THE RECOVERY AND BEHAVIOR OF FERTILIZER NUTRIENTS FROM THE ANAEROBIC DIGESTION OF POULTRY MANURE

by

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Chapter I

INTRODUCTION

Anaerobic fermentation of organic residues is a process resulting in the evolution of methane and carbon dioxide gases. This process occurs naturally in swamps, pond sediments and animal rumens where there is a rich source of organic matter and a lack of oxygen. The methane and carbon dioxide end products of anaerobic degradation account for 90% of the energy contained in original substrate materials consumed (McInerney and Bryant, 1981). This feature made the process popular for the stabilization of sewage sludges in the early twentieth century (Cillie et al., 1969); however, gaseous products were typically treated as a waste and vented to the atmosphere (Fry, 1973). Utilization of anaerobic fermentation for the capture of methane gas as a combustible fuel first occurred in Exter, England, in 1895 with a septic tank designed to provide energy for street lighting (NAS, 1977). The development of the process as a technology for recovering a high quality fuel from agricultural residues was first pursued to a large extent in India (Fry, 1973). Recently the Chinese have extensively developed the technology with 3.8% of the population utilizing methane derived from anaerobic degradation of night soils and agricultural residues (van Buren, 1980; and van Buren, 1979).

The greatest merit of anaerobic fermentation compared to other forms of energy recovery from biomass (such as direct combustion) is that the nutrient value of the raw materials is preserved. Therefore in addition to energy, fertilizer or feed can also be recovered from the biomass. Undoubtedly this factor contributes to the growing use of methane digesters in developing countries where acute fuel shortage has led to the loss of fertilizer nutrients through the direct combustion of agricultural residues such as livestock manures (DaSilva, 1980; Fry, 1973; and Barnett et al., 1978).

Interest in the utilization of methane digesters in the developed countries was sparked in the late 1970's when the price of petroleum based fuels rose sharply. Attention has been specifically focused on the treatment of sewage and livestock wastes. The use of anaerobic digestion for the primary treatment of sewage may again become important as methane captured can be used to power treatment processes. The large quantities of animal manures generated at localized facilities could potentially be treated by anaerobic digestion as an innovative means of capturing energy, reducing pollution and recovering the nutrient value from these wastes.

In 1972 the U.S. Department of the Interior estimated that 123.6 million Mg (dry weight and ash free basis) of readily collectible organic waste are generated within the United States each year. Using a healthy methane yield of $.31 m^3/kg$ of ash free dry matter they estimated the potential energy production from anaerobic digestion in the U.S. to be 1.43×10^{18} J/year (Anderson, 1972). This constitutes 7% of the United States' 1981 natural gas production of 2.1×10^{19} J/year and 2% of the 1981 total U.S. energy production of 6.8×10^{19} J/year (U.S. DOE, 1982). The U.S. Department of Agriculture in 1978 reported that the estimated production of readily collectible livestock and poultry manures in the U.S. is 47.3 million Mg (dry weight ash free basis) which constitutes almost 40% of the total U.S. readily collectible waste production (van Dyne and Gilbertson, 1978). This indicates the importance that anaerobic digestion of organic waste can play in the agricultural sector for energy production. Furthermore, the quantity of animal manures that can be readily collected contains 1.3, .45 and 1.1 million Mg of N, P, and K (van Dyne and Gilbertson, 1978). These nutrients which are recoverable during anaerobic digestion have the potential of serving a useful purpose as fertilizer or feed supplements in agricultural areas.

The recovery and application of N as a fertilizer to the land represents additional energy conservation beyond the production of methane by anaerobic decomposition. This is due to the large quantities of energy required to manufacture synthetic N. A kg of N requires the consumption of 1.5 m^3 of natural gas (mostly methane) which is equivalent to 5.5 x 10^7 J of energy (or 1.5 l of gasoline). This large energy input reflects 60% of the production cost and 32% of the retail price of N (Douglass, 1981). The other important macronutrients, P and K, require an energy investment for mining and processing. Likewise this energy consumption can be displaced by recycling P and K to the land.

Considering today's retail prices for N, P and K of .66, 1.23 and .35 dollars per kg, the total fertilizer value of the readily collectible animal manures in the U.S. today is worth 1.8 x 10^9 dollars per year. If prior to land application these manures were utilized for the production of methane by anaerobic digestion, their economic value would be greatly enhanced. Assuming the healthy methane gas yield of .31 m^3/kg of ash free solids used in the 1972 U.S. Department of Interior study and assuming today's retail price of natural gas of .21 dollars per m^3, the present economic value of methane recovered from readily collectible manures in the U.S. is worth 3.3 x 10^9 dollars per year. The combined energy and fertilizer value of the readily collectible manures from the agricultural sector is thus potentially worth 5.1 x 10^9 dollars per year. Therefore the agricultural sector has a large economic potential in the area of anaerobic digestion and land application of digested animal manures.

Nitrogen recovery during anaerobic digestion deserves the greatest attention since it is applied to agronomic crops in the largest quantities (Tisdale and Nelson, 1975). This is due in part to the comparatively large annual removal of N by crops and the relative ease by which N is lost from the soil by leaching, denitrification and volatilization (Brady, 1974; Tisdale and Nelson, 1975). Consequently N is the largest fertilizer expense for farmers.

The first objective of this study is to evaluate the recovery (in quantity) and changes in the quality of nutrients in poultry manure during digestion. The second objective is to compare the mineralization of untreated and anaerobically digested poultry manure organic N mixed with the soil inorder to determine the effects of the digestion process on N availability. The third objective is to compare the behavior of land applied N, recovered from anaerobic digestion, with poultry manure N and urea N in terms of N losses from the soil and corn yield. The final objective is to evaluate the ability of anaerobically digested poultry manure to reduce the P adsorption capacity of soils (and thus increase P availability to crops).

Chapter II

LITERATURE REVIEW

2.1 MICROBIOLOGY AND PHYSIOLOGY OF ANAEROBIC DIGESTION

Methanogenesis is the anaerobic decomposition of organic matter by the coordinated metabolism of several physiologically distinct groups of bacteria. The formation of methane can only occur in environments where inorganic electron acceptors such as O_2, NO_3^-, NO_2^-, SO_4^{2-}, and SO_3^{2-} are not available (Bryant, 1979; Hashimoto et al., 1980; Zehnder et al., 1982). In such environments only CO_2 (generated during degradation) and protons are utilized as inorganic electron acceptors (McInerney and Bryant, 1981; Zehnder et al., 1982).

2.1.1 Interrelationship of Metabolic Groups

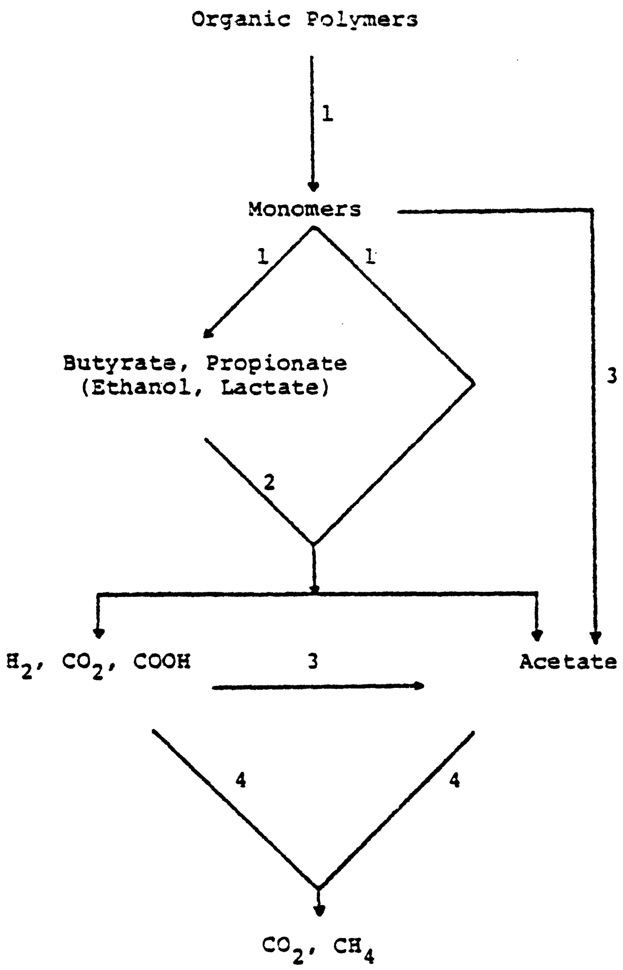
At least four different metabolic groups of bacteria have been isolated from anaerobic digesters. Each can be distinguished on the basis of substrates utilized and metabolic end products formed (Zeikus, 1982). The four groups include:

1. the fermentative bacteria which hydrolize complex organic polymers and ferment the resulting monomeric constituents into a broad spectrum of products (H_2, CO_2, organic acids and alcohols);

2. the hydrogen producing acetogenic bacteria which ferment organic acids (larger than 2 carbons) to acetic acid, H_2 and CO_2;
3. the homoacetogenic bacteria which can synthesize acetic acid from H_2 and CO_2 or produce acetate as the sole fermentation product from the catabolism of sugars; and
4. the methanogenic bacteria which produce methane by a reduction of CO_2 coupled with the oxidation of H_2 or formate, or by cleaving acetate (Zeikus, 1982; Zehnder et al., 1982; Bryant, 1979; McInerney and Bryant, 1981; Hashimoto et al., 1981a; Hashimoto et al., 1980).

The interrelationship of these four metabolic groups during anaerobic decomposition is illustrated in Figure 1.

The four metabolic groups do not function independently of each other. The metabolism of each group depends on the production and consumption of metabolites in the other groups (Bryant, 1979). The methanogens perform a pivotal role in the anaerobic digestion process because their unique metabolism directs the flow of carbon and electrons by removing extracellular intermediates which regulate the thermodynamic efficiency of interspecies metabolism (Zeikus, 1982). The methanogens are also essential to anaerobic



1) Fermentative bacteria

2) Hydrogen producing acetogenic bacteria

3) Homacetogenic bacteria

4) Methanogenic bacteria

Figure 1. The four metabolic groups in the complete anaerobic degradation of organic matter (Hashimoto et al., 1981a).

degradation as they are the only metabolic group capable of catabolizing acetate and hydrogen to gaseous products. Their absence would cause an accumulation of reduced fatty acids and alcohol products of the fermentatives, which would contain almost the same energy as the original substrates (McInerney and Bryant, 1981; Bryant, 1979). When the methanogens are present 90% of the energy in the original substrate is released to the atmosphere as CO_2 and CH_4 gases. The remainder of the energy is distributed into a relatively small yield of microbial cells and heat loss (McInerney and Bryant, 1981; Mattocks, 1981).

2.1.2 Fermentatives

The first step in the anaerobic degradation of organic matter is the hydrolysis of organic polymers by extracellular enzymes produced by the fermentative bacteria (Price and Cheremisinoff, 1981). Polysaccharides such as cellulose, hemicellulose, pectin and starch are hydrolized to sugars and oligosaccharides. These sugars are then fermented, primarily by the Embden-Meyerhof-Parnus pathway, to pyruvate, generating electrons in the form of nicotinamide adenine dinucleotide (NADH) (McInerney and Bryant, 1981). Since the fermentatives of anaerobic digestion constitute a complex mixture of obligate anaerobes, the types of products formed from pyruvate will depend on the fermentative pathways available to a given organism. The possible pathways involved in carbohydrate catabolism of anaerobic fermentatives are outlined in a generalized scheme in Figure 2. The scheme shows the consumption and production of reducing equivalents, NADH, and the points of substrate level phosphorlation represented here as ATP. A well balanced anaerobic digestion would perhaps have acetate, butyrate and porpionate organic products formed in the largest quantity by the group 1 fermentatives (Mackie and Bryant, 1981) with lactate, ethanol, and formate being produced to a lesser extent (Bryant, 1980; McInerney and Bryant, 1981). The fermentative species isolated from anaerobic digesters which are responsible for these organic acids (and solvents) belong to genera such as Bacteroides, Clostridium, Butyrivibrio, Eubacterium, Bifidobacterium, Lactobacillus and others (McInerney and Bryant, 1981).

2.1.3 Hydrogen Producing Acetogenic and Homoacetogenic Bacteria

The acetogenic bacteria catabolize the products of the first stage (mainly propionate and butyrate) to acetate, H_2 and CO_2 (Hashimoto et al., 1980a). The stoichiometry and standard free energy changes involved in the catabolism of

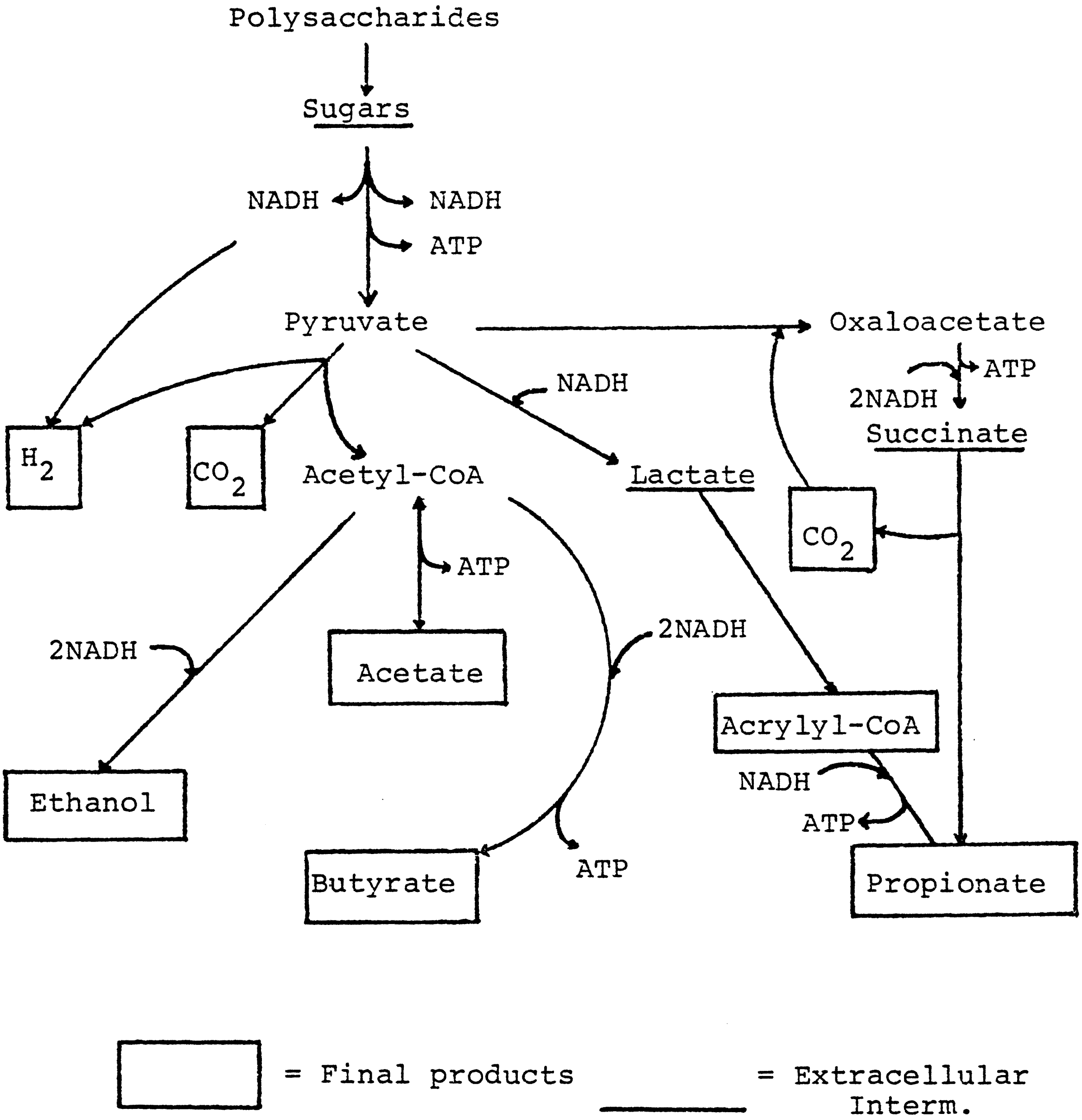


Figure 2. Pathways utilized by anaerobic fermentatives. From (Bryant, 1979; Ferry, 1983)

propionate and butyrate are illustrated in Figure 3. Observing the standard free energy change of these important acetogenic reactions one notices the large positive values indicating the necessity for removing products to thermodynamically favor these reactions (McInerney and Bryant, 1981; Hashimoto et al., 1980a; Bryant, 1979). If the H_2 gas, a product of these reactions, is externally supplied to the medium the utilization of propionate and butyrate is inhibited (Hashimoto et al., 1980a). Thus it is important for the methanogens to utilize H_2 and maintain a low H_2 concentration in the medium for the acetogenic reactions to proceed (Bryant, 1979). The species of acetogenic bacteria and the mechanisms of their metabolism are only recently being discovered (Zeikus, 1982).

In contrast to the H_2 producing acetogenic bacteria the homoacetogenic bacteria have a highly thermodynamically favorable metabolism as they utilize H_2 and CO_2 as substrates for the production of acetate. Thus the homoacetogenic bacteria may be of some importance in the anaerobic ecosystem by lowering the concentration of H_2 (Zeikus, 1982; McInerney and Bryant, 1981).

Substrate	Stoichiometry	$\Delta G'o$(kJ/mole) pH7
Propionate	$CH_3CH_2COO^- + 3H_2O \longleftrightarrow$ $CH_3COO^- + HCO_3^- + H^+ + 3H_2$	+76.1
Butyrate	$CH_3CH_2CH_2COO^- + 2H_2O \longleftrightarrow$ $2CH_3COO^- + H^+ + 2H_2$	+48.1

Figure 3. Stoichiometry and free energy changes in the catabolism of propionate and butyrate by acetogenic bacteria (McInerney and Bryant, 1981).

2.1.4 Methanogens

The methanogens constitute a diverse group of bacteria that belong to the Archaebacteria. They are considered an ancient group as evidenced by oligonucleotide sequencing of 16s ribosomal ribonucleic acid (rRNA), an organic polymer which has been highly conserved throughout evolution (Balch et al., 1979). Further evidence for their ancient evolutionary split from Eubacteria is also suggested from their unique cell wall and lipid compositions (Balch et al., 1979). Recently the methanogens have been divided into 3 orders based on 16s rRNA sequencing data, the Methanobacteriales, Methanoccales and Methanomicrobiales (Balch et al., 1979).

Methanogenic bacteria catabolize most substrates by anaerobic respiration and as a group lack the metabolic capacity for fermentation. Methanogens apparently obtain their energy through oxidative phosphorlation of high energy nucleotide phosphates (Ferry, 1983; McInerney and Bryant, 1981). Almost all methanogens studied thus far are capable of using H_2 and CO_2 as substrates (Balch et al., 1979). The H_2 is oxidized and coupled with the reduction of CO_2 forming CH_4 gas. The transfer of electrons during this reaction supports oxidative phosphorlation (McInenerney and Bryant, 1981; Balch et al., 1979). The stoichiometry and free energy change during the oxidation of H_2 are illustrated in Figure 4.

Acetate and formate can also be used as substrates by certain species of methanogens. The stoichiometry of these reactions are also illustrated in Figure 4. The mechanisms that support oxidative phosphorlation during the catabolism of formate parallel those for H_2, whereby formate is utilized as the electron donor. The catabolism of acetate involves a cleavage of the substrate. However, the mechanism of energy production from acetate is less well understood than that of H_2 catabolism (Ferry, 1983). Formate is the substrate second in numerical importance to H_2 as it is utilized by a large number of methanogenic species (Balch et al., 1979). Acetate is quantitatively the most important substrate catabolized to CH_4 in anaerobic digestions of animal manures, despite the small number of species that have been identified as capable of its utilization (McInerney and Bryant, 1981). Various studies report that from 65 to 90% of the methane produced in anaerobic digesters and pond sediments comes from the methyl group of acetate (McInerney and Bryant, 1981; Bryant, 1979; Hashimoto et al., 1981a; Zeikus, 1982; Mountfort and Asher, 1978; Mackie and Bryant, 1981). Only three species capable of acetate catabolism have been identified; these include the mesophiles *Methanosarcina barkeri* and *Methanothrix soehngenii*, and a thermophillic strain of *Methanosarcina* (Zhender et al., 1982; Ferry, 1983; Huser et al., 1982). Since *M. barkeri* has a relatively low affinity for acetate compared to *M. soehngenii*, it is presently thought that the latter species is the most important producer of methane in the anaerobic digestion of organic wastes (Ferry, 1983). This belief is supported by numerous isolations of *M. soehngenii* from anaerobic digesters while *M. barkeri* is not isolated as frequently (Huser et al., 1982). In rumen environments organic acids are extremely limiting as they are absorbed into the animals blood stream through the stomach wall. Thus in these environments the methane is entirely produced by the oxidation of H_2 coupled to CO_2 reduction (Zehnder et al., 1982).

The growth rates of methanogenic bacteria are low relative to the fermentative bacteria. In a study comparing various metabolic phases of anaerobic digestion on defined media, the maximum specific growth rate of the fermentative phase on glucose was 7.2 day^{-1} while that of the methanogens on acetate was .49 day^{-1} (Ghosh and Kluss, 1978). Zehnder et al. (1982) cite specific growth rates of 1.08 to 1.2 day^{-1} in natural mixed cultures of methanogens utilizing H_2 as a substrate. On acetate substrates, these same authors

Substrate	Stoichiometry	ΔG'o(kJ/mole) pH7
H_2	$H_2 + HCO_3^- + H^+ \rightleftharpoons CH_4 + H_2O$	-135.7
Formate	$HCOO^- + H_2O + H^+ \rightleftharpoons CH_4 + 3HCO_3^-$	-130.7
Acetate	$C^*H_3COO^- + H_2O \rightleftharpoons C^*H_4 + HCO_3^-$	-31.0

C^* labeled with C^{14}

Figure 4. The stoichiometry and standard free energy of methane formation from ecologically important substrates (Bryant, 1979).

cite rates ranging from .08 to 1.44 day^{-1} for pure cultures. Due to these low growth rates, anaerobic digesters must utilize long retention times to avoid wash out of the acetate utilizing methanogens, or have some mechanism by which viable methanogens can be retained.

Methanogenic metabolism previously has been implicated as the rate limiting step during anaerobic digestion due to the slow growth rates (Ghosh and Klass, 1979). Recently, researchers are suggesting that the degradation of fatty acids (by acetogenic bacteria) is the rate limiting step of anaerobic digestion. This is evident from methane yields occurring in high rate digestions, of less than 5 days retention time, while organic acids formed by the fermentatives remain unutilized (Bryant, 1979; Hansson, 1982). The hydrolysis of organic polymers can be rate limiting in the digestion of cellulosic wastes (Bryant, 1979; Ghosh and Klass, 1978).

Successful anaerobic digestion of organic wastes requires specific environmental conditions because the methanogens are a sensitive group of bacteria. Even though some methanogens are capable of autotrophic energy production (from H_2 and CO_2), rich organic habitats are common for most. This is not because methanogens are fastidious, since as a group they are capable of growth on minimal media with few organic nutrients other than those required for energy (Bryant, 1979; Huser et al., 1982). The occurrence of methanogens in rich organic environments is related to the production of substrates required for methanogenesis by the more fastidious groups of bacteria.

2.2 ENVIRONMENTAL CONDITIONS AND PROCESS INHIBITION

Oxygen is highly toxic to the methanogenic bacteria;thus strict anaerobic conditions are essential for growth (McInerney and Bryant, 1981; Pfeffer, 1980). Methane production in anaerobic environments has been reported for temperatures ranging from 0° to 97°C; however, maximum methane production occurs in two temperature regimes, mesophilic and thermophilic, with temperature optimums of 35° and 55°C, respectively (Hashimoto et al., 1981a; Bryant, 1979; Zehnder et al., 1982). Methane production occurs in environments ranging from pH 5.5 to 8.5 with specific species of methanogens having more limiting pH ranges (Zehnder et al., 1982). Optimum pH ranges reported for methane production in anaerobic digesters are from 6.6 to 7.6 (Price and Cheremisinoff, 1981; Hashimoto et al., 1981a).

Optimum anaerobic digestion requires the presence of essential nutrients in proper proportions and concentrations. Animal manures usually contain all required nutrients in sufficient quantities (Hashimoto et al., 1981a). Other wastes which are highly cellulosic, such as municipal refuse, have been shown to be deficient in N and P (Hashimoto, 1980; McInerney and Bryant, 1981). The ratio of carbon to nitrogen (C:N) in substrates is an important parameter regulating the efficiency of anaerobic digestion (Fry, 1973; Price and Cheremisinoff, 1981). Sievers and Brune (1978) demonstrated that optimum C:N in terms of methane yield ranges from 15.5 to 19 in their experiments with swine wastes. Substrates with very high C:N may be deficient in N relative to the energy supply from the carbon (Fry, 1973). Digestion of substrates with C:N ratios between 20 and 30 may have sufficient N for nutrient supply but lack stability to changing environmental conditions. This may in part be related to the major role NH_3 plays as a pH buffer in anaerobic systems (Sievers and Burne, 1978; Hashimoto et al., 1980). At the other extreme, low C:N substrates provide an excess of N and allow an accumulation of NH_4^+N in solution. This can be inhibitory to methane production at high concentrations (Sievers and Burne, 1978; Bryant, 1979; Hashimoto et al., 1980).

The concentration of substrate loaded into a digester can be limited by NH_3 toxicity. This is particularly true for animal wastes which are inherently high in N. During the digestion process proteins are hydrolyzed and their amino acid constituents are mineralized, releasing ammonia into solution (Price and Cheremisinoff, 1981). Early researchers reported that failures in methane production corresponded with concentration of total NH_3 (NH_4^+ + NH_3) at levels greater than 1200 to 1400 mg/l (Albertson, 1961). The affect of NH_3 toxicity becomes greater at increasing pH due to greater dissociation of free NH_3 from NH_4^+. McCarty (1964) reported inhibition of high pH (>7.4) digestions to range between 1500 to 3000 mg/l total NH_3, while above 3000 mg/l, total NH_3 was toxic regardless of pH. More recent research indicates that methanogens can be slowly assimilated to tolerate high concentrations of total NH_3 (Melbinger and Dannelon, 1971; van Velsen, 1981). For example, the anaerobic treatment of swine wastes with added urea salts allowed for the production of methane at concentrations greater than 5000 mg/l total NH_3 with only a 27% decline in gas productivity compared to untreated manure (van Velsen, 1981).

In addition to ammonium salts, other ions can be inhibitory and toxic to methanogenic bacteria. Studies with the acetate utilizing methanogens show strong inhibition at concentrations of 3, 000, 8, 000 8, 000 and 12, 000 mg/l Mg, Ca, Na and K, respectively (Anderson et al., 1982). Heavy metals can cause toxicity to anaerobic systems and have been extensively discussed throughout the literature (Anderson et al., 1982). Hayes et al. (1978) studied the toxic limits of several heavy metals. The order of decreasing toxicity was found to be:

$$Ni > Cu > Cr > Pb > Zn$$

ranging from toxic concentrations of 30 mg/l for Ni to 600 mg/l for Zn. Since anaerobic digestion is sensitive to salts and heavy metals, the use of strong industrial wastes as substrates for methane production can be limiting if the concentrations of these constituents are high.

High loading rates of anaerobic digesters can result in an accumulation of volatile fatty acids (Albertson, 1961). As previously discussed, the fermentative bacteria metabolize at a faster rate than the acetogenic and methanogenic bacteria which allows for the accumulation of propionate and butyrate. These organic acids become toxic at concentrations in excess of 33 mM as demonstrated in several studies (Varel et al., 1977; McCarty and McKinney, 1961). The accumulation of volatile fatty acids must be avoided by not overloading an anaerobic digester beyond the capacity of methanogenic bacteria to utilize the products of fermentation.

Often volatile fatty acids accumulate as a result of other process inhibitions. Such accumulations have been shown in the cases of temperature shocks and inhibitory levels of total NH_3 (Anderson et al., 1982; van Velsen, 1981; Albertson, 1961). Thus it is advisable to reduce loading after a system shock since the growth rate and metabolic rate of the methanogens are reduced. Subsequently, the rate at which fatty acids are utilized is also reduced.

2.3 DESIGN OF ANAEROBIC DIGESTION PROCESSES

Anaerobic digestion systems have evolved into a wide range of designs reflecting several technical approaches. The particular design suited for a given application depends on numerous considerations. Perhaps the greatest consideration is the principle objective of the process, for example, whether waste stabilization or methane yield is the highest priority (Stafford et al., 1980). Considerations that are essential to the development of a design are: the type of waste to be utilized; heating requirements of the system; accessibility of the waste; availability of capital; and availability of labor (Stafford et al., 1980; NAS, 1977).

After the parameters of a system are defined, a design must then provide optimal conditions for methanogenic activity. Conditions which can be maximized in an anaerobic digestion process include: maintenance of a plentiful supply of viable bacterial cell mass; adequate supply of substrate; contact between the substrate and the cell mass; maintenance of optimal environmental conditions (absence of O_2, temperature, pH, absence of toxic materials, etc.) (Price and Cheremisinoff, 1981).

The simplest design for anaerobic digestion is the batch process. In this design organic slurries are loaded into a sealed tank and allowed to digest for a given time period. At the end of the digestion period the spent slurry is removed and the process is repeated with new materials (Horton, 1980). This type of digestion is suited for waste with large sized particles, such as crop residues, which would be subject to clogging in flow through type digesters. Batch systems are also suited for applications that lack continual supply of organic wastes (NAS, 1977).

Designs for anaerobic digesters are commonly continuous. These types of processes are fed substrates on a continual or semicontinual basis. The simplest continual type digesters were developed in both India and China (Horton, 1980). These designs are exemplified by the

Chinese digester which is essentially a pit lined with bricks and covered with a fixed dome. The organic wastes from households and pigsties are fed semicontinuously into the pit. As biogas pressure builds up, effluent is pushed out of the oulet dispensing the digested organic slurry (van Buren, 1979). A typical Chinese digester is illustrated in Figure 5.

Continual processes have also commonly been employed in the anaerobic treatment of sewage. In the 1950's the mixing of digester contents was developed for these treatment processes. The mixing process homogenizes the contents, providing enhanced contact between the substrate and the bacteria. Additionally mixing prevents gas blockage by scum layer formation (Price and Cheremisinoff, 1981; McCarty, 1982). These digesters are referred to as continually stirred reactors (CSTR) or high rate digesters. A CSTR reactor is illustrated in Figure 6.

Even though the CSTR contributed to increased productivities of anaerobic treatment processes by enhanced contacting, the bacterial cell mass is subject to wash out from the reactor. Thus the rate of wash out, controlled by the retention time of the system, determines the concentration of bacterial cell mass in the reactor. This in turn limits the loading of the CSTR reactors which

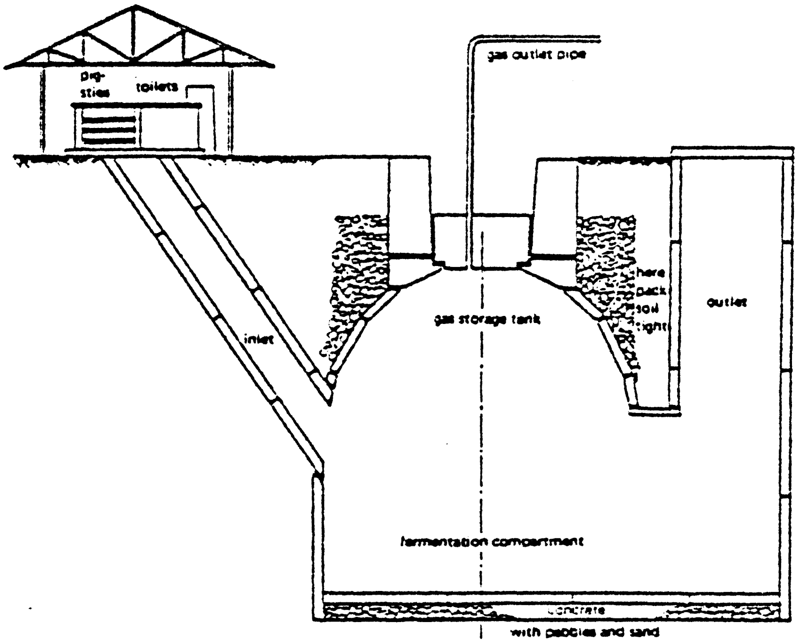


Figure 5. A Chinese biogas plant (van Buren, 1979).

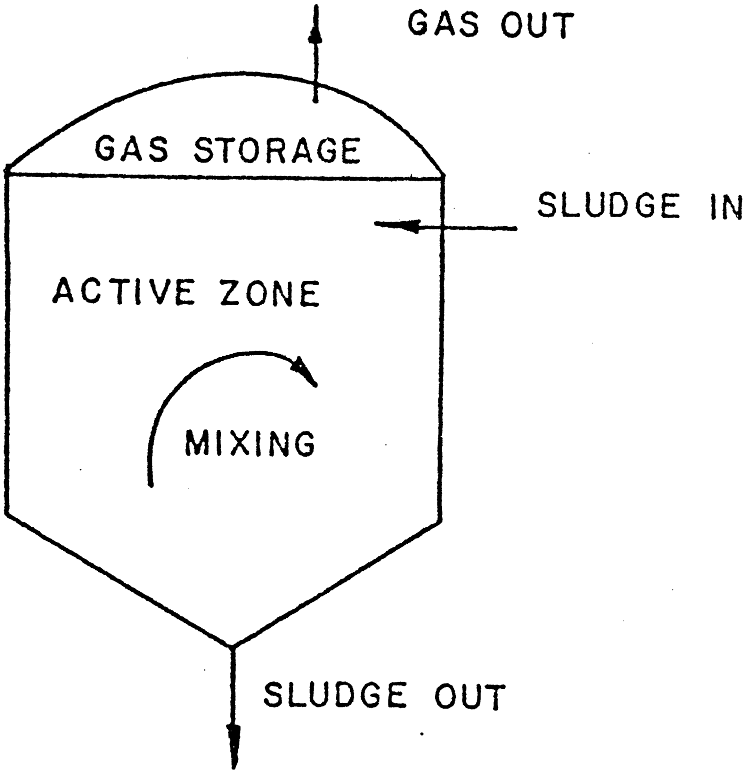


Figure 6. A conventional CSTR reactor (Price and Cheremisinoff, 1981).

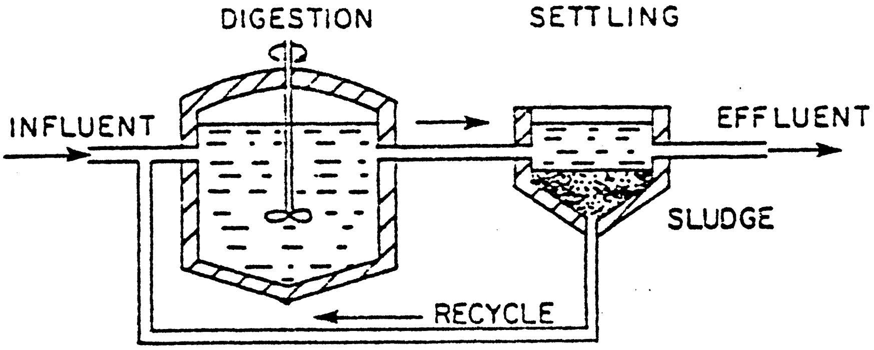
generally are not loaded beyond 6 kg volatile solids per m^3 per day.

The appreciation of maintaining a high cell mass, for increased loading and methane yield, has led to the development of other types of designs (McCarty, 1982). One such design involves the segregation of the sludge (which is concentrated with the cell mass) from the outgoing effluent stream for recycling into the digester (McCarty, 1982). A sludge recycle reactor is illustrated in Figure 7.

Other designs for maintaining a cell mass in the reactor involve the use of anaerobic filters. These are digesters filled with porous support matrices that retain the cell mass against hydraulic flow (Colleran et al., 1982; Lettinga et al., 1982). The support matrices utilized include porous rock (Barry and Colleran, 1982), clay slabs (Kennedy and van den Berg, 1982) and sludge blankets (Lettinga et al., 1980). The anaerobic filter reactors have primarily been developed for low strength wastes, typically less than 10, 000 mg/l chemical oxygen demand (COD). With these types of wastes, such as distillery, sugar refinery and potato processing wastes, low hydraulic retention times of less than 1 day, high loadings of up to 40 kg COD m^{-3} day^{-1} and high methane productivity have been successfully achieved without digester upset (Riera et al., 1982;

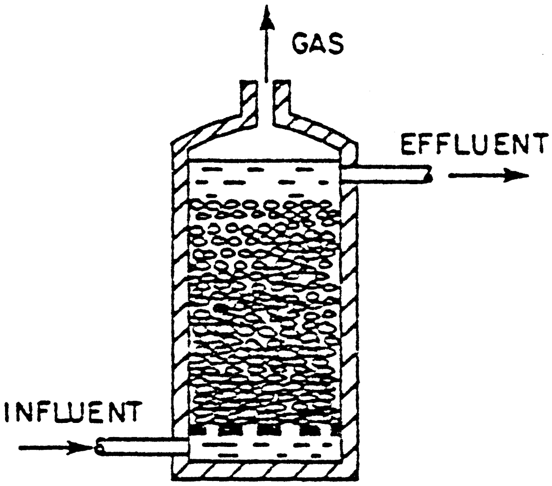
Lettinga, 1982; Braun and Huss, 1982). In the case of stronger wastes such as animal slurries, a laboratory fixed film reactor has been used for treating a 39, 000 mg/l COD piggery waste. A typical anaerobic filter digester and a sludge blanket digester are illustrated in Figure 7.

Another group of continual digesters belong to the plug flow category. Digesters of this type utilize an elongated reactor vessel. In contrast with the more conventional CSTR designs, the principle of the plug flow reactor is to prevent mixing. This allows the acid fermentation phase of digestion to occur at the influent end of the digester and remain separate from the methanogenic phase of the reaction which occurs at the effluent end of the digester. The formation of volatile fatty acids in the initial phase of fermentation thus will not inhibit the methanogens and the inhibitory end products (such as NH_4^+) only affect the latter portion of the digester. Plug flow reactors at the laboratory, and pilot scale have been compared in parallel operation with CSTR reactors at Cornell University. When utilizing each of these systems with high strength dairy manure wastes (13% total solids), the plug flow reactors provided a 10% enhancement in CH_4 production compared with the CSTR reactors and a 14 to 19% enhancement in volatile solids destruction during digestion (Hayes et al., 1980).



a) Sludge recycle

b) Anaerobic filter



c) Sludge blanket

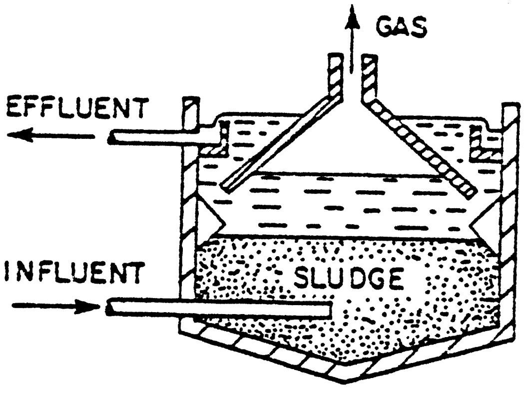


Figure 7. Sludge recycle, anaerobic filter, and sludge blanket reactors (McCarty, 1982).

