NUTRIENT MOVEMENT DURING WINTER RUNOFF FROM MANURE TREATED PLOTS

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ABSTRACT

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By

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Winter runoff from manure treated plots was observed for variations in water quality due to surface condition and length of buffer zone downslope from the manured area. Twelve plots were established on a Hillsdale, sandy loam soil with four percent slope. The surface conditions selected for evaluation were grass cover, corn stubble, and tilled surface. Each surface condition consisted of four plots, two control and two treated with 62.7 mton/ha of fresh dairy manure. The plots were 3 x 58 m with the treated area being 3 x 24. Runoff was collected at three points along the plot. The results presented here indicate that nutrient concentrations decrease as the runoff water moves downslope from the manured area. Two lengths of buffer zone were evaluated. Runoff collected at a location 12.2 m below the manured area showed a partial reduction in nutrient concentration and runoff collected 36.6 m below the manured area was of the same quality as control plot runoff.

The quality of runoff water was similar for all surface conditions when collected at the end of the plot. Indications were that the

grass cover was more effective in nutrient reduction within the manure treated area but, further research is needed for verification. The tilled surface plots reduced all four of the nutrient parameters compared in the runoff to background levels over a shorter distance than the other surface conditions compared.

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NUTRIENT MOVEMENT DURING WINTER RUNOFF

FROM MANURE TREATED PLOTS

By

Dale B. Thompson

A THESIS

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LIST OF SYMBOLS

COD	Chemical Oxygen Demand
TKN	Total Kjeldahl Nitrogen
T.S.	Total Solids
V.S.	Volatile Solids
NH_3	Ammonia (Concentrations given represent a combination of NH_4^+ and NH_3)
N	Nitrogen
T.P.	Total Phosphorus
A	Sample Site A
B	Sample Site B
C	Sample Site C
$\bar{x}$	Sample Mean
s	Sample Standard Deviation
*	Represents a significant difference in the data values being compared for a 95 percent confidence level (Table 6)
n	Represents no significant difference for a 95 percent confidence interval (Table 6)

CHAPTER I

INTRODUCTION

Public concern about deterioration of surface water quality in many agricultural areas has focused attention on surface runoff from agricultural land and animal confinement areas. Concerns about nonpoint source pollution from fertilizers and animal waste are based on the importance of nitrogen and phosphorus to eutrophication and the effects of pesticides and other chemicals on public health. The phenomenal increase in cost of commercial fertilizers has stimulated conservation and the desire for increased efficiency in utilizing the nutrients present in manure.

All land, regardless of use or management, contributes nitrogen and phosphorus to drainage or runoff water. Both nitrogen and phosphorus are present in runoff in soluble form and particulate forms. Nitrogen may enter the system dissolved in precipitation as well as being washed from surface vegetation. Phosphorus is associated with soil organic matter and clay minerals; most of the phosphorus in runoff is transported in these two forms. Limited amounts of phosphorus are, however, also transported as soluble orthophosphate. Future research must clarify whether the amounts of nitrogen and phosphorus added to surface waters as a result of land application of manure are significant in relation to other controllable and noncontrollable sources to justify action.

Recently some of the traditional methods for utilization and disposal of animal waste have been challenged by a growing number of environmentalists. Winter spreading of manure has been implicated as one of the less desirable methods of animal waste disposal. In order to avoid winter spreading, livestock producers would need sufficient storage to hold an entire winter's manure production. This would mean that costly new facilities for the handling and storage of manure would have to be installed. Several studies in Wisconsin have been undertaken to investigate the pollution potential of manure spread during the late fall, winter and early spring months so that a better evaluation of manure management alternatives could be made (Converse, et al.; Minshall, et al.; Witzel, et al.).

The many variables involved in this type of research often cause results and conclusions to be sitespecific. Slope and soil type are just two of the factors which change frequently and have a pronounced influence on management practices. Because of the large amount of variation between locations care must be taken in applying results to other areas. The extent to which we can extrapolate facts from one watershed or soil type to another must be considered in the development of future regulations and controls.

The goals of a land disposal system are to dispose of the waste and to optimize the use of nutrients available in animal waste, and at the same time, minimize the pollution potential. By using proper management and conservation practices the amount of runoff and erosion can be reduced thus reducing nutrient loss. Land application of animal waste is the most economical of the feasible means of recycling the nutrients found in manure. Experience and research have shown many times in the past that the addition of these nutrients improves soil fertility (Unger and Stewart, 1974). Frequently, however, these nutrients are applied in amounts in excess of what can be used by the growing plants. Present and future research must respond to questions concerning possible negative effects that accumulations, or movement (through runoff and leaching) of these nutrients, may have on the environment.

Thus there is a good chance that some of the organic matter or nutrients may be transported by rainfall or snowmelt to nearby surface water. Therefore, proper management is needed to minimize plant nutrient loss and to prevent surface water deterioration. This thesis is an attempt to clarify just what constitutes "proper" management.

CHAPTER II

OBJECTIVES

The major objective of this project was to evaluate the pollution potential from winter application of animal wastes to the land. In order to meet this objective three surface conditions were selected and compared. Water quality data from each surface condition were compared to determine the influence that surface condition may have had on the reduction of nutrient concentrations in winter runoff water.

A second objective was to evaluate the effectiveness of buffer zones downslope from winter spreading areas using selected nutrient concentrations to measure effectiveness. Buffer zones represent one of the few management alternatives available for reducing nutrient movement into surface waters through winter runoff. Two lengths of buffer zone were evaluated, one 12.2 m and a second 33.5 m downslope from the manure treated area.

A third objective was to simplify, if possible, the evaluation of runoff water quality. Chemical Oxygen Demand was used as a basis to compare relationships among the nutrients found in runoff water. Correlation coefficients from basic linear and curvilinear equations were used to compare pairs of nutrients and evaluate any possible relationship.

CHAPTER III

REVIEW OF LITERATURE

Land application has been selected as the most economical means of disposal of animal waste. Anytime animal waste has been applied to the soil surface without incorporation there is potential for nutrients to be transported by snowmelt or rainfall to surface waters. Nutrient content in runoff should be minimized for two very important reasons. First, to protect surface water quality and second, to prevent the loss of valuable plant nutrients. The quality of runoff from a treated field depends to some degree on the slope and the amount of infiltration which takes place. The infiltration rate is directly influenced by the soil structure and texture. The relative size of the soil particles and the proportion of sand, silt and clay determines the soil texture (Foth, et al., 1972). Poor soil structure (degree of aggregation) will decrease the amount of infiltration and increase runoff.

The quality and quantity of runoff is somewhat dependent upon the season of application and subsequent weather conditions. The physical condition of the soil (i.e., frost content, soil texture and structure) will affect infiltration and therefore the quantity of runoff (Storey, 1955). The quality of the runoff water will be influenced by the rate of application and the number of prior runoff events since the application.

Past research indicates that immediate incorporation results in the least amount of nutrient loss to the atmosphere and to surface water (Hensler et al., 1970). Land application of animal waste over prolonged periods will have both positive and negative effects on the soil. The application of animal manures usually increases the rate of infiltration but excessive application rates have been shown to decrease infiltration. The large percentage of organic matter found in manure is believed to be the major factor responsible for increased infiltration. Zwerman et al. (1970) found that a single application of 13.5 ton/ha of solid dairy manure increased soil infiltration by 27 percent in a continuous corn culture. Manure application did not influence infiltration where three of the four crops in a rotation were legumes because little plant material was returned to the soil. The build up of inorganic salts from excessive manure applications or irrigation water has been shown to decrease infiltration. Monovalent cations of sodium, potassium and ammonium tend to break down aggregates of soil structure and decrease infiltration rates (Unger and Stewart, 1974). The bulk density (mass per unit volume) is decreased with the addition of animal manure. Manure adds organic matter to the more dense mineral fraction of the soil making it easier to till, improves drainage and increases water-holding capacity. Solid animal manure will not always decrease bulk density, as recorded by Swader et al. (1972) but, it has been found beneficial in the majority of cases (Evan et al., 1974; Unger and Stewart, 1974).

Animal manure has been shown to increase hydraulic conductivity, decrease bulk density, increase water-holding capacity and increase aggregate stability (Unger and Stewart, 1974). All of these are beneficial to soil structure and crop growth. Improved soil structure will increase the infiltration rate and thereby decrease soil erosion and nutrient loss through runoff.

The season and method of manure application have been shown to have a large scale effect on the percentage of manure which remains in or on the soil. Midgley and Dunklee (1945) found that the amount of nitrogen lost in runoff from surface-applied manure during the winter was inversely related to the amount previously lost to the air by volatilization. Immediate incorporation with the soil has been shown to be the best way of reducing nutrient loss to the air and in runoff water (Hensler et al., 1970). In this study, as in most, fresh manure was applied to the surface without incorporation. Manure application on melting snow, or before a rainfall event, represents the worst possible case. Hensler et al. (1970) investigated the influence of the season of application on the nutrient losses from dairy manure. Winter application on frozen, snow covered ground resulted in a three-fold increase in the annual average nitrogen and phosphorus losses as compared with areas with no manure applied. Much of this loss resulted from one storm event which occurred only a few hours after the manure was applied to frozen soil. Minshall et al. (1970) found that the amount of nutrient getting into surface runoff from plots having manure incorporated into the soil in the summer was less than from check plots which received no manure. They also stated that the total amount of runoff from the check plots exceeded the average from all other plots by 78 percent. Indications were that this phenomenon became progressively worse each succeeding year. Depletion of readily degradable organic matter on these plots may have been the cause for the increase in runoff. This phenomenon seems to vary with the site and specific soil condition. Witzel et al. (1969) found that nutrient losses from winter and spring runoff from four small watersheds were the same even though some of the watersheds had winter spread manure while others did not. On one watershed, where the estimated fertilizer applications on a per acre basis were about double that of other areas, the loss of N and K was lower than other areas. Thus, it is evident that runoff characteristics will vary from one location to another independent of manure application and often due to variation in the general physical soil condition.

