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Volatilization, Plant Uptake And Mineralization Of Nitrogen In Soils Treated With Sewage Sludge

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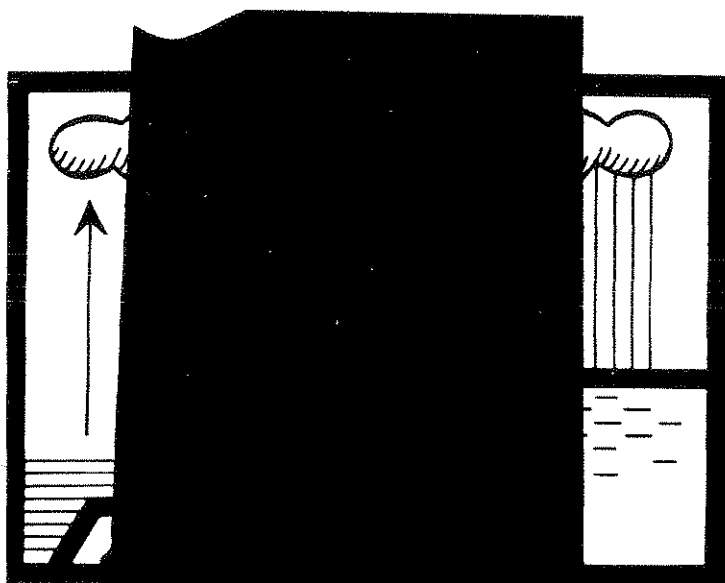
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VOLATILIZATION, PLANT UPTAKE AND MINERALIZATION OF NITROGEN IN SOILS TREATED WITH SEWAGE SLUDGE



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February 1981



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by

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ABSTRACT

The objectives of this project were 1) to quantify volatilization of ammonia after application of sewage sludge to the soil surface; 2) to evaluate nitrogen movement and plant uptake from soils treated with sewage sludge and 3) to determine the amounts of potentially mineralizable N in a wide-range of sewage sludges under laboratory conditions.

Ammonia volatilization from anaerobically-digested municipal sewage sludge (pH 7.3) applied to a Celina silt loam soil was measured under field conditions. Volatile-N losses were estimated by drawing air over the surface of sludge-treated soils enclosed in polyvinyl chloride cylinders (20.32 cm deep by 30.48 cm diameter) and trapping evolved NH_3 in acid. Air samples were taken for 12 minutes every three hours for four days. When the air samples were not being taken, the cylinders were uncovered and allowed to equilibrate with the atmosphere. Results obtained indicate that NH_3 -N loss was dependent upon the method of sludge application, initial soil moisture content and sludge pH. At $\sim -1/3$ bar soil moisture, less than 1% of the applied NH_4^+ -N was volatilized when sludge was incorporated as compared to 5 to 9.5% volatilization following a surface application of sludge. From 17.3 to 18.8% of applied NH_4^+ -N was volatilized from soils that were initially water saturated and treated with a surface application of sludge. Ammonia volatilization from acid sludge (pH 5.5) and $(\text{NH}_4)_2\text{SO}_4$ fertilizer salts was less than 1% of applied NH_4^+ -N.

In a separate study, an anaerobically digested municipal sewage sludge (pH 5.5) was applied to a Celina silt loam soil to evaluate N uptake by sorghum x sudan (*S. vulgare* x sudanese) and to determine N mobility in soils. The sludge was amended with 4 g KBr/liter so Br^- could serve as a tracer for water movement through the soil profile. The experimental treatments resulted in loading rates of 304 kg N/ha and 580 kg Br^- /ha for the 2 cm rate, 608 kg N/ha and 1160 kg Br^- /ha for the 4 cm rate, and 414 kg N/ha and 965 kg Br^- /ha for the $(\text{NH}_4)_2\text{SO}_4$ treatment. The crop was harvested 63 days and 107 days after application of sludge and soil samples were taken after 3, 63, and 107 days. The total yield of sorghum x sudan grown on plots receiving

sewage sludge or $(\text{NH}_4)_2\text{SO}_4$ applications was not statistically different from untreated plots. Recovery of total sludge N in plant tissue ranged from 7% to 27% while recovery of total N ranged from 8% to 33% if N in the soil to a depth of 90 cm and plant tissues was considered. Significant losses of sludge inorganic N occurred within 3 days of application. Since essentially complete recovery of Br^- was obtained and since no NH_3 volatilization was found, rapid immobilization of NH_4^+ may be responsible for the initial decrease in soil inorganic N. Fertilizer NH_4^+ was nearly quantitatively recovered.

The amount of mineralizable N in 24 sewage sludges was proportional to the total organic N content. The anaerobic digestion or composting of primary, raw or waste activated sludges results in reduced organic N levels and thus decreased amounts of potentially mineralizable N. This generalization is not true for sludges treated by a wet-air oxidation process since immobilization rather than mineralization of N occurred during soil incubations. The kinetics of both C and N mineralization were described by a single first-order rate equation. A comparison of N mineralization for a static and leaching incubation procedure indicated that the static method generally yielded more accurate values. This was likely caused by the removal of soluble organic N during leaching of sludge-soil mixtures with 0.01M CaCl_2 . The static incubation procedure is preferred because it is easier to set-up, requires less glassware, and involves only periodic subsampling of a soil-sludge mixture rather than leaching soil-sludge samples under a constant vacuum. Current guidelines used to calculate the amounts of sewage sludge applied to agricultural crops assume that 20 to 25% of the organic N is mineralized during the first year after application. The results of this study demonstrate the need to use a different N mineralization percentages for various sludge types. Realizing that a limited number of sludges were studied and that the incubations were conducted in the laboratory under optimum conditions, the following N mineralization percentages should be used to calculate the appropriate sludge application rate for agronomic crops: raw and primary sludges, 25%; waste activated sludges, 40%; anaerobically digested sludges, 15%; and composted sludges, 8%.

Introduction

Application of sewage sludge on agricultural and non-agricultural lands is being viewed as a viable disposal alternative by municipal treatment facilities. Application to soil not only is one of the most economical methods of sewage sludge disposal but it also can supplement the nutrient requirements of the crop grown on amended soils (Hinesly and Sosewitz, 1969; Stewart et al., 1975; Kelling et al., 1977a). However, some inherent problems exist with use of sludges on cropland, including the accumulation in soils of Cd and other metals, contamination of groundwater with NO_3^- , depression of yields due to soluble salts, and addition of potential human or animal pathogens. Thus, design of a sound land application system requires a knowledge of sludge-soil-plant interactions. From a practical standpoint, land application cannot be considered a panacea for disposal of all sewage sludge produced annually, especially in large cities with limited accessibility to cropland.

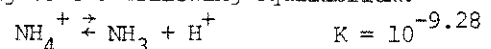
Two criteria limit annual application rates of sewage sludge to land: 1) heavy metals, particularly Cd and; 2) nitrogen. With continuous annual applications, heavy metals (Pb, Zn, Cu, Ni, Cd) added with the sludge will accumulate in soils. To maintain soil productivity, sludge application should cease once a critical amount of metals have been applied. The validity of the total metal loading approach requires further study. Irrespective of the approach, the soil pH should be maintained near neutrality to minimize any potential problems from phytotoxicity resulting from metal addition to soil.

The N content of sewage sludge applied to cropland and the N required by the crop will govern application rates for many sludges. Anaerobically digested wastewater sludges contain from 1% to 17% total N with approximately one-half of the N present in the NH_4^+ form (Somers et al.,

1976; Somers, 1977). The plant available N content (inorganic N plus a percentage of the organic N) of many sludges is used as the basis for calculating annual application rates for sludges on cropland. The NH_4^+ -N added in the sludge and the NH_4^+ released through decomposition of organic N can result in three potential problems. Excessive NO_3^- in the soil could be transferred to crops used for livestock feed and ultimately cause toxicity in livestock. Secondly, NO_3^- can leach into groundwater and cause a potential hazard to humans or animals consuming the NO_3^- laden water. Lastly, a problem resulting from NO_3^- leaching is eutrophication of lakes and streams. Consequently the fate of N applied to soil in sewage sludge is of vital importance if environmentally sound disposal practices for wastewater sludges on cropland are to be implemented.

I. Evaluation of NH_3 Volatilization Under Field Conditions

A significant mechanism for N loss from soils receiving sludge is NH_3 volatilization. The NH_4^+ and NH_3 forms of N exist in soil or soil-sludge according to the following equilibrium:



The distribution of NH_4^+ and NH_3 is controlled by pH and the partial pressure of NH_3 in the atmosphere. Any meteorological, soil and/or sludge condition that increases pH or decreases the partial pressure of NH_3 in the air are conducive to increased NH_4^+ losses through NH_3 volatilization. The pH of the soil-sludge system directly controls the ratio NH_4^+ to NH_3 and hence the degree of volatilization. For each mole of NH_3 lost to the atmosphere, a H^+ remains in solution resulting in a pH decrease. It follows that the buffering capacity of a soil-sludge system will influence loss since the pH will drop most rapidly in a poorly buffered system. This has been confirmed experimentally using soil-sand- NH_4^+ solution mixtures (Avnimelech and Laher, 1977).

It was shown that pH is of prime importance only when the buffering capacity of the soil is high, or when the concentration of NH_4^+ in the soil solution is low. Wastewater treatment such as dewatering (e.g. centrifuge, filter beds) and heat or air drying of sludge can affect the amounts of NH_4^+ applied to soils. The NH_4^+ -N content of a sludge slurry was decreased by 50% after six days of vigorous aeration (Molina et al., 1972). Upon air-drying of four municipal sewage sludges, 30% to 60% of the total N was lost and it appeared that a large proportion of the NH_4^+ -N was volatilized as the liquid phase evaporated (Ryan and Keeney, 1975).

Several laboratory experiments have been conducted to evaluate NH_3 loss from soils treated with sewage sludge. Eleven to 60% of NH_4^+ -N applied to clay loams, sandy loams, and sands can be lost by NH_3 volatilization (Ryan and Keeney, 1975). This data suggested that NH_3 volatilization losses decreased as the clay content of the soil increased. However, losses were not directly related to evaporation of soil water. Other researchers have noted a correlation between NH_3 loss and water evaporation (Wahhab et al., 1957; Ernst and Massey, 1960). King (1973) concluded NH_3 losses were significantly higher for surface applications of sewage sludge than for incorporated applications; however, the losses under both application systems were less than 1% of the total N applied. Following surface application of synthetic sewage sludge, as much as 26% of the added NH_4^+ -N was lost as NH_3 during 49 days of laboratory incubation (Terry et al., 1978). These studies showed that losses increased from 26% to 35% of added NH_4^+ -N when initial soil moisture content increased from 60% to 120% of water holding capacity. Incorporation reduced volatile-N losses to less than 10% of added NH_4^+ -N. Addition of a liquid sludge to a sandy clay loam soil with a Coastal bermudagrass (*Cynodon dactylon* L. Pers) cover reduced NH_3 losses from 36% to 20% as compared to surface applications to bare soils (King and Morris, 1974). A 4 to 6% loss and a 13% loss of NH_4^+ -N were measured when 228 and 456 kg NH_4^+ -N/ha, respectively were added to an alluvial sandy loam

soil (Premi and Cornfield, 1969).

Various approaches have been used to quantify NH_3 loss under field conditions including the determination of inorganic N in soil samples, measuring NH_3 flux in air over treated plots and, trapping NH_3 evolved from a fixed volume of soil. Thirty percent losses of NH_4^+ -N were reported from surface applied sewage sludge spread on a loam (pH 7.1) soil based on N determinations in soil samples taken one week after application (Stewart et al., 1975). Beauchamp et al. (1978) measured NH_3 flux by taking air samples at various heights above a soil surface treated with a liquid sewage sludge. Five days after application from 50% to 60% of the NH_4^+ -N was volatilized. During experiments with $(\text{NH}_4)_2\text{SO}_4$ fertilizer spread on a calcareous soil, Kissel et al. (1977) measured NH_3 volatilization in the field by trapping air drawn over microplots sealed for twelve minutes every three hours and found approximately 35% of the applied N was volatilized.

Sludge application rates should provide total plant available nitrogen equivalent to the N Fertilizer requirement of the crop grown, although some experience in applying 1 1/2 to 2 times the crop's N fertilizer requirement has not resulted in the development of groundwater problems (EPA, 1977). Volatilization of NH_3 from surface applied sludge should be taken into account when calculating NH_4^+ -N application rates as discussed above, as it has been shown that 50% or more of the NH_4^+ -N may be lost when sludge is surface applied and may be reduced to less than 10% if the sewage sludge is incorporated immediately following application (EPA, 1977; Terry et al., 1978). In view of the limited available data, the objectives of this study were to determine NH_3 volatilization under field conditions as a function of sludge pH, soil moisture, application rate and method of application by using a modified microplot technique originally developed by Kissel et al. (1977).

Materials and Methods

The system used to measure NH_3 volatilization from liquid sewage sludge applied in the field was patterned after the chamber system designed by Kissel et al. (1977). In essence the system

involved treating soil contained in polyvinyl chloride (PVC) cylinders with sludge, sealing the cylinders for short time intervals, flowing air through the sealed cylinders and trapping the NH_3 volatilized from the treated soil in acid. A schematic of the experimental system is shown in figure 1.1.

The PVC cylinders (20 cm long, 39 cm diameter) were fitted with five plexiglass intake parts (0.5 cm ID) and one exit part (1.0 cm ID) placed 0.5 cm from the top of the cylinder. After soil preparation by rototilling to a depth of 15 cm, the cylinders (lower edge was beveled) were driven into the soil until the intake and exit parts were flush with soil surface. After the soil within the cylinder was treated with sludge or fertilizer, NH_3 loss measurements were conducted as follows: an opaque plexiglass lid was placed over the cylinder and sealed with Permagum sealant. A vacuum pump (204 liters/min) was used to draw air through the NH_3 scrubber to remove background NH_3 , over the treated soil, and through an acid trap to collect NH_3 volatilized. Volatilization measurements were made for 12 minutes every three hours for four days after $(\text{NH}_4)_2\text{SO}_4$ or sludge application. Following the twelve minute measurement period, the cylinders were uncovered and allowed to equilibrate with the atmosphere.

The NH_3 scrubber and trap were 250 ml French Square bottles fitted with rubber stoppers and fritted glass dispersion tubes and contained either 50 mls of 1.0 M H_2SO_4 (scrubber) or 0.5 M H_2SO_4 (trap). The chambers, traps and scrubbers were connected with appropriate rubber tubing. A manifold was used so NH_3 loss measurements were performed simultaneously on four cylinders. The flow rate of air through the system was controlled for each cylinder by placing a valve in the tubing between the NH_3 trap and the manifold.

After each sampling period, the H_2SO_4 in the trap was quantitatively transferred to a 100 ml volumetric flask with deionized water and diluted to volume. The samples were transferred to 150 ml plastic bottles and refrigerated until analyzed for NH_4^+-N by steam distillation (Bremner, 1965).

The rate of NH_3 volatilization was calculated

by extrapolating the quantity of NH_3 trapped during 12 minute sampling period over the three or six hour period between samples. The first sample was taken three hours after sludge application. It was assumed that the rate of NH_3 loss was constant over the time period between the samples.

The soil used for this study was a Celina silt loam (Aquic Hapludalf, fine, mixed, mesic); pH 6.9; CEC, 9.2 meq/100g; total organic C, 1.12%; total N, 1020 mg/kg: Soil, sludge and meteorological characteristics during the May, June, and July experiments are shown in Table 1.1.

Anaerobically digested sewage sludge was obtained from West Lafayette and Frankfort, Indiana, municipal treatment plants. The source and properties of the sludges used in the May, June and July experiments are shown in Table 1.1. Total N was determined on wet sludge samples by semi-micro Kjeldahl digestion and steam distillation (Nelson and Sommers, 1972). Inorganic N was extracted from sludges with 2 M KCl followed by steam distillation for NH_4^+ and $\text{NO}_2^- + \text{NO}_3^-$ analysis (Bremner, 1965), pH was determined by direct measurement with a glass electrode.

Experiments were conducted to evaluate the following parameters; sludge pH, application rate, application method and initial soil moisture. For surface application, 2 cm and 4 cm (1500 mls and 3000 mls) of liquid sludge were applied to duplicate cylinders for each treatment. Depending on the percent solids of the sludge used, these rates correspond to 5 to 9 and 10 to 18 metric tons of solids/ha for the 2 cm and 4 cm application rates, respectively. To simulate injection of liquid sewage sludge, the upper 20 cm of the soil was removed from the cylinders, sludge was applied to the soil within the cylinders and then the soil was replaced. Application rates for the incorporated treatments were the same as the surface treatments. The effect of soil water was studied by saturating the soil around and within the cylinder for 24 hours prior to a surface application of sludge. The excess water remaining on the soil was removed immediately prior to surface applications of 2 cm and 4 cm of sludge. Two grams of granular

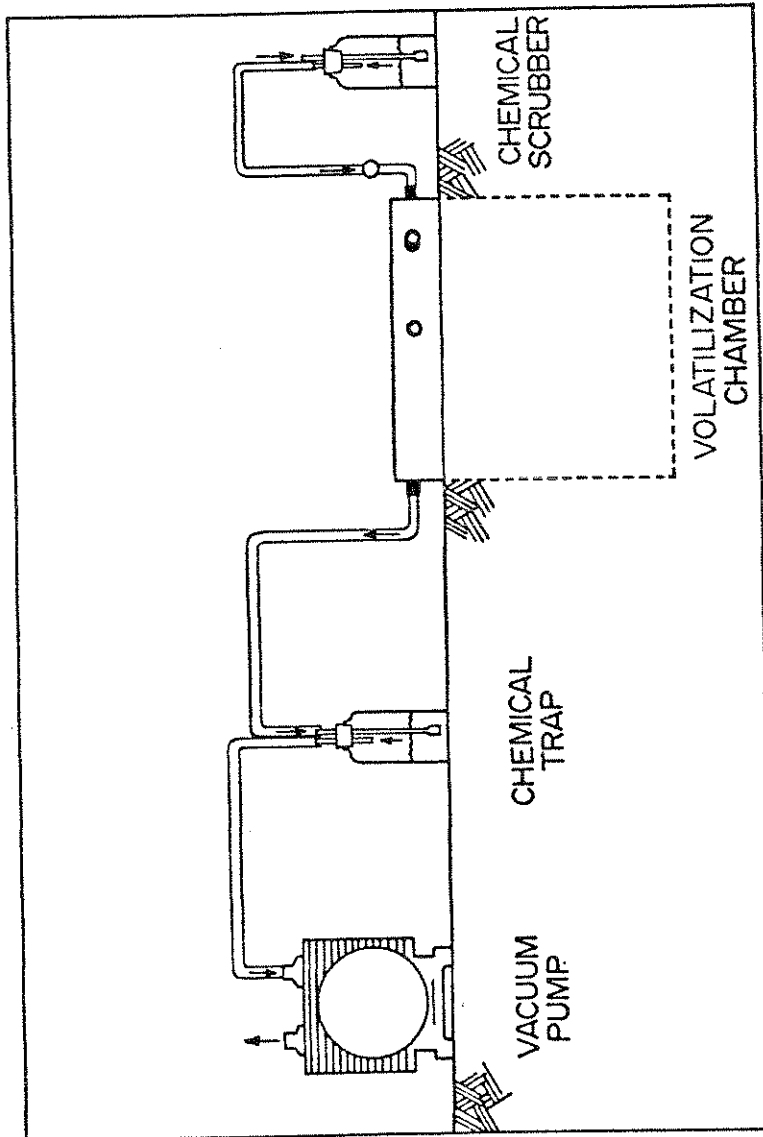


Figure 1.1. Basic Design of the Ammonia Collection System (Side View)

Table 1.1. Meteorological and soil characteristics for May, June and July, 1977 NH₃ volatilization experiment.

Parameter	May 18-20	June 14-17	July 8-11
Meteorological			
Air Temp, °C			
minimum	17	16	18
maximum	31	26	33
Relative Humidity, %	40	54	39
Pan Evaporation, cm/day	0.74	0.61	0.82
Soil			
Bulk Density, g/cc	1.0	0.9	1.1
pH	6.9	6.9	6.9
Sludge			
Source	W. Lafayette	Frankfort	Frankfort
Solids, %*	3.0	2.6	4.4
pH	5.5	7.3	7.1
Total N, %†	4.0	5.8	3.8
NH ₄ ⁺ -N, %†	0.9	1.3	0.9
(NO ₂ ⁻ + NO ₃ ⁻)-N, %†	<0.1	<0.1	<0.1

* wet-weight basis

† oven-dry basis

(NH₄)₂SO₄ was surface applied at rates corresponding to 414 kg NH₄⁺-N/ha. Duplicate microplots were left untreated to quantify ambient NH₃ volatilization. At the initiation of each experiment, soil samples were obtained between the cylinders for determination of bulk density and soil moisture. Bulk density and soil water were determined on a known volume of soil by drying at 110 °C for 24 hours and weighing.

The recovery of NH₄⁺ and (NO₂⁻+NO₃⁻) applied was evaluated by analysis of soil samples taken after the July trials. Five, one inch diameter soil cores were removed from each cylinder at depths of 0-7.5 and 7.5-15 cm, composited and, then frozen until subjected to N analysis. The soil samples were thawed and analyzed for NH₄⁺ and (NO₂⁻+NO₃⁻)-N by extraction with 2 M KCL and steam

distillation (Bremner, 1965).

Comments

Preliminary tests indicated that two traps were not needed to collect all the NH₃ volatilized during a 12 minute sampling period. When four cylinders were run simultaneously the vacuum pump (204 liters/min) enabled establishment of a flow rate of 10 exchange volumes per minute (15 liters/minute). Previous experiments with a similar system showed that 10 exchange volumes/minute or greater resulted in collecting 95% of the maximum NH₃ lost from calcareous soils treated with NH₄⁺-N fertilizer (Kissel et al., 1977). This agreed with earlier work by Fenn and Kissel (1973) who noted that NH₃ loss reached a maximum at 15 exchange volumes/minute. Results during the May experiment indicated that the NH₃ scrubber was

effective in removing ambient NH_3 in the air since negligible NH_3 was trapped from cylinders containing untreated soil. The results from this experiment are therefore reported on an uncorrected basis.

Results and Discussion

Evaluation of NH_3 Volatilization Methodology

Ammonia volatilization from liquid sewage sludge applied to soils was measured by periodically passing NH_3 -free air over sludge treated microplots enclosed in PVC cylinders and trapping the evolved NH_3 in acid. The principal advantage of this experimental system was that measurement of NH_3 loss could be obtained under actual field conditions and yet utilize a system requiring a minimum area. The major disadvantages of employing sealed cylinder systems for determining NH_3 evolution are (1) dissolution of NH_3 in water condensed on the surface of the apparatus, (2) variations in air and soil temperature during measurement (McGarity and Rajaratnam, 1973) and (3) alterations of the NH_3 flux resulting from sealing the cylinders. The design of the cylinder system used in this experiment and the method of sampling employed caused no visible condensation of water vapor within the cylinders. Even though soil and air temperatures were not controlled during the experiment, it appeared that the use of opaque plexiglass lids and the minimum time of sealing the cylinders (12 minutes/3 hours) should reduce fluctuations in air temperature within the system. It was assumed that N losses due to denitrification and immobilization were minimal because of the low levels of NO_3^- in both the soil and sludge at the beginning of each experiment. In experiments using animal manure, the efficiency of the system has been evaluated by placing manure in cylinders lined with plastic (i.e. the manure and soil do not interact) followed by measurement of NH_3 loss using the approach described (Hoff, 1978). In addition NH_3 loss was directly monitored by analyzing NH_4^+ -N on samples of manure. These experiments indicated that the NH_4^+ -N measured from the sealed cylinders was less than that obtained by analysis of the manure directly. The rate of NH_3 volatilization was decreased by sealing the cylinders, probably because of a lower air flow

across the soil surface. The cylinder system employed in the current experiment likely underestimates the actual amount of NH_3 lost from sludge amended soils. Perhaps the efficiency was lowered because volatile N compounds were released by the manure and not trapped by the H_2SO_4 . The results from this experiment are reported as measured realizing that the percent NH_3 losses may be greater by 50 to 100% if the system were continuously exposed to the atmosphere.