2.4 ANAEROBIC DIGESTER PERFORMANCE

Large variations in digester performance are reported in the literature. A large contributing factor to this difference is the varying operational conditions such as temperature, digester design, loading rates and feed stock. However, comparing the performance of digestions with similar conditions also indicates large variability. An examination of Table 1 illustrates this large variability for animal manures treated anaerobically in stirred continuous reactors with temperatures between 30 to 35°C. Biogas production from these selected studies vary from .072 to .693 m^3 per kg of volatile solids (VS) added, or on a m^3 per m^3 digester retention per day basis from .277 to 3.32, with methane compositions that vary from 50.6 to 82.8%. The yield of biogas is a function of manure type and loading rate (determined from solids concentration and retention time). However, the trends are difficult to obtain when comparing data of different studies.

An example of this difficulty is in the comparison of poultry manure data. Morrison et al. (1981) reports a yield of .677 m^3 biogas per kg VS added with a 10 day retention time (RT) and influent VS concentration of 4.61% while Gramms et al. (1971) used the same RT and slightly lower VS concentration of 3.84% report a yield of .313 m^3 per kg VS.

Table 1. Methane production and performance of poultry (P), swine (S), and cow (C) manures anaerobically digested in continuous mesophilic stirred reactors.

Feed	RV[1] m^3	Temp. C°	Loading kg VS/m^3/day	RT[2] days	VS[3] %	Biogas Yield m^3/kg VS added	Biogas Yield m^3/m^3 retent./day	CH_4 %	VSR[4] %	CODR[5] %	CH_4 per VSD[6] m^3/kg	Reference
P	96.7	35	1.98	30.5	5.93	.34	.74	55.6	53.0	-	.356	Converse et al., 1977a
P	96.7	35	1.95	42	8.02	.440	.86	62.2	59.9	40.8	.457	Converse et al., 1981
P	.004	32.5	3.84	10	3.84	.313	1.20	52.9	64.2	74.8	.258	Gramms et al., 1971
P	.004	32.5	3.84	15	5.76	.281	1.08	52.5	57.0	68.7	.259	Gramms et al., 1971
P	2.83	35	4.61	10	4.61	.677	3.12	-	-	-	-	Morrison et al., 1981
S	.0015	30	2.99	10	2.99	.239	.713	82.8	25.3	31.5	.782	van Velsen, 1981
S	.240	30	3.76	12	4.51	.314	1.18	76.3	27.8	40.3	.862	van Velsen, 1981
S	.240	30	2.27	20	4.36	.373	.850	75.2	37.6	44.3	.746	van Velsen, 1981
S	.005	30	6.74	10	6.74	.079	.534	67.6	12.4	14.3	.431	van Velsen, 1981
S	.004	32.5	3.84	15	5.76	.422	1.62	59.1	59.2	41.8	.422	Gramms et al., 1971
S	.450	35	4.00	15	6.00	.568	2.27	60.0	63.0	58.0	.541	Fischer et al., 1979
C	.710	35	6.22	10.4	6.49	.267	1.66	50.6	30.7	35.4	.440	Converse et al., 1977b
C	.003	35	6.32	10	6.32	.531	3.32	54.6	55.1	49.9	.526	Hashimoto, 1983
C	.003	35	4.21	15	6.32	.611	2.57	57.3	58.1	51.2	.602	Hashimoto, 1983
C	.004	32.5	3.84	10	3.84	.072	.277	65.2	19.4	9.33	.242	Gramms et al., 1971
C	.004	32.5	3.84	15	5.76	.098	.375	61.3	17.7	13.2	.339	Gramms et al., 1971

[1] Retention volume

[2] Retention time

[3] Volatile solids conc. of influent

[4] VS reduction

[5] Chemical oxygen demand reduction

[6] Methane per VS destroyed

A difference such as this may be due to the large acclimation period (>1.5 years) in the Morrison et al. (1981) study which perhaps enabled the methanogenic bacteria to adjust to high ammonia exposures. In contrast the Gramms et al. (1971) study only allowed for a 5 week acclimation period.

Another similar discrepancy, in the case of cow manure, is illustrated between a study of Hashimoto (1983) and that of Gramms et al. (1971). A loading of 4.21 kg VS per m^3 retention per day yielded .611 m^3 biogas per kg VS for the former study. This greatly exceeded .098 m^3 biogas per kg VS in the latter study which had only a slightly lower loading of 3.84 kg VS per m^3 per day. In the former study a sludge which was highly acclimatized to cow manure was used for seeding the digesters while in the latter study a sewage sludge was used. Thus the large differencs in performance of digesters with seemingly similar operational conditions appears to be due to the physiological condition, composition and concentration of the bacterial population.

Since the condition of the bacterial population varies from study to study, generalizations concerning the effect of loading rates on CH_4 production need to be made with data generated within the same study. Such relationships were established in the study of van Velsen (1981) in which various loading rates of swine manure were examined. The relationships of CH_4 yield versus RT and total solids (which contain approx. 70% VS) are illustrated in Figure 8.

One generalization evident from this figure is that CH_4 production per unit of solids added increases with increasing RT. This would be expected since longer residence time allows for greater decomposition. The greatest contribution of CH_4 by the solids occurs prior to 15 to 20 days retention depending on solids concentration. For a given RT the methane yield per unit of solids added is generally greatest for the lower solids concentrations. The difference becomes greater as RT is lowered. This indicates there is methanogenic inhibition due to overloading at low RT with high solids concentrations. Overloading causes process imbalances by supplying fatty acids faster than they can be utilized by the methanogens. As the fatty acids accumulate they inhibit the methanogens as previously discussed.

The reductions in solids listed in Table 1 range from low values of 11.4 and 9.33 to highs of 64.2 and 74.8% for VS and COD, respectively. High solids reductions are associated with high CH_4 productivity since the mass in the solids destroyed is recovered in the biogas. Thus for digestions with high CH_4 yields, considerable stabilization

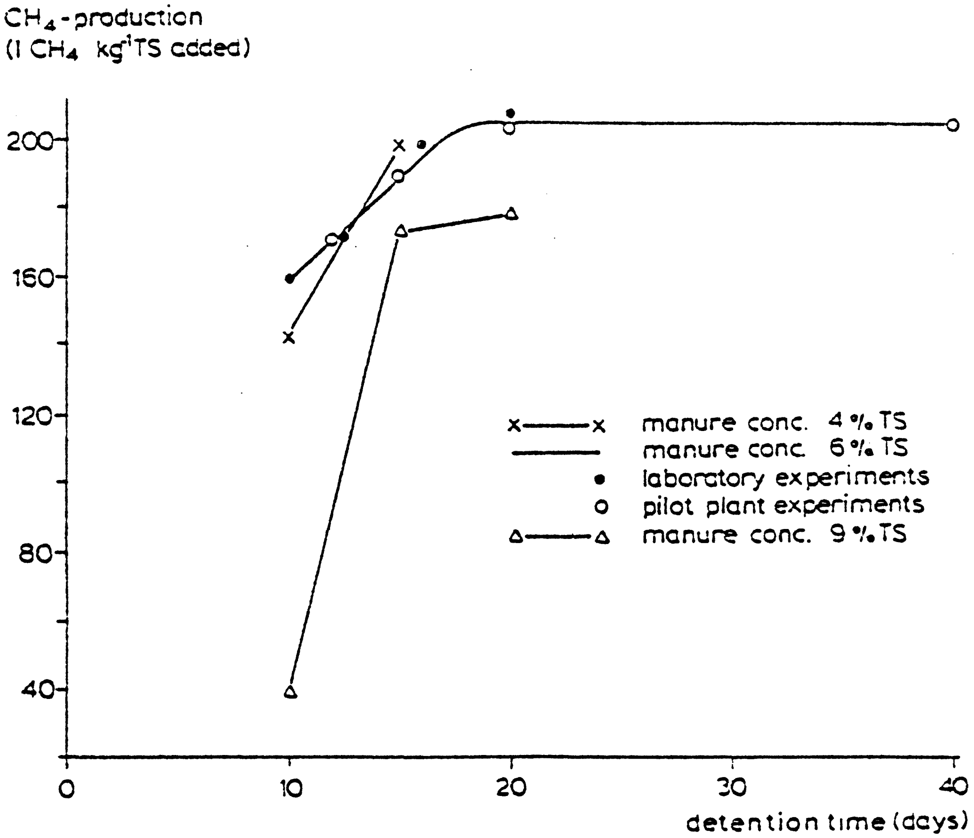


Figure 8. Relationship between solids concentration, retention time and methane yield for mesophilic (30°C) digestions of swine manure (van Velsen, 1981).

of the organic fraction can be expected (Cillie et al., 1969).

2.5 NUTRIENT RECOVERY DURING ANAEROBIC DIGESTION

While the anaerobic digestion of animal manures offers significant reductions in organic carbon, a unique attribute of the process is that nutrients important to plant growth are highly recovered (Hashimoto, 1980). As illustrated in Table 2, total N is essentially 100% recovered during the anaerobic digestion of animal manures. This has tremendous importance as N is the nutrient required by and applied to agronomic crops in the largest quantities (Tisdale and Nelson, 1975).

Nitrogen has been detected in trace quantities in biogas as NH_3. One study reports .021 mg N per liter of biogas from the anaerobic digestion of poultry manure. This would account for a .009% loss of the total N placed in the digester (Converse et al., 1981). This quantity is too small to detect from direct analysis of influent and effluent. Thus small deviations from a 100% recovery of total N shown for several studies in Table 2 can be attributed to errors associated with sampling and analyses.

Larger and significant losses of N will occur during anaerobic digestion if the N supplied is in the NO_2^- or NO_3^-

Table 2. Concentrations and recovery of ammonium N and total N during anaerobic digestion of poultry (P), swine (S) and cow (C) manures.

Feed	Temp. C°	RT[1] days	VS[2] %	Infl NH_4^+ mg N/L	Infl TKN[3] mg N/L	Infl NH_4^+/TKN %	Effl NH_4^+ mg N/L	Effl TKN mg N/L	Effl NH_4^+/TKN %	NH_4^+ Recov[4] %	TKN Recov %	Reference
P	35	42	8.02	5180	8820	58.7	7090	9220	76.9	131	100	Converse et al., 1981
S	30	15	5.19	1325	3230	41.0	2070	3520	58.8	152	106	van Velsen, 1981
S	35	15	6.00	1673	3900	42.9	2934	4080	71.9	168	100	Fischer et al., 1979
C	35	10	6.32	850	2820	30.1	1200	2970	40.4	135	101	Hashimoto, 1983
C	35	15	6.32	850	2820	30.1	1330	2810	47.3	149	94.9	Hashimoto, 1983
C	55	10	6.32	850	2820	30.1	1280	3070	41.7	143	104	Hashimoto, 1983
C	35	10.4	6.49	920	2566	35.9	1341	2867	46.8	142	109	Converse et al., 1977b

[1] Retention time

[2] Volatile solids conc. of influent

[3] Total Kjeldahl Nitrogen

[4] Recovery = (N conc. effl/N conc. infl) x (mass infl - mass biogas/mass infl) x 100

form. Nitrite and NO_3^- can be utilized for anaerobic respiration and become denitrified forming gaseous N_2O or N_2 (Ghosh et al., 1978). Snell (1943) demonstrated experimentally that N added as saltpeter, $NaNO_3$ could be recovered in the gas of anaerobically digesting sewage. However, only trace quantities of NO_3^- are present in animal manures as they are derived from anaerobic environments (gastrointestinal tracts).

Table 2 illustrates the increase of NH_4^+N concentrations in effluents from anaerobic digesters compared to the influents. This reflects the hydrolysis of proteins and mineralization of amino acids by the extracellular enzymes of fermentative bacteria. The enrichment of NH_4^+N has important implications in the behavior of the effluent as a fertilizer compared to its corresponding influent. This is because inorganic forms of N are readily absorbed by plant roots (Tisdale and Nelson, 1975). Thus one would anticipate that N in the effluent would be more readily available to plants compared to the influent. However, the NH_4^+ form of N is subject to greater losses from the soil by leaching and volatilization compared to organic forms of N, as will be discussed later.

The recovery of NH_4^+N in effluents of anaerobically digested animal manures ranges from 131% to 168% for the studies presented in Table 2. The highest recoveries occur with the swine manure and the lowest recovery occur with the poultry manure. There is not much data for N recoveries during anaerobic digestion of poultry manure. The one study shown in Table 2 may underestimate the average behavior of N in the digestion of poultry manure, since it was conducted at NH_4^+N concentrations (in the effluent) of 7090 mg/l. This concentration of NH_4^+N is in excess of that shown to cause partial inhibition of VS and COD reductions and accumulation of volatile fatty acids (van Velsen, 1981).

The cow manure experiments presented Table 2 had from 15 to 23.5% of the original organic N (total N - $NH^+{}_4N$) mineralized during digestion. The van Velsen (1981) swine manure study had 36%, and the Fischer et al. (1979) swine manure study had 51% of the original organic N mineralized during digestion. The poultry manure study had 44% of the original organic N mineralized. Thus the cow manure appears to have an organic N which is more resistant to degradation compared to the other manure types during anaerobic decomposition.

The poultry manure (of the cited study) contains almost twice as much NH_4^+N per unit of total N (TKN) than that of cow manure when comparing the two as an influent and as an effluent. This indicates that these two manure types perhaps behave quite differently as N fertilizers. The swine manure effluent has influent and effluent NH_4^+N:TKN ratios which are intermediary between those of cow and poultry manures but closer to poultry.

The enrichment of NH_4^+N during digestion has important implications for the distribution of N between liqud and solid associated fractions of the digester effluent. In a particle fractionation study of anaerobically digested beef cattle manure, the concentrations of organic N in the solids of centrifugate pellets were similar to those present in the composite effluents (Boening and Pfeffer, 1979). Since the pellet solids concentrations were 15 times higher than the supernatant solid concentrations, the organic N is most concentrated in this fraction. Thus the largest recovery of the effluent organic N is with the pellet fraction. Ammonium N concentrations of the pellet solids were on the average 63 times less concentrated than NH_4^+N in the composite effluent solids. Thus in contrast to organic N, the NH_4^+N of the effluent was recovered mostly in the supernatant fraction.

Hashimoto (1980) presents data demonstrating a 60% and 41% recovery of organic N and TKN, respectively, with the sieve plus pellet solids from sifted and centrifuged anaerobically digested cow manure effluents. With only 41%

of the TKN recovered in the separable solids, these data also demonstrate that NH_4^+N tends to segregate into the supernatant fractions of effluents.

The N recovered during digestion of animal manures has been shown to be of value as a feed supplement (Hashimoto, 1980; Mattocks, 1981; Marchaim et al., 1982). However, the NH_4^+N, associated with the liquid fraction cannot feasibly be segregated from the effluents for feeding (Mattocks, 1981). Thus the effluents of swine and poultry wastes, which have NH_4^+N to TKN ratios of 60% and greater, may be more practically utilized as a fertilizer for crops.

The recovery of other important fertilizer macronutrients such as P and K have not been as extensively studied. The recovery of total P (TP) and total K (TK) theoretically should be 100% as neither of these nutrients are volatile at temperatures used for digestions. The data of Converse et al. (1981) accounts for a 69.1% recovery of TP during anaerobic digestion of poultry manure. Fischer et al. (1979) present data that accounts for an 88.7% recovery of the TP during anaerobic digestion of swine manure. Converse et al. (1977b) account for TP recoveries ranging from 89% to 104% in various digestions of dairy manure. Hashimoto (1981b) presents data that accounts for an 85.4% recovery of TP for thermophilic digestions of beef cattle manure. These data illustrate a clear trend that TP recoveries of 100% are seldom measured. Since P is highly associated with solids, less than 100% recovery of TP may be an indication that solids are seldom completely recovered in effluent samplings.

Boening and Pfeffer (1979) present data from the fractionation of anaerobically digested cattle manure effluents which indicate that there is a high association of TP with the centrifugate pellet. The TP concentrations in composite and pellet solids were similar but the pellet contained almost a 15 times greater concentration of solids compared to the centrate. Thus like organic N the highest concentration of P is with the centrifugate pellet. These researchers also present data for soluble P which in their cattle manure influent ranged form 21 to 63% of the TP. In the corresponding effluent soluble P ranged from 8.5% to 13% of the TP which indiates that soluble P is transformed to insoluble forms of P during their digestions. The centrifugate pellet of the effluent contained soluble P to TP ratios of 25 to 30%, which shows that the soluble P is enriched with the sludge.

The recovery of TK during the anaerobic digestion of swine manure calculated from the data of Fischer et al. (1979) is 95.7%. Total K recoveries calculated from the thermophilic cow manure digestion data of Hashimoto (1981b) was 98.8%. Thus measured recoveries of TK are much closer to the theroetical recovery of 100% compared to TP. This would be expected as K is less associated with solids than P. In the solid fractionation studies of Boening and Pfeffer (1979), K is recovered mostly in the soluble form and low concentrations of K were present in centrifugate pellet solids.

Extractable K (in NH_4^+ acetate) recovery during the anaerobic digestion of poultry manure as calculated from the data of Converse et al. (1981) is 104%. Extractable K recoveries reported by Converse et al. (1977b) for various digestions of dairy manures ranged from 103% to 125%. Thus the general trend demonstrates a slight enrichment of extractable K during digestion. This indicates that a small amount of K not exposed to the extracting process in the influent is released during some digestions and can be extracted in digester effluents.

2.6 APPLICATION OF ORGANIC WASTES TO THE LAND AS FERTILIZER

Nutrients recovered from the anaerobic digestion of animal manures can be utilized as a fertilizer material. The availability of these nutrients for crop growth will depend on numerous transformations that can occur in the soil. The N of digested animal manures is in both organic and inorganic forms. The organic forms of N are mineralized to inorganic forms when these materials are applied to the soil. The NH_4^+N present in digester effluents, as well as that formed from mineralization, is subject to a large array of reactions depending on specific conditions in the soil. Some of the quantitatively most important transformations of N from NH_4^+N that can occur are: ammonia volatilization, nitrification, denitrification and leaching (Tisdale and Nelson, 1975).

2.6.1 Mineralization of Nitrogen

The mineralization of organic N from anaerobically digested sewage has been studied extensively (Parker and Sommers, 1983). Typically, the sludge fraction of the digested sewage materials are utilized for these studies. Two basic experimental approaches have been used. One method involves the incubation of soil-sludge mixtures with periodic sampling for inorganic N content (Parker and Sommers, 1983). A second line of methods involves periodic leaching of incubated soil-sludge mixtures with weak salt solutions and subsequent analysis of inorganic N in the leachate (Stanford and Smith, 1972).

Amounts of organic N mineralized (as a percent of organic N applied) from anaerobically digested sewage sludges mixed with soils have been reported as: 4 to 48% in a 16 week period (Ryan et al., 1973); 14 to 25% in a 13 week period (Magdoff and Chromec, 1977); 38% in an 8 week period (Hsieh et al., 1981); and 2 to 27% in a 16 week period (Parker and Sommers, 1983). Greater percentages of the applied organic N are mineralized when lower rates of N are mixed with soils (Ryan et al., 1973).

The relationship between cumulative inorganic N mineralized from organic matter versus the square root of the incubation time has been shown to be linear for untreated soils (Stanford and Smith, 1972). This relationship has also been shown to be linear for the mineralization of N from anaerobically digested sludge-soil mixtures (Stark and Clapp, 1980).

The rate of organic matter decomposition is affected by the pretreatment of sludge prior to utilization in the mineralization experiments. Terry et al. (1979a) reported significantly higher decomposition of liquid sludge compared with air dried or freeze dried sludges. Thus the treatment of the sludge used in a N mineralization experiment should be considered when interpreting results. Decomposition is enhanced under increased incubation temperatures as would be expected since the rate of biological activity is enhanced with higher temperatures (Terry et al., 1979a). Rates of sludge-soil mixture decomposition and N mineralization appear to be affected little by soil type (Terry et al., 1979a; Sommers et al., 1979). The rate of N mineralization, however, is affected greatly by the type of sludge used (Parker and Sommers, 1983; Sommers et al., 1979).

During the decomposition of organic wastes, native soil organic matter decomposes faster in waste-soil mixtures compared to the control. This process is known as 'priming' and has been observed in several studies. Terry et al. (1979b) reported from 100% to 150% enhanced decomposition of native organic C in an anerobically digested sludge-soil mixture compared to native C in the control treatment after 4 weeks of decomposition. Though N mineralization was not examined in this study the 'priming' phenomenon observed for C would be expected for organic N which is also released from the decomposition of organic matter. Similarly Jackson et al. (1977) observed a 'priming' of C phenomenon in organic matter decomposition of soils receiving high rates of poultry manure.

The relative availability to crops of total N in animal manures applied to the land has been estimated from a series of field and N mineralization experiments. The values of N available in the first growing season as a percent of the applied total N are 90, 90 and 50% for fresh litter free poultry, swine and dairy manure, respectively (Mathers and Goss, 1979). Thus, the organic N fraction of dairy manure appears to be mineralized to a lesser extent than the organic N of poultry and swine manure. However, when dairy manure lagoon effluent was utilized in a field experiment, 80% of the total N was demonstrated to be in the inorganic form 3 weeks after application (Quisenberry et al., 1981). This indicates that when the refractory components of the dairy manure are separated (with the lagoon sludge), the total N is considerably more available.

2.6.2 Ammonia Volatilization

When nitrogenous organic wastes are applied to the land the fraction of N in the NH_4^+ form is subject to gaseous losses from the soil by a process known as volatilization. Many factors contribute to the rate and quantity of NH_3 volatilization. One is pH of the waste-soil mixture. This is because the equilibrium between aqueous NH_4^+ and gaseous NH_3 shifts further to the NH_3 form as the hydroxyl ion concentration increases (Tisdale and Nelson, 1975; Terry et al., 1978). The concentration of NH_4^+ in solution influences volatilization since the process is caused by diffusion. With increasing NH_4^+ concentrations greater concentrations of dissolved NH_3 gas are formed by equilibrium dynamics. This in turn increases NH_3 volatilization by the development of concentration gradients between NH_3 in the soil and the overlying atmosphere (Terry et al., 1978; Vlek and Stumpe, 1978). Thus, high rates of NH_4^+ application to the soil and evaporation of soil water will both increase NH_4^+ concentrations in the soil solution and enhance NH_3 volatilization. Similarly, factors such as wind passing over the soil surface enhance diffusion gradients and volatilization (Vlek and Stumpe, 1978). Increasing temperatures allow for increased volatilization as diffusion processes are also enhanced with heat (Muck and Steenhuis, 1982; Vlek and Stumpe, 1978). Soil cation exchange capacity (CEC, the capacity of soil to adsorb cations on colloid surfaces) can decrease NH_3 volatilization by removing NH_4^+ from soil solution (Fenn and Kissel, 1976). Increased depths of applied NH_4^+ applications in the soil also decrease NH_3 volatilization by enhanced contact of NH_4^+ with the CEC and decreasing NH_3 concentration gradients between the soil and overlying air (Fenn and Kissel, 1976).

Quantities of NH_4^+N lost from the handling of nitrogenous waste can become significant. For a flow through anaerobic lagoon with a 60 day retention time receiving swine manure, volatilization of 65% of added N has been reported (Koelliker and Miner, 1973). In a study of various lagoon systems, from 3 to 60% of added N was accounted for by volatilization (Muck and Steenhuis, 1982).

Similarly large quantities of NH_3 lost from land application of nitrogenous waste have been reported. Hoff et al. (1981) reported that 65% of applied $NH^+{}_4N$ was lost by volatilization in 3.5 days when swine manure of pH 7.8 was broadcast to a loam (pH 7) in a greenhouse. In the field a swine manure of pH 6.4 broadcast to a soil of pH 6.4 resulted in 14% loss of applied $NH_4{}^+N$ in a 3.5 day period. A 2% loss of applied $NH_4{}^+N$ was reported in the field when the swine manure was injected into the soil and a 66% loss if manure was applied directly to a plastic liner. The research of Hoff et al. (1981) indicates that high manure pH and low soil incorporation cause high volatilization losses. In a comparison of broadcasted and subsurface injected swine manure, Safley et al. (1981) reported significantly lower yields of corn for the broadcast treatments. The lower yields indicate greater NH_3 volatilization losses occurred from the broadcast treatment compared to the incorporated treatment. Beauchamp et al. (1982) observed 24 to 33% of applied $NH_4{}^+N$ lost by volatilization from dairy manure broadcast to the land after a 7 day period. Lauer et al. (1976) reported 61% of NH_4^+N applied lost from dairy manure broadcast to the land in a 5 day period. Beauchamp et al. (1978) observed from 56% to 60% of applied NH_4^+N lost from anaerobically digested sewage sludge broadcast to the land in a 7 day period. Thus, NH_3 volatilization represents a potentially significant loss of N from land applied anaerobically digested animal manures since they contain a large NH_4^+N to total N ratios and have slightly alkaline pH's.

2.6.3 Nitrification

The NH_4^+ form of N can change to the nitrate (NO_3^-) form by a microbiological oxidation called nitrification. This transformation is caused by aerobic chemoautotrophic bacteria of the Nitrosomonas and Nitrobacter genera (Brady, 1974; Tisdale and Nelson, 1975). Generally, conditions of good aeration, mildly acid to mildly alkaline soils and temperatues of 20 to 30°C are necessary for optimal activity (Tisdale and Nelson, 1975). In conditions of high organic loadings to the soil nitrification can be inhibited due to heterotrophic competition for O_2 with the autotrophic nitrifying bacteria (Brady, 1974). With high organic additions, anaerobic conditions may result from the accumulation of CO_2 (from respiration) in the soil air and this may in part explain inhibition of nitrificaiton observed (Ryan et al., 1973). In several N mineralization experiments of sludge-soil mixtures, a delay in NH_4^+ nitrification is observed following the application of a sludge. This lag-phase usually lasts for 1 to 2 weeks (Ryan et al., 1973; Beauchamp et al., 1979).

The greatest significance of nitrification is that NH_4^+, a cationic form of inorganic N, is converted to NO_3^-, an anionic form. Nitrates are subject to greater leaching losses than NH_4^+ because the latter can be retained on the CEC of the soil. The quantities of applied N lost to leaching will depend on the quantity of N nitrified and subsequent flux of water through the soil profile. In general, the greatest volumes of water passing through a soil profile for a given quantity of water applied will be for coarser textured (lower percent clay) soils (Brady, 1974; Pratt et al., 1980). Thus NO_3^-N leaching losses are greatest on soils with higher sand contents. Highly significant losses of NO_3^-N by leaching have been demonstrated for the application of dairy waste water to a sand textured soil (Quisenberry et al., 1981).

2.6.4 Denitrification

After NH_4^+ is nitrified, the resulting NO_3^- is then subject to denitrification. Denitrification is a bacterial mediated conversion of NO_3^- or NO_2^- to NO, N_2O or N_2 gases. The latter are then evolved and lost from the soil (Firestone, 1982). The NO_3^- or NO_2^- is reduced as a consequence of being utilized as terminal electron acceptors of bacterial anaerobic respiration. Thus denitrification occurs only in anaerobic conditions. Anaerobic conditions need only occur in microsites within the soil to enable this process to proceed (Brady, 1974; Firestone, 1982). With increasing moisture contents in the soil, denitrification occurs to a greater extent as anaerobic microsites become more numerous. Denitification requires a supply of NO_3^-, thus the process would be insignificant in anaerobic environments which are not receiving NO_3^-, since the nitrification process does not occur in anaerobic conditions. A majority of the denitrifiers are heterotrophic organisms thus the rate of denitrification is generally positively correlated with the availability of organic substrates (Firestone, 1982).

2.6.5 Phosphorus Availability

Unlike N, P is generally very immobile in soils. Phosphorus forms relatively insoluble complexes with Ca, Fe and Al when applied to soils (Brady, 1974; Tisdale and Nelson, 1975). Likewise, clays and oxide particles that contain Al and Fe also can immobilize P. These insoluble forms of P are not highly available to plants. The formation of insoluble P from soluble forms of P is referred to as P sorption (Singh and Jones, 1976). For certian soils which are high in Fe and Al, 98% of applied soluble P can be sorbed by the soil (Kamprath, 1967).

Additions of organic matter to the soil can both increase and decrease the P avialability status of the soil. Researchers have suggested that P availability increases result from organic acids derived from organic matter decomposition which block sites of P sorption in the soil (Brady, 1974; Singh and Jones, 1976). Other researchers have suggested that availability decreases with organic matter application due to micribiol assimilation of P (Singh and Jones, 1976).

Additions of animal manures in large quantities to the soil have usually resulted in increased P availability. Singh and Jones (1976) added 5% by dry weight poultry manure to soil mixutures and observed that P sorption decreased drastically compared to the check soil. When treatments were equilibrated in P solutions, a given quantity of P sorption resulted in almost a five fold greater concentration of P in the equilibrating solution of the poultry manure treated soil compared to the check. Pratt and Laag (1981) applied 21 to 158 Mg solids/ha/yr of dairy manure to a soil (approximately .8 to 6% by weight manure solids to soil in the furrow slice). These manure treated soils sustained significantly higher levels of extractable P to a depth of .6 m in comparison to the check soil. The P availability was from 4 fold to 13 fold greater than the check plots for the lowest to highest rates of manure, respectively. Reddy et al. (1980) mixed poultry, swine and cow manure with soil at concentrations of approximately 1, 1.5, and 2.5 percent by weight solids to soil, respectively. Phosphorus sorption for the check soil was 5 fold greater than the cow manure treatment and 3 fold greater than the poultry manure, while no sorption was observed for the swine manure treatment. Thus, per unit of solids added, the swine manure decreased P sorption the greatest, followed by the poultry and cow manures, respectively. Thangudu et al. (1981) applied anaerobically digested sewage sludges to the land at rates of 11.2 to 67.2 Mg solids/ha/yr for 2 years (approximately .4% to 6% by weight solids to soil in the furrow slice). The available P of the treated plots were from 50% to 100% higher than the check plots. In the second year the treated plots had from 3 fold to 1.8 fold statistically greater levels of extractable P compared to the check for the highest and lowest rate treatments, respectively.

In all of the references cited above, the application rates of the wastes are at greater quantities than would be required to supply nutrients for ample crop growth. Thus conclusions concerning the available P status of the soil following organic waste applications at rates that are not excessive to crop needs are difficult to make from the literature. Additionally inorganic P is never added to check plots at rates equivalent to those added by the organic waste treatments. Therefore the component of the P availability and sorption characteristics in treated soils due to P added with the waste cannot be distinguished from the component due to organic matter residues preventing P sorption.

Chapter III

MATERIALS AND METHODS

3.1 NUTRIENT RECOVERY STUDIES

3.1.1 Pilot Scale Continuous Digestion

A 3.8 m^3 plug flow anaerobic digester, illustrated in Figure 9, was constructed from a steel tank in January of 1982. Operation was initiated on February 15, 1982, by loading the digester with 1.9 m^3 of seed sludge obtained from the Radford City (Virginia), Municipal Sewage Treatment Plant. Poultry manure from the Virginia Polytechnic Institute and State University Poultry Research Farm was diluted to a 6% total solids (TS) slurry and added to the digester to bring the contents to the retention volume of 2.7 m^3 used during the operation of the digester.

Continuous operation was maintained with daily feedings of approximately 6% TS poultry manure loaded at a volume that corresponded to a 30 day hydraulic retention time. Included in the feed was 10% (by solids basis) hammer milled corn cobs to ensure an adequate carbon to nitrogen ratio (C:N) for the digestion process. A constant temperature of 35°C was maintained with a thermostatically controlled propane fired hot water heater. Heated water was circulated through soft copper tubing, serving as heat exchangers,

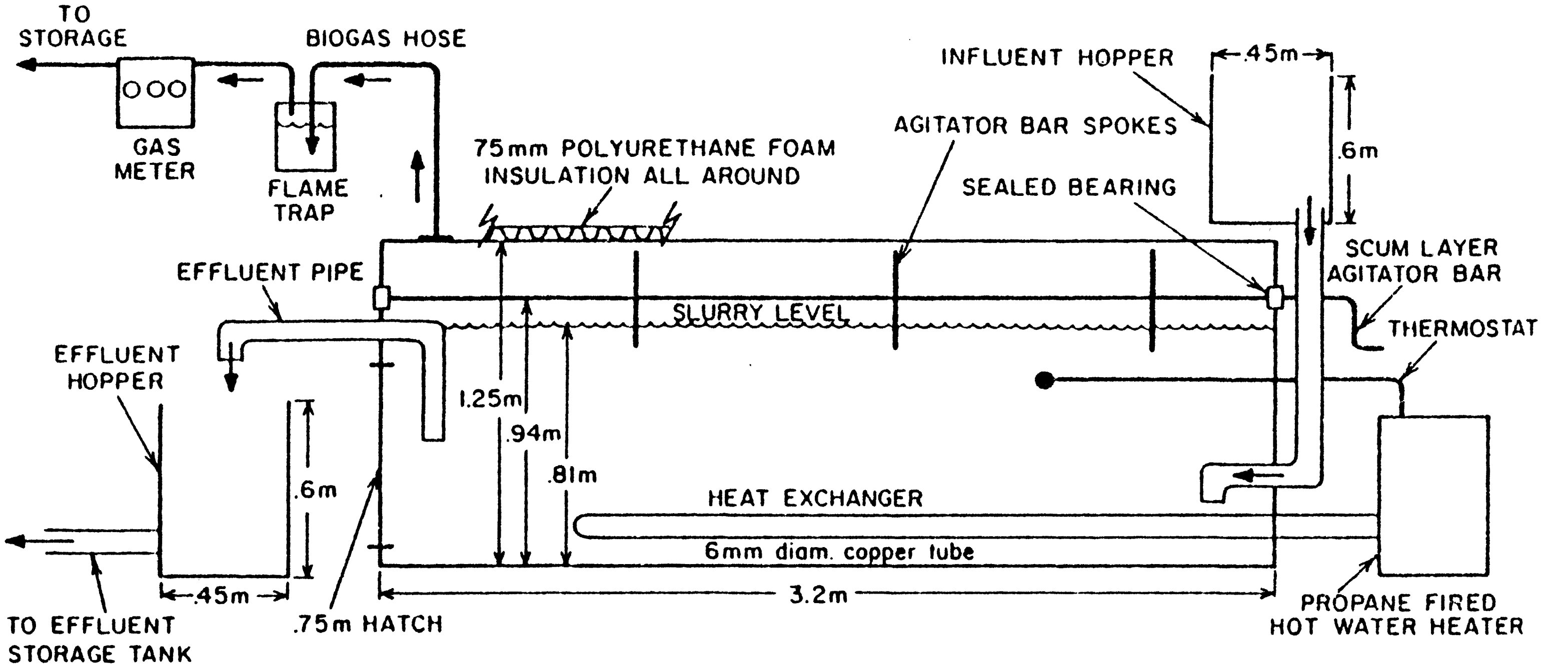


Figure 9. Diagram of pilot scale mesophilic plug flow continuous digester for the digestion of poultry manure.

placed on the inside of the tank. A stir bar with 300 mm spokes was turned vigorously for 5 minutes each day following feeding to prevent excessive scum layer formation.

Due to the difference in chloride concentration between the seed sludge and the poultry manure influent, the relative proportion of the original seed sludge remaining in the digester could be determined periodically. When 90% of the original seed sludge was washed out of the digester (6 weeks into operation) collection of effluent samples was initiated. Influent samples were collected from the onset of the digester operation. Samples were collected once every 5 days by stirring contents in the hoppers (influent and effluent) with a hoe and concurrently submersing a sample bottle. Effluent dispended from the digester was collected in a covered 3.8 m^3 tank for later use as a fertilizer in field grown corn (Zea mays L.) studies.

Samples collected on each fifth day of operation were analyzed for TS, pH, extractable NH_4^+N and TKN. Total solids were determined by drying in an oven at 105°C for 24 hours. The pH was determined with a combination electrode attached to an Orion research Ionanalyzer 901. Ammonium was extracted with 9 parts 2N KCl solution shaken with 1 part sample for 1 hour. The TKN samples were digested with 36N H_2SO_4 at 400°C following the Kjeldahl method (Bremner and

Mulvaney, 1982). Both NH_4^+N and TKN analyses were conducted utilizing steam distillation into boric acid indicator solution followed with a .005N H_2SO_4 back titration (Keeney and Nelson, 1981).

Extractable and total P, K, Ca and Mg, and extractable Mn, Zn, Cu and Fe were determined from composite influent and effluent samples. The composite influent sample was collected by subsampling several kg of poultry manure from numerous storage containers holding poultry manure used in the digester. These subsamples were mixed together and with hammer milled corn cobs in the same proportion used for feedng the digester. The composite effluent sample was collected from the effluent storage tank after mixing for 24 hours with a sludge pump. Samples were oven dried (105°C for 24 hours), ground with a mortar and pestel and .2 g of solids were extracted in duplicate with 20 ml of dilute double acid (.05N HCl and .025N and H_2SO_4) by shaking for 5 minutes. Total P, K, Ca and Mg were determined after digesting samples (run in duplicate) with perchloric acid (Lim and Jackson, 1982). All extracts and digests, except P, were analyzed with a Perkin Elmer Model 503 atomic absorption spectrophotometer following procedures outlined by Baker and Suhr (1982). Phosphorus was determined colorimetrically on a Hitachi model 100-20 spectrophotometer using the ammonium molybdate and ascorbic acid technique described by Olsen and Sommers (1982).

Immediately following the operation of the digester, the contents were drained. The remaining sludge was accessed through a port and sampled after mixing with a hoe. The digester sludge was analyzed for TS, NH_4^+N, TKN, extractable and total P, K, Ca and Mg, and extractable Mn, Zn, Cu and Fe with the previously indicated methods.

Gas was measured in a meter calibrated by directly measuring volumes collected in truck tire innertubes, using a simple water manometer to measure the pressure for standardizing to atmospheric pressure. The calibration period was conducted over the 24 hour feed cycle of the digester and repeated 3 times.

In order to calculate the distribution of nutrients between sludge and effluent fractions of the composite digested slurry, the mass of the digester sludge was estimated. This estimate was based on measuring the volume of sludge remaining in the digester after draining effluent, followed by taking a sludge sample for density determination.

In order to calculate nutrients recovered in a given fraction of the composite digested slurry, the following equations were utilized:

$$((Cs \times Fs)/Ci) \times ((Mi - Mg)/Mi) = Rs \qquad (1)$$

where Cs = concentration nutrient in sludge

Ci = concentration nutrient in influent

Fs = mass fraction of sludge in digested manure

Mi = mass influent

Mg = mass gas

Rs = recovery in sludge

and

$$((Ce \times Fe)/Ci) \times ((Mi - Mg)/Mi) = Re \qquad (2)$$

where Ce = concentratin nutrient in effluent

Fe = mass fraction of effluent in digested manure

Re = recovery in effluent

The total recovery of a nutrient during the digestion process is thus calculated as follows:

$$Rt = Re + Rs \qquad (3)$$

where Rt = total recovery. Since the mass of the gas was not directly measured, ideal gas laws and a composition of 70% CH_4 and 30% CO_2 were assumed in order to calculate the mass.

3.1.2 Laboratory Scale Batch Digestion

A follow-up laboratory batch digestion was conducted in the summer of 1982. The study was conducted with 3 replicates, each consisting of a 1.5 liter flask. The flasks were filled to a retention volume of 1 liter with a mixture of 10% ground corn leaves, 15% seed sludge and 75% poultry manure (by solids weight basis) to a final solids concentration of approximately 6%. The corn leaves were added to provide an adequate C:N for the digestion process. The seed sludge was obtained from the Radford City Municipal Treatment Plant.

