional empirical models based on octanol/water partition coefficients or water solubilities in accuracy, speed, and range of applicability.

The particle size distribution of the soil is fairly frequently reported as an important factor affecting the adsorption of pesticides (Huang et al., 1984; Karickhoff et al., 1979; Richardson, 1971). They insisted that a normal distribution of  $K_{oc}$  on particle size was apparent, which implies a low  $K_{oc}$  value for sand, increasing to a maximum for fine silt, then decreasing somewhat for clay-sized particles.

Huang et al. (1984) reported that besides organic matter, the noncrystalline to poorly crystalline Al and Fe components (sesquioxide) provide adsorption sites for organic compounds.

Other observed factors include dissolved humic acid (Carter and Suffet, 1982), ionic strength (Karickhoff, 1979), soil pH (Francis et al., 1972; Clay et al., 1988), and temperature (Francis et al., 1972).

It is clear that these factors affect the adsorption phenomena but, the groundwater at a particular location does not usually exhibit large variations in pH, temperature, or ionic strength, so these factors are usually neglected. Bailey and White (1970) mentioned the factors in detail, but they will not be described here.

#### **Recent studies about atrazine**

Lupi et al. (1988) developed a mathematical model to predict the effect of leaching on the contamination of groundwater sources generally located at several meters depth in soil. They improved and modified previously proposed models in an

effort to try to include the important factors such as water transport, rise due to capillarity, partition among soil-contained water, air and organic matter, and degradation processes. Organic carbon content at the soil surface of 1 – 2% and 2.5 Kg/ha of atrazine application were assumed in the simulation. According to the results, atrazine required at least 2 years to percolate significantly below 4m of depth in the lowest organic carbon content soil, and at least 3 years in the soil with the highest organic carbon content.

Bouchard et al. (1988) worked with atrazine and other neutral compounds to reveal that the nonequilibrium solute transport represented by the breakthrough curve (BTC) asymmetry was due to the sorption process itself. That is, the slow, nonaqueous phase diffusion within the organic carbon matrix and subsequent poor mass transfer between the solid and solute phase. For atrazine, higher organic carbon content surface soil ( $6.9 \pm 0.6 \text{ g Kg}^{-1}$ ) showed distinct asymmetric BTC's with a leftward shift and higher retardation factor (2.98). On the other hand, lower organic carbon content subsurface soil ( $0.33 \pm 0.01 \text{ g Kg}^{-1}$ ) showed almost symmetric BTC's and a lower retardation factor (1.25). The observation implied that low organic carbon loading of the aquifer material may allow rapid solute mass transfer between the organic carbon and aqueous phases. In this study, the measured equilibrium isotherms were linear so that there were no differences of mobilities of atrazine among different aqueous concentrations. But in the work by Rao and Davidson (1979), pesticides followed nonlinear Freundlich type equilibrium isotherms at high concentrations in soils. When the movement of atrazine through water-saturated soil columns was examined at two input solution concentrations (5 and  $50 \mu\text{g/ml}$ ), the break through curves (BTC's) showed that the mobility was significantly greater for the higher concentrations. The obtained BTC's were also asymmetrical, which could be attributed to nonequilibrium conditions existing in the



soil column during flow. They found  $K_{oc}$  values of  $121.8 \pm 25$  (mℓ/g) and  $1/n$  smaller than unit. A value of  $1/n < 1$  means that the amount of pesticide adsorbed by the soil continued to increase at a decreasing rate as the concentration increases. Brown and Flagg (1981) determined an empirical relationship between the octanol/water partition coefficients ( $K_{ow}$ ) and sediment sorption coefficients ( $K_{oc}$ ) for nine chloro-s-triazine and dinitroaniline compounds. They found that the set of sorbent and compounds followed linear isotherms. The resulting empirical equation was

$$\log K_{oc} = 0.937 \log K_{ow} - 0.006 \quad (r^2 = 0.95).$$

For atrazine especially, they obtained a  $K_p$  value of 7.07 with units of mℓ/g and a  $K_{oc}$  value of 216 with the same units.

Clay et al. (1988) determined the effect of soluble soil organic carbon (SSOC) during atrazine and cyanazine desorption equilibration and found that SSOC has no effect on those compounds hysteretic behavior. They proposed irreversible bonding of a metabolite as the major cause of the observed atrazine and cyanazine hysteresis.

## MATERIALS AND METHODS

### **Till samples**

The samples used in this study were Wisconsin aged oxidized glacial till collected from the saturated zone at the 6.5 – 9 foot depth at the ISU Agronomy/Agricultural Engineering farm near Boone using a Shelby tube. The sample was homogenized for the batch tests.

The composite material was analyzed using standard methods (Das, 1982) for the physical characteristics; moisture content by the difference after drying at 105°C – 110°C in the oven, grain size by sieving, and density by a mass per volume displacement method. The fraction of organic carbon content was determined by colorimetric determination of the chromous green color after digestion with sulfuric acid (Eik, 1988). Surface area was measured by the EGME (Ethylene Glycol Monoethyl Ether) technique presented by Heilman et al. (1965).

The parameters determined for the sample are summarized in Table 1, while a grain size distribution diagram is shown by Figure 3. The organic carbon fraction ( $f_{oc}$ ) is the ratio of organic carbon to the total weight of the sample. The value of  $f_{oc}$  is 0.00267.

### **Chemicals**

The solute investigated in this study was atrazine. Its full name is 2-chloro-4-(ethylamino)-6-(isopropylamino)-S-triazine and the chemical structure is shown in Figure 4. The physical and chemical characteristics of this solute are summarized in Table 2.

Experimental solutions were comprised of distilled-deionized nano pure water and optima grade (Fisher Scientific) acetone, hexane and methylene chloride for gas chromatography (GC) operation.