A problem commonly encountered in field experiments is replication of data obtained, both within a particular trial as well as between trials executed at different times during the year. Figure 1.2 shows the rate of NH_3 volatilization plotted against time for soils treated with a 2 cm surface application of alkaline (pH 7.3) sewage sludge. Data are presented for duplicate cylinders from the June experiment. The rates of NH_3 loss were similar for the duplicate cylinders indicating that NH_3 loss measurements are reproducible during a particular trial.

Ammonia loss exhibited diurnal fluctuations with higher losses occurring during the afternoon and lower losses of NH_3 evidenced at night. Similar diurnal fluctuations in NH_3 loss from surface applications of liquid sewage sludge were noted by Beauchamp et al. (1978). Volatilization measurements were terminated when the quantities of NH_3 volatilized from treated microplots were constant and approximately equal to the quantities of NH_3 volatilized from untreated cylinders.

To evaluate variability between experiments, losses of NH_4^+ -N are shown as a function of time after application for experiments conducted in June and July (Figure 1.3). The total NH_4^+ -N lost was slightly different between experiments, ranging from 5% to 8% of the NH_4^+ -N added for the June and July trials, respectively. In view of the low percent loss, the above values are acceptable. However, amounts of NH_3 loss are lower than those previously estimated for NH_3 losses from surface applied sewage sludge (Ryan and Kenney, 1975; Stewart et al., 1975; King, 1976; EPA, 1977; Beauchamp et al., 1978). Even if the percentage losses were increased by a factor

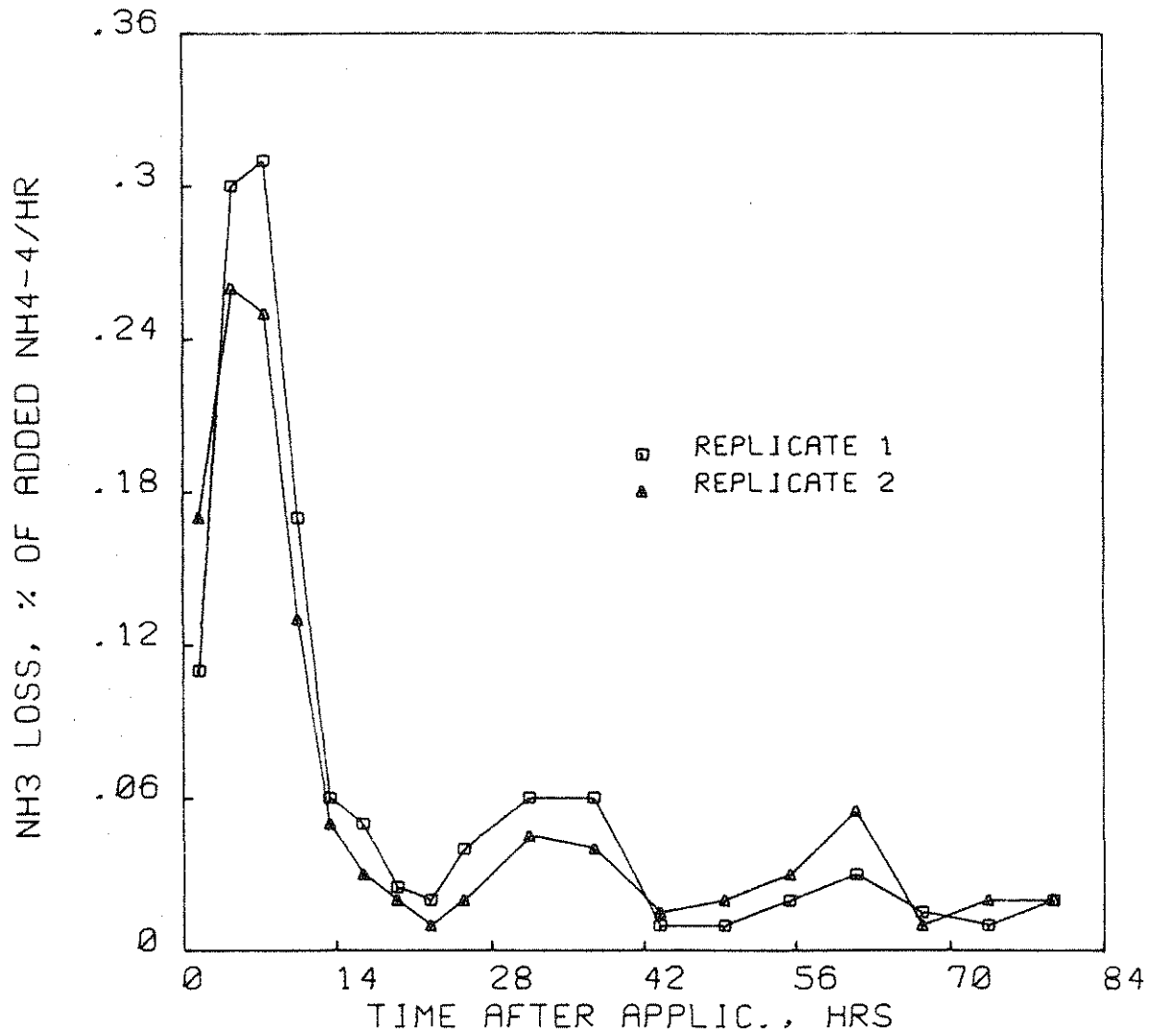


Figure 1.2. Rates of NH_3 loss from two cylinders treated with 2 cm of alkaline (pH 7.3) liquid sewage sludge, surface applied.

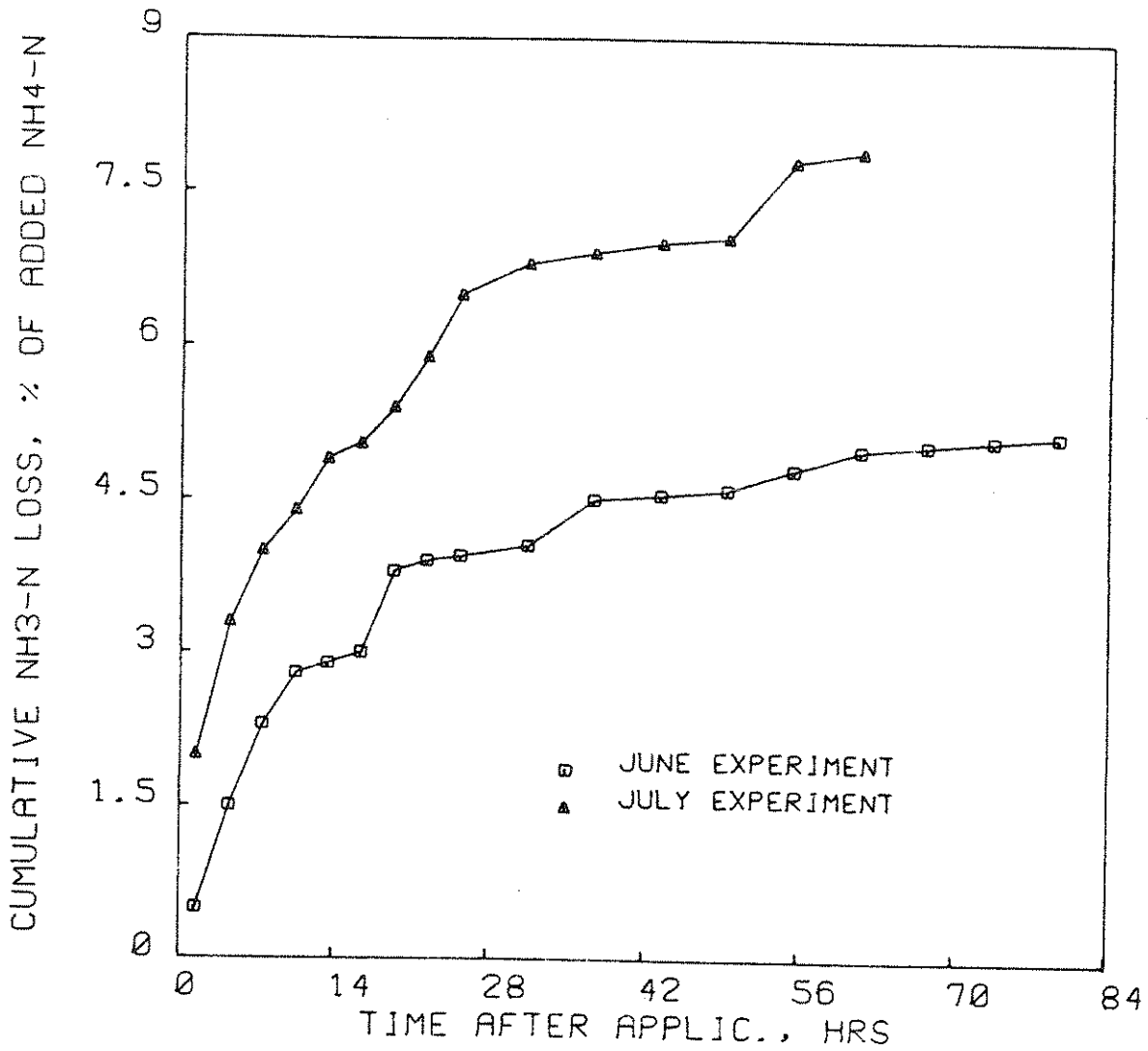


Figure 1.3. Cumulative loss of NH₄⁺-N due to volatilization from application of 2 cm of alkaline (pH 7.3) sewage sludge during the June and July, 1977 experiments.

of two, less than 16% of the NH_4^+ -N applied was volatilized. In general the data suggests that using sealed cylinders enables the measurement of NH_3 loss under field conditions in a reproducible manner. It should be noted that undetectable amounts of NH_3 were volatilized from untreated and $(\text{NH}_4)_2\text{SO}_4$ treated soils.

Factors Influencing NH_3 Volatilization

Initial Sludge pH

The effect of sludge pH on NH_3 losses was determined by applying sludges possessing initial pH's of 5.5 and 7.3. The pH of the sludge had a significant effect on the percentage of NH_4^+ -N lost as NH_3 (Table 1.2). For surface applied sludges, NH_3 losses for a pH 5.5 sludge were approximately 1% of added NH_4^+ -N while 5% to 9% losses of NH_4^+ -N were obtained for a pH 7.3 sludge. As shown by the equilibria for NH_4^+ and NH_3 , the high concentration of H^+ in the acid sludge would favor NH_4^+ in the liquid phase of the sludge and consequently losses of NH_3 were diminished from the acid sludge. Therefore, the sludge pH is an important parameter when NH_3 volatilization is considered for recommending rates for application of liquid sewage sludge on agricultural soils.

Sludge Application Rate

The rates of sewage sludge applied were selected to represent typical rates for fertilizing crops with N. The 2 and 4 cm of liquid sludge applied 5 and 18 metric tons of dry solids/ha, respectively. The quantities of NH_4^+ -N volatilized from 4 cm of surface-applied sewage sludge were nearly twice the NH_4^+ -N lost from 2 cm applications (Table 1.2). Results obtained in laboratory studies also indicate that doubling the rate of sewage sludge applied will increase NH_3 losses (Premi and Cornfield, 1969). On soils of pH 6.8, NH_4^+ -N loss due to volatilization increased from 4-6% to 13% of added NH_4^+ -N when 57 and 457 kg NH_4^+ -N/ha were added, respectively. Doubling the amount of sewage sludge added to the surface of soils increased the percentage of added NH_4^+ -N lost as NH_3 from 18% to 35% of added NH_4^+ -N (Ryan and Keeney, 1975). The authors concluded that NH_4^+ -N will continue to volatilize as long as the sludge liquid remained above the soil surface and was

not in contact with the cation exchange complex of the soil. Another possible explanation for increased NH_3 loss as sewage sludge rate increases is that the pH buffering capacity of the soil has a minimal effect on NH_3 volatilization until infiltration of the sludge liquid into the soil occurs (Avnimelech and Laher, 1977).

Method of Sludge Application

The method of application has a significant effect on NH_3 losses. Incorporation of the sewage sludge reduced volatilization losses of NH_4^+ -N from 7 to 9% to less than 1% when compared to a surface application of the alkaline sludge (Table 1.2). Others have noted similar decreases of NH_3 loss when liquid sewage sludges are incorporated into the soil (King, 1973; Terry et al., 1978). By incorporation of the sludge, NH_4^+ -N could interact with the cation exchange complex of the soil and thereby reduce the quantity of NH_4^+ -N in the soil solution subject to volatilization.

Initial Soil Moisture

The initial soil moisture content has a significant effect on volatilization from surface applied liquid sewage sludge. Previously saturating the soil before application of alkaline sewage sludge increased losses of NH_3 from 8-9% to approximately 18% added NH_4^+ -N (Table 1.2). By decreasing the rate of infiltration, either through high initial soil moisture, increased application rates or higher bulk density appear to result in increased NH_3 losses. As noted by other studies (Ryan and Keeney, 1975), increasing the length of time the aqueous NH_4^+ solution is exposed to drying conditions on the soil surface appears to increase losses of NH_4^+ -N from surface applied alkaline sludge. Essentially all the added NH_4^+ -N in excess of the exchange capacity of the soil could be lost by NH_3 volatilization if infiltration is slowed or impeded (Ryan and Keeney, 1975).

Recovery of Inorganic N

An alternative approach to evaluate NH_3 losses is soil analysis following infiltration of the sludge. After the July volatilization trial,

Table 1.2. Cumulative NH_3 loss from sewage sludge and $(\text{NH}_4)_2\text{SO}_4$ applied.

Application		Sludge pH*	Soil Moisture	NH_4^+-N Applied	Cumulative NH_3 Volatilized		
Method	Rate				kg/ha	%	
Surface	2	5.5a	10.2	59	0.8	1.3	
		7.3b	12.3	74	3.9	5.2	
		7.3c	9.5	84	6.6	7.8	
		7.3c	Sat ⁺	84	15	18.8	
	4	5.5a	10.2	118	1.1	0.9	
		7.3b	12.3	148	8.9	6.0	
		7.3c	9.5	168	16.5	9.4	
		7.3c	Sat ⁺	168	29.1	17.3	
	Incorporated	2	5.5a	10.2	59	0.02	<1
			7.3b	12.3	74	0.09	<1
		4	5.5a	10.2	118	0	0
			7.3b	12.3	148	0.15	<1
$(\text{NH}_4)_2\text{SO}_4$	-	--	10.2	441	0.5	<1	

*Letter denotes experiment conducted in May (a), June (b), and July (c).

Solids loading rates for 2 cm and 4 cm were:

(a) 6 and 12 mt/ha (dry)

(b) 5 and 10 mt/ha (dry)

(c) 9 and 18 mt/ha (dry)

⁺Soil saturated prior to sludge application

soil samples were taken from all cylinders and analyzed for NH_4^+ and $(\text{NO}_2^- + \text{NO}_3^-)-\text{N}$. The percentage of inorganic-N recovered from the soil immediately following measurement of NH_3 volatilization for four days ranged from 48% to 164% of the added inorganic N (Table 1.3). The inconsistent percentages of NH_4^+-N recovered at the 2 cm rate may be a result of inherent soil sampling and analytical errors. At the 4 cm rate of application, the percentage recovery approached 100%. The difficulties in using soil N analysis to calculate N balance sheets have been found in previous studies (Beauchamp et al., 1978). These authors only recovered 81% of the NH_4^+-N in soil samples collected four hours after surface application of sludge.

Calculation of Applied NH_4^+-N

Lauer et al. (1976) suggested that NH_3 flux over a field applied with manure decreased with time in an exponential manner. It has also been reported that NH_3 flux above soils treated with liquid sewage sludge follows a similar pattern, i.e. $d\text{NH}_4/\text{dt} = \text{NH}_{40}K$ where t = time and K = a rate constant (Beauchamp et al., 1978).

The following equation was developed to depict this relationship:

$$\ln(\text{NH}_3-\text{N})_t = \ln(\text{NH}_3-\text{N})_0 - Kt$$

where NH_3-N_t = quantity of NH_4^+-N (kg/ha) remaining at time t (hours); $(\text{NH}_3-\text{N})_0$ = quantity of NH_4^+-N (kg/ha) at $t = 0$; and K = rate constant (hour^{-1}). The data obtained from the cylinder studies was evaluated by a regression of $\ln(\text{NH}_3-\text{N})_t$ vs. time. The results of these calculations are summarized

Table 1.3. Recovery of inorganic N in soil after July NH₃ volatilization experiment.

Application Rate	Soil Moisture	Rep.	NH ₄ ⁺ -N Applied	Soil N _i *	NH ₃ Vol. [†]	NH ₄ ⁺ -N Accounted For
cm	%		kg/ha	----% of NH ₄ ⁺ -N applied-----		
2	9.5	1	84	155.8	7.8	164
		2	84	147.2	7.8	155
		Avg.	84	151.5	7.8	160
	Sat. [‡]	1	84	42.9	18.8	62
		2	84	29.5	18.8	48
		Avg.	84	36.2	18.8	55
4	9.5	1	168	88.4	9.4	98
		2	168	97.2	9.4	107
		Avg.	168	92.8	9.4	102
	Sat. [‡]	1	168	86.7	17.3	104
		2	168	57.1	17.3	74
		Avg.	168	71.9	17.3	89

*NH₄⁺ + NO₂⁻ + NO₃⁻; N_i in sludge treated soils was corrected for N_i present in control soils. The NH₄⁺ and NO₂⁻ + NO₃⁻ in non-sludge amended soil was 6.8 µg NH₄⁺-N/g and 8.1 µg NO₂⁻ + NO₃⁻-N/g. Calculations of KgN/ha were based on bulk density measurements obtained at termination of experiment.

[†]Volatilized (measured).

[‡] Soil saturated before application of sludge.

in Table 1.4. The highly significant regression coefficients (R) obtained indicate that the rate of NH₃ volatilized. Generally, for all treatments tested, the calculated NH₄⁺-N applied is well related to the actual NH₄⁺-N applied.

Volatilization of NH₃ from liquid sewage sludge applied to soils varies considerably depending upon sludge pH, method of application and initial soil moisture. Sludges with pH of 5.5 lost approximately 1% of NH₄⁺-N when surface applied as compared to alkaline sludges (pH 7.3) which lost 5% to 9% of added inorganic N. Incorporation of sludges reduced NH₃ volatilization losses 80-90% when compared to a surface application. Ammonium sulfate treated and untreated soils had undetectable levels of NH₃ volatilization. Application of alkaline sludge to previously saturated soil increased the time required for infiltration of sludge liquid and the time soluble NH₄⁺-N was subject to loss, and resulted

in 18% losses of applied NH₄⁺-N by NH₃ volatilization.

The experimental system of measuring NH₃ losses provides an inexpensive and simple way of quantifying NH₃ losses under field conditions, and could be used as an aid in quantifying NH₃ losses from NH₄⁺-N compounds applied to soils of various initial moisture contents, textures, temperatures, and buffering and cation exchange capacities. Increasing the flow rate in the system is recommended to approximate more closely the wind-speed occurring naturally and thus the rates of NH₃ volatilization.

II. Determination of Nitrogen Movement, Plant Uptake and Transformation.

The application of anaerobically digested municipal sewage sludge to agricultural land is being viewed not only as an economical method for cities to dispose of the end products of wastewater treatment but also as a potential source of

Table 1.4. Calculated and measured $\text{NH}_4^+ \text{-N}$ at the beginning of the study based on the linear regression equation: $\ln(\text{NH}_4^+ \text{-N})_t = \ln(\text{NH}_4^+ \text{-N})_0 - Kt$.

Application		Soil Moisture Content †	Sludge pH	Slope (K)	Correlation Coefficient	$\text{NH}_4^+ \text{-N}$ Applied	
Method	Rate					Actual	Calculated
	cm	%		$\times 10^4$	R^{\S}	-----kg/ha-----	
Surface	2	10.2	5.5	19.6	0.97	77	77
		12.3	7.3	4.8	0.89	77	75
		9.5	7.3	8.6	0.95	84	81
		Sat [†]	7.3	22.0	0.93	84	77
	4	10.2	5.5	8.6	0.89	154	154
		12.3	7.3	6.0	0.94	148	145
		9.5	7.3	11.0	0.94	168	161
		Sat [†]	7.3	25.0	0.98	168	161
Incorporated	2	10.2	5.5	0.43	0.78	77	74
		9.5	7.3	0.04	0.78	74	74
	4	10.2	5.5	0.16	0.84	154	148
		9.5	7.3	0.02	0.70	148	148

* $(\text{NH}_4^+ \text{-N})_t$ = quantity of $\text{NH}_4^+ \text{-N}$ (kg/ha) remaining at time t (hours).

$(\text{NH}_4^+ \text{-N})_0$ = quantity of $\text{NH}_4^+ \text{-N}$ at time = 0.

K = rate constant (hour^{-1}).

[†]Soil saturated before sludge applied.

‡Oven-dry weight basis.

§All R values were significant at 0.01 significance level.

nutrients for crops. However, the use of sewage sludges on soils will not significantly impact fertilizer consumption since the amount of sludge generated presently will fertilize <2% of the agricultural lands (Sommers, 1977).

Nitrogen added to soils in sewage sludge may be lost through several mechanisms including denitrification and leaching of NO_3^- , and volatilization of NH_3 . The plant available N content of the sludge being applied and the N needs of the crop grown can be considered to determine the optimum rate of sludge application on soils in order to minimize NO_3^- leaching. Anaerobically digested sewage sludges contain from 1% to 17% total N (dry-weight basis) with 2% to 38% of the total N in the NH_4^+ form (Sommers, 1977).

The N available for plant uptake includes the NH_4^+ and NO_3^- present in the sludge plus a fraction of the organic N which is mineralized during the growing season. Current estimates regarding organic N mineralization range from 20% to 25% for the first year after sludge application (Keeney et al., 1976; Sommers and Nelson, 1976). A decay series for N mineralization of 30-15-7.5-3.25-2.0% of the remaining organic-N mineralized/year has been recently proposed (Sommers and Nelson, 1978).

Several studies have been conducted to determine the response of crops to nutrients applied to soils in sewage sludges. Responses similar to those obtained with conventional fertilizer materials have been found for the

following crops after application of sewage sludge: grass clover swards, rye (Secale cereale L.) and barley (Hordeum vulgare L.) (Coker, 1966a, 1966b, 1966c); Coastal bermudagrass (Cynodon dactylon L. Pers) (King and Morris, 1972b); rye, corn (Zea mays L.) and sorghum x sudan (Kelling et al., 1977a, 1977b); snap beans (Phaseolus vulgaris L. var Tendergreen) (Dowdy et al., 1978); corn and bromegrass (Bromus inermis) (Soon et al., 1978). Liquid sewage sludge applied annually to Coastal bermudagrass and rye resulted in recovery of 9% and 24% of applied N, respectively, while 63% of a 724 kg N/ha fertilizer application was assimilated by the crops (King and Morris, 1972b). Coker (1966a) applied sludge at rates of 70 and 132 kg N/ha and observed 24% to 46% recovery of N by clover. In this study, N recovery ranged from 28% to 32% for a 70 kg N/ha fertilizer application. Recovery of applied N by corn following surface application of sludge at rates of 400 to 1600 kg N/ha average 3% and 12%, respectively (Stewart et al., 1975). Multiple croppings of rye, sorghum x sudan and corn over a three year period on soils treated with sewage sludge indicated that 7% to 46% of the applied N was recovered in the crops (Kelling et al., 1977a, 1977b). Previous studies have indicated that N in sewage sludge is readily available to plants. In most studies, the recovery of sewage sludge N by crops ranges from 5% to 25% of the N applied. These low N recoveries may be explained, in part, by the inability of soil analysis to quantify sludge organic N remaining in the soil, but it could also be due to extensive losses through NH_3 volatilization, NO_3^- leaching, and denitrification. Of these, NH_3 volatilization is a significant N loss mechanism with surface application methods whereas it is minimized when sludge is incorporated immediately after application. The potential for NO_3^- leaching exists whenever plant available N applied to soils in sewage sludge exceeds the N requirement of the crop being grown. Several studies have shown increased NO_3^- in soils at depths below the root zone (Braids et al., 1970; Hinesly et al., 1972; King, 1973; Kelling et al., 1977a, 1977b). Most studies measuring NO_3^- movement have

used NO_3^- determinations on soil or soil solution samples collected from the soil profile. A complicating factor in evaluating NO_3^- movement is the natural background of NO_3^- leaching from soils. It is advantageous to use an approach where movement of material from the sludge can be differentiated from the naturally occurring ions. An ion of similar mobility as NO_3^- , such as Cl^- or Br^- has been used for such purposes. Several studies have recently shown the reliability of using Br^- as a "tracer" for the relative mobility NO_3^- in soils (Smith and Davis, 1974; Onken et al., 1975, 1977). The objective of this study was to evaluate the effect of surface and incorporated application of sewage sludge to soils on N uptake by sorghum x sudan and the mobility of NO_3^- in the soil.