Samples for TS, pH, $NH_4{}^+N$, TKN and extractable and total P, K and Ca were collected prior to the digestion by homogenizing the influent in a kitchen blender. Similarly the effluent samples were collected after 30 days digestion. Analyses were identical to those described in section 3.1.1.

During the digestion process a constant temperature was maintained at 35°C by placing the digester flasks in a styrofoam box with a 1 liter jar filled with water and heated by an aquarium heater. Gas volumes were measured by a water displacement method described by Gramms et al. (1971).

Calculations of nutrient recoveries were similar to those outlined in section 3.1.1 except for the following modificaiton. The composite contents following digestion were termed effluent. The effluent was fractioned into a supernatant and sludge fraction by centrifuging a 60 ml aliquot at 2000 rpm for 5 minutes. Nitrogen and K were directly measured in the supernatant fraction while P and Ca were directly measured in the sludge fraction. The nutrient concentrations in the corresponding unmeasured fraction were then calculated from the concentrations in the composite effluent, the measured fraction and the distribution of mass between the two fractions.

3.2 NITROGEN MINERALIZATION STUDY

A Hayesville loam (clayey, oxidic, mesic Typic Hapludult) was collected from the Ap horizon and passed through a 2 mm sieve. Equal parts of soil (dry weight basis) and acid washed distilled water rinsed quartz sand (1 mm to .5 mm size fraction) were mixed together. The mixture was then added to a set of 21 leaching tubes corresponding to a quantity of 15 g of the original soil placed into each tube.

The leaching tubes were constructed from polypropylene centrifuge tubes by removing the bases to form a cylinder 150 mm long with a 28 mm diameter. The bottom of each tube was capped with a modified cork. The cork was bored in the center and lined with a 5 mm diameter glass tube. To the side of the cork facing into the leaching tube, a perforated thin aluminum disc (100 mm in diameter) was placed over the bore . This disc supported a glass fiber filter (Gelman Science Inc., Type A-E) placed at the base of the leaching tube. The filter equilibration of the soil moisture content by applying suction to the base of the tubes. The filters had a maximum pore diameter of 3×10^{-4} mm which corresponds to an air entry pressure of .5 MPa. This is in large excess of .033 MPa of suction applied to the tubes for final moisture equilibration.

Three replications and seven treatments were arranged in a completely randomized block design. One treatment was the check (unamended). The other 6 treatments utilized 3 rates of poultry manure influent and the three rates of effluent corresponding to 100, 500 and 1000 µg TKN per g of soil. This is approximately equivalent to 1, 5 and 10 times the rate of the annual N application to conventionally cultivated corn. The effluent utilized in the study was obtained from the pilot scale plug flow digester described in section 3.1.1. Total Kjeldahl N of the influent and effluent was determined from the procedures also described in section 3.1.1.

The influent and the effluent were homogenized with a magnetic stir bar. As the influent and effluent were being homogenized, aliquots corresponding to the N application rates were transfered to the leaching tubes and dispensed onto the soil surface. The homogenizing process used prior to the transfer of the influent N was believed to be adequate. However, subsequent analysis indicated that the stir bar did not sufficiently homogenize some of the influent solids. Thus utilization of a blender is recommended for slurries that contain coarse particles.

Immediately following application of the treatments to the soil a glass rod was used to incorporate the slurries 10 mm into the soil. This was followed with a 100 ml aliquot (added 10 ml at a time) of .01M $CaCl_2$. The glass rods were removed while washing attached soil off with the .01M $CaCl_2$. A 25 ml nutrient solution devoid of N(.002M $CaSO_4.2H_2O$; .002M $MgSO_4$; .005M $Ca(H_2PO_4)_2$; .0025M K_2SO_4) was applied following the .01M $CaCl_2$. The leachate was collected in 1000 ml side arm flasks utilizing suction at .033 MPa.

After this initial leaching the remaining applied N in the tubes was assumed to correspond to organic N. The N mineralization study was initiated by placing the tubes in a 35°C constant temperature incubator. A pan of water was placed in the incubator to maintain the relative humidity near 100% and prevent drying of the soil in tubes from the .033MPa tension achieved by equilibration with suction. The tubes were also covered with wax paper punctured with three pinholes to further prevent drying yet not limit the exchange of air.

The leaching procedure (100 ml of .01 M $CaCl_2$ followed by 25 ml of N minus nutrient solution) was repeated at 7, 14, 28, 56, 84, 102, 130, 158, 186 and 234 days of incubation. Collected leachate was analyzed for NH_4^+N and NO_3^-N + NO_2^-N colorimetrically utilizing an automated analyzer (Scientific Instruments Corporation Model CFA-200). Ammonium N was determined by the indophenol blue method (Keeny and Nelson, 1982). Nitrate and NO_2^- forms of N (termed NO_3^-N for the remainder of this paper) were first reduced to NO_2^-N with a cadmium copper column and subsequently determined with the sulfanilamide method (Keeny and Nelson, 1982).

The cumulative inorganic N (NH_4^+N + NO_3^-N) leached during the course of the study was plotted against the square root of time. This relationship was estimated with a linear regression of the treatment averaged data (Little and Hill, 1978). Lines were fitted through an intercept of 0. Additionally the cumulative inorganic N leached up to a given date in the experiment was analyzed with ANOVA and

Duncan's multiple range test (Little and Hill, 1978). Similar statistical analyses were repeated using the data normalized against applied organic N, estimated in the following manner:

$$((\mathrm{CINt} - \mathrm{AVECINc})/\mathrm{ORGNt}) \times 100 \qquad (4)$$

where CINt = cumulative inorganic N leached from treated tubes

AVECINc = average cumulative inorganic N leached from check

ARGNt = organic N applied with treatment

The ORGNt was estimated with the following equation:

$$\mathrm{APPLN} - (\mathrm{INDOt} - \mathrm{AVEINDOc}) = \mathrm{ORGNt}$$

where APPLN = TKN applied

INDOt = inorganic N leached at day 0 from treated tubes

AVEINDOt = average inorganic N leached at day 0 from check

3.3 FIELD EXPERIMENT

Field experiments were conducted at two sites in the summer of 1982. The soils at Site 1 (Montgomery County, Virginia) and Site 2 (Floyd County, Virginia) are the Groseclose silt loam (clayey, mixed, mesic Typic Hapludult) and the Hayesville loam (clayey, oxidic, mesic Typic Hapludult), respectively. Selected chemical and physical properties of the 0 to 150 mm (furrow slice) and 150 to 300 mm depth intervals of these soils are shown in Table 3.

Site 1 was plowed and disced three weeks prior to treatment applications. Site 2 was not plowed prior to treatment applications as this site was located in a minimum till cornfield with the previous year's stubble on the soil surface.

A randomized complete block design was used in these experiments. Each of the 6 treatments were replicated 4 times. The six treatments utilized were as follows: a check treatment; urea N fertilizer applied at 146 kg ha^{-1} TKN; manure influent N applied at 146 kg ha^{-1} TKN and digester effluent applied at 73, 146 and 219 kg ha^{-1} TKN. The poultry manure influent was diluted to a 6.9% TS slurry and homogenized by mechanical agitation with a 2.6 m^3 hydroseeder tank. The homogenized poultry manure was then spread evenly onto the surface of the plots with a watering

Table 3. Physical and chemical[*] characteristics of the soils used in the field experiments.

Site number		1		2	
Soil series		Groseclose silt loam		Hayesville loam	
Parent material		limestone		granitic schist	
Depth interval	mm	0-150	150-300	0-150	150-300
Bulk density	Mg m^{-3}	1.25	1.49	1.14	1.51
Sand	%	25.3	22.9	45.2	41.4
Silt	%	59.6	56.4	30.3	26.2
Clay	%	15.2	20.7	24.5	32.4
pH		6.5	-	6.3	-
TKN^1	µg/g	1230	-	2660	-
NH_4^+-N	µg/g	3.45	2.72	11.7	6.04
NO_3^--N	µg/g	11.3	10.2	24.3	12.3
Extractable P	µg/g	35.0	-	4.52	-
Extractable K	µg/g	128	-	75.4	-
Extractable Ca	µg/g	528	-	660	-
Extractable Mg	µg/g	96.0	-	120	-

[*] Sampled 1 week after lime application and prior to treatment, P and K applications.

can. The effluent was collected from the pilot scale plug flow methane digester described in section 3.1.1 and similarly homogenized in the hydroseeder. The effluent was then sprayed from the hydroseeder evenly over the surface of the plots. All treatments were disced lightly (75 mm into the soil) from 2 to 4 hours following the application.

Prior to application of treatments, the experimental sites were sampled for pH and extractable, P, K, Ca and Mg and analyzed at the Virginia Soil testing Laboratory in Blacksburg. Based on these analyses lime, P and K were applied to ensure adequate pH and adequate nutrient levels for corn growth. Two weeks prior to treatment applicaitons, 2.25 and 3.9 Mg ha^{-1} of $CaCO_3$ were applied to Sites 1 and 2, respectively, and disced in 75 mm. Immediately prior to treatment applications, P and K were brought to equal applied levels with fertilizer (40 kg ha^{-1} P and 37 kg ha^{-1} K for both sites). This was done by deducting the quantity of extractable P and K added with the influent and effluent treatments. Extractable P and K of the influent and effluent materials were determined with the dilute acid extraction procedures discussed in section 3.1.

Each experimental plot was 4.6 m wide by 6.1 m long. Each block consisted of 6 experimental plots and a 1 m border area was placed between blocks. Pioneer 3369A hybrid corn was planted four days after treatment applications in rows parallel to the length of the plots. The rows were spaced .76 m apart so that each plot contained 4 guard rows and 2 center rows. Granular Furidan was applied with the seeds at 17 kg ha^{-1} for insect control. Dual herbicide was applied at 2.5 ha^{-1} and Atrazine at 2.25 kg ha^{-1} for weed control.

Soil samples were obtained from the 0-150 mm depth interval at 0, 7, 14, 34, 54, 88 and 147 days after treatment application for Site 1 and at 0, 7, 14, 32, 52, 81 and 154 days after treatment application for Site 2. Inorganic N reported for the day 0 samples was calculated from the N measured in the soil (prior to treatment application) and that applied with the treatments. Inorganic N reported at all other dates are based from direct measurements from the soil samples. Inorganic N was also measured from samples taken from the 150-300 mm depth interval collected at 0 and 34 days at Site 1 and at 0, 32 and 81 days at Site 2. Samples for this depth interval on day 88 at Site 1 were not collected because of excessive soil strength.

Inorganic N was determined from 2N KCl extracts. The extraction utilized 50 ml of 2N KCl that was shaken with 5 g (dry weight basis) soil for one hour. Analysis of the filtered extracts were colorimetrically determined with an automated analyzer (Scientific Instruments Corporation Model CFA-200). The procedures for NH_4^+N and NO_3^-N determinations are described in section 3.2.

Inorganic N is reported as kg N per ha in the 0-150 mm (furrow slice) and 150-300 mm depth intervals. Conversions from N concentration in the soil to N content in the ha furrow slice and lower depth interval required a bulk density. The bulk density was directly measured by collecting 20 mm diameter by 150 mm long undisturbed cores with a soil probe. Thirty cores were collected at each depth from each experimental site and bulk densities were determined from oven dried soil mass (105°C for 24 hours).

Ammonia volatilization losses were estimated from applied inorganic N which was not recovered in day 7 samplings. The estimate accounts for N mineralized from indigenous organic N of soil in the check plots. The equation for the estimate is as follows:

$$AVOLe = -1x\ ((NSoil7t - NSoil0t) - (NSoil7c - NSoil0c)) \quad (5)$$

where

AVOLe = estimated ammonia N volatilization losses

NSoil7t = inorganic N measured on day 7 (treated plot)

NSoil0t = inorganic N measured in soil and applied material on day 0

NSoil7c = inorganic N measured on day 7 (check plot)

NSoil0c = inorganic N measured on day 0 (check plot)

The estimated ammonia losses are based on several assumptions. The first is that significant denitrification did not occur in the first week. This is a relatively safe assumption to make since a majority of the N applied was in the NH_4^+ or urea form. Prior to denitrification, nitrification must occur first. The data revealed that some nitrification was occurring in the first week but by the time the nitrates appeared, there was not sufficient time for significant denitrification. This is especially true since the soil was relatively dry. A second asumption requires that insignificant leaching of applied N occurred beyond a depth of 150 mm. This is also a relatively safe assumption since rainfall did not occur until two weeks after treatment applications. A third assumption is that there was no immobilization. This would be expected as the C:N ratios of the poultry manure and effluent were low (never measured above 10). A fourth assumption is that there was insignificant mineralization of organic N applied with infuent and effluent treatments during the first week. This is not a safe assumption as N mineralization data of the effluent and influent revealed a significant amount of organic N is mineralized in the first week. However, the effluent applied TKN was only 12% organic N, thus the contribution of mineralized N to the alteration of the estimate would not be that great. This influent applied TKN was 54% organic N of which only a partial fraction would be expected to have been mineralized. Nitrogen mineralization data of the influent N at 35°C with optimal moisture revealed that up to 40% of the organic N could be mineralized in one week. However, in the field, temperatures were much lower so the actual amount would be much less. A fifth assumption is that indigenous soil organic N was mineralized at the same rate in the check plots as in the treated plots. This assumption may not be valid as data from the previously mentioned mineralization study indicated that there was a 'priming' effect. The result of these assumptions, those involving the mineralization of organic N, would however, only cause the estimated losses to be slightly lower than the true losses. Thus the estimated losses are still a good indicator of the NH_3 losses. A final assumption is that insignificant NH_3 losses occurred following the first week. While it is possible that some volatilization continued past the first week, an estimate based on losses of inorganic N past the first week would be undistinguishable from leaching, denitrification and crop uptake. Again since the effect of this assumption would only result in an underestimation, the estimated NH_3 losses can still be considered indicative of the true loss. Since urea N is entirely organic, the estimate assumed that this form of N was completely mineralized by week 1. Thus urea N was included in the NSoil0t term of equation 5.

Tissue analyses were conducted on ear leaf samples collected at early silk. The leaves were dried, ground, ashed and prepared for analysis according to methods described by Jones and Steyn (1973). An atomic absorption spectrophotometer, Perkin and Elmer Model 503, was utilized for the analyses of plant tissue K, Ca and Mg (Issac and Kerber, 1971). Phosphorus was determined colorimetrically with a Hitachi model 100-20 spectrophotometer using the procedure described in section 3.1.1. Prior to ashing, ground leaves were digested with a kjeldahl digestion (Bremner and Mulvaney, 1982). Total N of these digests were analyzed colorimetrically with sodium salicylate, sodium nitroprusside and sodium hypochlorite (EPA, 1974) using the automated analyzer.

The experimental plots were harvested at 147 and 154 days after treatment applications for Sites 1 and 2, respectively. Yields were measured from the center two rows of each experimental plot. Grain was weighed at field moisture and was oven dried to enable reporting yields at

15.5% moisture. Silage yields were determined by weighing field moist fodder, subsampling for oven dried moisture determinations and adding the weight of oven dried grain. Silage yields are reported on a dry matter basis.

The yield of grain, silage yield and percent N in the ear leaf were compared with TKN applied (NAPPLO), total N applied recovered on day 7 (NREC7) and soil inorganic N of the 0-150 mm depth interval on day 7 (NSoil7). The comparisons were made with a Mitscherlich plant growth model using a nonlinear statistical curve fitting program (Helwig and Council, 1979). Mitscherlich curves were chosen for the determinations of regressions because they are commonly used for relating yield as a function of plant nutrient supply (Tisdale and Nelson, 1975; Ware et al., 1982). The NREC7 term is NAPPLO minus the estimated NH_3 N volatilization losses. This term is an estimate of applied N remaining after the volatilization losses are discounted.

The inorganic N and NO_3^-N to inorganic ratio were analyzed at each sampling date with ANOVA and Duncan's multiple range test to determine statistical significance (Little and Hill, 1978). The N, P, K, Ca and Mg in the ear leaf at early silk were analyzed similarly. Inorganic N in the 150-300 mm depth interval at 34 and 32 days after treatment application for Sites 1 and 2, respectively, are reported and statistically analyzed as the increased quantity of inorganic N over the content measured on day 0. This provides a relative indicator of N leaching from the treated plots since the absolute quantity of N leached cannot be estimated from the data. Inorganic N for this depth at day 81 is reported and statistically analyzed as the content measured, since at this date, inorganic N was lower than that measured on day 0.

3.4 PHOSPHORUS SORPTION STUDY

A laboratory phosphorus sorption study was initiated in June 1982. The study utilized 4 treatments, a check treatment and anaerobically digested poultry manure applied at 3 rates. The soil used in the study was a Hayesville loam collected from Site 2 of the field experiments. The anaerobically digested poultry manure (effluent) was obtained from the pilot scale plug flow digester described in section 3.1.1.

The oven dried soil and oven dried effluent (105°C for 24 hours) were each ground with a mortar and pestel and passed through a sieve with .5 mm openings. The effluent solids were applied to the soil at rates of 100, 500 and 1000 µg TKN applied per gram of soil, corresponding to approximately 1, 5 and 10 times the N applied to conventionally grown corn. The rates were based on the TKN concentrations associated with a unit weight of solids prior to oven drying (acknowledging NH_3 would be lost during drying). Nitrogen was chosen as the determining factor for the application rates of the treatments as N is typically the factor determining the rate of organic waste application to crops.

In terms of solids added, these rates corresponded to 753, 3765 and 7530 µg effluent solids applied per g of soil. Extractable P of the effluent solids was determined with 20 ml of dilute acid (.05N HCl and .025N H_2SO_4) shaken for 5 minutes with .2 g of effluent solids (Olsen and Sommers, 1982). The extractable P applied with the effluent soilds was equivalent to 9.87, 49.4 and 98.7 µg P per gram soil.

The effluent solids were mixed with the soil by placing 200 g of soil and the corresponding quantity of effluent in a 250 ml square plastic bottle and shaking laterally for 3 hours. After shaking, water was added until the moisture content corresponded to .033 MPa tension. The soil and effluent were mixed further with a glass rod. The moisture content that corresponded to .033 MPa was determined by equilibrating a saturated sample of the ground and sieved soil placed on .1 MPa stone with .033 MPa air suction applied under the stone. The bottles were then covered with wax paper perforated with 3 pin holes to avoid excessive drying while ensuring aeration. The bottles were incubated in a 25°C incubator. A pan of water was kept in the incubator to maintain the relative humidity near 100% to further prevent drying.

Phosphorus sorption isotherms modified from the procedures outlined by Fox and Kamprath (1970) and Singh and Jones (1976) were conducted after 0, 30 and 90 days of incubation. Soil from the incubator was oven dried, and 1.5 g of soil was placed in each of a series of 100 ml centrifuge tubes. The soil was equilibrated with 25 ml of 0, 5, 10, 20, 40, 80 and 160 mg P/l solutions. At the onset of equilibration, 2 drops of toluene were added in each tube. Each treatment was equilibrated in duplicate; however, only averages are reported. The equilibration process was conducted by incubating at 25°C for 6 days. During the equilibration period, tubes were shaken for .5 hours every 12 hours. At the end of the equilibration period, the solution was filtered and colorimetrically analyzed for P using the procedure described in section 3.1.1.

Phosphorus sorption was determined from the disappearance of P from the P solutions during equilibration. Phosphorus sorption is graphed as a function of the final equilibration solution P concentration (EPC).

To facilitate comparison of the results with field observations, extractable P was determined for the soils from the field experiments described in section 3.3. The phosphorus in soil samples collected at several dates during the course of the field experiments was extracted with 20 ml of dilute acid (.05N HCl and .025N H_2SO_4) shaken with 5 g of oven dried soil. The extractable P was analyzed by the previously discussed colorimetric method. The P concentration at a given sampling date was statistically analyzed with ANOVA (Little and Hill, 1978). Linear regressions (Little and Hill, 1978) were also calculated for the relationship of soil extractable P concentration versus effluent solids applied at Site 1, since a clear trend was evident at this site.

Chapter IV

RESULTS AND DISCUSSION

4.1 RESULTS OF THE PILOT SCALE DIGESTER

4.1.1 Biogas Yield: Pilot Scale

The biogas yields from the pilot scale mesophilic continuous digester from day 60 to 90 of operation are plotted in Figure 10. The average daily gas yield was .752 m^3 of biogas per m^3 of retention volume. On a solids basis, the biogas yield was .39m^3 per kg of solids loaded into the digester. If the methane composition is assumed to be 70% and the concentration of volatile solids (VS) in the total solids (TS) is also assumed to be 70%, then the yields obtained are comparable to those reported in other studies of poultry manure digestions operated with similar retention times (Converse et al., 1977a; Converse, et al., 1981; and Gramms et al., 1971).

The energy equivalence of the biogas yield is 10, 130 kJ produced per kg of poultry manure solids added. This is equal to the energy contained in .32 liters of gasoline. Since each day an average of 5.2 kg solids were added, the daily energy production from the pilot scale digester is equivalent to that contained in 1.7 liters of gasoline.

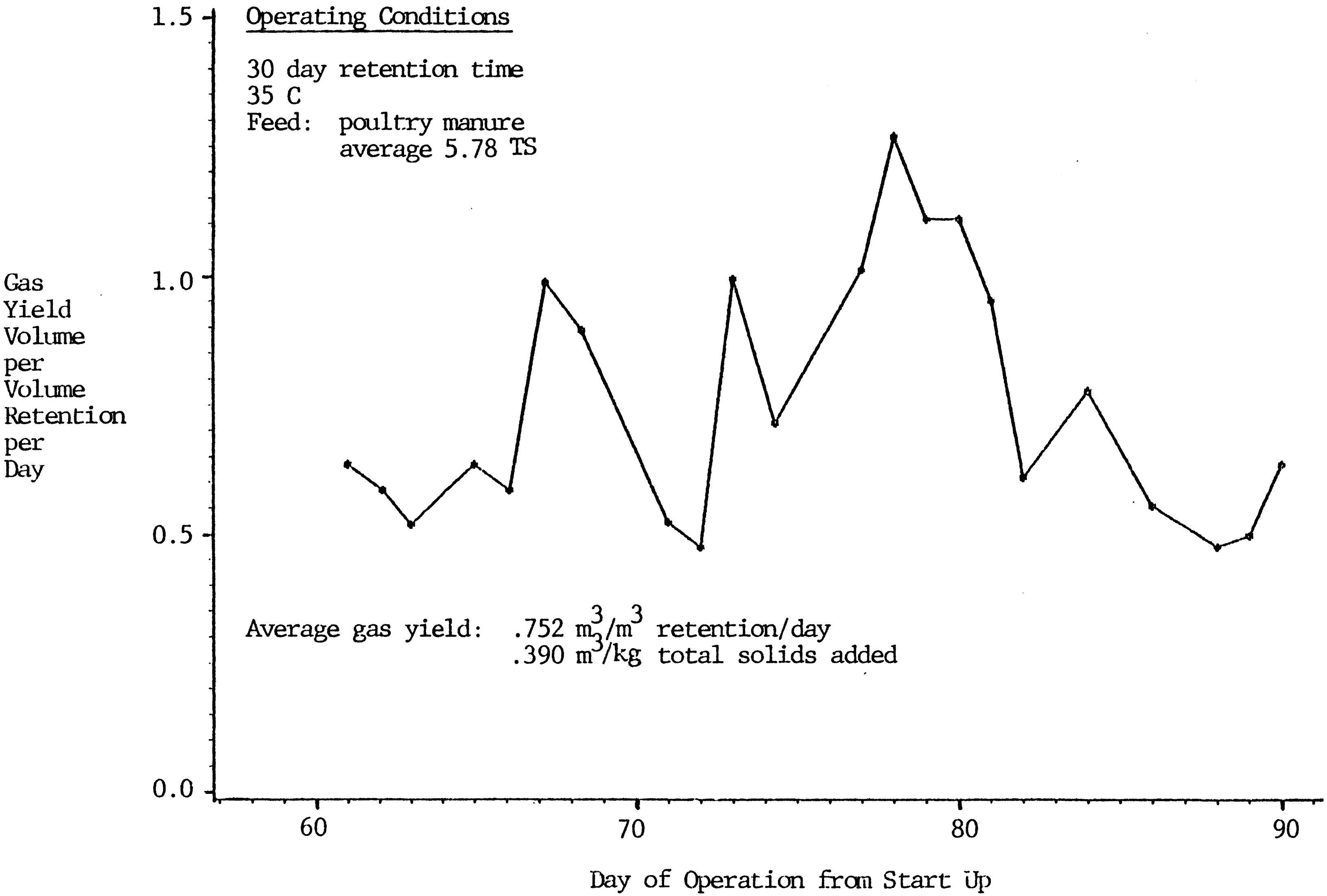


Figure 10. Biogas yields from day 60 to 90 of operation for the pilot scale mesophilic plug flow continuous digester.

4.1.2 Total Solids and Mass Recovery: Pilot Scale

The total solids concentrations of the poultry manure influent, corresponding effluent and sludge are shown in Table 4. The average effluent concentration of 3.15% was almost half that of the influent, 5.8%. The reduction of solids in the effluent is due to both a conversion of the influent organic matter to gaseous products and to the settling of refractory constituents. These settled solids developed into the digester sludge which had a concentraiton of 16.9% solids.

Considerable variation in the influent solids concentration is evident from the standard deviation of approximately 1 percentage unit of solids. This variation was due to the day to day differences in the moisture content of the manure collected for digester operation. The effluent solids concentration also had considerable variation of approximately .95 percentage units. This variation was due to the effluent pipe placement which was located 250 mm above the base of the digester. As such, some solids washed out as they were settling to the sludge bed. Thus the variation in effluent solids can be attributed to daily variations in the wash out of these solids.

Table 4. Comparison of total solids, pH ammonium N and total N of poultry manure influent slurries, corresponding effluent and digester sludge from a mesophilic pilot scale continuous plug flow anaerobic digester.

Material	Parameter	Total Solids %	pH	NH_4^+-N[1] mg/l	TKN[2] mg/l	NH_4^+-N/TKN %
Influent	Average	5.78	-	2240	3940	57
	Low	4.58	6.56	1780	3050	42
	High	6.74	7.48	2850	4670	77
	S.D.[3]	.981	-	336	519	10
Effluent	Average	3.15	-	3690	4420	83
	Low	2.24	7.43	3280	4130	75
	High	4.84	8.17	3840	4840	89
	S.D.	.944	-	194	222	5.6
Sludge	1 sample	16.94	-	2690	6700	40

[1] Extractable in 2N KCl

[2] Total Kjeldahl Nitrogen

[3] Standard Deviation

The recovery of the influent mass is given in Table 5. Of the influent mass, 97.7% was recovered in the composite of the effluent and digester sludge. The biogas accounts for the remaining mass. Most of the mass (91.7%) was recovered with the effluent and the sludge accounted for the other 6%.

The composite solids recovery (shown in Table 5) was 67.8% of the influent solids. If the mass of the biogas is used as the sole basis of determining solids recovery (assuming that biogas mass equals the mass of solids destroyed) then 60.2% of the solids could be considered recovered which is close to the measured value. Of the solids recovered, 74% were with the effluent and 26% remained with the sludge.

4.1.3 Recovery of Nitrogen: Pilot Scale

The concentrations of NH_4^+N (Table 4) in the influent, effluent and sludge were 2240, 3690 and 2690 mg/l, respectively. A distinct increase in the NH_4^+N concentration of 65% was evident in the effluent compared to the influent.

The TKN concentrations of the influent, effluent and sludge (Table 4) were 3960, 4420 and 6700 mg/l, respectively. The TKN concentration of the effluent was 12%

Table 5. Recovery of mass, solids, total and extractable forms of macronutrients during the anaerobic digestion of poultry manure in a pilot scale mesophilic plug flow continuous digester.

Material	Mass	Solids	NH_4^+-N[1]	TKN[2]	Extr[3]P	Total[4]P	Extr K	Total K	Extr Ca	Total Ca	Extr Mg	Total Mg
	% of influent											
Composite[a]	97.7[b]	67.8	159	113	75.1	66.7	113	121	56.7	64.2	51.9	62.5
Effluent	91.7	50.0	151	103	45.6	48.1	108	116	30.8	44.4	27.6	40.7
Sludge	6.01	17.8	7.61	10.2	29.5	18.6	4.66	4.92	25.9	19.8	24.3	21.8

[1] Extractable in 2N KCl

[2] Total Kjeldahl Nitrogen

[3] Extractable in dilute acid

[4] Perchloric digest

[a] Effluent and sludge fractions combined

[b] Remaining 2.3% of mass is biogas

higher than that of the influent. This increase is partially due to a concentration effect that results from the loss of mass with biogas. The concentration of TKN in the digester sludge was 70% higher than the influent TKN due primarily to the much higher solids (containing organic N) concentration of the sludge.

The standard deviations of the NH_4^+N and TKN of the influent (shown in Table 4) were 15% and 13% of the means, respectively. In contrast, the standard deviations of the NH_4^+N and TKN of the effluent were 5.3% and 5% of the means, respectively. This indicates that biogas effluent is a more homogeneous N carrier than the corresponding influent poultry manure. This suggests that N fertilizer recommendations could be made with greater certainty for digested animal manures compared to untreated untreated manures.

The NH_4^+N to TKN ratios are presented in Figure 11. The average NH_4^+N :TKN for the influent was 57% NH_4^+N which contrasts the average of 83% NH_4^+N present in the effluent. The sludge TKN was 40% NH_4^+N indicating that the majority of the N in the sludge solids was in the organic form. The effluent accounts for 94% of the mass in the recovered composite slurry. Thus the composite slurry (a hypothetical mixture of the effluent and sludge) has a similar NH_4^+N:TKN ratio (80% NH_4^+N) to that of the effluent. This indicates that only a small component of the effluent NH_4^+N enrichment can be attributed to the segregation of organic N rich particles into the sludge fraction.

The effect of the anaerobic digestion process on the quality of the N in the composite slurry material remaining after digestion was to convert a material from 57% NH_4^+N to 80% NH_4^+N per TKN. The calculated recoveries of added NH_4^+N and TKN are shown in Table 5. The recovery of NH_4^+N in the composite slurry was 159%. The quantity of recovered NH_4^+N was 59% greater than the NH_4^+N originally added to the digester. This NH_4^+N comes from the mineralization of the poultry manure organic N.

The recovery of TKN was 113%. As discussed previously, the theoretical TKN recovery cannot exceed 100%; thus, the deviation from 100% must be attributed to errors introduced from sampling and analysis. Sampling procedures most likely introduced the majority of the errors as samples were collected once every five days. While the effluent samples collected in this manner would be representative of all the material placed in the digester, the influent samples would only represent 20% of the actual material used. Thus the influent sample apparently underestimated the TKN. Additional sampling errors were introduced from the sludge

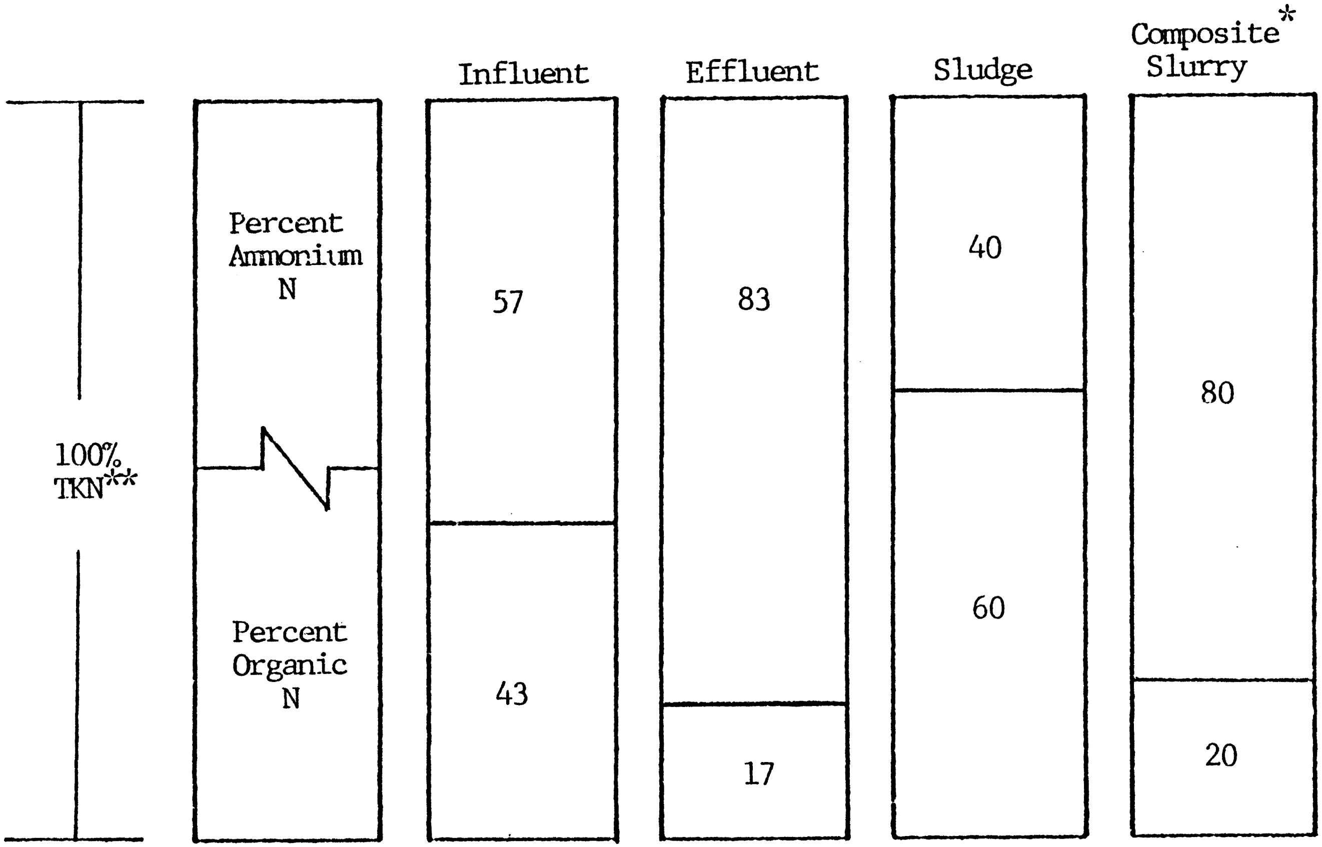


Figure 11. Ratios of extractable ammonium N to organic N in poultry manure influent, corresponding effluent, digester sludge and composite digested slurry from a pilot scale mesophilic plug flow continuous digester.

*Mixture of effluent and sludge **Total Kjeldahl Nitrogen which was analyzed from one composite sample. Homogenization of the sludge was also somewhat limited as access to the sludge was restricted.

The percent of the original organic N (TKN - NH_4^+N) that was mineralized to inorganic N during the digestion process is estimated to be 60%. This estimate assumes that the influent TKN (used in estimating influent organic N) was that which could be calculated from the effluent and sludge TKN, mass recovery data and a theoretical TKN recovery of 100%. Additionally, the assumed influent TKN was used to calculate an assumed influent organic N from the measured influent NH_4^+N:TKN ratio. This was done as the effluent TKN was considered to be more representative of the true TKN than that measured for the influent.

The majority of the recovered NH_4^+N, 95% (see Figure 12), was distributed in the effluent fraction. Similarly, most of the recovered TKN, 91% (Figure 12), was distributed in the effluent fraction. Thus, essentially most of the fertilizer N was associated with the effluent fraction. This would be expected as NH_4^+N, which constitutes the largest component of the recovered TKN, is a highly soluble ion. Consequently, very little N remained in the sludge.

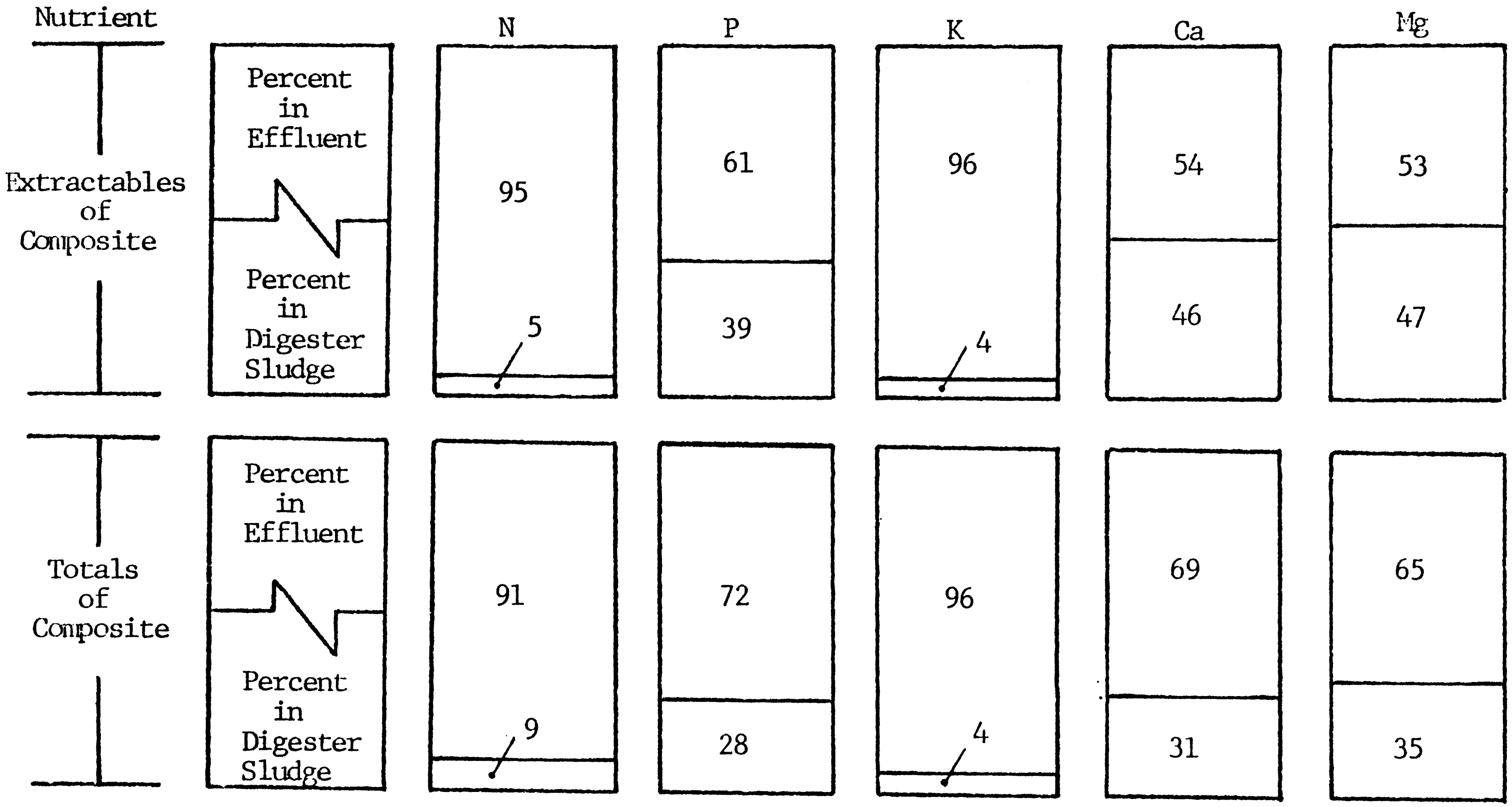


Figure 12. Distribution of extractable and total N, P, K, Ca and Mg in the effluent and digester sludge of the composite digested slurry from anaerobic digestion of poultry manure in a pilot scale mesophilic continuous digester.