**Table 1.** Parameters of till sample

Parameter	Value
Water content g/g ---	0.1692
Bulk density g/cm <sup>3</sup> ---	1.77
Particle density, g/cm <sup>3</sup> ---	2.65
d <sub>50</sub> (mm) ---	0.06
Uniformity coefficient --- (d <sub>60</sub> /d <sub>10</sub> )	41.82
Percent sand (%)	47
Percent silt (%)	44
Percent clay (%)	9
Fraction organic carbon content (f <sub>oc</sub> )	0.00267
Soil pH	8.1
Specific surface (m <sup>2</sup> /g)	36

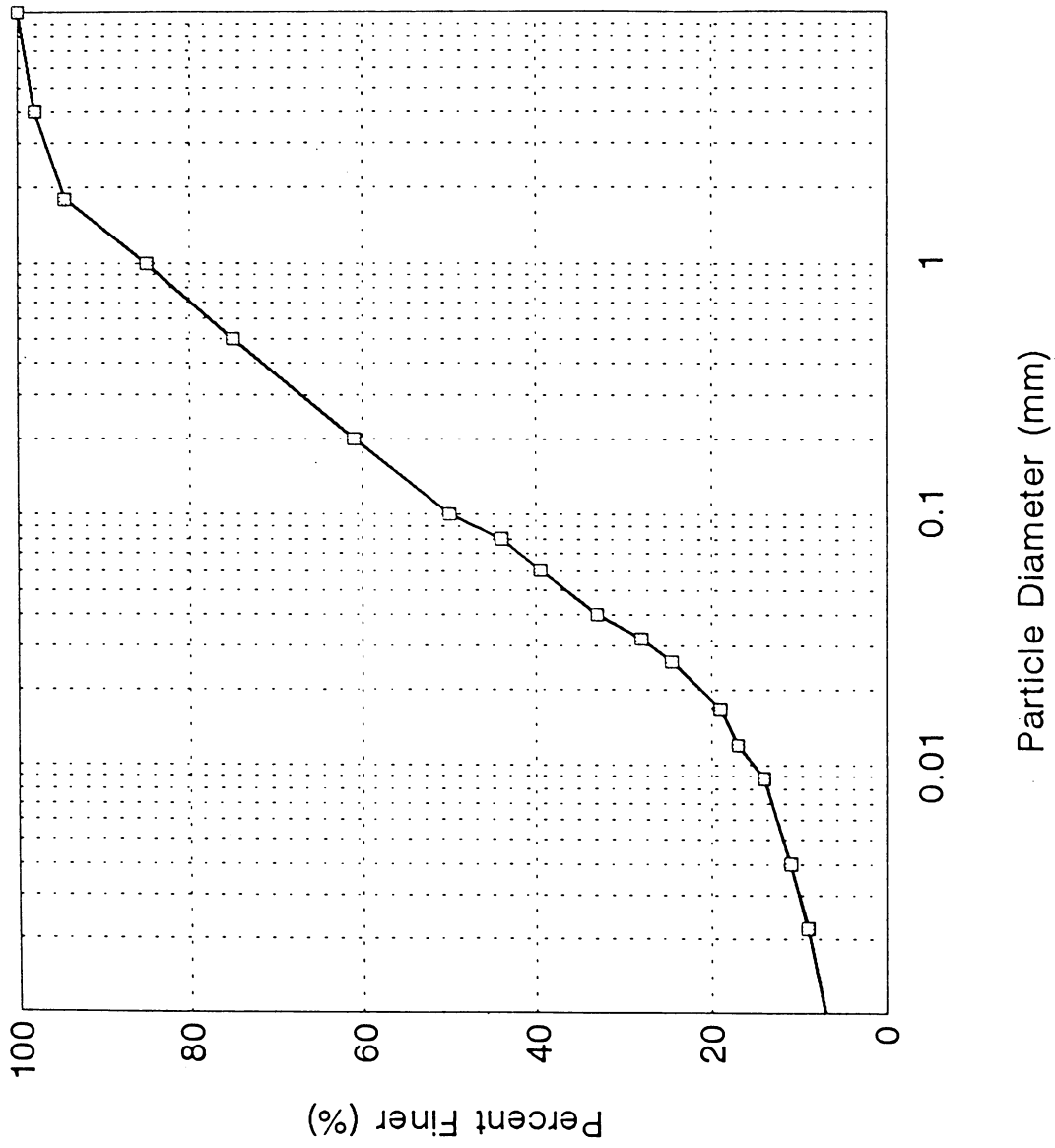


Figure 3. Grain size distribution

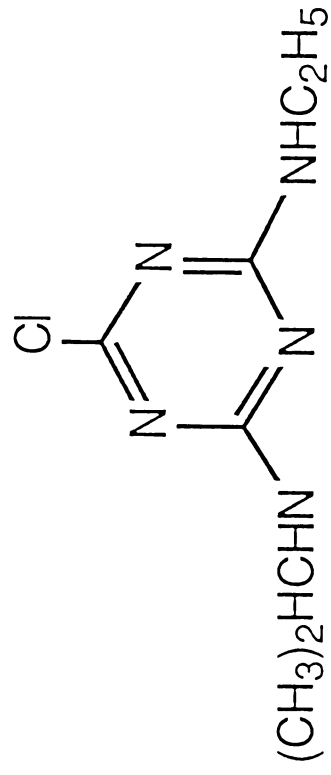


Figure 4. Chemical structure of atrazine

**Table 2.** Atrazine physiochemical parameters

Parameter	Property
Trade name	Aatrex
Molecular formula <sup>a</sup>	C <sub>8</sub> H <sub>14</sub> ClN <sub>5</sub>
Molecular weight <sup>a</sup>	216.06
Water solubility @ 25°C (ppm)	70
Half-life in soil (days) <sup>b</sup>	60
Melting point (°C) <sup>a</sup>	171 – 174
K <sub>ow</sub> (octanol-water partition coefficient)	2.33

<sup>a</sup> Merk Index (1976).

<sup>b</sup> Rao and Davidson (1979).

