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EFFECTS OF WATER QUALITY ON SOIL PROPERTIES AND HERBICIDE LEACHING

by

GAYLAN F. GODDARD, B.S.

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## CHAPTER I

### INTRODUCTION

Vast acreages of the Texas High Plains are devoted to the production of grain sorghum and related crops. Large quantities of herbicides are used in these crops to control weeds throughout the growing season. The s-triazine herbicides, of which propazine is a prominent member, are dominately used for weed control in grain sorghum and related crops. Propazine's effectiveness stems from its relative immobility in the soil, which allows it to remain localized in the zone of weed seed germination.

Movement of propazine is determined largely by the amount of water moving through the soil with the soil characteristics altering this movement. Since ionic solutions affect many chemical reactions, they might also be expected to affect propazine movement. The possibility that different water qualities and wetting and drying cycles influence the position and activity of propazine in the soil should be investigated. This information could prove useful when new sources of irrigation water are used.

Because of the potential need for such information, a herbicide leaching study was initiated to observe any trends in the leaching characteristics of propazine as affected by three water qualities and three application frequencies. Samples were taken at three depths

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inside double ring infiltrometers for herbicide extractions. Analyses were made after extraction using gas chromatography. Additional samples were taken for determinations of organic matter, aggregate stability, bulk density, and infiltration rates. These samples were taken to determine if there had been any changes in soil physical condition caused by continued use of sewage effluent. A visual study of the different flocculation rates caused by the three water qualities was also conducted.

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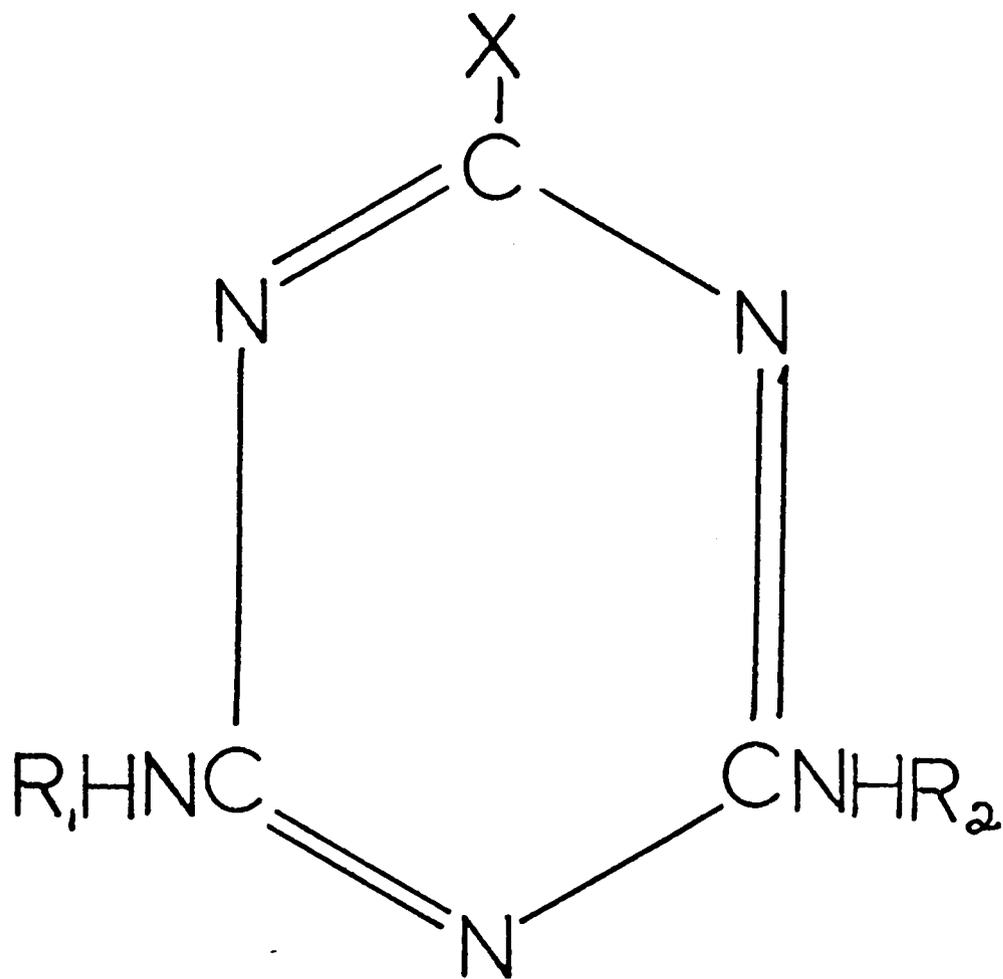
## CHAPTER II

### LITERATURE REVIEW

The retention of herbicides at the soil surface is the basis for many preemergent herbicides. The primary means by which herbicides are localized at or near the surface is adsorption by soil colloids. This may be detrimental because of reduced phytotoxicity.

The triazines as a class of herbicides are generally adsorbed on the soil particles within a few inches of the surface and are fairly resistant to further movement (Figure 1). Nearpass (24) found that 97% of the soil adsorption of simazine occurred within 30 minutes. Dawson et al. (6) found that after six years of continuous simazine application 86% to 100% of the simazine applied and recovered from the soil was found within four inches of the surface.

Propazine/2-chloro-4,6-bis (isopropyl amino)-s-triazine/7  
(Figure 1) is commonly used as a means of weed control in sorghum on the Texas High Plains. Its effectiveness as a herbicide is due, in part, to the environment to which it is subjected. Ercegovich (9) listed seven processes that enter into detoxification of herbicides. These are: 1) volatilization, 2) adsorption, 3) leaching, 4) chemical alteration, 5) photodecomposition, 6) plant removal, and 7) microbial degradation. Of these seven processes, leaching and adsorption are generally inversely related. Since there are no practical analytical methods for the detection and quantitative analysis of degradation



	X	R <sub>1</sub>	R <sub>2</sub>
<b>Chlorotriazines</b>			
Simazine	Cl	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>
Atrazine	Cl	C <sub>3</sub> H <sub>7</sub>	C <sub>2</sub> H <sub>5</sub>
Propazine	Cl	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>
<b>Methoxy triazines</b>			
Atraton	OCH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub>	C <sub>2</sub> H <sub>5</sub>
Prometon	OCH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>
<b>Methyl mercaptotriazines</b>			
Ametryne	SCH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub>	C <sub>2</sub> H <sub>5</sub>
Prometryne	SCH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>

Figure 1.--Common Triazine Herbicide Structures

products, the short time interval between treatment initiation and sampling would preclude degradation.

This review of literature will only be concerned with the environmental factors that affect leaching and adsorption. Leaching depth is dependent on the herbicide solubility and the degree of adsorption encountered in soils. Greater leaching depths are found with the more soluble herbicides and in soils with low herbicide adsorption. The relationship between solubility and leaching depth of the s-triazines is not as important as it is for other classes of herbicides. The adsorption phenomenon is a result of an attractive force between a solid surface and a liquid or vapor. This attraction is due to the fields of force originating from the solid surface and the ions or molecules of the liquid or vapor material.

Numerous papers may be found in the literature that report on the factors and mechanisms involved in leaching and adsorption. These factors may be combined into two broad categories, soil characteristics and herbicide characteristics. The important soil characteristics include organic matter, clay type and content, cation exchange capacity, pH, and soil moisture content. Herbicide characteristics include number, type, and location of the constituent groups, pH, and solubility in water.

#### Soil Characteristics

Of the two groups of factors that affect herbicide behavior, the soil exerts the main effect on leaching and adsorption. The herbicide molecules come into direct contact with the various soil particles present. Because of this, and the physical and chemical nature of the

various soil particles being different, one would expect different herbicide reactions on different soils. Organic matter generally adsorbs herbicides in larger quantities than does clay, but in soils of relatively low organic matter content, such as those found on the High Plains, the type and amount of clay is the major factor governing adsorption and leaching.

#### Organic Matter

Numerous investigators have reported on the effects of organic matter content on the adsorption, leaching, and persistence of herbicides (7, 10, 16, 18, 34, 35, 40). These studies showed organic matter content and herbicide adsorption to be correlated. Organic matter may have a high surface area that is equal to or greater than that of montmorillonite and vermiculite clays. Organic matter also exhibits a high cation exchange capacity (CEC). Bailey and White (1) give the CEC of organic matter as two to four times that of montmorillonite. Burnside et al. (4) found organic matter content and adsorption to be correlated with monuron, but atrazine adsorption was found to be inversely related. This is contrary to the results obtained from five triazines by Talbert and Fletchall (36). They found that atrazine and the general group of chloro-triazines were strongly adsorbed by organic matter with prometone and prometryne, methoxy and methylmercapto triazines respectively, not being adsorbed to as large an extent. They found the order of adsorption for the triazine herbicides to be propazine > atrazine > simazine > prometone > prometryne. Such inconsistencies may be found throughout the literature, which indicates uncontrolled factors and makes drawing conclusions difficult.

In most instances these inconsistencies are due to a failure to take into consideration other factors that may affect adsorption, such as pH, moisture content, and relative concentration of other adsorbing species. Sheets et al. (31) and Day et al. (7) described the relationship between adsorption and organic matter as the concentration of herbicide resulting in 50% growth reduction in indicator plants (ED<sub>50</sub>). Sheets found that of the four soil properties--organic matter, total clay, cation exchange capacity, and pH--organic matter was the best single predictor of the adsorption of simazine. Upchurch et al. (40) found that for each 1% increase between 1% and 40% in organic matter content an additional 0.46 pounds per acre of simazine would have to be added to maintain 50% grass control.

Not only the total content but also the type of organic matter present has been found to be important. Two studies by Bouchet (3) have shown this to be the case. In one study he found that simazine was adsorbed very strongly by humic acids, but the herbicidal activity was not lost. In the other experiment he found that free organic matter extracted from an organic sand also adsorbed and deactivated simazine. Also in accordance with these findings, McGlamery et al. (20) found that the adsorption by an acidic humic acid was approximately ten times greater than for a neutral humic acid.

