THESIS

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SPRINKLER IRRIGATION WITH
SIMULATED SECONDARY WASTEWATER
EFFLUENT OF A TILE DRAINED SOIL
CROPPED IN BROMEGRASS AND CORN

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SPRINKER IRRIGATION WITH SIMULATED SECONDARY WASTEWATER EFFLUENT OF A TILE DRAINED SOIL CROPPED IN BROMEGRASS AND CORN

By

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ABSTRACT

SPRINKLER IRRIGATION WITH SIMULATED SECONDARY WASTEWATER EFFLUENT OF A TILE DRAINED SOIL CROPPED IN BROMEGRASS AND CORN

By

Steven Alexander Grant

A tile drained soil cropped in bromegrass and corn was irrigated with simulated secondary municipal effluent at 100 and 200 cm/year. The efficacy of additional N and K fertilization was tested. The dry matter production, grain yield and nutrient content of the crops were measured. The concentrations of nutrients were determined in the soil and in water from drainage tiles, wells and irrigation. The flow rates of water in the tile drains were monitored continuously.

Corn took up more nutrients than bromegrass, mainly because the dry matter yield of corn was greater. The tile drainage water concentration of NO_3^--N and P, however, was typically less under grass than that under corn. Crop yield and nutrient removal by corn were increased with N fertilization. Fertilization with N and K increased yield and nutrient removal by grass.

THIS THESIS IS DEDICATED

TO

ROGER NEWELL

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INTRODUCTION

As every agronomist knows, a weed is a plant growing out of place. Similarly, pollutants are chemicals which find their way into environments where they do not belong. As with weeds, man must determine the anomalousness of the chemicals which make them pollutants. Unlike weeds, man determines, consciously or not, the distribution of pollutants. With this role in determining the fate of pollutants goes both the responsibility and the ability to separate pollutants from the environment.

One form of pollution is municipal wastewater. The general problem of the disposal of municipal wastewaters is that when released to rivers and lakes they stimulate growth of aquatic flora. If the chemicals in wastewater could be used to fertilize crops rather than aquatic algae, then effective land disposal could have the additional benefit of increased crop production. This is the strategy behind land application of municipal wastes. Of course, systems in the real world do not always work as they do in theory, but if the idea is sound, a place can be found for the idea. This study is one small part in the process of bringing this promising idea to fruition.

CHAPTER I

LITERATURE REVIEW

Waste Disposal on Land

Though the application of various kinds of sewage to land is the object of current scientific investigation, the concept is hardly new. The current interest in land application of sewage is reexamination of an older, though probably less well understood, practice. Wolman (1977) cited two earlier examples of land disposal: (1) The use of night soil as fertilizer, an ancient practice that is still observed widely in Asia; (2) in nineteenth century Europe many communities disposed of their sewage by irrigation of crop land. Virtually none of these irrigation systems are in operation today. The encroachment of the expanding cities upon the disposal sites was a factor in their disappearance.

Though there has been some application of sewage waters to crop land in the United States, the spread of the method was spurred by Congress. In response to growing public concern about water pollution, the Congress enacted the 1972 Amendments to the Federal Water Pollution Control Act which set a national goal to eliminate the discharge of pollutants into navigable waters by 1985. One of the several types of pollution the Amendments addressed was municipal sewage, which is wastewater of residential and non-industrial commercial origin (Metcalf and Eddy, Inc., 1972). The Amendments required municipalities, if they were to receive federal funds for sewage treatment, to consider land application as a possibility (Jacobs, 1977).

Many of the wastewaters put on croplands are treated prior to application. There are two general objectives of wastewater treatment: (1) primary treatment is the removal of particulate matter from the wastewater; and (2) secondary treatment is the reduction of the biological oxygen demand (B.O.D.) of the organic compounds in the wastewater by microbiological consumption (Jacobs, 1977).

Untreated wastewaters may be very different from city to city. Once treated, however, these wastewaters are remarkably similar among municipalities. For example, in a survey of 809 municipal wastewater treatment plants, Gakstatter and Allum (1978) reported small standard errors of the mean concentrations of phosphorus (P) and nitrogen (N) in treated wastewaters. They identified two basic types of communities, those which attempted to restrict P pollution and those which did not. In communities which did not take measures to limit P pollution, the mean phosphate P concentration was 4.5 ppm and the total P was 6.1 ppm. In those that did, the mean concentration of phosphate P was 1.2 ppm and the mean total P concentration was 1.8 ppm. In the same study, the mean inorganic N content was 6.1 ppm, while the mean total N content was 15.0 ppm. Jacobs cited 25 ppm as a typical organic carbon (C) content in treated municipal wastewater.

Noy and Feinmesser (1977) listed possible advantages of irrigation with wastewater. Three advantages were presented: (1) treated wastewater is an inexpensive source of irrigation water; (2) it can also be a source of nutrients in addition to fertilizer; and (3) wastewater irrigation is an inexpensive final treatment of wastewater. They cite five disadvantages to this approach: (1) whereas irrigation demand is seasonal, municipal wastewater supply is continuous; (2) particulates in the wastewater may clog irrigation equipment and soil pores; (3) some soluble constituents of wastewater may be toxic to plants; (4) the range of crops which receive sewage may be limited by health regulations; and (5) the combination of the crop and soil may be unable to remove enough of the nutrients to prevent contamination of the groundwater.

Movement of Water and Ions Through Soil

Almost all non-gaseous substances that move through soil do so in solution. Hence, to understand the movement of various solutes, including possible pollutants, the flow of water in soil must be considered. In the following review, flow in water saturated soils is emphasized since most solutions to tile drainage problems assume water saturation of the soil. No doubt one motivation of this assumption is to make the problem more tractable. Unsaturated flow problems are more difficult to handle mathematically. It is doubtful that the assumption of saturated flow is much in error, since drainage tiles are inserted to reduce the height of the water table, below which the soil is saturated.

Water moves along gradients of potential energy. Taylor and Ashcroft (1972) have summarized the basics of soil water energetics. The total soil water potential energy (Ψ_t), the relative ability of the water to do work, is the sum of the water's chemical potential

(μ_w or Ψ_w) and the potential due to the water's height above a datum, the gravitational potential ($\Psi_t = \Psi_w + \Psi_z$). The chemical potential, in turn, is the sum of the matric, solute and pressure potentials ($\Psi_w = \Psi_m + \Psi_s + \Psi_p$). The matric potential (Ψ_m) is due to the forces of attraction between soil and water. Since these forces restrict the soil water, Ψ_m is usually negative, and Ψ_m becomes more negative as the water content decreases. The solute potential (Ψ_s) is that due to the presence of solutes. In general, the solute potential decreases as the concentration of solutes increases. In the absence of membranes, solutes have little effect on the total water potential and water flow because their contribution, relative to the other components of water potential, are usually small. In addition, the ability of the soil to restrict the migration of solutes is limited and the effect of solute concentration differences are lessened. The pressure potential (Ψ_p) is due to the weight of the overlying water. Unsaturated soils exert no pressure potential other than that due to atmospheric pressure. Water in soils generally is thought to move along gradients of hydraulic potential (Ψ_h), the sum of the matric, pressure and gravitational potentials ($\Psi_h = \Psi_m + \Psi_p + \Psi_z$).

The cornerstone of the theory of water flow in soil is Darcy's Law (Childs, 1957)

$$\frac{Q}{At} = -Kw \frac{\Delta\Psi_h}{\Delta s} \qquad (1)$$

where: Q = quantity of water passed across A in time t
A = area
t = time
Kw = hydraulic conductivity
s = distance

This may be rewritten as

$$V = - Kw \frac{d\Psi_h}{ds} \qquad (2)$$

where V is the darcian velocity (=Q/At) and the hydraulic gradient is written in its derivative form. Equation (2) can be broken down to its various vector components:

$$V_x = -Kw \frac{\partial\Psi_h}{\partial x}, \; V_y = -Kw \frac{\partial\Psi_h}{\partial y}, \; V_z = -Kw \frac{\partial\Psi_h}{\partial z}. \qquad (3)$$

The equation of continuity can be written as

$$\frac{d\Theta}{dt} = -(\frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z}) \qquad (4)$$

where Θ is the soil moisture content. Substituting (3) in (4) assuming that Kw is constant and that the soil is saturated ($\frac{d\Theta}{dt} = 0$), then

$$\frac{\partial^2\Psi h}{\partial x^2} + \frac{\partial^2\Psi h}{\partial y^2} + \frac{\partial^2\Psi h}{\partial z^2} = 0 \qquad (5)$$

which is Laplace's equation (Kirkham and Powers, 1972). In deriving Laplace's equation, three explicit assumptions have been made, the violation of any brings to question the applicability of the equation for flow through soils. It has been assumed that the soil in question is saturated, that the hydraulic conductivity is uniform throughout the soil and that Darcy's Law, with its associated assumptions, completely describes the flow of water in the soil. These assumptions are true of few if any soils in either the laboratory or the field. Since the equation is widely used to describe water flow through soil, the benefits must outweigh the errors inherent in its use. The advantages of using Laplace's equation are considerable. The equation is used in many other disciplines, so that a problem with the same boundary conditions as a soil problem may have already been solved. Another benefit of the wide, interdisciplinary use of Laplace's equation is that many different approaches are available to aid in its solution to a specific problem. Some solutions of flow to drains using Laplace's equation will be presented later.

In order to adequately describe the movement of solutes through soils, a formula must contain an approximation of both the movement of substances through soil without reaction and the interaction of the ion with the soil. One way to do this is to add a term representing this interaction to the differential equation describing flow through porous media. One-dimensional flow of a non-reacting solute in porous media may be represented by

$$J_s = vC - D\frac{\partial C}{\partial s}$$

where: J_s = solute flux
v = darcian velocity
C = solute concentration
D = disperson coefficient
s = distance.

Combining this equation with the equation for the conservation of mass and adding a term to represent the interaction with soil yields

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial s}\left(D\frac{\partial C}{\partial s}\right) - \frac{\partial}{\partial s}(vC) + f_n(C,\ s,\ t,\ldots), \qquad (7)$$

where f_n is some function which describes the release or removal of the solute by the soil. Assuming that both dispersion and velocity are uniform ($\frac{\partial C}{\partial s} = 0$, $\frac{\partial v}{\partial s} = 0$) equation (7) reduces to the more familiar equation:

$$\frac{\partial C}{\partial s} = D\frac{\partial^2 C}{\partial s^2} - v\frac{\partial C}{\partial s} + f_n \qquad (8)$$

Equation (8) can be solved numerically or analytically, depending upon the boundary conditions and the nature of the term f_n (Nielsen et al., 1972).

The adequate description of the term f_n is particularly elusive. Certainly the variety of soils and the numerous minerals found in soils make the job difficult. In addition, different solutes react by different mechanisms with the same soil. Most soil-solute interactions are between soil minerals and ions in solution. Two types of mechanisms will be reviewed here, non-specific site adsorption and specific site adsorption. Non-specific site adsorption is the simplest soil-ion interaction (Nye and Tinker, 1977). Three aspects of the ions and the soil materials affect this interaction. (1) The sign and amount of electrical charge carried by the soil mineral and the ion will affect the behavior of the two together. All soils and most soil minerals have a net negative charge and the retention by soil of some anions, such as the chloride ion (Cl^-) and the nitrate ion (NO_3^-) is almost nil. For this reason, in abiotic soils the two ions behave almost identically. Because Cl^- and NO_3^- move similarly in soils, the ratio of concentration of the two ions has been used to give an indication of the movement and loss of NO_3^- in the soil profile. Soils vary

considerably in their amount of charge and the amount of cations which will be adsorbed varies likewise. In general, divalent ions are more greatly attracted to the soil than are monovalent ions.
(2) The chemical potential of both the ion and the mineral surface affect adsorption. The chemical potential of either cannot be measured directly or even calculated with a great degree of certainty. Many authors have attempted to formulate a relation between ionic chemical potential and adsorption similar to the thermodynamic dissociation constant (Bolt, 1967). One such formula is

$$K_N = \frac{(N^+)^2}{N^{++}} \frac{Ao^{++}}{(Ao^+)^2} \tag{9}$$

where: N^+ = fractional amount of monovalent cations adsorbed
N^{++} = fractional amount of divalent cations adsorbed
Ao^+ = activity of monovalent cations in solution
Ao^{++} = activity of divalent cations in solution
K_N = constant.

(3) To a large degree, the rate of adsorption is limited by the rate of diffusion of the ion to the mineral surface and the geometry of the soil matrix and the size of the hydrated ion will affect the diffusion and adsorption of the ion. The ammonium ion (NH_4^+) has virtually the same hydrated radius as the potassium ion (K^+) and in sterile soil the two ions behave almost identically (Bohn et al., 1979).

Unlike the interactions of soil cations and anions such as Cl^- and NO_3^-, the sorption of P by soil is site specific. Before reviewing the details of the interactions between soil and P, I would like to begin this section with a few general notes which point out the special qualities of P both as a nutrient in the soil and a pollutant in natural waters. Unlike N, no stable gaseous forms of P exist in nature (Van Wazer, 1973). Thus water is the major carrier of P from and within the soil. Unlike K, P makes up only a fraction of a percent of the earth's crust (Van Wazer, 1958). Further, in those rocks which bear P, it is usually a minor constituent (McKelvey, 1973). Though P is capable of holding several valences, the quinquevalent is the only common form. The group of compounds known as phosphates, which is any combination of molecules with the PO_4^{-3} ion, make up nearly all natural P. Larsen (1967) in his review of the soil P literature warned his readers that the words "phosphorus", meaning the element, and "phosphate", meaning the group of compounds, are often used interchangeably.

Phosphorus is essential to life; it is a fundamental constituent of nucleic acids and ATP, which control, respectively, cellular replication and cellular energy transfer. Given P's scarcity and critical position in biologic nutrition it is not surprising that small changes in P concentration can have dramatic changes in biological productivity. Algal growth in lakes is one example of this change in activity. Schindler (1976) cited several workers who have shown a correlation between P concentration in lakes and phytoplankton abundance, ". . . regardless of the latitude, size or trophic state of water bodies studied or time period considered." The central role P can play in proliferation of aquatic plants has made it a pollutant to natural waters.

Since P loss by soil would damage the soil's ability to sustain a crop and possibly contribute to the deterioration of natural waters, how well the soil retains the nutrient is very important. Separate studies have indicated that P is conserved, that is, less P leaves than is added, whether the land is a farmland (Bargh, 1978), woodland (Bargh, 1977) or a sewage disposal site (Kardos and Hook, 1976).

Returning to the model of solute flow in soil (Equation 8) f_n, the term describing the removal from or release to the solution, of the solute, in this case P, may be affected by the other forms of P in the soil matrix. There are three forms of P associated with soil solids; mineral, organic and adsorbed.

The type of P minerals found in soil is affected by the pH and the chemical activities in solution of Ca^{+2}, Fe^{+2}, Fe^{+3} and Al^{+3}. Most mineral P in unfertilized calcareous soils is apatite (Larsen, 1967). Fertilizer amendments may cause the precipitation of dicalcium phosphate or octacalcium phosphate, but both of these are transient and will degenerate into an apatite. The effect of sewage effluent application upon soil P has hardly been investigated. Lance (1977) found that the behavior of their soil receiving effluent was consistent with an adsorption-precipitation reaction of calcium phosphates, but he did not discover the P mineral precipitated. Another group went to the trouble to discover the phosphate mineral precipitated in a soil irrigated with sewage. Van Riemsdijk et al. (1978) studied a soil receiving a sewage effluent for 50 years. Based on the soil and sewage composition, they expected to find an increase in soil calcium phosphate. They found, however, that an iron phosphate, Sterrettite, had precipitated in the soil, probably from P in the effluent.

Phosphate adsorbs to two different soil minerals. Experimental evidence indicates that phosphate may adsorb to either the surface sesquioxides (iron or aluminum oxides) of many soil minerals or on surfaces of the calcite mineral. The adsorption of P to the sesquioxides is more energetic than that to calcite (Holford and Mattingley, 1975). Surface sesquioxides are found in many crystalline and amorphous soil minerals. In a ligand exchange reaction, one of oxygens of the PO_4^{-3} ion displaces one of the hydroxyls bonded to a surface sesquioxide (Parfitt, 1978). Once this bond between the sesquioxide and the PO_4^{-3} oxygen is established, a second oxygen may bind to another sesquioxide, forming a bridging complex between the PO_4^{-3} ion and two sesquioxide atoms on the surface of the mineral (Parfitt et al., 1975). Apparently phosphate can also bind by ligand exchange with sesquioxides chelated to the soil organic matter (Parfitt, 1978).

Apparently the adsorption of phosphate on calcite surfaces is followed quickly by the precipitation of calcium phosphate crystals. Images from a scanning electron microscope showed the growth of apatite crystals on the calcite exposed to phosphate solution (Stumm and Leckie, 1970). Three steps are seen in the precipitation process. (1) With the initial adsorption of phosphate, a monolayer is formed on the calcite surface. Kuo and Lotse (1972) suggested that this adsorption was caused by the displacement by the phosphate ion of hydroxyl ions, water molecules and carbonates adosrbed on the calcite surface. (2) In time, the adsorbed phosphate tends to nucleate on the surface. (3) Following nucleation, crystallization and the formation of a calcium phosphate mineral begins.

Since both the sesquioxide and calcite adsorption sites will be found in soils, the relative abundance of each will determine the adsorption characteristics of the soil. In the development of an equation to describe phosphate adsorption of soils, Holford and Mattingly (1975) assumed the soil had two adsorption sites, one "high energy" and the other "low energy." They felt the equation accurately predicted phosphate sorption capacity of soils. The high energy site, they found, was closely correlated with extractable Fe while the low energy site was best correlated with soil calcite.

In most calcareous soils, the equilibrium concentration of phosphate will be determined by solubility of calcium phosphate minerals (Lindsay and Moreno, 1960). In most soils, if P has not been added, the calcium phosphate mineral will be an apatite. Since equilibrium is rarely achieved in soils, adsorbed P can have a greater influence upon phosphate concentration in soil solutions. Murrmann and Peech (1969) argued that the concentration of P in soils shaken for 108 hr was dependent upon adsorbed, not mineral P.

It is impossible to accurately predict the effect soil organic P has upon solution P. Surely some of the organic P is mineralized during the course of a growing season, but it is difficult to say how much, by what organisms or at what rate (Cosgrove, 1977). A few things can be said with some certainty. Not surprisingly, most of the soil organic P comes originally from plants and animals. Contributions of organic P from these two sources are rapidly assimilated by soil microorganisms, so that while virtually all organic P comes from plants and animals the fraction of soil organic P derived directly from them is quite small. Virtually all organic P in soil comes after microbial metabolism. The mineralization rate of these soil organic P compounds depends upon their water solubility, which is usually very low (Cosgrove, 1977).