4.1.4 Recovery Of K, P, Ca and Mg: Pilot Scale

This study of K, P, Ca and Mg recoveries from the pilot scale continuous digestion can only be considered as a preliminary investigation. This results from the nature of the sampling program. Analyses were conducted on single composite samples of influent poultry manure, effluent and digester sludge. The influent sample was based on a random set of subsamplings taken from various containers of manure which were used for loading in the digesters. The sludge sample was based on samples with limited homogenization (discussed in section 4.1.3). However, despite obvious sampling errors, results are still reported as clear trends in the behavior of the nutrients recovered are indicated.

The concentrations of dilute acid extractable and total P, K, Ca and Mg are shown in Table 6 for the influent, effluent and digester sludge. Both extractable and total K concentrations were noticeably lowered by 34% and 35%, respectively, in the sludge fraction compared to the effluent fraction. Figure 13 shows the extractable to total ratios of K. The influent total K was 95% extractable. This indicates that most of the K in poultry manure is in an ionic form which is readily extractable.

The recoveries of extractable and total K are illustrated in Table 5. Extractable K recovery was 113%. A

Table 6. Concentrations of extractable* and total** P, K, Ca and Mg of poultry manure influent, corresponding effluent and digester sludge from a pilot scale mesophilic plug flow continuous digester.

Material	P		K		Ca		Mg	
	Extr	Total	Extr	Total	Extr	Total	Extr	Total
	mg/l							
Influent	832	1722	1960	2070	4465	5874	419	427
Effluent	413	904	2300	2615	1500	2670	126	189
Sludge	4070	5336	1520	1694	19227	19312	1694	1545

*Extracted with dilute acid

**Perchloric digest

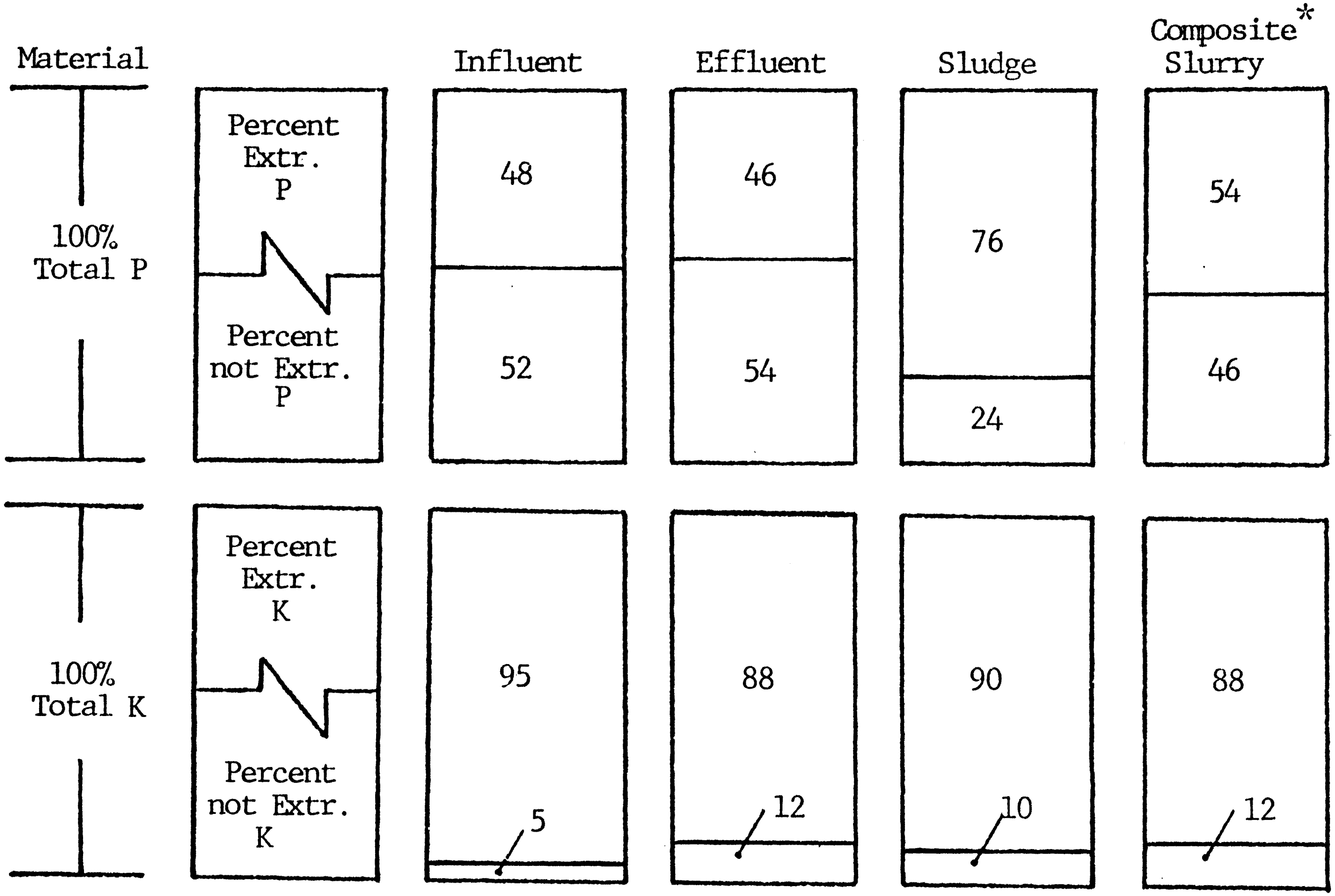


Figure 13. Ratios of extractable to unextractable forms of P and K in poultry manure influent, corresponding effluent, digester sludge and composite digested slurry from a pilot scale mesophilic plug flow continuous digester.

*Mixture of effluent and sludge

greater than 100% recovery of an extractable nutrient is theoretically feasible as enrichment can be attributed to the release of previously unextractable forms. However, since a slight decrease in the extractable to total K ratio was observed in the composite digested slurry compared to the influent, the larger than 100% recovery observed here is attributed to sampling errors. This is supported further by the measured 121% recovery of total K. The theoretical 100% recovery of total K was exceeded, clearly indicating that the influent samples underestimated the quantity of K actually fed into the digester.

The distributions of recovered extractable and total K in the composite digested slurry are illustrated in Figure 12. Both extractable and total forms of K were distributed 96% in the effluent fraction. The distribution of K indicates that most of the influent K placed in the digester will be recovered with the effluent. This would be expected as K is highly water soluble. Consequently, only insignificant quantities of K remained in the sludge.

The concentrations of total and extractable P, Ca and Mg in the influent, effluent and sludge are shown in Table 6. The majority of observed decreases in P, Ca and Mg concentrations in the effluent compared to the influent can be attributed to the segregation of these nutrients into the sludge. Extractable P, Ca and Mg concentrations of the sludge were 9.9, 12.8, and 13.4 times higher, respectively, than the concentrations observed in the effluent. Similarly, total P, Ca and Mg concentrations of the sludge were 5.9, 7.2 and 8.2 times higher, respectively, than the concentrations observed in the effluent. These high concentrations of P, Ca and Mg present in the sludge fraction indicate that these nutrients are not highly soluble. Rather an association of these nutrients with the solids is implicated as these nutrients are enriched with the solids.

The extractable to total ratios of P in the influent, effluent, sludge and composite digested slurry are shown in Figure 13. the ratio of 48% extractable P to total P in the influent is comparable to the 46% observed in the effluent and the 54% observed for the composite digested slurry. However, the sludge fraction contains a greater proportion of extractable P (75%) per unit of total P. A component of P in organic wastes is usually incorporated in the organic matter as it is a constituent of many organic molecules. The fine organic particles of the effluent appeared to contain a significant component of incorporated P. The coarser sludge particles apparently had less incorporated P and a greater proportion of readily extractable P, perhaps associated with newly formed inorganic precipitates.

The extractable to total ratios of Ca and Mg in the influent, effluent, sludge and composite digested slurry are shown in Figure 14. The extractable Ca and Mg in the influent accounted for 76 and 98%, respectively, of the total Ca and Mg. However, the extractable Ca and Mg in the effluent fraction was only 56 and 67%, respectively, of the totals. This contrasted the sludge extractable to total ratios of 100% for both Ca and Mg. The composite digested slurry was similar to the effluent as the effluent constitutes most of the mass.

The Ca and Mg of the effluent solids were thus less available to dilute acid extractions than the influent solids or the sludge solids. This is perhaps due to increased sorption by colloidal particles dispersed in the effluent. A component of these sorbed cations apparently resist extraction. Conversely, the coarser sludge solids lack the surface area for similar sorption. The Ca and Mg of the sludge must be associated with newly formed inorganic precipitates (perhaps hydroxides) since they were completely dissolved during the extraction process.

The recoveries of extractable and total P, Ca and Mg are shown in Table 5. Extractable P and total P were only 75.1 and 66.7% recovered, respectively. The extractable and total Ca were only 56.7 and 64.7% recovered, respectively.

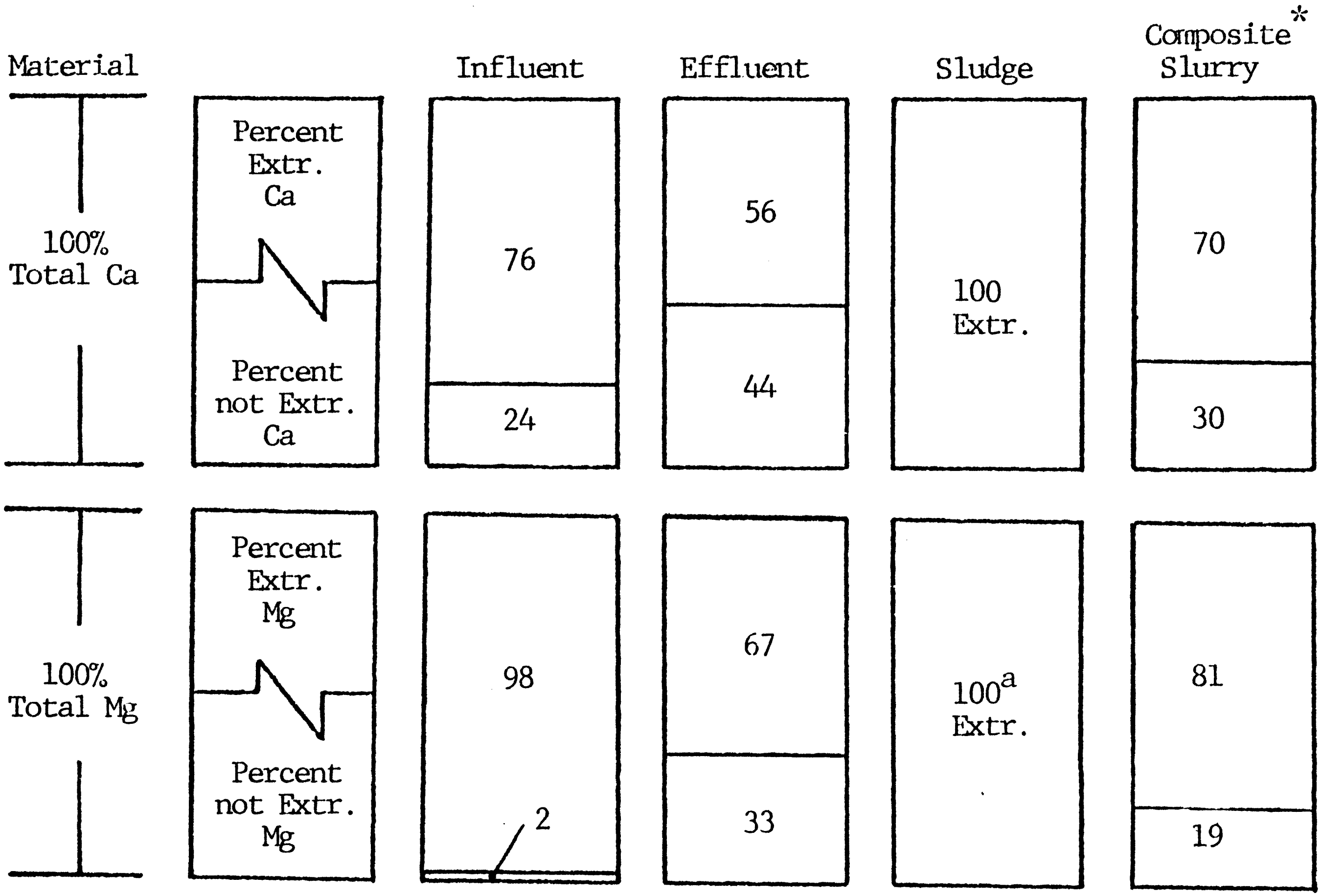


Figure 14. Ratios of extractable to unextractable forms of Ca and Mg in poultry manure influent, corresponding effluent, digester sludge and composite digested slurry from a pilot scale mesophilic plug flow continuous digester.

*Mixture of effluent and sludge. [a]Assumed 100% since Total<Extr.

The extractable and total Mg were only 51.9 and 62.5% recovered, respectively. In all cases, the less than 100% theoretical recoveries of these solid associated nutrients can be attributed to unrepresentative sampling. This clearly indicates that the effluent and sludge samplings did not adequately represent all of the recovered solids. The stored effluent sampled was homogenized by recirculation with a pump. The TS concentration of this sample was only 72% of the TS measured from the effluent samples collected in a more rigorous fashion for the N recovery study (see Table 4). The homogenizing process therefore did not sufficiently suspend some of the effluent solids. Additionally, problems associated with homogenizing the digester sludge perhaps contributed further to the low recovery of the P, Ca and Mg.

The recovered extractable P, Ca and Mg (Figure 12) were preferentially concentrated with the sludge solids, because 39, 46 and 47%, respectively, were distributed with the sludge (which was associated with only 26% of the recovered solids). The enrichment of these nutrients in the sludge may have been due to the formation of hydroxide precipitates that settled out of the effluent. The distributions of total P, Ca and Mg were more closely allied to the solids distribution between the effluent and sludge fractions.

Thus the distribution of solids in mass fractions recovered from the digestion of animal manures is indicative of the total P, Ca and Mg distributions.

4.1.5 Recovery Of Cu, Mn, Fe and Zn: Pilot Scale

The concentrations of extractable Cu, Mn, Fe and Zn are shown in Table 7. The extractable Cu, Fe, Mn and Zn concentrations were 6.8, 8.1, 8.8 and 6.3 times greater, respectively, in the sludge than the effluent. These micronutrients were thus highly enriched in the sludge fraction.

The recoveries of extractable Cu, Mn, Fe and Zn are reported in Table 8. The recoveries of extractable Cu and Fe were 145 and 142 percent, respectively. This seems contrary to the less than 100% recoveries of other nutrients highly associated with the solids. However, Fe and Cu were obviously contributed from materials used in the construction of the digester. The tank utilized was a steel tank which had rusted surfaces exposed to the digester contents. These surfaces could have easily provided additional Fe to the digester slurry. Similarly, a soft copper tube was utilized as a heat exchanger. Since the influent Cu concentration was low (6.9 mg/l), only a small dissolution of Cu from the tube would have been necessary to

Table 7. Concentrations of the extractable* forms of several trace nutrients in poultry manure influent, corresponding effluent and digester sludge from a pilot scale mesophilic plug flow continuous digester.

Material	Cu	Mn	Fe	Zn
	mg/l			
Influent	6.94	42.2	24.9	25.1
Effluent	7.56	21.0	25.2	15.8
Sludge	51.7	184	203	99.9

*Extracted in dilute acid

cause this greater than 100% recovery. The recoveries of extractable Mn and Zn were 71.7 and 81.6 percent, respectively. These recoveries are similar to those observed for P. Thus, lower than 100% recoveries can be attributed to problems associated with representative recovery of solids in effluent and sludge samplings.

The distributions of extractable Cu, Mn, Fe and Zn in the effluent and sludge fractions of the digester sludge are shown in Figure 15. Extractable Cu, Mn, Fe and Zn were similarly distributed 31, 37, 35 and 29% the sludge fraction. These distributions correspond closely to the distribution of solids between the effluent and sludge fractions. However, in the case of Mn and Fe, there was a minor preferential concentration in the sludge solids.

4.2 RESULTS OF THE LABORATORY SCALE DIGESTER

Due to the problems encountered with representative samplings in the pilot scale study, a laboratory batch digestion was performed to more carefully study the recovery of nutrients.

Table 8. Recovery[*] of the extractable[**] forms of several trace nutrients during the anaerobic digestion of poultry manure in a pilot scale mesophilic plug flow continuous digester.

	Cu	Mn	Fe	Zn
Material	% of influent			
Composite[1]	145	71.7	142	81.6
Effluent	99.9	45.5	93.0	57.7
Sludge	44.7	26.2	49.2	23.9

[*] Recovery accounts for mass lost with biogas

[**] Extracted in dilute acid

[1] Effluent and sludge fractions combined

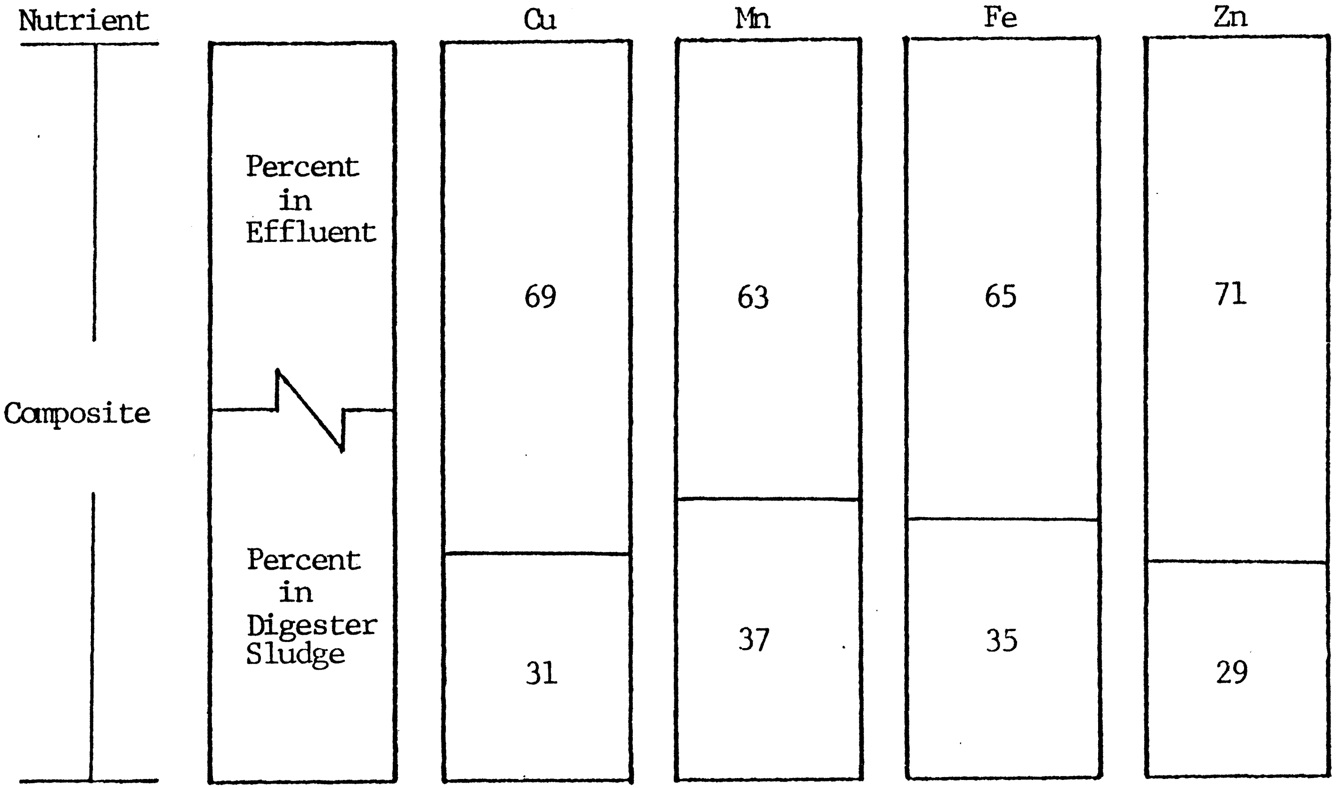


Figure 15. Distribution of extractable* forms of several trace nutrients in the effluent and digester sludge fractions of the composite digested slurry from anaerobic digestion of poultry manure in a pilot scale mesophilic plug flow continuous digester.

*Extracted in dilute double acid

4.2.1 Biogas Yield: Laboratory Scale

The average cumulative biogas yield from 3 laboratory scale batch digesters is shown in Figure 16. A noticeable decline in gas yields began after the fifth day of digestion. By the eighth day, gas yields had essentially ceased. Thus the seed sludge inoculum applied at 15% of added solids was not sufficient to maintain a stable and physiologically healthy population of methonogenic bacteria. The gas which was evolved, did however, contain methane as the gas was combustible.

4.2.2 Total Solids and Mass Recovery: Laboratory Scale

The total solids concentration of the poultry manure influent and corresponding effluent are shown in Table 9. The average TS of the composite digested slurry (termed effluent in this study) was 5.43%. This was 14% less than the solids concentration of the influent. The effluent was fractioned into supernatant and sludge by centrifugation. The average TS of the supernatant was 2.66%. The average TS of the sludge was 17.9% which was 6.7 times more concentrated than the supernatant.

The recoveries of influent mass and solids are given in Table 10. The mass recovery of 99.8% was close to 100% since low gas yields contributed to minor losses of mass

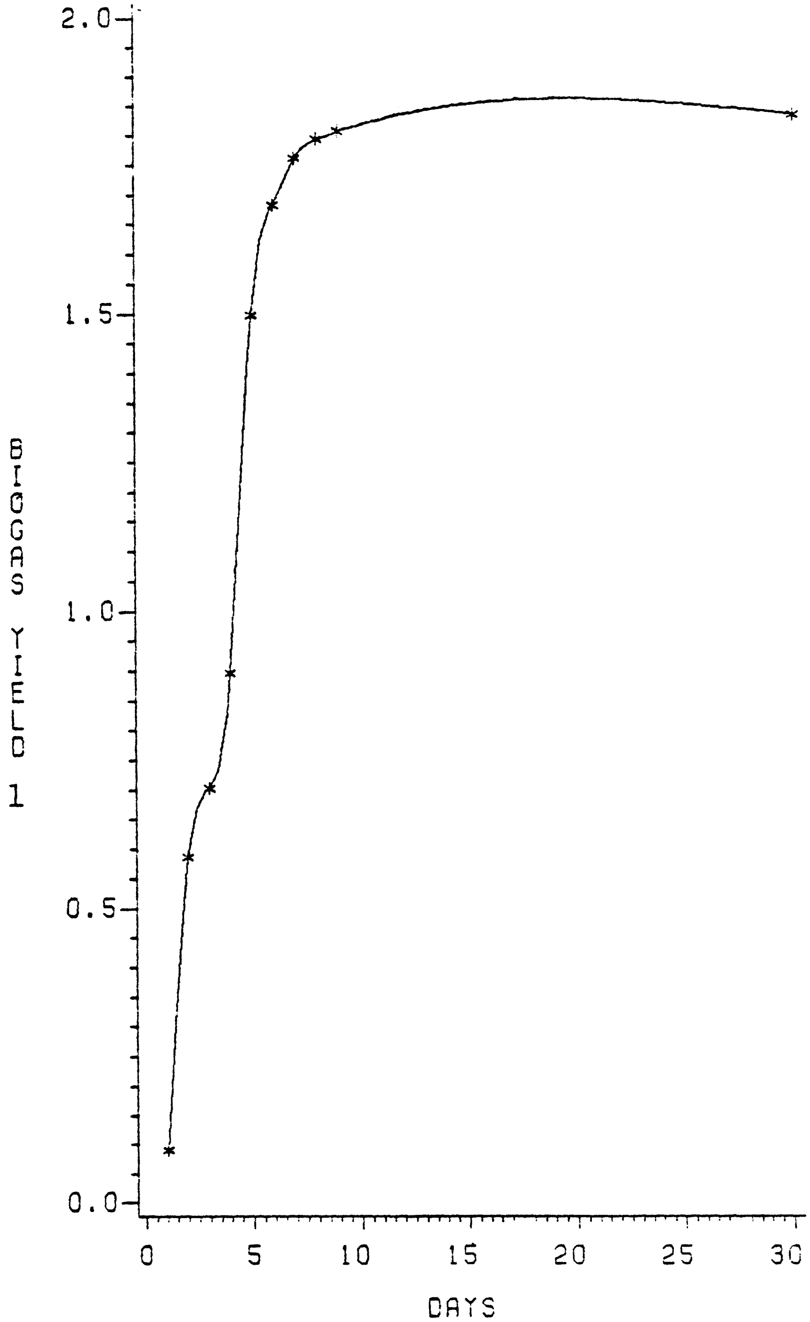


Figure 16. Cumulative biogas yield* of the batch anaerobic poultry manure digestion (35°C, 30 days retention). Cubic spline interpolation.

*Average of 3 replications, standard deviation at day 30 = 0.85L.

Table 9. Concentration of solids, ammonium N and total N, and ammonium N to total N ratios for influent and effluent of the anaerobic batch digestion of poultry manure (35°C, 30 days retention)[a].

Sample	Fraction of Effl Mass %	Total Solids %	NH_4^+N** mg/l	TKN† mg/l	NH_4^+N/TKN %
Ave Infl[1]	-	6.32	1390	3980	34.9
S.D.*	-	.13	81	25	2.2
Ave Effl[2]	100	5.43	2100	3910	53.7
S.D.	0	.12	35	62	1.6
Ave Spnt[3]	81.8	2.66	2080	3430	60.8
S.D.	.46	.27	40	99	3.0
Ave Sldg[4]	18.2	17.9	2160	6040	35.7
S.D.	.46	1.0	47	229	.91

[1] Ave Infl = average influent

[2] Ave Effl = average effluent

[3] Ave Spnt = average supernatant fraction of effluent

[4] Ave Sldg = average sludge fraction of effluent

*S.D. = 1 standard deviation

**Extractable ammonium in 2N KCl

†Total Kjeldahl Nitrogen

[a] Average of 3 replications

from the effluent. The recovered mass was distributed approximately 82% in the supernatant and 18% in the sludge. Greater segregation of sludge in this study compared to sludge formed by settling solids in the pilot scale study is due to the centrifugation process.

The average measured recovery of influent solids was 85.6% for the effluent. If the mass lost with the gas is used as a basis of calculating solids recovery, then the recovery would be 96.8%. The lower measured recovery may result from the loss of volatile constituents (perhaps accumulated in the methane inhibited digestion) by oven drying. The recovered solids were distributed 40% in the supernatant and 60% were distributed in the sludge of the effluent. The centrifugation process enabled a 2.3 fold greater removal of solids with the sludge compared to the settling that occurred in the pilot scale digestion.

4.2.3 Recovery of Nitrogen: Laboratory Scale

The concentrations of NH_4^+N and TKN are shown for the influent, effluent and the supernatant and sludge fractions of the effluent in Table 9. The concentration of the effluent NH_4^+N was enriched by 51% compared to the influent. No large differences in NH_4^+N concentrations were observed between the supernatant and sludge fractions. The enrichment of the $NH_4{}^+N$ in the effluent is caused by the mineralization of organic N during digestion. The TKN concentration in the effluent was comparable to the TKN of the influent as would be expected when insignificant mass is lost with the gas (since there is no concentration effect). However, the TKN concentration of the sludge was 76% higher than the supernatant fraction. The enriched concentration of TKN in the sludge can be explained by the higher solids concentration of the sludge.

The $NH_4{}^+N$ to TKN ratios of the influent, effluent and fractions of the effluent are also shown in Table 9. The original influent was 34.9% $NH_4{}^+N$ per TKN. This $NH_4{}^+N$:TKN ratio is much smaller than that observed for many influent samples in the pilot scale study (see section 4.1.3). The poultry manure used in this study, which was 35.5% $NH_4{}^+N$ to TKN, was obviously stored longer than that used for the pilot scale study. While in storage, significant ammonia volatilization must have occurred to alter the characteristic $NH_4{}^+N$ to TKN ratio observed previously.

The $NH_4{}^+N$ to TKN ratio of the effluent was 53.7%. The $NH_4{}^+N$ to TKN ratio of the supernatant fraction was 60.8% which was 70% greater than that of the sludge fraction. The $NH_4{}^+N$ to TKN ratio was higher in the supernatant fraction since the organic N was associated with the solids.

The recoveries of NH_4^+N and TKN during digestion are shown in Table 10. The recovery of NH_4^+N was 151% indicating that during digestion there was a 51% relative increase in the quantity of NH_4^+N. This was comparable to the NH_4^+N recovery of the pilot scale study. However, the influent NH_4^+N concentration in the laboratory scale batch digestion study was lower. Thus a comparable relative increase in NH_4^+N during digestion indicates a smaller absolute quantity was mineralized. The estimated mineralization of N during digestion was 27.4% of the influent organic N. This is only 46% of the proportion of organic N mineralized in the pilot scale plug flow digester. The significantly reduced mineralization of organic N in this study compared to the pilot scale study, might be attributable to the highly inhibited production of methane. The justification of this hypothesis resides in the importance of methanogenic activity for a high level of activity from all other metabolic groups involved in anaerobic degradation. The recovery of TKN during the digestion was 96.8% which is close to the hypothetical recovery of 100%.

The distribution of recovered NH_4^+N and TKN in the supernatant and sludge fractions of the effluent are illustrated in Figure 17. The supernatant fraction

Table 10. Percent recovery* of mass, solids, extractable and total nutrients during anaerobic batch digestion of poultry manure (35°C, 30 days retention) in composite and fractions of the effluent slurry.

Sample	Mass	Solids	Extr[1] NH_4^+ N	TKN[a]	Extr[2] K	Total[b] K	Extr[2] P	Total[b] P	Extr[2] Ca	Total[b] Ca
Composite	99.8	85.6	151	96.8	108	104	97.3	96.6	103	101
Supernatant fraction	81.7	34.1	123	70.6	100	87.1	40.5	36.3	23.0	20.8
Sludge fraction	18.1	51.5	28.3	25.2	7.6	17.0	56.8	60.3	79.5	79.9

*Average of 3 replications, concentrations of influent and effluent shown with standard deviations in Tables 9 and 11. Note recovery accounts for mass lost with the biogas.

[1] Extractable in 2N KCl

[2] Extractable in dilute double acid (H_2SO_4 and HCl)

[a] Total Kjeldahl Nitrogen

[b] Perchloric digest

accounted for 81% of the effluent NH_4NH. Thus NH_4^+N was again observed to be highly water soluble and associated with the liquid fraction of the digested slurry. A larger distribution of NH_4^+N in the sludge in this study compared to the pilot scale study, can be attributed to the larger mass of sludge recovered with centrifugation. The liquid filled pores between the solids would contain most of the NH_4^+N associated with the sludge, some NH_4^+N would be adsorbed to the sludge solids. The supernatant fraction contained 73% of the TKN recovered in the effluent. The distribution of TKN in the sludge beyond that accounted for by the NH_4^+N is due to the organic N of the solids. The greater distribution of TKN in the sludge in this study compared to the pilot scale study can be attributed to both greater recovery of solids with the sludge by centrifugation and the greater organic N content of the influent materials.

4.2.4 Recovery Of K, P and Ca: Laboratory Scale

The concentrations of extractable and total K are shown in Table 11 for the influent, effluent and fractions of the effluent. The concentrations of extractable and total K in the supernatant were 225 and 14.3% higher, respectively, than the sludge. Thus the extractable K was highly enriched in the liquid fraction.

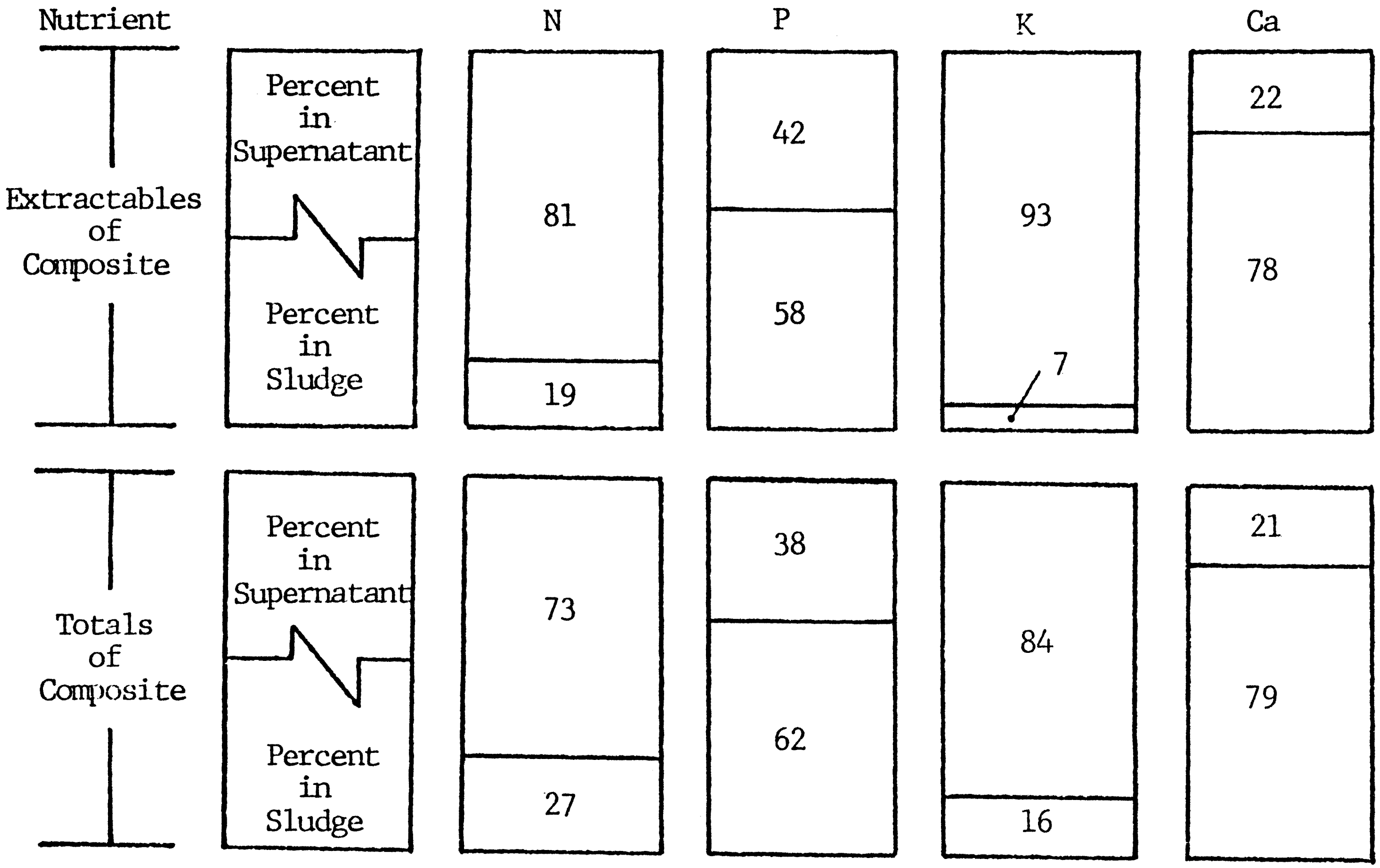


Figure 17. Distribution of extractable and total N, P, K and Ca in supernatant and sludge fractions of the composite effluent from anaerobic batch mesophilic digestion of poultry manure.

Table 11. Concentration of extractable and total forms of K, P and Ca, and extractable to total ratios of K, P and Ca for influent and effluent of the anaerobic batch digestion of poultry manure (35°C, 30 days retention)[a].

Sample	Extr[**] K	Total[†] K	Extr K / Total K	Extr P	Total P	Extr P / Total P	Extr Ca	Total Ca	Extr Ca / Total Ca
	mg/l	mg/l	%	mg/l	mg/l	%	mg/l	mg/l	%
Ave Infl[1]	1440	1650	88.1	1170	1220	95.7	3260	4190	78.5
S.D.[*]	60.8	265	10.0	25	34.6	1.1	90.7	509	9.2
Ave Effl[2]	1550	1720	90.3	1140	1220	93.2	3343	4240	79.8
S.D.	108	36.1	7.9	20	15.3	1.7	157	506	11.9
Ave Spnt[3]	1770	1760	100	590	626	94.0	874	936	93.2
S.D.	237	225	0	61.5	44.4	3.8	116	94.1	3.5
Ave Sldg[4]	545	1540	33.6	3660	4050	90.4	14260	18420	77.7
S.D.	477	1220	5.9	295	191	4.4	832	1480	8.2

[1] Ave Infl = average influent

[a] Average of 3 replications

[2] Ave Effl = average effluent

[3] Ave spnt = average supernatant fraction of effluent

[4] Ave sldg = average sludge fraction of effluent

[*] S.D. = 1 standard deviation

[**] Extractable in dilute double acid (H_2SO_4 and HCl)

[†] Perchloric digest

The extractable to total ratios of K in the influent, effluent and effluent fractions are also shown in Table 11. The average extractable to total K ratio in the influent was 88.1% indicating, as discussed previously, that K in poultry manure is highly soluble. The effluent extractable to total K ratio was 90.3% which was similar to the influent. The supernatant total K was 100% extractable. This contrasted sharply with the extractable to total K ratio of 33.6% in the sludge. The ratio of the sludge seems unrealistic and perhaps results from an overestimation of total K in the sludge. This explanation is likely since the K in the sludge was indirectly calculated from effluent and standard deviation of the sludge total K was 80% of the mean.

The recoveries of extractable and total K are shown in Table 10. Extractable and total K recoveries were 108 and 104%, respectively. The recovery of total K was close to the theoretical value of 100%.

The distribution of K in the supernatant and sludge fractions of the effluent is illustrated in Figure 17. Extractable and total K were 93 and 84%, respectively, distributed in the supernatant. The majority of the K was again observed to be distributed with the liquid fraction of the digested slurry.

The concentrations of extractable and total P and Ca are shown in Table 11. Extractable and total P concentrations of the sludge fraction were 6.2 and 6.5 times higher than those in the supernatant. Extractable and total Ca concentrations of the sludge fraction were 16.7 and 19.7 times higher than those in the supernatant. These high enrichments within the sludge were also observed in the pilot scale study. However, Ca enrichments were higher in this study due to the greater distribution of solids in the sludge fraction by centrifugation.

The extractable to total ratios of P and Ca are also shown in Table 11. The extractable to total P ratio of the effluent was 95.7%. This is an unusually high ratio. The particular sample of manure used in this experiment did not have the representative ratio observed elsewhere (see Figure 13). In this study, the extractable to total ratio of Ca in the supernatant fraction was noticeably higher than the ratio in the sludge fraction. This is opposite the trend observed in the pilot scale study (see Figure 14). The difference between the studies is perhpas due to the incorporation of colloidal particles into the sludge by centrifugation. These particles were previously hypothesized to hold sorbed Ca and Mg cations from exraction by dilute acid.

The recoveries of extractable and total P and Ca are shown in Table 10. Extractable P and Ca recoveries were 97.3 and 103%, respectively. Total P and Ca recoveries were 96.6% and 101%, respectively. The recoveries of total P and Ca were both close to the theoretical recovery of 100%. This indicates that with laboratory conditions, where representative samples of all input and output materials from the digestion process can be obtained, realistic recoveries of the solids associated nutrients can also be obtained. Since extractable P and Ca recoveries were only slightly greater than those obtained for the total forms, no obvious release of unextractable P and Ca occurred during digestion.