The reasons for land disposal are to dispose of waste and to optimize the use of nutrients available in animal waste, and at the same time, to minimize the pollution potential. By using proper management and conservation practices the amount of runoff and erosion can be reduced thus reducing nutrient loss. Ketcheson et al. (1973) observed that chopped corn stover reduced the amount of phosphorus lost through soil erosion. Soil phosphorus (P) loss was reduced by 65 percent and fertilizer phosphorus loss was reduced by 97 percent in runoff water from corn stover fields. The reduction of soil erosion and associated P in the runoff stover fields suggests that stover may reduce the impact of rain drops on soil and consequently result in less soil and P being brought into suspension.

Cross et al. (1971) found that excessively high rates of manure (260 T/acre) can have a negative effect on the physical soil structure; the highest rate of manure reduced the hydraulic conductivity of the soil. Large quantities of Na and K were present in the top layer of the soil decreasing the movement of the water through the soil. Lower application rates (40, 120 T/acre) had the effect of improving the physical condition of the soil by increasing the geometric mean diameter of water stable soil aggregates. The higher application rate went beyond the beneficial point.

In this experiment, fresh dairy manure was spread on frozen soil but several other methods of handling manure are currently in use and will be mentioned briefly. Hensler et al. (1970) worked with four methods of manure handling and storage. They found that on the average fresh, fermented or stacked, and anerobic liquid dairy manure gave similar increases in crop yield but were superior to yields from aerobic liquid manure. Most aerobic manure treatment has been all but ruled out because of the reduction of available plant nutrients and the high cost of operation. Winter-applied manure resulted in higher losses of N, P and K than spring-applied manure for all methods of handling.

Spreading fresh manure year round requires a regular labor input but makes use of conventional equipment available at a lower capital cost to the operator. Interruptions in daily hauling throughout the year due to inclement weather or growing crops are major drawbacks in the operation of this system. Stacking of manure for temporary storage has proved to be a feasible alternative but required good management to prevent excessive leaching and surface water pollution. Undesirable features of stacking include objectionable odor at the time of spreading and certain limits on the season of spreading. The best time for spreading winter storage may conflict with other farming operations at the busiest time of the year. Hensler et al. (1970) says that fermented (stacked) manure ranks high as a fertilizer for corn because of the nutrient recovery by the crop and the flexibility in application time. When stacked manure is applied to corn ground after the spring thaw, scheduling conflicts may arise where time before planting is limited. Time is an important factor which must be considered along with nutrient conservation and pollution potential for the various methods of handling animal waste. The management system chosen must fit well in the farm operation schedule as well as meet requirements for maintaining environmental quality.

The pollution potential of winter spread manure depends, to a large extent, on the physical state of the soil. Frost structure has much to do with winter infiltration capacity of soils. Storey (1955) uses two terms to describe the structure of frozen soil for the North Central region. Concrete frost structure has many thin ice lenses, many small ice crystals and is extremely dense. Concrete freezing has been observed most frequently in cultivated fields or areas with sparse vegetative cover. It often occurs in compacted soils or soils settled by a heavy rain. Honeycomb freezing is characterized by a loose porous structure easily broken into pieces. It is found most frequently in meadows and pastures. Storey concluded from available data that concrete type frost formed in practically all soils which have been largely depleted of humus and in compacted soils irrespective of the humus content. As little as one inch of concrete frost prevents infiltration of rain or melting snow while infiltration may be good in the case of honeycomb freezing.

Frozen soils may greatly increase the potential for surface runoff by restricting infiltration from snow melt. Midgley and Dunklee (1945) concluded that in determining nutrient losses from manure applied to snow covered fields, the amount of snow was more important than physical characteristics of the land. Adverse weather conditions (e.g., snowmelt or rainfall) usually cause increased nutrient loss when they occur during or shortly after manure application. Klausner et al. (1974) investigated surface runoff losses of inorganic nitrogen and total soluble phosphorus from fields spread with dairy manure. Their results indicated that manure disposal during active thaw periods can result in increased nutrient losses. Losses were minimized when manure was applied and then covered with snow, melting at a later date. Klausner's 35 metric ton/ha rate of application, applied to frozen soil and then covered with snow, resulted in nutrient losses that differed little from areas that received no manure. On control plots nutrient losses from a field or watershed will originate primarily from residual soil fertility (Klausner et al., 1974), leaching of organic material on the surface (Timmons, 1970) and from precipitation.

The amount of plant residue left on the soil and other management practices have been shown to have an effect on runoff quality. Zwerman et al. (1974) investigated two systems of soil management. One involved the removal of all plant residue at harvest time and is denoted as poor management. The other involves the reincorporation of plant material with the soil (good management). Corn harvested for silage is classified as poorly managed soil since all of the plant residue is removed from the field. Corn harvested for grain allows for the reincorporation of the plant when the soil is plowed. In Zwerman's study the addition or subtraction of organic residues on the same plots has persisted for sixteen years. This investigation showed that substantial reduction in nutrient losses (N,P) can be produced by lowering the loading rate and/or improving the soil structure. Even when spreading under adverse weather conditions, a two-thirds reduction in nitrogen and phosphorus losses to the environment was achieved by maintaining soil structure by return of plant residues.

Several researchers have stated they believe that well managed soil and surface conditions (i.e., plant residue or vegetation) will have an effect on nutrient losses from frozen soil. Zwerman et al. (1974) presented data showing reduction of N and P in runoff due to corn plant residue on the soil surface. Young and Mutchler (1975) indicated that there was only a slight difference in nutrient losses from manured and unmanured corn plots but higher nutrient losses were found from manured alfalfa plots than unmanured alfalfa plots. The indication is that certain surface conditions are more likely to retain nutrients from manure than others. Upon investigation Young and Mutchler found very little difference in the thawing rates from manured verses unmanured alfalfa plots. Many experiments have been performed in order to correlate the amount of nutrients lost with varied application rates. Most of the results show that only excessively high rates of manure application result in high nutrient losses in runoff. This experiment and several others indicate that there are variations in runoff from different surface conditions with equal amounts of manure.

Management practices also influence the volume of water that will infiltrate or run off a field. Manure and plant residue have both been indicated as having effects on runoff. Converse et al. (1975) observed the average runoff from plots for three years and reported that runoff from the check plots was significantly greater than from manured plots. Similar observations have been made by other investigators (Witzel et al., 1969, and Young and Mutchler, 1975). The number of runoff events which occur on the research plots and the intensity of each event must be considered. Doyle et al. (1975) concluded that the concentrations of the nutrients investigated (N,P,K and Na) were dependent on the number of rains previously leaching the manure, but was independent of the total rainfall and the amount of runoff collected.

Rainfall intensity is a decisive factor in the movement of pollutants in runoff as observed by several researchers (Miner et al., 1966 and Swanson et al., 1971). The calculated average rainfall intensity does not reveal short periods of very intense rainfall which may cause significant erosion and increase the concentration of nutrients in the runoff. Each runoff event will be influenced by the source of the runoff water and the duration of precipitation or snowmelt. Both will affect the movement of material and also the amount of infiltration which can take place. Short periods of intense rainfall are likely to cause more runoff than longer light showers.

It appears probable that temperature and moisture conditions in the manure and soil have a strong influence on the release of nutrients into runoff (Doyle et al., 1975). As indicated earlier, some researchers have found that accumulation of organic matter from previous applications of manure on soil may affect moisture content and temperature which in turn affect runoff. The season of application affects runoff quality in two major ways. The first and most obvious is whether the soil is frozen. A second influence is that of temperature and moisture content of the manure on the surface. High temperatures will tend to cause N to be lost through volatilization (Adreano et al., 1974). High temperatures will increase evaporation and tend to dry out the manure on the surface. Runoff events which follow will be affected by the amount of water the manure is able to absorb before runoff begins.

CHAPTER IV

EXPERIMENTAL PROCEDURES

The experimental area, composed of twelve plots, was established in the Fall of 1975 to collect runoff water from areas where manure was spread on frozen soil. The test area was located on a moderately well drained loam textured glacial till (classified Hillsdale, Sandy Loam). Dimensions of the plots were 3 x 58 meters (10 x 190 feet). Three sample sites were located on each plot at specific distances down slope. The first, sample site A, was located 12.2 meters (40 feet) from the upper end. The second, sample site B, was located 36.6 meters (120 feet) from the upper end or 24.4 meters (80 feet) downslope from sample site A. The third, sample site C, was located at the lower end of the plot. Figure 1 illustrates plot arrangement and location of sample sites.

Fresh dairy manure was applied on January 10, 1976 to the upper 24.4 meters of the plot at the rate of 62.7 mton/ha (28 tons/acre). Stanchion barn manure, with a moderate amount of straw bedding, was applied to the plot uniformly with a pitchfork. The manure was applied on a 10 cm (4") snow cover while temperatures were below freezing. Every attempt was made to imitate current practice in dairy-farming. During the following two days approximately 18 cm (7") of snow fell and covered the manure. Natural precipitation was the only source of runoff water throughout this experiment. The first significant runoff event occurred thirty-one days after application.