The chemistry of P in solution is no less complex than it is in its mineral and organic forms. At neutral pH, solution phosphate is composed almost entirely of two ions, HPO_4^{-2} and $H_2PO_4^{-1}$ (Novozamsky and Beek, 1976). They each make up about half of the solution phosphate. The range of the concentration of phosphate-P in soil solution is typically 0.1 to 1.0 ppm (Larsen, 1967). Larsen, using stability constants tabulated by Sillen and Martell (1964), suggested that while experimental evidence was limited, some solution phosphate is present complexed with a metal ion, such as Fe^{+2}, Fe^{+3}, Ca^{+2} or Mg^{+2}.

The soil solute interactions presented thus far have been studied in soils not subject to water flow. Salt sieving, the restriction of the passage of ions in solution flowing through soils, has recently been the object of scientific interest. Salt sieving is one example of a coupled phenomena. In order to understand salt sieving, coupled phenomena should be briefly reviewed.

Energy may be dissipated by the movement of either energy or matter. The flow of energy and matter is across potential gradients. For example, these equations describe the flux of heat, a diffuser, electricity and water (Katachalsky, 1963):

$$Q = L_{11}(\Delta T/\Delta s) \qquad (10)$$

$$J_D = L_{22}(\Delta \Pi/\Delta s) \qquad (11)$$

$$I = L_{33}(\Delta E/\Delta s) \qquad (12)$$

$$J_v = L_{44}(\Delta P/\Delta s) \qquad (13)$$

where: Q = flow of heat
T = temperature
s = distance
J_D = movement of a diffuser
Π = osmotic potential
I = flow of electrical current
E = electrostatic potential
J_v = flow of water
P = hydraulic pressure
L_{nn} = constant

Equation (10) is Fourier's Law, equation (11) is Fick's Law, equation (12) is Ohm's Law and equation (13) is Darcy's Law.

For reasons of brevity that will be clear later, equations (10) - (13) will be written:

$$J_1 = L_{11}F_1$$

$$J_2 = L_{22}F_2$$

$$J_3 = L_{33}F_3$$

$$J_4 = L_{44}F_4$$

where J_n is a flux of either mass or energy and F_n is the appropriate gradient.

In 1808, Rous noted that an electrical potential applied to a pair of porous electrodes strattling a water saturated clay would induce the flow of water. His interest piqued, Rous applied a hydraulic pressure gradient across the same system and the flow of electrical current began. The combination of these two phenomena is known as electrokinetic coupling. Darcy's Law and Ohm's Law do not completely describe this sytem. The fluxes of electricity and water are coupled and can be described, using the symbols from equations (10) - (13), by:

$$J_3 = L_{33}F_3 + L_{34}F_4 \qquad (14)$$

$$J_4 = L_{43}F_3 + L_{44}F_4 \qquad (15)$$

Similarly, the Seebeck and Peltier effects demonstrate, respectively, the effects of temperature gradients on the flow of electrical current and an electrical potential gradient upon heat flow. There are many examples of coupled phenomena (Katalchatsky and Curran, 1965). The two equations (14) and (15) which describe the electrokinetic effect, can be written in matrix form:

$$J_3 = L_{33}L_{34} \quad F_3$$
$$J_4 = L_{43}L_{44} \quad F_4 \qquad (16)$$

In 1931 Lars Onsager asserted that, for a set of coupled phenomena for which the formulas are derived correctly, the matrix of L coefficients is symmetric. For the electrokinetic case above, this means that

$$L_{43} = L_{34}.$$

The validity of this approach has been demonstrated repeatedly for a variety of coupled phenomena (Miller, 1960).

As was stated earlier, salt sieving is a coupled phenomena (Groenevelt and Bolt, 1969). In the terminology of coupled phenomena, the important interactions in ion flow through soil can be represented as:

$$J_v = L_v F_v + L_{vD} F_D + L_{vE} F_E \quad (17)$$

$$J_D = L_{Dv} F_v + L_D F_D + L_{DE} F_E \quad (18)$$

$$I = L_{Ev} F_v + L_{ED} F_D + L_E F_E \quad (19)$$

where: J_v = flux of water

J_D = flux of salt relative to the flux of water

I = flux of electricity

$F_v = -(\Delta P/\Delta s)$

$F_D = -(\Delta \Pi/\Delta s)$

$F_E = (\Delta E^-/\Delta s)$

$\Delta\Pi = RT\Delta C$

P = hydraulic pressure

C = concentration

E = electrical potential

s = distance

Groenevelt et al. (1978) calculated theoretical values for the L coefficients to describe the flow of water, ions (Na^+ and Cl^-) and electrical current through a clay membrane. The flow of current was restricted unless a wire connects one face of the membrane with the other. With the wire absent, there was no current and $I = 0$. At steady state flow, ionic balance was maintained and $\Delta E^- = F_E = 0$ (Nielsen et al., 1972). Using these two conditions, we can calculate the reflection coefficient, σ, which is defined as the ratio of the flux of ions relative to that of water. For the situation where $I = F_E = 0$, the reflection coefficient is:

$$\sigma = \frac{J_D}{J_v}, \text{ and} \quad (20)$$

$$\sigma = \frac{L_{Dv} - \frac{L_{ED}}{L_{Ev}} + L_{D}}{L_{v} - \frac{L_{ED}}{L_{EV}} + L_{vD}} \qquad (21)$$

Using the values for the coefficients provided by Groenevelt et al. (1978) the value of the reflection coefficient may be determined:

$$\sigma = \frac{(6.20 \times 10^{-10}) - \frac{3.70}{.105} + 2.39 \times 10^{-8}}{(1.09 \times 10^{-10}) - \frac{3.70}{.105} + 6.20 \times 10^{-10}} = -0.64 \qquad (22)$$

This value for the reflection coefficient does not mean that the concentration of salt on the effluent side of membrane is constant, rather it means that the concentration drops as the rate of water flow increases.

If the osmotic gradient is very small or the ions under consideration are a small fraction of all ions in solution, we may assume $\Delta\Pi = F_D = 0$. In this case, the reflection coefficient is:

$$\sigma = \frac{J_D}{J_v} = \frac{L_{Dv}}{L_v} = \frac{6.20 \times 10^{-10}}{1.09 \times 10^{-10}} = 5.69 \qquad (23)$$

which indicates that the ions under consideration will increase in concentration as flow increases.

The experimental studies of salt sieving show that the effects of hydraulic pressure vary depending on experimental conditions. Kemper reviewed his own work in a collection of articles edited by Nielsen et al. (1972). Kemper forced .01 N NaCl solutions through clay membrances with hydraulic pressure gradients of 5, 10 and 17 bars. He found that the ionic concentration in the effluent decreased as the pressure increased, which is predicted qualitatively by equation (22).

He noted that in investigations where higher pressure gradients were used, the effluent ion concentrations increased rather than decreased with increasing pressures.

Such a study is one performed by Kharaka and Smalley (1976) who studied the effluent concentration in ion solutions of several salts forced by pressures ranging from 7 to 180 bars. While the flow of ions in all cases was restricted relative to the flow of water the data showed that the effluent concentration of most types of ions increased with increasing pressure. The authors argued that the increased hydraulic drag on the hydrated ions at higher flow rates explained the behavior. If this was the case, then L_{vD} was dependent upon J_v and, therefore, was dependent upon L_v, a violation of premises of the general non-equilibrium model that the coefficients are independent of the gradients (Groenevelt, 1971). Nonetheless, whether the nonequilibrium model applies in all cases or not, the theory and experimental evidence indicate that the concentration of ions passing through soil is affected by the hydraulic pressure gradient. Furthermore, whether the ionic concentration of the effluent increases or decreases depends on the nature of the soil, hydraulic gradient, ionic solution and water velocity.

Flow of Water and Ions to Tile Drains

What particular investigators attempt to understand about the flow of water through soil to tile drains depends on the purpose of the tile and the nature of the investigation. Soils are drained for two reasons: (1) If a soil has poor natural drainage, a tile system may be installed to drain the soil, lower the water table and allow better root development by the crop; and (2) a sometimes congruent purpose of tile drainage, especially in arid areas, is to facilitate salt removal from the surface of the soil. Tile drains are also studied for reasons other than those relating directly to their agricultural use. One may want to study tile drainage because the solution flowing in tiles drains may contribute to surface water pollution. Phosphorous is a potential pollutant. The concentration of P in soil solution decreases as its path length through the soil increases (Reneau and Pettry, 1976). Ryden et al. (1973) suggested that tiles may increase the concentration in surface waters because the path length through soil is shortened considerably. In addition, many researchers have used the concentration of ions in tile water as an estimate of the nature of the soil solution passing through the root zone to the groundwater. The indications from the literature on the efficacy of sampling tile water for this purpose are contrary. Ivanov et al. (1977) wrote, "Drainage water is found to reflect clearly the changes in the soil." Thomas and Barfield (1974), however, contended that tile drainage water is an unreliable indicator of NO_3^- loss by leaching. Two articles (Sharpley et al., 1977 and Karlen et al., 1976) have reported wide and apparently flow dependent changes in the concentration of P in tile water. If only because of convenience, the practice of using tile drainage water as representative of the leaching water will probably continue.

Several groups of investigators have been forced to examine limited aspects of tile flow. Since the answers for each of these groups come only with great ingenuity and effort, it is natural that knowledge about water flow to drain tiles is not comprehensive. Many questions that would seem to be important are unanswered. How much of the water which is applied finds it way to the tile? What is the path of water to the drain? What is the nature of the soil through which the water passes, saturated or unsaturated, oxidized or reduced? How do macropores affect the behavior of water flow? What are the dynamics of water flow in the tile drains following irrigation or rain? On these questions, the literature is either silent or equivocal. Most of what is known about water in tile drained fields comes from three areas: (1) field observations, (2) mathematical analysis and (3) physical analogues.

Four things have been learned from field observations. (1) In tiled soils the water table tends to be lowered. (2) The water table in these soils is curved, with the maximum height at the midpoint between two tiles and the lowest height directly above the tiles (Engelund, 1957). (3) In fact, unless the tile is malfunctioning, the water table above the tile is not higher than the top of the tile (Luthin and Haig, 1972). (4) Recently, Meek et al. (1978) analyzed the ionic and gaseous constitutents of tile water entering from various points around the circumference of the tile. They found, not surprisingly, that water entering the tile from above reflected a more aerobic environment than the water entering the tile from below.

In order to understand the possible chemical fluxes to the tile water from the soil a dynamic picture of the contributions from the various portions of the soil should be developed. Neither of the two most widely used mathematical approaches gives a comprehensive picture. Since both approaches arrive at an analytic solution which assumes an impermeable barrier below the tile, theory requires all the water entering the surface must flow out the tile, an assumption that is not always satisfied. The two theories of water flow that have found wide use are potential theory, based upon the applicability Laplace's equation, and Dupuit-Forchheimer (D-F) theory, based upon Darcy's Law and the assumptions that flow along all streamlines is horizontal and independent of distance from the water table. While solutions of the D-F theory of water flow to tiles have been capable of predicting transient flow, the approach was incapable of describing realistically the path of water, the streamlines, to tile drains (Kirkham and Powers, 1972). Solutions based upon potential theory suffer from an opposite setback. While the streamlines are correct, the approach has been incapable of analytically predicting transient behavior.

Transient behavior in water flow to tiles has been approximated using potential theory by a series of steady states. This approach has been found acceptable by Childs (1947), Kirkham (1964) and Van Schilfgaarde (1974). Using a Fourier expansion of Laplace's equation, Kirkham (1958) was able to solve analytically the streamline and hydraulic potential distribution for a tile drained soil. A drawing of this distribution is presented in Figure 1. In a later article, Kirkham (1964) assumed that the fall of the water table after the cessation of water application was identical to a series of water

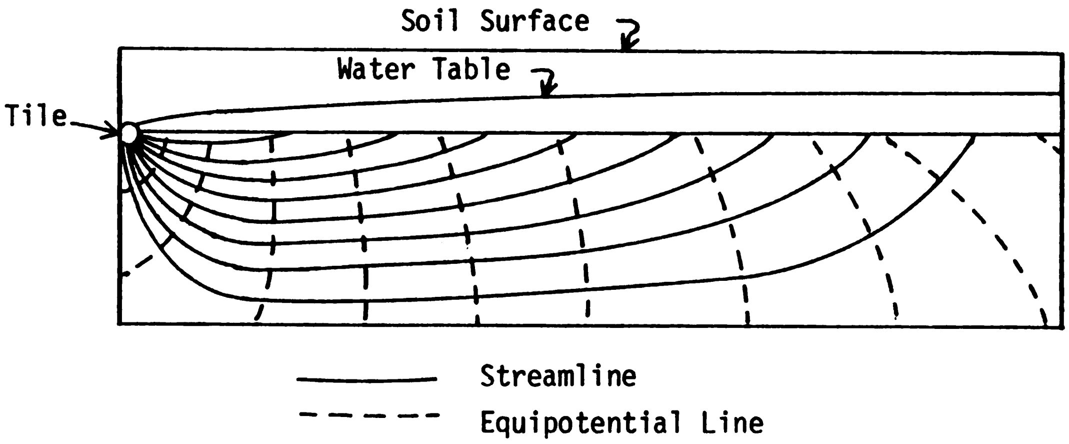

Figure 1. Theoretical distribution of streamlines and equipotential lines in a tile drained soil (After Kirkham, 1956).

table heights associated with ever decreasing water application rates. The results of this method indicate that water flow with streamlines originating furthest from the tile always make up the greatest proportion of the tile flow. Because the height of the water table near the tile is lower, the proportion of water flow from streamlines originating nearest the tile, though starting high, quickly dissipate.

As with Kirkham, Childs, in an earlier article (1947), assumed that a series of steady state solutions would simulate the falling water table. As was discussed in the review of coupled phenomena, Ohm's Law, which describes the flow of electricity, has exactly the same mathematical form as Darcy's Law, which describes the flow of fluids through porous media. Using this fact, Childs (1943) constructed several electrical analogues of cross sections of tile drained soils. This method gave the first precise description of the flow net of streamlines and equipotential lines about a tile drain. Because Childs assumed a much higher water table initially, his results were contrary to Kirkham's. Childs found that the first flow of water to the tile after the cessation of water application was dominated by contributions of streamlines originating close to the tile.

In general, laboratory models of tile drainage systems have not been used to understand transient behavior of water flow to tile drains. Rather, the method has been used to evaluate various materials and methods which would be difficult to study in the field. A recent article by Luthin and Haig (1972), for example, examined the effect of tile diameter, the placement of holes in the tile and water table height upon tile flow.

Three articles have found peculiarities in the concentrations of ions in water flowing from tile drains. Thomas and Barfield (1974) have suggested that the contribution of NO_3^--N from a tile drain to a drainage ditch was many times greater than that from any other source in a Kentucky field. They concluded that estimate of leachate loads based upon the concentration of NO_3^- in tile drains could be greatly in error. Two articles have shown variations of the P concentration in tile drainage water. Both Sharpley et al. (1977) and Karlen et al. (1976) observed that P concentration water from tile drains increased with flow rate. Each presented a different explanation. Sharpley et al. stated that most of the P in the water was associated with particulate matter and implied the increase in P concentration was due to increased suspension of particulate matter in the tile drainage water with increased flow. Karlen et al., citing great heterogeneity in the soil at the experimental site, suggested that faster flow of water through sand smears in the soil profile caused the peaks in the P concentration.

Thomas and Barfield argued that denitrification was less in water flowing to tile drains because the soil in the region of the tile was aerobic. At two times in the 1972 season, Thomas and Barfield measured the flow rate and NO_3^- concentration in tile drains and a ditch draining the experimental site. The authors observed only two sources of water flowing to the ditch from the field, subsurface drainage and tile drainage. The NO_3^- concentration and volume of subsurface drainage water was calculated from the difference of both the NO_3^- and water loads from the ditch and the tile drains. Their results seem to show that while the water from the tile was a minor constituent of water flowing in the ditch, most of the NO_3^- in the tile drainage was many times greater than the NO_3^- concentration measured in the ditch and that calculated for the subsurface flow water. The results suggested to the authors that water flowed to the tile drains through portions of the soil that were mainly aerobic. The NO_3^- in this water was not lost by denitrification. Water flowing to the drainage ditch by subsurface drainage entirely through the soil passed through a more anaerobic environment conducive to denitrification.

Thomas and Barfield attempted to show the uncertainty of relying on tile concentrations of NO_3^- for estimates of leachate concentration. Results by other authors question whether changes in denitrification rates were the cause of the differences in the NO_3^- concentrations. (1) Almost certainly much of the NO_3^- flowing in the ditch was removed from solution. A report on NO_3^- pollution by the National Research Council (1978) stated that unlike NO_3^- in groundwater, NO_3^- in surface waters is rapidly consumed by aquatic plants. (2) The field measurements by Meek et al. (1978) showed that much of water flowing into the tile comes from reduced portions of the soil. (3) Denitrification has been shown in aerobic soils in both the field and the laboratory (Greenwood, 1961; Allison, 1966). (4) As noted by Thomas and Barfield, anaerobiosis is only one of the environmental determinants of microbial denitrification. The other main determinant is the supply of that organic C which can be metabolized by the denitrifying bacteria. Most of this C is located close to the soil surface. The concentration of organic C at the depth of a typical tile drain is practically nil. Thus, while Thomas and Barfield have suggested disquieting inconsistencies in the concentration of NO_3^- in tile drainage water, they were unable to adequately demonstrate the behavior or conclusively explain its cause.

Two groups of investigators have found anomolies in the tile drainage water P concentration. The soil at the experimental site used by Karlen et al. (1976) was very heterogenous. The concentration of P in the tile drainage water varied greatly. A figure presented by the authors showed a maximum of 0.75 ppm P and a minimum of 0.13 ppm during a 100 hour period. The maximum concentration was roughly coincident with maximum flow following an irrigation. The authors hypothesized the existence of sand smears in the soil profile. Some of the irrigation water, they argued, flowed rapidly through the smears. They assumed that little or none of the solution P was adsorbed to the soil in the smear. The P peak was caused, they suggested, by the rapid and unencumbered flow of P to the tile.

Sharpley et al. (1977) observed roughly the same behavior at a New Zealand experimental site. The soil they used was much different from the one used by Karlen and his coworkers. Because it often indicates the relative abundance of sesquioxides and calcite, pH is an important indicator of the amount and type of P adsorption in soils. The soil at the site used by Karlen et al., a Conover loam, was derived from calcareous till and had a neutral to alkaline pH. The pH of the soil used by Sharpley et al., a Tokomaru silt loam, was low, normally between 5.2 and 5.7. It is likely that the two soils had quite different P adsorption properties. Whereas, the Conover soil used by Karlen et al. was very heterogenous, the Tokomaru silt loam, which was derived from a coarse loess was very homogenous (During, 1972). In fact the group in New Zealand reported that the entire experimental area, covering 112 ha, was all the same series.