The distributions of recovered P and Ca in the fractions of the effluent are shown in Figure 17. Extractable and total P distributions were 58 and 62%, respectively, distributed in the sludge. The distribution of both forms of P were almost identical to the solids distribution between supernatant and sludge fractions of the effluent. This also was shown for total P in the pilot scale study. Extractable Ca was preferentially concentrated in the sludge solids as 78% was distributed in the sludge (which accounted for 60% of the solids distribution). This was similarly observed in the pilot scale study. Total Ca was also preferentially concentrated in the sludge solids. The greater distribution of P and Ca in the sludge of this study, compared to the pilot scale study, is related to the greater recovery of solids in the sludge from the centrifugation process.

4.3 NITROGEN MINERALIZATION STUDY

The N mineralization study was conducted to determine the release of inorganic forms of N from organic N applied to the soil with poultry manure influent and biogas effluent.

4.3.1 Initial Leaching

The inorganic N present in the initial leachate (on day 0) is shown for the various treatments in Table 12. The quantity of inorganic N leached from a given application rate of TKN was consistently higher for the effluent treatments. This was expected since the biogas effluent TKN was composed of a greater percentage of NH_4^+N compared to the influent as shown in Figure 18. The quantities of inorganic N leached at day 0 from the effluent-soil mixtures were significnatly higher than those from the corresponding influent-soil mixtures by 21.6 and 15 percent, respectively, for the low and mid rates of applied TKN. The effluent-soil mixture with the high rate of applied TKN had 1.5% more inorganic N leached at day 0 compared to the high rate influent-soil mixtures. This difference was not statistically significant. The check treatment had significantly less inorganic N leached when compared to the treatments with applied TKN.

Table 13 shows the amount of organic N applied with the treatments as calculated from applied TKN and inorganic N leached. The organic N of the low, mid and high rate treatments of influent were 3.04 times, 68 and 2.7% greater than the corresponding organic N contents of the effluent treatments.

The significance of the differences between organic N quantities of the low rate treatments were masked by the variations in the organic N of the higher rate treatments. The relative proportions of organic N and NH_4^+N of the applied TKN (as calculated from the initial leaching data) are illustrated in Figure 19. The relative organic N of the influent and effluent treatments was significantly different for both the low and mid rates of applied TKN. The difference between the relative organic N of the influent and effluent applied at the highest rate was very small. The NH_4^+N and organic N per TKN was such that the influent material was not statistically similar between any of the

Table 12. Initial inorganic N* leached, prior to the onset of the N mineralization experiment, from soil, poultry manure influent N and biogas effluent N soil mixtures.

Treatment		Inorganic N
Type	TKN[1] appl μg/g soil	μg/g soil
Check	0	46.7[f][2]
Influent	100	111[e]
Influent	500	399[c]
Influent	1,000	889[a]
Effluent	100	135[d]
Effluent	500	459[b]
Effluent	1,000	902[a]

*Average of 3 replications

[1] Total Kjeldahl Nitrogen

[2] Means followed by the same letter are not significantly different at the 5% level (Duncan's Multiple Range).

Table 13. Organic N[*] of treatments estimated from applied N remaining[**] in soil following the initial leaching of poultry manure influent N and biogas effluent N soil mixtures.

Treatment		Organic N
Type	TKN[1] appl µg/g soil	µg/g soil
Influent	100	35.9^{c}[2]
Influent	500	148a
Influent	1,000	158a
Effluent	100	11.8^{c}
Effluent	500	88.1^{b}
Effluent	1,000	144a

[*] Average of 3 replications

[**] (appl TKN) - (inorg N leached from treatment - ave inorg N leached from checks)

[1] Total Kjeldahl Nitrogen

[2] Means followed by the same letter are not significantly different at the 5% level (Duncan's Multiple Range).

rates. This discrepancy was due to problems with homogenizing the poultry manure as discussed previously in section 3.2. The poultry manure slurry was initially shaken by hand and placed on a magnetic stirrer. The stir bar apparently did not adequately suspend some of the larger solids. While the first aliquots of poultry manure were removed from the slurry and applied to the leaching tubes, a representative sample of the poultry manure was obtained. This is evident since the NH_4^+N:TKN ratios of the low rate treatment (first one prepared) was comparable to the NH_4^+N:TKN ratio of the poultry manure measured directly (see Figure 18). However, by the time the second set of tubes were prepared (those corresponding to the mid rate), some of the larger solids, which contained large proportions of the manure organic N, were settling. Thus aliquots removed were lower in organic N. This is evident from the higher NH_4^+N:TKN ratio of the middle rate influent (see Figure 19). Similarly, the solids continued to settle so that the final set of tubes (those corresponding to the highest rate) had the highest NH_4^+N:TKN ratio (see Figure 19). Homogenization was apparently not a problem with the effluent samples, as the NH_4^+N:TKN ratios of the effluent samples were more comparable between the various rates.

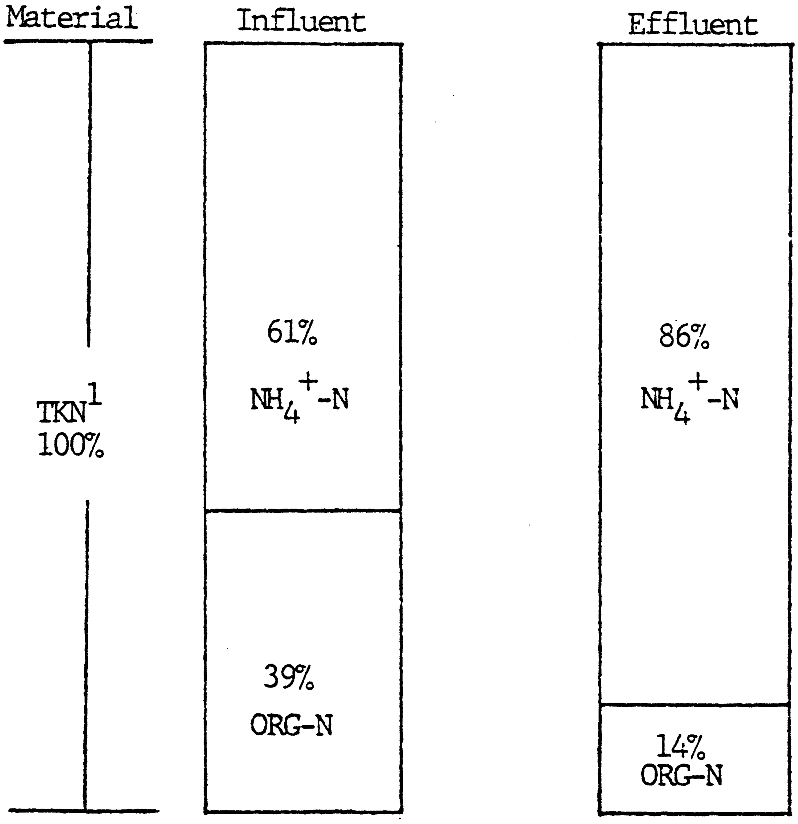


Figure 18. Ratio of ammonium N* and organic N** as a percent of total N, defined by direct measurement of materials used as treatments in the N mineralization study.

[1] Total Kjeldhal Nitrogen

*2N KCl extractable

**(TKN - NH_4^+N)

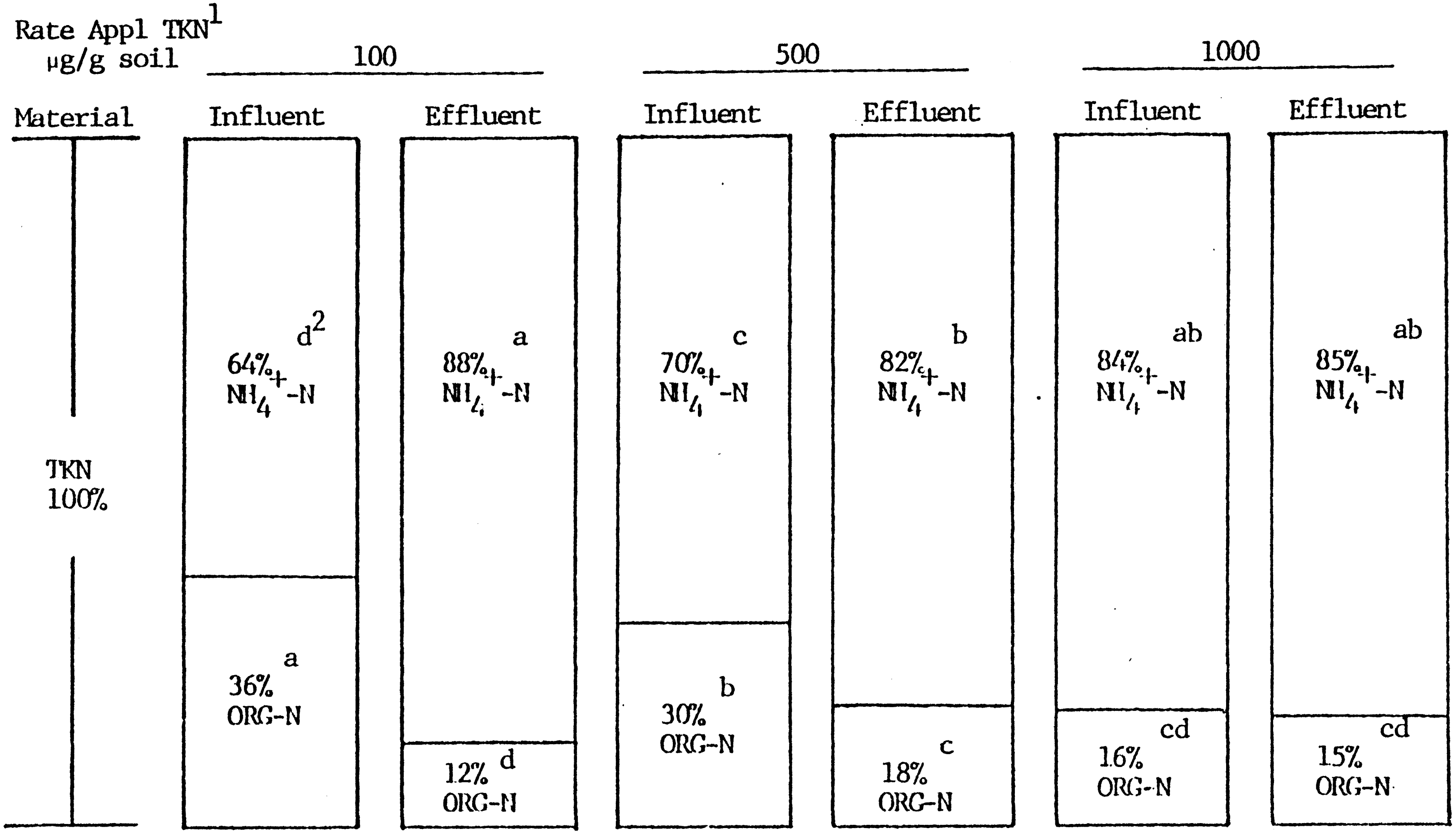


Figure 19. Ratio* of ammonium N and organic N as a percent of total N applied estimated from the initial leaching data.

[1] Total Kjeldahl Nitrogen *Average of 3 replications

[2] Means for a given form of N followed by the same letter are not significantly different at the 5% level (Duncan's Multiple Range).

4.3.2 Mineralization

Table 14 shows the cumulative inorganic N leached, indicating the cumulative mineralization of organic N from the treatments following the initial leaching. After seven days, all of the treated soils had significantly greater mineralization of organic N than the check soil. Mineralization of organic N from the soil with the low rate of applied effluent was almost equivalent to that of the soil with the low rate of influent. The mineralization of organic N was significantly 25.7 and 14.2% greater in the effluent treated compared to influent treated soil for the mid and high rates of application, respectively.

The trends established during the first week continued through 28 days. Cumulative inorganic N leached remained similar for both treatments at the low rate. Cumulative inorganic N of the mid and high rate effluent treatments were 15.4% and 11.8% statistically higher, respectively, than those of the corresponding influent treatments.

By 56 days into the incubation, no statistically significant differences between effluent and influent at a given rate of application were present. However, there were statistical differences between all treatments with different rates of applied TKN.

Table 14. Cumulative inorganic N[*] leached (μg/g soil) from soil, poultry manure influent N and biogas effluent N soil mixtures at various dates following day 0 leaching.

Treatment		Days after Day 0 Leaching									
Type	TKN[1] appl μg/g soil	7	14	28	56	84	102	130	158	186	234
Check	0	37.6^{f}[2]	70.7^{e}	111^{e}	156^{d}	191^{d}	235^{f}	277^{d}	299^{e}	322^{e}	338^{e}
Influent	100	52.2^{e}	86.4^{de}	127^{de}	192^{c}	239^{c}	292^{ed}	329^{c}	357^{cd}	385^{cd}	403^{cd}
Influent	500	73.5^{d}	109^{c}	162^{c}	236^{b}	282^{b}	336^{cd}	383^{b}	411^{bc}	439^{bc}	458^{bc}
Influent	1,000	106^{b}	142^{b}	203^{b}	294^{a}	351^{a}	412^{a}	459^{a}	487^{a}	517^{a}	539^{a}
Effluent	100	52.3^{e}	89.1^{d}	136^{d}	189^{c}	228^{cd}	266^{ef}	307^{cd}	336^{de}	364^{de}	379^{de}
Effluent	500	92.4^{c}	139^{b}	187^{b}	262^{b}	303^{b}	350^{bc}	391^{b}	427^{b}	455^{b}	470^{b}
Effluent	1,000	121^{a}	169^{a}	227^{a}	318^{a}	361^{a}	396^{ab}	442^{a}	468^{ab}	497^{ab}	518^{ab}

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[*] Average of 3 replications

[1] Total Kjeldahl Nitrogen

[2] Means in columns followed with the same letter are not significantly different at the 5% level (Duncan's Multiple Range).

Linear regressions of the cumulative inorganic N leached from the soil (mineralized) versus the square root of time (days) are shown for all the treatments in Figure 20. The equations and the coefficients of determination, R^2, are also shown in the figure. The linear regressions accounted for most of the variation in the data as R^2 ranged from .995 to .998. Thus the data plotted in this manner was adequately described with the fitted lines.

Since the applied organic N varied considerably among treatments, the data were normalized in order to express the amount of N mineralized as a percent of the original organic N applied. The normalized data are presented in Table 15. The first obvious trend is that the low rate effluent treatment had statistically higher values than all of the other treatments throughout the entire experiment. The normalized cumulative inorganic N of this treatment became as much as 5.5 times greater than the corresponding influent treatment by day 28. At the end of the experiment, this treatment was 2.3 times higher than the corresponding influent treatment.

While differences between other treatments were not statistically significant, important trends can be observed. The mid rate effluent treatment had a normalized cumulative inorganic N which was 3 times greater than the corresponding

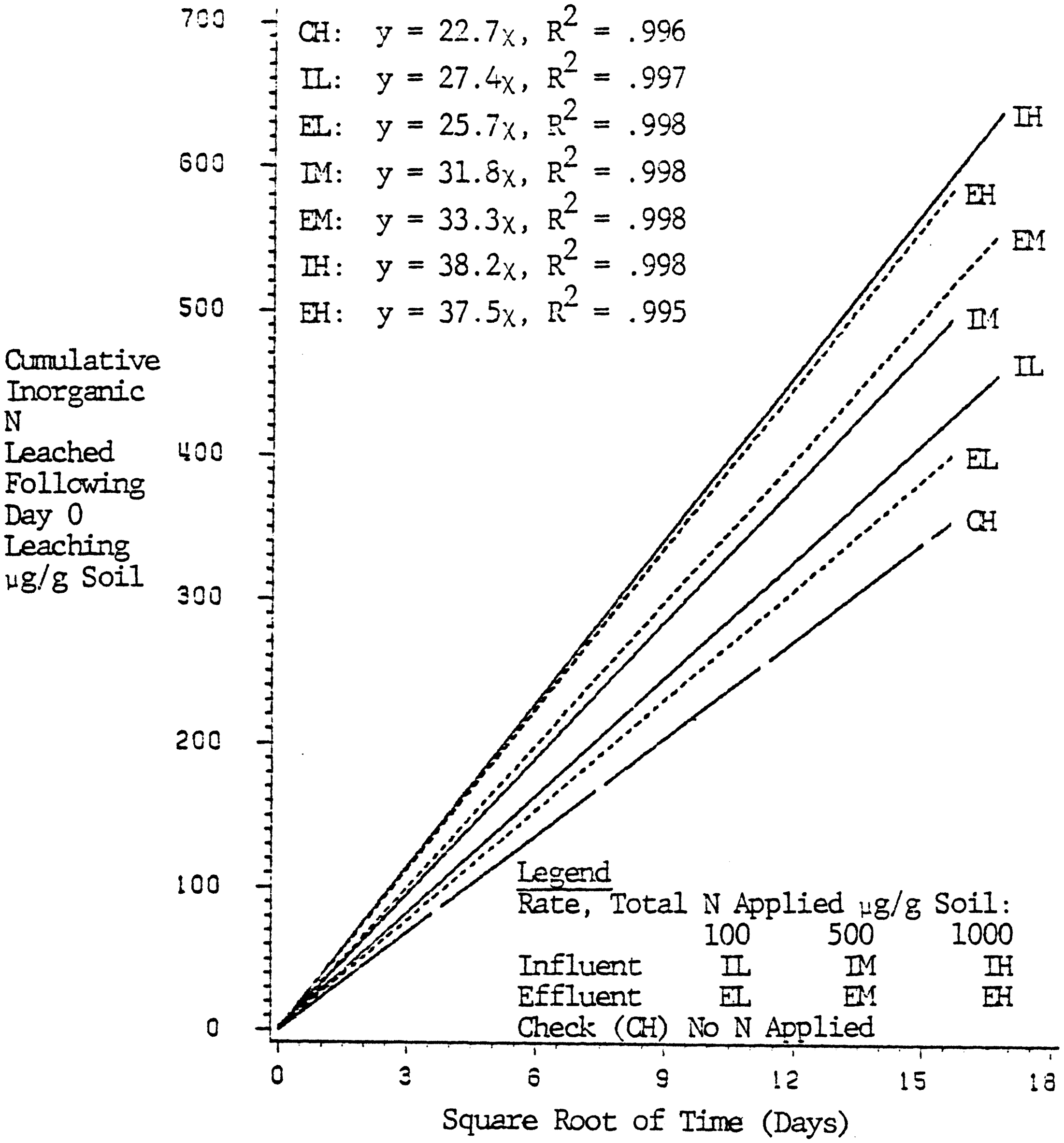


Figure 20. Linear regression of inorganic N* leached from soil, poultry manure influent N and biogas effluent N soil mixtures, versus the square root of time.

*Average of 3 replications

Table 15. Normalized[*] cumulative inorganic N[**], leached from poultry manure influent N and biogas effluent N soil mixtures, expressed as a percent of organic N applied with treatments.

Treatment		Days after Day 0 Leaching									
Type	TKN[1] appl μg/g soil	7	14	28	56	84	102	130	158	186	234
Influent	100	39.9^{b}[2]	42.6^{b}	42.9^{b}	96.0^{b}	128^{b}	155^{b}	142^{b}	156^{b}	169^{b}	172^{b}
Influent	500	24.3^{b}	25.8^{b}	34.9^{b}	53.9^{b}	61.3^{b}	68.5^{b}	72.1^{b}	76.2^{b}	79.5^{b}	81.6^{b}
Influent	1,000	43.3^{b}	45.5^{b}	59.0^{b}	87.9^{b}	102^{b}	113^{b}	118^{b}	120^{b}	125^{b}	128^{b}
Effluent	100	140^{a}	175^{a}	236^{a}	311^{a}	348^{a}	291^{a}	292^{a}	363^{a}	401^{a}	392^{a}
Effluent	500	62.4^{b}	77.8^{b}	87.0^{b}	119^{b}	127^{b}	130^{b}	129^{b}	144^{b}	150^{b}	149^{b}
Effluent	1,000	60.6^{b}	70.8^{b}	83.9^{b}	117^{b}	123^{b}	116^{b}	119^{b}	122^{b}	128^{b}	131^{b}

[*] $\frac{\text{(cum. inorg. N of treatment - cum. inorg. N of check)}}{\text{(org. N applied with treatment)}}$

[**] Average of 3 replications

[1] Total Kjeldahl Nitrogen

[2] Means in columns followed with the same letter are not significantly different at the 5% level (Duncan's Multiple Range).

influent by day 14. At the end of the experiment, this treatment was still 1.8 times higher than the corresponding influent.

The highest rate effluent treatment had normalized cumulative inorganic N that was 56% higher than the corresponding influent by day 14. By 102 days into the experiment, this treatment was consistently less than 5% greater than the corresponding influent.

Greater N mineralization was therefore observed from effluent treatments at the mid and low rates. This indicates that the effluent organic N is more readily degraded than the corresponding influent organic N. Higher rates of mineralization for the effluent per unit of organic N applied can be attributed to the segregation of decay resistant solids of the influent in the digester sludge. Furthermore, the solids suspended in the effluent were most likely reduced in size during the digestion process. Thus the effluent solids would have more surface area exposed for microbial degredation in the soil compared to the influent solids.

The greater similarity in organic N mineralization observed between the influent and effluent treatments at the highest rate is due to the absence of larger solids in the aliquots of influent applied to the high rate treatment.

Greater mineralization of N from the effluent in the early part of the incubation is most likely related to the smaller size of effluent solids.

During the course of the experiment, all of the treatments except the mid rate influent had normalized cumulative inorganic N that exceeded 100%. This indicates that the quantities of organic N mineralized in the soil-slurry mixtures were greater than those applied with the effluent or influent. Thus, indigenous organic N from the soil was mineralized in the treated soils faster than it was in the check soil. This phenomena is known as the 'priming' effect. Normalized cumulative inorganic N exceeded 100% by day 84 for the lowest and highest rate of influent. Normalized cumulative inorganic N exceeded 100% by day 7 for the lowest rate of effluent and by day 56 for the mid and high rates of the effluent.

Values reached 401 and 150% of applied organic N mineralized by day 186 for the low and mid rates, respectively, and 131% at day 234 for the high rate of applied effluent. These values seem high in comparison with previous N mineralization studies of sludges which were derived from the anaerobic digestion of sewage (see section 2.6.1). However, the material in this study was different in behavior because the effluent utilized was from the fraction of the digested manure that lacked the sludge. Thus, instead of containing the most decay resistant, largest and most inert solids, the effluent used here contained soluble, fine and readily degraded solids. Additionally, the substrate of the anaerobic digestion process studied was considerably more degradable than raw sewage. Other reasons that contribute to the differences are that the sludges in other studies (see section 2.6.1) are often pretreated in various manners, such as air drying and freeze drying. Also, application rates in large excess of fertilizer rates are often utilized.

In this study, the effluent was applied in the liquid form and since it contained a high proportion of inorganic N, the application rate of organic N was very small. In the lowest effluent treatment, the application averaged 11.8 µg organic N per g of soil. This small amount of organic N was applied with 543 µg (dry weight basis) of effluent per gram of soil. This mass of effluent would contain bacteria, enzymes, vitamins, nutrients and organic energy to 'prime' the indigenous rate of soil organic matter degradation. Thus, a greater than 100% recovery of inorganic N from the small amount of organic N applied (with the low rate effluent treatment) by day 7 should not be considered an unrealistic result. Similarly, 2715 and 5430 µg (dry weight basis) of effluent were applied with the organic N of the mid and high rate treatments, respectively.

Linear regressions were also fitted to the normalized cumulative inorganic N leached (following the initial leaching) versus the square root of time in days. These are illustrated with the line equations and R^2 values in Figure 21. The R^2 values for these lines were also high, ranging from .947 to .987. Thus, the regressions fitted in this manner were successful in describing the normalized N mineralization data.

Figure 21 illustrates the trends discussed previously, the large differences in normalized mineralization between the effluent and influent at the low and mid rates of TKN and the similarity between these two treatments at the high rate of TKN. The figure also illustrates that the slopes of the normalized cumulative inorganic N lines decrease with increasing rates of applied effluent. This illustrates substrate saturation which is common to all enzymatic and microbiological systems. Two factors could have contributed to the substrate saturation observed. Firstly, as greater amounts of organic N are supplied, the relative mineralization rate becomes proportionally less. Secondly, as greater amounts of effluent solids are added, their contribution to the 'priming' effect becomes proportionally less.

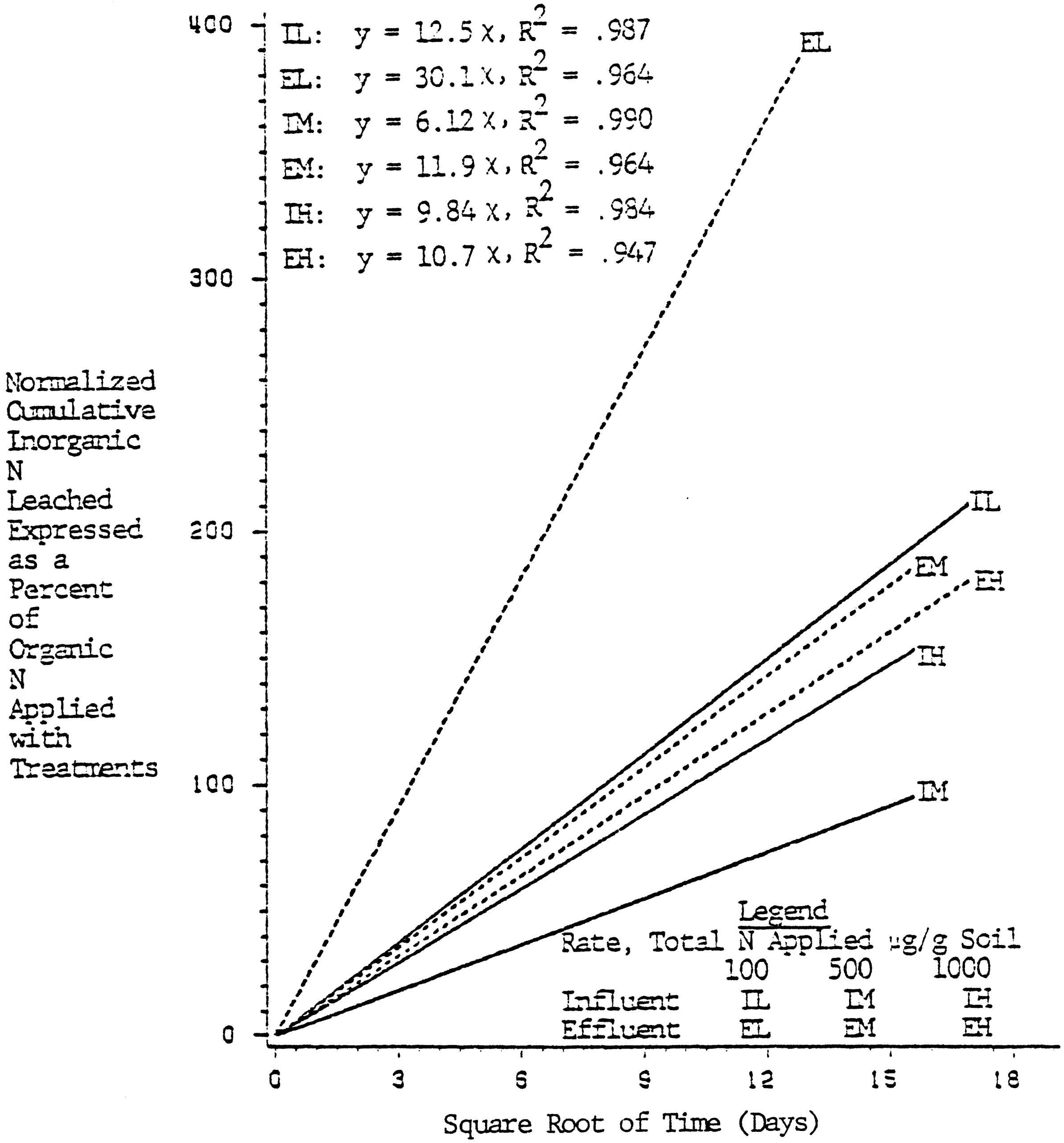


Figure 21. Linear regression of normalized* inorganic N** leached from poultry manure influent N and biogas effluent N soil mixtures, versus the square root of time.

$$^{*}\frac{(\text{cum. inorg. N of treatment} - \text{cum. inorg. N of check})}{(\text{org. N applied with treatment})}$$

**Average of 4 replications

This trend was also observed for the low and mid rates of influent; however, the high rate did not fit the pattern. Table 13 shows that the highest rate of applied influent TKN actually supplied only 7% more organic N than the middle rate of influent. Since this organic N was probably associated with more easily degraded solids than the mid influent rate, the higher slope observed here is understandable. Additionally, this organic N was supplied with twice the amount of effluent solids to further promote the 'priming' of indigenous soil organic N degradation.

4.3.3 Nitrification

Table 16 shows the cumulative NO_3^-N leached from the treatments during the course of the incubation. When compared with Table 14, the relative contribution of NO_3^-N to the inorganic N leached can be observed. At day 7 the cumulative NO_3^-N accounted for approximately 50% of the leached inorganic N for the treated soils. By day 14, the cumulative NO_3^-N accounted for approximately 60% of the cumulative inorganic N for all the treatments except the mid and high rates of influent which were 48 and 43% NO_3^-N:inorganic N, respectively.

After 28 days of incubation, the NO_3^-N:inorganic N ratios of the cumulative inorganic N were 68 to 75% NO_3^-N

Table 16. Cumulative nitrates N* leached (μg/g soil) from soil, poultry manure influent N and biogas effluent N soil mixtures at various dates following day 0 leaching.

Treatment		Days after Day 0 Leaching									
Type	TKN[1] appl μg/g soil	7	14	28	56	84	102	130	158	186	234
Check	0	17.8^{d}[2]	42.3^{d}	78.7^{e}	123^{d}	156^{f}	196^{d}	222^{d}	229^{d}	247^{d}	256^{d}
Influent	100	22.7^{cd}	52.1^{cd}	86.8^{e}	147^{d}	192^{de}	232^{cd}	264^{cd}	274^{cd}	297^{cd}	307^{bcd}
Influent	500	23.8^{cd}	52.6^{cd}	121^{cd}	175^{c}	217^{cd}	263^{bc}	302^{bc}	314^{bc}	336^{bc}	345^{bc}
Influent	1,000	29.0^{c}	61.5^{c}	114^{c}	202^{b}	255^{b}	313^{ab}	358^{a}	374^{a}	402^{a}	413^{a}
Effluent	100	21.8^{d}	49.4^{cd}	90.9^{de}	140^{d}	178^{ef}	211^{d}	243^{d}	258^{cd}	281^{cd}	287^{cd}
Effluent	500	44.5^{b}	87.2^{b}	130^{b}	202^{b}	241^{bc}	286^{ab}	322^{ab}	339^{ab}	362^{ab}	367^{ab}
Effluent	1,000	65.2^{a}	112^{a}	165^{a}	253^{a}	296^{a}	329^{a}	371^{a}	382^{a}	408^{a}	420^{a}

*Average of 3 replications

[1] Total Kjeldahl Nitrogen

[2] Means in columns followed with the same letter are not significantly different at the 5% level (Duncan's Multiple Range).

for most treatments. The highest rate of influent however, had a lower NO_3^-N:inorganic N (56%). By 56 days, the cumulative NO_3^-N accounted for 74 to 80% of cumulative inorganic N except for highest rate of influent which had 69% NO_3^-N:inorganic N. After 84 days of incubation, all treatments had similar NO_3^-N:inorganic N ratios that ranged from 70 to 80%.

A slight lag period of nitrification was thus observed with the treatments having only 50% NO_3^-N:inorganic N ratios at the first week of incubation. The lag period appeared to last only 2 weeks except for the highest rate influent treatment. These treatments had longer delays in nitrification, perhaps due to a large supply of organic C. Thus, O_2 competition from heterotrophic microorganisms could have slowed the nitrification process.

After 28 days of incubation, the NO_3^-N accounted for a majority of the mineralized inorganic N. Therefore, the incubation procedure provided sufficient aeration to sustain adequate nitrification.

4.4 FIELD EXPERIMENTS

A field study was conducted to investigate the behavior of N recovered from the anaerobic digestion of poultry manure in terms of plant growth. The biogas effluent N was compared with poultry manure influent N and synthetic urea N as a fertilizer for corn at two sites.

4.4.1 Soil Inorganic N

The soil inorganic N content in the furrow slice versus time after the application of the treatments are shown graphically in Figure 22 and 23 for Sites 1 and 2, respectively. Tables 17 and 18 present data numerically so that statistical differences can be observed. At both sites the inorganic N in the check and urea treated plots were statistically similar at day 0. This is because the N in urea was initially in the organic form. The only differences observed between urea and check plots were due to variations in the native inorganic N content of the soil. Effluent applied at the mid rate was statistically higher than the influent treatment as the effluent used was 87.6% and the influent used was 46.1% NH_4^+N:TKN.

By day 7, significant drops in the inorganic N of the effluent treatments occurred at both sites. Due to these decreases, differences in inorganic N content between the

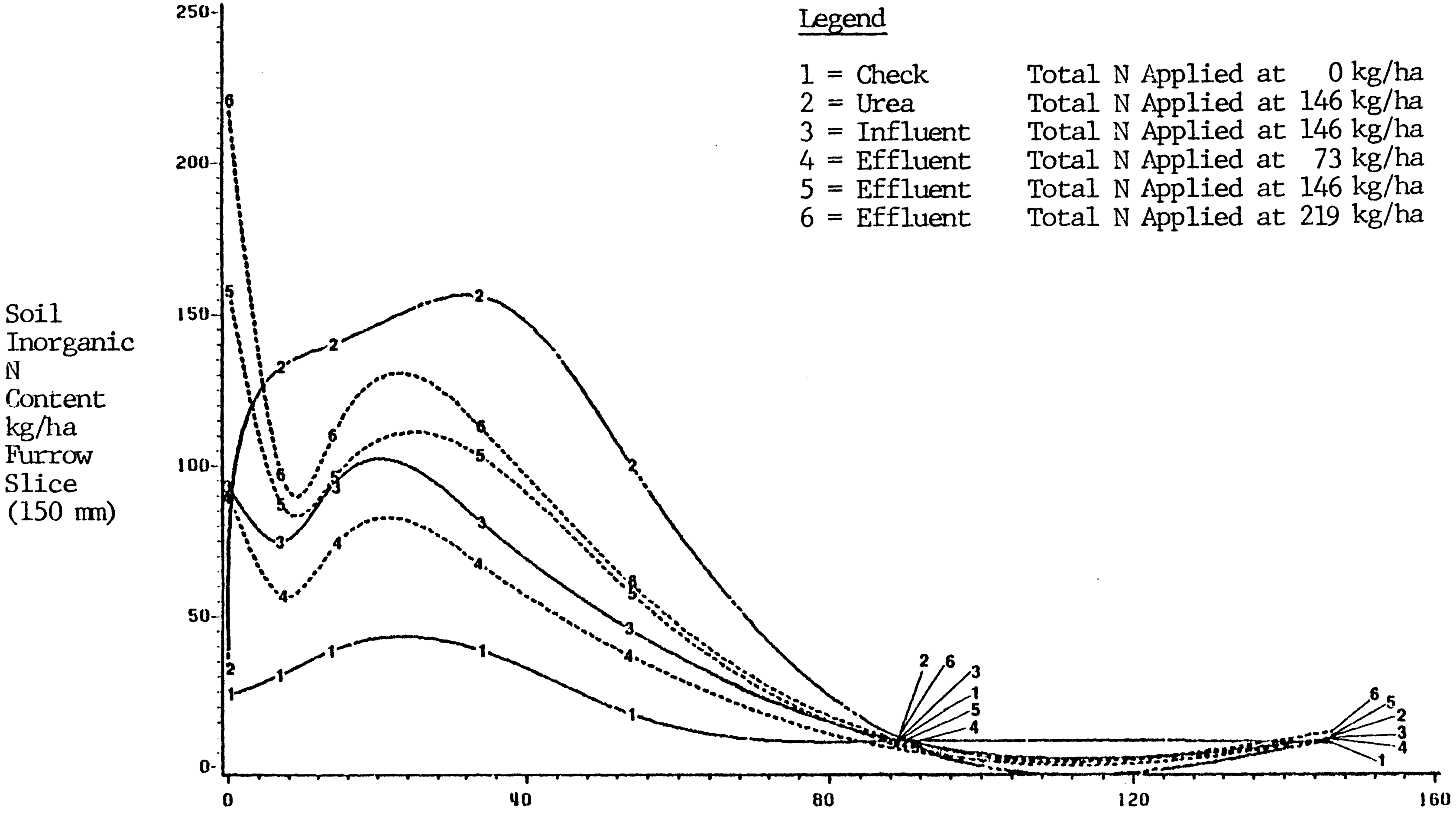


Figure 22. Soil inorganic N* content of field grown corn plots treated with urea N, poultry manure influent N and biogas effluent N, versus days after treatment application (Site 1). Data interpolated with cubic spline functions.

*Average of 4 replications

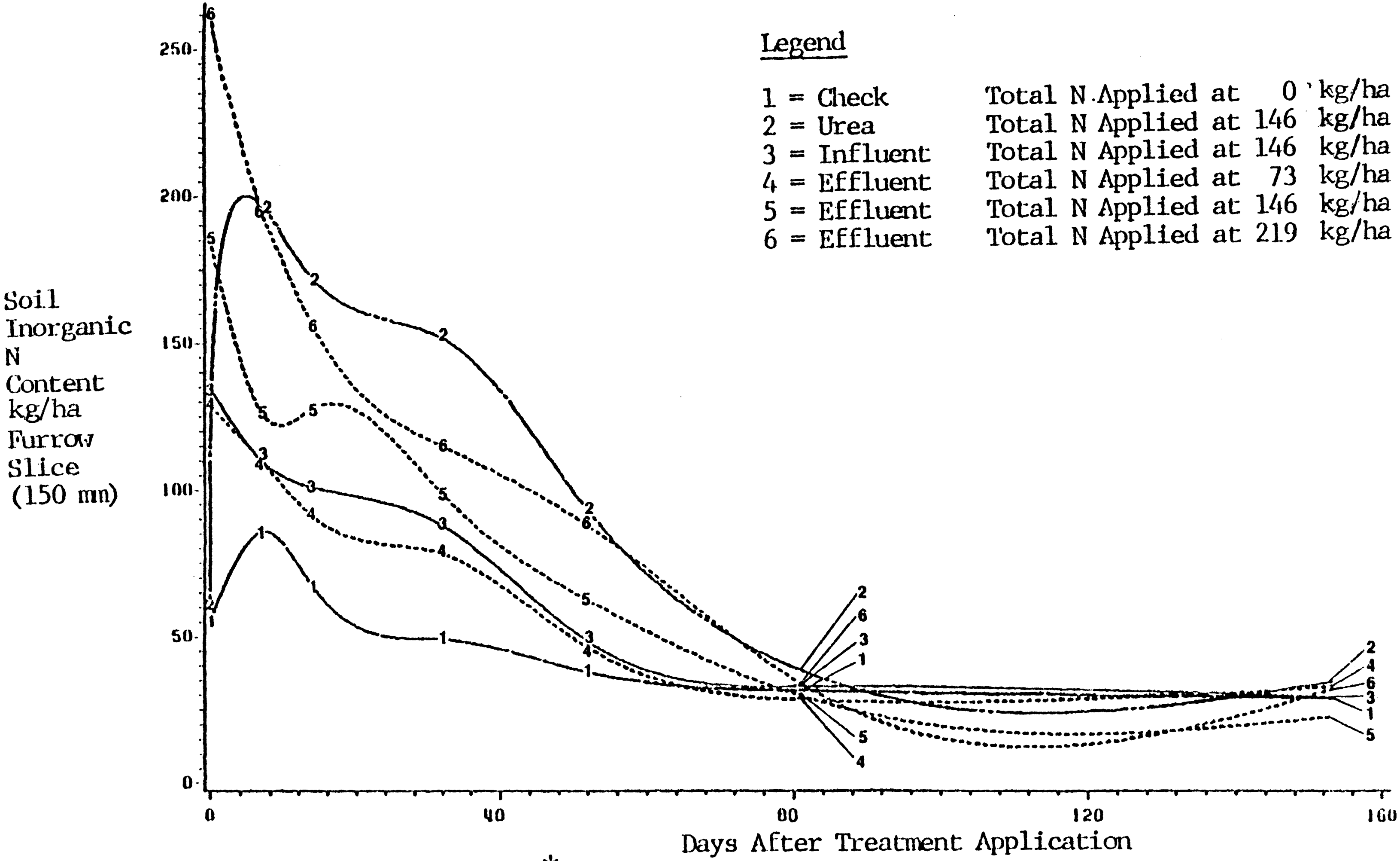


Figure 23. Soil inorganic N* content of field grown corn plots treated with urea N, poultry manure influent N and biogas effluent N, versus days after treatment application (Site 2). Data interpolated with cubic spline functions.