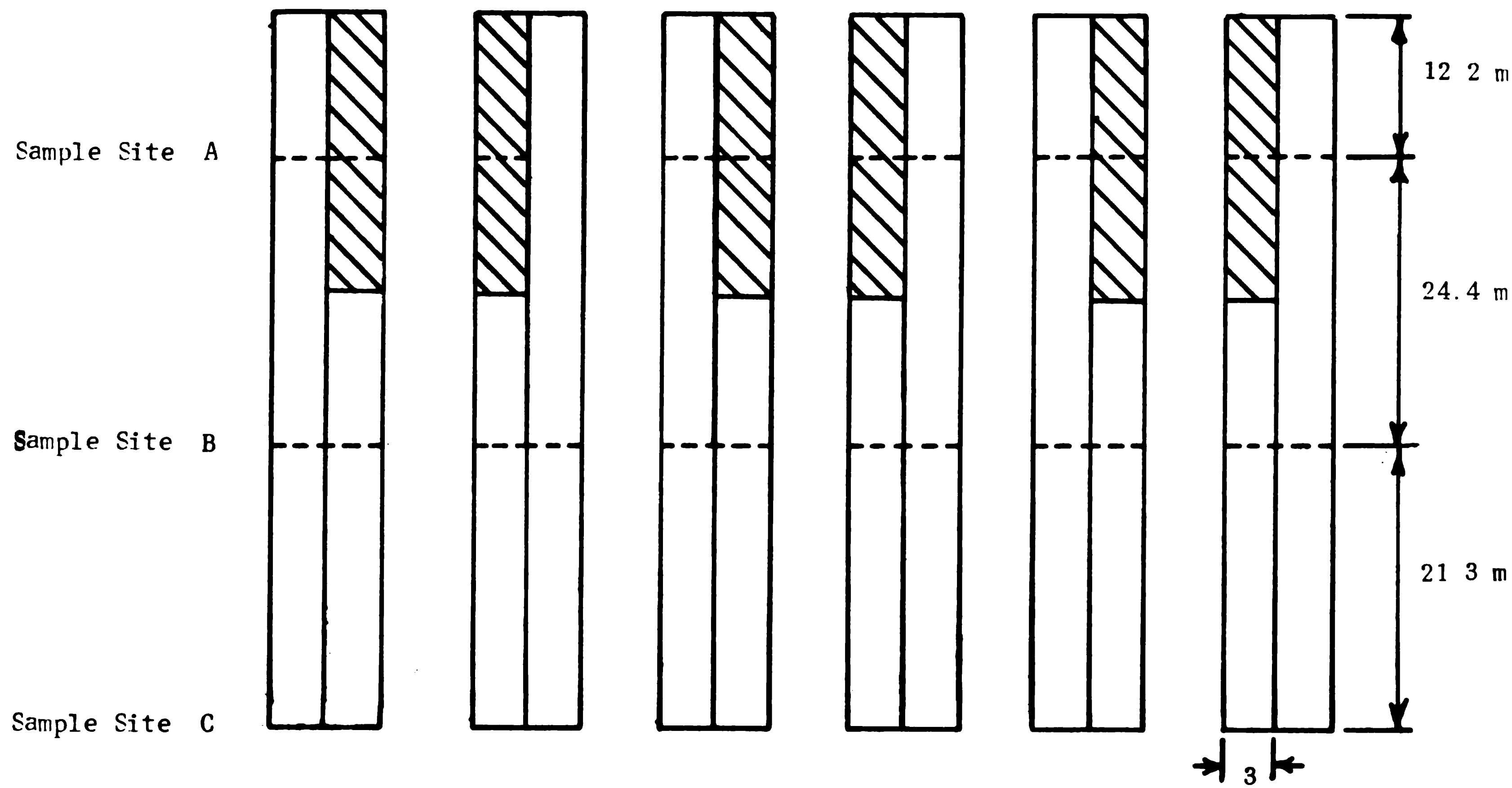

FIGURE 1 Plot Arrangement and Sample Sites

= Manure Treated Area

Samples were taken from 208 liter (55 gallon) reservoirs after mixing for one minute. All samples were refrigerated at 4° C until laboratory analysis was completed.

Description of Surface Conditions

Three surface conditions were tested and each was replicated twice (both with and without manure) making four plots of each surface condition. Grass cover was chosen for a surface condition to simulate effects of winter runoff on year round vegetative cover. Orchard grass was sown with a grain drill at the rate of 34 kg/ha (30 lb/ac). A fairly uniform cover was formed on the plots except on areas where cutting and leveling operations had removed the topsoil.

Field corn was planted across the slope in 93 cm rows (46,950 plants/ha) in preparation for the other two surface conditions. Manure was applied prior to the tillage operations at the rate of 33.6 mt/ha (15 t/ac). The test area was sprayed prior to emergence with a mixture of herbicides to control weeds. In the fall the corn was chopped for silage leaving about 20 cm (8") stubble. Four plots were left in this condition and hereafter will be referred to as corn stubble.

The third surface condition was created by working the remaining corn stubble down with a discing operation. The area was worked over twice, first parallel to the slope and the second time perpendicular to the slope. This operation was done to simulate a fall tillage operation which often takes place on the farm. The tilled field was assumed to be a significantly different surface condition since the corn stubble was dislodged and partially covered up with soil.

Description of Collecting Apparatus

In order to collect a representative sample from a runoff event, reservoirs were installed to hold the water until a sample could be taken. Barrels 208 liters in volume were buried in the ground with approximately 8 cm of side wall above the ground. Sections of wood plank were attached to the bottom of each barrel to prevent hydraulic pressure from pushing it up out of the ground. The plank dimensions were 4 x 25.4 x 122 cm (2 x 10 x 48 in.). The plank protruded 30 cm on either side of the barrel providing more than enough force to counteract the flotation force. The plank was attached with two steel straps welded to opposite sides of the barrel rim (Figure 2). The barrels were lined with plastic liners (up to 4 mm thick) to prevent interference from metal rust in the water samples. Problems were encountered at first with water seeping in between the barrel and the liner but, this was remedied by completely sealing the area around the sample inlet tube. The outer seal was made with roofing cement. All other seals in areas exposed to runoff water were sealed with silicone calking. The barrels were covered with a removable dome-shaped metal cover to keep animals and direct precipitation out.

Each plot was bordered by galvanized sheet metal strips. The sheet metal strips were 20 cm wide and placed in the soil vertically 10 cm deep with 10 cm above the soil surface. Each strip was 3 meters long and placed so that the uphill end of the sheet overlapped on the inside of the next to prevent water from escaping. The metal strips were placed in a groove made in the soil and then pushed or driven in, if necessary, with a hammer and a block of wood. The groove was made with a 51 cm diameter disc, with a thickness of 5 mm, mounted on a weighted tool bar. The tool bar was mounted on a three point hitch and was weighted with 181 Kg (400 lb) of tractor weights. The sheet metal strips were placed in the groove immediately after it was made. This was done to minimize the amount of debris that could fall into the groove before the strip was introduced. Also, due to some variation in soil moisture, the groove may tend to cave in on itself. On several occasions rocks were encountered and the disc rose up out of the ground and over them. This required digging with a shovel to remove the rocks and refilling before the strip could be installed.

Several different methods of collecting a portion of the total runoff from the plot were tried. The first method consisted of a 10 cm diameter plastic tile line with the upper one-third cut out laying across the plot, perpendicular to the plot length (Figure 3). The tile was buried so that the upper edge was flush with the ground surface and was extended through the plot border to the collection barrel. The runoff water was to flow into the tube until it filled up and then overflow on the downslope side. The plastic tile had what was called a "flow limiter" to restrict flow into the barrel. The flow limiter consisted of a round disc made of sheet metal with a 5 mm diameter hold drilled in it. It was placed inside the tile and sealed with silicone calking. The flow through the hold varied with the head in the tube but averaged 19 liters (5 gallons) per hour. The purpose of the flow limiter was to get a representative sample over several hours of runoff. Without it, the barrel would have filled up with the initial flow rather than getting a composite or mixture of all the water passing the collection point.

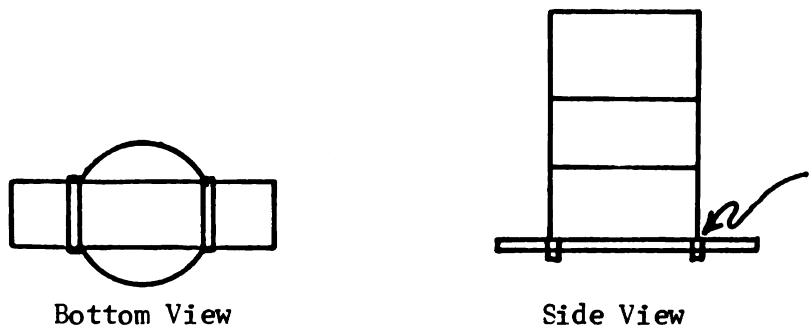

Figure 2 Sample Reservoir Barrels and Anchoring Plank

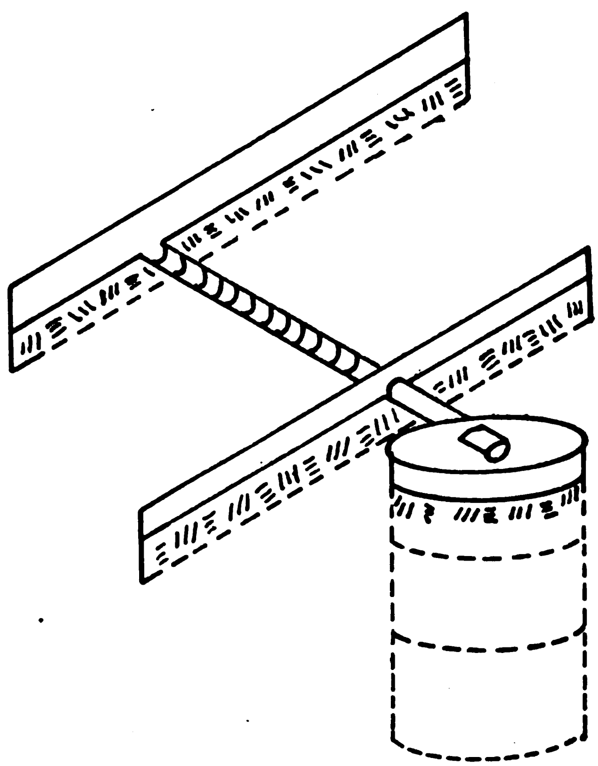

Figure 3 Sample Collection Appartus ; Site A

This method of collection was found to have several drawbacks. The major problem encountered was that water tended to follow the outside edge of the tile and run out of the plot underneath rather than into the tile. The small hole in the flow limiter also plugged with particulate organic matter occasionally. The diameter of the hole was increased to allow large particles to enter.

A second method of collection was used at the B locations. A small depression in the soil surface was made across the plot perpendicular to the plot length. The depression was approximately 2.5 cm deep and 7.5 cm wide. Plastic tile 10 cm (4 inches) in diameter extended through the plot border and 12 cm into the depression running across the plot. The tile had a flow limiter sealed in the plot end and was connected to the sample barrel at the other. This method proved to be more successful because it offered less obstruction of flow and allowed for collection of a portion of the runoff water while the runoff continued past that point uninterrupted. This factor may have had a large effect on the value and significance of the data collected downslope at site C. The same problem of hole plugging arose at this site and the holes were then also enlarged. In order to prevent water from seeping around the tile at the border, a sheet metal collar was devised to fit the outer diameter of the tile. The collar was sealed to the tile with silicone calking and cemented with concrete into place, in line with the plot borders.