Sharpley et al. examined the behavior of P in the tile in more detail than did Karlen and his coworkers. The object of the New Zealand study was to estimate how frequently an investigator should sample the water in streams, subsurface drainage, tile drains and surface runoff in order to get an accurate estimate of P loading. Three types of P from all these sources were monitored: dissolved inorganic P (DIP), total dissolved P (TDP) and total P (TP). DIP and TDP were that P remaining after a sample was passed through a 0.45 μm filter. Particulate P was estimated by the difference between TP and TDP.

The results presented in graphs in the article by Sharpley et al. showed that TP varied with flow in streams, tile drains and surface runoff. The difference between the maximum and the minimum concentration of TP was greatest in the tile drainage water. The behavior of the TP concentration during a flow event was similar in water sampled from tile drains and streams, where the highest concentration of TP was at or near the maximum flow. Based on these results, Sharpley et al. argued that during maximum flow turbulence would also be highest. Turbulent flow would bring particulate matter into suspension. Much of the P and thus much of the increase in P concentration during rising flow rates, they argued, must be associated with newly suspended particulate material. The behavior TP in streams and the tile drains was not identical. Unlike the TP concentration in water from the stream, the peak TP concentration and the peak water flow in the tile drains did not coincide. The peak TP (and DIP) concentration in the tile drainage water led the peak flow rate consistently by about 1.5 hours.

Nitrogen Transformations in Soil

Five transformations in the N cycle may have an effect upon N applied to croplands in sewage: (1) immobilization of inorganic N, (2) mineralization of organic N, (3) volatilization of ammonia (NH_3), (4) nitrification of NH_4^+ to NO_3^- and (5) denitrification of NO_3^-. Volatilization of NH_3 from water, and by implication from the soil solution, is controlled by pH. The ammonium (NH_4^+) stays in solution. The loss of one proton from this ion forms NH_3 which is readily volatilized. The conversion of NH_4^+ to NH_3 is fostered by alkaline conditions. The rate and absolute amount of loss are increased by increases in temperature. The collodial property of soil limits volatilization of NH_3. Losses by NH_3 volatilization have been reported from the water above rice paddy soils, from manures in feed lots (Lauer et al., 1976), from sewage in sludge ammended soils (King, 1973) and from plant surfaces (Denmead et al., 1974). Once the NH_3 source is incorporated into the soil, losses are lessened. There is little possibility that NH_3 volatilization losses are large from sewage irrigated soils once the wastewater has entered the soil.

Mineralization is the conversion of organic N to inorganic forms, usually NH_4^+. The organisms which mineralize organic N are so numerous and diverse that the process probably occurs under virtually all environmental conditions. By far the largest portion of soil N is the organic fraction, indicating that in most soils the process is slow. For reasons which are not clear, mineralization of organic N is increased by alternate wetting and drying. The addition of inorganic N also accelerates the breakdown of humus, probably by stimulating microbial activity in general (Alexander, 1977). Apparently organic N added to soil as sewage is rapidly mineralized. Both Lance and Whisler (1972) and Broadbent et al. (1977) found that virtually all organic N in wastewater applied to soil columns was mineralized.

In many secondary wastewaters, organic N is a minor constituent. For example, 4% of the total N in wastewater used in a study by Lance and Whisler (1972) was organic. Wastewater application may spur mineralization of soil organic N. For example, using ^{15}N Broadbent et al. (1977) found that as much as half of the NO_3^- leaving a soil column continuously amended with simulated wastewater was derived from soil organic N. Apparently this additional NO_3^--N came from organic N which had been mineralized, then nitrified.

Immobilization of soil inorganic N is the opposite of mineralization. Immobilization is the assimilation of inorganic N into organic molecules as constituents of organisms. The balance in soil between mineralization and immobilization is affected by the ratio of organic C to organic N. Anything which increases the ratio, such as the addition of organic C, tends to spur N immobilization while a decrease in the ratio may bring about an increase in mineralization

(Alexander, 1977).

Nitrification, the conversion of NH_4^+ to NO_3^-, is also thought to be complete in soils amended with secondary wastewaters (Broadbent et al., 1977). Nitrification is an aerobic process. Lance and Whisler (1972) attributed the success of the process to the ability of the soil to adsorb NH_4^+ during saturation. When a soil was irrigated with wastewater and soil was saturated, the NH_4^+ was retained by the soil exchange complex. When it drained, the soil became aerobic again, and the sorbed NH_4^+ was nitrified.

Denitrification is the reduction of NO_3^- to gaseous N. Bacteria are the only organisms which have been shown to have the capacity to denitrify. Fifteen genera of bacteria are capable of denitrification (Payne, 1973). The bacteria are obligate aerobes which use NO_3^- as an oxidant when O_2 is unavailable. Most of these bacteria are heterotrophs which use NO_3^- as the terminal acceptor of electrons donated by substrate organic C. Nitrate N is not assimilated in the denitrification pathway. Denitrifying bacteria can be found in abundance in most soils. The extent of denitrification in soils is to a large degree dependent on the soil environment. In laboratory experiments denitrification is favored by the presence of organic C, the absence of O_2, saturation by water, elevated temperatures and a neutral to slightly alkaline pH (Nommik, 1956). Water saturation stimulates denitrification because it severely restricts the diffusion of O_2 in the soil. The O_2 concentration in saturated soils is rapidly depleted by biological respiration and oxidation of reductants (Howeler and Bouldin, 1971).

Anoxia, the absence of O_2, does not have to be complete in soils for denitrification to occur. In a review of N balance studies in soils typically below field capacity, Allison (1966) found unaccounted losses which usually amounted to about 15% of applied N. He attributed much of these losses to denitrification. The energetics of electron transfer in the oxidation of organic C may help to explain why denitrification can proceed in aerobic soils. The energy yields from the transfer of one mole of electrons from organic C to the four major inorganic oxidants are: to O_2, 26.5 kcal; to NO_3^-, 18 kcal; to SO_4^{-2}, 3.4 kcal; to CO_2, 2.4 kcal (Payne, 1973). By this approach the energy yield of electron transfer to NO_3^- is 68% as energetic as that to O_2. Another explanation for denitrification in aerobic soils has been developed separately by Currie (1961) and Greenwood (1961). They suggested that the restriction of O_2 diffusion in soil aggregates would create anoxic sites in the center of the aggregates where denitrification could occur. The diffusion of O_2 from the surface through the soil is a factor in denitrification. Since O_2 moves primarily by diffusion in soil, the concentration is lower further from the surface. In a simple experiment Jones (1974) measured the NO_3^- lost after 28 days at two depths in a soil maintained at 90% saturation. The soil section between the surface and 7.5 cm depth lost no NO_3^-, while the section between 7.5 and 17.5 cm lost between 73% and 83% of the NO_3^- present at the beginning of the experiment.

While anoxia may not restrict the ability of denitrifiers to metabolize organic C substrate, anoxia can restrict the capacity of microorganisms to transform complex organic compounds to a form which denitrifers can readily use. Denitrifiers, like most heterotrophs, rapidly metabolize simple carbohydrates. "Readily mineralizable" organic C is that C quickly oxidized by aerobic heterotrophs. The denitrification capacity of soils is strongly correlated with both "glucose equivalent" organic C and "readily mineralizable" organic C (Burford and Bremner, 1975). Some bonds in organic C can only be broken under aerobic conditions (Focht and Verstraete, 1977). Perhaps what limits denitrification is not organic C but forms of organic C that denitrifiers can use under continuously anoxic conditions.

Denitrification is enhanced by the same things which increase the amounts of simple carbohydrates in soil. A simple though inelegant method to increase the carbohydrate concentration and denitrification is to add glucose or methanol to the soil (Kohl et al., 1976; Lance et al., 1976). Cycles of wetting and drying can also increase denitrification. Reddy and Patrick (1975) found that the most frequent cycle of wetting and drying removed the greatest amount of nitrogen by denitrification. Apparently, this procedure allows enough aeration to break down organic C to a more mineralizable form while preventing the O_2 content from rising high enough to inhibit denitrification. The rhizosphere, that volume of soil immediately adjacent to the plant root, has higher denitrification rates than the bulk soil. Woldendorp (1962), the first author to investigate the phenomena in detail, concluded that the stimulation of denitrification was due to the consumption of O_2 around the root and the exudation of carbohydrates by the root. Studies have shown considerable organic C exuded by roots. Barber and Martin (1976) measured the CO_2 evolved from planted pots containing sterile and non-sterile soil. The difference in CO_2 evolved was taken to be due to the root exudation of organic C. The results indicated that root exudation was equal to 18-25% of the total dry matter accumulation by the plant. Using a different method, Johnen and Sauerbeck (1977) estimated the annual production of carbonaceous root exudate. They reported that in one year a hectare of wheat would exudate some 650,000 kg of organic C. Palpably, the addition of large quantities of organic C would stimulate heterotrophic microbial activity, including denitrification if no other factor is limiting.

Many investigators have attempted to elicit the relationship between plants and denitrification. The results have not been consistent due, perhaps, to a lack of uniformity both in the plants studied and in the methods used to assay denitrification. Garcia (1975), measuring the activity of N_2O reductase in pot soils, both planted in rice and not planted, found greater denitrification in the planted soils. He concluded the enhancement was due to the development of an anaerobic zone about the roots, the presence of root exudates and the presence of larger numbers of denitrifiers in the rhizosphere. A study by Brar (1972) with excised roots found that denitrification measured by N gas evolution was greater with than without roots. He concluded that denitrification was enhanced in the rhizosphere because the concentration of O_2 was lowered near the root. Volz et al. (1976) studied two plots, one planted in barley (Hordeum vulgare L.), the other fallow. The plots were irrigated with water containing 100 ppm NO_3^--N and 46 ppm Cl^-. At various depths in the soil, they measured the concentration of glucose,

NO_3^--N and Cl^- as well as the redox potential. They found that the NO_3^--N loss was greater in the planted plot. They concluded that the organic C exuded by the roots moved with the NO_3^- in soil solution. This organic C, they thought, stimulated denitrification by accelerating microbial activity and reducing the redox potential.

Investigators measuring denitrification in soils containing corn (*Zea mays* L.) roots have been less successful showing an enhancement of denitrification. Bailey (1976) measured NO_3^- loss and N gas evolution in microcylinders containing soil with and without corn seedling roots. His data showed no significant increase in denitrification in the microcylinder with the corn seedling root. Patriguin et al. (1978) measured denitrification by acetylene inhibition in soils with and without corn roots. Denitrification was greatest before the plant roots began to grow rapidly. After the plant root began to grow denitrification dropped. They concluded that the roots maintained the NO_3^- concentration below that at which the bacteria could denitrify.

Management of Irrigated Soils to Maximize N Removal

Nitrate pollution of the groundwater may have several undesirable effects. (1) The presence of NO_3^- in the groundwater will almost undoubtedly contribute to the N load of surface waters, with the attendant problem of increased aquatic plant productivity. (2) Recently, nitrosamines have been shown to be carcinogens. While the biochemical connection between NO_3^- and nitrosamines may be tenuous, until more is known, it cannot be discounted (National Research Council, 1978). (3) Nitrate has been shown to cause methemoglobinemia in human infants.

This sometimes fatal blood disorder has been caused by using well water high in NO_3^- to make infant formula (Lee, 1970).

Four factors have been shown to be important in decreasing N content in water leached from cropland; the crop, the soil, irrigation scheduling and, if the soil is sewage irrigated, chemical amendments. Many authors have pointed out that some forage crops maintain a low NO_3^- concentration in the soil. Most researchers have attributed the low concentration to either plant uptake or changes in the behavior of the soil microorganisms. MacLean (1977) studied the uptake of fertilizer NO_3 by corn, timothy (Phleum pratense L.), bromegrass (Bromus inermis L.) and orchardgrass (Dactylis glomerata L.). The above ground portion of the corn crop contained less of the applied N than any of the grasses. At the highest fertilization rate, 448 kg/ha, the corn removed an average 19% of the applied N while bromegrass removed 43%. Warncke and Barber (1974) estimated the rate of N uptake by roots of bromegrass, corn, sorghum (Sorghum bicolor L.) and soybean (Glycine max L.). They also measured the minimum NO_3^- concentration maintained in solution about the roots of these plants. Bromegrass roots maintained a lower NO_3^- concentration than corn or any of the other plants. Overman and Nguy (1975) studied the N uptake over a season by corn, sorghum-sudan grass (Sorghum vulgare Pers. X Sorghum sundanese Stapf) and kenaf (Hybiscus cannabinus L.) in a soil irrigated at high rates with sewage effluent. While the N uptake of kenaf and sorghum-sudan grass dropped rapidly after 50 days, the uptake of corn remained consistent during the growing season.

Since early in this century, many authors have reported that the concentration of NO_3^- was less under grasses and forage crops than that under row crops (Lyon et al., 1923; Kolenbrander, 1969; Zwerman et al., 1972; Low, 1973). Lately, this fact has been used to reduce the NO_3^- leaching under irrigated soils. Avinimelech and his co-workers (1978) found that NO_3^- pollution of the groundwater was reduced under irrigated Rhodes grass (Chloris gayana Kunth) and alfalfa (Medicago sativa L.). They speculated that the low NO_3^- concentration under these forage crops was due to denitrification induced by low O_2 tensions found under these crops. Levin and Leshem (1978) concluded that the reduced NO_3^- concentration under forages was due to nitrification inhibition. Feigin et al. (1978) also found the NO_3^- concentration lower under an irrigated Rhodes grass sward. They thought that the grass had stimulated denitrification.

The first explanation for the depression of NO_3^- concentration under grasses to receive much attention was nitrification inhibition. Theron (1950) originally suggested that grass roots somehow acted to inhibit the conversions of NH_4^+ to NO_3^- in soils. The work of Munroe (1976), Moore and Waid (1971) and Rice (1976) has shown that nitrification was depressed in the presence of grass roots. This explanation has been attacked, sometimes vituperously (Purchase, 1974), by several authors including Theron himself. With ingeneousness rare in scientific literature, Theron, in a later article (1963), repudiated his own theory, and suggested the mechanism which depressed the soil NO_3^- concentration under grass was an inhibition of net soil mineralization. This explanation has also been suggested by Huntjens

(1971a, 1971b) and by Kissel and Smith (1978).

Several aspects of the soil can affect the reduction of the NO_3^- concentration in irrigated lands. Avnimelech et al. (1978) found that soils high in clay reduced NO_3^- leaching, presumably by enhanced denitrification. Lance et al. (1976) found that the concentration of NO_3^- in the soil leachate was inversely related to infiltration rate of the soil. Lance and Whisler (1972) claimed that NH_4^+ adsorption was important to facilitate nitrification, though Broadbent et al. (1977) stated that nitrification in sewage amended soils was almost always complete.

Results on the effect of irrigation scheduling upon soil NO_3^- are contradictory. Reddy and Patrick (1975) found that frequent flooding (every 2 days) maximized N loss by denitrification. Lance and Whisler (1972) found that while all of the NH_4^{+4} and organic N was transformed to NO_3^- during a similar schedule, the maximum N loss was found in soils flooded for longer periods, up to 23 days.

Apparently the amount and quality of organic C found in secondary sewage effluent is insufficient to denitrify much of the N applied to the soil. Lance and Whisler (1976) found that the addition of glucose or methanol to the effluent before irrigation would increase N loss. Lance et al. (1976) found that mixing sewage effluent with high NO_3^- soil filtrate stimulated denitrification of the filtrate in the soil.

CHAPTER II

MATERIALS AND METHODS

Introduction

This report details an investigation made as part of an ongoing study of the irrigation of cropland with stimulated secondary wastewater effluent. This investigation, begun in 1973 and ended in 1978, was supported by the Michigan State University Agriculture Experiment Station with special funding from the Michigan Legislature. Descriptions of the experimental site for the study and the initial results may be found in Karlen (1975) and Karlen et al. (1976). Here I report the data collected during the 1977 and 1978 growing seasons. While some experiments spurred by field observations were conducted in the laboratory virtually all the information came from samples or data collected at the experimental site. Since the project spanned several years, the experiment changed as time progressed. As more was learned about the response of the soil and plants to irrigation, the crops, the irrigation rate and the chemical application rates were changed appropriately. In addition, from year to year different types of data were collected in the field as questions were resolved and new lines of inquiry were developed. Because the experiment changed with time, the description of the materials and methods may be confusing. To avoid this possibility, it will be noted in the text when a procedure was done and why a new one was initiated. A brief explanation will be given at that time for these transitions.

Description of the Site

Size, Relief and Soil

The same experimental site was used in all five years of the wastewater study. The site was 0.68 ha block, 185.3 m long by 36.6 m wide. The longer dimension was oriented directly east-west. In the morning, when sprinkler irrigation commenced, the winds were generally from the southwest. If the wind velocity exceeded 24 kilometers per hour, the drifting of water became excessive and the irrigation was stopped. The site was slightly rolling. The highest point, running most of the width of the plot, was located in the center of the plot. The maximum change in relief was less than 3 meters over the whole site. Even though considerable amounts of water were applied to the site runoff and erosion were observed infrequently. The soil was heterogeneous. Nominally, the soil at the experimental site was of the Conover series, a fine loamy mixed mesic Udollic ochraqualf. This soil was formed from calcareous till. The Ca content in the soil at the site was very high throughout the profile. Soils of the Conover series are somewhat poorly drained. In 1970, the experimental area was tile drained at a depth of 1.05 m. The tiles ran along the width of the plot and were spaced every 15 m.

Plots and Subplots

Throughout the simulated wastewater experiment, four treatments were always in effect. In 1973 and 1974, the entire area was planted in corn which was irrigated at four rates; 25 cm, 50 cm, 100 cm and 200 cm annually. Little or no potential contamination of the groundwater was found at the 25 and 50 cm rates. Beginning with the 1975 season and continuing to the end of the experiment, two crops, corn and bromegrass, were irrigated at two rates, 100 and 200 cm/year. There were 12 plots located at the experimental site (see Figure 2). Each treatment was conducted on three adjacent plots.