Materials and Methods

Materials

The soil used during this investigation was a Celina silt loam (Aquic Hapludalf, fine, mixed, mesic); pH 6.9; CEC 9.2 meq/100 g; organic C, 1.12%; total n, 1020 mg/kg; Bray $\text{P}_1 - \text{P}$, 44 mg/kg; and exchangeable K, 111 mg/kg, respectively. The research plots were located at the Purdue University Agronomy Farm, West Lafayette, Indiana.

An anaerobically digested sewage sludge was obtained from the sewage treatment plant in West Lafayette, Indiana. The chemical characteristics of the sludge were determined as described previously (Somers et al., 1976) and are listed in Table 2.1.

Experimental Design

The basic experimental design enabled the evaluation of N uptake by sorghum x sudan from surface and incorporated applications of liquid sewage sludge and the determination of N mobility in soils. A completely randomized block design (four replicates/treatment) was employed with the following treatments:

1. Surface applied sludge - 2 cm and 4 cm rates
2. Incorporated sludge - 2 cm and 4 cm rates
3. Surface applied sludge - 2 cm and 4 cm each applied with N-Serve 24E at 5 kg/ha

Table 2.1. Composition of liquid digested sewage sludge from the West Lafayette Sewage Treatment Plant.

Parameter	Range	Mean
-----g*-----		
Solids	0.9-6.5	3.8
Ash	24-45	28
Total N	3.6-5.6	4.2
NH ₄ ⁺ -N	0.6-2.6	1.1
(NO ₂ ⁻ + NO ₃ ⁻)-N	<0.01	<0.01
P	0.08-0.8	0.75
Br ⁻	ND†	ND†

* Basis except for solids (wet-weight).

† Not detectable. All data expressed on an oven-dry solids.

4. (NH₄)₂SO₄ - 414 kg N/ha
5. Control - no sludge or fertilizer applied.

The plot area was plowed and disced prior to sludge application. For plots receiving a surface application of liquid sludge, 6 cm high earthen dikes were constructed around the plots. Twenty cm deep furrows were excavated in the plots simulating knife injection of sludge. Before application, the sludge was amended with 4 g KBr/liter so Br⁻ could serve as a tracer for water movement through the soil profile. The sludge was pumped onto 2.7m x 3.4m plots at 190 and 380 liters of liquid sludge/plot for the 2 cm and 4 cm application rates, respectively, on May 17-18, 1977. Each plot received the entire amount of sludge in one application. For the incorporated treatment, the trenches were immediately covered with soil to prevent drying of the sewage sludge on the soil surface. The average loading rates were 304 kg N/ha and 580 kg Br⁻/ha for 2 cm and 608 kg N/ha and 1150 kg Br⁻/ha for the 4 cm application rate (Table 2.2). Granular (NH₄)₂SO₄ fertilizer was applied at 414 kg N/ha. After three days, all the plots were disced and sorghum-sudan (*S. vulgare* x *sudanese*, Var. FFR #74) was planted. The crop was harvested from a 1.8m x 3.4m area of each plot on July 20th (63 days after application) and September 7th (107 days), 1977.

After weighing the entire harvest, a subsample was taken for moisture determination (dried at 105°C) and the remainder dried in a forced air oven at 60°C and ground to 40 mesh in a Wiley Mill. Soil samples were taken 3, 62 and 107 days after application of sludge. Five, 2.5 cm diameter core samples were taken at depths of 0-15 cm, 15-30 cm, 30-60 cm, and 60-90 cm from each plot, composited by depth and air-dried. Soils were ground to pass a 10 mesh sieve before analysis.

Analytical Procedures

The soil and sewage sludge samples were analyzed for NH₄⁺-N and (NO₂⁻ + NO₃⁻) - N by 2 M KCl extraction and steam distillation (Bremner, 1965). Total N was determined by semi-micro Kjeldahl digestion and steam distillation on plant (Nelson and Sommers, 1973) and sludge (Nelson and Sommers, 1972) samples. Total P concentrations in the sludge were measured colorimetrically after digestion with HClO₄ and HNO₃ (Sommers and Nelson, 1972). Heavy metal concentrations were determined by atomic absorption after HNO₃ - HClO₄ digestion.

All Br⁻ activity measurements were performed with an Orion 94-35A Br⁻ electrode and an Orion 90-02-00 double junction reference electrode attached to an Orion Model 701A pH meter (Onken et al., 1975). The concentration of Br⁻ in soil

Table 2.2. Total loading rate of various components for the 2 cm and 4 cm sludge application rates.*

Component Added	Sludge Application Rate ⁺	
	2m	4m
Dry solids, mt/ha	2-12 (7)	4-24 (19)
Total N, kg/ha	106-484 (304)	212-968 (608)
NH ₄ ⁺ -N, kg/ha	46-80 (58)	92-160 (116)
(NO ₂ ⁻ + NO ₃ ⁻) - N, kg/ha	0.2-0.6 (0.4)	0.4-1.2 (0.8)
Organic N, kg/ha	60-407 (241)	120-814 (482)
P, kg/ha	13-47 (44)	26-94 (88)
Br ⁻ , kg/ha	339-773 (580)	678-1546 (1160)

* Oven dry weight basis.

+ The range is shown with the mean in parenthesis. The fertilizer treatment was 414 kg N/ha ((NH₄)₂SO₄) and 965 kg Br/ha (KBr).

samples was determined in water extracts (50 ml water:25 g soil) after shaking samples for 24 hours. The ionic strength of the extract was adjusted by adding 1 ml of 0.5 M NaNO₃. Bromide concentrations in sewage sludge were also determined with a Br⁻ electrode. However, an internal standard method was necessitated by the presence of interferences extracted from the sludge. Five mls of liquid sludge were diluted to 100 mls with 0.5 M NaNO₃ and shaken for 24 hours on a wrist-action shaker. After the NaNO₃ extraction, the Br⁻ concentration was measured in (1) 25 mls of extract + 10 mls of 0.5 M NaNO₃ and (2) 25 mls of extract + 10 mls of 80 µg Br⁻/ml in 0.5 M NaNO₃. The Br⁻ concentration in each sample was corrected for the Br⁻ level. Bromide in plant samples were determined in a similar fashion. Bromide was extracted from plant tissue with 0.5 M NaNO₃ (solution:solids, 25 mls 0.5 M NaNO₃:1 g plant material) added to the plant material at 80°C (i.e. a procedure similar to that used for NO₃⁻ extraction from plants). After shaking for 24 hours on a wrist action shaker, the samples were centrifuged at 2150 x g for 10 minutes. An internal standard method similar to that described above was used for the plant samples. The Br⁻ concentration was determined in 25 mls of extract

diluted to 35 mls with 10 mls of 0.5 M NaNO₃ and in 25 mls of extract treated with 10 mls of 400 µg Br⁻/ml in 0.5 M NaNO₃. The appropriate correction equations were calculated for each sample.

Laboratory Experiment

A bulk sample of Celina silt loam soil from the area used for the field experiment was collected to assess short-term losses of N from soils treated with sewage sludge in a laboratory study. The soil was air-dried and ground to pass a 10 mesh sieve.

The sludge was obtained from the West Lafayette wastewater treatment plant. The chemical and physical characteristics of the sludge used are listed in Table 2.1.

The lab incubation study involved treating soils contained in a short glass column with sludge or (NH₄)₂SO₄, incubating the column in an aeration system to allow collection of CO₂ and NH₃ evolved and analyzing the soil sample to assess changes in total N and inorganic N.

Fifty grams of soil adjusted to 8.7% moisture content (oven-dry weight basis) were placed in 10 cm long by 2.2 cm (ID) diameter glass tubes and sealed at one end with a rubber stopper. The soil

was packed to a bulk density of 1.2 g/cm^3 . The soil columns were treated with 2 cm (7.5 mls/column) and 4 cm (15 mls/column) of liquid sludge or $(\text{NH}_4)_2\text{SO}_4$ (20 mg). The amount of total N applied was equivalent to 225 and 450 kg N/ha for the 2 cm and 4 cm application rates, respectively, or 107 kg N/ha as $(\text{NH}_4)_2\text{SO}_4$ to simulate a fertilizer treatment.

After treatment of the columns with sewage sludge or $(\text{NH}_4)_2\text{SO}_4$, the columns were placed in a closed aeration apparatus similar to that used by Terry et al. (1978) and incubated in the dark at 21°C . Scrubbers containing $1 \text{ M H}_2\text{SO}_4$ and 1 M KOH solutions were used to remove NH_3 and CO_2 , respectively, from the air prior to passage through the apparatus. The air flow rate was 50 ml/minute through the system. The NH_3 and CO_2 evolved from the system were trapped in 25 mls of $0.5 \text{ M H}_2\text{SO}_4$ and 25 mls of 0.5 M KOH , respectively. The H_2SO_4 in the NH_3 trap was diluted to 50 mls with deionized water and an aliquot removed for NH_3 determination by steam distillation (Bremner, 1965). The CO_2 evolved was analyzed by treating the KOH with 5 mls of 1.5 M BaCl_2 and titrating residual alkalinity with standard HCl using phenolphthalein as an indicator.

Duplicate treated and untreated columns were removed from the incubation apparatus one hour and 1, 3 and 7 days after initiation of the experiment and subjected to soil analysis. The soil plus sludge or $(\text{NH}_4)_2\text{SO}_4$ was removed from the glass column, placed in a 1000 ml Erlenmeyer flask, and extracted with 500 mls of 2 M KCl . Following centrifugation at $2500 \times g$ for 10 minutes, NH_4^+ and $(\text{NO}_2^- + \text{NO}_3^-)\text{-N}$ in the KCl extract were determined by steam distillation (Bremner, 1965). The soil was washed with deionized water and then dried in a forced air oven at 60°C . After grinding the soil to pass a 40 mesh sieve, the oven-dried soil was analyzed for total N by semi-micro Kjeldahl digestion (Nelson and Sommers, 1972). All data were obtained from analysis of duplicate samples.

Results and Discussion

Yield of Sorghum - Sudan

The effect of sewage sludge and $(\text{NH}_4)_2\text{SO}_4$ application on the yield of sorghum - sudan is shown in Table 2.4. Crop yields from treated plots were greater from Harvest 2 than from Harvest 1; however, there was no statistical difference between treatments for a particular harvest. Higher amounts of precipitation and increased density of the grass stand between Harvest 1 and Harvest 2 were probable causes of the increased yields observed from Harvest 2 (Table 2.3).

Differences in total yields of the sorghum - sudan were statistically insignificant for all plots including the control, sewage sludge or $(\text{NH}_4)_2\text{SO}_4$ treatments. Although N uptake was greater from treated plots as compared to control plots, the sorghum - sudan did not respond to N-P-K or other nutrients added with the sewage sludge, the N added in $(\text{NH}_4)_2\text{SO}_4$ or the K added as KBr. The similar N uptake (Figure 2.1) and yields (Figure 2.2) observed for all treatments may have been a result of high native soil fertility in the plot area. Plant yields were measured on plots treated with N-Serve, a nitrification inhibitor, to see if inhibition of nitrification would decrease N losses through leaching and denitrification. No statistical differences was found between yields obtained with surface applied sludge in the absence and presence of N-Serve. Typically, the greatest yield responses are found with N-Serve when N is applied in the fall. In this study, sludge was applied in the spring and thus, even if losses of N occurred during the growing season, they were not of a magnitude which depressed plant yields. In addition, it is likely that a large percentage of the N-Serve was lost through volatilization. The minimal plant response to N applied as $(\text{NH}_4)_2\text{SO}_4$ or sludge suggests that a relatively large pool of labile organic N may have been present in the soil and became available for plant uptake during the growing season.

For all sludge treated plots, the N content in plant tissues was increased over that found for control plots (Table 2.4). The %N in plants

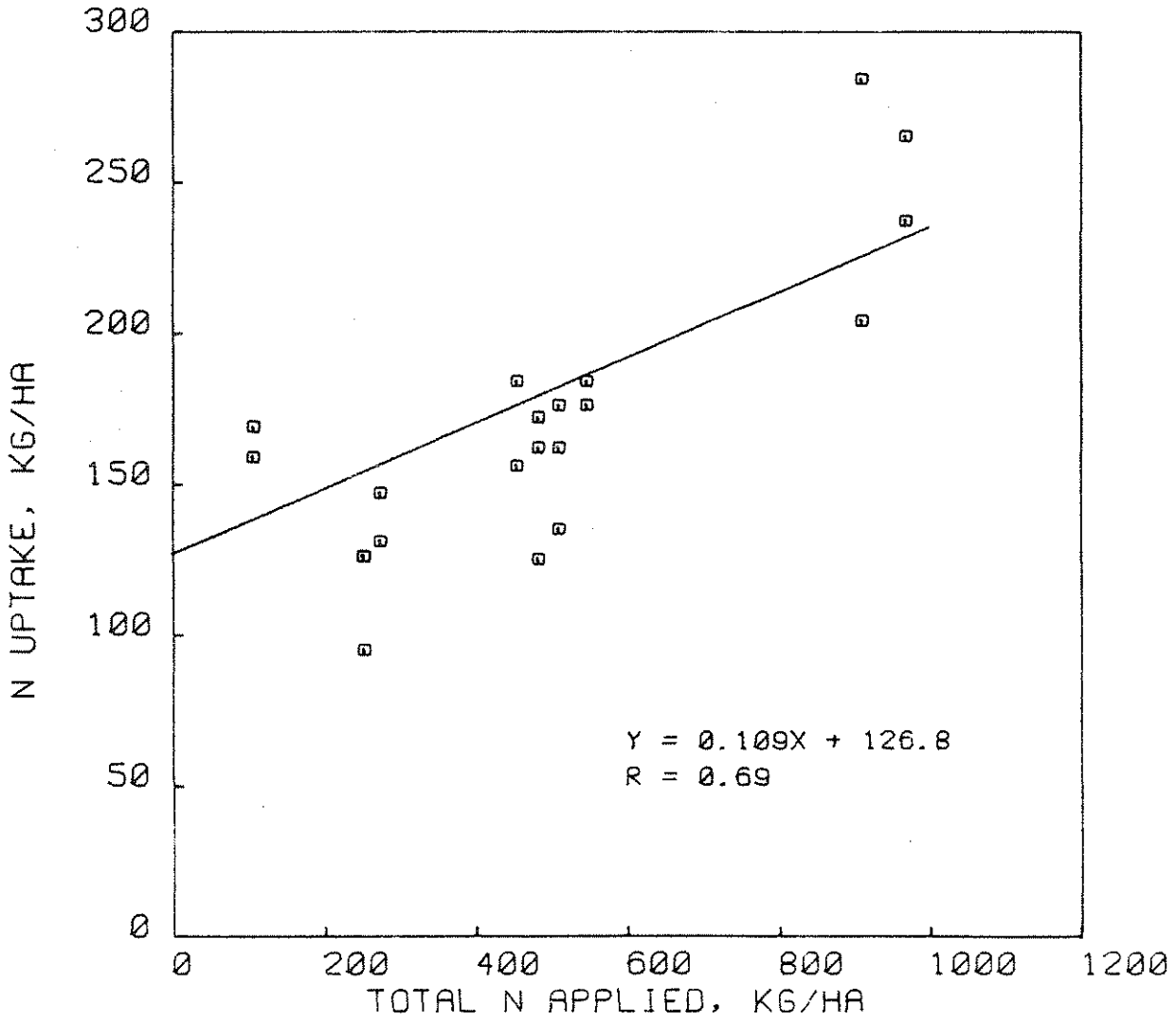


Figure 2.1. The relationship between total N applied in sewage sludge and cumulative uptake of N by sorghum-sudan.

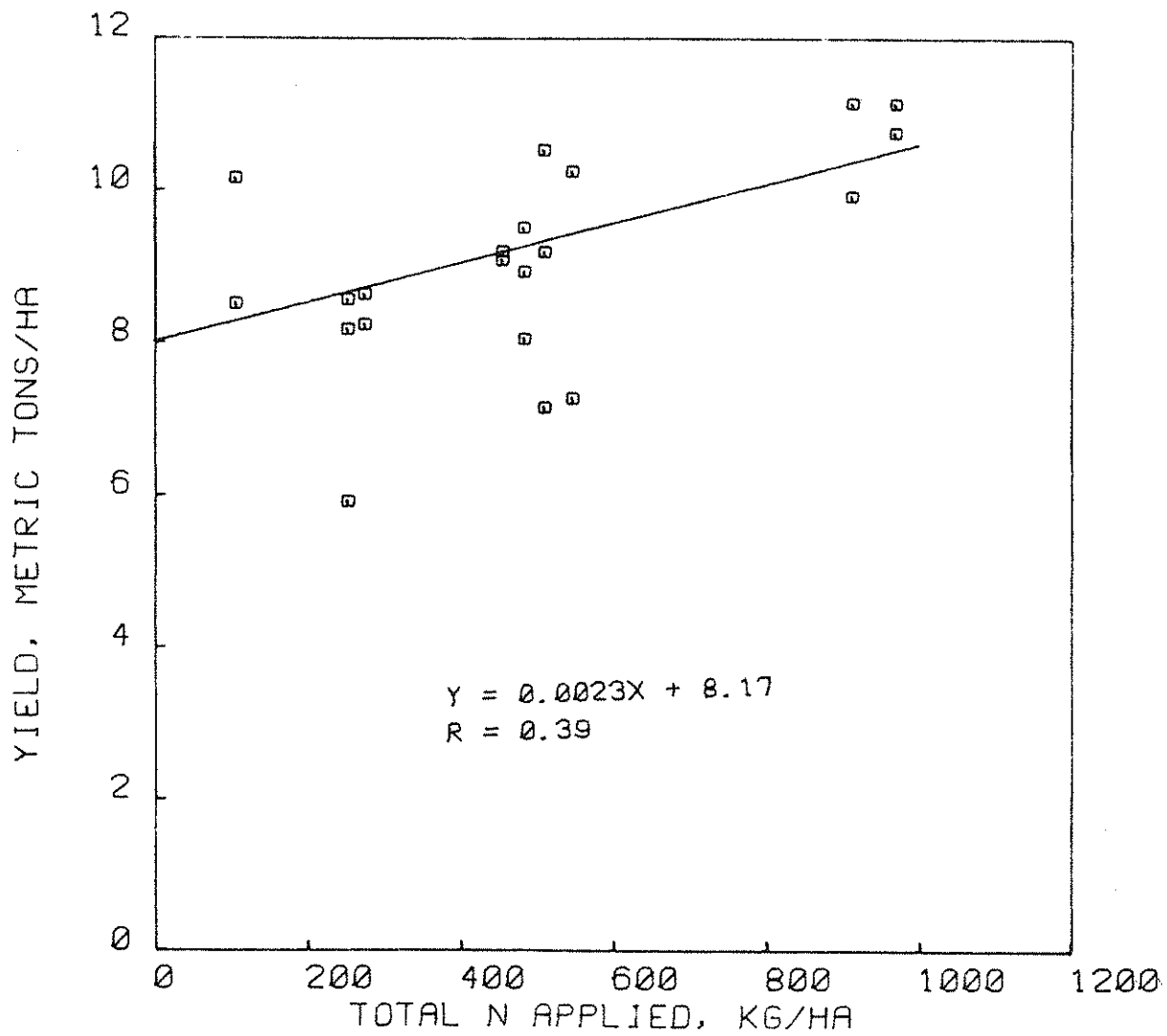


Figure 2.2. The relationship between total N applied in sewage sludge and cumulative yield of sorghum-sudan.

Table 2.3. Cumulative precipitation and pan evaporation at 63 and 107 days after sludge or fertilizer treatment.*

Days After Application	Precipitation		Pan Evaporation
	cm		
3	1.7		2.1
63	10.3		44
107	39.0		110

* Data obtained from the meteorological station, Purdue University Agronomy Farm, West Lafayette.

Table 2.4. Yield and composition of sorghum x sudan harvested 63 and 107 days after treatment with sewage sludge or $(\text{NH}_4)_2\text{SO}_4$.

Treatment	1st Harvest			2nd Harvest			Total		
	Yield	N	Br	Yield	N	Br	Yield	N-uptake	Br uptake
	kg/ha	-----%		kg/ha	-----%		-----kg/ha-----		
Control	4710a*	1.3a	0.2a	3755a	1.1a	0.2a	8465a	103	17
$(\text{NH}_4)_2\text{SO}_4$	3233a	2.4a	2.8b	5903b	2.0c	0.7b	9136a	196	132
Surface applied sludge									
- 2 cm	4613a	1.9b	4.7c	5493b	1.7bc	1.3c	10106a	181	288
- 4 cm	4395a	2.2bc	2.8bc	5355b	1.7bc	1.1bc	9750a	188	182
Incorporated sludge									
- 2 cm	3325a	1.9b	3.5bc	4638b	1.4b	0.9bc	7963a	138	158
- 4 cm	3710a	2.4c	2.7b	6010b	1.9c	0.9bc	9720a	203	154
Surface applied sludge									
2 cm + N-Serve	3388a	2.1bc	3.0bc	5498b	1.5b	0.9bc	8886a	154	151
4 cm + N-Serve	3877a	2.4c	3.5bc	5023b	1.5b	1.0bc	8900a	168	186

* Values in same column followed by same letter are not significantly different at the 0.05 level by Duncan's Multiple Range Test.

decreased from Harvest 1 to Harvest 2 and may be a result of lower soil N availability, leaching losses of N caused by increased precipitation between the two harvests, or increased dry matter production to lower the N content. Percent N in the sorghum - sudan harvested after 63 days from all sludge treated plots was significantly higher than the

control plots (Table 2.4). The crop grown on the $(\text{NH}_4)_2\text{SO}_4$ and 4 cm sludge treated plots (surface, incorporated, and surface + N-Serve) averaged 2.4%N for Harvest 1; however for Harvest 2 the N level in the sorghum - sudan had decreased to 1.7%N. The 2 cm sludge application rates (surface, incorporated, surface + N-Serve) averaged 2% and

1.5%N in shoots for harvests 1 and 2, respectively.

Nitrogen uptake in the above ground plant tissue ranged from 25 to 100 kg N/ha for sludge-treated plots (Table 2.5). The recovery of total N applied in plant shoots averaged 23% to 15% for the plots receiving 2 cm (surface and surface + N-Serve) and 4 cm (surface and surface + N-Serve) application, respectively. Seven and 14% of the total N applied was recovered in the sorghum - sudan grown on the 2 cm and 4 cm incorporated applications, respectively. The lower N recovery for the 2 cm incorporated, 4 cm incorporated, surface, and surface + N-Serve treatments were probably a result of various N losses (i.e. leaching, denitrification).