The third method of sample collection was used at the C locations. At the lower end of the plots the border tapered off into a "V" shape. At the base of the "V" there was a 10 cm diameter tile connected to three barrels in a series. There was not a flow limiter at this point, all of the runoff entered the barrels. All of the runoff water from the plot entered through the tile and mixed in the first barrel. When the first barrel was full it overflowed into the second and the second into the third. All runoff in excess of capacity overflowed into a drainage ditch from the third barrel in the sequence. The three barrels at the end of the plot were connected in series near the top of each by a 5 cm diameter plastic tube (Figure 4).

One problem, unique to the barrels at site C, was the settling of large amounts of eroded soil on the bottom. Resuspending the extra soil sediment required thorough agitation. The amount of sediment appeared to be heavier in the first barrel of the sequence. This would seem reasonable because heavier particles would tend to fall out of suspension after the velocity of flow was reduced by entering the barrel. The runoff water mixed slowly in the first barrel until it was full and then began to overflow, dropping the particles in suspension as the velocity decreased. Proper agitation and thorough pumping, as described above, assured that sediment did not accumulate from one runoff event to the next.

Sampling Procedure and Analysis

Samples for laboratory analysis of runoff water were taken from the barrel reservoirs adjacent to the plots. The barrel capacity was approximately 170 liters (45 gallons) when full to the inlet tube. The barrels containing runoff water were agitated thoroughly using a gasoline-powered centrifugal pump. Samples were very rarely taken if the barrel contained less than 40 liters of runoff water and then designated "small volume samples." The barrels were mixed for one

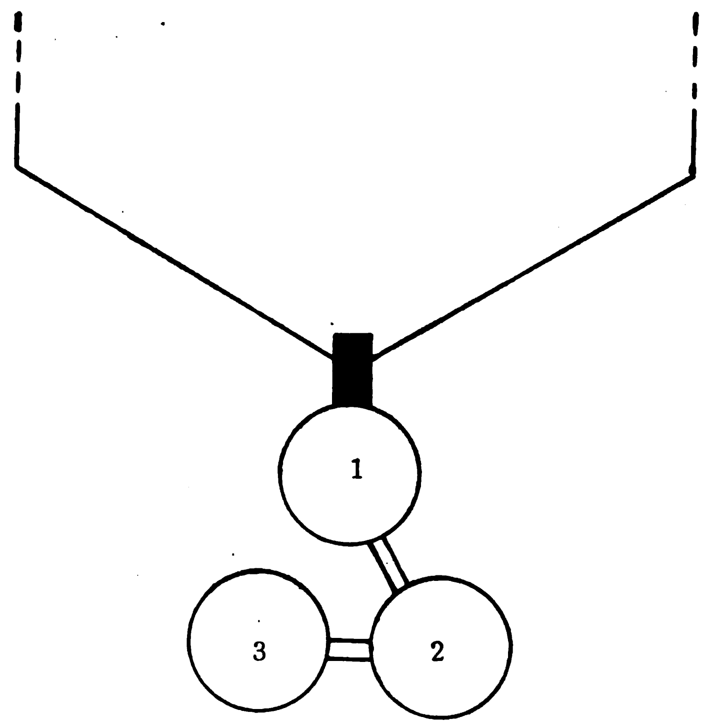

Figure 4 Sample Collection Apparatus, Site C

note: Samples taken from first barrel in series.

minute with the pump and then the sample was taken by submerging the 300 ml sample bottle into the center of the barrel. The sample bottle was extended down into the barrel by means of a bottle holder. Sample bottles were marked according to plot number, sample site, and the date. A small head space was left in the sample bottle to allow for shaking to get the solids back into suspension. The samples were then transported to the laboratory where they were refrigerated at 4° C until laboratory analysis was completed.

The parameters of runoff selected for analysis were based on their importance to surface water quality. Nitrogen and phosphorus are generally limiting factors in aquatic systems and are therefore critical in the rate of eutrophication. Chemical Oxygen Demand was selected to represent the oxygen demand that the runoff would exert on the surface water. The COD value represents a maximum amount of oxygen demand, and this procedure allowed for processing of a large number of samples between events. Volatile solids was selected as an indicator of dissolved and suspended organic compounds. Total Solids was used as an indicator of the total residue present in the runoff. Total residue included dissolved salts, organic materials, and soil particles which were carried by the runoff water.

The analysis of total and volatile solids involved taking the weight of a porcelain crucible four times on a Mettler balance. The Mettler balance allows the weight to be read to the fifth decimal place. The clean dry crucible was weighed and labeled weight A. The dish was then filled with a 65 to 70 ml portion of the runoff sample, re-weighed and labeled B. The porcelain containers were then oven dried at 103° C for 24 hours, cooled in a dessicator, weighed and labeled C. To arrive at the value for total solids in parts per million mg/l the following formula was used:

$$\frac{C - A}{B - A} \times 10^6 = mg/l$$

The analysis for volatile solids continued on past this point with the same porcelain container being placed in a furnace at 550° C for 20 to 30 minutes. The container was allowed to cool and a final weight was taken and labeled D. To arrive at volatile solids in ppm, the following formula was applied:

$$\frac{C - D}{B - A} \times 10^6 = ppm$$

A portion of the sample was measured for specific conductance. The instrument used was calibrated with a standard .05 Molar potassium chloride solution which has a specific conductance of 6.66 micromhos/cm. The instrument was then zeroed for distilled water. The Chemical Oxygen Demand test (COD) indicates the quantity of oxidizable organic matter in a sample. The test was run according to the procedure in Standard Methods for the Examination of Water and Wastewater (thirteenth edition) using potassium dichromate as the strong chemical oxidant.

Total Kjeldahl nitrogen measures the amount of ammonia and organic nitrogen present in the sample using procedures outlined in Standard Methods. Sample aliquots to be used for analysis of TKN and total phosphorus were prepared with a strong acid digestion. Mercuric oxide, potassium sulfate and concentrated sulfuric acid were added to the sample. Immediately after the samples were allowed to cool a precipitate appeared in the bottom of the flask. The precipitate was forced back into solution by a series of pH changes with 10 molar sodium hydroxide and 2 Molar potassium iodide. The distilled water blanks were subjected to the same digestion. The samples were then analyzed by the ascorbic acid method and color was developed. The light transmittance was measured with a Beckman spectrophotometer (R) at 880 nanometers. A series of problems in sample preparation developed, but were corrected by the pH changes. Sulfides and silica are known to interfere in concentrations greater than 10 mg/1. Any silica not already digested was removed with a millipore filter (R). The samples turned orange occasionally, probably due to formation of a mercury compound. The addition of potassium iodide for the pH change eliminated the mercury ions by complexing them with the iodine.

The ammonia concentration was determined using an Orion selective ion reference electrode. The samples were pretreated by shaking in .01 N hydrochloric acid to get maximum NH_4^+ in solution. The solution was then made strongly basic and the reading was taken. Readings were compared with a known standard to determine actual ammonia concentration.

CHAPTER V

RESULTS AND DISCUSSION

The methods used for analysis for runoff water have not been fully established. Many problems occur in the chemical analysis of runoff due to the lack of homogeneity and interference from particles of eroded soil. Organic matter from both the manure and the plant material from the cover crop of the previous year find their way into the samples. Large particles such as these make it difficult to get a uniform or homogeneous aliquote from the sample for each of the laboratory tests to be run. Improved methods had to be found which would give a truer picture of the runoff content. Some methods require that an aliquot be digested with strong chemicals. Problems of soil interference may develop when the digested sample contains soil. Any of the laboratory problems encountered may tend to mask the true concentration of the element in question. I feel however, that we have mastered the more serious problems encountered in the laboratory analysis. Improvements are yet to be made in sample collection methods and preparation. Variation between replicate tests on the same sample were created by the lack of homogeneity within the sample. The runoff data has been arranged in tables. The mean values presented in the tables have large standard deviations associated with them. The number of samples used to calculate the mean values in Tables 1-4 are given below Table 1. The mean values will be utilized only to illustrate trends in nutrient concentrations; conclusions will be drawn from the data after further statistical analysis which is presented in Table 6 on page 45. Most of the results analyzed here, unless otherwise stated, are based on a 0.05 level of significance.

Chemical Oxygen Demand (COD)

The data were divided into treated and control plots and then further broken down and separated into the three surface conditions. The first step was to look at the gross mean and standard deviation for each site (i.e., A, B, C) for all three surface conditions together. Mean values for COD are found in Table 1. The purpose of comparing COD in a composite form was to evaluate the general effect of buffer zones on reducing movement of organic materials downslope from the manured area.

The mean treated COD values decrease from A to B to C respectfully as the runoff moves downslope. The standard deviations are very large suggesting wide variations between sample locations and events. The mean COD values for all control plots show a reverse trend and increase as runoff progresses downslope. Comparison of the composite COD values for site C indicates a higher concentration of COD for control plots than treated plot runoff. One-way analysis of variance--which will be discussed in a later section--indicated that there was no significant difference between treated and control plot runoff at site C (see Table 6). The COD values from control plots are considered to be background levels of COD present in the runoff. If the control plot COD value is subtracted from the treated plot runoff COD value that result should be the approximate value of COD you would

TABLE 1

CHEMICAL OXYGEN DEMAND

COD (mg/l)

	Composite of All Three Surface Conditions					
	Treated			Control		
	A	B	C	A	B	C
Mean Value	389.9	156.0	67.8	47.5	77.9	91.9
Std. Dev.	267.1	139.4	52.1	32.7	65.5	98.5

	Treated			Control		
	A	B	C	A	B	C
Grass Surface						
Mean Value	155.80	81.83	65.75	42.33	57.83	69.50
Std. Dev.	59.25	14.81	8.96	32.13	9.54	12.02
Corn Stubble						
Mean Value	499.86	182.17	70.63	51.00	84.25	56.00
Std. Dev.	267.24	61.03	78.86	38.18	61.37	59.25
Tilled Surface						
Mean Value	586.38	186.38	66.58	46.00	44.67	122.50
Std. Dev.	210.50	179.69	41.06	41.27	30.89	116.97

	Number of Samples[1]					
	Treated			Control		
	A	B	C	A	B	C
Grass Surface	(10)	(6)	(4)	(3)	(6)	(2)
Corn Stubble	(7)	(7)	(8)	(2)	(4)	(5)
Tilled Surface	(8)	(12)	(12)	(5)	(4)	(8)

[1]The numbers in parenthesis indicate the number of samples used to calculate the mean values in Tables 1-4.

expect to get in runoff due to the presence of the manure.