Prior to 1973, a bromegrass sod was established at the experimental site. In the spring of that year, a preplant mixture of paraquat and atrazine was applied to the experimental area and the entire site was planted in corn. In 1974, the site was again planted with corn. For these two seasons, plots 1, 2 and 3 were irrigated at 25 cm/year, plots 4, 5 and 6 received 200 cm/year, plots 7, 8 and 9 received 100 cm/year while plots 10, 11 and 12 were irrigated at 50 cm/year. In 1975, the plots 1, 2, 3, 10, 11 and 12 were planted with bromegrass. Plots 1, 2, 3 received 100 cm/year. Plots 4, 5 and 6 continued in corn and continued to receive 200 cm/year in simulated secondary effluent. Plots 7, 8 and 9, in corn, again received 100 cm/year. Plots 10, 11 and 12, while in bromegrass, received 200 cm/year. Each year corn, but not bromegrass, received a starter fertilization consisting of 37 kg/ha N, 18 kg/ha P and 22 kg/ha K. In addition, all twelve plots were divided into four subplots to test the efficacy of additional K and N fertilization on the yield of the two crops. In each plot, two subplots received 112 kg/ha of N fertilizer in addition to any starter fertilization; the other two subplots received no additional N. Similarly, two subplots in

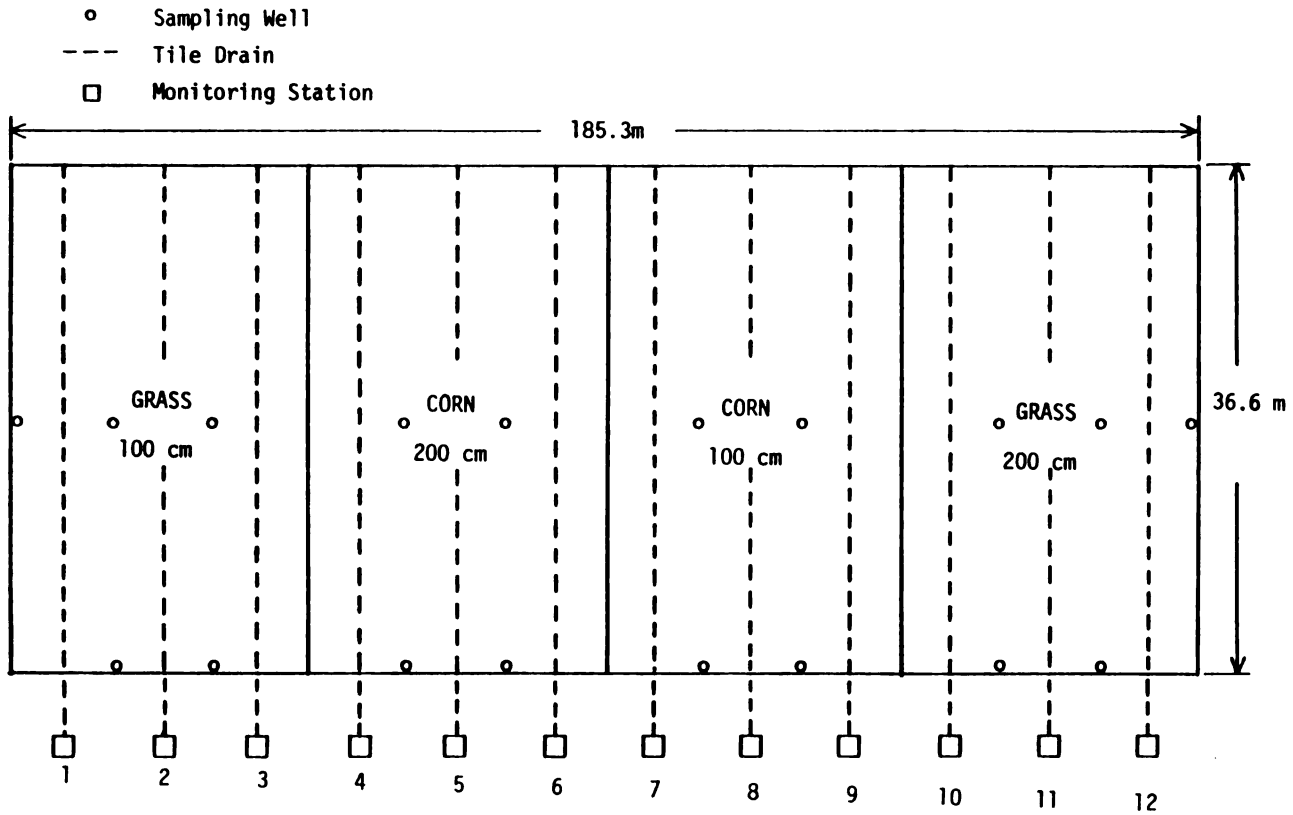

Figure 2. Simulated secondary municipal effluent experimental area.

each plot, one which received additional N, one which had not, received an additional fertilization of 93 kg/ha K. The other two subplots received no additional K.

Tile Lines

As was alluded to earlier, the tiles, in addition to draining the site, were also used to estimate leaching losses of ions and water. Tile lines were located below the center of each plot at a depth of 1.05 m. Before being intercepted by a major tile which carried the water off the site each tile line passed through a subsurface monitoring station. In the station, the tile line was exposed to reveal a special plexiglass tile section with two features. (1) A stoppered port in the plexiglass tile section allowed samples to be taken of the tile water. These samples were removed to the laboratory for chemical analysis. (2) The tile section contained a 60° weir, which allowed the water flow rate to be estimated by measuring the height of water behind the weir. The height of the water in the tile behind the weir was measured continuously by a Stevens type F, Model 61 water stage recorder. Each weir was calibrated individually by regression to one of two formulas:

$$\text{in 1977:} \quad F = ah^{b} \tag{24}$$

$$\text{in 1978:} \quad F = (c + dh)^{5/2} \tag{25}$$

where: F = water flow rate (liters/min)

h = height of water behind the weir

a,b,c,d = constants.

Equation 25 described the increase in flow with tile water height more accurately than did Equation 24. The correlation coefficient between flow rate and the height of water behind the weir using Equation 25 was $r^2 = 0.998$ or better. Qualitatively, the fit (Figure 3) was excellent.

Sampling Wells

Since the concentration of NO_3^- in the tile drainage water may have been a poor indicator of leaching losses, 26 sampling wells were established on the perimeter and at various locations within the plot areas in 1975. An estimate of the water table height was formed by measuring the height of water standing in the wells. A sampling well consisted of a 5-cm diameter non-perforated PVC pipe inserted in an augur hole dug to a depth of 2 to 3 m. Figure 2 shows the location of the wells.

Description of the Simulated Waste Water

Preparation

Secondary treated municipal wastewater was not available at the experimental site. A facsimile of East Lansing's secondary effluent was made at the site. Fresh water, containing about 25 ppm Cl, was piped to the site from an irrigation well. A solution containing a combination of NaCl and 12-6-6 liquid fertilizer was injected into the pipe supplying water to the sprinklers on the site. Ammonium and urea made up most of the N in the liquid fertilizer. It was noted that the injection solution produced a white precipitate when mixed with the well water. While we did not find out what it was, it was probably a phosphate salt. The concentration of a phosphate P in

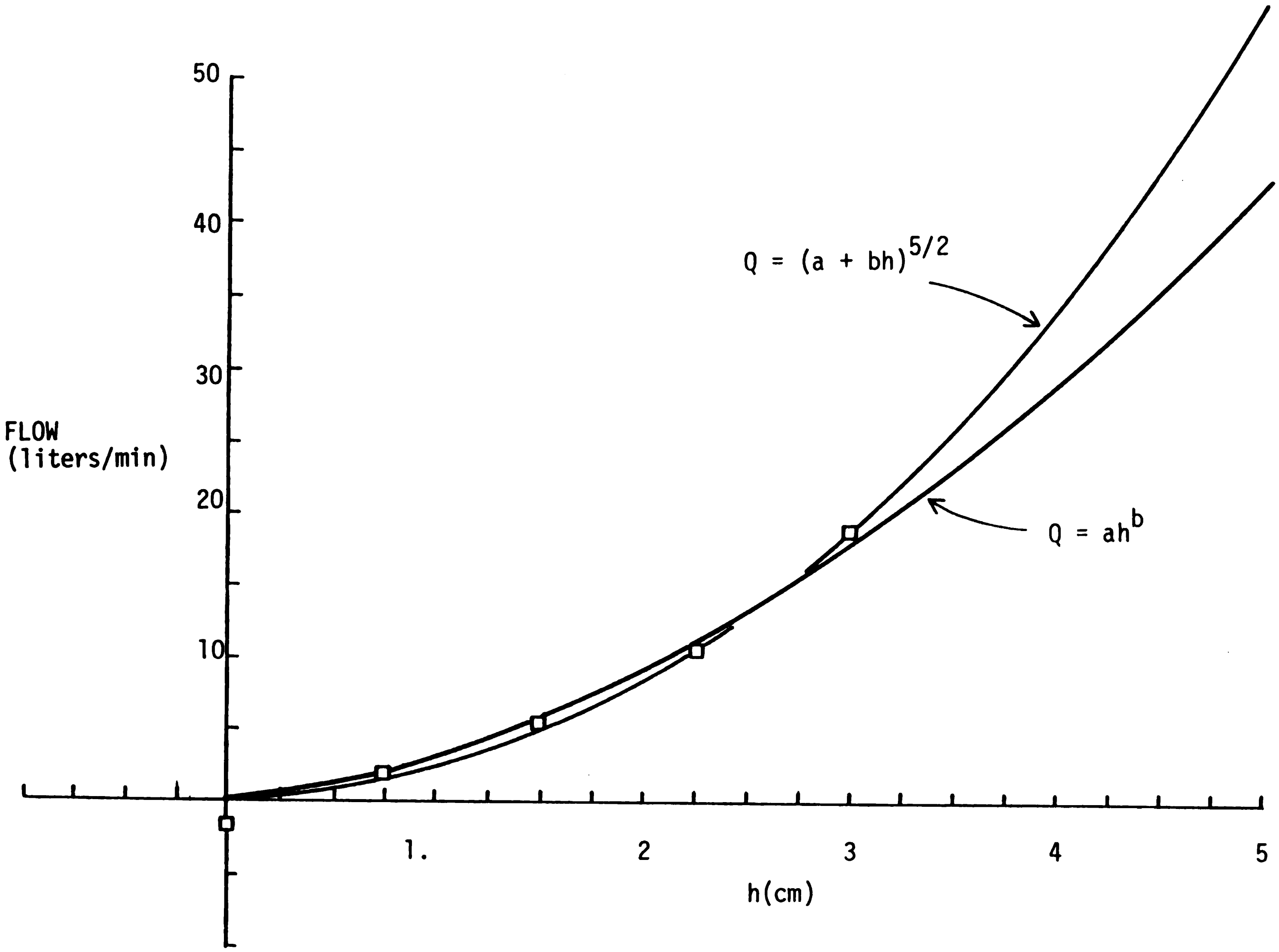

Figure 3. Comparison of two equations to describe the relation between height behind a weir and tile water flow rate.

the simulated wastewater was supposed to be 2.2 ppm. The typical concentration of phosphate P in the simulated wastewater in 1977 and 1978 was 1.3 ppm. While not conclusive, this drop in concentration suggests that some of the phosphate added to the irrigation water did not remain soluble.

Irrigation

Irrigation water was brought to each plot by a single pipe set down in the middle of the plot. Elevated sprinklers were fastened to each pipe at 9.1 m intervals. Two types of sprinklers were used; three full-circle Rainbird 9/64" nozzles in the interior of the plot and two Rainbird 3/32" semi-circle nozzles at either end. The irrigation water was applied at a rate of 0.78 cm/hr for 3 hours. Thus, the plots received 2.5 cm of stimulated effluent per irrigation. In practice, the plots receiving 200 cm/year were irrigated 6 times weekly, plots receiving 100 cm/year, 3 times weekly.

Sampling

Soil

The soil from the experimental site was sampled to a depth of 274 cm twice annually from 1973 through 1978. Samples were taken at the following depths: 0-15 cm, 16-30 cm, 31-60 cm, 61-90 cm, 91-122 cm, 123-152 cm, 153-213 cm, 214-274 cm. The soils were taken from the field, air dried and stored until analysis.

In 1977 and 1978, an investigation on the effects of supplemental fertilizer was initiated. After 1977 surface soil samples were taken in each subplot. To maintain consistency, after the initiation of the fertilizer experiment in 1977, the deeper semi-annual samples from each plot were taken from the check subplot, to which no additional fertilizer was added. In the fall of both years, soil was taken from the top 15 cm of all 48 subplots, air dried and stored until analysis.

In 1978, 3 forms of N were determined in soil samples taken to a depth of 274 cm. The procedure is presented in a later section.

Water in Tiles and Wells

Irrigation was sometimes halted to harvest crops or because of breakdowns in the supply of well water to the site. If irrigation was not interrupted, tile water samples were collected weekly. Tile water was withdrawn by suction through sampling ports in the plexiglass tiles at the monitoring stations which also housed the water stage recorders.

Water in sampling wells was collected as time permitted in 1975, 1976 and 1977, but not in 1978. Well water was drawn by applying a suction to a collection flask attached to a 3.5 m length of tygon tubing. The height of water in the well was measured during this operation. All water samples were stored in 250 ml polyethylene bottles. Within two hours after sampling, the water samples were brought to the lab and stored at $4^{o}C$ until they were analyzed.

Phosphate and Potassium vs. Pressure Experiment

In an effort to discover a relationship between effluent concentrations of phosphate and K with hydraulic head, a soil column experiment was set up. Soils from the experimental site were collected from 2 depths, 0-0.5 m and 0.5-1 m. These soils were air dried, passed through a 10 mesh screen and packed in the order as taken from the field to a depth of 1 m in four 10 cm I.D. PVC pipes. Twenty liters of solution with phosphate and K concentrations similar to the simulated effluent were passed through the soil in each pipe. The hole at the bottom of each pipe was stoppered and according to a randomized scheme heads of water were maintained above each soil at 5, 10, 20 and 50 cm. After 8 hours, the stoppers were removed and water samples were taken from each tube every five minutes for 50 minutes. The samples were stored at 4°C until the end of the experiment and then analyzed for phosphate and K.

Plants

A 15 m section of one row of each hybrid in each corn subplot was cut in the fall. The corn plants were weighed, a subsample for chemical analysis was oven dried then ground to pass through a 40 mesh sieve.

The grass in each subplot was cut twice yearly. The size of the area cut varied, but in general, an area 13.5 m^2 was cut. These samples were also weighed, subsampled, dried and ground to pass through a 40 mesh screen.

Laboratory Analysis

Soil

All soil samples, with the exception of those analyzed for N in 1978, were analyzed at Michigan State University Soil Testing Service

Laboratory. Samples were air-dried, ground to pass through a 10 mesh screen and analyzed for extractable P, exchangeable Na^+, K^+, Ca^{+2} and Mg^{+2} and soluble Cl^-. Phosphorus was extracted from the soil with 0.03 N NH_4F and 0.025N HCl at a 1:8 soil-solution ratio, shaken for 5 minutes. Color development was accomplished by using ammonium molybdate and 1, 2, 4-aminonapthosulfonic acid (Jackson, 1958). Cations were extracted with 1N NH_4OAc solution (pH 7). Potassium and Na^+ concentrations were determined using a Coleman flame photometer. A Perkin-Elmer 303 atomic absorption spectrophotometer was used to measure the concentration of Ca^{+2} and Mg^{+2}. Samples to be measured for soluble Cl^- were shaken with saturated $CuSO_4$ for 30 min. After filtration, the concentration of Cl^- was measured using an Orion specific ion electrode.

Soil Nitrogen Determinations of the 1978 Growing Season

Field soil samples were collected three times for N analysis. The soil was sampled to a depth of 274 cm or as far as possible. These depths were as follows: 0-15 cm, 31-60 cm, 61-90 cm, 91-122 cm, 123-152 cm, 153-213 cm and 214-274 cm. 0-15 and 15-30 samples were collected using a soil probe with which perhaps 10 subsamples in a plot were mixed to make up one sample. The samples taken from 30 cm and below were obtained from the same hole with an auger. Often, the lower samples could not be brought up because the sampling depth was below the water table and the soil was not retained by the auger.

All samples were placed in plastic bags and taken to the laboratory. Here three subsamples were weighed and analyzed. One subsample, weighing about 20 g, was used for NH_4^+ determinations. These samples were shaken with 20 ml of 2N KCl, centrifuged and the supernatant analyzed for NH_4^+ by micro-Kjeldahl distillation. A second subsample was weighed, shaken with 20 ml of saturated $CaSO_4$ solution and filtered. The filtrate was analyzed for NO_3^--N using a Technicon Auto-Analyzer. The third subsample was weighed, placed in an oven and reweighed to determine the water fraction in the soil.

Denitrification Incubation Experiment

Air dried soils were sampled from each block at 3 depths; 0-15, 15-30, 30-60 cm were used in the experiment. Two subsamples were taken from each sample; one subsample was wetted and dried before analysis and the other subsample was used directly. Other than wetting and drying, all subsamples were treated identically. Fifteen g of soil were placed in a 125 ml plastic bottle to which 75 ml of 200 ppm N as KNO_3 were added. The bottle was then capped and shaken. The bottles were then kept in the dark at 25°C for 7 days. Following the 7 days of incubation, the bottles were shaken and the contents filtered. The filtrate was analyzed for NO_3^- using an Orion specific ion electrode.

Denitrification Assay by Acetylene Inhibition

The measurement of denitrification by acetylene (C_2H_2) inhibition of nitrous oxide reduction was conducted on several soil samples in

September 1980. Since N_2O is readily measured with a gas chromatograph, the method has been shown to be an effective measure of denitrification (Smith et al., 1978). The rate of N_2O evolution from soil in an anoxic environment in the presence of C_2H_2 was measured for 2 hours following the addition of NO_3^- solution. Denitrification during this period has been designated "Phase I" by Smith and Tiedje (1979), representing the denitrification rate before the derepression of nitrate reductase synthesis following extensive periods of anoxia.

Soils were sampled two years after the cessation of the simulated secondary sewage effluent project. The experimental site had laid bare for the time after the end of the project. Soils at five different locations in and around the experimental site were sampled to a depth of 15 cm. One sample was taken in a plot which was planted in corn, another sample was taken in a plot which had been cropped in bromegrass. Both plots had been irrigated at 100 cm/year. These soil samples were designated "Corn 100" and "Brome 100" respectively. A third sample was taken from a bromegrass sod 20 m from the experimental site. Two samples were taken in an irrigated corn plot 30 m from the original site. One sample, called "Corn A" was taken right next to the corn stalk. Another sample, called "Corn B" was collected at mid-row, 37.5 cm from the stalk. All soils were the same type, Conover loam. The soil was near field capacity with a moisture content (by weight) of 22% to 28%. The samples were passed through a 4 mm sieve and stored without drying for two weeks in sealed plastic bags at 4^oC.