*Average of 4 replications

Table 17. Soil inorganic N and nitrate N content*, kg/ha furrow slice (150 mm), at various dates in field grown corn plots (Site 1).

#	Treatment Type	TKN** appl (kg/ha)	Sampling Date (days after application of treatments)													
			0		7		14		34		54		88		147	
			Inorg N	NO_3N	Inorg N	NO_3N	Inorg N	NO_3N	Inorg N	NO_3N	Inorg N	NO_3N	Inorg N	NO_3N	Inorg N	NO_3N
1	Check	0	23.7^{d}[1]	17.6^{a}	30.6^{d}	24.1^{b}	38.8^{d}	32.6^{d}	38.7^{d}	28.2^{d}	17.5^{c}	9.39^{c}	8.66^{a}	3.68^{a}	8.15^{b}	5.47^{b}
2	Urea	146	33.5^{d}	25.0^{a}	133^{a}	56.0^{a}	140^{a}	125^{a}	156^{a}	145^{a}	99.8^{a}	87.7^{a}	10.9^{a}	7.74^{a}	9.50^{ab}	8.51^{ab}
3	Influent	146	93.5^{c}	20.3^{a}	74.7^{cb}	50.6^{a}	93.5^{bc}	84.3^{bc}	81.3^{c}	72.2^{c}	45.3^{bc}	33.7^{bc}	9.56^{a}	6.73^{a}	9.31^{ab}	7.62^{ab}
4	Effluent	73	90.8^{c}	22.3^{a}	56.7^{cd}	44.4^{a}	72.6^{c}	66.8^{c}	66.7^{c}	54.2^{c}	36.4^{bc}	28.9^{bc}	6.41^{a}	3.56^{a}	9.26^{ab}	7.18^{ab}
5	Effluent	146	158^{b}	22.8^{a}	87.4^{b}	57.2^{a}	95.2^{bc}	90.3^{bc}	103^{b}	93.9^{b}	57.1^{b}	44.0^{b}	8.30^{a}	5.73^{a}	9.57^{ab}	8.42^{ab}
6	Effluent	219	219^{a}	21.7^{a}	96.8^{b}	56.9^{a}	110^{b}	105^{ab}	112^{b}	103^{b}	60.2^{b}	51.5^{b}	9.74^{a}	6.81^{a}	12.1^{a}	10.4^{a}

*Average of 4 replications

**TKN = Total Kjeldahl Nitrogen

[1] Means in columns followed by the same letter are not significantly different at the 5% level (Duncan's Multiple Range).

Table 18. Soil inorganic N and nitrate N content*, kg/ha furrow slice (150 mm), at various dates in field grown corn plots (Site 2).

	Treatment	Sampling Date (days after application of treatments)													
	TKN appl	0		7		14		32		52		81		154	
# Type	(kg/ha)	Inorg N	NO_3N	Inorg N	NO_3N	Inorg N	NO_3N	Inorg N	NO_3N	Inorg N	NO_3N	Inorg N	NO_3N	Inorg N	NO_3N
1 Check	0	56.0^{d}[1]	38.6^{b}	85.7^{b}	63.4^{c}	67.3^{c}	60.0^{c}	49.1^{c}	39.5^{d}	38.0^{c}	31.1^{c}	31.6^{b}	18.7^{bc}	28.7^{a}	22.9^{a}
2 Urea	146	60.2^{d}	40.3^{ab}	197^{a}	164^{a}	172^{a}	160^{a}	152^{a}	145^{a}	93.3^{a}	88.0^{a}	38.5^{a}	28.4^{a}	34.8^{a}	28.6^{a}
3 Influent	146	135^{c}	45.2^{ab}	110^{b}	87.5^{c}	101^{bc}	93.5^{bc}	88.0^{c}	80.9^{bc}	48.5^{c}	42.7^{c}	32.9^{ab}	22.3^{abc}	29.1^{a}	23.7^{a}
4 Effluent	73	129^{c}	46.7^{a}	110^{b}	86.0^{c}	91.0^{bc}	85.0^{bc}	78.3^{c}	71.5^{c}	46.2^{c}	41.0^{c}	28.5^{b}	17.9^{c}	33.0^{a}	26.9^{a}
5 Effluent	146	185^{b}	40.0^{ab}	126^{b}	102^{bc}	128^{ab}	121^{ab}	98.7^{bc}	91.2^{bc}	62.4^{b}	56.6^{b}	29.1^{b}	19.9^{bc}	22.9^{a}	17.8^{a}
6 Effluent	219	261^{a}	42.4^{ab}	194^{a}	134^{ab}	156^{a}	149^{a}	115^{b}	105^{b}	88.0^{a}	82.7^{a}	34.0^{ab}	24.5^{ab}	32.5^{a}	25.8^{a}

*Average of 4 replications

**TKN = Total Kjeldahl Nitrogen

[1] Means in columns followed by the same letter are not significantly different at the 5% level (Duncan's Multiple Range).

mid rate effluent and influent treatments were not significant. The large decreases in inorganic N in the effluent treatments can be attributed to NH_3 volatilization and will be discussed in greater detail later. The urea treated plots had large increases of inorganic N by day 7. Thus, the mineralization of urea by urease was rapid.

The check plot had increased inorganic N levels by day 7 at both sites. The increase was small for the plowed site (1). However, for the minimum till site (2), large increases were observed. This perhaps results from increased microbial activity after discing at this site.

Two weeks after application, the soil inorganic N contents of the effluent and influent treatments were increased over the day 7 values at Site 1. The increases were noticably greater than the small increases that were evident in the check and urea treatments (see Figure 22). These increases were probably due to mineralization of applied organic N. The mineralization of organic N in the field appeared to occur at the same rate for the influent and effluent treatments. This is indicated by the nearly parallel slopes of the lines between days 10 and 25, corresponding to these treatments in Figure 22. These results can be compared with the N mineralization study (section 4.3.2). The mineralization of organic N from effluent-soil mixtures was shown to be similar to that of influent-soil mixtures despite greater levels of applied organic N in the influent treatments.

Similar trends in the same period were not as easily observed with the Site 2 data since the inorganic N of the check plot was decreasing rapidly. However, the decreases of inorganic N between days 7 and 32 for the 2 lower rates of effluent and the influent treatments were similar. Since these decreases were less than those from the check and urea treatments, mineralization of applied organic N was implied.

At site 1, the inorganic N content of the urea treatment was statistically greater than those of all the other treatments from day 7 through 54. During this period, the inorganic N content of the urea treatment ranged from 27 to 66, 47 to 75 and 50 to 120% greater than those from the high and mid rate effuent and influent treatments, respectively. At Site 2, the inorganic N content of the urea treatment was statistically greater than those from all other treatments from day 7 to 52 except for the high rate effluent treatment. During this period, the inorganic N content of the urea treatment ranged from 2 to 32, 34 to 56 and 70 to 92% greater than those from the high rate and mid rate effluent and influent treatments, respectively.

The higher soil inorganic N contents in the urea treatments are attributable to lower losses of NH_3 in comparison to the effluent and slower mineralization of influent organic N. Additionally, the effluent also has a component of organic N which would not be mineralized as rapidly as the urea N.

The inorganic N content of the soil was always greater in the mid rate effluent treatment compared to the influent treatment which had the same rate of applied N. The difference was only significant on day 34 at Site 1 and on day 52 at Site 2. Thus despite large volatilization losses, the effluent maintained slightly greater levels of inorganic N because the influent N was composed of a larger component of organic N.

The large decreases in inorganic N that were evident at both sites after 40 days resulted from crop uptake and perhaps to a lesser extent from leaching and denitrification. By 80 days, the inorganic N contents were similar for all treatments at both sites.

The quantities of inorganic N increased over the day 0 value in the 150-300 mm depth interval are shown in Table 19 for day 34 at Site 1 and in Table 20 for day 32 at Site 2. The quantities of inorganic N accumulated over the quantity originally present in the lower depth interval were not statistically different between treatments at Site 1. The value in the check plot was 27 kg/ha which was similar to the value for the lowest effluent treatment. The remaining treatments at Site 1 had values that ranged from 35 kg/ha for the urea treatment to 40 kg/ha for the influent treatment. The highest value from the treatments was only 13 kg/ha greater than the value present in the check. This indicates that leaching losses of N from the furrow slice were relatively small compared to the losses previously attributed to NH_3 volatilization.

The quantity of inorganic N accumulated in the lower depth interval was highest for the urea treatment at Site 2. This indicates that leaching was greatest for the urea treatment which was expected as this treatment had the greatest levels of inorganic N in the furrow slice after day 7. The accumulated inorganic N accounted for 16% of the N applied. The values observed for the other treatments were small by comparison.

Table 21 shows the inorganic N content of the 150-300 mm depth interval at day 81 for Site 2. The inorganic N levels corresponded to the inorganic N contents of the furrow slice between days 14 and 52.

Table 19. Increased quantity of inorganic N in the 150-300 mm depth interval at Day 34 compared to Day 0 (Site 1).

#	Treatment Material	TKN[1] Appl. (kg/ha)	Inorganic N kg/ha
1	Check	0	27.2 a[2]
2	Urea	146	34.9 a
3	Influent	146	40.4 a
4	Effluent	73	25.8 a
5	Effluent	146	36.7 a
6	Effluent	219	36.1 a

*(Inorg N Day 34) - (Inorg N Day 0)

**Average of 4 replications

[1] Total Kjeldahl Nitrogen

[2] Means that are followed by the same letter are not significantly different at the 5% level (Duncan's Multiple Range).

Table 20. Increased quantity* of inorganic N in the 150-300 mm depth interval at Day 32 compared to Day 0 (Site 2).

#	Treatment		Inorganic N
	Material	TKN[1] Appl. (kg/ha)	kg/ha
1	Check	0	3.81b[2]
2	Urea	146	27.1a
3	Influent	146	9.76b
4	Effluent	73	9.39b
5	Effluent	146	11.9b
6	Effluent	219	11.8b

*(Inorg N Day 32) - (Inorg N Day 0)

**Average of 4 replications

[1] Total Kjeldahl Nitrogen

[2] Means that are followed by the same letter are not significantly different at the 5% level (Duncan's Multiple Range).

Table 21. Inorganic N content* of the 150-300 mm depth interval at Day 81 (Site 2).

#	Treatment Material	TKN[1] Appl. (kg/ha)	Inorganic N Content kg/ha
1	Check	0	13.4^{c} [2]
2	Urea	146	25.7^{a}
3	Influent	146	16.6^{c}
4	Effluent	73	14.9^{c}
5	Effluent	146	17.7^{bc}
6	Effluent	219	24.0^{ab}

*Average of 4 replications

[1] Total Kjeldahl Nitrogen

[2] Means that are followed by the same letter are not significantly at the 5% level (Duncan's Multiple Range).

4.4.2 Nitrate N

The NO_3^-N contents measured in the furrow slice are provided in Table 17 for Site 1 and Table 18 for Site 2. By day 14 at both sites, the trends observed for the inorganic N were closely followed by the NO_3^-N. This is expected since NO_3^-N accounted for most of the inorganic N past day 14.

The NO_3^-N:inorganic N ratios are presented graphically in Figures 24 and 25 for Sites 1 and 2, respectively. The ratios are also presented numerically in Appendices 1 and 2 to show statistical differences. At Site 1, the NO_3^-N:inorganic N on day 7 ranged from 43 to 79%. By day 14, the treatments with applied N had ratios of 90 to 95%. Thus the nitrification process lagged in the first week. The amount of lag was related to the quantity of inorganic N present at day 7. This lag period perhaps reflects the time required for the nitrifiers to adjust to the new levels of inorganic N. The nitrifiers in the plots which were supplied with the greatest amounts of inorganic N had the longest lag period. This was evident from the significantly low ratio in the urea treatment at day 7.

After day 14 the NO_3^-N:inorganic N ratios were corresponded to the inorganic N content. The check treatment consistently had the lowest ratio. The low rate

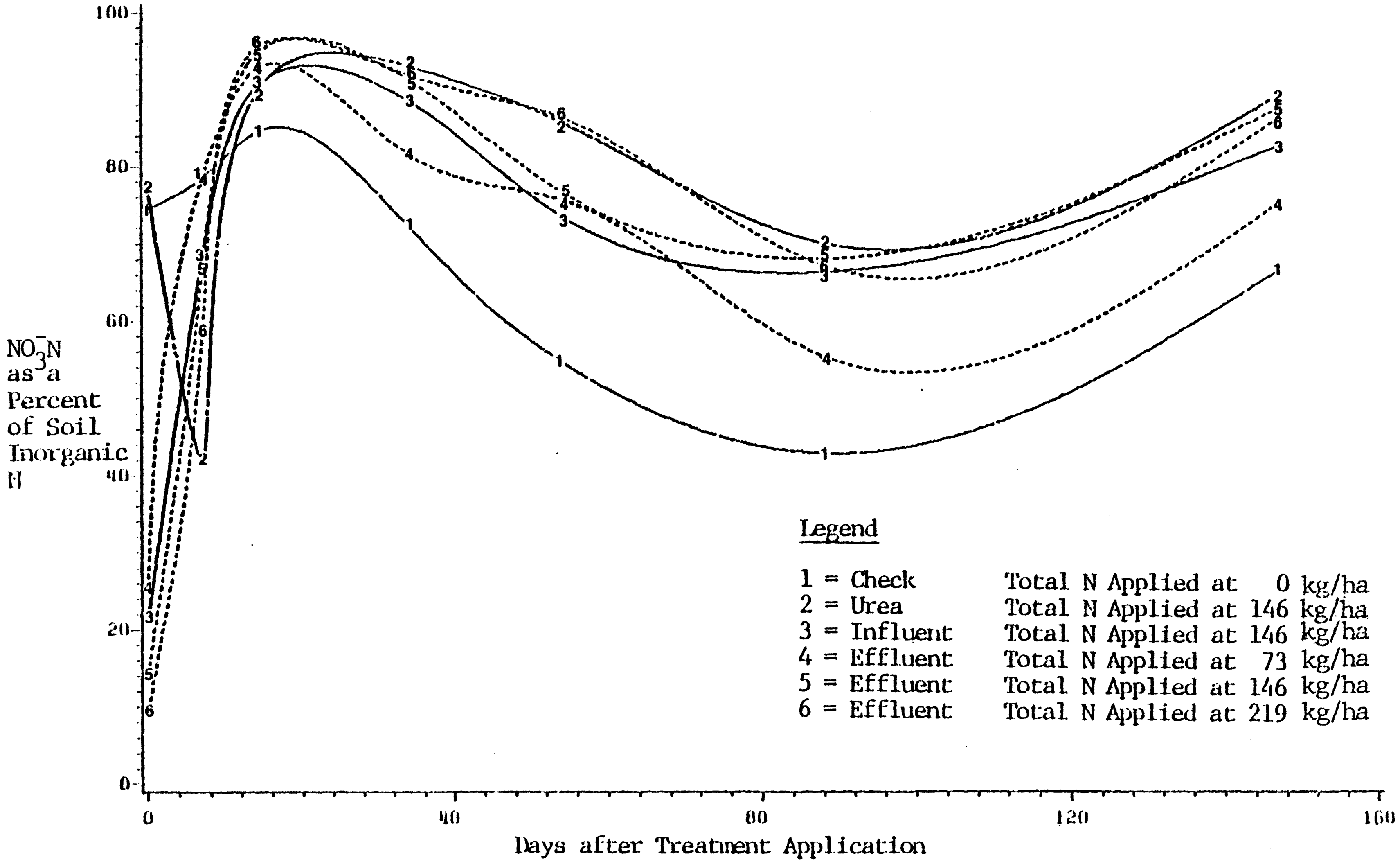


Figure 24. Nitrates N as a % of soil inorganic N* of field grown plots treated with urea N, poultry manure influent N and biogas effluent N, versus days after treatment application (Site 1).

*Average of 4 replications.

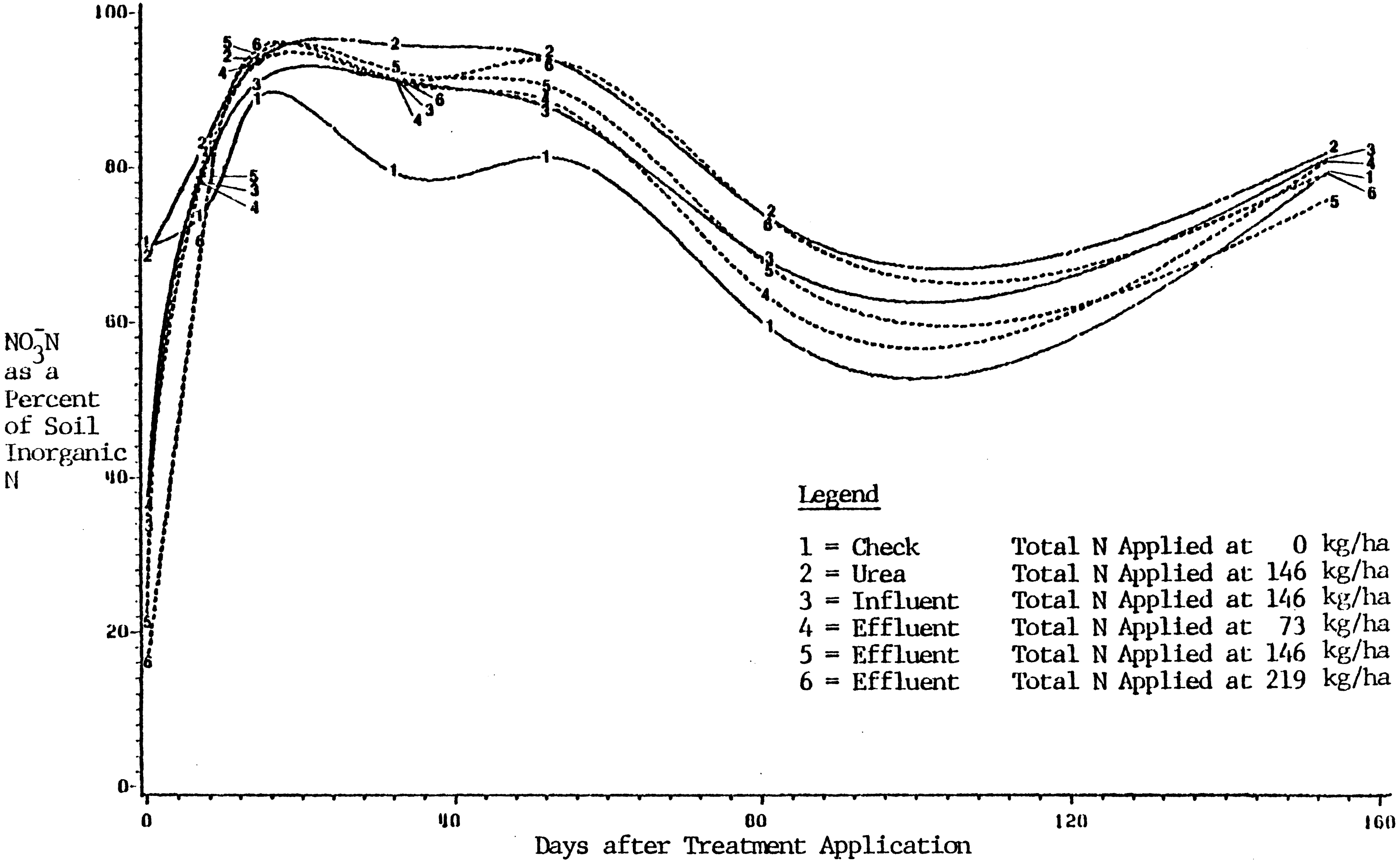


Figure 25. Nitrates N as a % of soil inorganic N* of field grown plots treated with urea N, poultry manure influent N and biogas effluent N, versus days after treatment application (Site 2).

*Average of 4 replications.

effluent treatment generally had the next lowest ratio. This trend resulted from the manner in which all of the inorganic N present was nitrified except for a distinct quantity, which was the same for all treatments regardless of the soil inorganic N content. This can be observed from examining any given date past day 14 in Table 17. As an example, on day 34 the NO_3^-N content was generally about 10 kg ha^{-1} less than the inorganic N content in all of the treatments.

The trends observed at Site 1 were also observed in Site 2. However, there did not appear to be an obvious lag phase of nitrification. Thus the NO_3^-N:inorganic N ratios at day 7 were not inversely related to the inorganic N content of the soil.

4.4.3 Ammonia Volatilization

The estimated NH_3 volatilization losses from the treatments are given in Table 22 for Site 1 and Table 23 for Site 2. At Site 1, the volatilization losses from the effluent treatments ranged from 61 to 68% of the applied NH_4^+N and 53 to 59% of the applied TKN. In comparison, volatilization lost from the influent was 38 and 18% of the applied NH_4^+N and TKN, respectively. The estimated loss from the urea was 37% of the applied TKN.

Table 22. Estimated ammonia N volatilization losses* from soil treated with urea N, poultry manure influent N and biogas effluent N (Site 1).

Treatments[1]		Estimated Ammonia N Volatilization Losses		
Material	TKN Appl (kg/ha)	kg/ha	Percent of NH_4^+N Appl	Percent of TKN Appl
Urea	146	53.3^{bc2}	-	36.6^{b}
Influent	146	25.7^{c}	38.3^{b}	17.6^{c}
Effluent	73	40.9^{c}	64.2^{a}	56.2^{a}
Effluent	146	77.8^{b}	61.0^{a}	53.4^{a}
Effluent	219	129^{a}	67.6^{a}	59.2^{a}

*Average of 4 replications

[1] Total Kjeldahl Nitrogen

[2] Means in columns that are followed by the same letter are not significantly different at the 5% level (Duncan's Multiple Range).

Table 23. Estimated ammonia N volatilization losses* from soil treated with urea N, poultry manure influent N and biogas effluent N (Site 2).

Treatments		Estimated Ammonia N Volatilization Losses		
Material	TKN[1] Appl (kg/ha)	kg/ha	Percent of NH_4^+N Appl	Percent of TKN Appl
Urea	146	38.7 ^{b} [2]	-	26.6 ^{b}
Influent	146	54.8 ^{ab}	81.7 ^{a}	37.6 ^{ab}
Effluent	73	48.7 ^{ab}	76.4 ^{a}	66.9 ^{a}
Effluent	146	88.8 ^{ab}	69.6 ^{a}	60.9 ^{a}
Effluent	219	96.5 ^{a}	50.4 ^{a}	44.1 ^{ab}

*Average of 4 replications

[1] Total Kjeldahl Nitrogen

[2] Means in columns that are followed by the same letter are not significantly different at the 5% level (Duncan's Multiple Range).

The volatilization of NH_3N per unit of NH_4^+N applied from the effluent was approximately 69% greater than from the influent. This is due to the higher pH of the effluent used in the field experiments (pH=7.95) compared to the influent (pH=7.10). The tendency for the effluent to be of a more alkaline pH in comparison with the corresponding influent was also observed previously in Table 4. Higher pH solutions cause greater equilibrium concentrations of NH_3 and thus promote NH_3 volatilization.

The volatilization of NH_3 per unit of applied TKN from the effluent was approximately 3.2 fold greater than that from the influent. The reason for the larger difference based on TKN is because a majority of the influent N is in the organic form. In contrast, a majority of the effluent N is in the NH_4^+N form.

The estimated NH_3 losses from the effluent were generally 54% greater than that estimated for the urea fertilizer. However, if the true losses from the urea were as large as the estimated losses, then the differences between soil inorganic N of the effluent and urea that are observed (following day 14) would not be as large. Thus, it appears that the losses of NH_3 from the urea plots were overestimated. This was due to the assumption (used in the estimation) that the urea N was 100% mineralized by day 7.

By viewing Figure 22, a rise in the inorganic N of the urea plot is evident between days 7 and 34. This was probably caused by the mineralization of a final component of the applied urea which was not mineralized during the first week. An estimate based upon the inorganic N present at day 34 would indicate that 26.4% of the applied TKN was volatilized from the urea, which is about half that lost from the effluent treatments.

At Site 2, the volatilization losses from the effluent treatments were 76, 70 and 50% of the applied $NH_4{}^+N$ and 67, 61 and 44% of the applied TKN for the low, mid and high rates, respectively. The lower rates at Site 2 thus had greater volatilization losses than the higher rates on a percent of applied N basis. This is because Site 2 is a minimum till site and had corn stubble on the soil surface. When the low rate was applied, a large proportion of the effluent was absorbed by the stubble. The $NH_4{}^+N$ soaked in the stubble did not come into contact with the soil CEC. The higher rates had proportionally less of the effluent absorbed by the stubble. This was because the stubble became saturated with effluent. Thus, the higher rates had proportionally more of the $NH_4{}^+N$ in contact with the CEC and less $NH_4{}^+N$ was available for NH_3 volatilization.

The volatilization loss from the influent was 82% of the NH_4^+N which was greater than that lost from the effluent per unit of NH_4^+N applied. This was opposite the trend observed at Site 1 and can be explained in terms of the influent's interaction with the surface stubble. The influent slurry applied was more viscous than the effluent slurry applied and adhered to the stubble more than the effluent. The volatilization loss from the influent as a percent of TKN applied was 38%. Since the effluent N was composed mostly of NH_4^+N, the NH_3N losses were greater than that from the influent. At this site the effluent applied at the mid rate had 62% greater losses of TKN by volatilization in comparison to the influent applied at the same rate of N.

The NH_3N volatilized from the urea treated plots was estimated at 26.6% of the applied TKN. The estimate (based from day 7 data) at this site was more reliable than that from Site 1 since no further mineralization from urea N past day 7 is indicated from the soil inorganic N data (see Figure 23). Since the urea N was applied in a granular form, the N was not subject to absorption by the stubble. Thus, the NH_3N loss from urea at this site was very similar to the estimate based on the day 34 data of Site 1. The N volatilization loss from urea ws 44% of that lost from effluent applied at the same rate of N.

The N volatilization losses from the slurries applied at both sites were high despite incorporation of the treatments in the soil. Thus, the largest component of the volatilization must have occurred in the several hour period between application and discing. The materials were applied on warm dry sunny days at both sites which allowed for some of the slurry to dry. Considerable volatilization could have also continued after incorporation as many soil aggregates saturated with the slurries were observed on the soil surface after the discing operation. Thus, immediate incorporation of the effluent and influent slurries into the soil at application is highly recommended to prevent large volatilization losses. Heavy discing to maximize the incorporation of applied NH_4^+N with the soil CEC is also recommended. Additionally, application of the slurries to the surface of soils covered with stubble or mulch should be avoided.

The effluent N is evidently subject to greater losses of N by volatilization than the corresponding influent N and the urea N fertilizer. The effluent contains a greater proportion of its TKN in the NH_4^+N form in comparison to the influent. Thus a greater proportion of the effluent TKN is available for volatilization. Additionally, the pH of anaerobically digested effluent is typically higher than the corresponding influent.As a consequence effluent NH_4^+N can be converted to NH_3 more rapidly. The volatilization losses were lower for the urea N since at the critical period (hours) following application, the urea was in the organic form.

4.4.4 Plant Tissue Nutrient Analyses

The concentration of N in the corn ear leaves at early silk are shown in Table 24 for Site 1 and in Table 25 for Site 2. The total N concentration of the corn leaves at Site 1 generally corresponded to the soil inorganic N contents of the furrow slice after day 14. However, the influent treatment had an ear leaf N that was slightly higher than that of the middle rate effluent treatment. In the soil, the inorganic N of the influent treatment was observed to be lower than that of the effluent treatment applied at the same rate.

The total concentration of the corn ear leaves at Site 2 also generally corresponded to the soil inorganic N contents of the furrow slice after day 14. The influent treatment at this site again was observed to have slightly higher ear leaf N than that of the effluent treatment. The high rate effluent treatment had almost identical ear leaf N

Table 24. Concentration of earleaf N* at early silk of field grown corn on untreated, urea N, poultry manure influent N and biogas effluent N treated soil (Site 1).

Treatment			Concentration N in Ear Leaf % of dry weight
#	Type	TKN[1] appl kg/ha	
1	Check	0	2.28^{b}[2]
2	Urea	146	2.96^{a}
3	Influent	146	2.75^{a}
4	Effluent	73	2.63^{ab}
5	Effluent	146	2.72^{a}
6	Effluent	219	2.89^{a}

*Average of 4 replications

[1] Total Kjeldahl Nitrogen

[2] Means followed with the same letter are not significantly different at the 5% level (Duncan's Multiple Range).

Table 25. Concentration of earleaf N[*] at early silk from field grown corn on untreated, urea N, poultry manure influent N and biogas effluent N treated soil (Site 2).

Treatment			Concentration N in Ear Leaf % of dry weight
#	Type	TKN[1] appl kg/ha	
1	Check	0	2.59c[2]
2	Urea	146	3.06a
3	Influent	146	3.02ab
4	Effluent	73	2.76bc
5	Effluent	146	2.98ab
6	Effluent	219	3.07a

[*] Average of 4 replications

[1] Total Kjeldahl Nitrogen

[2] Means followed with the same letter are not significantly different at the 5% level (Duncan's Multiple Range).

to that of the urea treatment. This corresponded to the similarities of soil inorganic N contents of the high rate effluent and urea treatments after day 52.

Little statistical differences were observed between ear leaf N concentrations of treatments at either site except for the significantly lower values for the check. At Site 2 the low rate effluent also had significantly lower ear leaf N than some of the treatments with high soil inorganic N contents.

The concentrations of ear leaf P, K, Ca and Mg are shown in Table 26, for Site 1 and Table 27 for Site 2. At both sites there were no relationships between the treatments and the Ca and Mg concentrations. Thus, there was similar uptake of these nutrients in all of the treatments.

At Site 2, K concentrations in the ear leaves were similar in all of the treatments and there were no observable trends. However, at Site 1, the ear leaf K of the check treatment was significantly lower than those of the influent, mid and high rate effluent treatments. Thus, the K uptake was affected by low N supply.

At both sites, statistical differences in the P concentrations of the ear leaves were observed. Ear leaf P tended to be low for the check treatment and low rate

Table 26. Concentrations[*] of earleaf P, K, Ca and Mg at early silk of field grown corn on untreated, urea N, poultry manure influent N and biogas effluent N treated soil (Site 1).

Treatment			P	K	Ca	Mg
#	Type	TKN[1] appl kg/ha	% of dry weight			
1	Check	0	$.238^{c}$[2]	2.38^{b}	$.494^{a}$	$.225^{a}$
2	Urea	146	$.334^{a}$	2.53^{ab}	$.483^{a}$	$.241^{a}$
3	Influent	146	$.314^{ab}$	2.65^{a}	$.500^{a}$	$.225^{a}$
4	Effluent	73	$.292^{b}$	2.48^{ab}	$.470^{a}$	$.225^{a}$
5	Effluent	146	$.323^{ab}$	2.58^{a}	$.446^{a}$	$.228^{a}$
6	Effluent	219	$.337^{a}$	2.63^{a}	$.473^{a}$	$.210^{a}$

[*] Average of 4 replications

[1] Total Kjeldahl Nitrogen

[2] Means in columns followed by similar letters are not significantly different at the 5% level (Duncan's Multiple Range).

Table 27. Concentrations* of earleaf P, K, Ca and Mg at early silk from field grown corn on untreated, urea N, poultry manure influent N and biogas effluent N treated soil (Site 2).

Treatment			P	K	Ca	Mg
#	Type	TKN[1] appl kg/ha	% of dry weight			
1	Check	0	.225c[2]	2.10a	.380a	.348a
2	Urea	146	.278ab	2.18a	.419a	.350a
3	Influent	146	.284a	2.18a	.389a	.339a
4	Effluent	73	.252bc	2.10a	.395a	.353a
5	Effluent	146	.271ab	2.00a	.399a	.324a
6	Effluent	219	.262ab	2.03a	.418a	.358a

*Average of 4 replications

[1] Total Kjeldahl Nitrogen

[2] Means in columns followed by similar letters are not significantly different at the 5% level (Duncan's Multiple Range).

effluent treatment. Since fertilizer P was applied to bring the extractable P to equal levels for all of the treatments, the differences in ear leaf P might be attributed to the interaction of N and root development. Treatments which supplied adequate levels of inorganic N to the soil perhaps had more extensive root growth in comparison to treatments with low soil inorganic N. Since P is a soil immobile nutrient, poor root development results in low P uptake.

4.4.5 Grain and Silage Yield

The grain and silage yields for the field study are shown in Table 28 for Site 1 and Table 29 for Site 2. The grain yields at both sites were not significantly different for treatments with N applications greater or equal to 146 kg ha^{-1}. These treatments, however had significantly higher yields than the check.

The high rate effluent had the third highest yield at Site 1 and the highest yield at Site 2. Nitrogen volatilization losses were 34% greater for this treatment at Site 1 compared to Site 2. Therefore, the higher yield in comparison to the other treatments at Site 2 is attributable to lower losses of N.

The urea treatment which sustained significantly higher levels of soil inorganic N throughout the growing season at

Table 28. Grain and silage yields* from field grown corn treated with urea N, poultry manure influent N and biogas effluent N (Site 1).

#	Treatment Material	Treatment TKN[1] Appl. kg/ha	Grain Yield[2] Mg/ha	Silage Yield[3] Mg/ha
1	Check	0	4.72 c[4]	13.4 c
2	Urea	146	8.90 a	19.9 a
3	Influent	146	8.81 a	18.8 ab
4	Effluent	73	7.40 b	17.0 b
5	Effluent	146	8.17 ab	16.6 b
6	Effluent	219	8.69 a	17.7 ab

*Average of 4 replications

[1] Total Kjeldhal Nitrogen, [2] 15.5% moisture, [3] dry weight basis

[4] Means in columns that are followed by similar letters are not significantly different at the 5% level (Duncan's Multiple Range).

Table 29. Grain and silage yields* from field grown corn treated with urea N, poultry manure influent N and biogas effluent N (Site 2).

Treatment Material	 TKN[1] Appl. kg/ha	Grain Yield[2] Mg/ha	Silage Yield[3] Mg/ha
Check	0	4.30 c[4]	10.8[a]
Urea	146	5.47 ab	12.1[a]
Influent	146	5.42 ab	12.3[a]
Effluent	73	4.88 bc	11.4[a]
Effluent	146	5.37 ab	12.3[a]
Effluent	219	5.95 a	12.8[a]

*Average of 4 replications

[1] Total Kjeldahl Nitrogen

[2] 15.5% moisture

[3] dry weight basis

[4] Means in columns that are followed by similar letters are not significantly different at the 5% level (Duncan's Multiple Range).

Site 1 also had the highest grain yield. At Site 2, the high rate effluent treatment had the highest grain yield despite having slightly lower soil inorganic N contents in comparison to the urea treatment. Similarly, grain yields from the influent treatment at both sites were higher than those from the corresponding rate of effluent.

Thus, the content of inorganic N in the soil during the period of crop growth, does not necessarily account for the behavior of the applied N in terms of grain yield. Applied organic N could possibly be mineralized rapidly and absorbed by corn roots with a high rate of turn-over. In this manner effluent N from the high rate treatment at Site 1 could have provided more N to the crops than the urea N while concurrently having a lower soil inorganic N content. Similarly, the influent treatment perhaps had a higher N turn-over rate compared to the mid rate effluent because of its greater organic N fraction. The higher ear leaf N values observed previously for the influent treatments at both sites compared to the effluent is further evidence that the influent provided greater quantities of N to the crop.

The silage yields generally followed the trends recognized with the grain yields at each of the sites. The silage yield, like the grain yield and ear leaf N, was higher for the influent treatment than that of the corresponding rate of effluent. At Site 1, the silage yield from the urea treatment was significantly higher (19.9%) than that from the corresponding rate of effluent. This difference is most likely attributable to the large volatilization losses from the latter treatment. The silage yields at Site 2 were not significantly different between treatments, however the yield from the check and low rate effluent treatments were noticably lower.

At both sites the grain and silage yields between treatments of equal N application were statistically similar except for the 1 difference in silage yields noted previously. Thus despite large differences in NH_3 volatilization losses, similar yields were maintained. This is perhaps attributable to small increases in yield response to additional N past a given level of N.

The lower yields at Site 2 compared to Site 1 are attributable to low soil P. The soil apparently had a high P sorption capacity and maintained the soil P at low levels for crop needs (<10 mg/g) (Donohue and Gettier, 1982). Additionally, ear leaf P (see Table 27) at this site was at the lower end of the P sufficiency range for corn (Donohue and Hawkins, 1977).

4.4.6 Mitscherlich Regressions

The parameters and R^2 values of Mitscherlich curves fitted to yield and ear leaf N versus applied N (NAPPLO), applied N recovered after volatilization losses (NREC7) and soil inorganic N content following the period (7 days) of greatest volatilization (NSoil7) are shown in Tables 30 and 31 for Sites 1 and 2, respectively. The parameters and R^2 values of curves utilizing only the check and effluent data are shown in Tables 32 and 33 for sites 1 and 2, respectively. An overview of the relationships presented in the tables indicates that the Mitscherlich curves describe the yield responses of grain and silage and the response of ear leaf N to NAPPLO, NREC7 and NSoil7. Additionally, the fitted relationships account for a large percentage of the observed variation due to the high R^2 values.

The BO parameter is the predicted maximum yield or ear leaf N with an infinite supply of N. The BO parameters for relationships fitted to Site 1 data were similar to the highest observed yields and ear leaf N. This indicates that maximum yields and N uptake were approached at Site 1. The BO parameters at Site 2 were unrealistically high for grain and silage yields fitted to NAPPLO in comparison to observed yields. This data conformed to a linear pattern and thus was fitted to the lower portion of the Mitscherlich curve.

Table 30. Parameters of Mitscherlich fitted relationships between average grain and silage yield, earleaf nitrogen and nitrogen applied, recovered and measured for field grown corn utilizing check, urea, poultry manure influent and biogas effluent treatments (Site 1).