There are three major factors which may contribute to the decrease in mean COD values as runoff moves downslope on treated plots. First is the dilution effect created by the addition of runoff water due to snow melt or precipitation. The treated area extends down 24.4 m from the top of the plot. Site B is located 12.2 m downslope from the manured area. This leaves a large area for dilution of the runoff before it gets to sample site B. The runoff is even further diluted by the time it reaches site C.

The second factor important in reducing COD as the runoff moves downslope is adsorption nutrients onto the surface of the soil particles. The finer the soil texture the greater the surface area and greater the active area of adsorption. This is the most important factor because it prevents the contents of the runoff from entering surface waters diluted or otherwise. Some infiltration and nutrient adsorption may take place even on frozen soils. By this mechanism the nutrients can be retained for the benefit of plant growth. This mechanism was discussed in greater detail in another section.

A third mechanism is that of settling and screening. Settling of particles of organic matter takes place when the velocity of flow is reduced by the irregular soil surface or some obstruction (i.e., tractor tracks, low puddle areas or crop ridges). Screening is done by plant material growing or uprooted on the surface which tends to physically remove particles from the runoff and retains them. Plant roots, stems and leaves are mostly responsible for this type of resistance to flow.

The mean values of COD were grouped by treatment and by surface condition. Grass and tilled control plot runoff both showed an increase in average COD with downslope distance. Corn stubble averages showed an increase from A to B and then a decrease to C. One-way analysis of variance indicates that there is no significant difference between any of the sites (A, B, or C) for control plots based on COD.

The treated plots show a decrease in average COD as you move downslope for all three surface conditions. The one-way analysis of variance test indicated these differences are significant at the 95 percent confidence level. The COD decrease is dependent on the three factors listed earlier. The mean values of COD seem to indicate that there is a difference between surface conditions at site A based on Chemical Oxygen Demand. The average COD at site B for grass plots appears to be lower but the analysis of variance indicates no significant difference between surface conditions for treated plots at site B.

Total Solids (T.S.)

Total Solids are determined by evaporation of the liquid portion of the sample and taking the weight of the residue. The mean values for total solids are listed in Table 2. It is very hard to draw conclusions from these data because of the extreme size of some standard deviations. The amount of total solids present in runoff is not completely a function of treatment of control although treatment does have an effect. Factors which affect soil erosion appear to be the major influence on values for total solids. Soil particles made up the major portion of the total residue. The amount of soil residue

TABLE 2A

TOTAL SOLIDS (mg/1)

	Treated			Control		
	A	B	C	A	B	C
Grass Surface						
Mean Value	537.4	428	385	465	461	352
Std. Dev.	268	212	54	268	177	172
Corn Stubble						
Mean Value	756	1720	745	494	457	882
Std. Dev.	389	2521	574	747	357	945
Tilled Surface						
Mean Value	635	438	1289	409	1582	2006
Std. Dev.	213	316	1190	392	864	1862

TABLE 2B

VOLATILE SOLIDS (mg/1)

	Treated			Control		
	A	B	C	A	B	C
Grass Surface						
Mean Value	239	146	169	157.5	144	98
Std. Dev.	71	57	57	85	44	18
Corn Stubble						
Mean Value	386	355	212	382	154	191
Std. Dev.	211	267	119	74	61	119
Tilled Surface						
Mean VAlue	470	191	167	179.5	296	309
Std. Dev.	155	149	93	91	111	143

was high and extremely variable and therefore, masked other solids present in the runoff. I believe that the amount of soil in our samples is not representative of what is lost in a normal situation. Soil loss may have increased due to interruption and manipulation of flow by the sampling apparatus.

Certain trends can be seen in the mean values of total solids and volatile solids. These trends should not be assumed valid unless further research gives reinforcement due to the extreme degree of variation and large standard deviations. Mean values for grass plot total solids show a decrease as runoff moves downslope. The opposite trend is seen in the corn stubble and tilled surface where the total solids increase as the runoff moves downslope.

Volatile Solids (V.S.)

The average value of volatile solids on the grass plots decreases with downslope distance for both treated and control plots. The standard deviations indicate the values are less variable than those for total solids. In calculating volatile solids the soil fraction does not interfere or mask the results since V.S. is only the amount of ignited organic material. Average volatile solids tend to decrease moving downslope for treated corn stubble and tilled surfaces. Trends in control plot runoff are not clear for volatile solids. Corn stubble control plot runoff data indicate a decrease from A to B with a small increase from B to C. Control plots from the tilled surface show an increase in volatile solids with downslope distance. As mentioned above, control grass plots show a decrease in V.S. with downslope distance. There appears to be three different patterns developed for the three surface conditions.

Total Kjeldahl Nitrogen (TKN)

The average value of Total Kjeldahl Nitrogen for treated plots for all three surface conditions shows a decrease in TKN as you move downslope (Table 3). In general, the average for control plot runoff TKN shows a decrease from A to B and then the mean is unchanged from B to C. Background levels of TKN from all control plots fall within the range of 12-16 mg/l when all sites for each surface condition are averaged. When the control values are separated by site the corn stubble and tilled surface appear to have a larger mean TKN than the grass plot runoff at site A. The grass may be the factor which has reduced the amount of TKN. The mean TKN values are also higher for treated corn stubble and tilled surface than for treated grass plot runoff at site A. Here again there is some form of nitrogen adsorption and/or absorption taking place, probably due to the grass cover.

Ammonia (NH_3)

The average values for ammonia for both treated and control runoff show a decrease in concentration as you move downslope. The ammonia concentrations for corresponding sites are almost equal for the treated corn stubble and tilled surface runoff. Concentrations were lower for treated and control grass plots for site A and B than for the other two surface conditions. The ammonia was probably absorbed by the grass cover or soil. Background levels of ammonia from all control plots were higher than those detected at site C of all treated plots. This indicates that there is probably no ammonia getting to site C from the manured area. In summary, the corn stubble and tilled surface

TABLE 3

TOTAL KJELDAHL NITROGEN

TKN (mg/l)

	Treated			Control		
	A	B	C	A	B	C
Grass Surface						
Mean Value	4.95	1.88	.70	1.07	1.52	.90
Std. Dev.	3.55	2.10	.41	.50	1.36	.71
Corn Stubble						
Mean Value	18.03	4.72	.39	3.15	1.53	.70
Std. Dev.	15.18	4.08	.32	.49	.92	.60
Tilled Surface						
Mean Value	17.17	3.47	.35	1.00	.93	.35
Std. Dev.	14.11	4.72	.33	.35	.53	.35

TABLE 4

AMMONIA CONCENTRATIONS

NH_3 (mg/l)

	Treated			Control		
	A	B	C	A	B	C
Grass Surface						
Mean Value	23.47	14.54	12.83	10.63	14.60	5.3
Std. Dev.	12.38	19.98	9.69	5.63	14.67	
Corn Stubble						
Mean Value	41.88	24.62	10.23	20.33	14.40	14.00
Std. Dev.	23.88	13.61	6.31	4.04	7.16	7.48
Tilled Surface						
Mean Value	42.25	18.35	10.99	24.28	11.15	11.72
Std. Dev.	27.04	9.84	7.46	15.81	5.58	5.07

runoff had similar amounts of ammonia in runoff from treated and control but the grass plots have comparatively lower concentrations.

Phosphorus (P)

Phosphorus is usually found in close association with soil particles and organic matter. Losses from soil occur through crop removal, leaching, and mostly through erosion. The major loss of phosphorus associated with soil was through soil erosion. A larger percentage of total phosphorus was lost however, in particulate organic matter from manure and plant material. The phosphorus associated with organic matter is bound by ester linkages and will not be separated without some chemical reaction--either by microbes or laboratory analysis. Because of the close relation of P and organic matter, the trends in movement of P should be similar to those observed for COD, which is a measure of the amount of oxidizable organic matter present. Similarity may diverge when the influence of soil erosion becomes more dominant. In the analysis of winter runoff, 59 percent of the samples with phosphorus concentrations greater than 1 mg/l were taken directly from the manured area on treated plots at site A. Only 18 percent of the samples with over 1 mg/l were from treated B locations. The remaining 23 percent of the samples with concentrations greater than 1 mg/l were from sites B and C of the control plots due mostly to erosion of the soil. Only one sample was found to have a P concentration greater than 1 mg/l at a C location. There are no set limits at present for phosphorus levels entering surface water. The amounts of phosphorus in flowing water with only a slight loading rate are generally less than 100 mg/cu.m (.1 mg/l) total phosphorus (Vollenweider, 1968 and Keup, 1968). Most phosphorus concentrations which have been monitored depend on waste discharged, for the most part, and levels of several hundred mg/sq m are not uncommon. Serious cases exceed 1000 mg/sq m (1 mg/l). Assimilation rates of phosphorus and up-take by stream biota are rapid, but a majority of the load is carried downstream in dissolved and particulate suspension to the receiving lakes or reservoirs of reduced flow velocities (Wetzel, 1975).