### Laboratory batch test procedure

Batch equilibrium sorption isotherms were determined using six concentrations of atrazine on till samples. The sorption isotherm was measured in duplicate on mixtures of 50 g of soil and 100 mL of each concentration solution in 250 mL Erlenmeyer flasks. The six initial concentrations were approximately 50  $\mu\text{g/L}$ , 100  $\mu\text{g/L}$ , 200  $\mu\text{g/L}$ , 500  $\mu\text{g/L}$ , 700  $\mu\text{g/L}$ , and 1,000  $\mu\text{g/L}$ . The flasks were sealed with aluminum foil covered stoppers and placed in a shaker at 25°C for 24 h. Kinetic studies (Tsai, 1990) indicated that equilibrium was achieved in 20 h or less.

After equilibration the samples were centrifuged at 17,000 rpm for 10 min in stainless steel centrifuge tubes. A 40 mL supernatant sample was taken for further analysis. The initial and final solution concentrations of the atrazine were determined by variation of USEPA Method 619 (USEPA, 1982), which will be described below, and the amount sorbed was calculated by mass balance.

The 40 mL supernatant sample was poured into a 250-mL separatory funnel and extracted four times with 15 mL methylene chloride by shaking 2 min vigorously, with periodic venting to release excess pressure for each of the extractions. The solution was allowed to stand for 10 min to separate the organic layer from the water phase. The methylene chloride extracts were collected in a 250-mL Erlenmeyer flask and filtered through a drying column containing 10 cm of anhydrous sodium sulfate to catch any remaining water. The extract was collected in a Kuderna-Danish (K-D) concentrator, which were assembled by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. The Erlenmeyer flask and the column were cleaned with 20 mL of methylene chloride to complete the quantitative transfer. One clean boiling chip was added to the evaporative flask and a three-ball Snyder column was attached.

The K-D apparatus was placed on a hot water bath, 65 – 70°C, so that the concentrator tube was partially immersed in the hot water and the entire lower rounded surface of the flask was bathed with hot vapor. 15 – 20 min was required to reduce the apparent volume of liquid to 1 mL. Then the K – D apparatus was allowed to stand at room temperature until it cooled down completely.

50 mL of hexane and a new boiling chip were added. The temperature of the water bath was increased to about 80°C. During evaporation of hexane, the evaporative flask and the Snyder column was wrapped with a good insulator to keep the process going on. When the mouth of the Snyder column became fully dry, the K – D apparatus was removed from the bath and allowed to stand for 10 min.

The volume of liquid was adjusted to exactly 2 mL by blowing argon gas or adding hexane. The concentrated sample was transferred to a vial with a teflon taped cover and stored in a refrigerator.

For desorption isotherm, the 40 mL aliquot of supernatant removed for adsorption determination was replaced by 40 mL of nano pure water. During the centrifuge, the soils coagulated strongly to make soil cakes. The flasks were shaken by hand first to break and disperse the soil cake, then shaken for 24 h as previously described, and recentrifuged. The desorption equilibration process was repeated three times. The other processes for extraction and analysis were the same as described above.

A Perkin Elmer sigma 1 gas chromatograph (GC) was used to determine the concentration of each sample with a nitrogen/phosphorous (N/P) thermionic detector in the nitrogen mode. The gas column utilized was 1.8 m long x 2 mm (inside diameter) and was packed with 5% Carbowax 20M – TPA Supelcoport (80/100 mesh).



During GC operation, the injection temperature was 250°C, the oven temperature was 200°C, the carrier gas was helium, the carrier flowrate was 30 mL/min and the sample injection volume was 5.0  $\mu\text{L}$ . For these operating conditions, the peak retention time for atrazine is 13.2 min. For the 40 mL original sample size, the detection limit for atrazine was 0.5  $\mu\text{g/L}$ .

#### **Standard curves and recovery efficiency**

The peak intensities from GC were calibrated with standard curves obtained as follows. Standard curves were made with eight standard solutions in acetone to cover the lowest and the highest concentrations of the batch tests.

To estimate the recovery efficiency, four concentrations of 1,000  $\mu\text{g/L}$ , 500  $\mu\text{g/L}$ , 250  $\mu\text{g/L}$  and 100  $\mu\text{g/L}$  of atrazine solutions were analyzed following the extraction and concentration procedure used in the batch tests.

## RESULTS AND DISCUSSION

### Recovery efficiency

The recovery factor was assumed to be constant and obtained from a linear regression of the data, as shown in Figure 5. A zero-intercept in the curve was also assumed. Within the concentration range of the experiment, this assumption appears to be valid statistically ( $R^2 = 0.99$ ). The plot was made for concentration expected vs concentration observed. Then the slope was the efficiency of the GC method. The recovery efficiency was obtained as  $89 \pm 1\%$ . Because the recovery error limit was large, the numbers obtained in this study should be taken to be as an estimated range.

### Adsorption

The adsorption of atrazine on the tills followed linear adsorption isotherms for the original concentration range of  $50 \mu\text{g}/\ell$  to  $1,000 \mu\text{g}/\ell$  of atrazine. The  $K_F$  and  $n$  values of the Freundlich isotherm equation were calculated as follows:

$$\log K_F = -3.56 \pm 0.17 \text{ (m}\ell/\text{g)}$$

$$1/n = 0.93 \pm 0.14$$

or

$$0.00019 < K_F < 0.00041 \text{ (m}\ell/\text{g)}$$

$$0.93 < n < 1.27$$

where the unit of the amount of atrazine adsorbed was in  $\mu\text{g}/\text{g}$  and, equilibrium concentration, in  $\mu\text{g}/\ell$ . Within the statistical error limit, the  $n$ -parameter could be considered as unity. The result and the isotherm curve are represented in Table 3 and Figure 6, respectively. The data points are scattered broadly along the isotherm line. This is because the batch tests used a very low concentration range. In the