All plots were amended with Br^- to obtain information on the extent of water and NO_3^- movement in soils receiving sludge. In greenhouse experiments with sorghum, Chao (1966) concluded that Br^- was readily absorbed by plants. If Br^- is to be used as a tracer of water movement, uptake of Br^- by the crop has to be determined in soils and plants. Bromide uptake was significant, and $>1\%$ Br^- was noted in most plant tissues. The Br^- content of plant tissue was increased as a result of Br^- application. Bromide concentrations ranged from 2.8% to 4.7% in sorghum - sudan harvested 63 days after sludge or $(\text{NH}_4)_2\text{SO}_4$ applications. For Harvest 2, the percentage of Br^- in shoots ranged from 0.7% to 1.3% (Table 2.4). Low precipitation between initiation of the experiment and the 63 day harvest may have resulted in higher Br^- concentrations in the plant zone and thus increased Br^- concentrations in the plants (Table 2.3)

N Balance

From 8% to 33% of the total N applied was recovered by the plant or remained in the soil 107 days after application of $(\text{NH}_4)_2\text{SO}_4$ or sewage sludge (Table 2.5). This percentage recovery is similar to the 9% to 24% of the sludge N recovered by Coastal bermudagrass (King and Morris, 1972b), the 3% to 12% recovery of N in corn grown on soils amended with sewage sludge (Stewart et al., 1975) and the 7% to 46% recovery of sludge applied N in

rye and corn (Kelling et al., 1977a, 1977b).

Not all the N applied from sewage sludge is available for plant uptake in a given growing season. All the inorganic N added initially plus 20% to 25% of the organic-N has been estimated to be available to crops in the first year after sludge application (Keeney et al., 1976; Sommers and Nelson, 1976). The N recovery percentages calculated, assuming that 25% of the organic N is mineralized, is also shown in Table 2.5. Using these assumptions, 20% to 81% recovery of the "available N" in the sludge was accounted for in the crop or in the soil profile. Approximately 32% to 87% of the Br^- was either incorporated into plant tissue or remained in the soil 107 days after treatment with sewage sludge or $(\text{NH}_4)_2\text{SO}_4$.

Essentially 100% of the inorganic N in the sewage sludge or fertilizer applied to the soil was in the NH_4^+ -N form; however, three days after sludge application, the concentration or amount of $\text{NH}_4^+ + (\text{NO}_2^- + \text{NO}_3^-)$ -N in the soil was not significantly higher in the sludge treated plots than in the control plots (Tables 2.7, 2.8, 2.9). In the $(\text{NH}_4)_2\text{SO}_4$ treated plots, a significant increase in the NH_4^+ concentration in the soil was found three days after application. Low inorganic-N losses from NH_3 volatilization were measured in an independent field study and found to be $<1\%$ of applied inorganic N (Part I). Denitrification was assumed to be small since low concentrations of $(\text{NO}_2^- + \text{NO}_3^-)$ -N existed in the sludge and soil at the time of sludge application. Thus, N may have been lost from sewage sludge through a mechanism other than NH_3 volatilization or denitrification.

By 107 days after application of sewage sludge or fertilizer, the amount of inorganic N had increased significantly in the 30-60 cm and 60-90 cm depths (Table 2.9). This increased inorganic N below the roots zone has been found by other researchers (Braids et al., 1970; Hinesly et al., 1972; King, 1973; Kelling et al., 1977a, 1977b).

The fallability of soil sampling to estimate N balance sheets in soil-plant systems has been shown previously (Stewart et al., 1975; Beauchamp et al., 1978). Assuming that Br^- and inorganic N

Table 2.5. Total N recovered by plants and inorganic-N remaining in the soil 107 days after sewage sludge or $(\text{NH}_4)_2\text{SO}_4$ application.

Treatment	Soil*	Plant†	Total	Total Applied	Recovery [‡]			
					Total N	N _i + 25% organic N§	%	
			kg N/ha					
Control	57	103	160	---	---	---	---	
$(\text{NH}_4)_2\text{SO}_4$	100	196	296	414	136	33	33	
Surface applied sludge								
- 2 cm	65	181	246	411	86	21	54	
- 4 cm	203	188	391	723	231	32	81	
Incorporated sludge								
- 2 cm	60	188	188	368	28	8	20	
- 4 cm	74	203	277	725	117	16	38	
Surface applied sludge								
- 2 cm + N-Serve	23	154	177	190	17	9	20	
- 4 cm + N-Serve	32	168	200	436	40	9	21	

* kg $(\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-)$ -N/ha at 107 days, assuming a bulk density of 1.2, 1.3, 1.4, 1.5 g/cm³ for the 0-15, 15-30, 30-60 and 60-90 cm depths, respectively.

† Total N in shoots only from both harvests.

‡ Treatment-control.

§ $(\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-)$ -N applied initially plus 25% of organic N added.

Table 2.6. Total Br⁻ recovery by sorghum - sudan and soil Br⁻ 107 days after sewage sludge or $(\text{NH}_4)_2\text{SO}_4$ application.

Treatment	Soil*	Plant†	Total	Total Br ⁻ Applied	Recovery of Br ⁻	
					kg/ha	Percent of added
			kg Br ⁻ /ha			
Control	20	14	37	---		
$(\text{NH}_4)_2\text{SO}_4$	366	132	498	965	461	48
Surface applied sludge						
- 2 cm	153	288	441	665	404	61
- 4 cm	232	182	414	1177	377	32
Incorporated sludge						
- 2 cm	340	158	498	532	461	87
- 4 cm	377	154	531	1073	494	46
Surface applied sludge						
- 2 cm + N-Serve	201	151	352	565	315	56
- 4 cm + N-Serve	410	186	596	1140	559	49

* kg Br⁻/ha at 107 days, assuming a bulk density of 1.2, 1.3, 1.4 and 1.5 g/cm³ for the 0-15, 15-30, 30-60 and 60-90 cm depths, respectively.

† Br⁻ in shoots only.

(Treatment-control ÷ Br⁻ added) x 100.

Table 2.7. Concentration of $\text{NH}_4^+\text{-N}$ in soil at various depths 3, 63 and 107 days after sewage sludge or $(\text{NH}_4)_2\text{SO}_4$ application.

Treatment	Time After Application	Depth (cm)			
		0-15	15-30	30-60	60-90
		--- $\mu\text{g NH}_4^+\text{-N/g}$ ---			
Control	3	5	4	3	1
	63	3	2	ND*	ND
	107	3	4	3	3
$(\text{NH}_4)_2\text{SO}_4$	3	103	20	9	7
	63	4	4	ND	ND
	107	5	3	2	2
Surface applied sludge - 2 cm	3	9	6	3	3
	63	5	1	ND	ND
	107	4	3	3	3
- 4 cm	3	31	5	3	0
	63	7	2	ND	ND
	107	7	9	3	3
Incorporated sludge - 2 cm	3	5	5	3	0
	63	5	1	ND	ND
	107	7	9	3	3
- 4 cm	3	9	6	3	1
	63	8	2	ND	ND
	107	5	3	4	1
Surface applied sludge - 2 cm + N-Serve	3	7	6	4	1
	63	5	2	ND	ND
	107	1	2	1	1
- 4 cm + N-Serve	3	13	6	3	2
	63	6	2	ND	ND
	107	4	3	1	1

*ND, not determined.

Table 2.8. Concentration of $(\text{NO}_2^- + \text{NO}_3^-)\text{-N}$ at various depths 3, 63, 107 days after sewage sludge or $(\text{NH}_4)_2\text{SO}_4$ application.

Treatment	Time After Application	Depth (cm)			
		0-15	15-30	30-60	60-90
		--- $\mu\text{g } (\text{NO}_2^- + \text{NO}_3^-)\text{-N/g}$ ---			
Control	3	7	6	4	5
	63	3	2	ND*	ND
	107	2	2	1	1
$(\text{NH}_4)_2\text{SO}_4$	3	21	14	7	7
	63	140	17	ND	ND
	107	6	2	8	4
Surface applied sludge - 2 cm	3	12	6	3	3
	63	17	2	ND	ND
	107	3	3	2	1
- 4 cm	3	15	8	3	4
	63	40	3	ND	ND
	107	7	4	14	14
Incorporated sludge - 2 cm	3	5	6	3	3
	63	20	1	ND	ND
	107	4	3	2	1
- 4 cm	3	6	5	4	4
	63	45	4	ND	ND
	107	7	3	2	2
Surface applied sludge - 2 cm + N-Serve	3	7	6	4	4
	63	12	1	ND	ND
	107	1	1	1	0
- 4 cm + N-Serve	3	6	5	4	3
	63	25	2	ND	ND
	107	1	4	0	0

*ND, not determined.

Table 2.9. Inorganic-N remaining in soil at various depths 3, 63, 107 days after sewage sludge or $(\text{NH}_4)_2\text{SO}_4$ application.

Treatment	Time After Application	Depth (cm)*				Total in Profile	
		0-15	15-30	30-60	60-90		
	--- days ---	----- kg N_i /ha -----					
Control	3	22	20	30	28	100	
	63	10	8	ND†	ND	---	
	107	9	12	17	19	57	
$(\text{NH}_4)_2\text{SO}_4$	3	223	68	70	64	425	
	63	259	42	ND	ND	---	
	107	20	10	43	27	100	
Surface applied sludge	- 2 cm	3	38	24	26	28	106
		63	40	6	ND	ND	---
		107	12	12	22	1	65
	- 4 cm	3	83	26	26	18	153
		63	85	10	ND	ND	---
		107	26	26	73	78	203
Incorporated sludge	- 2 cm	3	18	22	26	14	80
		63	45	4	ND	ND	---
		107	12	12	22	14	60
	- 4 cm	3	27	22	30	23	102
		63	95	12	ND	ND	---
		107	22	12	26	14	74
Surface applied sludge	- 2 cm + N-Serve	3	26	24	30	23	103
		63	31	6	ND	ND	---
		107	4	6	8	5	23
	- 4 cm + N-Serve	3	34	22	30	23	109
		63	56	8	ND	ND	---
		107	9	14	4	5	32

* $(\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-)$ -N remaining in soil assuming a bulk density of 1.2, 1.3, 1.4 and 1.5 g/cm^3 for the 0-15 cm, 15-30 cm, 30-60 cm, 60-90 cm depths, respectively.

†ND, not determined.

added to the soil from the sludge or fertilizer is equally distributed and no loss of Br^- or inorganic N occurs, application of sludge or fertilizer to soils should not alter the ratio of Br^- :inorganic N (N_i) in the soil. The ratio of Br^- : N_i in the sludge and in the soil three days after treatment are listed in Table 2.10. The Br^- : N_i ratio was significantly increased for all the sludge treatments, however, the ratio remained the same for the fertilizer treatment. It was concluded that the increase in the Br^- : N_i ratio was a result of low N_i recovery in soil samples

and not losses of Br^- by leaching which was assumed to be minimal during the three days of sludge drying. The unexplainable losses of N_i prompted the laboratory incubation study to help assess N transformations and losses from sewage sludge applied to soils.

Laboratory Experiment

The results of the laboratory incubation study are shown in Table 2.11. Recovery of total N from soil samples treated with sewage sludge was approximately 100% when the soil was analyzed one

Table 2.10. Ratio of Br^- :inorganic N (N_i) in sewage sludge or $(\text{NH}_4)_2\text{SO}_4$ initially and in the soil 3 days after application.

Treatment	Br ⁻ :N _i ratio in*		Relative Increase In Br ⁻ :N _i ratio 3 days After Application†
	Material Applied	Soil After 3 days	
$(\text{NH}_4)_2\text{SO}_4$	2.3	2.4	1.0
Surface applied sludge			
- 2 cm	9.3	29	3.1
- 4 cm	9	29.8	3.3
Incorporated sludge			
- 2 cm	8.5	58	6.8
- 4 cm	7.5	43.8	5.8
Surface applied sludge			
- 2 cm + N-Serve	11	46.8	4.3
- 4 cm + N-Serve	11	36	4.3

* Br^- and N_i ($\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-$)-N in kg/ha

† Calculated by $(\text{Br}^-:\text{N}_i)_{t=3 \text{ days}} \div (\text{Br}^-:\text{N}_i)_{t=0}$

hour after sludge application. The 60% recovery of added N_i from soils treated with granular $(\text{NH}_4)_2\text{SO}_4$ after one day compared to approximately 90% recovery of N_i from the sludge treated soils may be a result of inherent errors in the method of $(\text{NH}_4)_2\text{SO}_4$ application. Three days after application of sludge, 70% and 79% of the total N applied was recovered from the soils receiving 2 cm and 4 cm sludge applications, respectively, while 93% of an $(\text{NH}_4)_2\text{SO}_4$ treatment was recovered. By seven days after application, only 53% of the sludge N was recovered from the 2 cm surface treatment, while 84% and 74% of the total N applied was recovered from the 4 cm surface and $(\text{NH}_4)_2\text{SO}_4$ treatments, respectively. Ammonia volatilization losses of 2%, 45%, and 25% of the applied N_i for the $(\text{NH}_4)_2\text{SO}_4$, 2 cm surface, and 4 cm surface treatments, respectively, were found during the seven day incubation. The initial pH of the sludge was 7.3 and, as shown previously, was likely responsible for the effect of NH_3 volatilization.

The liberation of CO_2 -C indicated that microbial activity was increased by sludge addition, suggesting N immobilization could be

occurring in the soils within 7 days after sludge addition (data not presented). The decrease in organic N content of soils surface treated with 2 cm and 4 cm of liquid sewage sludge with time indicates an unexplainable loss mechanism of organic N not measured during the field study. The 35% recovery of organic N in soils from the 2 cm liquid sewage sludge application rate as compared to 88% recovery of organic N from the 4 cm application rate may be a result of inherent analytical errors associated with total N determinations in soil samples. This is also shown by a 91% to 96% recovery of total N when the sum of total N recovered at a given time is compared to the one hour total N recovery for the treatment.

Table 2.11. Recovery of NH_4^+ - N, $(\text{NO}_2^- + \text{NO}_3^-)$ - N, organic-N, and total-N from the laboratory incubation study.

Treatment*	Time days	N Recovered				Sum	Total N recovery Based on ⁺	
		Org.	NH_4^+	$\text{NO}_2^- + \text{NO}_3^-$	NH_3 Vol.		Trt-Ctrl	Trt'/Trt
mg N Incubation Unit								
Control	0	41	0.2	0.5	--	42	--	--
	1	43	0.4	0.4	0	44	--	--
	3	39	0.4	0.4	0	40	--	--
	7	41	0.1	0.2	0.5	42	--	--
$(\text{NH}_4)_2\text{SO}_4$	1	45	3.8	0.3	0	49	93	
	3	41	3.1	0.8	0	45	93	
	7	42	3.0	0.3	0.6	46	74	
Surface applied sludge - 2 cm	0	49	3.3	0.2	0	53	97	100
	1	47	3.2	0.3	0.2	51	62	96
	3	45	2.3	0.4	0.5	48	70	91
	7	44	1.5	0.5	2.0	48	53	91
Surface applied sludge - 4 cm	0	57	6.3	0.4	0	64	97	100
	1	53	6.0	0.4	0.4	60	70	94
	3	51	5.5	0.6	0.9	58	79	91
	7	55	3.8	0.4	2.2	61	84	95

* mg NH_4^+ , $(\text{NO}_2^- + \text{NO}_3^-)$ -N and organic N added were 3.32, 0.03 and 8.00, respectively, for the 2 cm rate and twice these amounts for the 4 cm treatment. NH_4^+ -N added was 5.4 mg for the $(\text{NH}_4)_2\text{SO}_4$ treatment.

⁺ Trt-Ctrl, [treatment total N at time t - control total N at time t]/N added x 100

Trt'/Trt, [treatment total N at time t/treatment total N at time = 0] x 100

III. Characterization of Organic N mineralization

Following application to soil, a portion of the organic matter contained in sewage sludge is subject to decomposition by the soil microbial population. Several studies have shown that from 10 to 25% of the organic C found in sewage sludge is decomposed during the first year after addition to soil (Miller, 1974; Sommers et al., 1979). Concurrent with the evolution of CO_2 is the liberation of NH_4^+ during sludge decomposition (i.e., N mineralization) provided the C/N of the organic matter is less than $\sim 20/1$. The mineralization of organic N is an important consideration when calculating the appropriate sludge application rate for crop production because the N mineralized is readily oxidized to NO_3^- and will be leached into ground water if present at levels in excess of the N requirement of the crop grown.

Laboratory incubation procedures have been used to assess N mineralization in soils amended with sewage sludge. The majority of studies involve amending a soil sample with sewage sludge and incubating the mixture for varying periods of time. Subsamples are removed from the incubation system and analyzed for inorganic N (NH_4^+ and NO_3^-). The difference in inorganic N between an unamended and sludge amended soil sample represents the amount of sludge organic N mineralized. This calculation assumes that sludge addition does not increase mineralization of soil organic N. Mineralization of organic N (N_0) from an anaerobically digested sludge was found to range from 4% to 48% of the N_0 during a 16 week incubation period (Ryan et al., 1973). The percent N_0 mineralized decreased as the amount of N_0 added to the soil was increased from 47 to 1,880 mg N_0/kg soil. Soil analysis indicated that neither amino acids nor hexosamines were decreased appreciably during incubation. In contrast, Sabey et al. (1975) studying N_0 mineralization of an anaerobically digested sludge added to soil at rates ranging from 22.4 to 224 metric tons/ha found that similar amounts of N_0 were mineralized (36 to 41% of N_0) at all application rates. Significantly lower N_0 mineralization (2.3 to 4.2% of N_0) has been found in

some studies using both anaerobically digested and activated sludges (Premi and Cornfield, 1971). Based on plant uptake of N, it has been estimated that 4 to 29% of the sludge N_0 can be mineralized and thus made available for crops (Sabey, 1977).

Several studies have evaluated N_0 mineralization for different types of sludges. Magdoff and Chromec (1977) found that N_0 mineralization ranged from 14 to 25% for anaerobically- and from 36 to 41% for aerobically-digested sludges during a 13 week laboratory incubation period. The amount of N_0 mineralized in raw-, digested- and activated-sludges has been found to be 7%, 21% and 60%, respectively, for a 42 day incubation (Stephenson, 1955). Epstein et al. (1978) evaluated N_0 mineralization using a leaching procedure and found that composting decreased N_0 mineralization for a digested sludge from 42% to 7% of N_0 and for a raw sludge from 43% to 4% of N_0 . This study also showed that sludge application to soil resulted in increased N immobilization during the initial phase of decomposition. Immobilization of N may be a significant process in many soils treated with sewage sludges. Approximately 20% of the inorganic N initially present in a soil amended with sewage sludge may be converted into relatively stable forms of organic N (Terry et al., 1981). The mineralization of sludge N_0 has been found to decrease from 11 to 3% as the C/N ratio increases. In addition to sludge properties, the characteristics of the soil may influence the rate of mineralization (Tester et al., 1977).

Estimates of N_0 mineralization have also been obtained from field experiments. Based on soil analysis, Kelling et al. (1977) concluded that approximately 50% of the N_0 applied was mineralized within 3 weeks after sludge application. It was also shown that 25% and 15% of the N_0 added was mineralized during the 2nd and 3rd years, respectively, after application. A similar level of N_0 mineralization ($\sim 50\%$) was obtained by Magdoff and Amadon (1980) from a field experiment. The amount of N_0 mineralized during a laboratory incubation for 17 weeks was comparable to that estimated from field data. Soil samples obtained from field plots treated with different

types of sludges and subsequently incubated in the laboratory have shown that mineralizable N is increased by sludge application but any differences due to sludge types was not apparent after a 4 year decomposition period under field conditions (Stark and Clapp, 1980).

Two basic procedural approaches have been used in the studies cited above. One approach involves incubating a soil-sludge mixture and periodically determining the inorganic N content of the mixture. Alternatively, a soil-sludge mixture is placed in a leaching tube and the inorganic N mineralized is periodically removed from the system by leaching with a dilute salt solution (Stanford and Smith, 1972). The leachate is then analyzed for NH_4^+ and NO_3^- . The latter approach has been used extensively to evaluate the mineralizable N status of diverse soils and has been more recently applied to studying N_0 mineralization in sludge amended soils (e.g., Epstein et al., 1978). The leaching technique is more cumbersome and time-consuming than a simple, static soil incubation system. Thus, if similar mineralization data were obtained from the leaching and static systems, the static procedure would be the method of choice for routine estimation of N mineralization in soils amended with sewage sludge.

The objectives of this study were: 1) to determine N mineralization for a variety of sewage sludges obtained from different regions of the U.S.; 2) to compare the leaching and static incubation methods for studying N mineralization and; 3) to evaluate several extraction procedures for predicting potentially mineralizable N in sewage sludges.

MATERIALS AND METHODS

Materials

The sludges used in the experiments were obtained from several regions of the United States and were chosen to represent a wide variety of sewage treatment processes. The actual sewage treatment processes evaluated in this experimental work are shown in Table 3.1 and include primary,

primary plus waste activated, raw-CaO treated, raw-Zimpro treated, waste activated, anaerobically digested, aerobically digested, raw-CaO treated and composted, and anaerobically digested and composted. All sludges were air-dried and shipped to Purdue University. After receipt, each sludge sample was ground to less than 60 mesh prior to use.

The soil used in the lab incubations was a Fincastle silt loam (fine-silty, mixed mesic Aeric Ochraqualf). The soil was collected at the Purdue Agronomy Farm located north of West Lafayette, IN., air-dried and ground to less than 20 mesh. The pH of the soil was 5.9.

Methods

Analytical methods utilized in the experimental work were as follows: organic and inorganic C were determined by the wet combustion procedure described by Allison (1960); inorganic C was also determined in selected sludges as described by Bundy and Bremner (1972); total N was measured using a micro-Kjeldahl procedure (Nelson and Sommers, 1972); total N in 0.01M CaCl_2 leachate samples was determined by micro-Kjeldahl digestion using a reduced iron pretreatment (Nelson and Sommers, 1975); inorganic N was estimated using the steam distillation method described by Bremner (1965) for 2M KCl extracts and 0.01M CaCl_2 leachates.

Several extraction procedures were evaluated to predict the mineralizable N content of sewage sludges, as a comparison to the N mineralization results obtained with soil incubations. Two different methods were evaluated. Inorganic N released by autoclaving was determined essentially as described by Smith and Stanford (1971). A 0.5-g sample of sludge was extracted with 25-ml of 0.01M CaCl_2 followed by filtration and determination of NaOH-distillable N (primarily NH_4^+) by steam distillation and acidimetric titration. A duplicate sludge sample was suspended in 0.01M CaCl_2 and autoclaved for 4 hours at 121°C. After autoclaving, NaOH-distillable N was determined in the 0.01M CaCl_2 extract. The difference between NaOH-distillable N in the 0.01M

Table 3.1. Sludge treatments.

Type of sludge	Source of Sludge		Comments
	Designation	City	
Primary	P	Grand Haven, MI	-
Primary + Waste Act. Raw + CaO ⁺	PWA	Seattle, WA	-
	RL	Blue Plains, D.C.	CaO + FeCl ₃ added
Raw and Zimpro [‡] treated	RZ 1	Grand Rapids, MI	-
	RZ 2	Oshkosh, WI	-
Waste activated	WA 1	Chicago, IL	FeCl ₃ added
	WA 2	Seattle, WA	-
Aerobically digested	AeD	Medina, OH	-
Anaerobically digested ^π	AnD 1	Anderson, IN	CaCO ₃ added
	AnD 2	Baltimore, MD	FeCl ₃ added
	AnD 3	Chicago, IL	FeCl ₃ added
	AnD 4	Chicago, IL	Imhoff
	AnD 5	Columbus, OH	-
	AnD 6	Frankfort, IN	-
	AnD 7	Glenwood Springs, CO	-
	AnD 8	Grand Rapids, MI	-
	AnD 9	Marion, IN	CaCO ₃ added
	AnD 10	Tucson, AZ	-
	AnD 11	Waukesha, WI	-
	AnD 12	Wisconsin Rapids, MI	-
	AnD 13	Zanesville, OH	-
Raw + CaO and composted	RLC	Blue Plains, DC	CaO + FeCl ₃ added
Anaerobically digested and composted	AnDC 1	Baltimore, MD	FeCl ₃ added
	AnDC 2	Los Angeles, CA	Polymer added

⁺Raw sludge = mixture of primary plus secondary sludge.

[‡]Treatment at elevated temperature and pressure.

^πMixture of primary and secondary sludge was normally treated.