The mean values for total phosphorus are presented in Table 5. The highest concentrations of total phosphorus usually occur at site A in the treated plots. This was due primarily to the large amounts

TABLE 5

PHOSPHORUS CONCENTRATIONS

P (mg/l)

	Treated			Control		
	A	B	C	A	B	C
Grass Surface						
Mean Value	1.73	.63	.70	1.05	.63	
Std. Dev.	.90	.14	.18	.78	.22	
Corn Stubble						
Mean Value	1.59	1.18	.47	.81	.87	.38
Std. Dev.	.83	.80	.25	.48	.56	.14
Tilled Surface						
Mean Value	1.91	.75	.85	.65	.49	.47
Std. Dev.	1.06	.61	.61	.11	.31	.32

of organic matter in the runoff which can be deduced from the COD values. Several high concentrations were recorded on control plots on occasion. These high concentrations of phosphorus occurred coupled with higher-than-normal values of total solids and COD in control plot runoff.

One-way analysis of variance indicates that there is a significant difference between the sites (A vs. B vs. C) on treated grass and tilled surface plots. No significant difference in P concentrations appeared on the corn stubble plots (Table 6). The only other comparison which indicated a significant difference between P values was on line 19 where treated A was compared with control A runoff from the tilled surface. When treated B and control B are compared (line 20) there is no significant difference. The conclusion is that the tilled surface was successful in reducing P concentrations at site B.

The majority of the comparisons made in Table 6 indicate that there was no significant difference in phosphorus concentrations attributable to variations in surface condition.

Correlations Between Test Parameters

One of the objectives of this research was to define the parameters and methods which would be most valuable in evaluating winter runoff. One way in which to simplify runoff analysis would be to reduce the number of tests performed on each sample. I had hoped to find correlations between test results which would allow development of an equation to predict the concentration of one parameter from the concentration of another. This would allow prediction of levels of a parameter of runoff with reasonable accuracy without having to do a time consuming laboratory analysis. The coefficients used were obtained from the values of all twelve sample sets. To accomplish this one must begin with an analysis of a parameter which is considered to be reliable and gives consistent results with a minimum of laboratory time. The laboratory procedure which was chosen to be the basis of the comparisons is Chemical Oxygen Demand (COD).

Results from tests for COD were compared with Total Solids (T.S.) and then with Volatile Solids (V.S.). Because I was interested only in the correlation between the two parameters and not the magnitude of the value I considered both treated and control plots together. Values from each sample for COD and T.S. were entered into a program for linear regression analysis. The data and results were grouped by sample date and will be referred to as sample sets. Each correlation coefficient was derived from the values of COD and T.S. for a specific date. Occasionally more than one sample set will be grouped to get a correlation and this will be referred to as a composite set. Table 8 in the Appendix lists the correlation coefficients derived from the linear regression for both Total Solids and Volatile Solids plotted against COD. First we will consider COD versus Total Solids. Correlation coefficients show a high degree of correlation for the first three runoff events. The first three events occurred on three consecutive days of snowmelt. The source or cause of the runoff event seems to have a direct effect on the degree of correlation between T.S. and COD. During snowmelt events the runoff is released in a manner which usually results in a low runoff velocity and good correlation. Events created by rainfall have a negative effect on the correlation of T.S. and COD. Hence, the theory that T.S. is increased during

rainfall events by the impact of raindrops which dislodge and carry material along in the runoff. Total Solids seem to be highly variable and dependent largely upon plot conditions during rainfall events. The amount of erosion and organic material in runoff depend to some extent on the rainfall intensity. During a very intense rain there is a greater chance of erosion and movement of organic material because runoff will exceed infiltration. Intense rainfall will tend to cause runoff to form small riverlets or rills where the velocity of moving water will increase and therefore increase the amount of material being carried downslope.

In event number four the source of runoff was still snowmelt but correlation between COD and T.S. dropped off drastically. One possible reason for the decrease in correlation was that the soil surface was in a saturated condition with the frozen layer approximately one inch below the surface. There was no infiltration due to the frozen layer. According to Schwab et al. (1966), "Areas where loose, shallow topsoil overlies a tight subsoil are most susceptible to erosion." The same reasoning can be applied here although the situation is slightly modified. The soil in a saturated condition as found in event number four gave higher total solids values and lower degree of correlation with COD.

The remainder of the sample sets (5 through 12) were taken after rainfall events. The soil became completely thawed several days after sample set four and remained unfrozen. The correlation between T.S. and COD was very low for sample sets 5-8 and then increased during events 9-11. Rainfall seems to be the most important factor which drove the correlation down in 5-8. However, in sample sets 9-11 there were also rainfall events which got a higher correlation. The total amount of precipitation leading up to or acting as the source for the series of events is similar for both cases (i.e., 9-11 and 5-8). The intensity of rainfall was higher for events 9-11 which would normally lower correlations (see Table 10 in the Appendix). The variables which have changed over the series of events (5-11) were the amount of time elapsed since the soil thawed and the temperature. The moisture content of the soil also had a chance to stabilize. The air temperature, and most likely the soil temperature, had increased over the elapsed time. In order to determine the cause for the variations in correlation between T.S. and COD one needs more detailed information on temperature, rainfall and rainfall intensity. Because of the general data recorded we can only theorize why the correlations broke down after the snowmelt events. The fact that the correlation between T.S. and COD is good for snow melt events is valuable. From these coefficients I deduce that soil erosion due to rain drop impact, soil moisture content, and other runoff characteristics has caused the breakdown of correlation between the T.S. and COD. Therefore, the eroded soil must have caused some kind of interference. To eliminate interference of soil minerals and other inorganic materials one can analyze the sample for volatile solids.

The amount of volatile solids can theoretically be predicted by substituting a value for COD into the equation for the line from the linear regression analysis of COD vs. V.S. The correlation between COD and V.S. is very high for sample sets 1-3. In sample set number four the correlation again drops off as it did in linear regression for T.S. The large amount of soil minerals in the samples from

event number four reduced the accuracy for most determinations. For sample sets 5-12 the same trend is seen as in analysis using T.S. but the values of correlation are much higher for events 5-8. The improvement in correlation of V.S. vs. COD compared with T.S. vs. COD was assumed to be due to elimination of soil particle interference which was high during that period of events. The correlation between COD and V.S. in the linear regression analysis was high enough to derive a reasonable equation for snowmelt events. The first three events, which were snowmelt events, were grouped into a composite set for analysis (see Figures 5 & 6). The program for linear regression analysis utilized the least squares method of determination. The constants given below were calculated for the straight line equation where x is the independent variable COD, and y is the dependent variable V.S. or T.S.

For COD vs. Volatile Solids:

$$y = 85.1 + 0.663\,x \qquad \text{when,} \qquad a(0) = 85.1$$

$$a(1) = 0.663$$

$$r = 0.981$$

For COD vs. Total Solids:

$$y = 91.8 + 0.886\,x \qquad \text{when,} \qquad a(0) = 91.8$$

$$a(1) = 0.886$$

$$r = 0.943$$

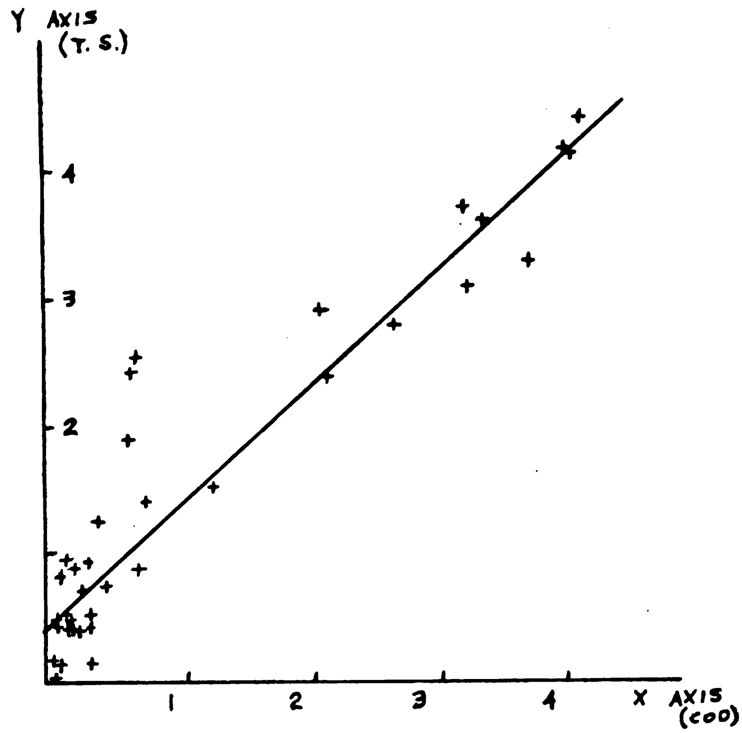

FIGURE 5 LINEAR REGRESSION ANALYSIS (Y= a(0) + a(1)X)
COD vs Total Solids.

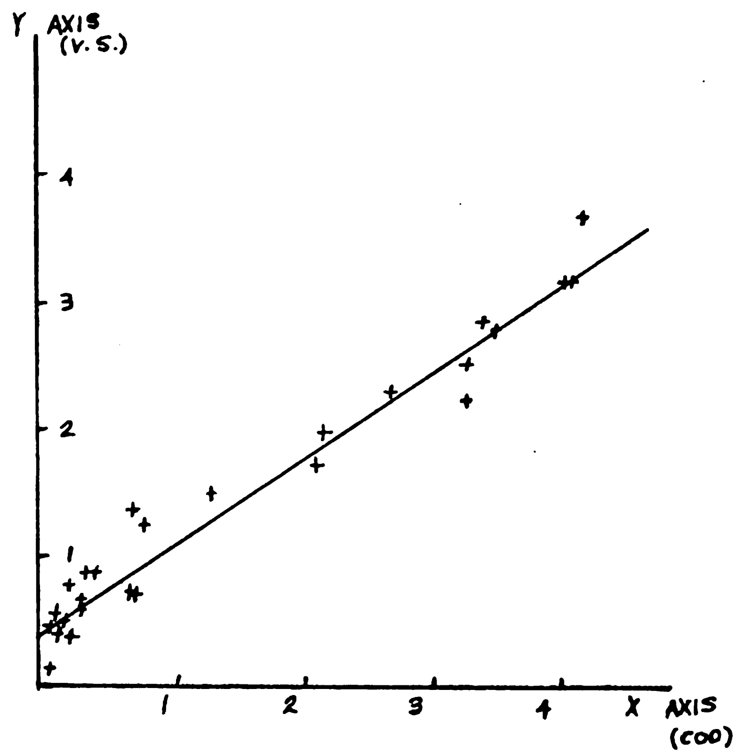

FIGURE 6 LINEAR REGRESSION ANALYSIS (Y= a(0) + a(1)X)
COD vs Volatile Solids.