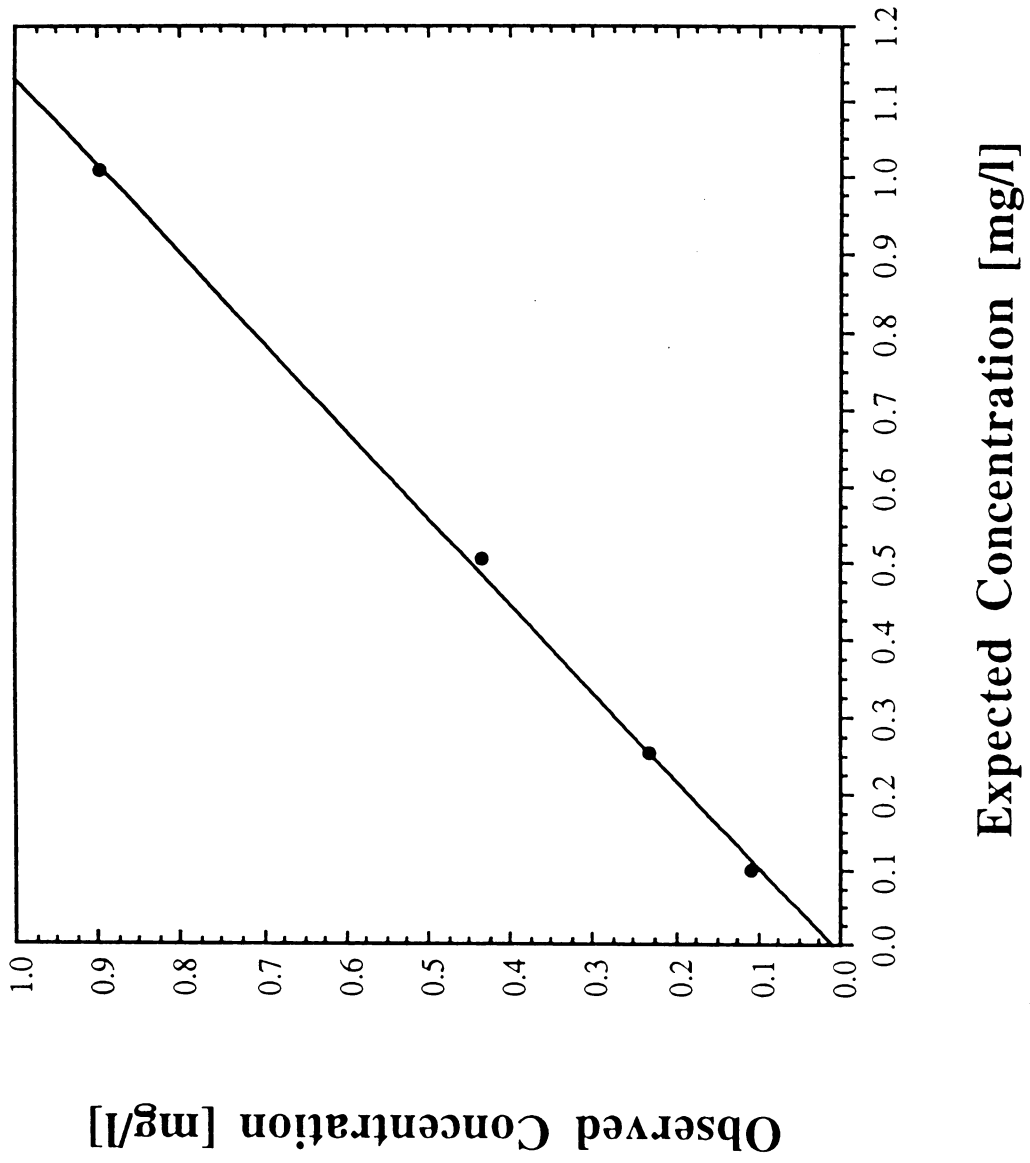


Figure 5. Recovery curve of atrazine from standard samples

**Table 3.** Result of atrazine adsorption isotherm

$C_0$ ( $\mu\text{g}/\ell$ )	$C_e$ ( $\mu\text{g}/\ell$ )	$q$ ( $\mu\text{g}/\text{g}$ )
50.4	44.0	0.0128
100.7	94.7	0.0120
201.4	178.7	0.0454
201.4	201.8	0.00001
503.5	429.0	0.149
700.8	602.2	0.196
1007.0	939.1	0.136
1007.0	931.2	0.152

$C_0$  : original concentration.

$C_e$  : equilibrium concentration.

$q$  : atrazine adsorbed in adsorption isotherm.