### Clay

Many soils in which herbicides are used are relatively low in organic matter, yet some show considerable adsorption. The clay content of the soil has been shown to have an influence on the behavior of herbicides applied to the soil (4, 10, 14, 23, 33). The clays, as

with organic matter, have large surface areas and charges. Thus, they have large potentials for adsorption. Of the common clay types, vermiculite, montmorillonite, illite, chlorite, and kaolinite, the former two have the greater surface areas and therefore would be expected to have the highest adsorption (1).

The expanding crystal lattice has an added influence on vermiculite and montmorillonite. Illite, kaolinite, and chlorite have lower surface areas, do not possess a readily expanding lattice, and would be expected to have lower adsorption potentials. Therefore, one would expect differences in adsorption, depending upon the type and amount of clay present. Talbert and Fletchall (36, 37) generally found adsorption to increase as the clay content increased. They studied triazine herbicides on different clay types and found that only kaolinite showed no adsorption of either atrazine or simazine. The order of the degree of adsorption for the clays was montmorillonite > illite > putnam clay > kaolinite. They also found that the adsorption exhibited by illite and montmorillonite was similar despite the larger cation exchange capacity exhibited by montmorillonite. They postulated that the triazine herbicide molecule might not be able to enter into the expanded lattice of montmorillonite. Bouchet (3) found simazine to be held by montmorillonite without losing its herbicidal activity, indicating that the herbicide molecule was probably tied up at the surface rather than entering into the expanded lattice structure. Harris and Sheets (15) found that simazine was more strongly adsorbed in soils higher in clay content relative to organic matter when montmorillonite made up the major portion of the clay. Grover (12)

found that the relative clay content had no significant effect on the toxicity of simazine. This deviation from the expected result was explained by the high moisture content of the soil during the study. This would tend to indicate that adsorbed simazine was freely and readily desorbed. Lambert et al. (18) found adsorption onto clay was more important when the herbicide molecule competed more effectively with water for adsorption sites. Most investigators who study the effect of soil components on herbicide adsorption generally concede that clay content contributes a major portion to the observed adsorption (4, 10, 14, 23, 33, 41).

Bailey and White (1) stated that there are two mechanisms by which herbicides are adsorbed onto the soil--physical and chemical. Physical adsorption arises from dipole-dipole interactions, dispersion interactions, ion-dipole interactions and induced dipole interactions. Chemical adsorption arises from bond formation between the herbicide and the adsorbing soil colloid. Chemical attractions are more stable as illustrated by the high heats of adsorption. Both types of adsorption may result in several monolayers being formed, the only difference being that in chemical adsorption the first monolayer is chemically bonded with all additional layers being physically bonded. In the 2:1 type expanding clays, montmorillonite and vermiculite, another type of adsorption may take place, adsorption of the complete molecule on the inner surfaces of the expanding lattice. Weber (42) found that adsorption of the s-triazines by montmorillonite was attributed to molecular adsorption at high pH values and to a combination of cation exchange and direct association with hydrogen ions on the clay at low pH values.

Nearpass (23) also observed that the adsorption of simazine occurred by proton association. Grover (12) observed that the adsorption forces for clays was much weaker than those for organic matter, indicating a difference in adsorption mechanism. These observations were made as a result of desorption studies on the two soil constituents. He also found that the herbicide was desorbed from the clay much more easily than from the organic matter. Turner and Adams (39) found that at the end of the equilibrium time, when using either anion or cation exchange resins, they were unable to detect the presence of any cations or anions that could have been released by the resins due to an exchange process with atrazine and atratone. This would mean that the adsorption of atrazine and atratone by the resins proceeded by a process other than direct exchange. McGlamery *et al.* (21) found that adsorption onto exchange resins was primarily due to hydrogen bonding rather than ionic bonding. This conclusion was drawn since all the atrazine was removed from the resin when washed with methanol. They concluded that adsorption took place at two binding sites and involved both nucleophilic and electrophilic adsorption.

Turner and Adams (39) also found that the particular cation with which the resin was saturated had an influence on the observed adsorption. In work conducted by Price (25) the nature of the saturating ion was also shown to affect adsorption. He found that the order of exchange was  $H^+ > OH^- > Cl^- > Ca^{++} > NH_4^+ > Na^+$  for both propazine and prometryne.

Doherty and Warren (8) showed that there was a relationship between the kind of organic matter present and the observed adsorption.

They postulated that since the mechanism thought to govern adsorption onto organic matter was hydrogen bonding, this difference should show up because of the different number of hydrogen bonding groups present in various types of organic matter. Scott and Weber (30) found that prometone was adsorbed onto montmorillonite and organic matter probably through hydrogen bonding. Hydrogen bonding in the organic matter was thought to be effected through association of the prometone and the hydrogens of the carboxyl groups of the organic matter. Sullivan and Felbeck (35) found, by the use of infrared absorption techniques, that the s-triazine herbicides were adsorbed by organic matter through ionic bonding and/or hydrogen bonding to the carboxyl group of the humic acid.

The general methods by which herbicide adsorption takes place has been described. The particular mechanism that governs the type of adsorption that takes place is highly dependent upon other conditions that exist. For example, the pH of the medium will exert effects on both the adsorbent and adsorbate that will cause a change in the adsorption mechanism. Conditions that tend to alter the adsorption mechanism are moisture content, pH of soil and herbicide solution, herbicide molecule characteristics, and the nature of the saturating element. Discussions of these will appear later in the review and the processes that apply will be discussed at that point.

#### Cation Exchange Capacity

Factors in the soil that contribute a major portion to the cation exchange capacity have already been discussed in the form of organic matter and clay content. However, because a soil has a high clay content does not necessarily mean that there will be an associated high CEC. The CEC associated with a particular soil is a function of the

clay and organic matter types, as well as the quantity present. Because the CEC of a soil is closely related to the organic matter and clay content, it might be expected that a high CEC would give rise to increased adsorption (5, 7, 21, 39). As pointed out by Turner and Adams (39), Mortland and Meggitt (22), McGlamery et al. (21) and Price (25) the predominant saturating cation has an influence on the amount of herbicide adsorbed. Corbin and Upchurch (5) found that the CEC of organic matter is increased as the alkalinity of the system is increased. They state that positively charged herbicides should be more highly adsorbed in soils of high CEC values thus becoming less subject to decomposition. Day et al. (7) found that CEC was a very reliable method of predicting the adsorption observed for a particular soil. Sheets et al. (31) found in their study of five soils that highly significant correlations existed between clay content and CEC and that high correlations existed between organic matter and CEC. They, however, warned against hasty interpretations of these correlations. Factors correlated significantly with the observed adsorption will usually give significant correlations with each other.

### pH

The pH of the soil solution could have two effects on adsorption of herbicides. They are: 1) the direct influence on the soil's physical and chemical processes by affecting the charge sites and 2) the effect on the dissociation of the herbicide molecule that could lead to either increased or decreased adsorption, depending upon the soil characteristics at that particular pH. Nearpass (24) stated that the triazines as a group are very weak bases and adsorption should,

to a large extent, be determined by the soil acidity. In another study by Nearpass (23) it was determined that as the soil became more acidic, there was an increased adsorption in the upper layers. McGlamery and Slife (20) went even further by saying that adsorption was increased as the pH fell below 6.0. This was attributed to increased van der Waals forces, since it is not believed that ionic or chemical forces become important until the pH nears the  $pK_a$  of the herbicide. The  $pK_a$  values for the s-triazines are very low, ranging from 1.8 to 5.2, and according to this theory there should not be any ionic or chemical influences on adsorption until the pH becomes rather low. They also found that desorption of the herbicide molecules was pH dependent. They theorized that the observed pH effect on organic matter was due to an increased ionic bonding caused by the protonation of the amino groups on the s-triazine molecules at lower pH values. They also attributed the pH effect to differences in the saturating ion on the exchange complex. Scott and Weber (30) carried the idea of protonation of the herbicide molecule further. They stated that when the pH is equal to the  $pK_a$  of the herbicide, 50% of the molecules are in the molecular form and 50% exist as protonated species. Harris and Warren (16) found that when two pH levels existed for the same soil, atrazine adsorption was much greater at the lower pH values. They also suggested protonation of the herbicide molecule as the main influence that pH had on adsorption. Protonation is thought to impart more cationic character to the herbicide molecule. Weber et al. (43) found that s-triazine herbicides were adsorbed in greater amounts when the pH was in the vicinity of the  $pK_a$  values. Prometryne, hydroxypropazine,

and prometone have  $pK_a$  values of from 4.05 to 5.20 with maximum adsorption occurring when the soil pH is 5.20, while propazine has a  $pK_a$  of 1.85 with maximum adsorption at pH 2.00.

### Moisture

The movement of various herbicides may depend upon the amount of water initially present in and later moving through the soil. The moisture level in many of the experiments reported in the literature was usually not controlled and could lead to some deviations from the expected results for a particular soil. It has been found that frequency of water application and total amounts applied influence the leaching depth of various chemicals in the soil (2, 4, 26, 27, 28, 44). It has been shown that the frequency, rather than the total amount applied, has the greater influence on the depth of leaching. Burnside et al. (4) found that the greatest amount of leaching occurred where the total rainfall amount was lowest, but almost all of the total fell within a short period of time. Grover (12) showed that the  $ED_{50}$  of simazine increased three fold when the moisture level fell from 60% to 30%. This would tend to show that simazine was forced onto the soil colloids resulting in less uptake by plants. He went on to say that under high moisture conditions, the availability of simazine was determined by the extent of adsorption on the hydrophobic sites (organic matter). Adsorption onto the hydrophilic sites will be insignificant because of a competition with large concentrations of water molecules. Lambert et al. (18) suggests that the clay fraction (hydrophilic sites) become more important for those herbicides that exert more competition for adsorption sites than does water. Stickler et al. (34) found a

general trend toward increased adsorption when the soil was dry at the time the experiment was initiated or when there was a natural drying of the soil during the experiment.

### Herbicide Characteristics

Differences between the leaching characteristics of different classes of herbicides as well as between herbicides within the same class have been noted in the literature (5, 31, 36, 39, 42). The three most important herbicidal characteristics that may enter into predicting the adsorption characteristics in soils are: 1) the number, type, and location of the substituent groups on the herbicide molecule, 2) pH and  $pK_a$  of the herbicide, and 3) water solubility of the herbicide.