Effect of Surface Conditions

Nutrient concentration from control and manured plots were compared to determine the influence that each of the three surface conditions had on reducing specific nutrients in runoff. The results from each control surface condition were compared to establish the amounts of naturally occurring nutrients and organic material in runoff water. There was no significant difference found between control plots for the three surface conditions based on analysis of variance. The nutrient concentration levels from control plots will be referred to as background levels. I have already compared treated versus control values for the same surface conditions in the discussion of mean values. The one-way analysis of variance test can be used to support observations and trends developed from looking at the mean values. Obvious trends can be seen looking at mean values but, because of the extreme standard deviations found one must use some other method of data analysis to clarify the results. Treatment and sample site data were grouped and compared in several combinations. Each combination is listed in Table 6 and sample sites are illustrated in Figure 1.

There are three different types of combinations which will serve to compare the results. Runoff samples from the three sample sites on each plot were compared (i.e., Grass A vs. Grass B vs. Grass C). Each sample site was compared with the corresponding one for all three surface conditions (i.e., Grass A vs. Corn A vs. Tilled A). In the third, each treated site was compared with the corresponding control site (i.e., Treated A vs. Control A). In Table 6 the stars (*) illustrate which nutrient analysis shows a significant difference

TABLE 6

ONE-WAY ANALYSIS OF VARIANCE

Combinations	Parameters TKN	NH_3	COD	T.P.
A vs. B vs. C				
1. Grass Treated	n	*	*	*
2. Grass Control	n	n	n	n
3. Corn Treated	*	*	*	n
4. Corn Control	n	*	n	n
5. Tilled Treated	*	*	*	*
6. Tilled Control	n	*	n	n
Grass A vs. Corn A vs. Tilled A				
7. Treated	n	*	*	n
8. Control	n	*	n	n
Grass B vs. Corn B vs. Tilled B				
9. Treated	n	n	n	n
10. Control	n	n	n	n
Grass C vs. Corn C vs. Tilled C				
11. Treated	n	n	n	n
12. Control	n	n	n	n
Grass Plots				
13. Treated A vs. Control A	n	n	*	n
14. Treated B vs. Control B	n	n	*	n
15. Treated C vs. Control C	n	n	n	n
Corn Plots				
16. Treated A vs. Control A	n	n	*	n
17. Treated B vs. Control B	n	n	*	n
18. Treated C vs. Control C	n	n	n	n
Tilled Plots				
19. Treated A vs. Control A	*	*	*	*
20. Treated B vs. Control B	n	n	n	n
21. Treated C vs. Control C	n	n	n	n

between groups that are entered in the combination indicated at the left. An "n" illustrates the fact that there was no significant difference for that specific nutrient analysis and combination.

A star on Table 6 indicates that I have rejected the null hypothesis which stated that the groups of values compared were the same under that particular set of circumstances. The stars are based on a 95 percent confidence level. Therefore, there is a 5 percent chance of making a Type I error by rejecting the null hypothesis. A Type I error involves the rejection of a null hypothesis which is true. That is, there is a 5 percent chance that I have indicated differences are significant when they are not. Each group used in the combination consists of all the data (snowmelt and rainfall runoff) gathered for that nutrient at the particular site in question.

First the plot data were broken down according to surface condition. There were four grass plots, two were control plots and two were treated. The values for COD from treated grass plots were lumped together into three groups. Each group contained the values from one of the sample sites (i.e., A, B or C). One-way analysis takes into consideration the amount of variation between values within the groups described above as well as the variation between the groups.

The first combination compares the three sample sites on the plot (A vs. B vs. C). By comparing sample sites on treated plots we can determine if the observed change in nutrient concentrations are significant. Comparing sites on control plots indicates that background levels remain constant for the most part, as you move downslope on the plot. Line 1 indicates that there is a significant difference in COD and ammonia between sample sites on treated grass plots.

TKN appears to be the asme for all sites on the treated grass plots. On grass control plots, background levels of nutrients are similar for all sites (line 2).

Line 3 indicates that there is a significant difference between the three sites on treated corn stubble, based on 3 nutrient parameters in Table 6. Sample sites on control corn plots are similar for amount of COD and TKN but, ammonia values show some variation between sites. In line 5, tilled surface treated plots are indicated to have significantly different levels of nutrients at each sample site. Tilled control plot sites are similar; based on TKN and COD. Ammonia levels vary here just as in the corn plots above.

The purpose of this first combination was to determine if nutrient concentrations changed significantly from one site to the next. The results show that treated plots have a significant change in nutrient concentration as you move downslope and that control plots generally remain the same except for ammonia. Ammonia is found at very low concentrations on control plots and by nature is very unstable, therefore, random fluctuations are not unusual.

The second type of combination compares respective sample sites on each of the three surface conditions. The combination (Grass A vs. Corn A vs. Tilled A) compares the runoff from each to determine whether there was a significant difference in runoff concentration between surface conditions. Line 7 indicates that on treated plots the surface conditions yielded significantly different concentrations of ammonia and COD at site A. Line 8 shows control plots to be similar based on TKN and COD but, again ammonia values show some variation between surface conditions at site A. Lines 9 and 10 illustrate no significant difference between surface conditions at site B for both treated and control. Lines 11 and 12 indicate the same phenomena at site C for all three surface conditions. This analysis then indicates that nutrient concentrations are essentially the same by the time runoff reaches the B location on all three surface conditions. Therefore, all three surface conditions are capable of similar nutrient removal within the buffer zone. Nutrient concentrations show a further reduction at site C but, appear to be the same level on all three of the surface conditions.

The third type of combination in Table 6 compares the treated sites with the control sites for the same surface condition. Using the three nutrient parameters we can determine if the nutrient level is significantly different on treated and control plots. If they appear the same, that means the surface has removed nutrients from the runoff to the point where it is equal with that of background concentrations on the control plots. Each surface condition will be discussed separately.

Grass Plots

Line 13 shows that treated and control plots at site A are significantly different based on COD, but similar for NH_3 and TKN. Line 14 indicates that there is still a significant difference in COD between treated and control at the B locations. This shows that COD has not yet been reduced to background levels on the treated plots at B. Line 15 illustrates that all three parameters are similar on treated and control plots at site C. Therefore, nutrient concentration reduction had been accomplished when runoff reached that point.

Corn Stubble Plots

Lines 16 and 17 indicate that sites A and B are similar for treated and control plots based on TKN and ammonia. COD values indicate that there is still significant difference between treated and control runoff at site B. Line 18 illustrates that there is no significant difference between nutrient levels for treated and control plots at site C. Therefore, the corn stubble was successful in removing nutrients to a point, similar to that of control plot concentrations.

Tilled Surface Plots

Line 19 indicates that there is a significant difference between tilled control and treated plots at site A. All three parameters indicate nutrients are higher on treated than controls at site A. Lines 20 and 21 indicate that there is no significant difference in nutrient concentration on treated and control plots at sites B and C. On the average, all three parameters were reduced to background levels by the tilled surface by the time runoff reached the B location.

Based on the results presented above each of the surface conditions were successful in reducing nutrient concentrations by the time runoff reached the C locations. I feel that COD is the most consistent and reliable analysis of the three parameters considered here. For the grass and corn stubble surfaces, significant amounts of COD still existed in runoff collected at site B. This means that the treated plot runoff contained more COD than control plots at site B. TKN and ammonia have been shown to be reduced to a point similar to that on control plots at site B. Nitrogen and phosphorus are readily adsorbed by soil particles. Organic material is not chemically bound to the soil as nitrogen

and phosphorus. Organic material may break away with raindrop impact or runoff water. The tilled surface was the only surface which appeared to have reduced all four parameters to background levels at site B (line 20). The tilled surface may be more effective in nutrient reduction as it appears here, but, a definite conclusion cannot be drawn from the limited amount of data presented. More research is needed to determine if the tilled surface has a greater capacity to reduce nutrients in runoff. The data presented here shows that there was a significant difference between runoff from treated and control plots and that nutrient reduction was accomplished by all three surface conditions by the time runoff reached sample location C.

Climatic Factors Effecting Runoff Quality

Total and volatile solids were analyzed by sample event to determine the difference climate may have made for snow melt and rainfall events. The source of runoff for the first four events was snowmelt. The remaining events (5-12) were rainfall events (see Table 10). Mean values for total solids show an increase in the amount of total residue for later runoff events (5-10). The most probable cause for the increase in total residue is soil erosion caused by rainfall impact. Water is released from snowmelt at a slower rate and lacks the impact of raindrops. Therefore, it is reasonable that the amount of soil erosion and total residue would be less for snowmelt events. The mean total solids show an uneven but constant increase through the rainfall events and then drops off considerably during the last two events. The results here indicate a real difference in total solids due to the source of runoff.

The source of runoff appears to have little effect on the values of volatile solids. The volume and/or intensity plays an important role in determining the amount of organic material moving in the runoff. Mean values for volatile solids from all events appear to be random with no pattern between rainfall and snowmelt events.

Total solids on the other hand was affected by the source of runoff. Earlier in the section on total solids the influence of raindrop impact was found to increase the amount of total solids during rainfall events. More soil particles were observed in samples from rainfall events due to soil erosion. The test for volatile solids eliminated interference from soil particles and therefore, was not affected by the source of runoff water. It is believed that an increase in rainfall intensity will increase the amount of soil erosion and increase the potential for movement of organic matter. Data from a nearby rain gauge are given in the Appendix (Table 10). The data given are the total accumulation of precipitation for the period prior to when each sample set was taken. Instantaneous rainfall intensities are needed to give the meaningful input to runoff analysis and these were not available for this experiment.