Three replicates of each soil sample were assayed for denitrification. Each replicate (11.76 g oven dry weight) was put into a 70 ml serum bottle. The bottle was stoppered and 1 ml chloramphenicol solution (365 mg/l) was injected into the bottle. The chloramphenicol was added to inhibit protein synthesis. The bottle was evacuated and flushed with argon (Ar) gas five times. Nitrate solution (4.2 ml) of varying concentrations was injected into the bottle to bring the total aquous concentration to 22.8 ppm NO_3^--N. Immediately, 5 ml C_2H_2 was injected into the bottle and the bottle was placed on a rotary shaker at 250 rpm. Every 24 minutes for two hours a 0.5 ml sample was taken of the serum bottle head space with a Pressure-lock syringe (Precision Sampling Corp., Baton Rouge, La.).

The N_2O concentration in the head space sample was measured using a Perkin-Elmer 910 gas chromatograph. This machine was equipped with a 2 m long, 0.32 cm diameter column filled with 8100 mesh Porapack Q. The gas chromatograph was equipped with a ^{63}Ni electron capture detector. The carrier gas was 5% methane, 95% Ar at a flow rate of 15 ml/minute.

The total N_2O content was calculated using the Bunsen absorption coefficient (Wilhelm et al., 1977), an index of the water solubility of the gas. The linear regression of the plot of N_2O content vs. time was used to calculate the rate of N_2O evolution.

Soil Organic Carbon

To get an indication of the relative potential for denitrification of the soils cropped in corn and bromegrass, the organic C content of the surface soil was measured. Carbon was determined in soil by ignition of 1 g oven-dried samples. The $CaCO_3$ content was estimated from the previously determined Ca content of the soil. Organic C was calculated by the difference.

Water

Field samples of water from drainage tiles, wells and irrigation lines were analyzed for Na^+, K^+, Ca^{+2}, Mg^{+2}, Cl^-, NO_3^--N and phosphate. Na^+ and K^+ were both determined with a Coleman Flame Photometer. These samples were diluted 1:10 to reduce interference by the high concentration of salts in solution. Samples for Ca^{+2} and Mg^{+2}, which were analyzed by using a Perkin-Elmer 303 atomic adsorption spectrophotometer, were also diluted. The dilution ratio was 1:50 in a solution to which La_2O_3 was added.

The Technicon Auto-Analyzer, an automated colorimeter, was used to estimate the solution concentration of NO_3^--N and phosphate P. Karlen (1975) found only nominal amounts of NO_2^--N in solution, so NO_3^--N was measured colorimetrically after reduction to NO_2^--N. The reduction is achieved by passing the sample solution through a cadmium copper column. Ammonium molybdate and ascorbic acid were used for color development to measure phosphate, also with the Technicon Auto-Analyzer.

Plants

Both corn and bromegrass samples were sent to the Ohio State University Plant Analysis Laboratory where they were analyzed spectrographically for P, K, Ca, Mg, Na, Cu, Fe, Zn, B, Mn, Al and

Ba. At Michigan State University the samples were analyzed for N by the semimicro-Kjeldahl method.

Statistical Analyses

Most statistical analyses presented here were performed on Michigan State University's Control Data Corporation 6500 computer. Most of the statistics were calculated using the Statistical Package for the Social Sciences (Nie et al., 1975).

Five specific subprogram routines were used. These were as follows:

1. BREAKDOWN calculated the sums, means, standard deviations and variances of a dependent variable.

2. PEARSON CORR computed Pearson product-moment correlations for pairs of variables.

3. SCATTERGRAM presented a two-dimensional plot of data points coinciding with the values of two variables being considered. Slopes and intercepts along with their significance were also computed.

4. ANOVA calculated an analysis of variance for factorial designs.

5. ONEWAY was used to calculate the Least Significant Difference (LSD) of a number of dependent variables due to one independent variable.

Those analyses not conducted with SPSS were calculated using M.S.U.'s STAT data package.

The calculation of the correlation coefficients between water height and tile flow was done using a Hewlett-Packard 25 programmable calculator. These data were plotted with the aid of a Hewlett-Packard 9845 desktop computer with hardcopy capacity.

CHAPTER III

RESULTS AND DISCUSSION

Concentration of Ions in Irrigation, Tile Drainage, and Soil Water

Concentration of Ions in the Irrigation Water

We attempted to approximate the concentration of the major inorganic ions found in East Lansing's secondary treated effluent by injecting a salt-fertilizer mixture into the irrigation water at the site. Table 1 presents an analysis of East Lansing's secondary treated sewage along with the projected concentration in the simulated effluent. Comparison with the data in Table 2 shows how closely the concentrations of ions in the irrigation water approached the concentration of ions in the real wastewater. The concentrations of all ions in the stimulated wastewater were reasonably close to what was intended to be manufactured at the site.

Since Cl^- will be given special attention in the body of this report, the nature of this anion will be investigated more extensively. The concentration of irrigation water Cl^- in 1977 must be taken with caution. Difficulties with the injection system caused huge variations in the Cl^- concentration. In some samples of irrigation water Cl^- concentrations were in excess of 1000 ppm. The concentrations of Cl^- in the irrigation water were much more variable in 1977 than 1978.

Table 1. Effluent composition. (From Karlen, 1975)

Constituent	East Lansing's Secondary[+]	Simulated
	ppm	
Total N	15.2	15.0
Nitrate N	3.1	3.5
Total P	4.9	3.3
Soluble P	1.1	2.2
K	8.6	6.2
Na	130	130[‡]
Ca	100	200
Mg	25	62
Cl	260	200[‡]

[+] In 1973 the simulated effluent contained 210 ppm Na and 324 ppm Cl.

[‡] This was the amount of Cl added. The irrigation water had an additional 25 ppm Cl from natural sources.

Table 2. Mean concentrations of ions in simulated wastewater and in water draining from tiles in 1977 and 1978.

	Wastewater	Tile Drainage Water				
		Grass-100 cm	Grass-200 cm	Corn-100 cm	Corn-200 cm	LSD (0.05)[‡]
	(ppm)					
				1977		
NO_3-N	2.73[+]	2.09	5.27	7.72	8.97	(1.12)
PO_4-P	1.62	0.35	0.50	0.49	0.74	(0.15)
K	8.2	8.9	3.5	3.9	5.2	(1.2)
Ca	205	217	215	207	208	(NS)
Mg	61.6	57.9	62.6	61.1	59.9	(3.2)
Na	148	112	128	106	111	(10)
Cl	313	247	241	205	212	(24)
				1978		
NO_3-N	3.18	3.25	5.42	6.58	8.52	(1.35)
PO_4-P	0.99	0.14	0.16	0.22	0.42	(0.09)
K	6.6	8.0	2.7	3.5	4.7	(0.9)
Ca	179	177	188	192	191	(9)
Mg	47.2	47.3	52.0	53.7	54.8	(3.2)
Na	138	113	130	115	123	(11)
Cl	227	206	240	207	221	(28)

[+] Total N for wastewater was 15 ppm.

[‡] LSD valid for tile drainage water, not wastewater

Since Cl^- was used as a tracer to estimate the leaching fraction leaving the root zone of the soil, this variability was unwelcome. Hence, the leaching fraction estimates in 1978 must be considered more valid than those in 1977.

As was noted earlier, virtually all N passing through the drainage tiles was in the form of NO_3^-. The majority of the N in the irrigation water was non-NO_3^--N, primarily urea and NH_4^+. The makeup and amount of the non-NO_3^--N in the irrigation water was not verified and this is a major failing in any interferences or conclusions made about the behavior of this nutrient once applied to the soil. The indications in the literature are that the urea in soil was rapidly hydrolized to NH_4^+ (Tabatabai, 1972) and that NH_4^+ was completely and quickly nitrified to NO_3^- in sewage amended soils (Broadbent et al., 1977). In this thesis, it is assumed that the concentration of total N applied was 15 ppm and that the N present as urea and NH_4^+ was rapidly converted to NO_3^-.

The concentration of phosphate P in the simulated secondary wastewater was below the projected soluble P concentration of 2.2 ppm. This discrepancy may have been due to precipitation of P when the salt, fertilizer and water were mixed. How much of the P which was applied to the soil either as a phosphate precipitate, as non-phosphate precipitate or as non-phosphate soluble P is conjecture.

Water and Ions in the Tile Drains

The calculated volume of water draining through the tiles in 1977 was less than 1978 (Table 3). The difference was substantial and

Table 3. Annual water drainage from the tiles in 1977 and 1978.

Plot or Block	1977	1978
	liters	
1	729,173	1,102,998
2	198,909	156,300
3	586,360	937,632
Grass - 100 cm	1,514,442	2,196,930
4	509,099	1,062,535
5	40,977	48,956
6	100,334	110,382
Corn - 200 cm	650,410	1,221,873
7	64,640	77,561
8	407,151	405,758
9	771,707	1,175,193
Corn - 100 cm	1,243,498	1,658,512
10	565,652	968,220
11	535,171	477,438
12	448,023	791,992
Grass - 200 cm	1,548,846	2,237,650
Total	4,957,196	7,314,965

cannot be explained by the use of different calibration formulas for the two years, because over the typical range of flow the two formulas are very similar. Another possibility is that the positioning of the floats used to measure tile water height was altered. This explanation is less probable because the increases in 1978 were consistent in most tiles with 1977 flow, which suggests an arithmetic variation during data manipulation rather than a physical variation in the field. The results indicate that between 50% to 75% of water applied by irrigation left via the tiles.

The theoretical development of tile flow does not allow lateral movement of subsurface water from the area about one tile to another tile or flow beyond the domain of the tiles altogether. Not much lateral movement out of the experimental area was indicated by the data. The high volumes of flow in tiles #1 and #12 did not indicate great amounts of water loss by flow east or west. That the flow east and west was probably small suggests that water movement north and south was also limited. There were wells placed north of the boundary of the experimental area. The water level in these wells was considerably less than that in the wells in the experimental area. Apparently, the loss of irrigation water by lateral movement out of the experimental site was limited.

The leaching fraction calculated using the ratio of Cl^- concentration is presented in Table 4. The leaching fraction, the volume of water leached below the tile drains during the portion of the growing season when water was sampled in the tile drains, was calculated by the following formula:

Table 4. Estimate of the leaching fraction of the individual tiles (liters/year)

Number	1977	1978
	liters	
1	704,347 (123)[+]	669,953 (117)
2	739,130 (129)	634,522 (111)
3	733,096 (128)	616,732 (107)
4	1,490,527 (130)	1,113,761 (97)
5	1,952,266 (170)	1,293,928 (113)
6	1,718,741 (150)	1,189,015 (104)
7	925,817 (161)	695,456 (83)
8	863,502 (150)	592,425 (97)
9	831,521 (145)	573,829 (100)
10	1,589,456 (138)	1,061,941 (93)
11	1,454,320 (127)	1,079,864 (94)
12	1,436,868 (125)	1,057,553 (92)
Total	14,439,591 (140)	10,587,979 (103)

[+] Number in parenthesis is leaching fraction expressed as a percentage of the amount of irrigation water applied over the year.

$$V_L = \frac{Cl_I}{Cl_L} V_I$$

where: V_L = leaching fraction (liters)

V_I = total irrigation volume for the season (liters)

Cl_I = mean concentration of Cl^- in the irrigation water (ppm)

Cl_L = mean concentration of Cl^- in the tile drainage water (ppm)

The estimates of the leaching fraction during 1977 should be viewed with caution. If we accept the estimates of leaching in 1978, then the amount leached was approximately equal the volume applied. If this is true, then the amount transpired from a plot was about equal to rainfall, which makes sense intuitively. The estimates of leaching volumes were used to calculate nutrient loss by leaching.

Seven ions: phosphate, NO_3^-, K^+, Ca^{+2}, Mg^{+2}, Na^+ and Cl^-, were monitored weekly in the tile water. Ammonium was evaluated intermittently. The typical NH_4^+-N content was well below 1 ppm and apparently not above the error inherent in the analytical method. The concentrations of the other seven ions in the tile water were analyzed statistically by irrigation rate and crop. This analysis is presented in Table 2.

The differences in the concentration of Cl^- in the tile water were not consistent from year to year. Given the fact that Cl^- is poorly retained by the soil and hardly taken up by crops, attempts to draw conclusions from this data is bound to be spurious. On the other hand, the tendency of Na^+ in tile water is clear. The concentration of Na^+ under plots irrigated at 200 cm per year was higher than those irrigated at 100 cm. This behavior is probably due to the higher amount of the ion which passed through the exchange complex of the soil.

The concentration of Mg^{+2}, Ca^{+2}, and K^{+} was significantly different in plots 1, 2 and 3, which were cropped in bromegrass and received 100 cm/year, than in the rest of the experimental area. There is no similar behavior of the other plots irrigated at 100 cm or the other grass plots. Under these three plots, Mg^{+2} and Ca^{+2} tended to be lower, whereas the concentration of K^{+} was substantially elevated.

The concentration of NO_3^--N was less in tile water under grass and also less at the lower irrigation rate. The depression of NO_3^--N concentrations under grass will be examined in more detail later in this thesis.

The concentration of phosphate in tile water was less under grass than under corn. As will be shown later, the corn crop took up more P than grass and one can only speculate on the mechanisms responsible. Lance (1977), in a study of the removal of sewage water P from soil columns, suggested that plant roots act somehow to keep P compounds in solution. Lance did not demonstrate or suggest how the plant roots were capable of doing this.

We have observed, as Karlen (1975) first demonstrated, that the concentration of phosphate in the tile drainage water rose as the flow rate of water in the tile increased. This behavior is contrary to any model in which sorption-desorption reactions of P in the soil are time dependent. This behavior was so peculiar that I investigated it further. Here, I will present the facts about the dynamic behavior of phosphate-P in the tile water. Following that, I will evaluate various hypotheses to explain this egregious phenomenon.

1. The phenomenon was the increase and decrease of phosphate P concentration during the tile flow subsequent to an irrigation.

2. The rate of water flow in the tile was highest about 30 minutes after the cessation of irrigation.

3. In 9 of the 12 plots the concentration of phosphate P in the tile drainage water was linearly correlated with K^+. (see Table 5 and Figure 4)

4. The concentration of phosphate P in the irrigation water was not similarly related with K^+.

5. The concentration of phosphate P and K^+ rose together as the flow event progressed. The maximum concentration of both ions fell after the peak. The maximum flow rate was not coincident with the phosphate P and K^+ concentration maxima (Figure 5).

6. This behavior was observed in tiles under both bromegrass and corn.

7. Both the linear correlation between phosphate P and K^+ and the flow related vagaries of the two ions, though marked, were less noticable early in the season and became progressively more distinct as the year progressed.

8. Returning to Table 6, the correlation was not significant between the concentration in tile water under plots 1, 2, and 3. The slopes of the regression lines relating the concentration of phosphate P with that of K for these tiles are much less than the other tiles. Unlike most other tile lines in the experiment, we

Table 5. Linear regression and correlation coefficient for the concentrations of PO_4-P and K in tile drainage water (μmoles liter^{-1})

Tile	No. of Samples	A^+	B	r^2
		1977		
1	12	11.04	.007	.011
2	13	- 5.32	.074	.304*
3	13	11.11	-.005	.003
4	14	- 27.44	.373	.820**
5	13	- 5.10	.242	.644
6	11	- 7.10	.220	.723**
7	12	9.00	.085	.380*
8	13	4.75	.113	.435**
9	10	- 0.90	.157	.871**
10	11	- 4.97	.188	.614**
11	11	- 5.03	.258	.659**
12	12	- 3.54	.234	.700**
		1978		
1	9	.10	.027	.543*
2	9	- .08	.021	.234
3	9	.50	.016	.244
4	9	3.29	.023	.006
5	8	- 3.18	.182	.441*
6	8	- 29.80	.361	.721**
7	7	- 17.74	.240	.688*
8	9	- 11.03	.202	.895**
9	9	- 4.73	.129	.862**
10	8	- 6.71	.145	.940**
11	8	- 2.17	.118	.571
12	8	- 5.65	.169	.653

$^+(PO_4) = A + B\ (K)$

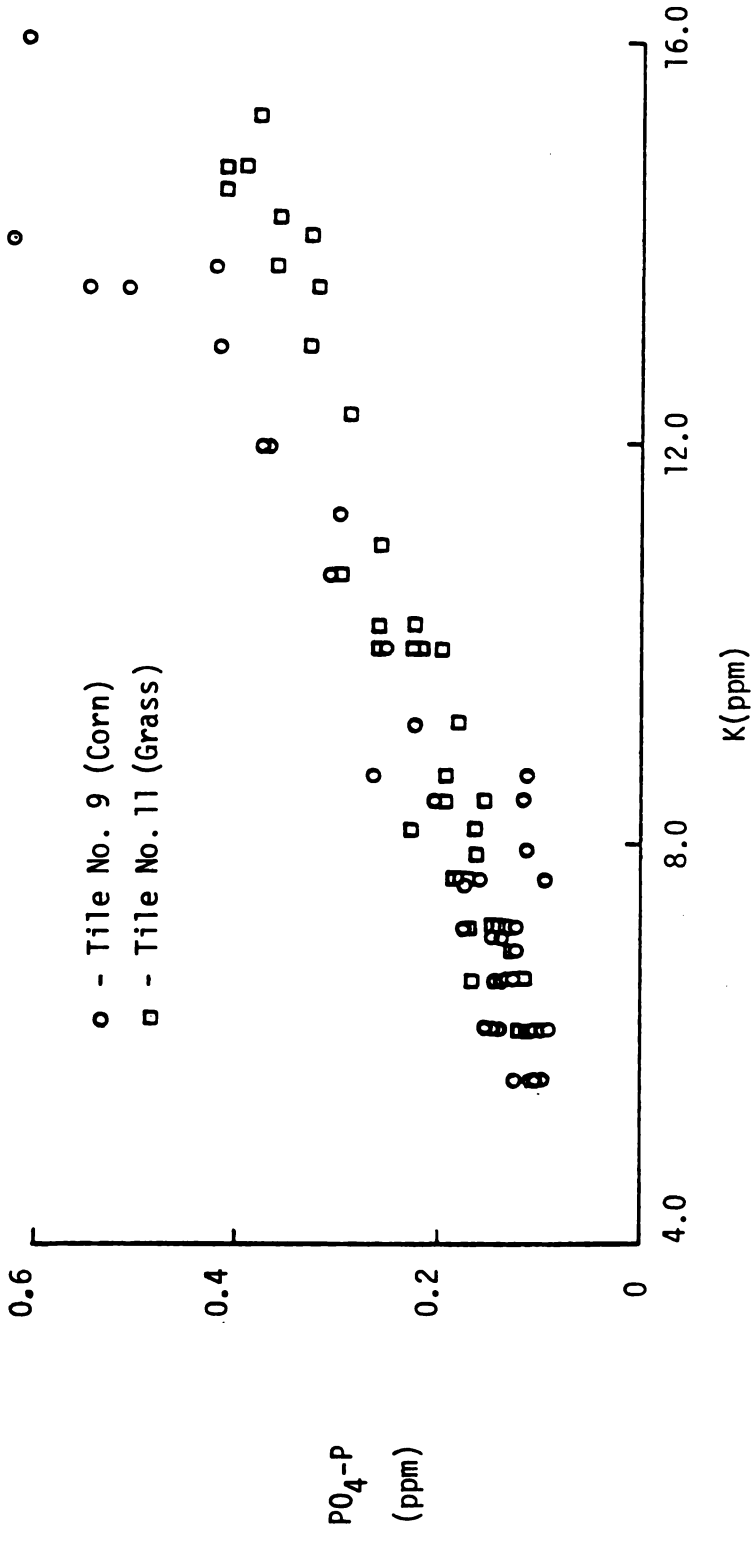

Figure 4. Plot of phosphate and potassium concentration in tile drainage for the 1977 growing season.