CaCl₂ extracts, in the presence and absence of autoclaving, was used as an estimate of potentially mineralizable N. The second approach involved measuring NH₄⁺ released from sludges by treatment with 1N H₂SO₄ plus KMnO₄ (0.1 or 0.5 N) (Stanford and Smith, 1978). Indigenous NH₄⁺ was determined in sewage sludge by extracting a 0.5-g sample of sludge with 25-ml of 1N H₂SO₄. The extract was separated by centrifuging and an aliquot analyzed for NaOH-distillable N (mainly NH₄⁺). A second sample was treated for one hour with 1N H₂SO₄ plus 0.1N KMnO₄. The extract was separated by centrifugation and an aliquot treated with NaOH to determine distillable N. This was also performed using 1N H₂SO₄ plus 0.5N KMnO₄. The difference between NH₄⁺ in H₂SO₄ and H₂SO₄ plus KMnO₄ was used as an estimate of mineralizable N.

Two experimental approaches were utilized in the laboratory to measure N mineralized in soil-sludge mixtures. The first was a leaching incubation (Stanford and Smith, 1972) while the second involved a closed system static incubation.

For the leaching incubation, 30-g of washed silica sand, 20-g of air-dry Fincastle soil and 0.267-g of air-dry sludge (equivalent to 30 mt/ha) were intimately mixed and placed in a 3.75-cm (id) PVC pipe containing a glass wool layer above a 1-hole rubber stopper fitted with glass tubing. A second glass wool pad was placed above the soil-sand-sludge mixture to maintain an undisturbed soil surface when 0.01M CaCl₂ was added for leaching. All soil-sand-sludge mixtures were run in duplicate and were incubated in the dark at 24°C. The soil-sand-sludges mixtures were leached at 0, 1, 2, 4, 6, 8, 12, and 16 week time intervals. Leaching was performed by adding three 50-ml portions of 0.01M CaCl₂ followed by 25-ml of minus-N nutrient solution (0.02M CaSO₄·2H₂O, 0.005M KH₂PO₄, 0.002M MgSO₄). The leachate was collected in 500-ml side-arm Erlenmyer flasks with the side-arm attached to a vacuum system so each tube was leached at approximately -0.3-bar tension. A Hg manometer was used to continuously monitor the tension applied. Total volume of leachate was calculated by weighing each 500-ml side-arm flask when empty and after collection of the leachate.

Inorganic N in all leachate samples was measured on a 25-ml aliquot and steam distilling with MgO for NH₄⁺-N and with Devardas alloy for NO₂⁻ + NO₃⁻-N (Bremner, 1965). Total N was measured in the first four leachates (0, 1, 2 and 4 weeks) by pretreating a 25-ml aliquot with reduced iron plus 0.5-ml of concentrated H₂SO₄, drying the samples for 16 hours at 105°C and then proceeding with micro-Kjeldahl analysis (Nelson and Sommers, 1975). The difference between inorganic and total N measurements on the leachate samples was used as an estimate of organic N leached from sludge-soil mixtures.

The static incubation system involved simultaneous measurement of both CO₂ evolved and N mineralized from soils amended with sewage sludge. Fincastle soil (100-g) was amended with 1.338-g of sludge (equivalent to 30 metric tons/ha), adjusted to approximately -0.3 bar water potential by addition of deionized H₂O and placed in a 1-liter Erlenmeyer flask. The flask was then attached to a manifold system enabling humidified CO₂-free air to be continuously passed over the soil-sludge mixture (see Terry et al., 1979). The flow rate of air was 8 ml/min and the flasks were incubated in the dark at 24°C. Carbon dioxide evolved from soil-sludge mixtures was trapped in 25-ml of 2N KOH. At 2, 5, 8, 15, 30, 57, 87 and 112 days, the KOH traps were removed from the system and a 5-ml aliquot was treated with 5-ml of 1.5M BaCl₂. The residual alkalinity was titrated with standard 0.5N HCl using phenolphthalein as an indicator. At 0, 7, 14, 28, 42, 56 and 112 days, the soil was thoroughly mixed and a subsample removed for determination of inorganic N. Approximately 3-g of moist soil were extracted with 15-ml of 2M KCl by shaking for 1 hour. An appropriate aliquot was analyzed for NH₄⁺ and NO₂⁻ + NO₃⁻ by steam distillation. Also, at 0, 56 and 112 days a small subsample (~ 1-g) was removed for determination of moisture content (drying at 105°C for 16 hours). All data were expressed on an oven-dry basis. The amounts of CO₂ evolved were corrected for the removal of soil subsamples from the flask during incubation. All data presented are the average of duplicate experimental systems.

It has been commonly assumed that N mineralization follows first-order kinetics (Stanford and Smith, 1972). The N mineralization data obtained in the leaching and static incubation systems were found to approximate first-order kinetics. Stanford and Smith (1972) used log transformed data to compute the rate constant (k) and potentially mineralizable N (N_p) in a variety of soils. Smith et al. (1980) evaluated this method and found that more precise estimates of k and N_p could be obtained from a nonlinear least squares calculation. The following development is essentially that described by Smith et al (1980).

If N mineralization follows first order kinetics, then

$$\frac{dN}{dt} = -kN \quad (1)$$

where N = concentration of mineralizable ($\mu\text{g N/g}$), t = time (weeks), and k = rate constant (weeks^{-1}). Equation 1 can be integrated from time t_p to time t yielding

$$\frac{\ln N_t}{N_p} = -k(t-t_p) \quad (2)$$

Setting $t_p = 0$ and rearranging

$$\frac{N_t}{N_p} = \exp(-kt) \quad (3)$$

In equation 3, N_t and N_p are final and initial concentrations of mineralizable N (N_p is used rather than N_0 for mineralizable N).

Data obtained in the laboratory incubations are the amount of N mineralized at various times so both N_t and N_p are unknown. One of the unknowns in Equation 3 can be eliminated because

$$N_t = N_p - N_m \quad (4)$$

where N_m = amount of N mineralized ($\mu\text{g N/g}$) during an incubation of time t. Substitution of Equation 4 into 3 yields

$$\frac{N_p - N_m}{N_p} = \exp(-kt) \quad (5)$$

In equation 5, N_m and t are known from experimental data leaving only N_p and k as unknowns.

Equation 5 can be solved iteratively using a nonlinear least squares regression technique.

Equation 5 is rearranged to give:

$$N_p - N_m = N_p \exp(-kt) \quad (6)$$

or

$$0 = N_m - N_p (1 - \exp(-kt)) \quad (7)$$

The objective of a least squares method is to minimize the deviations between the actual and predicted data using an estimate of N_p and k. The sum of squares of deviations is then

$$\sum_{i=1}^n d_i^2 = \sum [N_{mi} - N_p(1 - \exp(-kt_i))]^2 \quad (8)$$

where i represents each experimental data point.

The derivatives of Equation 8 with respect to N_p and k are evaluated and set equal to 0, or

$$\frac{d\sum d_i^2}{dN_p} = 0 \quad \text{and} \quad \frac{d\sum d_i^2}{dk} = 0 \quad (9)$$

$$\frac{d\sum d_i^2}{dN_p} = -2\sum [N_{mi} - N_p(1 - \exp(-kt_i))](1 - \exp(-kt_i)) = 0 \quad (10)$$

and

$$\frac{d\sum d_i^2}{dk} = -2\sum [N_{mi} - N_p(1 - \exp(-kt_i))](t_i N_p \exp(-kt_i)) = 0 \quad (11)$$

Solving Equations 10 and 11 for N_p

$$N_p = \frac{\sum [N_{mi}(1 - \exp(-kt_i))]}{\sum [(1 - \exp(-kt_i))]^2} \quad (12)$$

$$N_p = \frac{\sum [N_{mi} t_i \exp(-kt_i)]}{\sum [t_i \exp(-kt_i)(1 - \exp(-kt_i))]} \quad (13)$$

$$\begin{aligned} \text{Equations 12 and 13 are set equal and rearranged to} \\ \frac{\sum [N_{mi}(1 - \exp(-kt_i))] \sum [t_i \exp(-kt_i)(1 - \exp(-kt_i))]}{\sum [1 - \exp(-kt_i)]^2 \sum [N_{mi} t_i \exp(-kt_i)]} \\ = 0 \end{aligned} \quad (14)$$

A computer program was written in Basic-Plus to solve equation 14 for k by the bisection method. An accuracy of 10^{-5} was used to terminate the calculation. Once k is known, it can be substituted in either equation 12 or 13 to calculate N_p . The above procedure was also used to calculate the rate constant for organic C decomposition (i.e., CO_2 evolution) in the static incubation system.

RESULTS AND DISCUSSION

Sludge Composition

The sewage sludges studied are listed in 3.1. The majority of the sludges were anaerobically digested with a mixture of primary and waste activated sludges typically entering the digester. Other sludges evaluated included primary, primary plus waste activated, raw (commonly a mixture of primary and waste activated) plus CaO, raw plus Zimpro treatment (i.e., wet-air oxidation at elevated temperature and pressure), waste activated, aerobically digested and composted sludges. The source of the sludges along with some additional comments on sludge treatments are also shown in Table 3.1. It should be noted that sludge AnD 4 is the common sewage sludge being utilized by a cooperative regional research project (W-124) where barley is grown on soils amended with sludge at approximately 15 locations in the U.S..

The chemical characteristics of the sludges are presented in Table 3.2. The range in organic C content was from 7.47 to 35.61% with a mean of 21.22% (standard deviation = 8.02%). The primary, raw and waste activated sludges contained greater levels of organic C than the anaerobically digested sludges. The inorganic C content (primarily Ca or Mg carbonates) was obviously a function of CaO or CaCO₃ addition during sludge treatment. Because elevated CO₂ concentrations may result from microbial decomposition of organic matter during several sludge treatment processes, it is also likely that Ca or Mg carbonates will precipitate whenever the sewage influent contains appreciable concentrations of Ca or Mg. Two methods were evaluated for determining inorganic C in sludges. The results obtained (Table 3.2) suggest that the simple procedure of Bundy and Bremner (1972) will give a reasonable estimate if sludge inorganic C is <3%.

Table 3.2 also shows the amount of NH₄⁺, NO₂⁻ + NO₃⁻, and organic N in the sludges studied. It is difficult to generalize about the inorganic N concentrations because they are very dependent on the methods used for sludge drying prior to analysis. Anaerobically digested sludges are

devoid of NO₃⁻ when samples are collected directly from the digester (Sommers et al., 1976). Since several of the anaerobically digested sludges contained >500 mg NO₃⁻-N/kg, it is obvious that the sludge samples were slowly dried allowing nitrification to occur. Similarly, the NH₄⁺-N contents are likely a reflection of ammonia volatilization losses which occurred during air- or oven-drying of the sludges. The organic N levels in the sludges ranged from 5,009 to 68,137 µg/g with a mean of 21,750 µg/g (standard deviation = 14,510 µg/g). As was found for organic C, anaerobically digested sludges were quite variable in organic N content.

In general, the sludges used to study N mineralization represented a wide-range of treatment processes. The organic C and N concentrations found in these samples should bracket the majority of sludges produced.

Mineralization of Organic N

The amount of inorganic N released from soil-sludge mixtures in each incubation system (leaching and static) at the various sampling times is shown in Figures 3.1 to 3.12. All data presented represent the difference between the inorganic N(NH₄⁺ + NO₂⁻ + NO₃⁻) found after a particular time of incubation and that found in the system initially. A curvilinear relationship between N mineralized and time was found for nearly all sludges (Figures 3.1 to 3.12). In many cases, N mineralization was rapid during the initial 3 to 4 weeks and then the rate decreased significantly. The curvilinear relationship between N mineralized and time indicates that N mineralization can be approximated by first-order kinetics. The solid line shown in Figures 3.1 to 3.12 was calculated by nonlinear least squares regression assuming first-order kinetics. For most sludges, there is excellent agreement between the actual data points and the predicted values. These results show that first-order kinetics can be used to describe N mineralization in soils amended with sewage sludge. The agreement obtained between actual and predicted N mineralization values was

Table 3.2. Sludge properties

Type of sludge (see Table 3.1)	Organic C	Inorganic C ⁺		Organic N	Inorganic N	
		1	2		NH ₄ ⁺	NO ₂ ⁻ + NO ₃ ⁻
		----- % [‡] -----		----- µg/g [‡] -----		
P	28.39	1.99	2.10	42,115	2161	24
PWA	35.61	0.03		44,344	846	34
RL	21.91	1.23		23,191	62	42
RZ 1	32.11	0.53	0.55	13,197	183	0
RZ 2	32.91	0.17	0.20	17,370	165	14
WA 1	28.61	0.68	0.74	38,725	3717	40
WA 2	34.30	0.01	0.06	68,137	1704	42
AeD	17.39	0.14		25,190	1358	44
AnD 1	15.42	2.03	2.03	7,276	594	28
AnD 2	23.29	0.11	0.16	23,455	935	16
AnD 3	24.82	0.75		30,333	3760	33
AnD 4	16.80	1.08	1.56	16,545	339	1012
AnD 5	26.50	1.05		27,437	2015	22
AnD 6	10.39	1.87	1.76	10,481	56	783
AnD 7	20.59	0.07		18,903	1489	123
AnD 8	14.76	1.48		12,790	130	18
AnD 9	7.47	5.97	3.72	5,009	26	88
AnD 10	10.97	0.14		10,823	611	2104
AnD 11	25.04	0.81	0.87	20,058	493	547
AnD 12	15.57	0.16		16,917	2437	171
AnD 13	14.26	1.66		14,033	633	32
RLC	19.58	1.39		15,403	972	20
AnDC 1	18.62	0.35	0.49	13,100	171	88
AnDC 2	13.89	0.22		7,223	839	2142

⁺ Method 1, Bundy and Bremner (1972); Method 2, Allison (1960) with Ag(SO₄)₂ scrub.
[‡] Expressed on air-dry weight basis.

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more precise for the leaching than the static incubation method. The likely explanation for this trend is that once inorganic N removed from the leaching column is analyzed, subsequent sampling and analytical errors are not possible once this fraction of the N mineralized is removed. Both subsampling and analytical errors can occur in the static incubation system where inorganic N accumulates with time. Furthermore, some denitrification may have occurred in the static procedure even though the soils were maintained at -0.3 bars, resulting in fluctuations in the inorganic N content.

The amounts of N mineralized in the static procedure generally exceeded those obtained for the leaching method. The data presented in Figures 3.1 to 3.12 and in Table 3.3 indicate that greater amounts of N were mineralized in the static system for 16 of the 24 sludges studied. The average percentage of N mineralized for the leaching and static incubation procedures was 17.5 and 15.9% of the N_0 , respectively (Table 3.3). One possible explanation for lowered N mineralization percentages in the leaching method is the removal of potentially decomposable soluble organic N when the soil-sludge mixtures are leached with 0.01M $CaCl_2$. To evaluate this hypothesis, total N was determined on leachates collected after incubation for 0, 1, 2 and 4 weeks. The results obtained (Table 3.4) show that significant amounts of organic N are leached with 0.01M $CaCl_2$ from both the unamended and the sludge amended soils. The amount of organic N removed was equal to or exceeded the inorganic N for soils treated with sludge P, PWA, RL, RZ 1, RZ 2 and WA 1 at week 0. For nearly all sludges at 0 to 4 week incubation times, organic N constituted a significant proportion (>25%) of the total N leached from sludge amended soils. Similar levels of leachable organic N were obtained by Smith et al. (1980) for non-sludge amended soils. These data strongly suggest that the leaching procedure developed by Stanford and Smith (1972) will underestimate N_0 mineralization in soils because soluble organic N, presumable of relatively low molecular weight and susceptible to microbial

decomposition, is removed from the system and will not be detected by inorganic N analysis. Therefore, results obtained from the static incubation procedure should give a more reliable estimate of N_0 mineralization in unamended and sludge amended soils.

The percentage of sludge organic N mineralized during a 16 week incubation period is summarized in Table 3.3. Net immobilization of N occurred in soil treated with sludge RZ 1 (Zimpro treated raw sludge). The anaerobic sludges ranged from 2.1 to 26.7% of the organic N being mineralized. Waste activated sludges tended to mineralize greater amounts of organic N than the other sludge types. Mineralization of N_0 for composted sludges ranged from 4.5 to 12% (static procedure). A comparison of N_0 mineralization in a raw sludge treated with CaO before (RL) and after (RLC) composting indicates that composting reduced the amount of N mineralized from 27.9 to 9.4% of the N_0 . Similarly, composting has reduced N_0 mineralization in an anaerobically digested sludge from 13.7 (AnD 2) to 12% (AnDC) of the N_0 . Anaerobic digestion of waste activated sludge (WA 1) reduced N_0 mineralization from 33.1% to 23.5% (AnD 3) of the N_0 . In general, the greatest amounts of mineralizable N_0 are present in raw, primary or waste activated sludges. Further treatment (e.g., anaerobic digestion, composting) of these sludge types reduces the amount of N mineralization that will occur after the sludge is applied to soil.

The first-order rate constants and calculated estimates of mineralizable N are presented in Table 3.5. The rate constants ranged from 0.090 to 0.685 and from 0.140 to 1.000 week⁻¹ for the leaching and static procedures, respectively. A first-order rate constant was not calculated for sludges RZ 2 and AnD 1 in the leaching procedure because N mineralization was a linear function of time (i.e., a zero-order process). There was a general trend for the rate constant to increase with an increasing percentage of mineralizable N in the sludge; however, exceptions to this trend can be readily found. The calculated estimates of mineralizable N are essentially the same as the

Table 3.3. Comparison of leaching and static incubation methods for determining N mineralization in sewage sludge-soil mixtures.

Type of Sludge (see Table 3.1)	Cumulative N mineralized in ⁺		% of added organic N mineralized in [‡]	
	Leach	Static	Leach	Static
	μg/g		%	
P	63.7	88.8	11.2	16.0
PWA	261.9	246.3	43.9	42.1
RL	67.5	85.3	21.6	27.9
RZ 1	0	0	0	0
RZ 2	7.8	12.6	3.3	5.5
WA 1	160.5	169.3	30.8	33.1
WA 2	530.8	460.1	57.8	51.1
AeD	108.1	83.1	31.9	25.0
AnD 1	0.1	2.0	0.1	2.1
AnD 2	45.6	42.4	14.4	13.7
AnD 3	120.6	94.0	29.5	23.5
AnD 4	22.8	25.3	10.2	11.6
AnD 5	115.2	90.3	31.2	24.9
AnD 6	15.0	22.8	10.6	16.5
AnD 7	21.8	23.0	8.6	9.2
AnD 8	11.6	25.7	6.7	15.2
AnD 9	3.3	15.3	4.9	23.1
AnD 10	8.6	17.3	5.9	12.1
AnD 11	9.4	18.0	3.5	6.8
AnD 12	51.8	19.7	22.7	8.8
AnD 13	41.8	49.4	22.1	26.7
RLC	6.8	19.2	3.3	9.4
AnDC 1	9.3	20.7	5.3	12.0
AnDC 1	2.6	4.3	2.7	4.5
None	23.6	30.2	-	-

⁺ N mineralized in treated sample minus N mineralized in control, except for control.

[‡] [(N mineralized in treatment - N mineralized in control) ÷ sludge organic N added] x 100.

Corrected for inorganic N initially added in sludge.

Table 3.4. Comparison of inorganic and organic N leached from soil-sludge mixtures.

Sludge Type (See Table 3.1.)	Inorganic and organic N leached for an incubation period of weeks ⁺							
	0		1		2		4	
	N _i	N _o	N _i	N _o	N _i	N _o	N _i	N _o
	-----µg/g-----							
P	15.7	45.3	7.9	13.6	7.4	16.9	21.0	4.9
PWA	23.8	25.2	99.7	13.8	53.8	7.6	45.8	2.8
RL	11.1	26.0	6.8	13.9	6.3	14.1	25.3	3.1
RZ 1	10.9	13.8	0.0	5.6	0.7	6.6	2.7	2.2
RZ 2	10.9	18.4	0.0	6.6	0.7	4.5	1.8	1.2
WA 1	47.5	52.0	66.9	16.6	39.4	9.1	30.4	4.7
WA 2	-	-	263.6	28.2	142.6	15.3	75.3	7.0
AeD	22.4	13.5	49.0	8.8	26.8	8.4	14.4	6.0
AnD 1	-	-	2.0	9.3	0.0	12.5	2.3	1.1
AnD 2	21.5	16.7	15.2	10.0	13.6	6.1	9.1	2.9
AnD 3	37.5	29.0	62.0	12.6	23.2	9.2	19.2	2.9
AnD 4	25.9	13.2	11.3	9.6	8.0	24.4	6.4	4.7
AnD 5	-	-	44.4	12.1	25.1	5.4	24.9	3.5
AnD 6	20.4	14.2	6.7	12.7	4.2	15.3	7.4	1.8
AnD 7	24.3	13.1	11.0	7.6	7.8	3.1	7.4	3.0
AnD 8	11.4	17.2	3.2	9.0	3.1	10.5	7.5	1.1
AnD 9	-	-	3.9	9.2	1.0	10.4	5.1	3.0
AnD 10	42.9	14.0	5.9	11.9	5.2	8.0	5.4	1.4
AnD 11	20.7	11.4	9.7	10.8	1.9	8.4	3.5	1.9
AnD 12	42.5	14.7	25.7	9.0	12.8	4.2	11.4	2.0
AnD 13	13.3	12.9	14.7	9.9	10.2	3.9	12.4	1.6
RLC	-	-	6.6	14.3	1.0	15.5	5.0	3.2
AnDC 1	14.8	9.1	4.7	12.3	6.2	3.6	5.4	7.9
AnDC 2	35.7	10.8	5.0	13.5	2.8	4.1	4.3	1.5
none	11.7	7.0	5.1	13.0	3.5	1.4	1.9	0.0

⁺ N_i = NH₄⁺ + NO₃⁻ + NO₂⁻-N; N_o = total N - N_i.

Table 3.5. Rate constants for N mineralization and estimates of potentially mineralizable N in soil-sludge mixtures.

Sludge Type (see Table 3.1)	Rate Constant for system ⁺		Mineralizable N(N _o) for systems [‡]	
	leach	static	leach	static
	----- week ⁻¹ -----		----- µg/g -----	
P	.102	.198	110.6	120.4
PWA	.377	.616	268.5	242.3
RL	.106	.176	114.4	120.4
RZ 1	.135	.639	7.2	5.7
RZ 2	-¶	.124	--	51.4
WA 1	.424	.474	175.1	176.5
WA 2	.685	1.0	529.8	486.9
AeD	.413	.340	121.8	105.7
AnD 1	--	.141	--	37.3
AnD 2	.205	.286	68.8	67.0
AnD 3	.483	.625	133.3	115.1
AnD 4	.213	.209	45.8	56.6
AnD 5	.334	.531	132.9	104.7
AnD 6	.141	.214	42.6	52.6
AnD 7	.223	.173	44.8	52.9
AnD 8	.090	.140	46.7	61.1
AnD 9	.092	.198	35.4	47.3
AnD 10	.185	.239	33.4	39.6
AnD 11	.162	.619	34.9	38.1
AnD 12	.341	.354	70.3	47.9
AnD 13	.205	.229	66.3	75.3
RLC	.108	.154	36.3	53.7
AnDC 1	.160	.262	35.6	46.7
AnDC 2	.141	.251	28.5	31.0
none	.146	.318	25.4	27.6

⁺ First order rate constant obtained from non-linear least squares regression.

[‡] Calculated amount of potentially mineralizable organic N.

[¶] Data fit a zero order rather than first order equation.