Dependent Variable		Independent Variable	Parameters‡			R^2
	Units	Kg/Ha (furrow slice)	B0	B1	B2	
Yield Grain	Mg Ha^{-1}	NAPPL0[1]	9.03	.481	.0146	.9689***
Yield Silage	Mg Ha^{-1}	NAPPL0	18.37	.270	.0213	.7350***
N Earleaf	%	NAPPL0	2.96	.229	.0103	.8792***
Yield Grain	Mg Ha^{-1}	NREC7[2]	8.97	.474	.0294	.9920***
Yield Silage	Mg Ha^{-1}	NREC7	19.41	.299	.0196	.8027***
N Earleaf	%	NREC7	2.87	.207	.0292	.8770***
Yield Grain†	Mg Ha^{-1}	NSoil7[3]	9.47	-	.0258	.9296***
Yield Silage†	Mg Ha^{-1}	NSoil7	18.76	-	.0407	.7696***
N Earleaf†	%	NSoil7	2.86	-	.0498	.8932***
Yield Grain	Mg Ha^{-1}	N Earleaf (%)	10.08	117.5	2.365	.9704***

[1] NAPPL0 = Total N applied at day 0

[2] NREC7 = Applied total N recovered on day 7

[3] NSoil7 = Soil inorganic N content on day 7 (150 mm furrow slice)

† Two parameter model yield (or N Earleaf) assumed to be 0 when NSoil7 = 0 (B1 = 1)

* P = .05, ** P = .01, *** P = .001

‡ $y = B0(1 - B1\ e^{-B2\ X})$

Table 31. Parameters of Mitscherlich fitted relationships between average grain and silage yield, earleaf nitrogen and nitrogen applied, recovered and measured for field grown corn utilizing check and biogas effluent treatments only (Site 1).

Dependent Variable	Units	Independent Variable Kg/Ha (furrow slice)	Parameters‡ B0	 B1	 B2	R^2
Yield Grain	Mg Ha^{-1}	NAPPL0[1]	8.84	.464	.0141	.9999*
Yield Silage	Mg Ha^{-1}	NAPPL0	17.16	.217	.0397	.9419*
N Earleaf	%	NAPPL0	2.96	.228	.0085	.9807*
Yield Grain	Mg Ha^{-1}	NREC7[2]	8.78	.463	.0321	.9951*
Yield Silage	Mg Ha^{-1}	NREC7	17.16	.216	.0987	.9415*
N Earleaf	%	NREC7	2.96	.227	.0196	.9680*
Yield Grain†	Mg Ha^{-1}	NSoil7[3]	9.66	-	.0234	.9789***
Yield Silage†	Mg Ha^{-1}	NSoil7	17.51	-	.0494	.9084***
N Earleaf†	%	NSoil7	2.81	-	.0533	.9290***
Yield Grain	Mg Ha^{-1}	N Earleaf (%)	11.15	24.0	1.635	.9612*

[1] NAPPL0 = Total N applied at day 0

[2] NREC7 = Applied total N recovered on day 7

[3] NSoil7 = Soil inorganic N content on day 7 (150 mm furrow slice)

† Two parameter model yield (or N Earleaf) assumed to be 0 when NSoil7 = 0 (B1 = 1)

*P = .05, **P = .01, ***P = .001

‡ $y = B0(1 - B1\, e^{-B2\, X})$

Table 32. Parameters of Mitscherlich fitted relationships between average grain and silage yield, earleaf nitrogen and nitrogen applied, recovered and measured for field grown corn utilizing check, urea, poultry manure influent and biogas effluent treatments (Site 2).

Dependent Variable		Independent Variable	Parameters[‡]			R^2
	Units	Kg/Ha (furrow slice)	B0	B1	B2	
Yield Grain	Mg Ha^{-1}	NAPPL0[1]	8.22	.476	.0024	.9924***
Yield Silage	Mg Ha^{-1}	NAPPL0	16.64	.355	.0020	.9818***
N Earleaf	%	NAPPL0	3.34	.229	.0054	.9415***
Yield Grain	Mg Ha^{-1}	NREC7[2]	5.98	.275	.0151	.9279***
Yield Silage	Mg Ha^{-1}	NREC7	12.59	.147	.0233	.9025***
N Earleaf	%	NREC7	3.12	.173	.0198	.9892***
Yield Grain[†]	Mg Ha^{-1}	NSoil7[3]	6.00	-	.0166	.7713***
Yield Silage[†]	Mg Ha^{-1}	NSoil7	12.67	-	.0239	.6890***
N Earleaf[†]	%	NSoil7	3.13	-	.0220	.7716***
Yield Grain	Mg Ha^{-1}	N Earleaf (%)	8.09	4.86	.9044	.9177***

[1] NAPPL0 = Total N applied at day 0

[2] NREC7 = Applied total N recovered on day 7

[3] NSoil7 = Soil inorganic N content on day 7 (150 mm furrow slice)

[†] Two parameter model yield (or N Earleaf) assumed to be 0 when NSoil = 0 (B1 = 1)

*P = .05, **P = .01, ***P = .001

[‡] $y = B0(1 - B1\, e^{-B2\, X})$

Table 33. Parameters of Mitscherlich fitted relationships between average grain and silage yield, earleaf nitrogen and nitrogen applied, recovered and measured for field grown corn utilizing check and biogas effluent treatments only (Site 2).

Dependent Variable		Independent Variable	Parameters[‡]			R^2
	Units	Kg/Ha (furrow slice)	B0	B1	B2	
Yield Grain	Mg Ha^{-1}	NAPPL0[1]	10.54	.592	.0014	.9961**
Yield Silage	Mg Ha^{-1}	NAPPL0	15.51	.306	.0025	.9890**
N Earleaf	%	NAPPL0	3.62	.287	.0030	.9874**
Yield Grain	Mg Ha^{-1}	NREC7[2]	6.33	.322	.0131	.9996**
Yield Silage	Mg Ha^{-1}	NREC7	13.06	.180	.0178	.9900**
N Earleaf	%	NREC7	3.12	.175	.0198	.9870***
Yield Grain	Mg Ha^{-1}	NSoil7[3]	6.52	-	.0128	.9831***
Yield Silage	Mg Ha^{-1}	NSoil7	13.11	-	.0200	.9502***
N Earleaf	%	NSoil7	3.15	-	.0201	.9418***
Yield Grain	Mg Ha^{-1}	N Earleaf (%)	9.14	4.09	.7865	.9612*

[1] NAPPL0 = Total N applied at day 0

[2] NREC7 = Applied total N recovered on day 7

[3] NSoil7 = Soil inorganic N content on day 7 (150 mm furrow slice)

[†] Two parameter model yield (or N Earleaf) assumed to be 0 when NSoil = 0 (B1 = 1)

*P = .05, **P = .01, ***P = .001

[‡] $y = B0(1 - B1\, e^{-B2\, X})$

This was due to proportionally lower volatilization losses of N from the high rate compared to the low rate effluent treatment. The B0 paramters of yield and ear leaf N data fitted to NREC7 and NSoil7 were similar to the highest observed values at Site 2. Therefore, maximum yield and N uptake were also approached at Site 2.

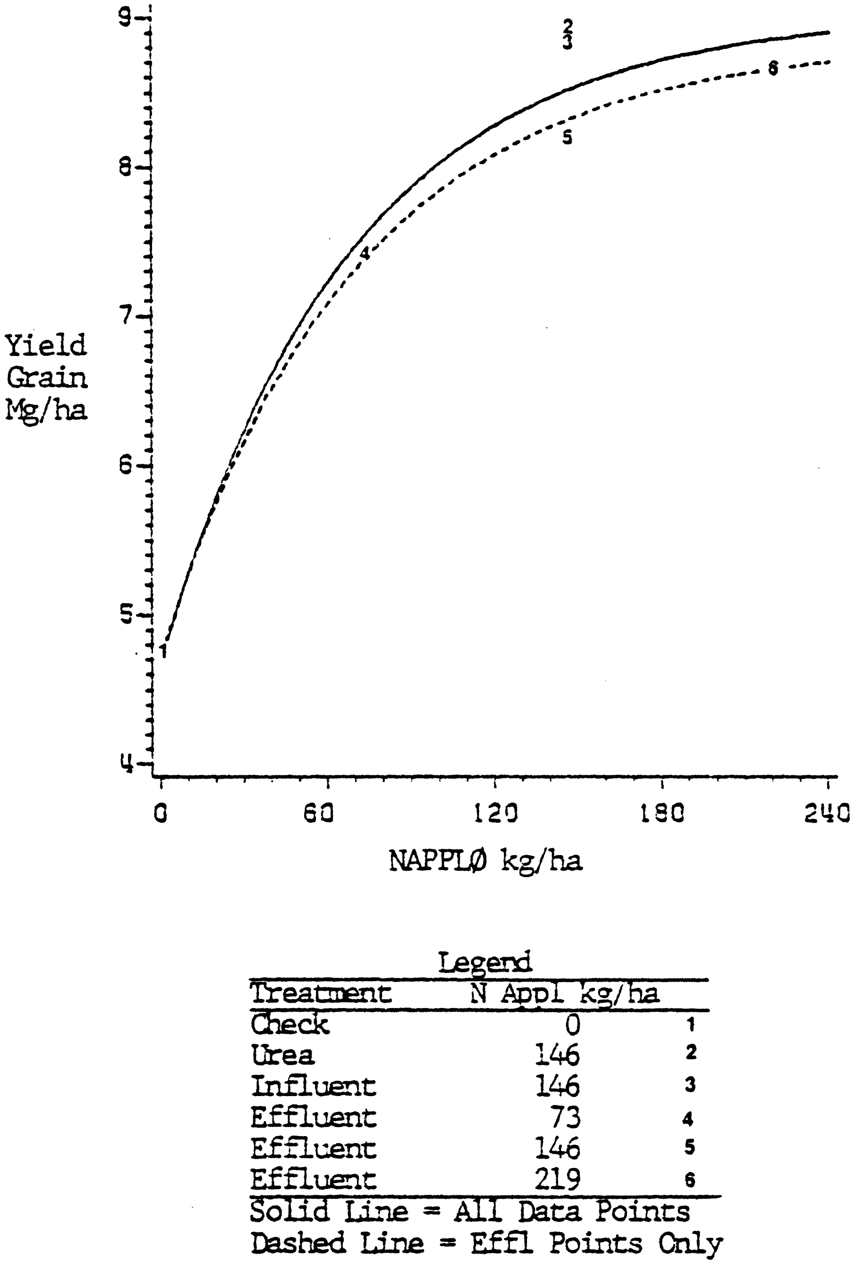
The R^2 values of the regressions from both sites were generally highest for grain yield compared to silage yield and ear leaf N fitted to NAPP10, NREC7 and NSoil7. This indicates that grain yield was most highly correlated with N supply. The one exception to this trend was the noticeably higher correlation of ear leaf N fitted to NREC7 at Site 2 when all the data points were utilized. Silage yields were least correlated (lowest R^2) to the N supply.

The R^2 values for yields and ear leaf N were generally highest for NREC7 compared to NAPP10 and NSoil7. This would be expected as the NAPP10 term does not account for volatilization losses of N and the NSoil7 term does not account for N mineralized from applied organic N. The high correlation of yield to NREC7 indicate that most of the applied organic N from both the influent and the effluent become plant available during the growing season.

The R^2 values of curves fitted to the effluent treatments were in most instances higher than those fitted to all the treatments. This results from higher correlations that are feasible when fitting fewer data points and greater homogenitiy in the behavior of N supplied with a single type of N carrier. When regressions were based on all the data points, differences in the mineralization and volatilization of applied N of the different materials accounted for some of the variation.

In order to facilitate comparison of the observed data with the Mitscherlich curves, plots of grain yield and ear leaf N versus NAPP10, NREC7, NSoil7 and grain yield versus ear leaf N were made. The plots of observed data and the Mitscherlich curves for the relationship between grain yield and NAPPLO are shown in Figure 26 for Site 1 and Figure 27 for Site 2. The data points representing the effluent at Site 1 were lower than the curve fitted to all the treatments. This is because there was greater volatilization of N from the effluent compared to the urea and influent treatments. The data from Site 2 conformed to a linear pattern. The typical yield response relationship was altered by differences in volatilization between the effluent treatments.

The plots of observed data and the Mitscherlich curves for the relationship between grain yield and NREC7 are shown in Figure 28 for Site 1 and Figure 29 for Site 2. The yield

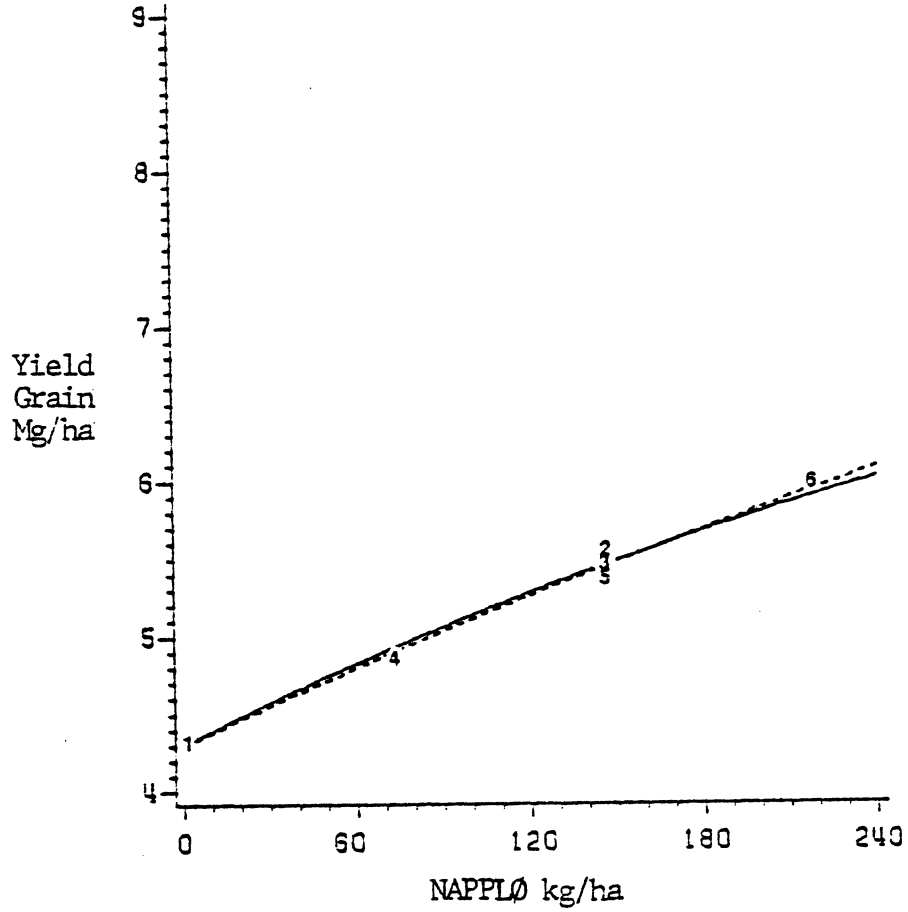


Legend

Treatment	N Appl kg/ha	
Check	0	1
Urea	146	2
Influent	146	3
Effluent	73	4
Effluent	146	5
Effluent	219	6

Solid Line = All Data Points
Dashed Line = Effl Points Only

Figure 26. Comparison of the observed and Mitscherlich fitted responses for the relationship between grain yield and total N applied with treatments (Site 1).



Legend

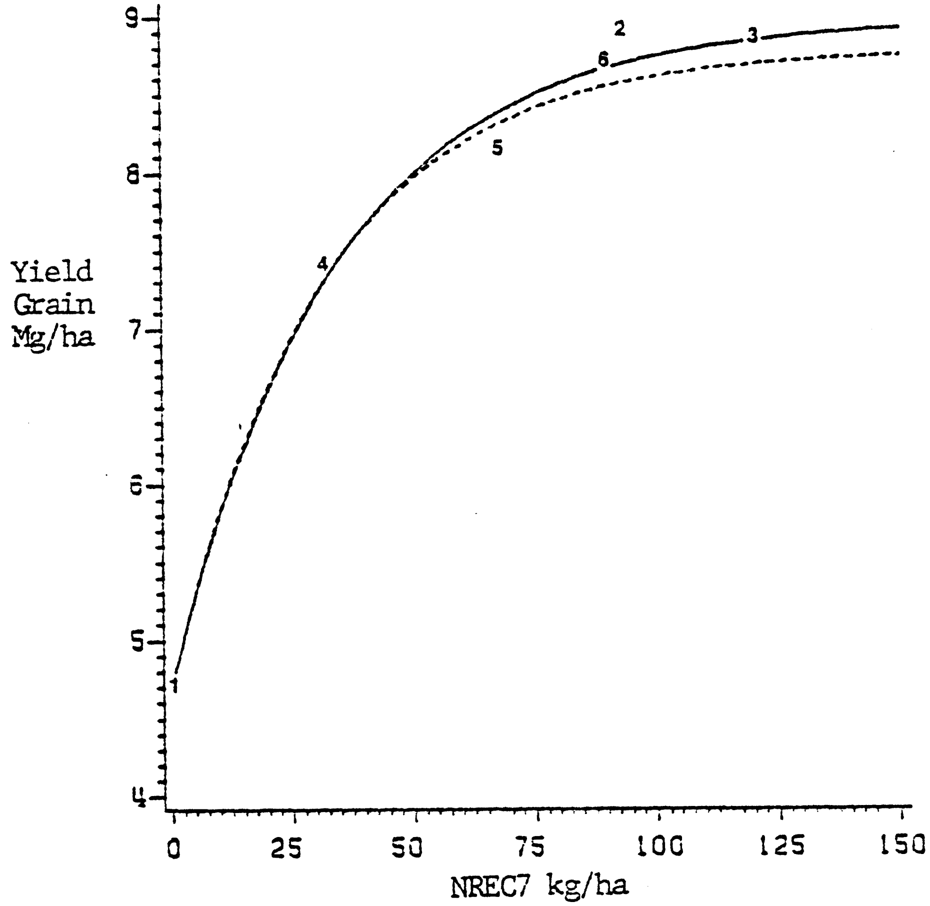
Treatment	N Appl kg/ha	
Check	0	1
Urea	146	2
Influent	146	3
Effluent	73	4
Effluent	146	5
Effluent	219	6

Solid Line = All Data Points
Dashed Line = Effl Points Only

Figure 27. Comparison of the observed and Mitscherlich fitted responses for the relationship between grain yield and total N applied with treatments (Site 2).

plotted against NREC7 for the data at Site 1 fitted a classic yield response relationship. The data point representing the urea treatment was slightly higher than the Mitscherlich curve fitted to all the data points. This apparently resulted because volatilization losses from the urea were smaller than those estimated (causing an underestimation of NREC7) as discussed previously. The influent data point was directly on the Mitscherlich curve indicating that a majority of the applied organic N became available during the growing season. The data from Site 2 plotted against NREC7 conformed to a typical Mitscherlich shape curve. The effluent data points on this plot were higher than the Mitscherlich curve fitted to all the treatments. Thus, the effluent had a higher yield for a given NREC7 than would be expected from the yield of either the urea or influent treatments. This indicates that accelerated mineralization of native soil organic N over the rate which was occurring in the other treatments may have occured. Evidence that the effluent 'primed' the soil organic N in this fashion was observed for this same soil in the laboratory mineralization study.

The plots of observed data and the Mitscherlich curves for the relationship between grain yield and NSoil7 are shown in Figure 30 for Site 1 and Figure 31 for Site 2. The

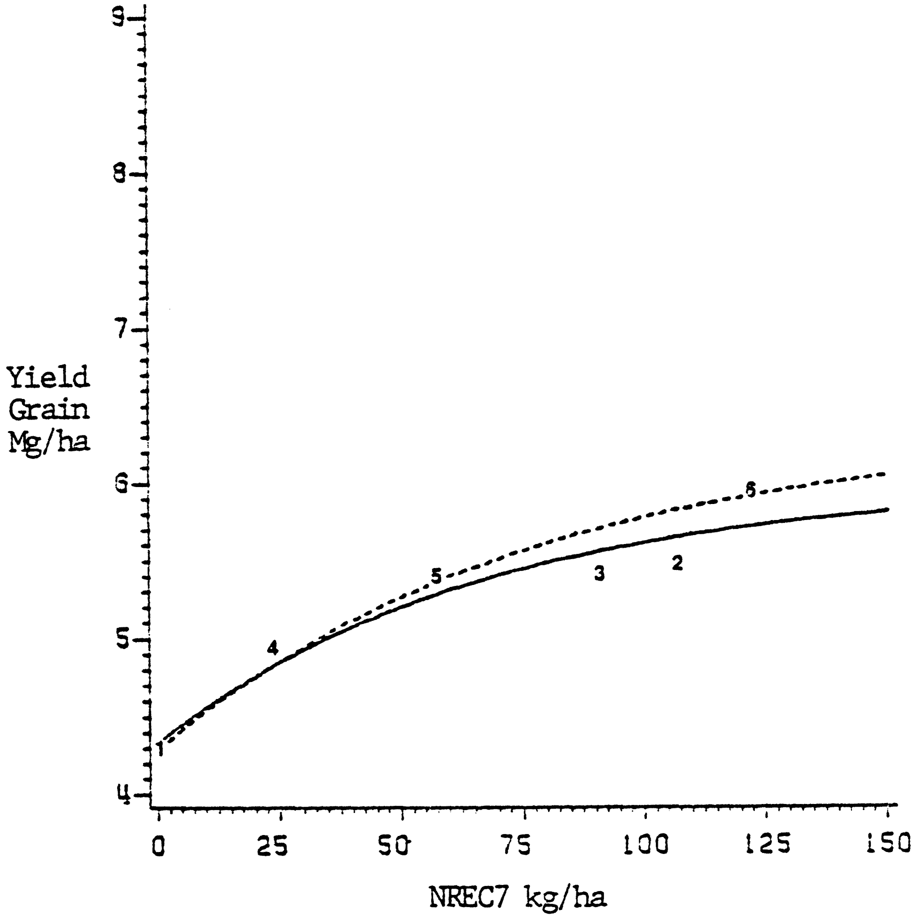


Legend

Treatment	N Appl kg/ha	
Check	0	1
Urea	146	2
Influent	146	3
Effluent	73	4
Effluent	146	5
Effluent	219	6

Solid Line = All Data Points
Dashed Line = Effl Points Only

Figure 28. Comparison of the observed and Mitscherlich fitted responses for the relationship between grain yield and applied total N recovered 7 days after treatment applications (Site 1).



Legend

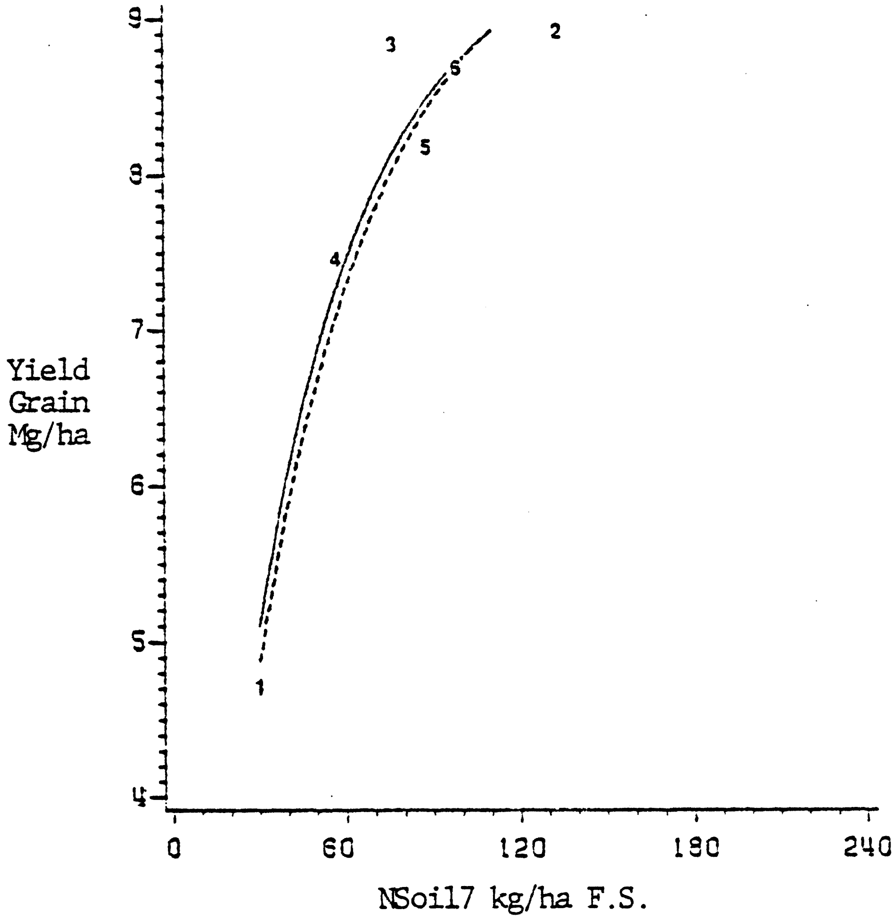
Treatment	N Appl kg/ha	
Check	0	1
Urea	146	2
Influent	146	3
Effluent	73	4
Effluent	146	5
Effluent	219	6

Solid Line = All Data Points
Dashed Line = Effl Points Only

Figure 29. Comparison of the observed and Mitscherlich fitted responses for the relationship between grain yield and applied total N recovered 7 days after treatment applications (Site 2).

Mitscherlich curves estimated from utilizing all of the treatments and from utilizing only the effluent treatments were nearly identical at Site 1. However, the yield from the influent treatment was higher and the yield from the urea treatment was lower than those that would be estimated from the Mitscherlich curve. This same observation was also evident at Site 2 . Thus, the inorganic N content of the soil one week after treatment application did not account for the N that was mineralized from the influent organic N. Similarly, it did not account for organic N mineralized from the effluent treatments since the yields from these treatments were higher at a given level of NSoil7 than that of the urea treatment. Yield from the urea treatment was underestimated as this treatment had little organic N remaining past the first week. These plots indicate that the applied organic N from the influent and effluent contribute to the yield of grain since a greater than expected yield is observed from regressions based on inorganic N.

The plots of observed data and the Mitscherlich curves for the relationship between ear leaf N and NREC7 are shown in Figure 32 for Site 1 and Figure 33 for Site 2. The ear leaf N was not as well correlated to NREC7 as grain yield at Site 1. The correlation is, however, better when observing

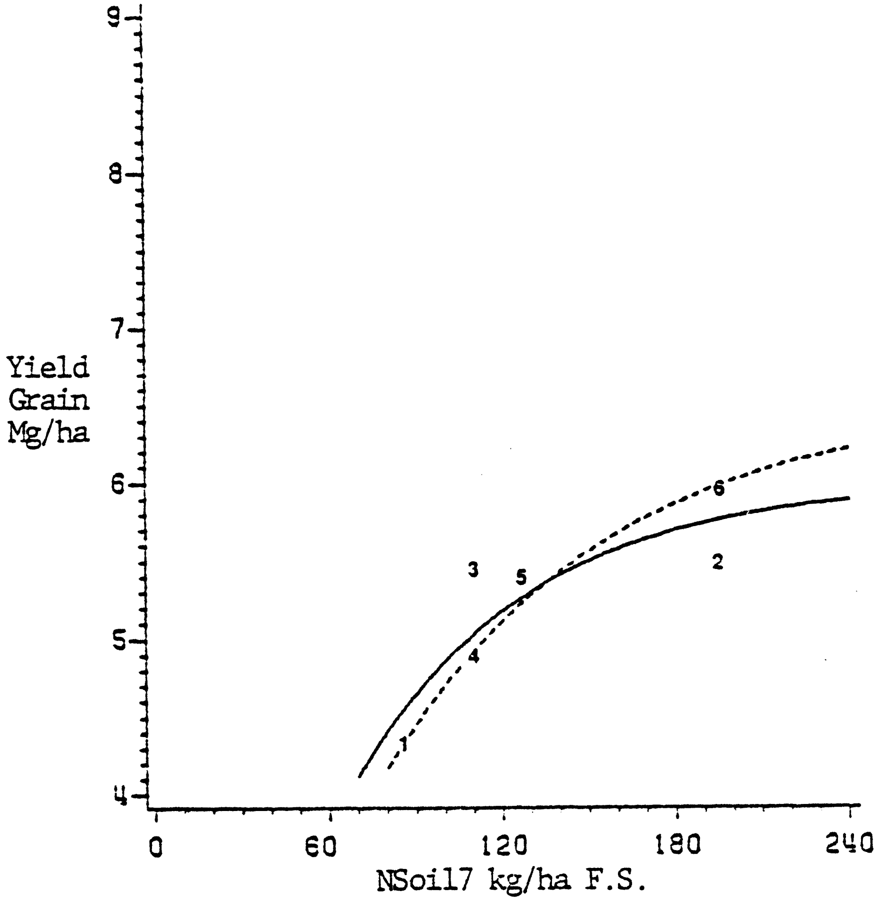


Legend

Treatment	N Appl kg/ha	
Check	0	1
Urea	146	2
Influent	146	3
Effluent	73	4
Effluent	146	5
Effluent	219	6

Solid Line = All Data Points
Dashed Line = Effl Points Only

Figure 30. Comparison of the observed and Mitscherlich fitted responses for the relationship between grain yield and soil inorganic N content of the 0 to 150 mm depth interval, furrow slice (F.S.), 7 days after treatment application (Site 1).



Legend

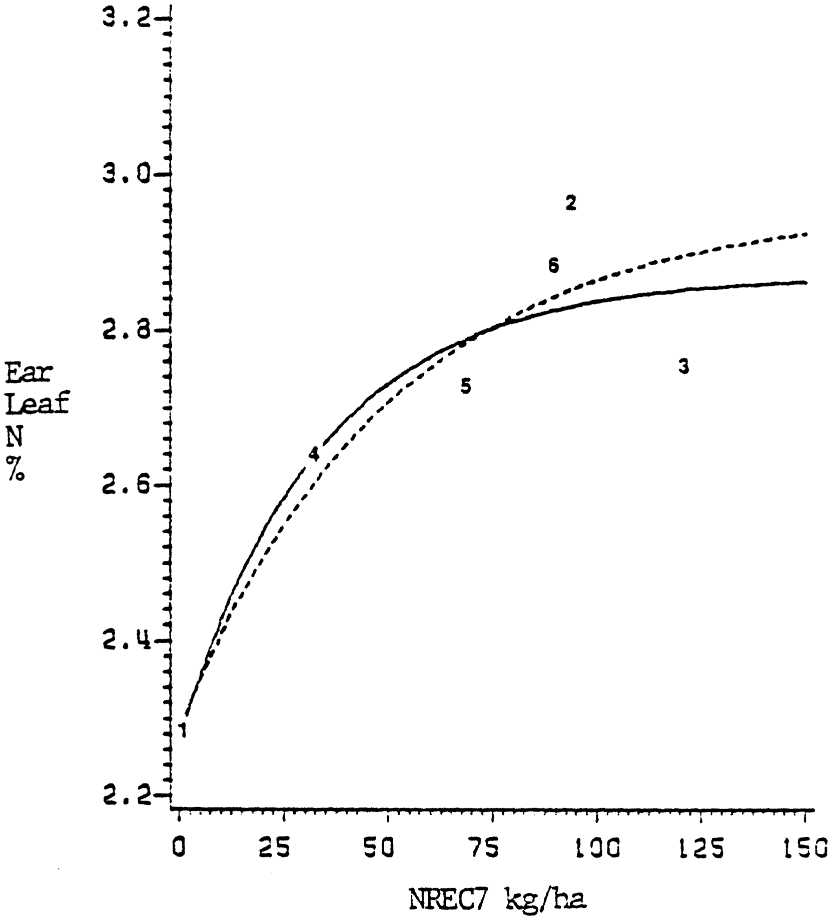
Treatment	N Appl kg/ha	
Check	0	1
Urea	146	2
Influent	146	3
Effluent	73	4
Effluent	146	5
Effluent	219	6

Solid Line = All Data Points
Dashed Line = Effl Points Only

Figure 31. Comparison of the observed and Mitscherlich fitted responses for the relationship between grain yield and soil inorganic N content of the 0 to 150 mm depth interval, furrow slice (F.S.) 7, days after treatment application (Site-2).

the effluent treatment point only. At Site 2, the ear leaf N was highly correlated to NREC7.

The plots of observed data and the Mitscherlich curves for the relationship between grain yield and ear leaf N are shown in Figure 34 for Site 1 and Figure 35 for Site 2. Most of the treatments had ear leaf N values that were correlated to yield. High B0 values for grain yields at both sites (Tables 30 and 32) indicated that yield plateaus were not achieved with yield relationships based on ear leaf N, despite the repeated observations that yield and ear leaf N plateaus were achieved with relationships based on applied N and soil N. Thus, the factors limiting yield at both sites appeared to be related to the uptake of N by the crop which limited the content of N in the leaves. A factor which could have limited the uptake of N at Site 1 may have been moisture supply. Factors contributing to the limitation of N uptake at Site 2 could have been a combination of low soil P (which was observed) and moisture supply.

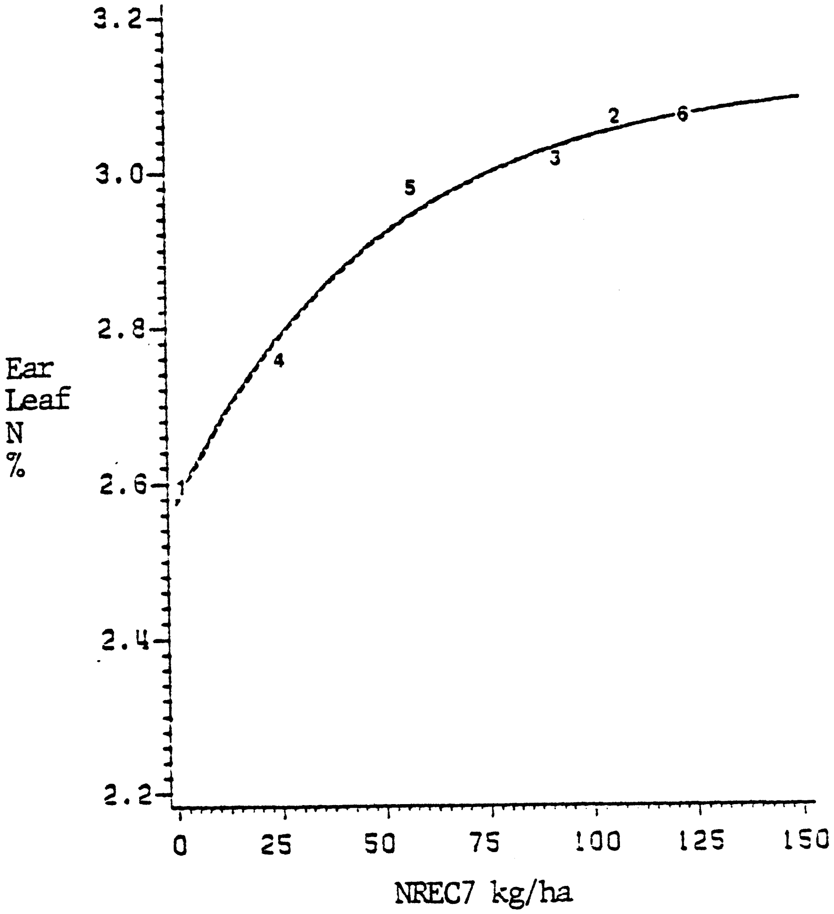


Legend

Treatment	N Appl kg/ha	
Check	0	1
Urea	146	2
Influent	146	3
Effluent	73	4
Effluent	146	5
Effluent	219	6

Solid Line = All Data Points
Dashed Line = Effl Points Only

Figure 32. Comparison of the observed and Mitscherlich fitted responses for the relationship between ear leaf nitrogen content at early silk and applied total N recovered 7 days after treatment application (Site 1).

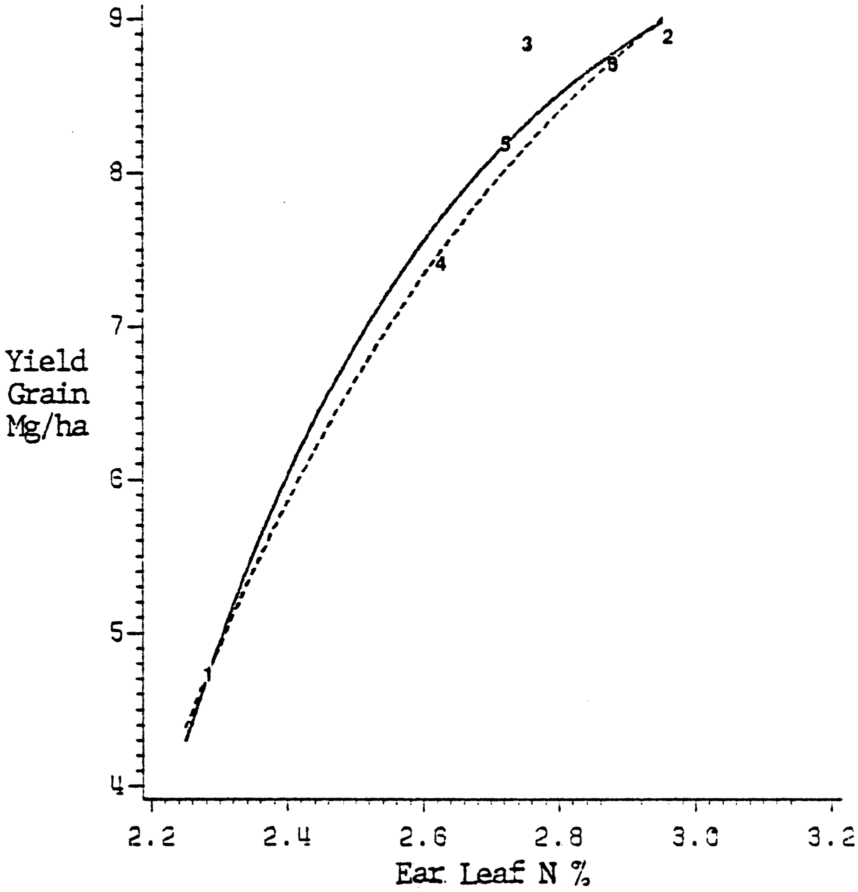


Legend

Treatment	N Appl kg/ha	
Check	0	1
Urea	146	2
Influent	146	3
Effluent	73	4
Effluent	146	5
Effluent	219	6

Solid Line = All Data Points
Dashed Line = Effl Points Only

Figure 33. Comparison of the observed and Mitscherlich fitted responses for the relationship between ear leaf nitrogen content at early silk and applied total N recovered 7 days after treatment application (Site 2).