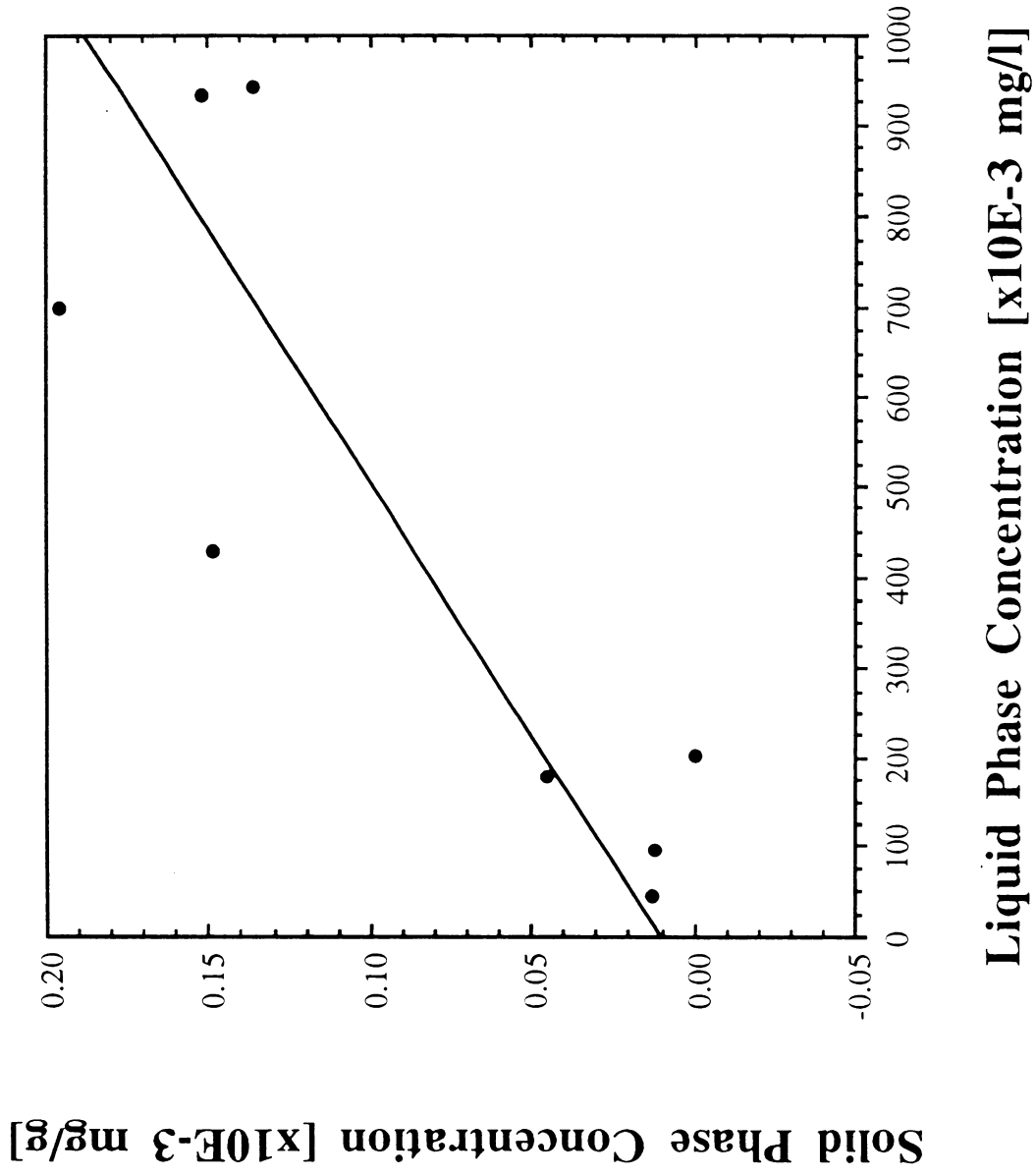


Figure 6. Adsorption isotherm for atrazine on oxidized till

low concentration range, the sensitivity of the result to the error of experiment should be very high compared with the case of higher concentration range.  $K_p$  value was obtained as 0.18 mL/g by linear regression with R squared value of 0.65. The R squared value is somewhat low because of the scattered data points. The other reason for the low R squared value could be the small number of observations. The  $K_{oc}$  value calculated according to equation (8) was 56.2 mL/g. And the retardation factor  $r_f$  by equation (6) was calculated to be 1.97.

On the other hand, because the recovery efficiency 89% was the average value obtained from four samples, the partitioning coefficients and other correspondent parameters were calculated for a recovery efficiency of 85%, 95%, and 99% for the purpose of comparison. These are summarized in Table 4 and shown in Figure 7. They give a possible range of the experimental results. From now on the calculations will be based on an assumed recovery efficiency of 89%.

Generally, organic carbon content in soil decreases very rapidly with depth. According to Lupi et al. (1988), organic carbon content decreases up to one twentieth from the surface to 1.5 m in depth, and under 1.5 m depth, logarithmically with depth. For a compound which has high  $K_{oc}$  value, the vertical distribution of that compound and transportation should have characteristic features that is, the gradient is big.

The comparison with the partition coefficients of atrazine on soil from other literature is shown in Table 5. Brown and Flagg (1981) worked with sediments from bottom of pond and obtained very high  $K_p$  value. A study of Rao and Davidson (1979) resulted in Strata of  $K_F$  values according to the organic carbon content. Higher organic carbon content soils tend to have higher  $K_F$  values.  $K_F$  of 5.16 by Clay et al. (1988) was still high because it was conducted using a surface soil. Bouchard et al. studied the vertical distribution of atrazine adsorption and obtained

**Table 4.** The linear isotherm partitioning coefficients ( $K_p$ ), organic carbon fraction partitioning coefficients ( $K_{oc}$ ), and the retardation factors ( $R_f$ ) for four recovery efficiencies

Recovery efficiency (%)	$K_p$ (m $\ell$ /g)	$K_{oc}$ (m $\ell$ /g)	$R_f$
85	0.07	26.2	1.38
89	0.18	67.4	1.97
95	0.32	119.9	2.72
99	0.42	157.3	3.26