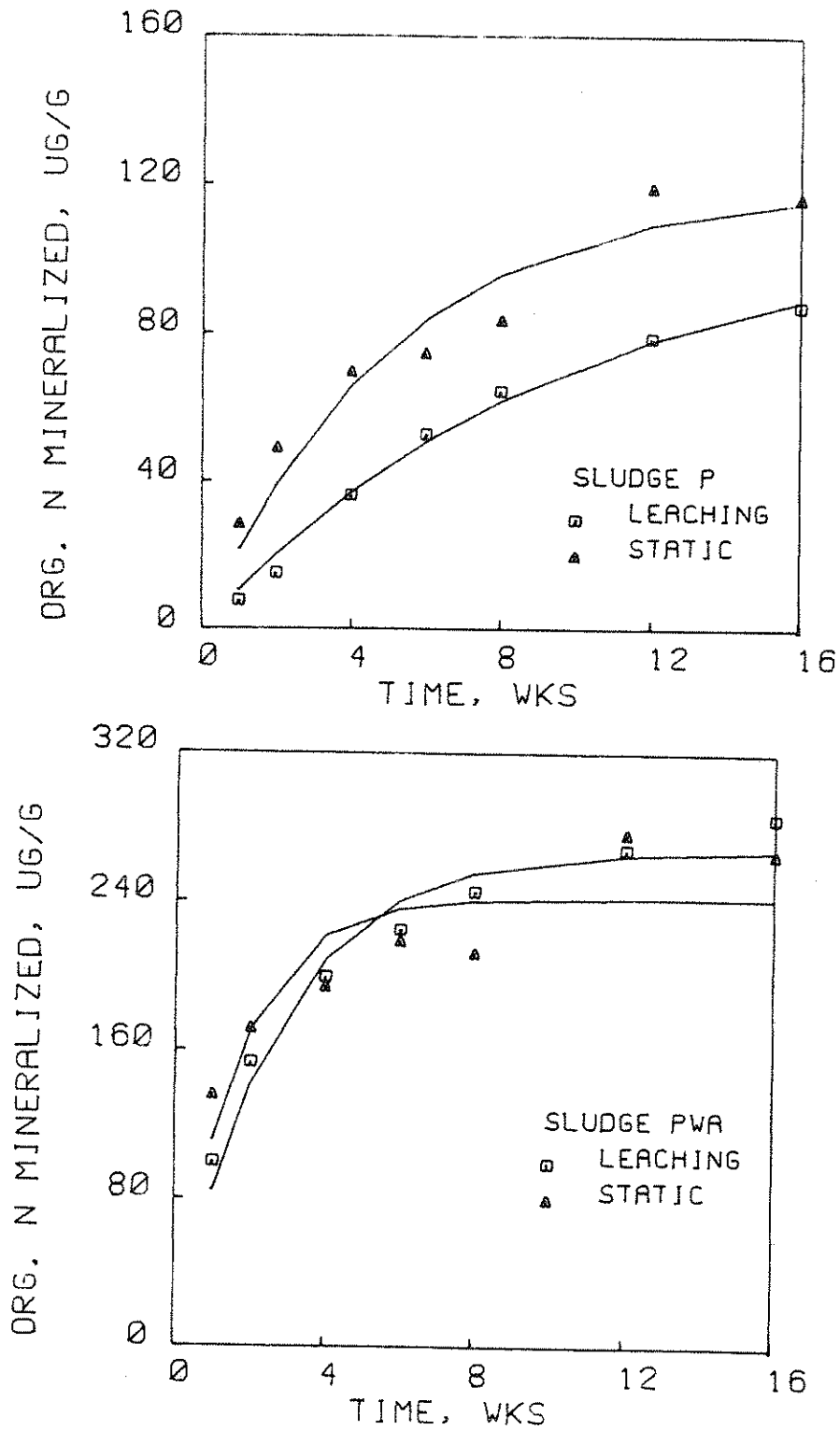


Figure 3.1. Comparison of N mineralized in Fincastle soil amended with primary sludge from Grand Haven, Michigan, (P) and primary plus waste activated sludge from Seattle, Washington, (PWA). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

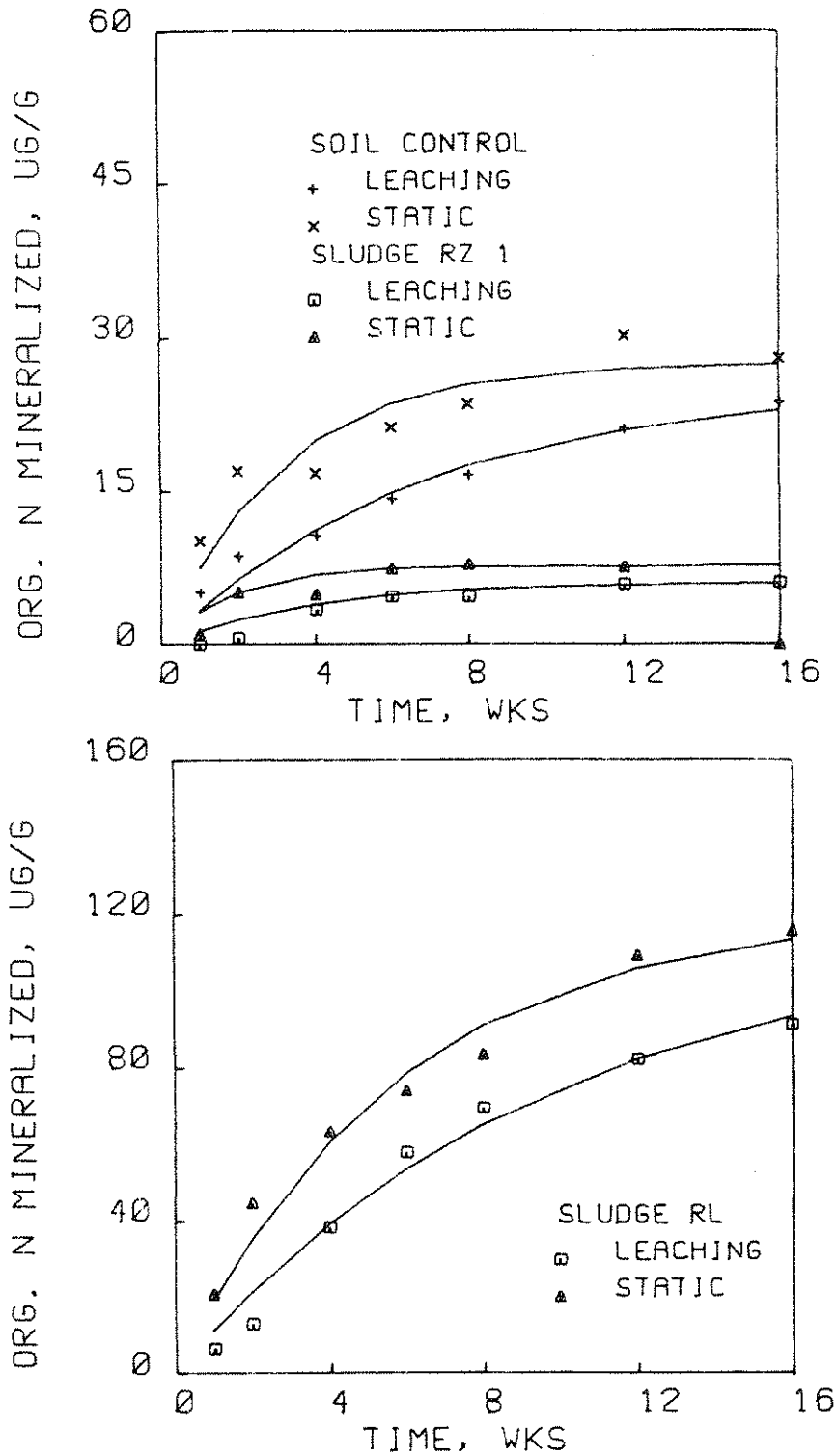


Figure 3.2. Comparison of N mineralized in Fincastle soil control and in Fincastle soil amended with raw plus Zimpro treated sludge from Grand Rapids, MI. (RZ 1) and raw plus CaO sludge from Blue Plains, D.C. (RL). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

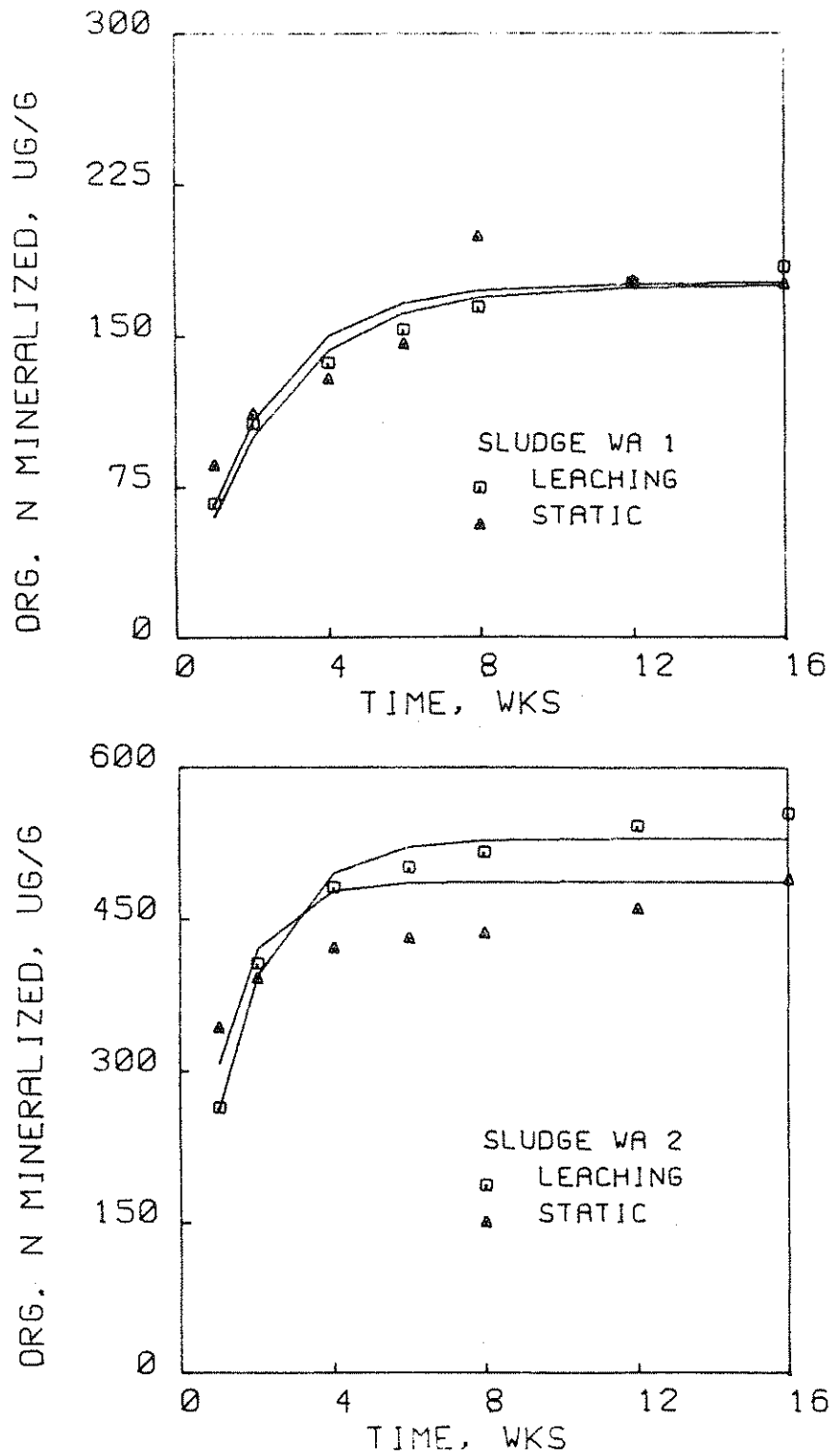


Figure 3.3. Comparison of N mineralized in Fincastle soil amended with waste activated sludges from Chicago, IL (WA 1) and Seattle, WA (WA 2). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

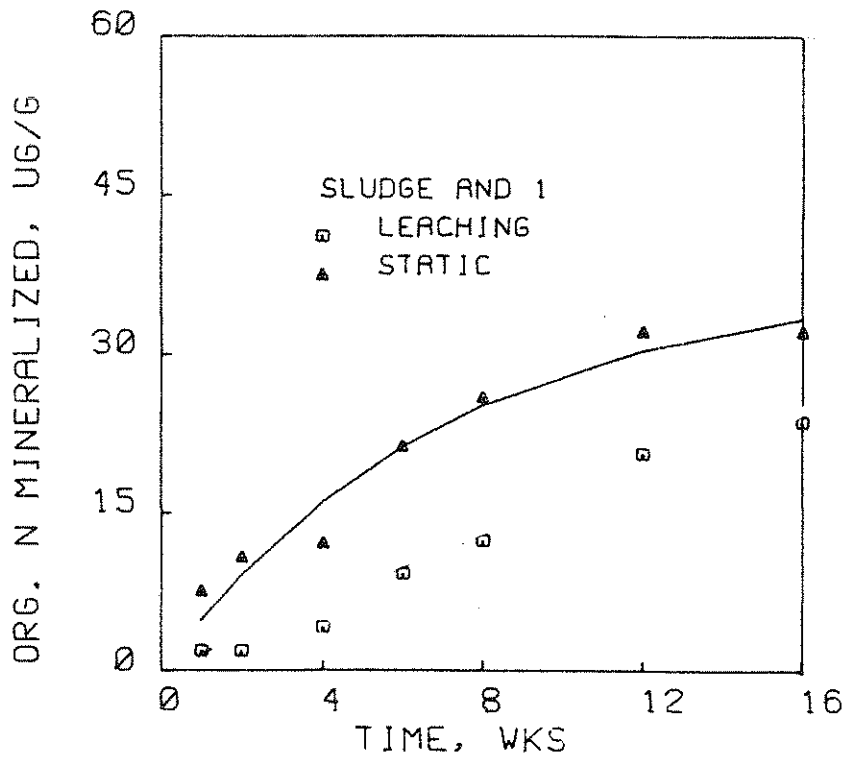
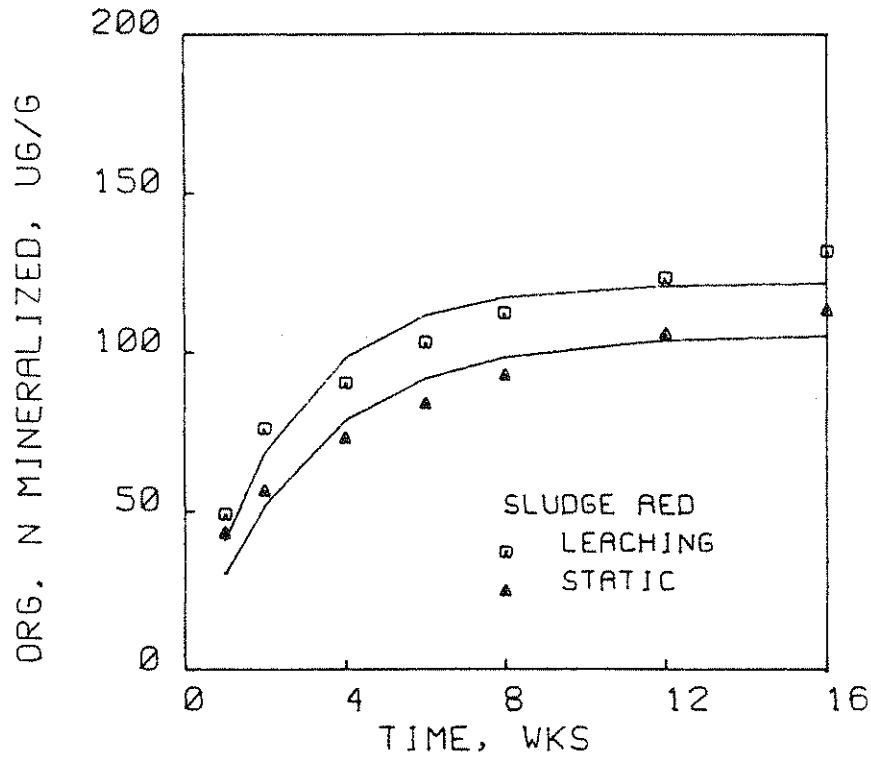


Figure 3.4. Comparison of N mineralized in Fincastle soil amended with aerobically digested sludge from Medina, OH (AeD) and anaerobically digested sludge from Anderson, IN (AND 1). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

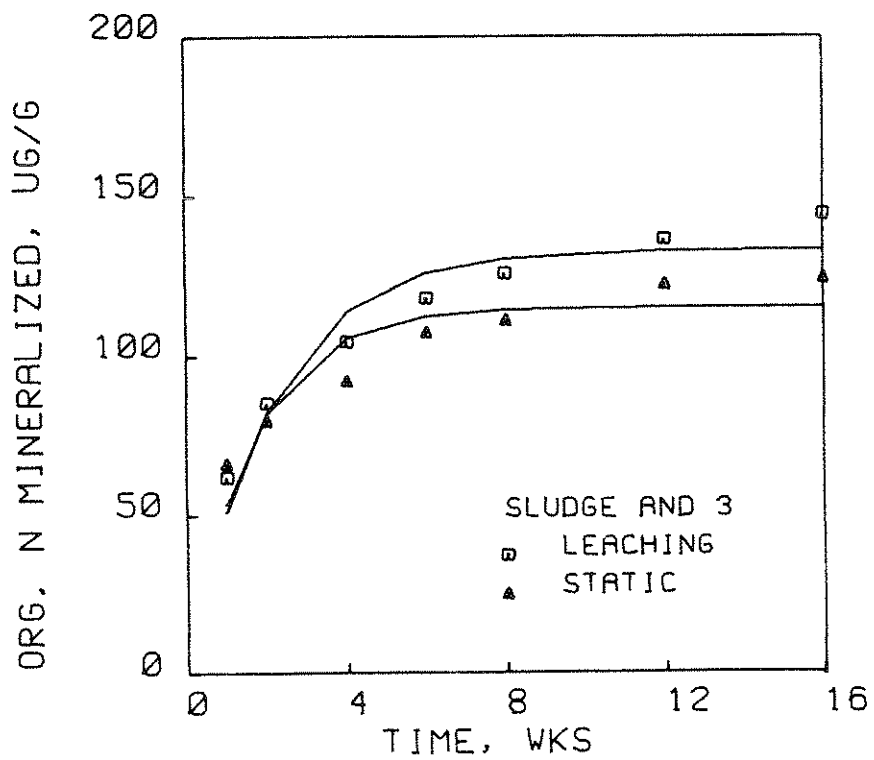
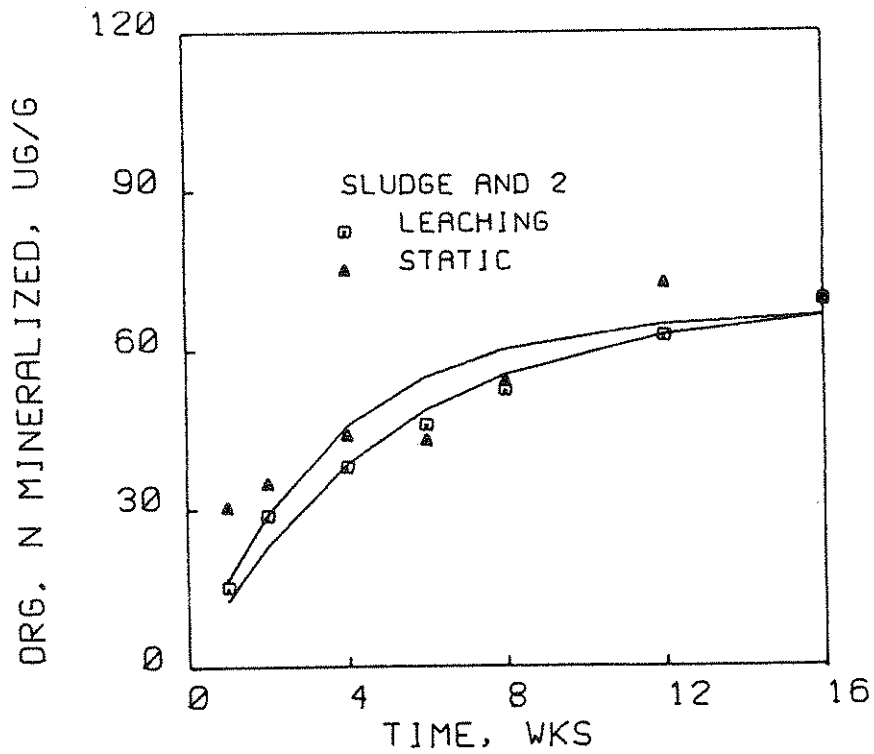


Figure 3.5. Comparison of N mineralized in Fincastle soil amended with anaerobically digested sludges from Baltimore, MD (AND 2) and Chicago, IL (AND 3). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

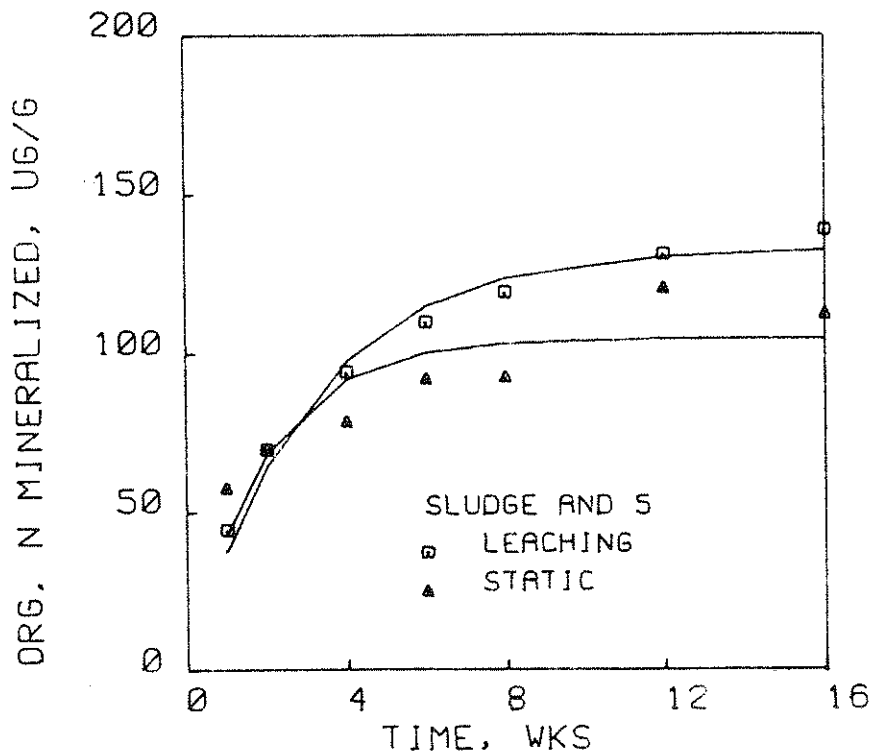
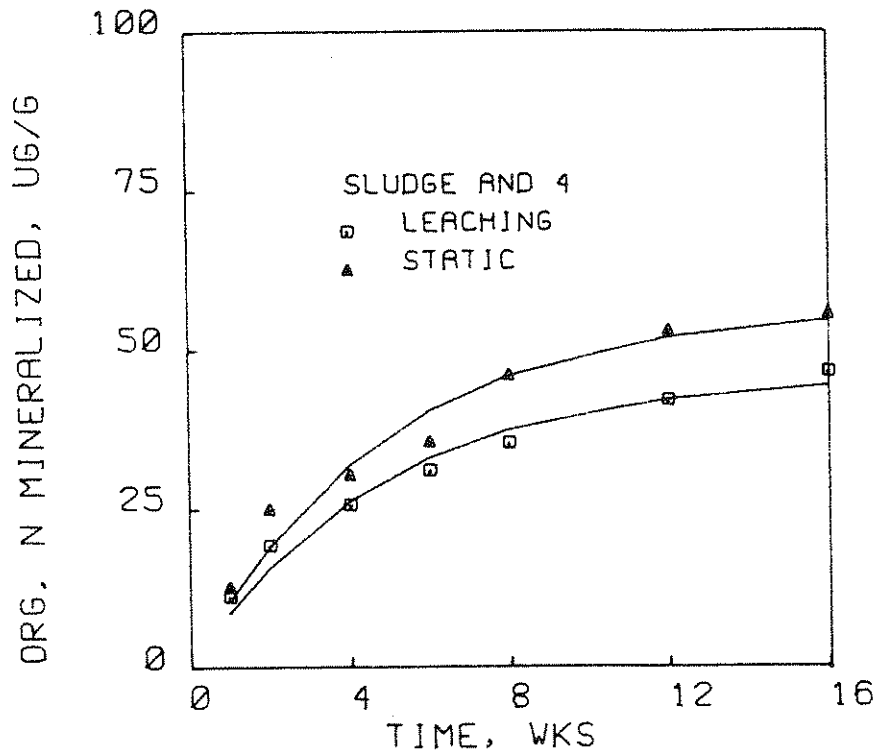