#### Number, Type, and Location of Substituent Groups

The number, type, and location of substituent groups affect the electron density which in turn affects the charge and relative strength of the charge. Corbin and Upchurch (5) state that those herbicide molecules that possess a positive charge should be adsorbed in greater amounts on soils of high CEC. Turner and Adams (39) contributed the observed differences in atrazine and atratone adsorption on cation exchange resins to the differences in electron distribution caused by the methoxy ( $-OCH_3$ ) group in the two position of atratone as compared to the chlorine ( $Cl^-$ ) of atrazine. Atratone was adsorbed in larger amounts on cation exchange resins. The methoxy group releases electrons to the ring structure which leaves a positive charge on the methoxy group, whereas chlorine withdraws electrons from the ring, making it more negative. Weber (42) and Price (25) found that the methylmercapto ( $-SCH_3$ ) triazines were adsorbed more strongly than those

containing  $-OCH_3$ ,  $OH^-$ , and  $Cl^-$  groups. Weber also found that those triazine herbicides with dialkylamino groups in the four and six positions were adsorbed more strongly than those containing only monoalkylamino groups or one of each. Talbert and Fletchall (36), however, found that the chlorotriazines were adsorbed more strongly with the relative order of adsorption being propazine > atrazine > simazine > prometone > prometryne. Sheets et al. (31) also showed this type of relationship for the triazines. It can be seen that the type of constituent in the two position and the number in the four and six positions affect the relative adsorption and phytotoxicity exhibited by herbicides.

### pH

The pH of the environment affects many biological and chemical systems, and also affects the extent of adsorption and desorption of colloidal systems. It would appear that the effect of pH on adsorption would be the degree of association or dissociation exhibited, whether of the soil or herbicide. Weber et al. (43) and Weber (42) observed that maximum adsorption was attained when the pH of the solution was near the  $pK_a$  value for the particular herbicide.

### Solubility

The solubility of the herbicide molecule should influence the distribution of the herbicide in the soil, with the more soluble being carried deeper into the soil. Rodgers (28) found that although there was a solubility effect, this was minor in comparison to the soil properties. Doherty and Warren (8) and Harris (14) found that although prometryne was nearly ten times more soluble in water than simazine, it moved much less in the soil. Harris (14) speculated that solubility

influences could be important in the movement of herbicides when high concentrations are involved.

#### Ion Effect on Herbicide Movement and Activity

There has been an ever growing tendency to combine several agricultural chemicals and apply these in one application in an effort to increase efficiency (17). There are opportunities for interaction to occur between the combined chemicals, either in solution or in the soil. Temple and Hilton (38) found that both ametryne and atrazine were more soluble in the presence of a cationic surfactant rather than an anionic or non-ionic surfactant. Frissel and Bolt (11) state that the adsorption of organic ions by clays in an aqueous environment is highly dependent upon the electrolyte concentration. The adsorption of acidic compounds onto montmorillonite was strong at very high salt levels. When looking at the effect of salt concentration on herbicide solubility, Nearpass (24) in contrast to Price (25) found that there was no change in solubility of the herbicide. He also found that there was no difference in adsorption when the predominating cation on the clay colloid was changed. He theorized from this that the importance of the predominating cation was merely to occupy adsorption sites which otherwise might be available to the herbicide.

## CHAPTER III

### METHODS AND PROCEDURES

#### HERBICIDE LEACHING

##### Field Procedure

The leaching study was conducted in conjunction with a three year sewage effluent-well water-fertilizer study on the Texas Tech University Research Farm at Pantex, Texas. Nitrogen fertilizer had been applied in this study at 0 and 180 pounds per acre. Three solutions, sewage effluent, well water and salt water were used in the leaching study. The sewage effluent and well water was obtained from the Atomic Energy Commission's Pantex Plant. The "salt water" was prepared by doubling the  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  content of well water by addition of suitable amounts of  $\text{NaCl}$ ,  $\text{MgSO}_4$  and  $\text{CaCl}_2$ . This, however, gave six times the  $\text{SO}_4^{=}$  and nine times the  $\text{Cl}^-$  content (Table I). A total of six inches of water was applied in each case with the only difference being in the number of applications. One-third of the application sites had a single 6-inch application, one-third had two treatments of three inches applied two days apart, and one-third had three treatments of two inches each applied two days apart. By using an arrangement such as this, data could be obtained that would reflect any differences in the leaching depth of propazine that might occur among any of the leaching solutions, wetting and drying cycles, continued use of sewage

Table I.--CONCENTRATION OF IONS OF INTEREST AND ESTIMATED AMOUNT OF EACH APPLIED TO THE SOIL EACH YEAR

ELEMENT	WELL WATER		SALT WATER		SEWAGE EFFLUENT	
	CONCENTRATION IN PPM	#/ACRE FOOT	CONCENTRATION IN PPM	#/ACRE FOOT	CONCENTRATION IN PPM	#/ACRE FOOT
Ca <sup>++</sup>	39	106	78	212	74.4	202.2
Mg <sup>++</sup>	21	57.1	42	114.2	31.9	86.7
Na <sup>+</sup> & K <sup>+</sup>	24	65.2	48	130.5	27.7	75.3
Cl <sup>-</sup>	12	32.6	118.5	321.1	18	48.9
SO <sub>4</sub>	14	38.1	98	266.4	----	----

effluent as an irrigation water source, fertilizer, or any of the possible interactions.

The experiment was conducted on a Pullman silty clay loam. From an earlier study on this soil by Rogers (29), the percentages of sand, silt and clay were 17.35%, 53.5%, and 29.1%, respectively. Calcium was the major exchangeable cation. The organic matter, cation exchange capacity and pH were found to be 1.10%, 20meq/100gm, and 6.5, respectively. The major clay components were found to be interstratified material, illite, and kaolinite with the interstratified material making up 50%-80% of the clay fraction. Of this interstratified material a considerable portion was that of a swelling component.

Double ring infiltrometers were used in the field leaching study. Equal water pressures in both inner and outer rings were maintained so that the water in the inner rings would move almost entirely straight down because of the buffer action imparted by the water from the outer rings. Both inner and outer rings were made in the farm shop from discarded items. The outer rings were made from 120-pound grease drums approximately 14 inches diameter. Rings to be used in the 6-inch applications were made 10 inches high and those for the 3- and 2-inch applications were made seven and six inches, respectively. The inner rings were made from 8-inch aluminum flow-line pipe with the same height as given above. One end of the aluminum pipe was beveled on the outer edge to aid in placement and to cause any soil distortion that might occur to be on the outer side. Ring placement was accomplished with the use of a  $\frac{1}{2}$ -inch plywood board. The board was placed

over the rings and a weight applied to the center thereby imparting a nearly equal force on all surfaces of the ring.

A solution of commercial propazine was prepared containing  $4.545 \times 10^{-3}$  grams/ml total material. Three ml (3 pounds active ingredient per acre) was then applied to each inner ring by mixing with approximately 25 ml of water for ease and uniformity of coverage. Water volumes corresponding to the three application amounts--six, three, and two inches--and the three water qualities--sewage effluent, well water and salt water--were applied to each of the appropriate inner rings. Well water was applied to each outer ring immediately after application to the inner ring was completed. Actual volumes applied to the outer rings were not controlled, since the only criteria was to have the same head on both rings. Close observations of the initial treatments showed that additional water in the outer rings was not necessary, since water in both rings infiltrated at approximately the same rate. Black plastic sheeting was then placed over both rings and held in place by rubber bands made from old inner tubes. The plastic sheeting was to reduce or eliminate losses by evaporation and animals and to eliminate addition by precipitation. After completion of each treatment, three sets of samples were taken within both rings with a 1-inch diameter hand sampler. Samples were taken at the 0-2, 2-4, and 4-8 inch depth increments and frozen in pint ice cream containers until time for analysis. Samples taken from the outer rings served as blanks for determination of the background and amounts of propazine initially present at each depth.

Moisture samples were taken outside the rings at the initiation of each treatment to get an indication of the initial moisture content. Sampling was accomplished by taking 1-by 8-inch core samples, which were dried and moisture contents calculated. Such a procedure gave information on the average moisture percentage throughout the leaching zone. Since the replications were completed in succession and no additional moisture was applied to the plots throughout the experiment, an indication of the effect that initial soil moisture content has on the leaching depth may be observed in the replications.

#### Analytical Procedure

Samples were kept frozen until time for analysis at which time they were pulverized in a mortar and pestle. During the time that the samples were stored they became essentially dry, containing four to five per cent moisture. Moisture samples were taken from each sample so that all calculations could be based on oven dry weight. Approximately 50 grams of each sample were weighed and placed in 300 ml flasks. Propazine extraction was conducted by adding 60 ml of reagent grade chloroform to each flask and shaking on a mechanical shaker for one hour. The flasks were then removed and filtered through Whatman No. 2 filter paper. The material was washed with two successive 30 ml portions of reagent grade chloroform and collected in a 300 ml round-bottom boiling flask. The extract was then evaporated to dryness on a flash evaporator operated at 40 degrees centigrade (C). When evaporation was complete, the residue was taken up in 5 ml of reagent grade chloroform. A portion of this 5 ml volume

was then transferred to a 4 ml glass sample vial and stored until time for analysis.

Gas-liquid chromatography was used in both qualitative and quantitative determinations of propazine contained in each sample. A Varian Aerograph, Series 1200, chromatograph equipped with a flame ionization detector and employing a five percent QF-1, 100/120, Varaport # 30 column was used for the analysis. Instrument settings throughout the complete analysis consisted of : injector temperature, 220 C; column temperature, 180 C; detector temperature, 240 C; and range,  $10^{-12}$  amps/mv. Compressed nitrogen was used as the carrier gas at a flow rate of approximately 30 ml/min. Hydrogen gas which served as fuel for the flame was supplied at approximately 25 ml/min. Air was supplied to the flame by an Oscar's Model 55 pump at a sufficient rate for proper flame operation. Output from the chromatograph was read on a Leeds and Northrup Speedomax H recorder with a chart speed of 30 inches per hour and a response time of 1.0 second.