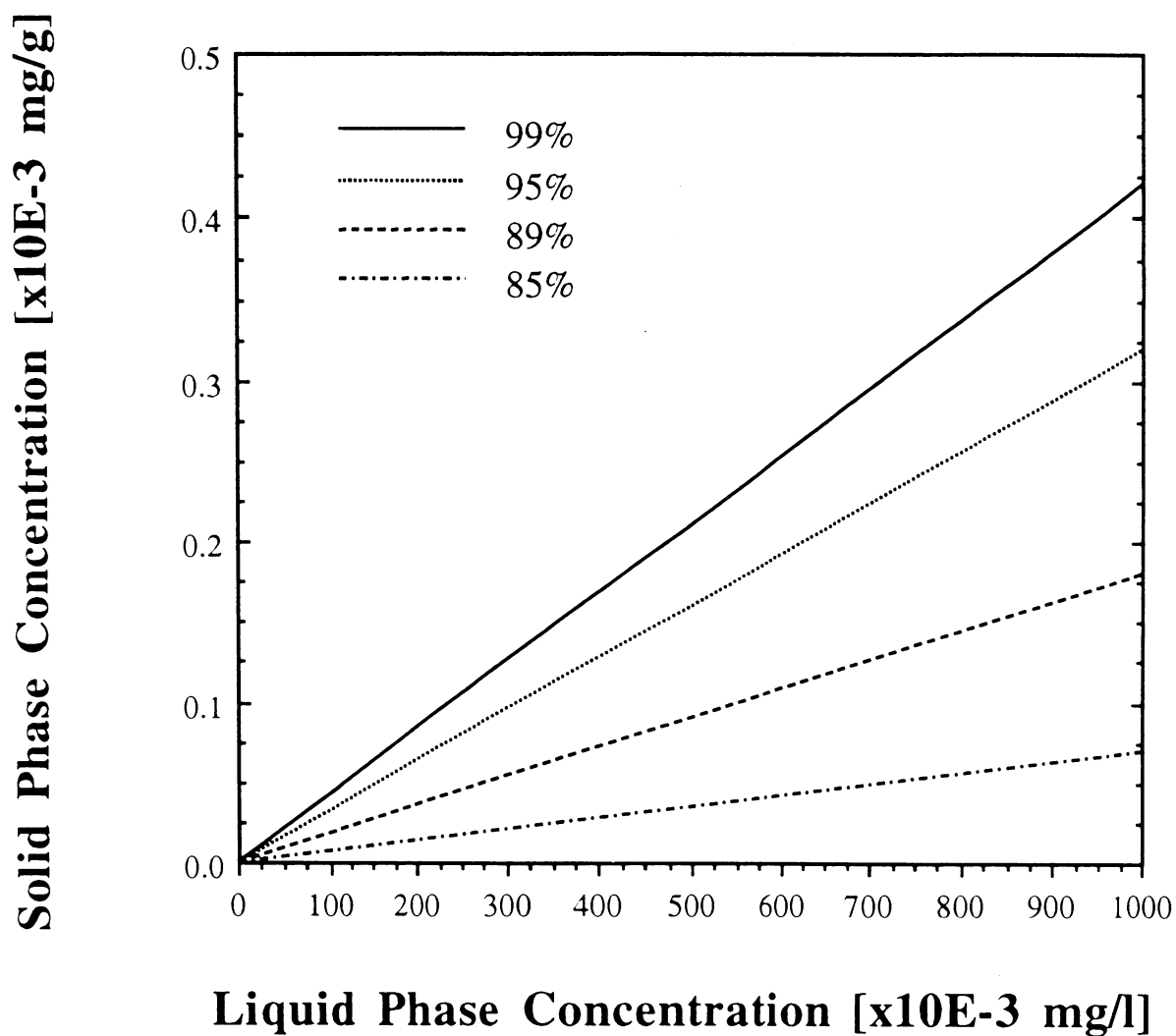


Figure 7. Adsorption isotherms on Wisconsin age glacial till of central-Iowa for four recovery efficiency



Table 5.  $K_F$  values of atrazine from literature

References	$K_p$ (mℓ/g)	$K_F/n$	$K_{oc}$ (mℓ/g)	$f_{oc}$	source of soil	$r_f$
Brown and Flagg (1981)	7.07		216		Pond sediment	
Rao and Davidson (1979)		6.03/0.73 0.89/1.04 0.62/0.79	155.8 98.9 110.7	0.0387 0.0090 0.0056		
Clay et al. (1988)		5.16/0.79			surface soil	
Bouchard et al. (1988)	0.07 0.32 0.45		212.1 123.1 65.2	0.00033 0.0026 0.0069	417 – 478 cm 290 – 340 cm surface	1.25 1.98 2.98
Sabatini (1989)	0.40		148	0.0027	30 ft	
-----						
This work						
Recovery efficiency						
85%	0.07		26.2	0.00267	6.5 – 9 ft.	1.38
89%	0.18		67.4			1.97
95%	0.32		119.9			2.72
99%	0.42		157.3			3.26

decreasing  $K_f$ 's from surface to subsurface. Sabatini (1989) worked with the low organic carbon content soils to get a  $K_p$  value of 0.40.

The till sample in the present study was from the subsoil (6.51 – 9 ft) so it contained a very low organic carbon fraction (0.00267). The  $K_p$  value of 0.18 from this study is low, as expected by the low organic carbon fraction. This implies that atrazine is not significantly retained by soil solids at this depth and, therefore, subject to potentially significant groundwater transport.