COD was analyzed by one-way analysis of variance comparing each surface condition separately for the two types of runoff events to determine if there was a difference in runoff quality. The data were broken down by surface condition to determine if the source of the runoff event had an effect on COD (Table 10 in the Appendix). COD was selected to illustrate the differences created by climatic factors because it was in my opinion the most representative analysis. The magnitude of the concentrations was such that treated and control plots were distinctly different. Of all the parameters, COD showed the least amount of overlap in concentration values which created significant differences between the locations sampled. Some of the other parameters had concentrations within a smaller range which offered less resolution for comparison. Problems arose in this method of comparison where data were limited to the point where no valid conclusions could be drawn. However, groups that were analyzed provide some valuable information. In general, data gathered during both snowmelt and rainfall events indicate that there is a significant difference between control plots and the treated A and B sites. This indicates that a significant amount of organic material is moving on all surface conditions for both types of runoff events. The tilled surface runoff appears to be different in that COD is the same for treated and control at site B indicating that less organic matter is moving on this surface condition. No conclusive statement can be made however based on the limited data.

A second method along the same lines was comparing treated A with treated B and treated B with treated C for each surface condition and type of runoff event separately. This gave the indication that the reduction in COD concentrations were significant as runoff moved downslope for both types of events. This was true for the grass and corn stubble surfaces. The tilled surface gave different results again consistant with those comparing treated and control plots. There was a significant difference between sites A and B on the tilled plots for both types of events, but sites B and C appear to be the same for both types of events. This indicates then, that the amount of organic matter in the runoff at site B is the same as at site C which was described earlier as being equal to background levels on tilled plots. The tilled surface appears to be reducing levels of organic matter in runoff more effectively then the other two surface conditions based on one year's data.

CHAPTER VI

SUMMARY AND CONCLUSIONS

Winter runoff from manure-treated plots was studied for variations in water quality due to three surface conditions (grass, corn stubble and incorporated stubble) and the length of buffer zone downslope from the manured area. The results presented here indicate that nutrient concentrations decrease as the runoff water moves downslope from the manured area. Nutrient concentrations on control plots were similar at all sample sites located along the slope; there was no significant difference between control plots of the three surface conditions. The extent to which dilution affected nutrient concentrations is unknown. Adsorption of nutrients by soil particles and the physical processes of settling and screening are probably the major factors responsible for nutrient reduction in the manured plot runoff. Based on the data gathered at this point, a buffer zone of 36.6 meters (120 feet) is effective in removing nutrients from runoff downslope from a manured area on a Sandy Loam soil.

Nutrient concentrations show a partial reduction at site B after a short buffer area. Ammonia and TKN values indicate that runoff concentrations were reduced to background levels for all three surface conditions at collection site B. Nitrogen was removed more rapidly than materials which contributed to COD. Amounts of COD remained higher than background levels at site B for runoff from both grass and corn stubble plot surfaces. There was no way of detecting if the material contributing to the COD originated in the manured area. The runoff may have picked up organic material as it flowed downslope from the treated area.

Average nutrient concentrations in the runoff from manured plots were less than or equal to those found on control plots at sample site C. The buffer zone was shown to be effective in nutrient removal for the surface conditions and slope set forth in this experiment.

Water quality data were used to determine the influence that surface condition may have had on nutrient concentrations in winter runoff. Runoff samples from three different surface conditions were compared and it was found that nutrient concentrations were indistinguishable from background levels at the end of the plot. Runoff from the three surface conditions sampled at site A differed significantly based on concentrations of ammonia and COD. Site A was located within the manured area. The treated grass plots had much lower values of ammonia and COD in the runoff than either of the other surface conditions at site A. At site B grass plot values were approximately one-half of the concentration at site A. The results suggest that the grass surface condition may be more effective in runoff control. Further research is needed to verify this phenomenon because of the limited number of samples collected in the present study. Variations in runoff volume were observed visually but could not be documented due to the lack of instrumentation. Grass plots seemed to have less runoff which may explain the improved water quality. Both the amount of infiltration and the runoff volume directly influence runoff quality. Results from the runoff collected at locations B and C indicated that there was

no significant difference in the nutrient concentrations from any of the surface conditions. The surface conditions appear to be similar in their capacity for nutrient reduction at site C below the manured area but there was some indication that the grass may be more effective within the manured area.

One-way analysis of variance indicates that the tilled surface condition was able to reduce all four of the nutrient parameters compared in this analysis to background levels at site B. I attribute the efficiency of nutrient removal on the tilled plots to surface roughness, depression storage and other physical-chemical factors which are characteristic of the tilled surface condition. The grass and corn stubble surfaces showed similar nutrient reduction at site C.

A linear relationship was found to exist between chemical oxygen demand and total solids values from snowmelt events. Linear regression analysis was used to determine if the relationship between these analysis could be used to predict one concentration from the concentration of the other. The relationship between the two variables was evaluated using the correlation coefficients. Correlations between the two variables broke down after the first three events when total solids values increased rapidly without a corresponding increase in COD. The rapid increase in total solids was attributed to increased soil erosion caused by rainfall and soil saturation. The relationship between COD and total solids is not a stable one and should not be used to draw any conclusions.

CHAPTER VII

SUGGESTIONS FOR FUTURE RESEARCH

The methods of sample collection need to be revised to prevent loss of runoff from the plot and to minimize distortion of the normal flow of runoff. Several problems arose during the course of runoff events. The most serious of the problems was the loss of runoff from the plot. The method of collection at site A consisted of a 10 cm diameter plastic tube with the upper one-third being cut away buried in the ground. A more complete description can be found in the procedure. At site A the water would follow the outside edge of the tile and run out of the plot underneath the tile rather than into the tile.

A second problem occurred when the small hole in the flow limiter plugged with organic material carried by the runoff water. This problem could be solved by placing a fine mesh screen at some point in the front of the hole. If this were done the material trapped should be collected, dried, and weighed. An average value of nutrient content would then be added to the value from liquid analysis. Regardless of the method used, large particles of organic matter must be removed from the liquid portion of the sample before laboratory analysis. There is no practical method of getting an equal amount of particulate organic matter into each aliquot for analysis. The large particles can be filtered in the laboratory. Filtration in the laboratory has several advantages. The results are likely to be more accurate and the amount of field hand work is minimized.

If flow limiters are to be used in the field, the holes must be large enough to prevent plugging. When screens and flow limiters are used in combination they must be used at all sample sites to maintain consistent sampling. The plugging problem did not arise until after several runoff events. Another area of concern was the amount of mixing taking place in the tube at site A. Good mixing occurred when the water entered the tube over the entire width, but in cases where water entered only at one isolated point (due to surface variations) stagnation may have occurred around the flow limiter. This may not be a serious problem when sampling directly from the manured area but may be of concern in other areas. The stagnation would cause the sample to be less representative of the entire event. In order to get a representative plot sample the whole volume of the collecting tube should be mixed constantly, especially near the area where the sample is being drawn off.

The effect that the grass surface condition had on runoff requires further research. Reduced runoff volumes on grass plots were noted in this experiment. The grass cover may increase infiltration and influence freeze-thaw cycles which will in turn affect runoff quality. Further research in this area may reveal a valuable management alternative for livestock producers using of land application wastes.

APPENDIX

APPENDIX

TABLE 7

LINEAR REGRESSION ANALYSIS

Total Solids vs. COD		Volatile Solids vs. COD	
Sample Set	Correlation Coefficient	Sample Set	Correlation Coefficient
Composite (1,2,3)	.946	Composite (1-3)	.981
1	.987	1	.989
2	.923	2	.970
3	.911	3	.984
4	.705	4	.404
5	.346	5&6	.787
6	.149		
7	.083	7	.726
8	.617	8	.533
9	.867	9	.971
10	.804	10	.959
11	.957	11	.915
12	.404	12	.896

TABLE 8

NUTRIENT CONTENT OF FRESH DAIRY MANURE

APPLIED TO RUNOFF PLOTS (1-10-76)

	Sample A	Sample B	Filtered*
COD (mg/l)	238,336	289,408	3540
NH_3 (mg/l)	45	198	14
TKN (mg/l)	769	774	42
Total P (mg/l)	602	561	65
Total Solids (% by wt.)	20.5	20.5	.38
Volatile Solids (% by wt.)	18.5	18.5	.23
Density (g/ml)	1.064	1.065	1.000

*Preparation of filtered sample:

38.5 grams of sample A mixed with 200 ml tap water refrigerated overnight. Then sample was filtered through a Whatman No. 3 filter paper and the filtrate was analyzed.

TABLE 9

CLIMATIC FACTORS EFFECTING RUNOFF QUALITY[1]

Combinations	Paramters	
	Snowmelt Events	Rainfall Events
Grass Plots		
1. Treated A vs. Controls	n	*
2. Treated B vs. Controls		*
3. Treated C vs. Controls		n
4. Treated A vs. Treated B		*
5. Treated B vs. Treated C		*
Corn Plots		
6. Treated A vs. Controls	*	
7. Treated B vs. Controls	*	
8. Treated C vs. Controls	n	
9. Treated A vs. Treated B	*	
10. Treated B vs. Treated C	*	
Tilled Plots		
11. Treated A vs. Controls	*	*
12. Treated B vs. Controls	n	n
13. Treated C vs. Controls	n	n
14. Treated A vs. Treated B	*	
15. Treated B vs. Treated C	n	n

Note: Blanks indicate insufficient data for analysis.

[1]Runoff quality comparisons based on COD data.

Climatic Factors Effecting Winter Runoff 1976

Events 1-4 were caused by snowmelt. During the first three events the soil was frozen but by the fourth day the upper layer had thawed (approx. 1"). By the time the fifth event occurred (nine days later) the soil had thawed even further. The remainder of the events occurred as a result of rainfall or a combination of snowmelt and rainfall. The total accumulation of rain is recorded in the table below. The average intensity calculated below does not indicate periods of very intense rainfall which tend to have a significant effect on the quality of runoff.

TABLE 10

RAINFALL DATA

Event	Inches Precipitation	Duration Hours	Average Intensity Inches/Hour
1 2 3 4	snowmelt events		
5	.31 1.15 1.28	3 15 snow	1.03 .07
6	.5	24	.021
7	.9	10	.09
8	.83	6	.138
9	1.16	9	.129
10	.51 1.20	20 24	.026 .05
11	.38	9	.042
12	None recorded by instruments		

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