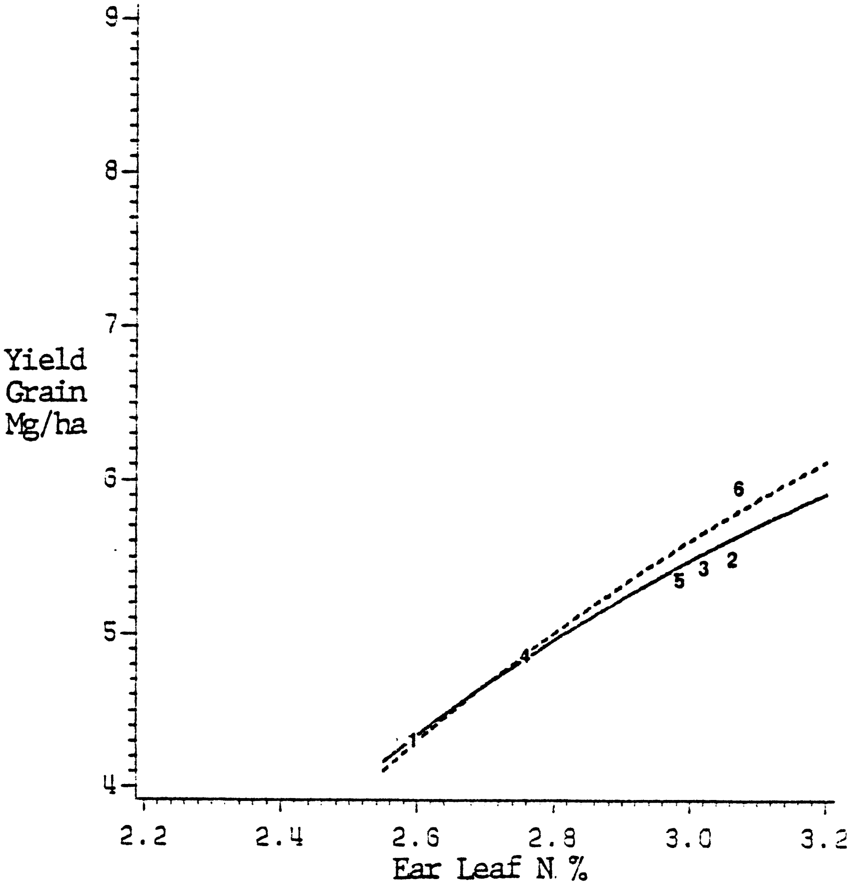


Legend

Treatment	N Appl kg/ha	
Check	0	1
Urea	146	2
Influent	146	3
Effluent	73	4
Effluent	146	5
Effluent	219	6

Solid Line = All Data Points
Dashed Line = Effl Points Only

Figure 34. Comparison of the observed and Mitscherlich fitted responses for the relationship between grain yield and ear leaf nitrogen content at early silk (Site 1).



Legend

Treatment	N Appl kg/ha	
Check	0	1
Urea	146	2
Influent	146	3
Effluent	73	4
Effluent	146	5
Effluent	219	6

Solid Line = All Data Points
Dashed Line = Effl Points Only

Figure 35. Comparison of the observed and Mitscherlich fitted responses for the relationship between grain yield and ear leaf nitrogen content at early silk (Site 2).

4.5 PHOSPHORUS SORPTION

A laboratory sorption study was conducted to observe the effect of organic matter added with anaerobically digested effluent on the sorption of added P by soil (from Site 2). Additionally, the available P status of the soil was measured from the field experiments at both sites to identify differences between treatments.

4.5.1 Laboratory Phosphorus Sorption Study

The relationship between the sorption of added soluble P and the final concentration of P in solution after a 6 day equilibration period are shown in Figures 36, 37 and 38 for 0, 30 and 90 days of incubation, respectively, after mixing effluent solids with the soil. Treatments 1, 2, 3 and 4 correspond to the check and effluent applied to the soil at 1, 5 and 10 times the field rate, rspectively. The relationship between P sorption and equilibrium P concentration (EPC) observed after 0 days of incubation illustrates that the effluent solids added to the soil at the field rate have no effect on reducing the P sorption characteristics of this soil. The treatments applied at 5 and 10 times the field rate were responsible for a slight reduction in P sorption. At 10 mg/l EPC, the P sorption from the check treatment was about 20% greater than that of the highest rate effluent.

The relationship between P sorption and the EPC at 30 days after incubation shows that at low EPC, the sorption of added P was similar for the check and the treatments with solids applied at 1 and 5 times the field rate. At high EPC, a slight increase in P sorption over the check was noticeable for the treatments with the two lower rates of effluent. This was perhaps due to greater microbial immobilization of available P during incubation from these treatments. If P were removed from the soil solution by incorporation into microbial tissue, then the equilibrium dynamics would cause P to be desorbed (freed) from sorbed positions in the soil during incubation. Thus, when equilibrated with added P, greater P sorption would be observed. Immobilization appeared to occur to a certain extent for all of the treatments at day 30 since there was greater sorption at a given EPC compared to those of the treatments equilibrated at 0 days of incubtion. Thus, the initiation of incubation appeared to be associated with a flourish of microbial activity. The treatments applied at 10 times the field rate had less P sorption at all EPC values on day 30. At 10 mg/l EPC, the P sorption from the check treatment was about 10% greater than that of highest rate treatment.

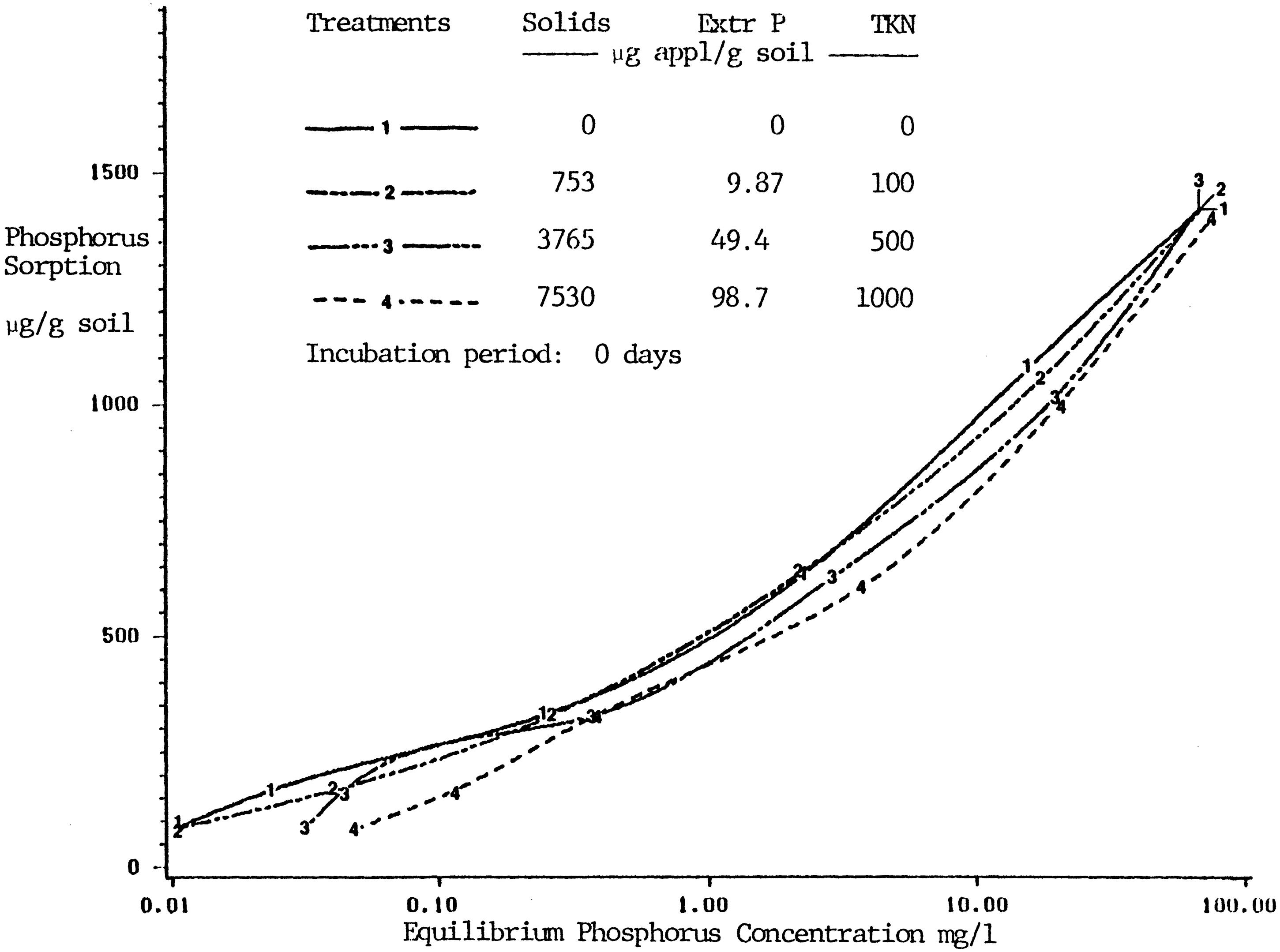


Figure 36. Phosphorus sorption characteristics of biogas effluent and soil mixtures equilibrated immediately following mixing.

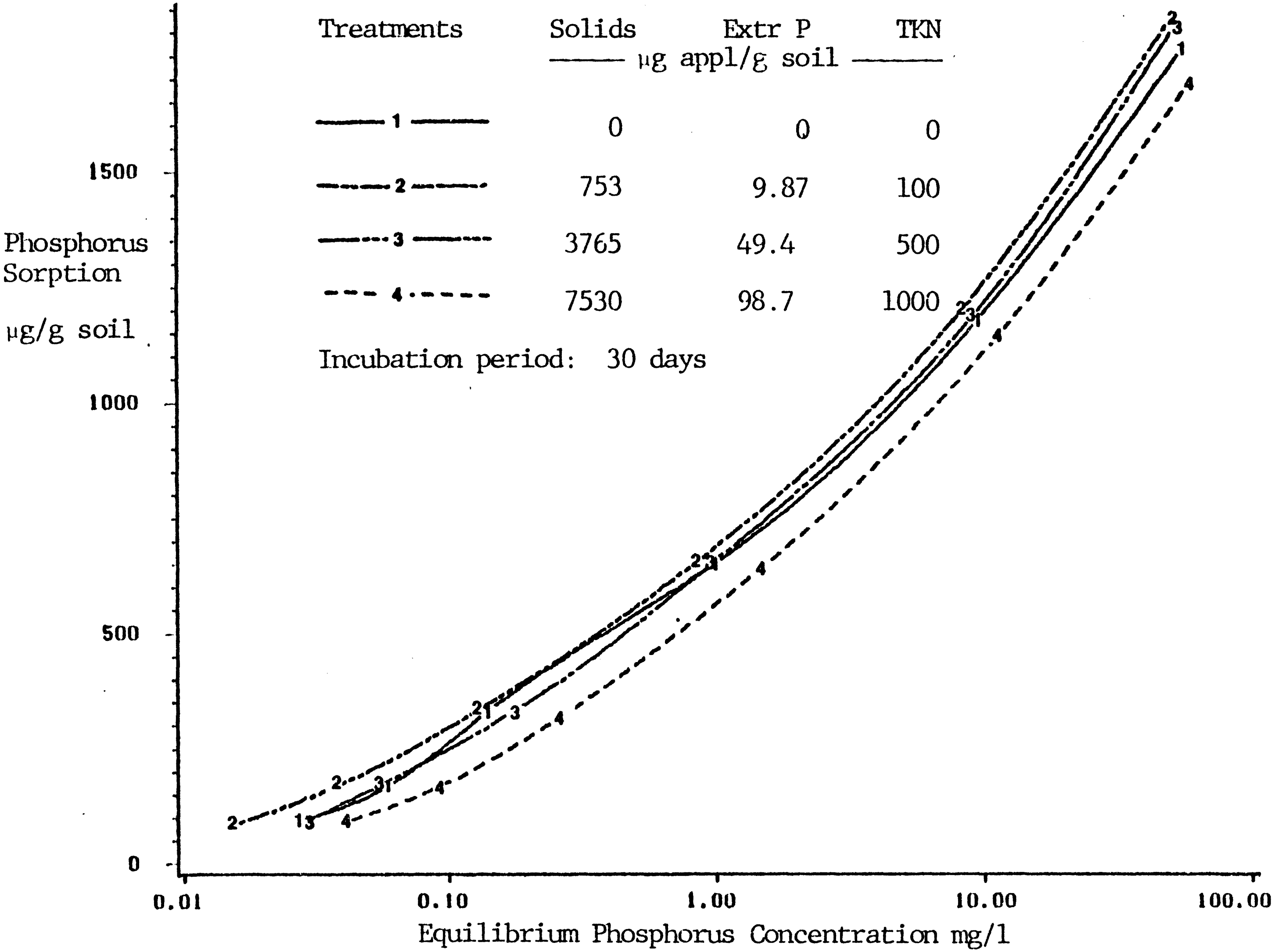


Figure 37. Phosphorus sorption characteristics of biogas effluent and soil mixtures equilibrated after 30 days of incubation.

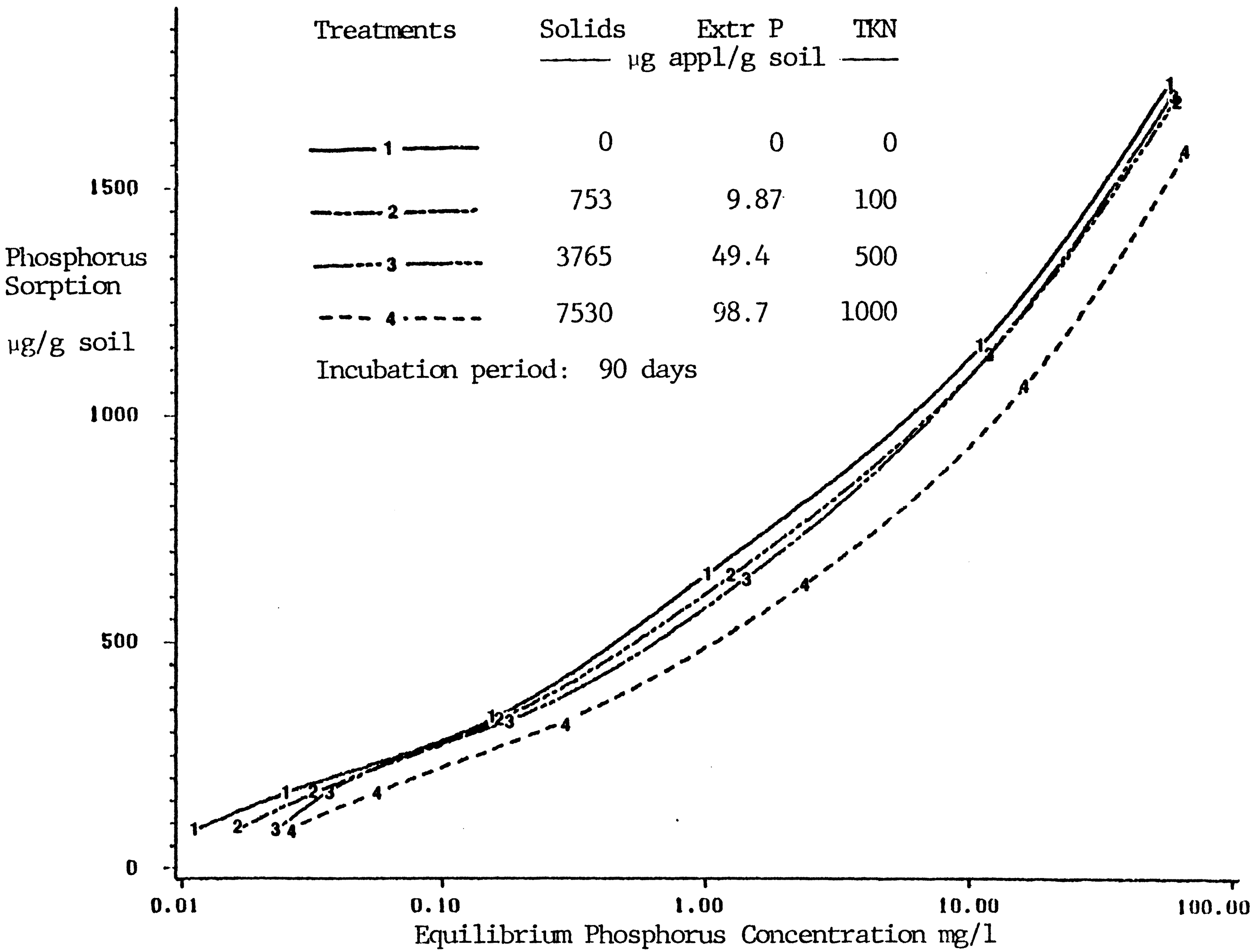


Figure 38. Phosphorus sorption characteristics of biogas effluent and soil mixtures equilibrated after 90 days of incubation.

The relationship between the sorption of added P and the EPC at 90 days after incubation again shows that at low EPC the sorption of added P was similar to the check and treatments with solids applied at 1 and 5 times the field rate. In the range of EPC, values between 1 and 10 mg/l P sorption was slightly decreased by the 2 lower rates of effluent in comparison with the check. Noticeably less sorption of P occurred from the highest rate effluent treatment at all EPC values. At 10 mg/l EPC, the P sorption from the check treatment was about 20% greater than that of highest rate effluent treatment.

Thus, for this soil (Hayesville loam), consistently noticeable declines in P sorption were only observed if effluent was applied at rates 10 times those anticipated for fertilizing crops. The soil, therefore, appears to have a high P sorption capacity since large quantities of organic solids must be added for a sufficient number of P sorption sites to be blocked.

4.5.2 Phosphorus Availability in Field Experiments

The extractable soil P observed from treatments on various dates at site 2 are shown in Table 34. Extractable soil P was not different between treatments. This is similar to the results from the laboratory study since the highest rate of effluent added in the field study corresponds to the lowest rate in the laboratory study. Thus noticeable declines in the P sorption of a Hayesville loam do not occur with the effluent applied at rates for fertilizing crops.

The extractable soil P observed from treatments at various dates at Site 1 are shown in Table 35. The extractable soil P was not statistically different between treatments. However, a clear correspondence between P availability and applications of effluent is evident at dates past day 7. This trend is illustrated in a plot of P availability at 34, 88 and 147 days after application versus the quantity of effluent solids applied with the treatments in Figure 39. In this figure, the increase in P availability appears to be linearly related to effluent solids applied. Thus, for the Groseclose silt loam, effluent applied at fertilizer rates resulted in a noticeable increase in P availability. Since at the onset of the experiment, all treatments were brought to equal levels of extractable P, the higher extractable P observed must be attributed to either the mineralization of applied extractable P (total P - extractable P) or the effect of applied organic matter on reducing P sorption. The P added

Table 34. Soil extractable phosphorus concentration* at selected times after the application of treatments in the field experiment (Site 2).

#	Treatment		Extractable P Concentration[2] $\mu g/g$		
	Material	TKN[1] Appl. (kg/ha)	Day 7	Day 32	Day 81
1	Check	0	6.0	5.8	8.8
2	Urea	146	7.8	6.0	7.8
3	Influent	146	7.0	6.3	9.8
4	Effluent	73	6.5	5.8	8.8
5	Effluent	146	6.5	5.5	6.3
6	Effluent	219	7.8	6.0	10.8

*Average of 4 replications

[1] Total Kjeldahl Nitrogen

[2] No statistical differences are observed between means at the 5% level (F test).

to the check treatment was almost four times greater than the unextractable P added with the highest rate of effluent. The soil extractable P of the check treatment was never enriched more than 8.6% above the value prior to fertilization. However, the high rate effluent treatment (receiving the same level of extractable P as the check) had soil extractable P levels that were enriched about 24% over the value prior to fertilization. Since this additional enrichment cannot be accounted for by the applied unextractable P, the majority of the enrichment perhaps can be attributed to decreases in P sorption by added organic matter.

While laboratory and field results indicated that the P sorption of the Hayesville loam was not decreased by effluent added at fertilizer rates, the field results indicated that the P sorption of the Groseclose silt loam was decreased by effluent added at fertilizer rates.

Table 35. Soil extractable phosphorus concentration[*] at selected times after the application of treatments in the field experiment (Site 1).

	Treatment		Extractable P Concentration[2] µg/g		
#	Material	TKN[1] Appl. (kg/ha)	Day 7	Day 34	Day 88
1	Check	0	38	35.5	36.3
2	Urea	146	42.5	40.8	38.3
3	Influent	146	41.8	43.0	41.8
4	Effluent	73	43.0	41.0	40.0
5	Effluent	146	40.3	43.8	42.5
6	Effluent	219	41.8	44.8	42.5

[*] Average of 4 replications

[1] Total Kjeldahl Nitrogen

[2] No statistical differences are observed between means at the 5% level (F test).

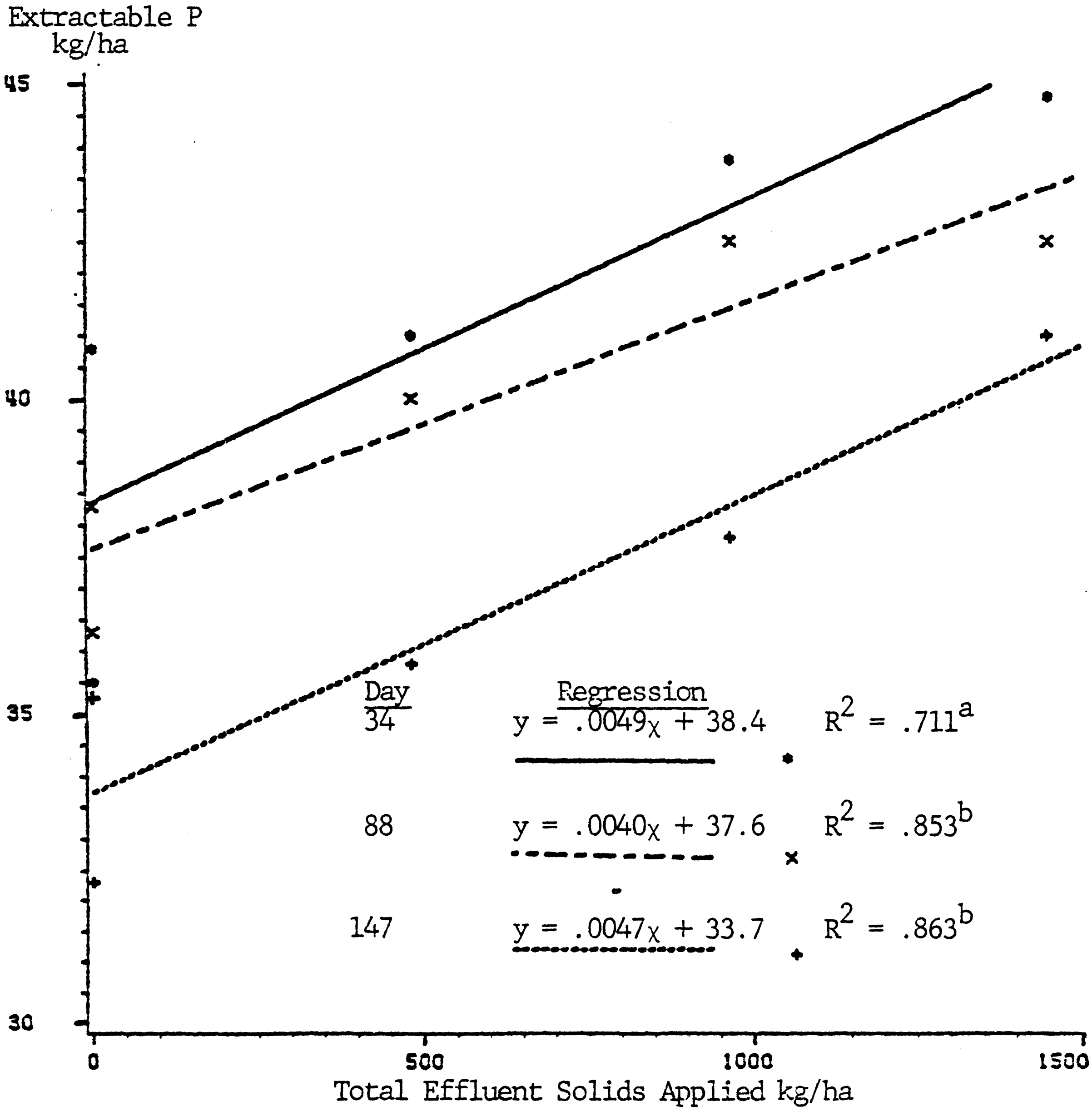


Figure 39. Relationship of effluent solids applied and soil extractable phosphorus at 34, 88 and 147 days after treatment applications. Extractable phosphorus was adjusted to equal levels for all treatments at day 0.

$^{a}P = .1$ $^{b}P = .05$

Chapter I

SUMMARY AND CONCLUSIONS

1.1 NUTRIENT RECOVERIES

1.1.1 Nitrogen

Both pilot and laboratory scale anaerobic digestions of poultry manure indicated N is completely recovered during digestion. Thus biogas can be produced from nitrogenous wastes without reducing the N value of the waste.

The average composition of the total N (TKN) of poultry manure influent used in the pilot scale plug flow digester was 57% NH_4^+N. During the digestion process, the influent N was converted to a digested slurry with a TKN composition of 80% NH_4^+N. Sixty percent of the original organic N placed in the digester was mineralized during the digestion process.

The average composition of the TKN in the influent of the laboratory batch digestion was 35% NH_4^+N. During the digestion process, the influent N was converted to a digested slurry with a TKN composition of 54% NH_4^+N. The percent of the original organic N placed in the digesters that was mineralized during the digestion process averaged 27.4%.

In both studies, a clear trend of organic N mineralization occurred during the digestion process. Thus the anaerobic digestion of poultry manure results in an enrichment of NH_4^+N in the digested slurry compared to the influent material. Organic N mineralization during digestion is reduced drastically if methanogenic activity is inhibited during the digestion process (as was the case in the batch digestion).

The distribution of both NH_4^+N and TKN in slurries recovered after the digestion of poultry manures were greatest in liquid associated fractions. Consequently, only small proportions of the recovered N are present in the sludge. In the pilot scale plug flow digester, only 5% of the NH_4^+N and 9% of the TKN were distributed in the sludge remaining in the digester. In the laboratory scale batch digestion, 19% of the NH_4^+N and 27% of TKN of the effluent were distributed in the sludge obtained after centrifugation.

Since most of the N of digested poultry manure is distributed in the liquid fraction and the N is composed primarily of NH_4^+N, the best use of digested poultry manure is as a N fertilizer. The recovery of the N as animal feed would be difficult due to the low recovery of the NH_4^+N in segregatable solids.

The recovered N in the effluent, however, would be of considerable bulk. The average N concentration of effluent collected from the pilot scale plant was .44% N. This is approximately 70 times less concentrated than conventional NH_4^+N solutions used commercially as fertilizers. This bulk would not be a limitation if the N could be used at the site of the digestion process and at the same time effluent is dispensed. However, if transportation and storage of effluent N were required, then the bulk would present logistical problems. Transportation would be necesary if cropland is not adjacent to the biogas facility. Storage would be necessary in most instances as optimal use of N fertilizer is typically seasonal.

A solution to these logistical problems may be feasible. Since N in the digested poultry manure is primarily in the NH_4^+N from, NH_4^+N can be volatilized (stripped) from the effluent. The resulting NH_3 can be recondensed into a concentrated NH_4^+N solution. Thus, we recommend that future research investigate the feasibility of practically performing such an extraction.

1.1.2 Potassium

Potassium is in a highly water soluble form in most manures. The influent of the pilot scale study had a total K which was 95% extractable. The average influent of the laboratory scale study had a total K which was 88% extractable.

No significant changes in the quantity of influent extractable K occurred during digestion. Thus extractable K placed in a digester should essentially be recovered during anaerobic digestion.

The K which is recovered following the digestion process, is also associated with the liquid fractions of the digested slurry. In the pilot scale study, 96% of the extractable and total K were in the liquid effluent. Consequently, only 4% remained in the settled sludge. In the laboratory scale study, 93% of the extractable K and 84% of the total K were distributed in the supernatant fraction of the digested slurry.

1.1.3 Phosphorus

Phosphorus in poultry manure was approximately 48% extractable and 52% unextractable. The extractable to total P ratio was not affected by the digestion process in either the pilot scale or laboratory scale digestion.

The recovery of extractable and total P during the pilot scale study was 75 and 67%. These low recoveries resulted from unrepresentative recovery of solids in the digested effluent and sludge fractions. In the laboratory scale study where representative samples were more easily obtained, recoveries of extractable and total P were near 100%.

Total P in the pilot scale study and both extractable and total P in the laboratory scale study had distributions indentical to the distributions of solids between liquid and sludge fractions of digested slurries. However, extractable P of the pilot scale study was preferentially concentrated in the solids of the sludge. Thus, P is highly associated with the slurry solids. Recovery of P as a fertilizer in the various fractions of digested slurries will depend on the distribution of solids. For example, in a plug flow digester where a majority of the solids are spilled over with the effluent, a majority of the P will be distributed with the effluent. Systems which have efficient removal of solids, such as clarifiers or centrifuges, will have a majority of the recovered P distributed in the sludge. Such sludges can be dried without P loss. Dried sludges would be sufficiently concentrated with the P to use as a fertilizer. The dried sludges were 3.2 and 2.3% P from the pilot and laboratory scale studies, respectively.

Since total P distributions in both studies were indicative of the solids distributions, we recommend that the total P be used as an indicator of solids recovery in mass balance studies of anaerobic digestions. Total P can be used to indicate if recovered solids were adequately reprsented in effluent samples. If the total P recovery is 100%, then samples can be considered reliable. Recoveries of less than 100% total P indicate that effluent samples did not include all of the solids actually present in the digested slurry.

1.1.4 Calcium and Magnesium

Calcium and Mg recoveries were similar to P in both studies. Extractable and total Ca and Mg in digested slurries were consistently related to the solids distribution between liquid and sludge fractions. In all cases, the Ca and Mg were preferentially concentrated in the solids of the sludge fraction.

The sludge can be dried to produce a concentrated Ca and Mg fertilizer. The dried pilot scale study sludge was 11.4% Ca and .91% Mg. Similarly, the dried sludge of the laboratory scale study was 10.3% Ca.

1.1.5 Micronutrients

Extractable Cu, Mn, Fe and Zn were associated with the solids of the digested slurry. The distributions of extractable Cu and Zn closely paralleled the distributions of the solids between the effluent and sludge of the pilot scale digester. The distributions of extractable Mn and Fe were to a small extent preferentially concentrated with the solids of the sludge. The dried sludge of the pilot scale digester was 305, 1086, 1198 and 590 µg per g solids Cu, Mn, Fe and Zn, respectively.

1.2 NITROGEN MINERALIZATION

Inorganic N recovered from effluent was greater than influent treated soil cores during an initial leaching. This reflects the greater proportion of inorganic N per unit of TKN applied in the effluent.

Higher mineralization observed from effluent per unit of organic N is attributed to the less refractory nature of the effluent organic N in comparison to the influent organic N. The effluent did not contain the sludge solids that settled to the base of the digester. Additionally, the digestion process reduces the size of the solids. Thus the effluent solids have more surface area for microbial degradation.

The slurry-soil mixtures in most cases had values of N mineralization that exceeded the applied organic N. Thus the indigenous soil organic N was being mineralized faster in the treated soils compared to the check. This 'priming' effect is attributed to vitamins, enzymes, microorganisms, nutrients and organic energy supplied with the slurries that enhance the degradation of soil organic N. The 'priming' effect was greatest for the effluent treatment at the lowest rate. This was because the influent and the high rate treatments supplied greater amounts of applied organic N and had slower mineralization rates.

A small lag period was observed for the nitrification process. This period was greatest for the highest rate of applied influent which had the greatest application of organic carbon. Therefore at high rates of poultry manure, a small inhibition of the nitrifying population occurs due to competition from heterotrophic organisms.

1.3 FIELD EXPERIMENTS

1.3.1 Behavior of Applied Nitrogen

The most noticeable difference in the behavior of the N applied with the poultry manure influent, corresonding biogas effluent and urea fertilizer was the large NH_3

volatilization losses that occurred from the effluent at both sites. Consequently, large drops in the soil inorganic N content of the effluent treatments occurred in the week that followed treatment applications.

Ammonia volatilization losses ranged from 53 to 59% of the applied effluent TKN and were not affected by application rate at Site 1. Volatilization losses ranged from 44 to 67% of the applied effluent TKN and were related to application rate at Site 2. The losses were greatest from the lowest rate as the applied effluent was absorbed by surface stubble present at Site 2. The applied $NH_4{}^+N$ absorbed in the stubble did not come into contact with the soil colloids and was thus more accessible to volatilization. Proportionally less effluent was absorbed by the stubble at higher rates of application as the stubble became saturated.

The volatilization losses from the influent were 200 and 62% less than those from the effluent at Sites 1 and 2, respectively. The major reason for the lower loss is because the influent N only contains half the $NH_4{}^+N$ of the effluent. A second reason is that the effluent has a higher pH than the influent. The higher pH increases NH_3 formation from $NH_4{}^+$ and thus results in greater volatilization.

The greatest component of the volatilization loss is suspected to have occured in the several hour period between application and discing. This is because warm sunny days during applications at both sites caused observable drying of applied slurries. In order to avoid large NH_3 losses of land applied effluent, we recommend immediate incorporation into the soil with heavy discing, preferably on overcast days. Additionally, surface applications should be avoided on soils which are overlain with stubble and mulches.

1.3.2 Plant Tissue Analysis

Ear leaf N contents generally corresponded to the soil inorganic N contents during the period of crop growth. However, the influent treatment had slightly higher ear leaf N than that of the mid rate effluent treatments at both sites, although higher soil inorganic N contents were observed for the effluent compared to the influent treatments. Therefore, the turn-over rate of influent organic N is suspected to be rapid.

The P contents of the ear leaves were lowest in treatments that had low soil inorgaic N. This indicates that P uptake is related to the supply of N. Low N is believed to have limited root development.

1.3.3 Yield

The grain yields at both sites were not significantly different among the influent, effluent and urea treatments applied at the same rate of N. However, the silage yield of the urea treatment was significantly (19.9%) higher than that of the corresponding effluent treatment due to large NH_3 volatilization losses from the effluent.

At both sites, the influent treatments had yields that were slightly higher than those of the corresponding effluent treatment despite lower soil inorganic N contents during the growing season. This indicates that the organic N of the influent is mineralized at a high turn-over rate, resulting in greater quantities of N supplied than that which would be expected from soil inorganic N content.

Mitscherlich type growth curves were fitted to yield and ear leaf N data as a function of applied N (NAPPLO), applied N recovered after volatilization losses (NREC7) and the soil inorganic N content following the period (7 days) of greatest volatilization (NSoil7).

The Mitscherlich regressions were highly correlated to NAPPLO, NREC7 and NSoil7 indicating that yield differences were due to variations in available N.

The Mitscherlich regressions of grain yield were more highly correlated to NAPP10, NREC7 and NSoil7 than silage yield or ear leaf N. Yields were most highly correlated to NREC7 because NAPP10 regressions did not account for NH_3 volatilization losses and NSoil7 did not account for inorganic N that was mineralized from applied organic N. High correlations of yield to NREC7 indicate that most of the organic N from the influent and effluent had become plant available during the growing season.

1.4 PHOSPHORUS SORPTION

The conversion of plant available P to insoluble forms (sorption) characteristically occurs in many soils. Research in the past has indicated that large additions of organic matter can reduce P sorption.

The laboratory P sorption study indicated that effluent must be applied at rates in large excess of crop nutrient requirements for noticeable declines by a soil with a high P fixing capacity. Results of the P availability status of field experiments confirmed that declines in P sorption do not occur with effluent applied at fertilizer rates.

The P availability status of a soil with a low P fixing capacity from the field experiments indicated that P sorption was decreased by effluent applied at fertilizer rates.

Chapter II

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Appendix 1. Nitrate N as a percent of soil inorganic N* content at various sampling dates for field grown corn plots (Site 1).

#	Treatment Type	TKN** appl (kg/ha)	Sampling Date (days after application of treatments) 0	7	14	34	54	88	147
1	Check	0	74.5^{a}[1]	78.6^{a}	84.5^{b}	72.2^{c}	54.8^{b}	42.9^{b}	66.3^{b}
2	Urea	146	77.3^{a}	42.6^{c}	89.6^{ab}	93.0^{a}	85.8^{a}	70.0^{a}	88.8^{a}
3	Influent	146	21.5^{b}	68.4^{ab}	90.4^{ab}	88.5^{a}	73.6^{a}	66.2^{a}	82.3^{a}
4	Effluent	73	24.5^{b}	78.6^{a}	92.6^{a}	81.5^{b}	75.7^{a}	55.3^{ab}	74.8^{ab}
5	Effluent	146	14.2^{c}	66.7^{b}	94.6^{a}	91.2^{a}	76.7^{a}	68.0^{a}	87.1^{a}
6	Effluent	219	9.8^{c}	59.2^{b}	95.4^{a}	91.8^{a}	86.3^{a}	67.1^{a}	85.8^{a}

*Average of 4 replications

**TKN = Total Kjeldahl Nitrogen

[1] Means in columns followed by a common letter are not significantly different at the 5% level (Duncan's Multiple Range).

Appendix 2. Nitrate N as a percent of soil inorganic N content[*] at various sampling dates for field grown corn plots (Site 2).

#	Type	TKN[**] appl (kg/ha)	0	7	14	32	52	81	154
	Treatment		Sampling Date (days after application of treatments)						
1	Check	0	69.7^{a}[1]	73.9^{a}	88.8^{b}	79.4^{b}	81.4^{c}	59.4^{b}	79.6^{a}
2	Urea	146	68.1^{a}	82.4^{a}	93.6^{ab}	95.8^{a}	94.2^{a}	73.4^{a}	81.9^{a}
3	Influent	146	33.4^{b}	78.9^{a}	90.8^{ab}	91.3^{a}	87.9^{b}	67.8^{ab}	81.2^{a}
4	Effluent	73	36.3^{b}	78.3^{a}	93.3^{ab}	91.1^{a}	88.7^{b}	63.2^{b}	81.0^{a}
5	Effluent	146	21.6^{b}	80.3^{a}	94.6^{a}	92.4^{a}	90.6^{ab}	67.1^{ab}	75.9^{a}
6	Effluent	219	16.2^{c}	70.1^{a}	95.3^{a}	91.5^{a}	93.9^{a}	73.2^{a}	79.4^{a}

[*] Average of 4 replications

[**] TKN = Total Kjeldhal Nitrogen

[1] Means in columns followed by a common letter are not significantly different at the 5% level (Duncan's Multiple Range).

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THE RECOVERY AND BEHAVIOR OF FERTILIZER NUTRIENTS FROM THE ANAEROBIC DIGESTION OF POULTRY MANURE

by

James Aaron Field

ABSTRACT

Nutrients of animal manures digested anaerobically for biogas production are highly conserved. The objectives of this study are to evaluate changes in the fertilizer value of poultry manure following digestion.

Total kjeldahl N (TKN) was completely recovered during digestion, however, NH_4^+N was 159 and 151% recovered from pilot scale plug flow and laboratory scale digesters. This indicates that added organic N is mineralized. Recovered N and K were associated with liquid fractions and P, Ca, Mg and micronutrients were associated with solids of digested slurries.

The mineralization of organic N from soil applied effluent was 2.3 times greater in comparison to influent over a 33.5 week laboratory incubation period. Higher mineralization is due to segregation of decay resistant solids into the settled sludge and the increase in surface area of suspended solids during digestion.

Significantly higher NH_3N volatilization (3 fold to 62%) of land applied effluent compared to influent is due to increases in pH and NH_4^+N:TKN during digestions. Yields of corn (<u>Zea mays</u> L.) grain at two sites were similar for effluent, influent and urea

treatments receiving identical N rates. However, the silage yield of the urea treatment was significantly 19.9% higher than that of the effluent at site 1. Yields and ear leaf N were highly correlated with applied N discounted for NH_3 N losses. This indicates that organic N of the effluent and influent become plant available during the growing season.