### **Desorption**

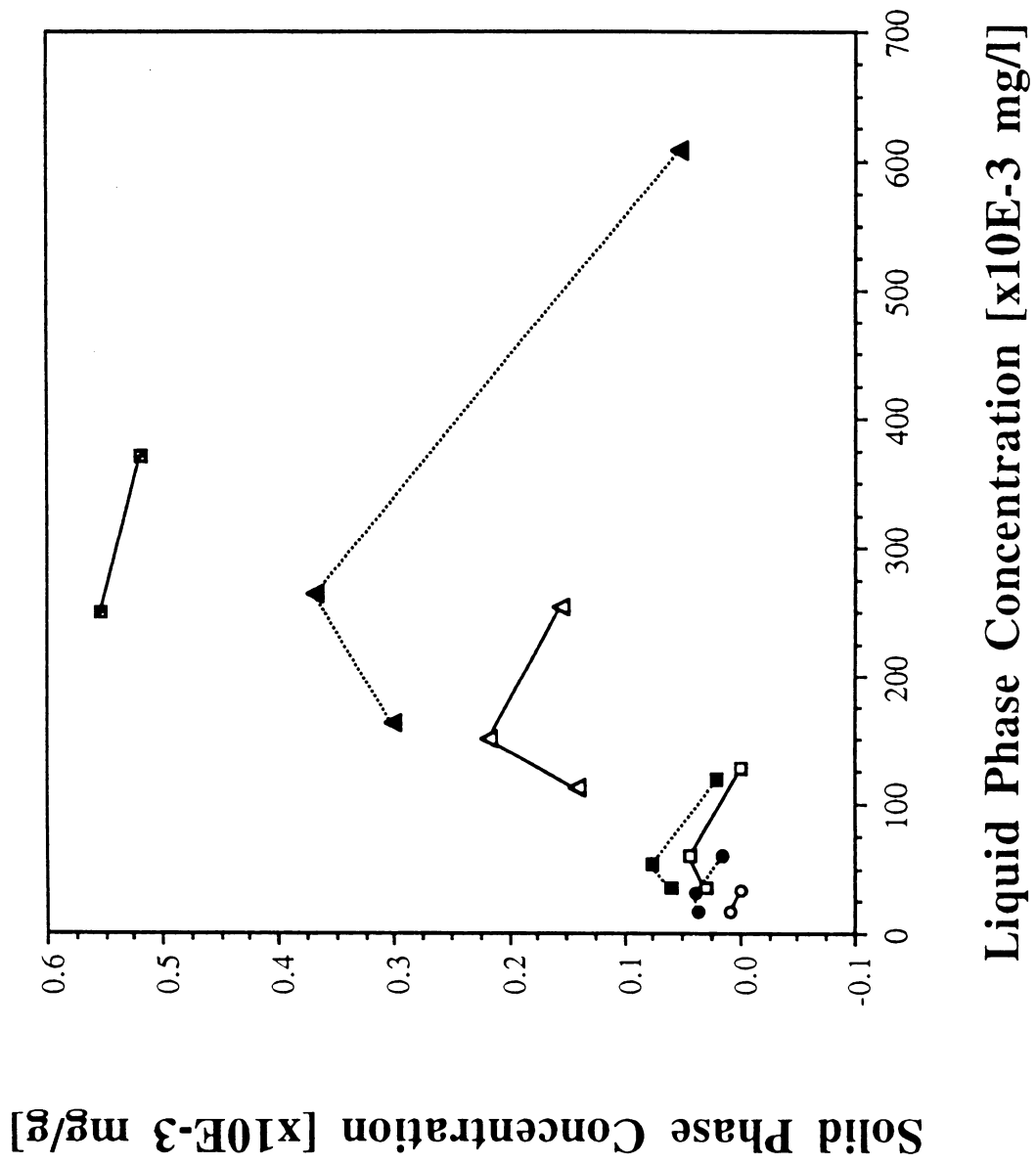
The results of the desorption isotherms are summarized in Table 6 and plotted in Figure 8. The desorption isotherms did not show any tendency of going up or going down or did not exhibit any consistent shapes. The most probable reason for the apparent increase in the amount of atrazine adsorbed on soil after dilution of the solution could be decomposition of atrazine. Lupi et al. (1988) cited the half life of atrazine in soil as 60 days. There was a discontinuance between the first desorption experiment and the second desorption experiment. In the present study, a time lag of one week could occurred between sample concentration and GC analysis and this could produce an underestimate of the aqueous concentration. The soil cakes formed during centrifuge could be considered another reason for the increased amount of adsorption in more dilute solution. It was hard to break the cakes even after 24 hours of shaking. Methods like sonication could help to break them. The reasons considered above presumably resulted in higher amounts of atrazine adsorbed. Instead of calibration of the concentration with the above, only the first desorption isotherms were plotted and factors compared with the adsorption isotherms in Figure 9. The discrepancy between the two isotherms exhibited an expected hysteresis. In general, hysteresis of atrazine is common on soil desorption

Table 6. Result of atrazine desorption isotherm

$Ce_1$	$q_1$	$Ce_2$	$q_2$	$Ce_3$	$q_3$
32.7	0.000136	16.9	0.0937	—	—
60.9	0.0165	32.1	0.0380	15.8	0.0378x
119.5	0.0208	55.2	0.0770	35.5	0.0598
126.3	-0.0112	60.9	0.0438	36.1	0.0309
253.7	0.156	150.5	0.217	111.6	0.140
371.5	0.520	250.8	0.554	—	—
608.2	0.0526	263.8	0.369	162.9	0.301

$Ce_i$ : equilibrium concentration in ith desorption isotherm ( $\mu\text{g}/\ell$ ).

$q_i$  : atrazine adsorbed in ith desorption isotherm ( $\mu\text{g}/\text{g}$ ).