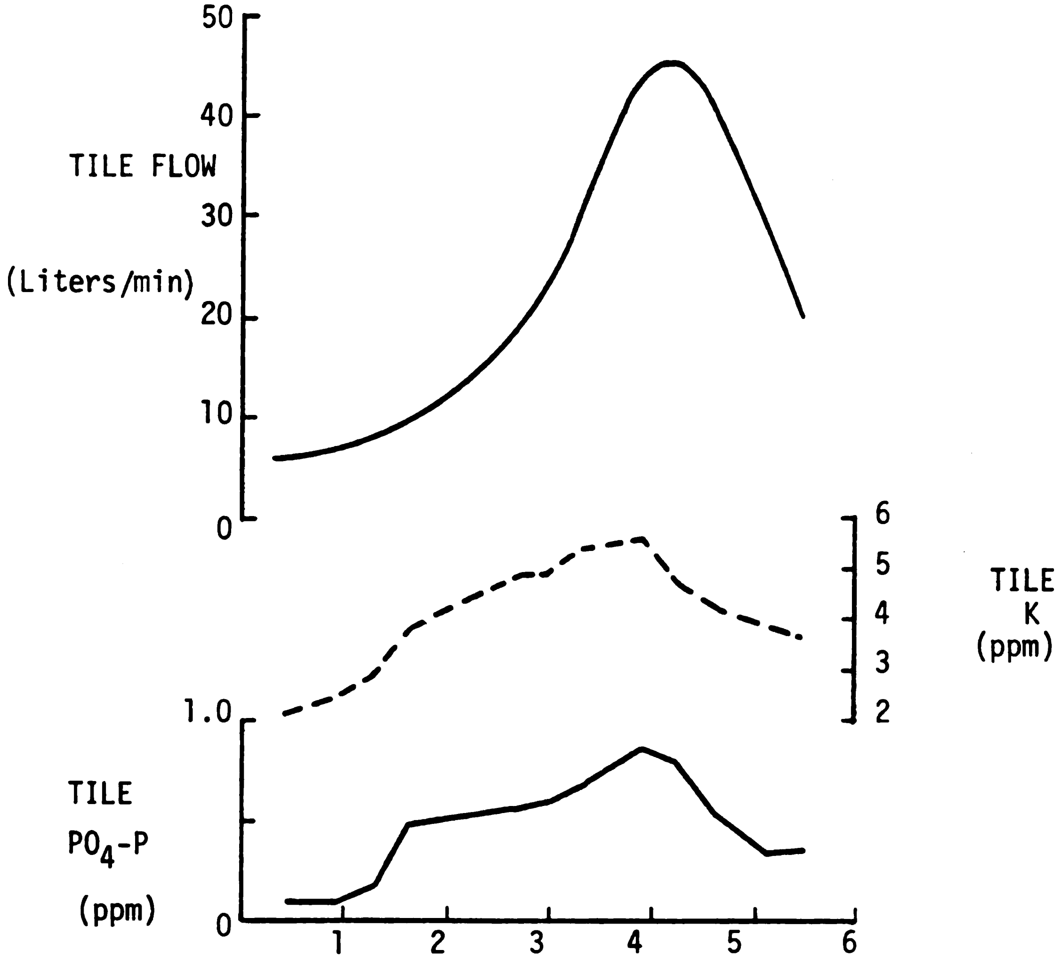

Figure 5. Changes in tile flow rate and concentrations of PO_4-P and K in the water draining from Tile #11, for a single flow event, 10-24-1978.

cannot say that there is a linear relationship between phosphate P and K^+ in tile drains 1, 2 and 3. Perhaps part of the lack of correspondence between the two ions in these tile drains is due to the higher concentration of K^+ in the tile drainage water.

I was unable to find out what caused this behavior of phosphate P in the tile drainage water. Four hypotheses exist to describe this phenomenon and I will critically examine them below. Whatever mechanism (or mechanisms) is at work clearly involves the soil. The correlation between the concentrations of phosphate and K^+ were closer coming out of the soil in the tile drainage water than it was in the irrigation water. In addition, the behavior became more distinct as the year progressed, and the cumulative load of the ions increased. Thus, I discount hypotheses which were based on the thought that water moved through portions of the soil profile with little or no reaction. While the mechanism need not have been instantaneous, it must have accounted for the coincidence of the cessation of irrigation and the peak ion concentration. Adsorption-desorption reactions in soil can be fast, but as far as I know, there is no specific relation between the sorption of P and K. While there are phosphate minerals which contain K, reactions of these minerals tend to be very slow. Since the precision of the behavior increased over the year, I am not inclined to discount the involvement of some sort of adsorption mechanism.

Several lines of inquiry can be dismissed quickly. Whatever caused the phenomenon, it was not due to changes in the electrical charge balance of the soil solution. Phosphate and K^+ were minor constituents of the soil solution and had opposite charge. Any change in the electrochemical balance that would cause one to increase would tend to decrease the other. The close behavior of the two ions suggests some sort of associated complex with K and phosphate. If an associated complex was the cause, the regression equations suggests that virtually all the P was associated with K and that the molar ratio of phosphate P to K was between 1:6 to 1:5. The association constants for HPO_4^{-2} and $H_2PO_4^-$ with K^+ presented by Larsen (1967) suggest only a small fraction of phosphate P would be associated with K. The valences of the three ions, K^+, HPO_4^{-2}, and $H_2PO_4^-$ are not consistent with a ratio of P:K higher than 1:2.

Several other suggestions cannot be dismissed so readily. The relative hydrated radius of the two ions would be expected to stay fairly constant. Thus if the two were moving in response to a nonelectrical gradient, one would expect constancy in the ratio of the two ion concentrations. The two ions may be complexed by a larger molecule, possibly organic, which dragged the two ions through the soil solution. Because the organic molecule was larger than most other ions in solution, its flow from soil to tile could be velocity dependent.

The first hypothesis to explain the behavior of phosphate P in tile drainage water was developed by Karlen (1975). He argued that the rapid flow of water through sand smears to the drains explained the peak behavior of phosphate in tile drains. In the soil, the argument went, there were sections with a lower ionic adsorption capacity and higher hydraulic conductivity than the rest of the soil. In these smears, the concentration of phosphate and K^+ in the soil solution was higher than in the rest of the soil. Since the conductivity was higher, as the irrigation proceeded the contribution of the solution from the smear to the tile drainage water increased. Thus, the concentration of the two ions in the tile water increased during an irrigation. The sand smear hypothesis is consistent with the flow of water through soils which are composed of two commingled portions, each with different hydraulic conductivities. The flow to the tiles, where the maximum flow was found after the cessation of water application is virtually identical to that of flow through macropores in soil (Thomas and Phillips, 1979). In theory, flow through macropores and through sand smears is similar in that the dynamics of flow is governed by two sectors of the soil, each having greatly different conductivities.

The hypothesis also poses many considerable failings. The sand smear hypothesis depends upon a convenient geometry in the subsoil. While only two tile drains were studied for the dynamic behavior of phosphate in the water 9 of the 12 tile drains showed significant correlations between phosphate and K indicating that, if the two behaviors were linked, the behavior was common in the field. Therefore, in a very heterogenous soil, if they were the cause of the behavior, sand smears must make a sizable portion of the flow to most of the tiles. Further, the soil used by Sharpley et al. (1977) in which the same behavior is observed was homogeneous probably without smears, sandy or otherwise. The model provides nothing to explain the correspondence of the concentrations of phosphate and K in the tile. Lastly, the model does not explain the repetitiveness of the behavior. To show why the model does not, the behavior of hypothetical model will be examined. Begin with two sectors of the soil, A and B. Both are connected to the tile drain and water flows through each to the tile drain. Assume that the conductivity and ion concentration is greater in A. Also assume that the volume of B is substantially greater than that of A. After one irrigation, the behavior would be that observed in the field, increasing flow and ion concentration in the tile. After irrigation stops, though, we can expect much of the solution in B to replace that in A. Thus, with the second irrigation, no appreciable change in the ion concentration would be observed. Therefore, the explanation is neither internally consistent nor does it adequately explain much of the behavior which has been observed.

The second explanation can be called the particulate hypotheses. According to this hypothesis, the behavior of P in tile lines was based upon the nature of flow in the tile drain. Phosphorus and K were adsorbed by minerals in the sediment of the tiles. As the flow rate in the tiles increased, so did turbulence, and sediment was suspended in the tile drainage water. Phosphorus and K previously adsorbed upon mineral surfaces were released into solution and the concentration of the two ions increased. This hypothesis was implied by Sharpley et al. (1977) to explain the increase in P concentration with the increase in tile drainage water flow. The hypothesis was presented obliquely. They noted that several investigators had observed a correlation between flow rate in rivers and runoff and the concentration of ions, including P. This was believed to be due to an increase in turbulence concomitant with the increase in flow. Turbulence caused the sediment to be brought into suspension. Their presentation may be faulted on two counts. (1) One of the articles they cite about the correlation of flow and ion concentration (the only one I was able to locate) showed a decrease in ion concentration in a river with an increase in flow. (2) While they present the general observation that "...an increase in suspensionate was observed in the tile," they failed to demonstrate that P associated with particulate matter was responsible for the increase in P concentration in tile water. This criticism is due largely to the fact that the Sharpley article is the only one on this aspect of tile flow to appear, and I have scrutinized it on an aspect fairly far removed from the main theme of the paper. The hypothesis was presented in passing and probably was not considered in great detail by the authors. Aside from the objections of the hypothesis inherent in the presentation of the article, there are two other criticisms. (1) The maximum tile flow rate, and I assume the maximum turbulence, and the peak concentrations of P and K do not coincide. (2) Since the chemistry of the adsorption or precipitation of P and K in sediments has not been shown to be related, the correspondence in the tiles draining the Conover study soil is unexplained.

A third hypothesis of the ion behavior in the tiles is based upon different path lengths of the soil water must have traveled to the tiles drains. Water and phosphate flowing from portions of the soil near the tile moved quickly into the tile. The concentration of phosphate in the soil solution flowing from portions near the tile drain was higher than in solutions flowing from portions further from the tile drain. This quickly flowing, high concentration solution caused a spike in the tile water concentration of phosphate during an irrigation.

This theory, like the sand smear theory, depends upon contributions of water from different sectors of the soil with different P and K concentrations. Two facts weigh in its favor. (1) P concentration in soil solution decreases with the increase in distance traveled and (2) according to models presented by Childs (1947) and Kirkham (1964) most of the water which is delivered to the tile along the shortest path lengths enters the tile soon after the end of water application. There is nothing to explain such persistent correlation between the phosphate and K^+ in the tile drainage water.

The last hypothesis to explain the peak beahvior of phosophate assumes that the soil about the tile drain acted as a semipermeable membrane allowing water to pass more freely than ions in solution. In the soil near the outside of the tile, the water pressure dropped dramatically from that due to the hydrostatic head to atmospheric pressure. This difference in water pressure increased as the irrigation proceeded and the water table rose. Increases in the pressure difference decreased the ability of the soil to act as a membrane, to restrict the passage of ions relative to water. More ions passed through the portion of soil close to the tile relative to the flux of water and the concentration of the ions in the tile drainage water increased. All ions behaved this way, only the behavior of phosphate and K were discernable because their concentrations were so much less than the rest.

Because little is known about the subject, it is difficult to evaluate the possibility that the soil about the tile acted as a semipermeable membrane. But, if one discounts macro-physical explanations such as the sand smear hypothesis and is unable to find satisfactory explanations in the sorption behavior of phosphate, there are few avenues left to follow. Studies in soils and clays have shown changes in the relative flux of ions to the flux of water due to changes in hydraulic head. To test this possibility, I measured the concentration of phosphate and K in leachate from soils maintained at four different hydraulic heads. No tendency was observed. The soil had been screened, the phosphate adsorption capacity had increased and the phosphate concentration in the effluent was very low. The field data has shown that the behavior was more pronounced the longer the soil has been irrigated with phosphate solution. Perhaps not enough P had passed through the soil in the laboratory to really test if hydraulic head has an effect upon ion concentration in the effluent water. I suspect that the variable head experiment did not adequately test the effect of pressure on phosphate and K^+ concentration in the effluent. A second fact supporting membrane hypothesis is that the concentrations of phosphate and K^+ were strongly and consistently related. No other explanation presented here, save the existence of a complexing molecule, can explain this fact. We can expect that the hydrated radii of HPO_4^{-2}, $H_2PO_4^-$ and K^+ remained consistent in the soil solution and if they are moved by non-electrical gradients, the ratio between them in solution would be consistent. If the cessation of irrigation affected the concentration of ions in the tile, and all information I have gathered supports this argument, then whatever mechanism was responsible, it must explain the speed and consistency of the soil system response. Looking only at the chemistry of P in soil we see that mineral dissolution and chemical desorption are too slow, as is chemical adsorption. Only physical adsorption or possibly membrane behavior of the soil react in times as quickly as we observed in the field.

Several formidable arguments go against this explanation. It has not been shown that the membrane behavior of soils is affected by pressure gradients as small as would be found at the tile drain. It has not been shown that soils act as a membrane with mixed electrolyte solutions. Indeed, it has not been shown that soils act as membranes at all, only pure clays have been used in experiments thus far. It has not been shown that the movement of phosphate is affected by this aspect of soil behavior. In fact, few anions have been investigated. The membrane hypothesis and the other three, are unable to adequately explain the peak behavior of phosphate and K^+ in the tile drainage water.

As noted above, the mean concentrations of NO_3^- in tile drainage water under grass was lower than in those under corn. Thomas and Barfield (1974) have contended that, because flow to tile lines is through aerobic soil, denitrification is reduced and the concentration of NO_3^- is greater in tile drainage water than in other subsurface water.

Using the measured soil NO_3^- concentration and the moisture content of soils collected in 1978, I calculated the NO_3^- concentration in the soil solution. The soil solution NO_3^- content calculated by this method should be more accurate than with most other ions in solution because NO_3^- is weakly attracted by most soils. The mean concentration of NO_3^- in soil solution in 1978 are presented in Table 6, as well as the mean drainage water concentration for the ion that year. The tile drainage water concentration were consistently less than those calculated for the soil solution. While these data do not establish the drainage water as a reliable estimate of leachate NO_3^- concentration, they do run counter to the argument by Thomas and Barfield that the NO_3^- concentration is typically much higher in the tile drainage water than in leachate from the soil.

Plant Response

The application of sewage to cropland has two aims; to remove potential pollutants and to produce a usable crop. The plant response in our experiment must be judged by similar criteria. Here three categories of crop response to irrigation rate and additional fertilizer will be presented; nutrient quality of the crop, crop production and annual nutrient removal by the crop.

The nutrient concentration of the bromegrass was consistently affected only by the irrigation rate (Tables 7 and 8). The calcium concentration of the bromegrass was higher in the plots irrigated at 200 cm/year.

Table 6. Calculated mean concentration of NO_3^--N in the solution of soils sampled at indicated depths and in water from tile drains, 1978.

Depth	NO_3^--N Concentration Grass-100 cm	 Grass-200 cm	 Corn-100 cm	 Corn-200 cm
(cm)	(ppm)			
0- 15	14.3	25.8	27.9	27.7
15- 30	16.4	19.0	26.1	37.5
30- 60	12.1	12.8	18.4	29.0
60- 90	10.3	11.4	15.0	19.6
90-120	13.1	9.8	12.9	18.2
120-150	11.5	8.4	11.5	18.5
150-210	10.8	7.8	11.4	16.6
210-270	11.4	9.7	12.3	17.7
Tile drains (120 cm)	3.3	5.4	6.6	8.5

Table 7. Influence of fertilization and irrigation rate on the nutrient concentration of grass in two cuttings, 1977.

Treatment	Nutrients				
	N	P	K	Ca	Mg
	(percent of dry weight)				
First cutting					
Check	1.81	.49	1.77	.64	.24
N	2.28	.55	2.29	.72	.34
K	1.73	.43	1.70	.62	.23
NK	2.43	.52	2.16	.69	.31
LSD (0.05)	(.47)	(.07)	(.31)	(NS)	(NS)
100 cm	2.02	.47	1.65	.58	.20
200 cm	2.11	.53	2.70	.76	.36
LSD (0.05)	(NS)	(NS)	(NS)	(NS)	(NS)
Second cutting					
Check	1.97	.67	1.54	.72	.16
N	2.06	.64	1.52	.70	.16
K	1.95	.65	1.64	.76	.18
NK	2.10	.64	1.56	.70	.16
LSD (0.05)	(NS)	(NS)	(NS)	(NS)	(NS)
100 cm	1.86	.60	1.48	.64	.16
200 cm	2.17	.70	1.05	.80	.17
LSD (0.05)	(.19)	(NS)	(NS)	(.05)	(NS)

Table 8. Influence of fertilization and irrigation rate on the nutrient concentration of grass in two cuttings, 1978

Treatment	Nutrients				
	N	P	K	Ca	Mg
	(percent of dry weight)				
First cutting					
Check	1.26	.27	2.16	.30	.12
N	1.25	.27	2.10	.29	.10
K	1.23	.26	2.20	.29	.11
NK	1.33	.26	2.13	.28	.10
LSD (0.05)	(NS)	(NS)	(NS)	(NS)	(NS)
100 cm	1.26	.27	2.15	.28	.10
200 cm	1.28	.26	2.15	.30	.11
LSD (0.05)	(NS)	(NS)	(NS)	(.02)	(NS)
Second cutting					
Check	1.26	.42	2.38	.54	.19
N	1.25	.40	2.44	.67	.26
K	1.23	.43	2.13	.56	.20
NK	1.33	.39	2.32	.61	.22
LSD (0.05)	(0.07)	(.02)	(0.28)	(0.07)	(.07)
100 cm	1.26	.41	2.45	.57	.23
200 cm	1.28	.41	2.18	.62	.21
LSD (0.05)	(NS)	(NS)	(0.20)	(0.05)	(NS)

As shown in Table 9, additional fertilizer had only one effect upon nutrient concentration in corn. Nitrogen fertilization increased N concentration in the crop. Phosphorus concentration was higher in corn grown in plots receiving the higher irrigation rate.