Figure 3.6. Comparison of N mineralized in Fincastle soil amended with anaerobically digested sludges from Chicago, IL (AND 4) and Columbus, OH (AND 5). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

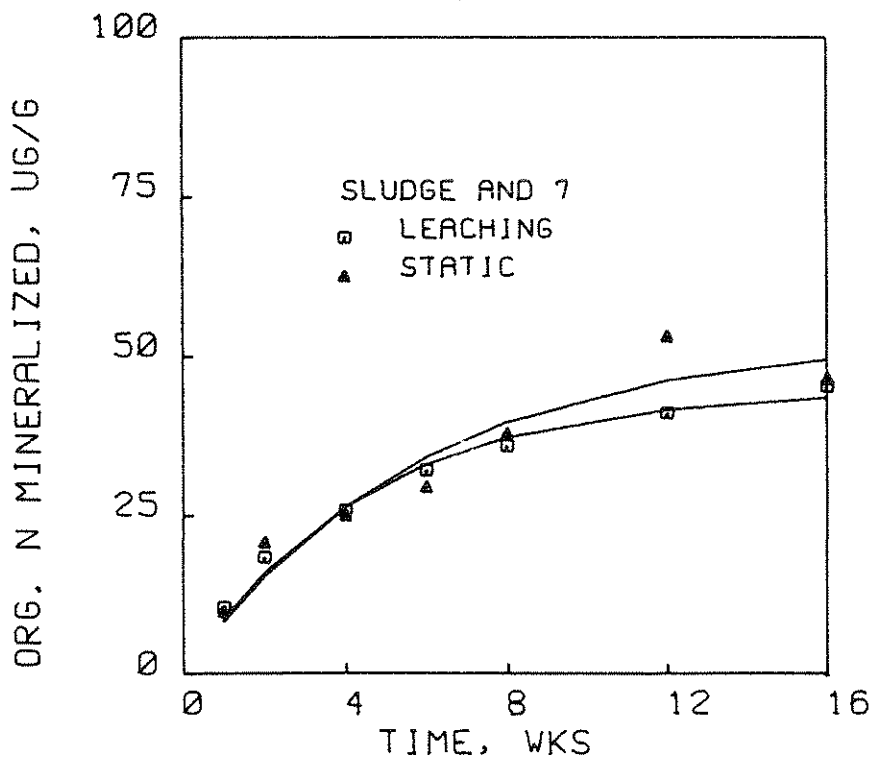
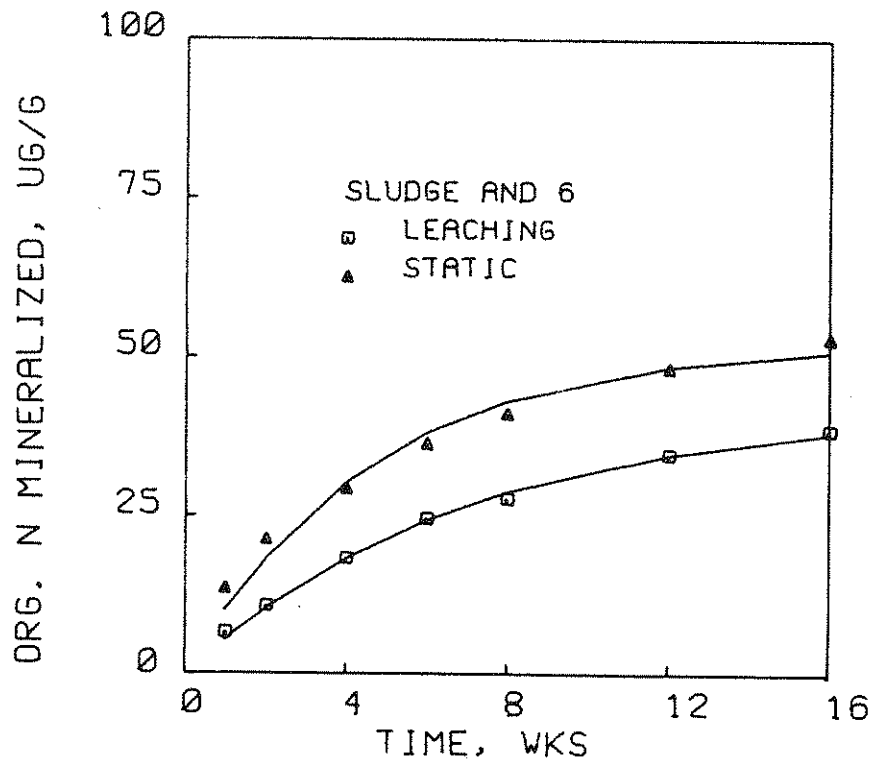


Figure 3.7. Comparison of N mineralized in Fincastle soil amended with anaerobically digested sludges from Frankfort, IN (AND 6) and Glenwood Springs, CO (AND 7). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

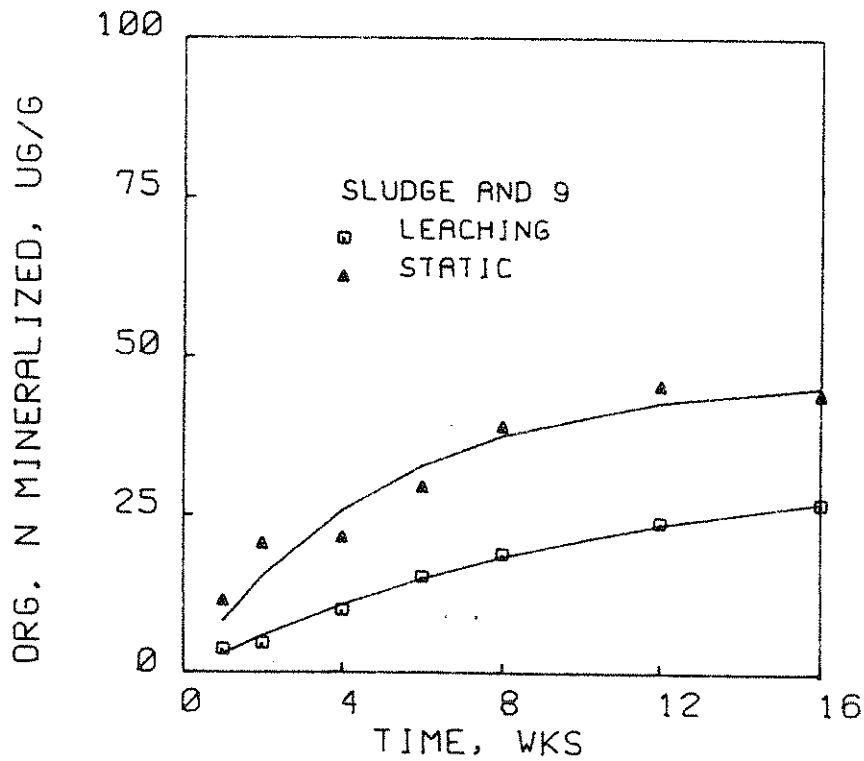
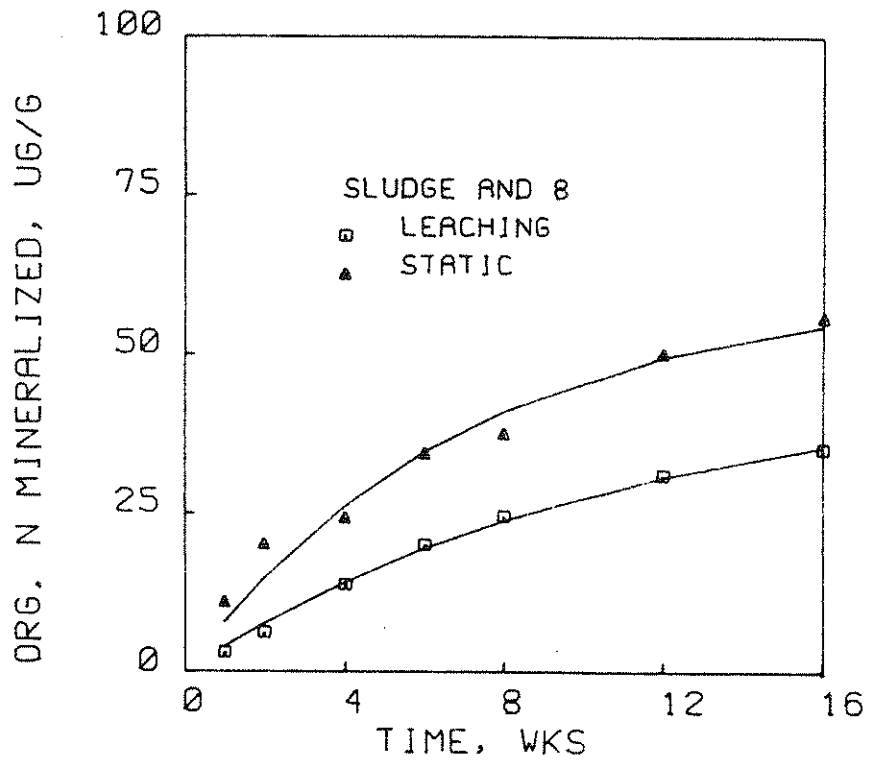


Figure 3.8. Comparison of N mineralized in Fincastle soil amended with anaerobically digested sludges from Grand Rapids, MI (AND 8) and Marion, IN (AND 9). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

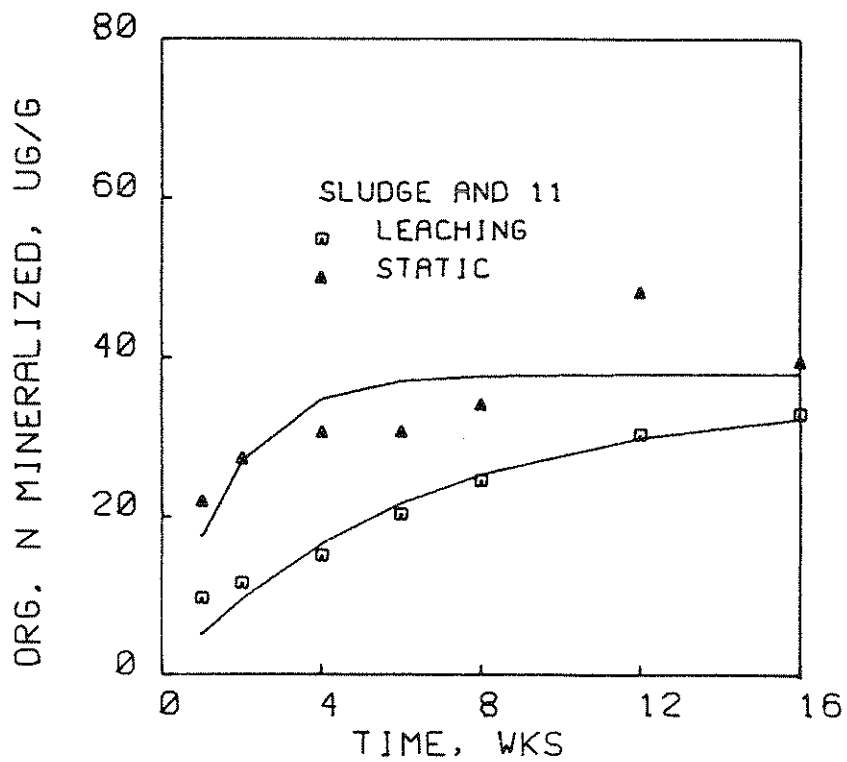
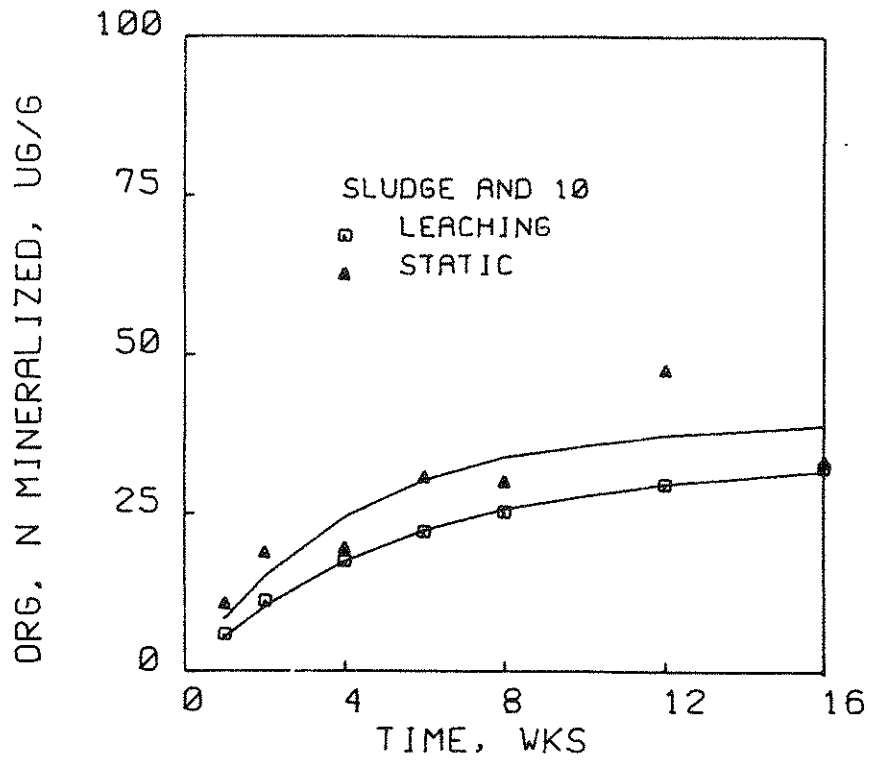


Figure 3.9. Comparison of N mineralized in Fincastle soil amended with anaerobically digested sludges from Tucson, AZ (AND 10) and Waukesha, WI (AND 11). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

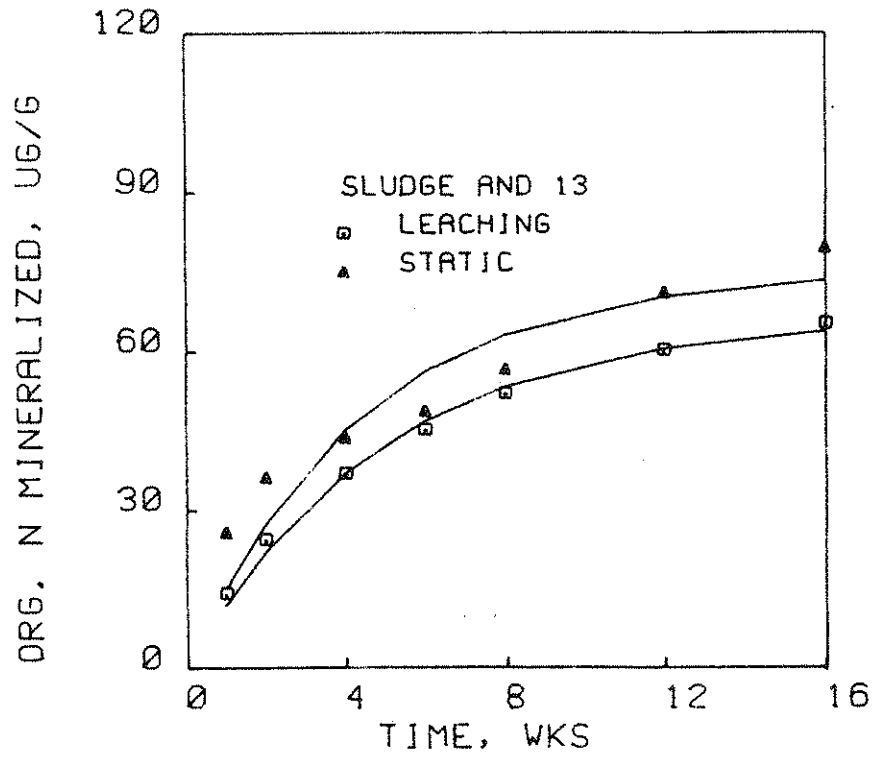
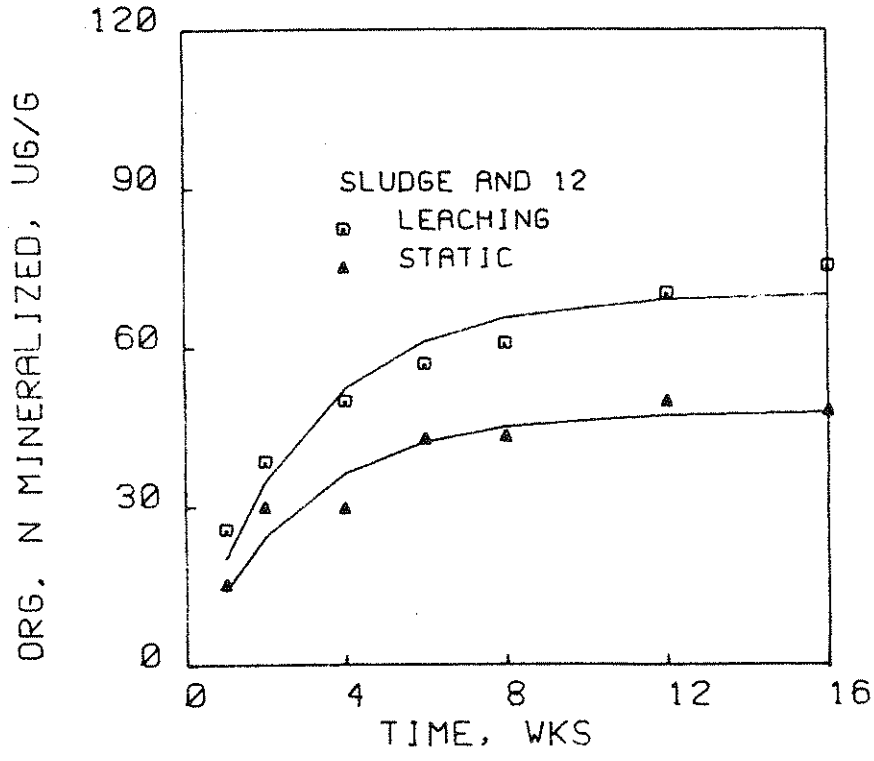


Figure 3.10. Comparison of N mineralized in Finncastle soil amended with anaerobically digested sludge from Wisconsin Rapids, WI (AND 12) and Zanesville, OH (AND 13). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

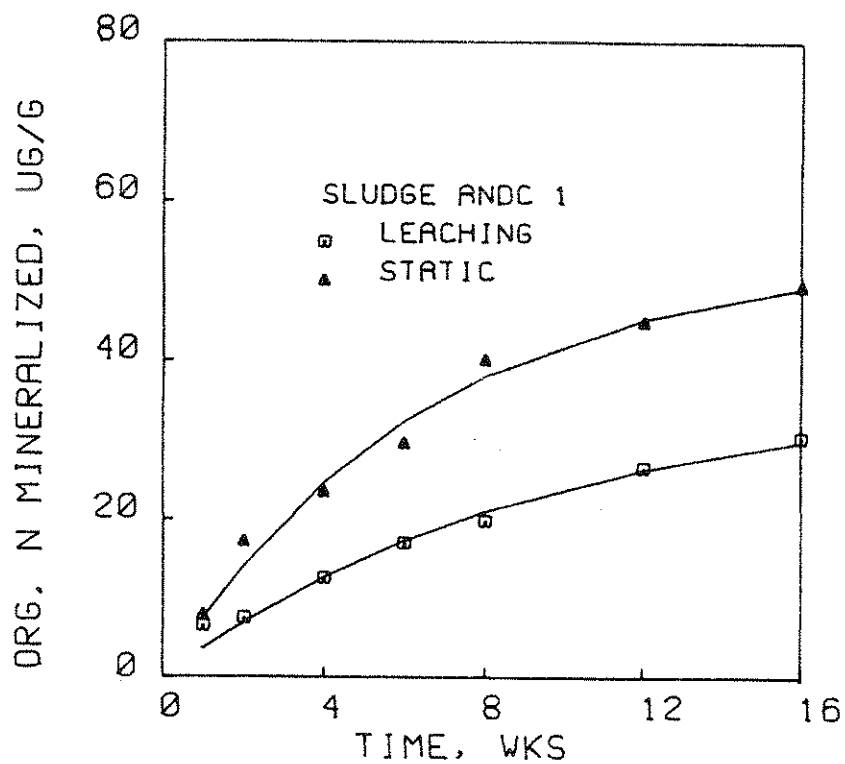
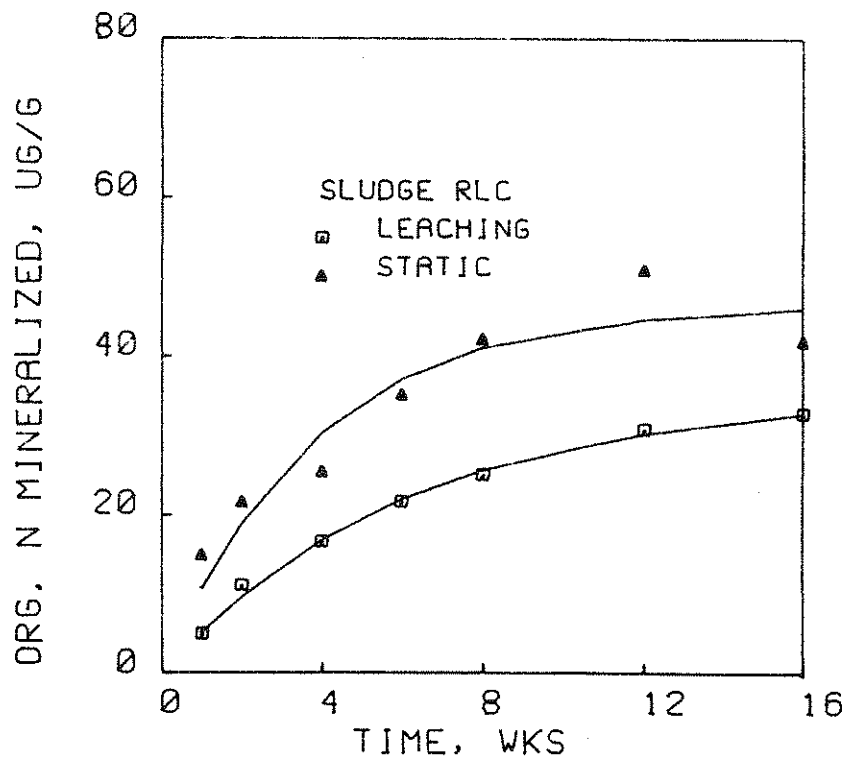


Figure 3.11. Comparison of N mineralized in Fincastle soil amended with composted sewage sludges from Blue Plains, DC (RLC) and Baltimore, MD (ANDC 1). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

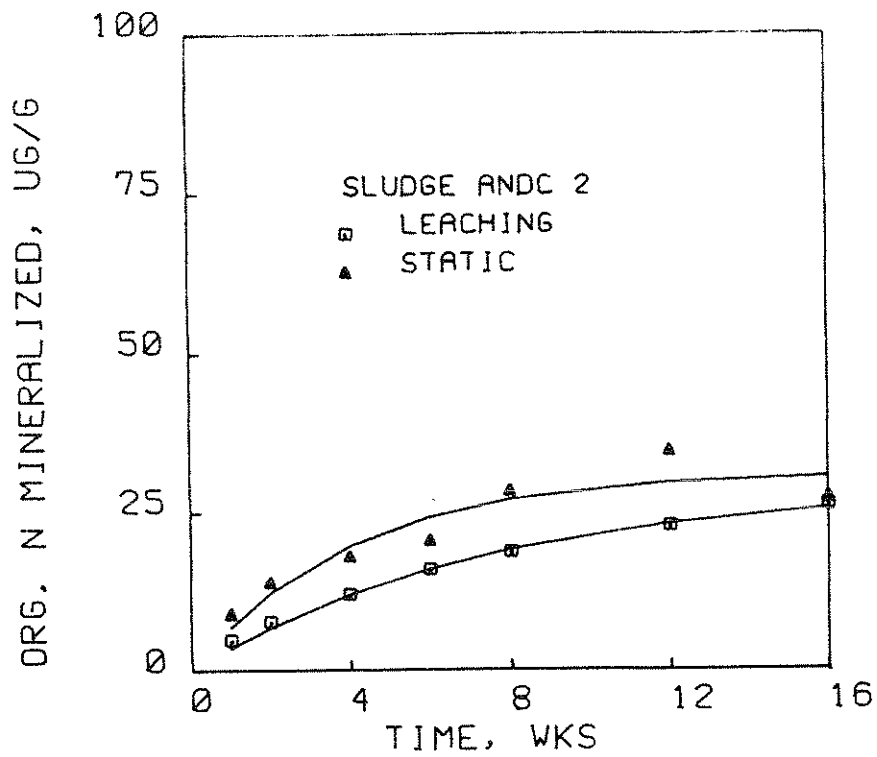


Figure 3.12. Comparison of N mineralized in Fincastle soil amended with composted sewage sludge from Los Angeles, CA (ANDC 2). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

actual values shown in Table 3.3 if the control is added to the sludge treatment values.