One microliter of each sample was injected into the chromatograph for analysis. This procedure was repeated until two chromatograms with approximately the same peak heights were obtained. The peak heights were then measured in millimeters (mm) from the beginning of the peaks to the highest point. An average of the two peak heights was then recorded as the value of the relative amount of propazine contained. Standard solutions containing 20 ng/ $\mu$ l and 100 ng/ $\mu$ l were used to obtain standard curves of 0-10 ng and 10-80 ng, respectively. The curves were obtained by plotting peak height in millimeters against concentration of propazine in ng/ $\mu$ l. In this way the concentration

in 1  $\mu$ l of the soil extract could be determined, which could be converted to  $\mu$ g/gram of soil by a conversion factor,

$\frac{5(\text{concentration in ng}/\mu\text{l})}{\text{weight of oven-dry soil}}$ . Final conversion was then made to express the concentration of propazine in each segment of the ring. This was accomplished by calculating the volume of each ring segment and multiplying by an average value for the bulk density. An average value of 1.33 grams/cm<sup>3</sup> was used for the bulk density of the 0-2 and 2-4 inch segments and 1.40 grams/cm<sup>3</sup> for the 4-8 inch segment. Values obtained from this procedure were totaled and the percentage of recovered propazine contained in each segment was recorded as the final value.

Samples taken as blanks were treated like the leaching samples except the two samples taken from the same water treatment were combined and thoroughly mixed. Moisture samples were taken and approximately 50 grams were taken for extraction.

#### ADDITIONAL INVESTIGATIONS

Additional studies directed at the effect of continued use of sewage effluent on soil physical conditions were also conducted. These were infiltration rate, bulk density, organic matter, aggregate stability, and herbicide flocculation as affected by water quality.

Both infiltration rate and bulk density were determined for the same sample. These samples were taken in the soft middle (furrow not packed by tractor wheels) of the original sewage effluent-fertilizer experiment. Four samples per replicate were taken in each treatment with a standard bulk density sampler. Samples were taken at a depth

of approximately 2-4 inches. Eight thicknesses of cheese cloth was placed over the lower end of the cylinder and held in place with rubber bands. These were then taken into the lab and placed overnight (12 hours) in shallow pans filled with water to let them become saturated. Another cylinder of the same type as those used to take the samples in the field was taped onto the soil core to serve as a water reservoir and placed over a funnel situated to collect into a graduated cylinder. An inverted erlenmeyer flask fitted with a two-hole stopper and glass tubing was used to maintain a constant head in the reservoir cylinder. The movement of water through the cylinders was allowed to reach a relatively constant rate (usually 30 minutes) before readings were recorded. Collection times were variable depending on the rate at which water infiltrated the soil. Values for infiltration rates were recorded in inches per hour and were averages of two observations.

Bulk density was determined for the same samples as above. After completion of the infiltration experiment, the soil cores were oven dried, and the bulk density in  $\text{grams/cm}^3$  was then determined for each sample.

Organic matter and aggregate stability were determined on the same samples. Two series of samples were taken across the original experiment, one near the upper end and another toward the middle of the field. Samples were taken in the middle of each treatment at two locations, bed and furrow, and at two depths, 0-2 and 2-4 inches. The aggregate stability of each sample was determined by a wet sieving process using four screens of decreasing size. These were 4.76 mm,

2.0 mm, 1.0 mm, and 250 microns, respectively. A 25 gram soil sample was weighed and placed on the top screen, and the sieving process continued for 10 minutes at two strokes per second. At the end of this time the sieves were removed and the fraction of soil found on each screen was collected, dried, weighed, and percentages calculated. The final value recorded was the percentage of the original 25 gm that was recovered from the four combined sieves.

Organic matter was determined by an oxidation process using 10 ml of 0.4N chromic acid. The acid-soil was boiled for five minutes and titrated with fresh ferrous ammonium sulfate using ortho-phenanthroline as an indicator. Organic matter content was determined and recorded as percentages by weight. This method was given by Hanna (13).

A study was conducted to determine what effects the various water qualities used in the leaching study would have on the commercial herbicide. This study consisted of weighing 1.0 gram samples of the commercial herbicide into each of three test tubes of 50 ml volume. Forty milliliters of each quality of water was added to the prospective tubes and shaken to get the herbicide into suspension. These were then set aside and observed. Preliminary results of this procedure showed that the flocculation rate observed with the increased salt content tube was much faster than that observed in either the well water or sewage effluent tubes. Because of this behavior, three additional tubes were prepared and water corresponding to each of the concentrations of calcium (78ppm), sodium (48 ppm), and magnesium (42ppm) found in the salt water was prepared. This was to get an indication of which ion or ions were contributing to the flocculation

rate observed in the salt water. The tubes were shaken and mounted on a display board and pictures were taken at various time intervals to give an indication of the sedimentation rate.

## CHAPTER IV

### RESULTS AND DISCUSSION

#### PROPAZINE LEACHING

Results from the leaching portion of the study were highly variable and will be discussed separately under each variable that went into making up the study.

Results from each depth were reported as a percentage of the total amount of herbicide recovered. This was necessary because of the variability in results. This method, however, had the limitation that only results between treatment variables at the same depth could be compared at one time. The trends set in the 0-2 inch samples would generally be reversed in one or both of the lower depths. Because the results in the three depths were based on 100%, higher percentages in the upper depths would result in correspondingly lower percentages in one or both of the lower depths. Means of the data are plotted in the graphs with individual data points to show the high degree of variability.

#### Depth

Sampling depth showed significant differences in all phases of the study with all interactions being significant. As might be expected, higher concentrations of propazine were found in the surface two inches, followed by successively lower amounts at the other depths (Figure 2). An average over the entire experiment of 73% of the propazine recovered was found in the surface two inches. The 2-4 inch

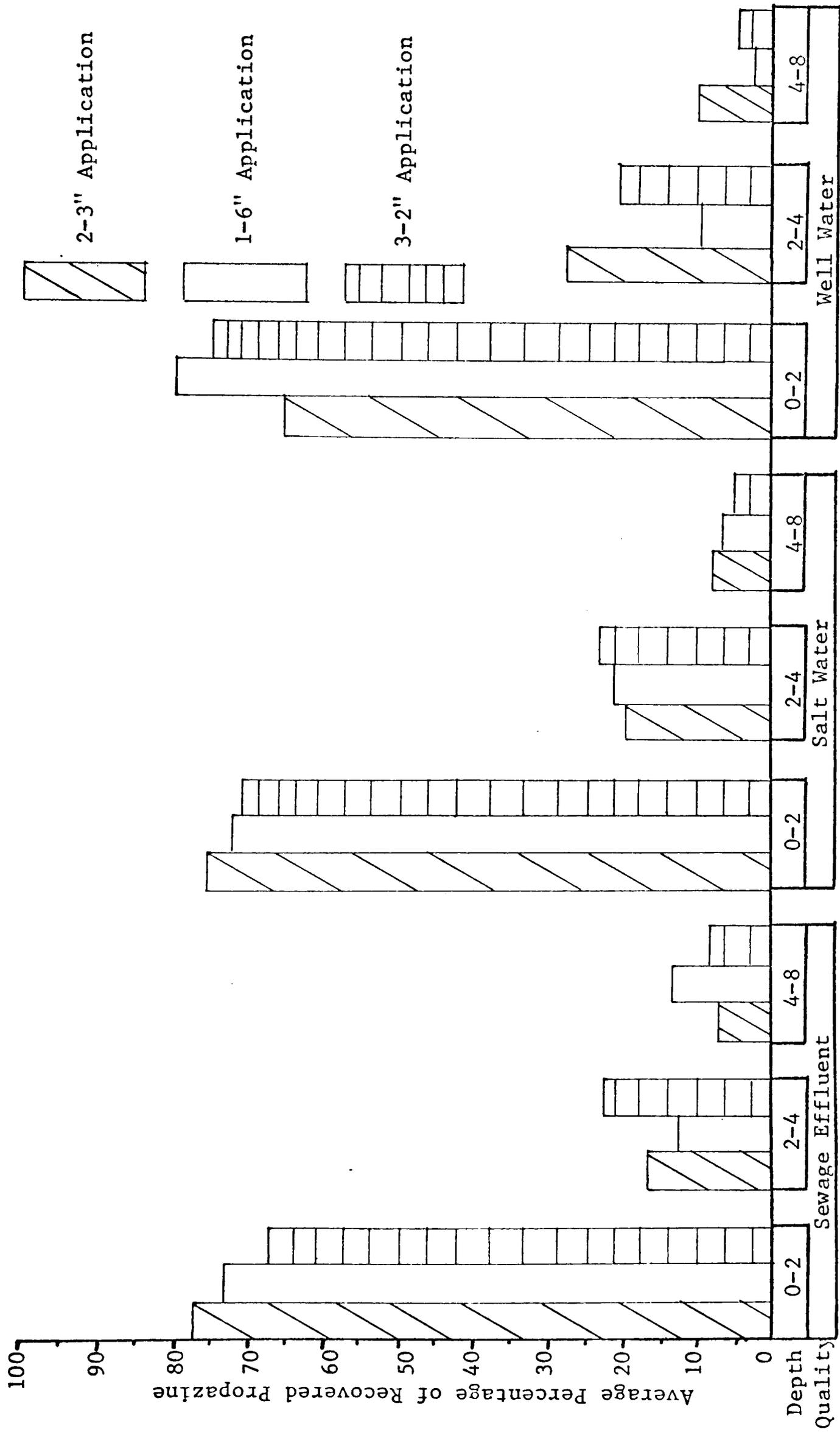


Figure 2.--Leaching Characteristics as Affected by Water Quality, Application Frequency, and Sampling Depth.

depth yielded 20% of the total amount recovered followed by 7% at the 4-8 inch depth. Values obtained from the 0-2 inch depth ranged from a high of 100% to approximately 17% of the total amount of propazine recovered, showing the high amount of variability involved in the study. This variability could have been due to soil differences in the immediate area of ring placement or poor extraction recoveries in the lab. As the study progressed in the field, the depletion of soil moisture caused the soil to crack, exposing the lower depths. Areas such as this caused excessively rapid penetration into the lower profiles and occasionally resulted in movement to the outside of the rings. Since the leaching water was applied shortly after application of the propazine, complete adsorption may not have taken place, and the rapid penetration into the profile and occasional washouts around the rings may have resulted in loss of the propazine.

Since the extraction procedure consisted only of shaking the soil with chloroform, the amount of moisture present in the soil would affect contact between the chloroform and the soil because of the immiscibility of the two liquid phases. Extractions in which there were higher moisture contents would cause the chloroform to be held away from the soil surface and extraction would progress through a partitioning of the propazine into the water and from the water to the chloroform. However, the recovery involved in this situation would also be low because of the low solubility of propazine in water. This would be important only in a few isolated samples since the majority of the samples had dried and contained only 4%-5% moisture.