The dry matter yield of bromegrass was increased by additional irrigation and fertilizations. Table 10 shows that only the combination of N and K fertilization consistently increased dry matter production.

Irrigation rate did not have a significant effect on dry matter production or grain yield of corn, as shown in Table 11. Of the two corn varieties grown in the experiment, Pioneer 3780 yielded more silage and grain than did Funks 4444. Nitrogen fertilization, but not additional K, increased grain and silage production.

The major determinant of nutrient removal was dry matter yield of the crop. Corn took up more N, P and K than did bromegrass (Table 12). Increased irrigation rate stimulated removal of N, P and K by bromegrass and increased the removal of P by corn (Table 13). Phosphorus removal was unaffected by additional fertilization. Of the two corn varieties, Pioneer 3780 removed more of the nutrients than did Funks 4444. More N was added to the crops as fertilizer than was removed by the induced increase in production. The increase in N uptake by corn in subplots receiving additional N fertilization was a 40.9 kg/ha, the increase in subplots receiving both N and K was 52.9 kg/ha. In subplots cropped in bromegrass the increases in N removal for these treatments were 30.5 and 65.2 kg/ha

Table 9. Influence of fertilization and irrigation rate on nutrient concentration of corn silage in 1977 and 1978.

Treatment	Nutrients				
	N	P	K	Ca	Mg
1977	percent of dry weight				
Check	.96	.48	1.15	.31	.20
N	1.08	.43	1.14	.29	.19
K	.94	.43	1.11	.28	.20
NK	1.08	.39	1.13	.27	.18
LSD (0.05)	(.05)	(.05)	(NS)	(NS)	(NS)
100 cm	1.00	.40	1.14	.27	.20
200 cm	1.03	.47	1.12	.30	.19
LSD (0.05)	(NS)	(.07)	(NS)	(NS)	(NS)
1978					
Check	1.08	.33	1.22	.34	.24
N	1.09	.32	1.11	.32	.25
K	1.03	.33	1.21	.33	.24
NK	1.12	.34	1.23	.36	.25
LSD (0.05)	(0.07)	(NS)	(NS)	(NS)	(NS)
100 cm	1.02	.27	1.11	.28	.21
200 cm	1.14	.38	1.27	.39	.27
LSD (0.05)	(0.05)	(.05)	(.14)	(.05)	(.03)

Table 10. Influence of fertilization and irrigation rate on dry matter yield of bromegrass in 1977 and 1978.

Treatment	1977 First cutting	1977 Second cutting	1977 Total	1978 First cutting	1978 Second cutting	1978 Total
	(metric tons/ha)					
100 cm						
Check	2.69	1.40	4.09	4.95	2.32	7.27
N	4.52	1.77	6.29	5.31	3.66	8.98
K	2.63	1.22	3.85	4.64	2.69	7.33
NK	4.68	1.59	6.17	5.68	4.15	9.83
LSD (0.05)	(1.59)	(NS)		(NS)	(NS)	
200 cm						
Check	5.50	1.59	7.08	5.80	4.34	10.14
N	5.68	1.34	7.02	5.37	4.40	9.77
K	4.34	1.65	5.98	5.86	4.82	10.69
NK	8.06	1.53	9.59	5.74	5.19	10.93
LSD (0.05)	(1.59)	(NS)		(NS)	(NS)	
Fert. Treat. Av.						
Check	4.09	1.47	5.56	3.60	5.07	8.67
N	5.07	1.53	6.59	4.52	4.88	9.40
K	3.48	1.22	4.70	3.66	5.31	8.97
NK	6.29	1.59	7.88	4.88	5.50	10.38
LSD (0.05)	(1.10)	(NS)		(0.55)	(0.55)	
Water Treat. Av.						
100 cm	3.60	1.53	5.13	5.13	3.18	8.30
200 cm	5.86	1.40	7.27	5.68	4.70	10.38
LSD (0.05)	(1.59)	(NS)		(0.55)	(0.55)	

Table 11. Yield of corn, as silage and grain in 1977 and 1978, as affected by fertilization, effluent application rate and corn hybrid.

Treatment	Silage Yield[+] 1977	Silage Yield[+] 1978	Grain Yield 1977	Grain Yield 1978
	—(metric ton/ha)—		— (quintal/ha)—	
Fertilization				
Check	14.9	13.4	85	58
N	17.3	16.7	107	97
K	15.7	13.8	85	59
LSD (0.05)	(1.3)	(1.4)	(8)	(4)
Water rate				
100 cm	17.0	15.3	99	75
200 cm	16.3	15.4	95	80
LSD (0.05)	(NS)	(NS)	(NS)	(NS)
Corn variety				
Pioneer 3780	17.6	16.4	107	86
Funks 4444	15.7	14.2	86	70
LSD (0.05)	(1.3)	(1.0)	(3)	(5)

[+] Dry weight.

Table 12. Effect of crop and corn variety on uptake of N, P and K in 1977 and 1978.

	Nutrient Uptake		
Treatment	N	P	K
	(kg/ha)		
Crop (1977)			
Bromegrass	121.0	31.6	113.2
Corn	170.8	71.2	185.9
LSD (0.05)	(27.1)	(5.8)	(18.3)
Variety (1977)			
Pioneer 3780	178.8	68.4	172.6
Funks 4444	162.8	74.1	199.1
LSD (0.05)	(17.4)	(6.7)	(15.4)
Variety (1978)			
Pioneer 3780	179.0	54.7	195.7
Funks 4444	154.6	46.3	169.9
LSD (0.05)	(20.5)	(7.4)	(23.9)

Table 13. Effect of irrigation rate and additional fertilization on uptake of N, P and K by corn and bromegrass in 1977 and 1978.

Treatment	Crop Uptake					
	Corn			Bromegrass		
	N	P	K	N	P	K
	(kg/ha)					
1977						
Irr. Rate						
100 cm	169.3	67.1	178.0	93.4	24.3	76.5
200 cm	172.2	75.4	193.7	144.0	37.8	143.7
LSD (0.05)	(NS)	(6.4)	(NS)	(38.2)	(7.3)	(29.2)
Fertilization						
Check	144.8	70.5	169.2	102.2	31.1	99.7
N	188.4	74.4	196.5	132.7	34.9	129.8
K	149.5	67.3	169.2	80.5	22.8	79.3
NK	200.6	72.8	208.6	167.4	38.3	144.3
LSD (0.05)	(15.1)	(NS)	(17.6)	(47.8)	(5.3)	(52.7)
1978						
Irr. Rate						
100 cm	157.9	41.6	169.3			
200 cm	175.7	59.4	196.3			
LSD (0.05)	(NS)	(5.7)	(23.8)			
Fertilization						
Check	145.3	44.4	165.2			
N	183.4	52.8	183.2			
K	143.3	45.6	168.0			
NK	195.3	59.2	214.8			
LSD (0.05)	(24.5)	(10.0)	(32.1)			

respectively. Since both crops received 112.1 kg/ha N as additional fertilizer 50% or less of the additional N was not taken up by the crops. The efficacy of additional N fertilization must be judged by two factors: (1) the load of fertilizer N finding its way to the groundwater and (2) the economic benefit from the increased crop production. As will be shown in the next section, much of the added N not removed by the crop did not find its way to the groundwater. This disparity was most pronounced under grass. The danger of N pollution may be less than indicated by incomplete N removal by the crop.

Changes in the Soil

During the 1977 and 1978 seasons, the chemical components measured (extractable P, exchangeable Na^+, K^+, Mg^{+2} and Ca^{+2} and soluble Cl^-) changed little. Table 14 presents the concentration of these ions in Fall 1978. The distribution of extractable P in the soil profile, shown in Table 15, varied greatly from time to time but no real trend was discernible in 1977 and 1978. Comparing the concentrations of extractable P in 1977 and 1978 with those in spring 1973, it is clear that considerable amounts of P had accumulated in the soil profile since the beginning of the experiment. The only obvious change in the profile distribution between 1977 and 1978 was a small increase in the P concentration in the lower depths.

Calcium and Mg^{+2} concentrations varied greatly from sample to sample but showed no tendency for accumulation or loss. Potassium, on the other hand, had a higher concentration in the soil profile

Table 14. Concentrations of extractable P and exchangeable K, Ca, Mg and Na in soil samples at given depths (Fall, 1978).

Depth (cm)	P	K	Ca	Mg	Na
	(μg/g soil)				
0 - 15	126	72	1655	242	140
15 - 30	36	69	1351	234	135
30 - 60	14	71	1596	291	147
60 - 90	7	62	2410	314	175
90 - 120	3	49	3092	279	129
120 - 150	2	31	3072	201	96
150 - 210	1	30	3164	194	95
210 - 270	1	35	4200	193	89

Table 15. Extractable phosphorus concentrations in the soil profile for Spring of 1973 and Spring and Fall of 1977 and 1978.

Depth (cm)	4-73	4-18-77	11-11-77	4-18-78	11-22-78
	(μg P/g soil)				
0 - 15	9	107	98	109	126
15 - 30	8	77	44	65	36
30 - 60	5	7	10	13	14
60 - 90	3	4	4	6	7
90 - 120	3	2	3	5	3
120 - 150	2	1	3	3	2
150 - 210	2	1	2	2	1
210- 270	2	1	2	2	1

each spring than the subsequent fall. The concentration of K^+ in the soil in spring 1978 were greater than those in fall 1977.

Sodium behaved the opposite of K^+. The concentration was higher in fall than spring. This is consistent with a build-up of Na^+ during the irrigation season followed by leaching during the winter and spring snow melt. Surface samples taken in each subplot showed little real variation. Each year, the subplots received the same fertilizer treatment so any effects which were additive would have been able to accumulate. The irrigation rate affected K^+ accumulation in samples taken in 1978. The K^+ concentration was less in the plots irrigated at 200 cm/year. In 1978, the concentration of K^+, Ca^{+2} and Mg^{+2} were lower in the corn plots. Consistently, the K^+ concentration was greater in soil from subplots receiving additional K fertilizer.

The Depressive Effect of Grasses Upon the Concentration of NO_3^-

As the data presented in Table 2 show, the concentration of NO_3^- in tiles under grass was less than that under corn. These mean values, while statistically significant, do not tell the whole story. As can be seen from Figures 6 and 7, the concentration of NO_3^- in tiles under corn was much more variable than that under grass. The concentration of NO_3^- under grass was fairly constant throughout the growing season, whereas the concentration of the ion under corn was typically quite high in the spring and fall and only approached the concentration found in the tiles under grass during the middle of the season, when the growth of corn was greatest. The mean concentrations of NO_3^- in wells under grass and corn point out the disparity between the

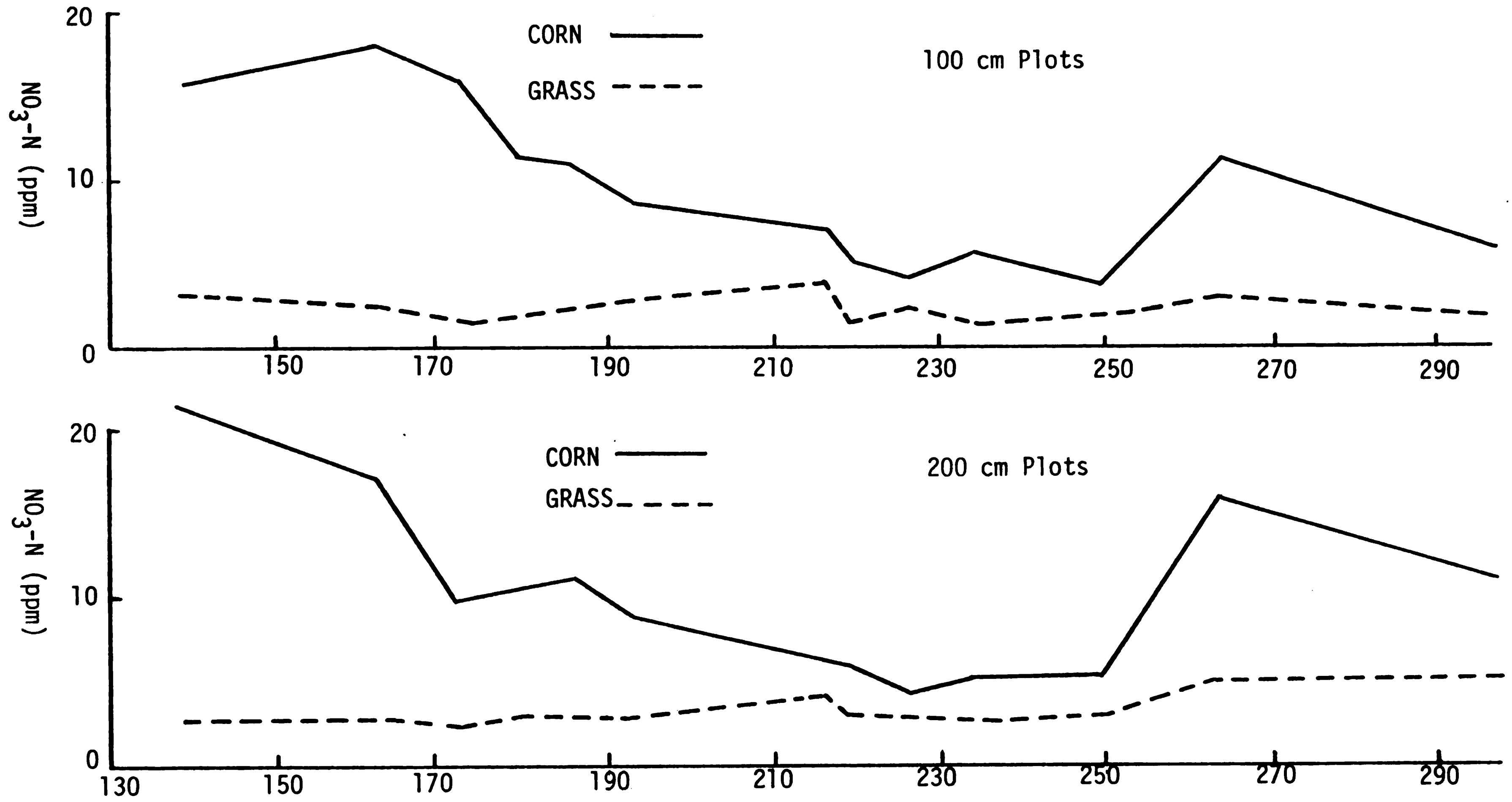

Figure 6. Concentration of NO_3-N in the tile drainage water under two crops at two irrigation rates in 1977.

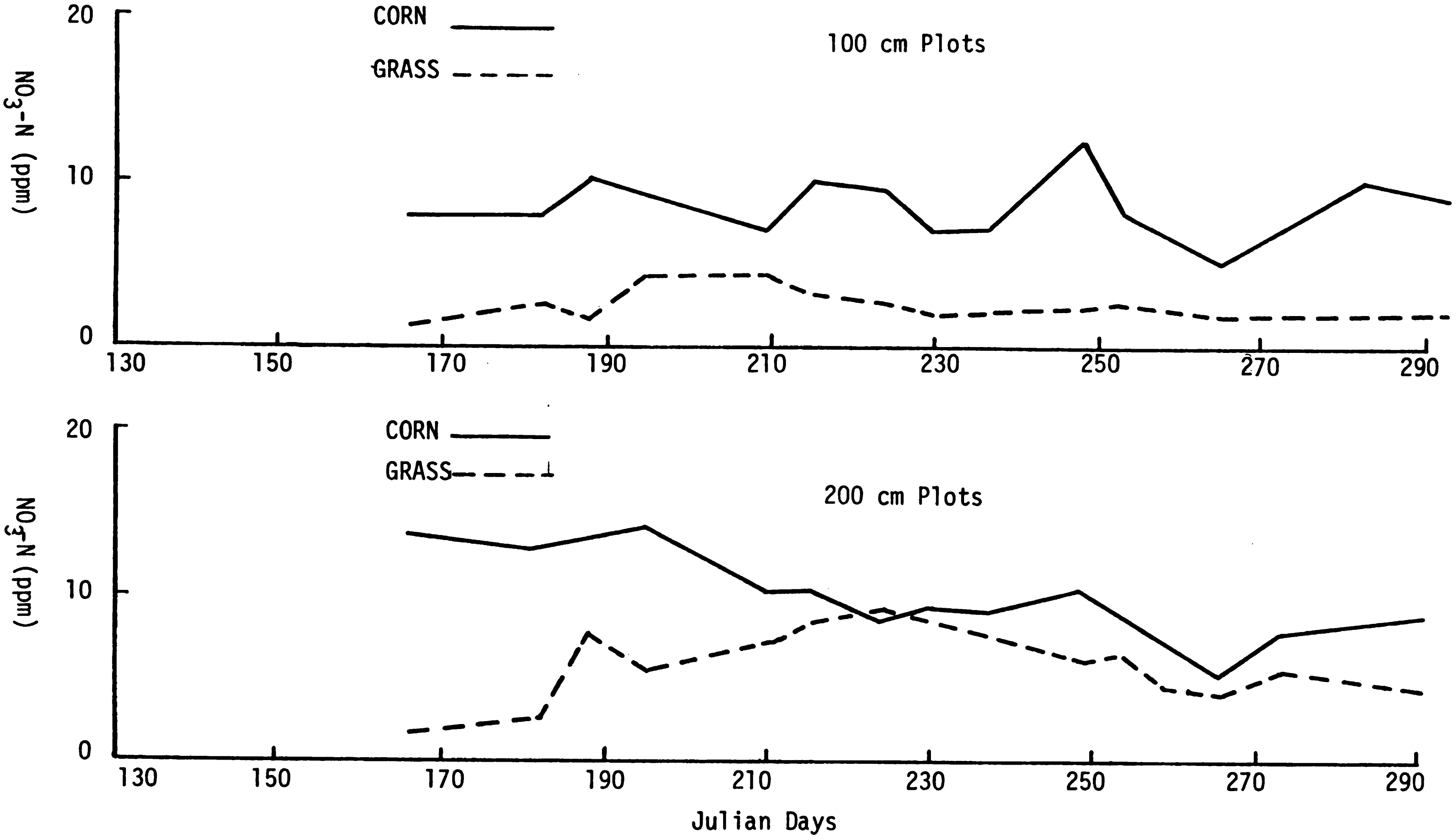

Figure 7. Concentration of NO_3-N in the tile drainage water under two crops at two irrigation rates in 1978.

two concentrations even more dramatically. In 1977, the mean concentration of NO_3^--N in water taken from wells located in grass plots was 1.04 ppm whereas in samples taken from wells in the corn plots the mean concentration was 11.15 ppm. By implication the soil water leached to the groundwater from soil cropped in corn contained substantially more NO_3^- than that from soil under grass.