**Figure 8.** Desorption isotherms for atrazine on oxidized till from Ames

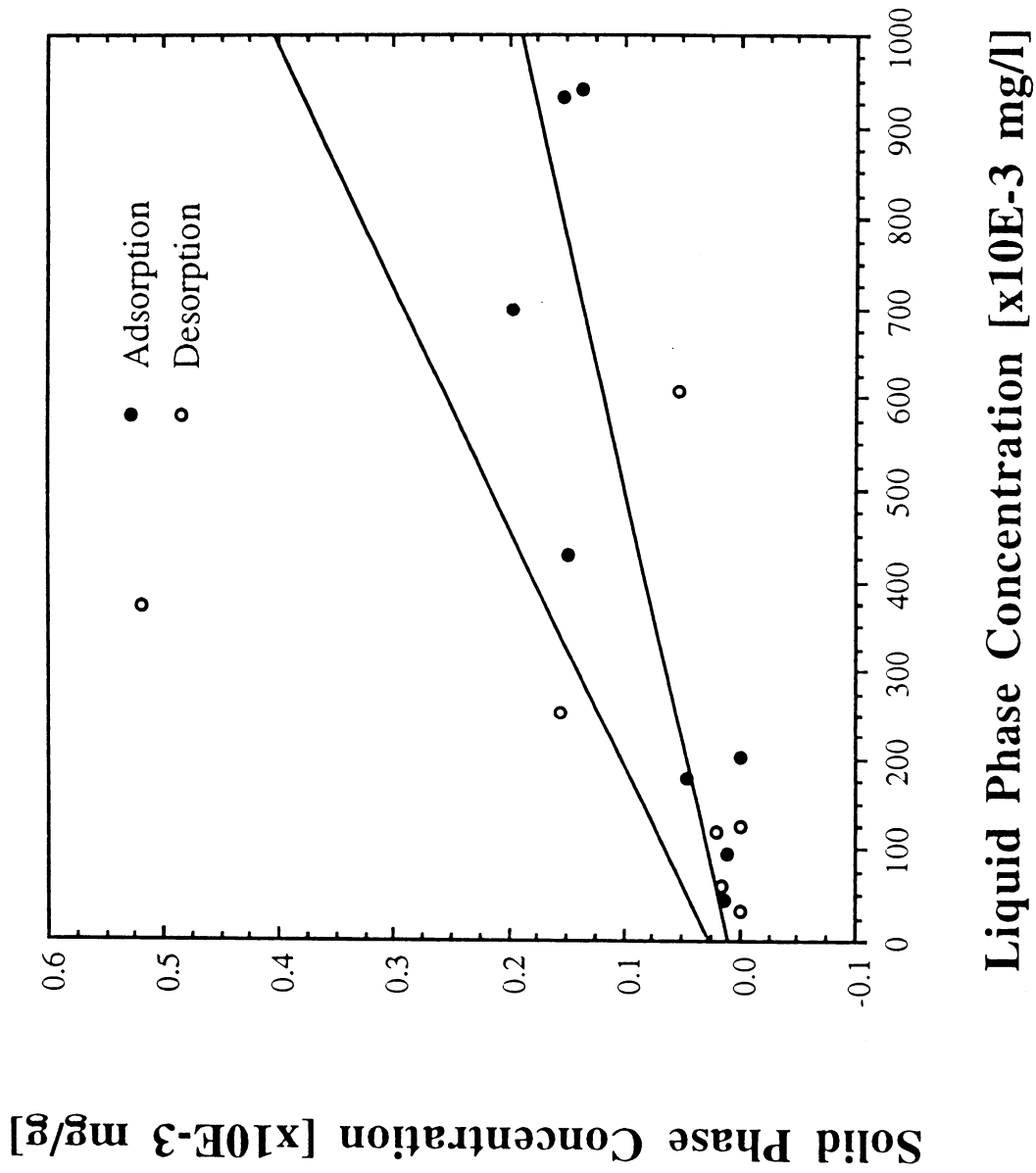


Figure 9. Adsorption isotherms and first desorption isotherms for atrazine on oxidized till from Ames

isotherms because 20% of atrazine is assumed to be changed to a nonextractable form bound to the soil (Clay et al., 1988).

### Field application

The field scale transportation of atrazine can be estimated with the results of this study and the hydrogeological parameters of the site. Darcy devised an equation experimentally explaining the relationship between the discharge,  $Q$ , and the hydraulic head gradient. Equation (12) shows this relationship in general terms:

$$Q = KA \left( \frac{dh}{d\ell} \right) \quad (12)$$

in which  $K$  is proportionality constant,  $A$  is cross-section area and  $dh/d\ell$  is the hydraulic gradient. If Equation (12) is divided by  $A$  it yields an expression for velocity of flow. That is,

$$V = \frac{Q}{A} = -K \left( \frac{dh}{d\ell} \right) \quad (13)$$

The average linear velocity is obtained from dividing the velocity by the effective porosity and is the average velocity at which water is actually moving through the pores. This velocity is represented by equation (14);

$$V_x = \frac{Q}{nA} = - \frac{Kdh}{nd\ell} \quad (14)$$

where

$V_x$  is the average linear velocity  
 $n$  is the porosity.

If the average linear velocity is divided by the retardation factor, it results in the Equation (7). As a conclusion of this study, the velocity of the solute front in Equation (7) will be roughly estimated. The hydrogeology and details of the study

site was not measured for this study. It is estimated that the hydraulic conductivity (K) ranges from  $1 \times 10^{-4}$  cm/s to  $1 \times 10^{-3}$  cm/s. The hydraulic gradient  $dh/dl$  has values between 0.02 and 0.04. The porosity is calculated from the bulk density and particle density to get 0.33. The distance atrazine can travel in one dimension is from  $1.0 \times 10^2$  cm/yr to  $2.0 \times 10^3$  cm/yr. Using retardation factor 1.97, the calculation was summarized in Table 7.

**Table 7.** Velocity of the solute front

Parameter	range		unit
	min	max	
K	$1 \times 10^{-4}$	$1 \times 10^{-3}$	cm/s
n	0.33	0.33	—
dh/d $\ell$	0.02	0.04	
Retardation factor	1.97	1.97	
$V_c^*$	$0.3 \times 10^{-5}$	$0.6 \times 10^{-4}$	cm/s
	$1.0 \times 10^2$	$2.0 \times 10^3$	cm/yr

$$*V_c = \left( \frac{K dh}{nd\ell} \right) / (\text{Retardation factor}).$$



## CONCLUSION

The adsorption isotherm of atrazine on Wisconsin age oxidized glacial till in central-Iowa was evaluated by batch study. The sorption obeyed linear isotherm. For a recovery efficiency of 89% the sorption partitioning coefficient estimate was 0.18 l/g and the retardation factor was 1.97. The desorption isotherm exhibited hysteresis.

The linear velocity of atrazine in the groundwater in the oxidized till is estimated to range from 100 cm/year to 2,000 cm/year.

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## ACKNOWLEDGEMENTS

The author wishes to thank Professor LaDon Jones for his support and guidance throughout this study and his understanding and patience with the author's special circumstances.

Thanks also to Jim Gaunt and Dave Schoeller for the help with G. C. operation. C. Tsai is thanked for his works in the material preparation.

Thanks are due to Shirley Standley for her help with typing and kind encouragement.

The author also wishes to thank her parents and parents-in-law for their love and understanding.

Finally, the author's husband and her son and daughter are deeply thanked for their love, support, and sacrifices.