### Quality of Leaching Water

As a consequence of reporting the data as percentages of the total amount recovered, comparisons can be made only between water qualities at the same depth. The three water qualities showed no significant differences at any depth with the means of the 0-2 and 2-4 inch depths for each water quality being only 2% removed from the overall means of these depths (Figure 2). This was also observed at the 4-8 inch depth. However, the overall mean percentage recovered at this depth was approximately 42% and 33% less in those leached with well water and salt water, respectively, as compared to sewage effluent.

This apparent difference may, as stated earlier, be more a result of the way the data is presented rather than actual differences due to treatment. The differences between the high and low percentages among the three water qualities were 2% and 4% at all depths. However, when working with the lower end of the scale, a change of 3%-4% made a larger difference than at the upper end. In this case there was only a decrease of 4% in the relative amounts recovered between water qualities at the 0-2 inch depth as compared to 42% in the 4-8 inch depth.

### Application Frequency

There were no significant differences among any of the three application frequencies. However, it might appear from Figure 2 that a trend in the 0-2 inch depth may have been established in the sewage effluent and salt water leached samples. The same general trend would be expected from each water quality because of their similar concentration of common ions. This behavior is not what would be

expected under true wetting and drying cycles. However, in this study, evaporation was kept low and drying was held to a minimum. It would be expected under alternate wetting and drying cycles that there would be a decrease in the wetting depth, resulting in decreased herbicide movement. Since there was no actual drying taking place, no major differences would be expected to occur.

#### Irrigation Water Type

The quality of irrigation water used for the previous three years failed to show any significant difference in the leaching behavior of propazine. If there had been any difference, it would have been due to a change in the major exchangeable cation and/or soil physical characteristics resulting from continued use of sewage effluent. Average values from the entire experiment showed increased leaching in those samples that were irrigated with well water (Figure 3). If this is a valid observation, it would appear that there have been some changes in the adsorption characteristics in those samples taken from sewage effluent irrigated plots. The changes in adsorption characteristics could be a result of several factors, each contributing a small portion to the observed results. Changes in soil physical conditions, with the exception of organic matter, would influence the rate in which water moved through the soil. In actual field conditions this would have a marked influence on the leaching characteristics of herbicides. However, with the use of infiltration rings, the same amount of water moves into the soil from each ring. Therefore, if there are actually differences observed in the use of infiltration rings, these may be

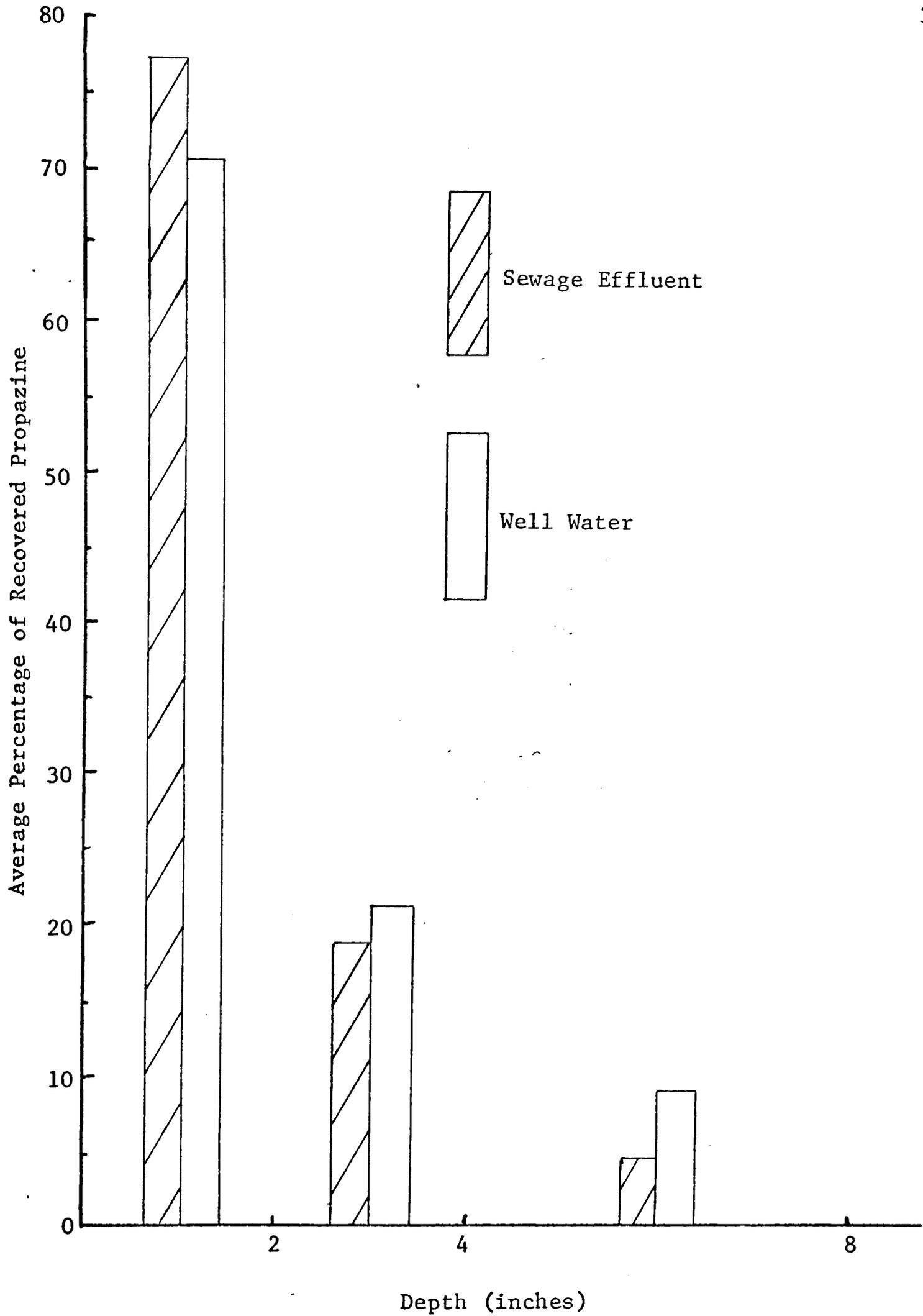


Figure 3.--Leaching Characteristics as Affected by Irrigation Water Quality and Sampling Depth.

due to changes in the amount and/or type of major exchangeable cation. The rate of water penetration could also effect any observed differences.

#### Fertilizer

There was no significant effect observed in propazine leaching as affected by fertilizer rate. However, in the field it was noticed that there was a difference in the soil moisture content with lower percentages being found in the non-fertilized plots. The plots that had been fertilized produced more foliage than those that had no fertilizer. This extra foliage seemed to shade the ground, cutting down on the moisture losses. There seemed to be slightly higher percentages of propazine retained in the upper two inches of soil samples taken from non-fertilized plots (Figure 4). Lower percentages were recovered from the lower levels of the soil profile. This difference in percentages could be due to the moisture effect and, on a long range basis, to the difference in the organic matter returned to the soil each year.

#### Soil Moisture Content

A moisture variable was not originally designed into the experiment but resulted because of the limitation on the number of infiltration rings. Only enough rings were made to complete one-half replication at any one time. The rings were moved such that each replication was completed in one week's time. Because of this arrangement, four weeks was needed to complete the field study. During this time each replication was essentially conducted under different moisture contents.

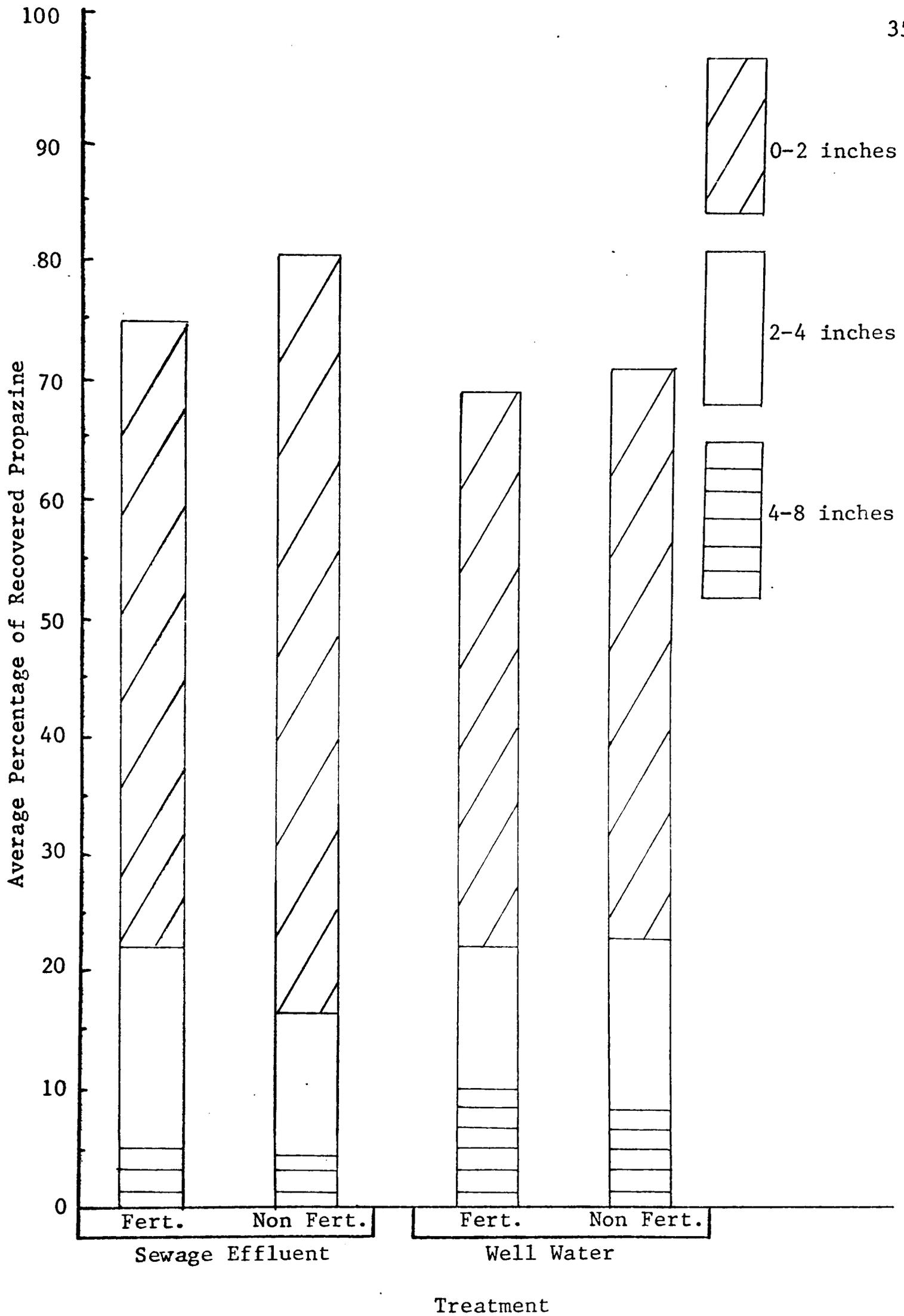


Figure 4.--Leaching Characteristics as Affected by Irrigation Water Quality and Fertilizer.