There are four possible explanations for this disparity in the solution concentration of NO_3^-. (1) The corn may have simply taken up less of the nutrient than grass. (2) As mentioned in the literature review, many authors have suggested that nitrification inhibition acts to reduce the NO_3^- content below grasses. Perhaps this was the cause. (3) Theron (1965) has suggested that plants, specifically grasses, are capable of reducing the net mineralization of soil organic N. If mineralized organic N was a contributor to the soil solution N then such an inhibition mechanism by grasses could reduce NO_3^--N loss. (4) Soils cropped with grass have been shown to have a greater denitrification potential than soils under other crops. Perhaps enhanced denitrification under grass was the cause of the relatively lower NO_3^- concentration under grass.

As was pointed out earlier, corn took up more N than bromegrass. This is opposite of what one would expect if crop uptake was the cause of the disparity. In fact, the differences in mean NO_3^- tile water concentrations were more pronounced in 1977 than in 1978. And while corn took up more N than grass in both years, the difference was greater in 1977. Crop uptake is a highly unlikely explanation for the differences in tile water NO_3^- concentration.

I was unable to adequately evaluate the possibility that increased net mineralization of N was responsible for this disparity. There was substantially more organic N in the soil than either of the major inorganic N forms, NO_3^- and NH_4^+. Broadbent et al. (1977) using ^{15}N in a study of nitrification-denitrification relations in wastewater amended soils, has shown that mineralized organic N is leached from irrigated soil columns as NO_3^--N. Small changes in the net mineralization rate could easily surpass any affects by the transformations of NH_4^+ and NO_3^-. One method to evaluate net mineralization is to monitor the changes in organic N over the course of the season. This was done during the 1978 season. The changes in NO_3^- concentration which were to be explained were small, hence high sensitivity in discerning the concentration of organic N was required. The variability of organic N unfortunately is very large. For example, in order to detect a real difference in the concentration of the mean organic nitrogen of 25 μg N/g soil, one would have to evaluate 125 samples of soil for each treatment. Thus, while the tendency of the organic N from the surface horizon seems to indicate that the loss of organic N was greatest in the corn soil, the results for the entire profile are not statistically significant (Table 16). A circuituous indication of the relative mineralization rate could be inferred from the invariability and paucity of NH_4^+ in the soil profile (Table 17). NH_4^+ is the major product of mineralization. Small changes will tend to indicate small rates of mineralization. Generally, the distribution of NH_4^+ in the soil profile was homogeneous.

Table 16. Mean organic N concentration in soil sampled at three depths and cumulatively to 60 cm+.

Depth	Mean Organic N Concentration				
	Grass - 100	Grass - 200	Corn - 100	Corn - 200	LSD(0.05)
(cm)	(kg/ha)				
0 - 15	2433	2754	1952	2079	299
15 - 30	907	1420	1160	1142	NS
30 - 60	725	614	1002	1184	NS
Σ	4065	4788	4114	4405	

+Soil was sampled 10-77, 4-78, 9-78.

Table 17. Mean NH_4-N concentrations in soil sampled at indicated depths for three periods of the 1978 growing season.

Depth	Spring			Summer			Fall		
	Grass	Corn	LSD(0.05)	Grass	Corn	LSD(0.05)	Grass	Corn	LSD(0.05)
(cm)	(μg NH_4^+-N/g soil)								
0 - 15	1.9	1.2	(NS)	3.1	2.7	(NS)	4.4	1.7	(NS)
15 - 30	0.8	1.4	(NS)	3.3	2.0	(NS)	2.9	3.2	(NS)
30 - 60	1.3	1.1	(NS)	3.5	2.1	(NS)	2.9	2.2	(NS)
60 - 90	1.0	0.8	(NS)	2.7	1.6	(NS)	2.2	1.7	(NS)
90 -120	0.6	0.8	(NS)	2.6	1.7	(NS)	2.3	1.4	(NS)
120 -150	1.9	1.1	(NS)	2.9	1.9	(NS)	1.2	1.5	(NS)
150 -210	0.9	0.9	(NS)	3.2	1.5	0.9	2.2	1.5	0.5
210 -270	2.0	1.0	(NS)						

Though the subject is controversial in the literature, I think the evidence holds that some plants have a depressive effect upon nitrification, but that this caused the lower NO_3^- concentration here is doubtful. First, Broadbent et al. (1977) has stated that under sewage irrigation nitrification of NH_4^+ was essentially complete. Second, the changes in NH_4^+ concentration in the soil above the tile are not statistically significant. Furthermore, the trends of the average concentrations of NH_4^+ indicate enhanced nitrification under corn, not bromegrass. Lastly, the changes, in whatever direction, are too small to account for the measured differences in NO_3^- concentration.

Denitrification in field soils may be evaluated in many ways. Five of these approaches were used in the simulated wastewater study experimental site. Two of the estimates of NO_3^- loss used the concentration of Cl^- in samples in the irrigation water, tile drainage water and soil. Because NO_3^- and Cl^- have the same charge and hydrated radii, the physical behavior of the two ions in soils is virtually identical. Changes in the concentration of each ion in the soil due to physical causes, especially dilution and concentration due to wetting and drying, will be the same. Chloride was used to estimate the volume of NO_3^- leached from the site in calculating a N balance for the site. The method used was similar to that used by Pratt et al. (1978). Their method was based on the assumption that Cl^- is a conservative ion in the soil water of irrigated fields. They also assumed that Cl^- flowed concommitant with water through the soil profile. If these assumptions are true, then

$$V_I Cl_I = V_L Cl_L$$

where: V_I = volume of irrigation water
Cl_I = concentration of Cl^- in the irrigation water
V_L = volume of leachate water
Cl_L = concentration of Cl^- in leachate

The amount of NO_3^- lost in the leachate was calculated by multiplying the NO_3^--N concentration in the tile drainage with the leachate volume, V_L. There are several possible problems with this approach. (1) Natural sources of Cl^- would increase the estimate of leachate volume. Since the mean Cl^- concentration in the irrigation water was quite high (270 ppm) this was probably not a problem. (2) Anion exclusion would make the Cl^- move more rapidly in the soil than the carrier water. Since NO_3^- and Cl^- move identically, while the estimate of V_L may be in error, the amount of NO_3^- calculated by this method should be correct. (3) If a steady state in the flow of the ions in the leachate water has not been achieved, erratic or misleading results would be calculated. Obviously, a steady state is rarely found in the ion flux through field soils. Unfortunately, there are no criteria for what variation in the NO_3^- and Cl^- concentrations may be allowed for the steady state assumption to be invoked.
In their study, Pratt et al. (1978) stressed the importance of determining the variability of inorganic N in soil samples before a N study is established, but gave no comprehensive guidelines.

A soil N balance for each crop at each irrigation rate was calculated for the 1978 growing season. This balance is presented in Table 18. Soil accumulation (or loss) or N was calculated using the NO_3^--N and NH_4^+-N concentrations in the top 120 cm of the soil in spring and fall of 1978. "Leaching" losses were calculated using the method of Pratt et al. (1978). The calculated accumulation of inorganic N during the 1978 growing season was greater in the soil cropped in bromegrass than that in corn. The unaccounted losses of N were greater in grass soils than the corn soils.

The second use of Cl^- in field studies of NO_3^- movement is to calculate the ratio of the concentration of the two ions in soil samples collected at various depths in the soil profile. Focht (1978) in his review of the various methods to assay denitrification argued that this method was more qualitative than quantitative. He thought that the method could be used to indicate denitrification in soils where N balance studies found unaccounted N losses. Plots of NO_3^--N/Cl^- ratios in soils sampled at various depths in 1978 are presented in Figures 8 and 9. In both the corn and bromegrass plots, the concentration of NO_3^- dropped relative to the concentration of Cl^-. This loss substantiates the N loss in the soil profile indicated by the N balance study, possibly due to denitrification. The relative constancy of the ratios lower in the profile, especially later in the year, indicates that the steady state assumption, used in the calculation of the N balance, may have been valid.

We can expect that the soil at the experimental site was saturated much of the time. If this is true, then the readily available organic

Table 18. Estimated gains and losses of nitrogen by the soil in 1978.

	Grass				Corn			
	100 cm		200 cm		100 cm		200 cm	
Irrigation	152		305		152		305	
Fertilization	56		56		93		93	
Total Application[+]	208		361		245		398	
Plant Uptake	105	(50)[‡]	133	(37)	153	(62)	159	(40)
Soil Accumulation (Loss)	23	(11)	40	(6)	(16)	(-7)	5	(1)
Tile Loss	41	(19)	76	(21)	76	(31)	65	(16)
"Leaching"	37	(18)	102	(28)	70	(29)	180	(45)
Total Loss[§]	165	(79)	275	(76)	207	(84)	344	(86)
Unaccounted Loss[++]	43	(21)	86	(24)	38	(16)	54	(14)

[+] Sum of irrigation and fertilization gains.

[‡] Numbers in parenthesis represent N loss expressed as a percentage of total application.

[§] Sum of Plant Uptake, Soil Accumulation and Tile losses.

[++] Total Application less Total loss.

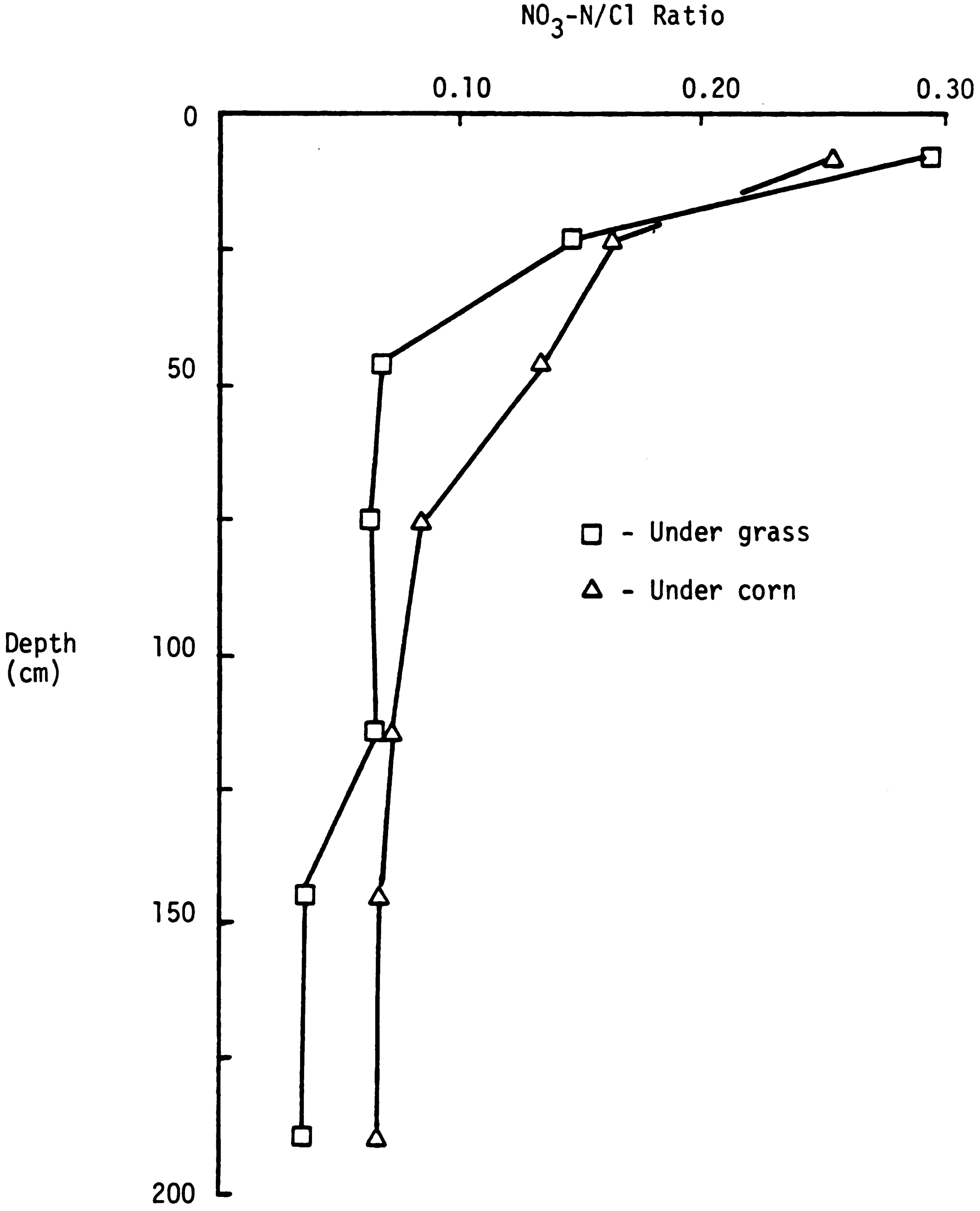

Figure 8. Mean NO_3-N/Cl Ratio in soil at indicated depths, Spring-1978.

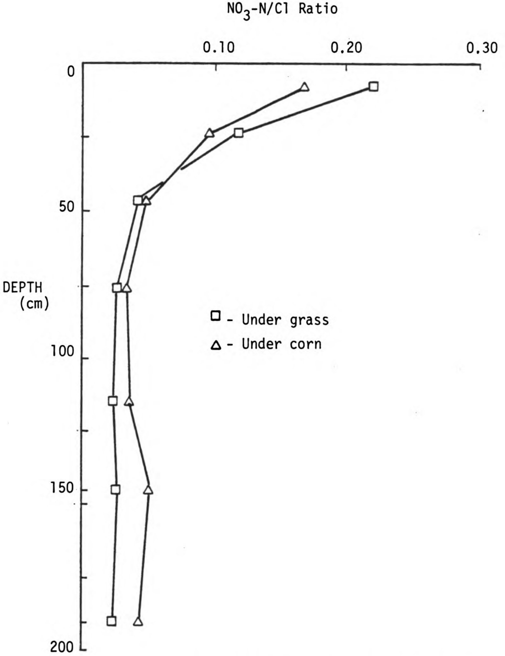

Figure 9. Mean NO_3-N/Cl ratio in soil at indicated depths, Fall-1978.

C would be a main determinant of denitrification rate. Hence, by a third method, several authors have shown a correlation between soil organic C and potential denitrification. With this in mind, the organic C content of the surface soils was determined. The results are presented in Table 19. The organic C content of the grass soil was greater than the corn soil.

Table 19. Mean organic carbon content of surface soil (0 - 15 cm) in 1978.

Organic Carbon Content				
Grass		Corn		LSD (0.05)
100 cm	200 cm	100 cm	200 cm	
%				
1.76	1.87	1.28	1.47	0.40

The correlation between denitrification and organic C is generally weak. A more direct (fourth) method is to incubate a soil saturated with a NO_3^- solution. Since assimilation of NO_3^--N by microorganisms in saturated soils is generally small, the disappearance of NO_3^--N is a measure of potential denitrification of the soil (Focht, 1978). The potential denitrification in the top 60 cm of the soil collected in the spring and fall of 1978 was determined. This data is presented in Table 20. The potential denitrification measured by this method was greatest in the grass soils. The amount of denitrification represented by the difference of the denitrification potential of the two soils was sufficient to explain the differences in N unaccounted for in the calculation of the N balance.

Table 20. Mean percent NO_3^--N lost after 7 days of incubation.

	NO_3^--N Loss				
	Grass		Corn		
Depth	Spring	Fall	Spring	Fall	LSD (0.05)
	%				
0 - 15	54	23	36	11	8
15 - 30	9	4	7	3	2
30 - 60	2	5	2	1	2

The measurement of N_2O production from soil following C_2H_2 injection is a fifth means of monitoring denitrification. In the summer of 1980 Phase I denitrification assays were conducted on five soil samples. Two samples were collected from the abandoned simulated secondary wastewater experimental site. One sample was collected in what had been a corn plot, another from what had been a bromegrass plot. As can be seen from Table 21 there was no significant difference in the denitrification rate in these two soils presented as "Corn 100" and "Brome 100" respectively. The denitrification measured in soil collected from an established bromegrass sod was larger than that in any other soil assayed. Two soil samples were taken from an irrigated corn plot showed different denitrification rates. The soil collected at mid-row ("Corn B") had a significantly higher denitrification than the soil sampled next to the corn stalk ("Corn A"). The implication, again, is that denitrification _in situ_ was greater in soils cropped in bromegrass than soils cropped in corn.

Table 21. Comparison of denitrification rates as determined by C_2H_2 inhibition.

Soil	Denitrification Rate
	µgN.g $soil^{-1}$. hr^{-1}
Bromegrass	11.74 a
Corn A	1.08 b
Corn B	2.51 c
Brome 100	4.35 c
Corn 100	1.82 bc

[+] Rates followed by same letter are not statistically different at the 5% level of probability as determined by the Mann-Whitney test (Snedecor and Cochran, 1967).

Thus, I discount nitrification inhibition and crop uptake as the major cause of the difference in NO_3^- concentration in drainage water. Although indications are that net mineralization of organic N was not responsible for the differences in NO_3^- concentration, the possibility cannot be discounted. Evidence from several lines of inquiry suggests that enhanced denitrification under grass may have been responsible for most of the differences in NO_3^- concentration under the two crops.

CHAPTER IV

SUMMARY AND CONCLUSIONS

Simulated secondary municipal effluent was applied by sprinkler irrigation to a tile drained soil cropped in bromegrass and corn. The effluent was applied at two rates, 100 and 200 cm/season. The efficacy of additional N and K fertilization was also tested.

The yield and nutrient concentration of the crops were measured. The nutrient concentration was determined in the soil, tile drainage water, well water and irrigation water. The flow rate of water in the tiles was monitored continuously.

1. The concentration of both phosphate and NO_3^- in water draining from tiles under grass was less than that under corn.

2. Between 50 and 75% of the irrigation water was lost through the tile drains.

3. There was a strong linear relation between the concentrations of K and phosphate P in the tile drainage water. The concentration of these ions in the tile water varied during an irrigation. This peak was roughly 1/2 hour before peak flow in the tile.

4. The concentration of NO_3^- in the tile water was found to be less than that calculated for the soil solution.

5. Mainly because its dry matter production was greater, the nutrient removal by corn was greater than that by bromegrass.

6. Additional N, but not K, fertilization increased yield and nutrient removal by corn.

7. The combination of additional N and K fertilization increased yield and nutrient removal by bromegrass.

8. The yield and nutrient removal of bromegrass, but not corn, was increased at the greater irrigation rate.

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