Although there were no significant differences between replications, there was a trend toward a greater percentage of that amount recovered being located in the 0-2 inch segments. Correspondingly lower amounts were recovered in the 2-4 and 4-8 inch segments (Figure 5). Of the samples taken from the 4-8 inch depth in the third replication, 72% contained a non-measurable amount of propazine, as compared to 16% and 33% for the first and second replications, respectively. The decrease in the relative amounts moved into the lower levels followed the same decrease that was observed in the moisture percentages. This might indicate that the depth of leaching was influenced by the moisture content at the time of initiation. Such results would be expected because more of the leaching solution would be tied up in the hydration of the soil particles and less would be available for movement through the soil.

#### ADDITIONAL INVESTIGATIONS

##### Infiltration Rates

Results from the infiltration study showed that there had been no significant changes in infiltration rates with the continued use of sewage effluent as a water source. This result might, however, be expected since the sewage effluent did not differ greatly in quality from the well water. As shown in Figure 6, very large variations were encountered between samples, the standard deviation being 0.61. The variations were due to different root concentrations and to cracks that developed in the soil as a result of drying. The differences in

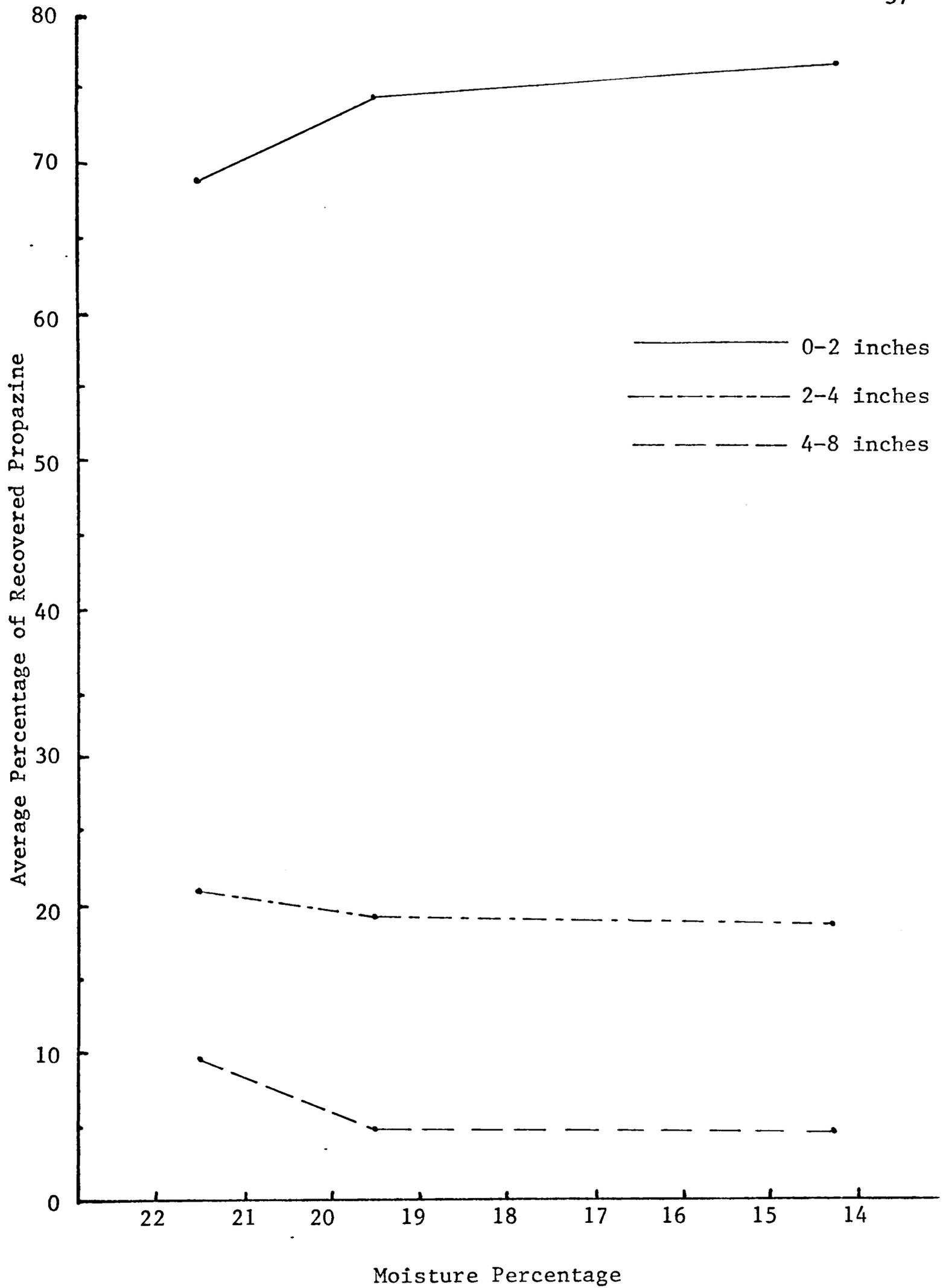


Figure 5.--Leaching Characteristics as Affected by Soil Moisture and Depth of Sampling.

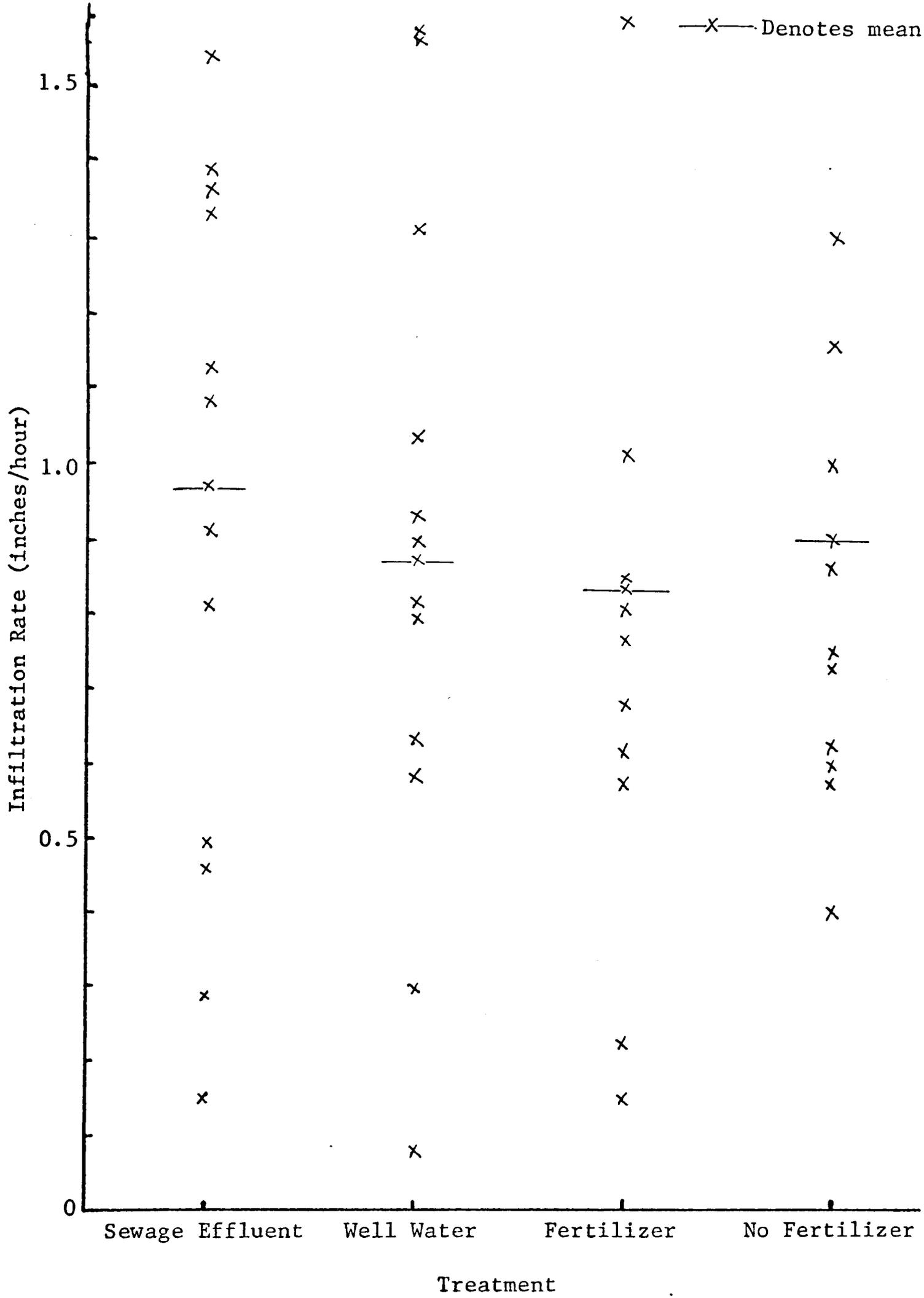


Figure 6.--Effects of Irrigation Water Quality and Fertilizer on Infiltration Rate.

infiltration rates could not be related to differences in bulk density, since these values were fairly constant, with a standard deviation 0.07 (Figure 7).

#### Bulk Density

Bulk density was not affected by the continued use of sewage effluent. The reasons used to explain the variations in infiltration rates apparently did not affect bulk density to as large an extent. In both experiments the effects of fertilizer was non-significant.

#### Organic Matter

Organic matter determinations failed to show any significance between either irrigation water type, fertilizer, location or depth at which samples were taken. However, there was a significant difference in the location in which samples were taken from the field (Figure 8). Higher organic matter values were obtained at the upper end or the end at which water was released onto the field. This difference could possibly be due to a slightly increased slope at the lower end of the field, which would cause the flow rate of water to increase and the amount of water entering the soil to decrease. Also, because of the slope, the soil was more shallow and possibly less fertile than that at the upper end of the field. These factors, alone or combined, could result in reduced plant growth. Over a period of years this would result in a lower soil organic matter content.

#### Aggregate Stability

Results of the aggregate stability study showed no significance between any of the major treatments. Samples taken from the furrow showed more stability than those taken from the bed. Also, here again,

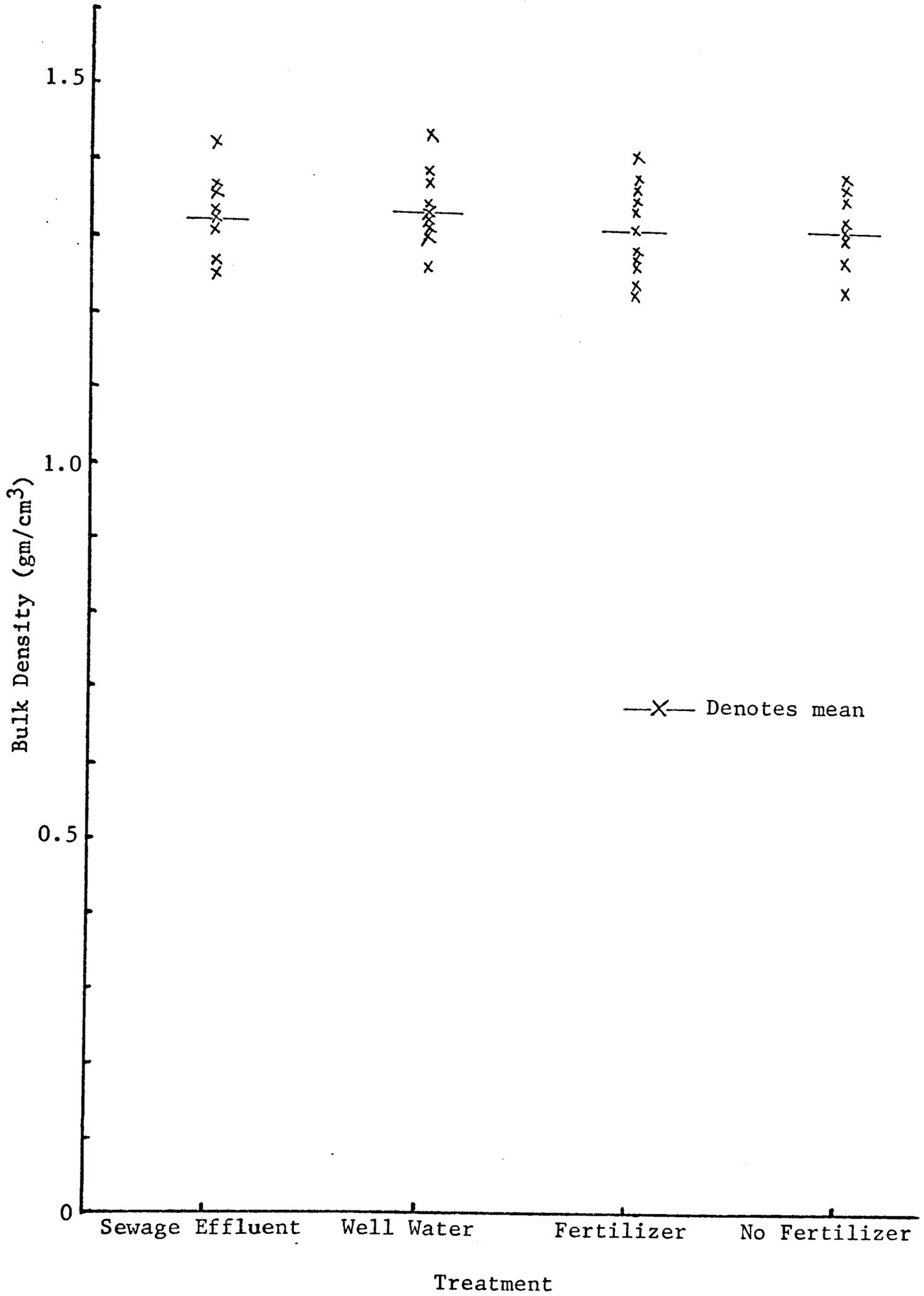


Figure 7.--Effects of Irrigation Water Quality and Fertilizer on Bulk Density.

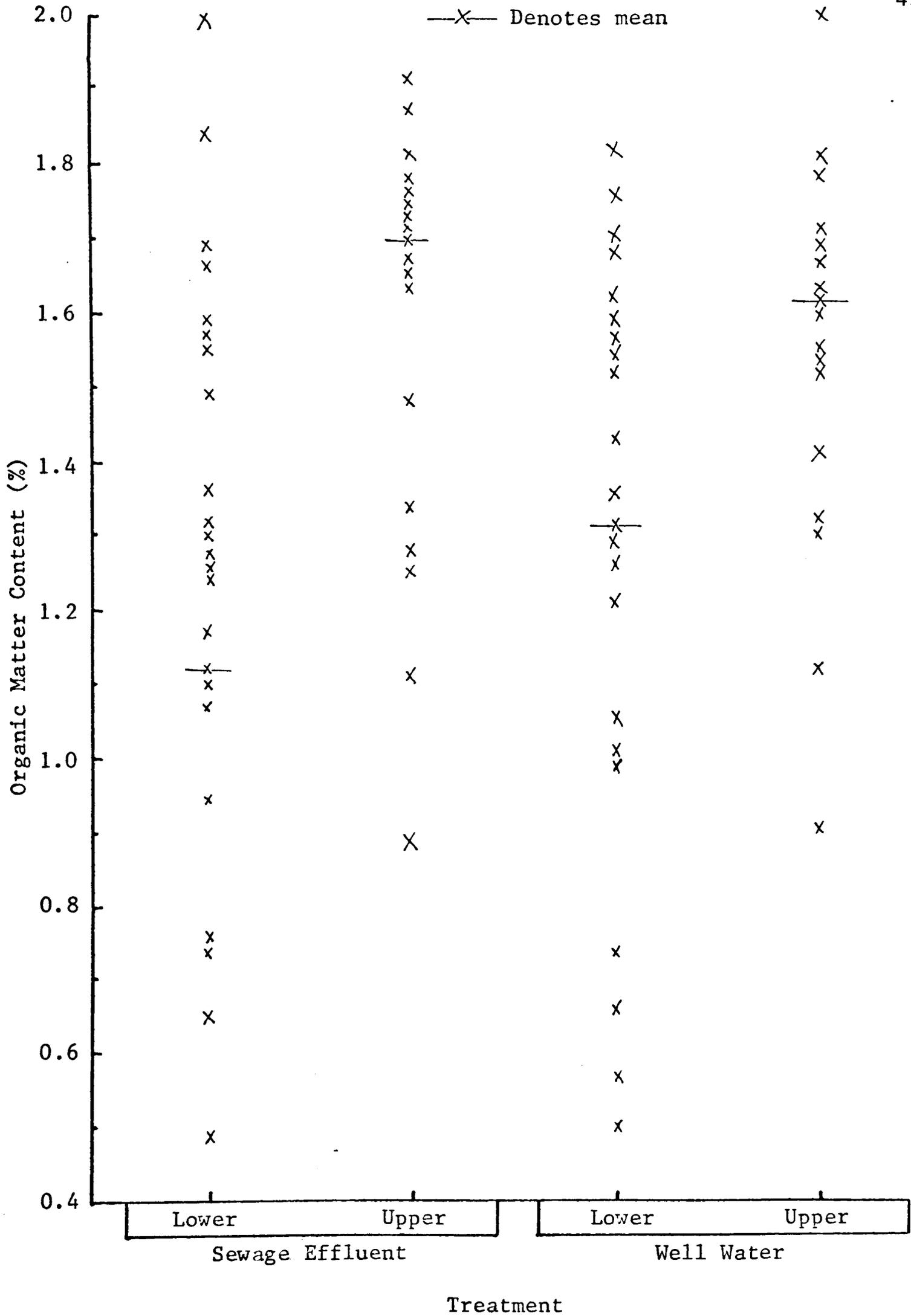


Figure 8.--Effects of Irrigation Water Quality, Field Location, and Sampling Location on Organic Matter Content.

there was a significant difference in the location in the field from which samples were taken. As with organic matter, samples from the upper end showed more stability. These effects, as well as the high degree of variability in results, may be seen in Figure 9. The standard deviation for the samples was 20.27. The fact that more of the soil from the furrow remained on the screens was probably due to mechanical compaction. Organic matter has a major influence in the role of aggregate stabilization. With this in mind, it would appear that the results obtained from the aggregate stability and organic matter portions of this study reinforce this finding. Where there was higher organic matter content, there was also more stable soil aggregates.

#### Flocculation

Results of the flocculation experiment can best be shown by comparing Figures 10 and 11. From these photographs it may be seen that the majority of the flocculation was due to the calcium in the solution with a small percentage being due to the magnesium. Wettable powder herbicides usually incorporate an Attapulgite clay as a carrier. A suspension of herbicide would be expected to react similarly to a clay suspension. Flocculation of clay particles are found to decrease in the order  $\text{Ca} > \text{H} > \text{Mg} > \text{K} > \text{Na}$ . This would appear to be a possible explanation for the observed results.

Price (25) found there to be a solubility change when the herbicide was in an ionic solution. This change was more pronounced in commercial preparations than in technical grade herbicides. Such results would tend to indicate that the herbicide molecule may be

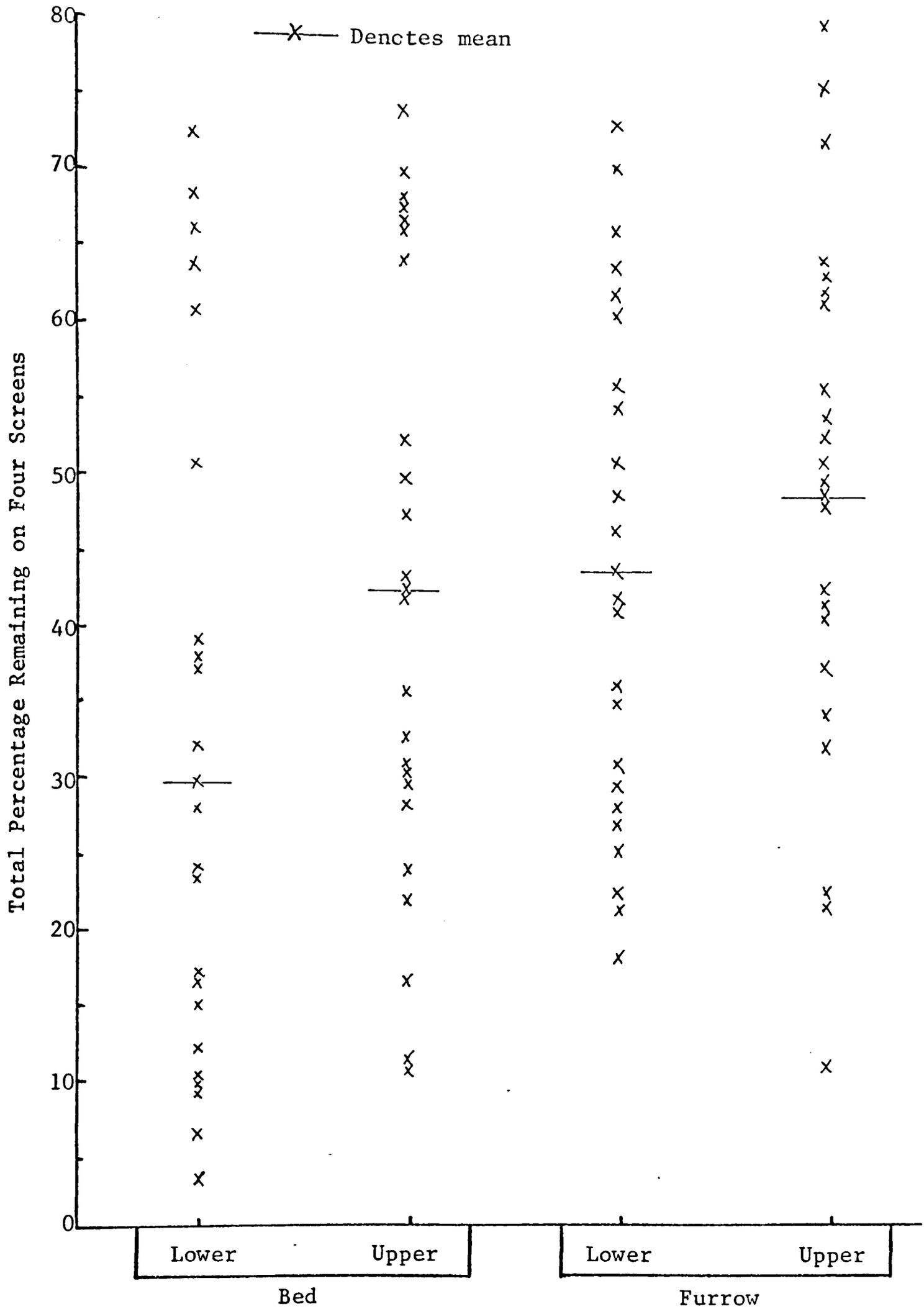


Figure 9.--Effects of Field Location and Sampling Location on Aggregate Stability.

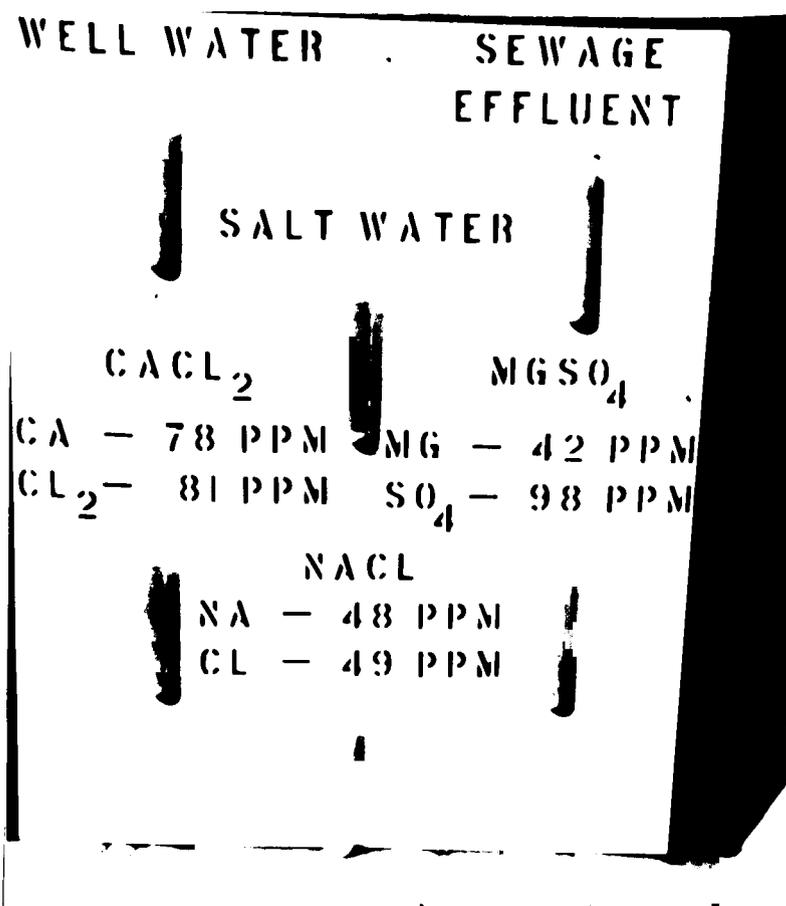


Figure 10.--Effects of Water Quality on a Propazine Solution After One Hour.

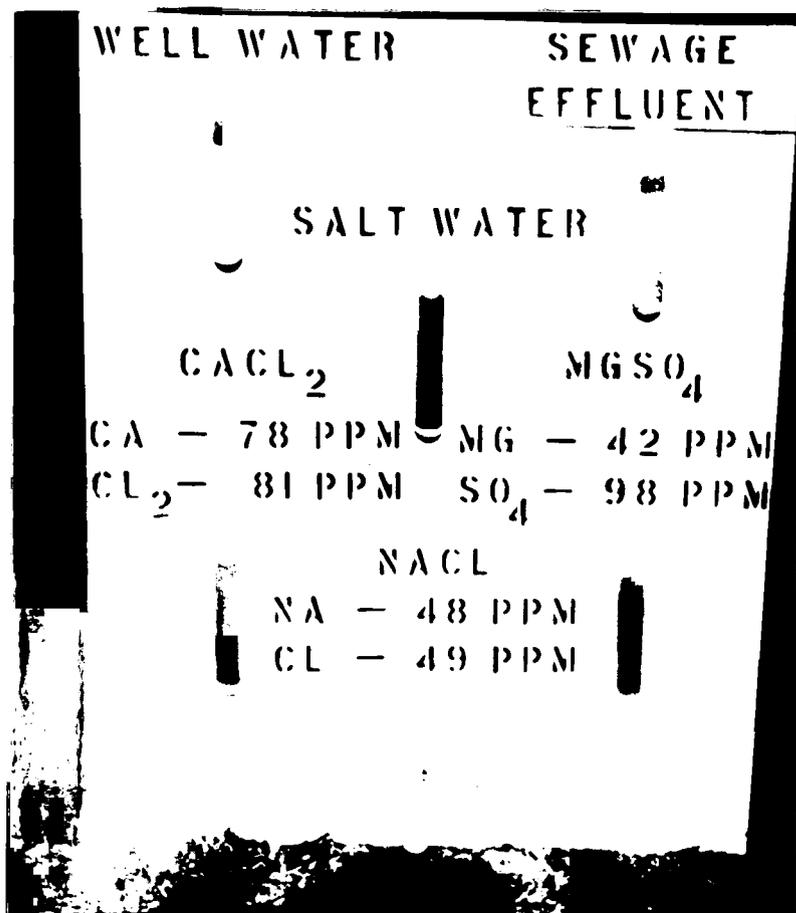


Figure 11.--Effects of Water Quality on a Propazine Solution After Seven Hours.

either adsorbed onto the clay colloid or physically trapped between precipitating particles. Considering this and results from the present study, the importance of water quality may exert itself not only in the soil but also during application. Because of the tendency of herbicides to flocculate when using water containing high salt concentrations, special care may be needed to insure adequate even mixing of the solution during application.

## CHAPTER V

### SUMMARY AND CONCLUSIONS

Leaching depth was significant in all water treatments with approximately 73% of the propazine recovered being located in the 0-2 inch segment. From this it may be concluded that propazine is not susceptible to leaching in a Pullman silty clay loam soil when a total of six inches is used as a leaching solution.

Each of the treatments, quality of leaching water, application frequency, irrigation water type, and fertilizer failed to show any statistically significant differences in the leaching characteristics of propazine. This does not, however, indicate that these variables are not capable of causing differences in leaching characteristics under other conditions.

Although initial soil moisture content was not significant, there seemed to be a correlation between amounts recovered from the lower depths and soil moisture content. As the soil moisture content decreased, the percentage of propazine recovered from the lower depths also decreased.

This work indicates that the continued use of sewage effluent did not affect the soil from the standpoint of organic matter, aggregate stability, infiltration rate, or bulk density. These findings are not surprising since the sewage effluent varied only slightly in quality from that of well water. These results cannot be used to make

inferences about sewage effluent or water qualities that are greatly different from those used in this experiment.

Herbicide suspensions made in the three water qualities showed that there was a difference in the flocculation rates caused primarily by the calcium in the solutions. On the basis of these results it would be advisable when using water high in calcium and magnesium salts to provide adequate agitation to overcome the flocculation.

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