Decomposition of Organic C

The static incubation system also allowed an evaluation of organic C decomposition in the Fincastle soil amended with sewage sludge. The amounts of CO₂ evolved are shown in Table 3.6 and in Figures 3.13 to 3.18. The nonlinear least squares regression technique was also applied to the CO₂ evolution data to compute first-order rate constants. The rate constants for CO₂ evolution ranged from 0.210 to 0.739 week⁻¹. Decomposition of organic C was overestimated for sludges RL, AnD 1, AnD 9, RLC and AnDC 1 due to the presence of appreciable inorganic C (primarily Ca and Mg carbonates). As shown in Table 3.6, in excess of 50% of the CO₂ liberated was evolved during the initial 30 days of incubation. Even though first-order kinetics adequately describe the decomposition of sludge organic C, the release of CO₂ after 57 days may be nearly a zero-order process. These data indicate that a single rather multiple first-order equations may be appropriate to predict decomposition of sludge organic C (e.g., Gilmour and Gilmour, 1980).

A comparison of organic C and N mineralization is presented in Table 3.7. For most sludges, the ratio of C mineralized to N mineralized is greater than 1. Sludge RZ 1 showed marked N immobilization but significant amounts of organic C decomposition. This sludge possessed a C/N of 24.3/1 which was responsible for N immobilization. Excluding the sludges containing inorganic C, from 1.5 to 61% of the sludge organic C was decomposed during a 16 week incubation period. As was shown for N mineralization, organic C decomposition was greatest in the primary and waste activated sludges. The decomposition data obtained are consistent with other studies reported in the literature. It must be realized that these calculation assume that sludge addition does not enhance decomposition of soil organic C.

Prediction of N Mineralization

Two different chemical extractants were evaluated to predict the amount of mineralizable N contained in sludges. The first method involved determining the NH₄⁺ released from sludge during autoclaving in 0.01M CaCl₂. The results obtained suggest that from 2.7 to 13.5% of sludge organic N is recovered as NH₄⁺-N after autoclaving (Table 3.8). For most sludges, autoclaving removed 4 to 5% of the organic N. The second procedure measured the amount of NH₄⁺ released from sludge organic N by treatment with 1N H₂SO₄ containing either 0.1N or 0.5N KMnO₄. The NH₄⁺ released by 1N H₂SO₄ + 0.1N KMnO₄ was similar to that recovered by autoclaving (i.e., 2.5 to 7.7% of the N₀). Increasing the concentration of KMnO₄ from 0.1 to 0.5N essentially doubled the amount of NH₄⁺ released. By comparing the percentages shown in Tables 3.3 and 3.8, it is obvious that the amounts of N mineralized from sludge N₀ during incubation in soil cover a significantly wider range than those values obtained by the chemical extractants studied.

Simple correlation analysis was conducted to evaluate the relationships between various parameters of N mineralization (Table 3.9). As expected, the concentrations of Organic C and N in sludges were significantly correlated (r = 0.73). Similar results were obtained by the static and leaching procedures as shown by correlation coefficients for µg N mineralized/g soil (r = 0.991), for N mineralized as a percentage of sludge organic N (r = 0.901), and for the first-order rate constant (r = 0.759). The chemical extractants (autoclaving and H₂SO₄ + KMnO₄) for estimating mineralizable N in sludges yielded correlation coefficients ranging from 0.504 to 0.605 for the static incubation procedure and from 0.550 to 0.815 for the leaching incubation technique. In contrast, correlations between the organic N content of the sludge and N mineralization were 0.922 and 0.906 for the static and leaching procedures, respectively. However, these correlations were decreased by 0.07 to 0.15 if N₀ mineralization was expressed as a percentage of the organic N present. There-

fore, the total organic N content of sludge was a better predictor of mineralizable N in sludges than inorganic N released by either autoclaving or extraction with $H_2SO_4 + KMnO_4$.

Summary

The amount of mineralizable N_0 in sewage sludge was proportional to the total organic N content. During sewage sludge treatment processes, it is likely that the same types of N mineralization processes are occurring as after incorporation into soil. The anaerobic digestion or composting of primary, raw or waste activated sludges results in reduced organic N levels and thus decreased amounts of potentially mineralizable N. This generalization is not true for sludges treated by a wet-air oxidation process since immobilization rather than mineralization of N occurred during soil incubations. It appears that the potential for N immobilization is greatest when the overall C/N ratio of the sludge exceeds 20/1.

The kinetics of both C and N mineralization were described by a single first-order rate equation. The rate constants for N mineralization obtained in this study are comparable to those presented in the literature. As expected, the addition to soil of sludge containing mineralizable N_0 resulted in increased rate constants.

A comparison of N_0 mineralization for the static and leaching incubation procedures indicated that the static method generally yielded more accurate values. This was caused by the removal of soluble organic N during leaching of sludge-soil mixtures with 0.01M $CaCl_2$. Since the organic N lost could have been decomposed in a subsequent incubation period, the leaching procedure will underestimate the amount of mineralizable N in many sludges. In addition, the static incubation procedure is preferred because it is easier to set-up, requires less glassware, and involves only periodic subsampling of a soil-sludge mixture rather than leaching samples under a constant vacuum.

Current guidelines used to calculate the amounts of sewage sludge applied to agricultural

crops assume that 20 to 25% of the organic N is mineralized during the first year after application (e.g., Sommers et al., 1980). The results of this study demonstrate the need to use a different N mineralization percentages for various sludge types. Realizing that a limited number of sludges were studied and that the incubations were conducted in the laboratory under optimum conditions, the following N mineralization percentages should be used to calculate the appropriate sludge application rate for agronomic crops: raw and primary sludges, 25%; waste activated sludges, 40%; anaerobically digested sludges, 15%; and composed sludges, 8%. Sludges treated with a wet-air oxidation process should be evaluated for N mineralization by a static incubation method prior to calculating a sludge application rate because of the potential for N immobilization.

A simple procedure to determine the mineralization of N in sludge amended soils would be to utilize a soil-sand-sludge mixture as described by Bremner (1965). In this procedure, 30-g of silica sand are mixed with 10-g of soil and 6-ml of H_2O are added to adjust the moisture content. The addition of sand to the soil enables the attainment of optimum water relations in all soil textures and eliminates the need to determine the water holding capacity of each soil studied. The amount of sludge added should be within the 15 to 40 metric ton/ha range to approximate a realistic rate of sludge application for crop production. The difference in inorganic N at time 0 and 16 weeks would approximate the amount of N_0 mineralization expected during the first year after sludge application. Unfortunately, a chemical extractant has not been developed which accurately predicts the amount of potentially mineralizable N in sewage sludge.

Table 3.6. Carbon Dioxide evolution from soil-sludge mixtures.

Sludge Added (See Table 3.1)	Cumulative CO ₂ - C evolved for an incubation period of, days								Rate Constant ⁺ week ⁻¹
	2	5	8	15	30	57	87	112	
	----- µg/g -----								
P	465	904	1226	1644	2045	2274	2454	2564	0.580
PWA	236	1131	1646	2135	2490	2752	2935	3086	0.632
RL	264	669	1022	1379	1715	1923	2115	225	0.503
RZ 1	155	378	563	845	1235	1607	1955	2138	0.217
RZ 2	193	368	513	704	869	1120	1291	1407	0.342
WA 1	244	705	964	1242	1534	1734	1908	2033	0.545
WA 2	287	1506	1978	2472	2838	3076	3274	3445	0.739
AeD	168	375	488	644	818	931	1051	1135	0.488
AnD 1	137	211	260	333	477	620	779	910	0.212
AnD 2	131	305	462	617	822	1019	1181	1292	0.322
AnD 3	156	392	549	733	952	1147	1291	1389	0.395
AnD 4	82	173	242	323	457	576	693	791	0.251
AnD 5	172	408	562	744	1017	1247	1442	1575	0.330
AnD 6	81	160	205	277	391	483	573	677	0.263
AnD 7	117	217	287	390	531	664	778	841	0.314
AnD 8	147	254	337	440	590	733	844	931	0.343
AnD 9	176	273	349	417	531	636	723	795	0.488
AnD 10	46	116	167	232	321	397	517	592	0.210
AnD 11	217	317	399	490	670	848	983	1148	0.313
AnD 12	68	126	219	325	405	521	614	692	0.274
AnD 13	196	354	442	565	749	892	1036	1106	0.413
RLC	141	257	354	489	637	734	845	924	0.408
AnDC 1	75	165	215	290	398	482	572	670	0.289
AnDC 2	68	123	167	216	308	405	492	556	0.232
none	35	92	136	254	338	386	470	534	0.270

⁺ First order rate constant obtained from non-linear least squares regression.

Table 3.7. Relationships between C and N mineralization in soil-sludge mixtures from the static incubation system.

Sludge Type (See Table 3.1)	Sludge C/N	Mineralization of sludge ⁺		Ratio of C mineralized to N mineralized
		Org. C	Org. N	
-- % of added ---				
P	6.74	51.4	16.0	3.21
PWA	8.03	51.4	42.1	1.22
RL	9.45	56.3 [‡]	27.9	2.02
RZ 1	24.33	34.6	0	--
RZ 2	18.95	18.8	5.5	3.42
WA 1	7.39	37.6	33.1	1.14
WA 2	5.03	61.0	51.1	1.19
AeD	6.90	25.2	25.0	1.01
AnD 1	21.18	16.5 [‡]	2.1	7.86
AnD 2	9.93	23.1	13.7	1.69
AnD 3	8.18	24.6	23.5	1.05
AnD 4	10.16	10.6	11.6	0.91
AnD 5	9.66	27.7	24.9	1.11
AnD 6	9.91	9.8	16.5	0.59
AnD 7	10.89	10.9	9.2	1.18
AnD 8	11.54	19.4	15.2	1.28
AnD 9	14.91	25.9 [‡]	23.1	1.12
AnD 10	10.14	3.4	12.1	0.28
AnD 11	12.50	16.5	6.8	2.43
AnD 12	9.20	7.3	8.8	0.83
AnD 13	10.16	30.2	26.7	1.13
RLC	12.71	14.6 [‡]	9.4	1.55
AnDC 1	14.21	5.1 [‡]	12.0	0.43
AnDC 2	19.24	1.5	4.5	0.33

⁺ [(C or N mineralized in sludge treated soil - C or N mineralized in control) ÷ C or N added] x 100.

[‡] Organic C decomposition overestimated because of CaCO₃ dissolution.

Table 3.8. Amounts of NH_4^+ -N released from sewage sludges by autoclaving in 0.01M CaCl_2 and oxidizing with 0.1N and 0.5N KMnO_4 in 1N H_2SO_4

Sludge (See Table 3.1)	NH_4^+ -N released by					
	Autoclaving in 0.01M CaCl_2		1N H_2SO_4 + 0.1N KMnO_4		1N H_2SO_4 + 0.5N KMnO_4	
	$\mu\text{g/g}$	% ⁺	$\mu\text{g/g}$	% ⁺	$\mu\text{g/g}$	% ⁺
P	1466	3.5	1042	2.5	2420	5.7
PWA	1500	3.4	1120	2.5	2162	4.9
RL	692	3.0	789	3.4	1471	6.3
RZ 1	379	2.9	857	6.5	1802	13.7
RZ 2	526	3.0	984	5.7	2075	11.9
WA 1	2309	6.0	798	2.1	1899	4.9
WA 2	2514	3.7	1463	2.1	2914	4.3
AeD	1150	4.6	1118	4.4	2055	8.2
AnD 1	467	6.4	196	2.7	527	7.2
AnD 2	1433	6.1	663	2.8	1345	5.7
AnD 3	1686	5.6	692	2.3	1686	5.6
AnD 4	750	4.5	516	3.1	1120	6.8
AnD 5	1374	5.0	750	2.7	1618	5.9
AnD 6	429	4.1	410	3.9	1004	9.6
AnD 7	1062	5.6	691	3.7	1558	8.2
AnD 8	526	4.1	377	2.9	897	7.0
AnD 9	137	2.7	205	4.1	498	9.9
AnD 10	701	6.5	837	7.7	1451	13.4
AnD 11	857	4.3	662	3.3	1295	6.4
AnD 12	2291	13.5	544	3.2	1179	7.0
AnD 13	604	4.3	468	3.3	800	5.7
RLC	750	4.9	1100	7.1	2299	14.9
AnDC 1	516	3.9	721	5.5	1501	11.5
AnDC 2	673	9.3	525	7.3	884	12.2

⁺ Percent of sludge organic N released as NH_4^+ -N.

Table 3.9. Correlation coefficients (r) between sludge characteristics and N mineralization parameters.

FACTOR	1	2	3	4	5	6	7	8	9	10	11
1. Organic C, %	1.00	.734	.656	.469*	.624	.636	.566	.503*	.493*	.713	.769
2. Organic N (No), %		1.00	.922	.772	.699	.906	.833	.756*	.794	.745	.785
3. Static, µg Nm/g			1.00	.879	.810	.991	.881	.789	.684	.672	.667*
4. Static, Nm as % No				1.00	.680	.857	.901	.684	.528	.504*	.483*
5. Static, k					1.00	.843	.792	.754	.605	.508*	.504*
6. Leach, µg Nm/g						1.00	.904	.846	.716	.661	.652
7. Leach, Nm as % No							1.00	.889	.756	.581	.564*
8. Leach, k								1.00	.815	.543*	.550*
9. 0.01M CaCl ₂ , µg NH ₄ ⁺ -N/g sludge									1.00	.493*	.552
10. 0.1N KMnO ₄ , " "										1.00	.969
11. 0.5N KMnO ₄ , " "											1.00

* Significant at p= 0.05; all other correlations significant at p = 0.01.

+ µg Nm/g - µg N mineralized/g soil-sludge mixture in static or leaching incubation procedure; Nm as % No - percentage of sludge organic N mineralized in soil for static or leaching incubation procedure;

k - first order rate constant for N mineralization in static or leaching incubation procedure.

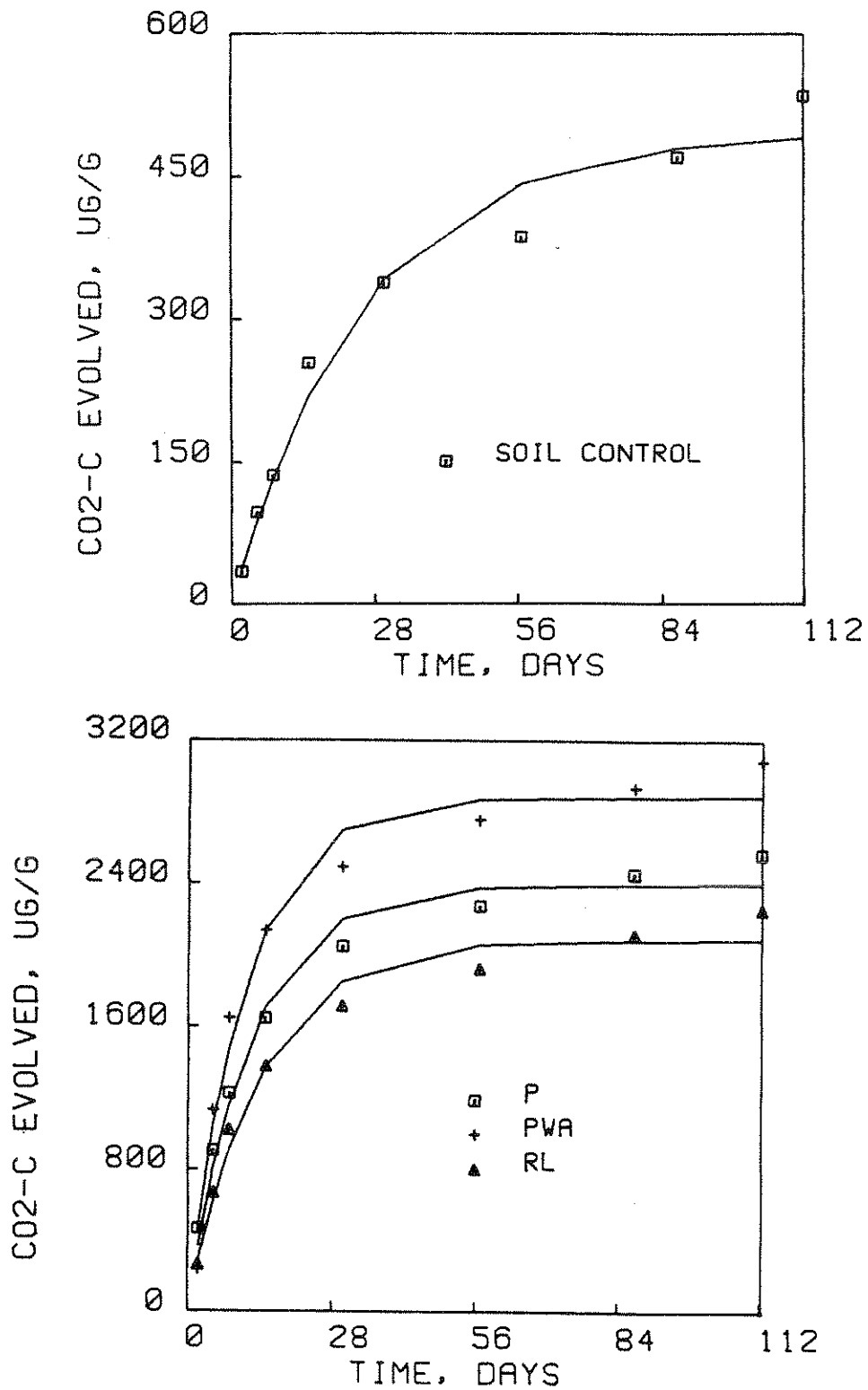


Figure 3.13. Carbon dioxide evolution from Fincastle soil control and Fincastle soil amended with primary sludge from Grand Haven, MI (P), primary plus waste activated sludge from Seattle, WA (PWA) and Raw plus CaO sludge from Blue Plains, D.C. (RLC). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

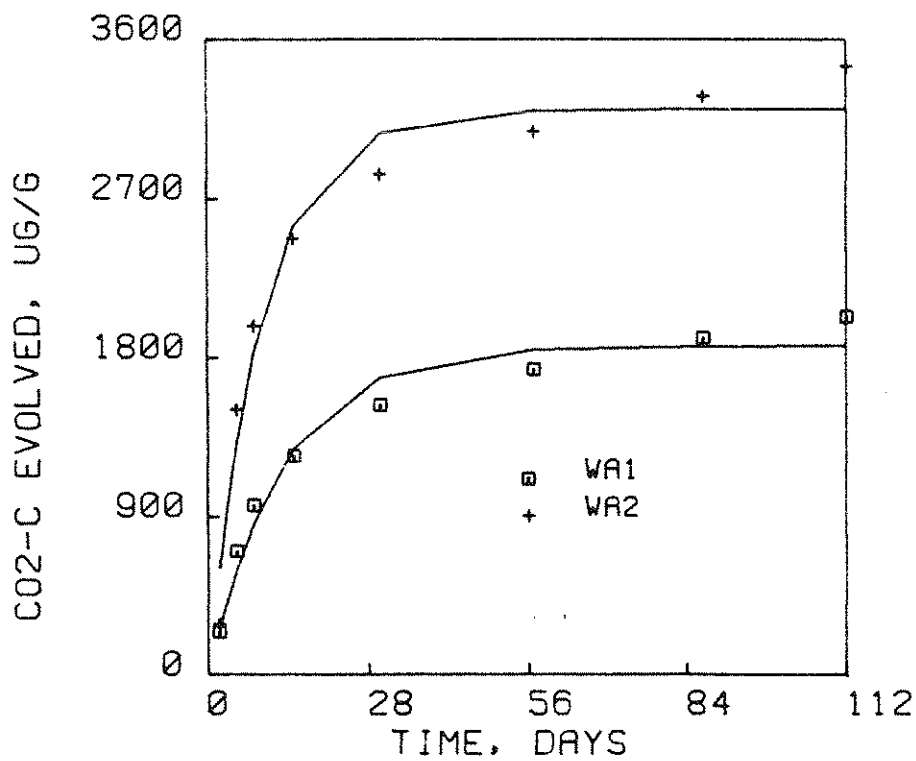
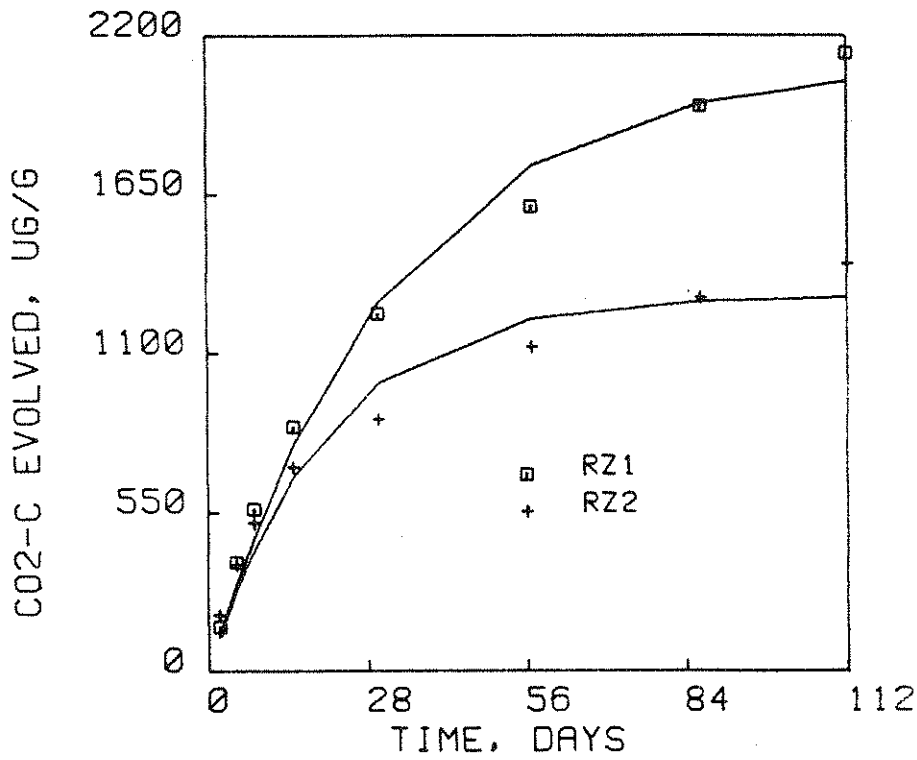


Figure 3.14. Carbon dioxide evolution from Fincastle soil amended with raw and Zimpro treated sludges from Grand Rapids, MI (RZ 1) and Oshkosh, WI (RZ 2) and waste activated sludges from Chicago, IL (WA 1) and Seattle, WA (WA 2). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

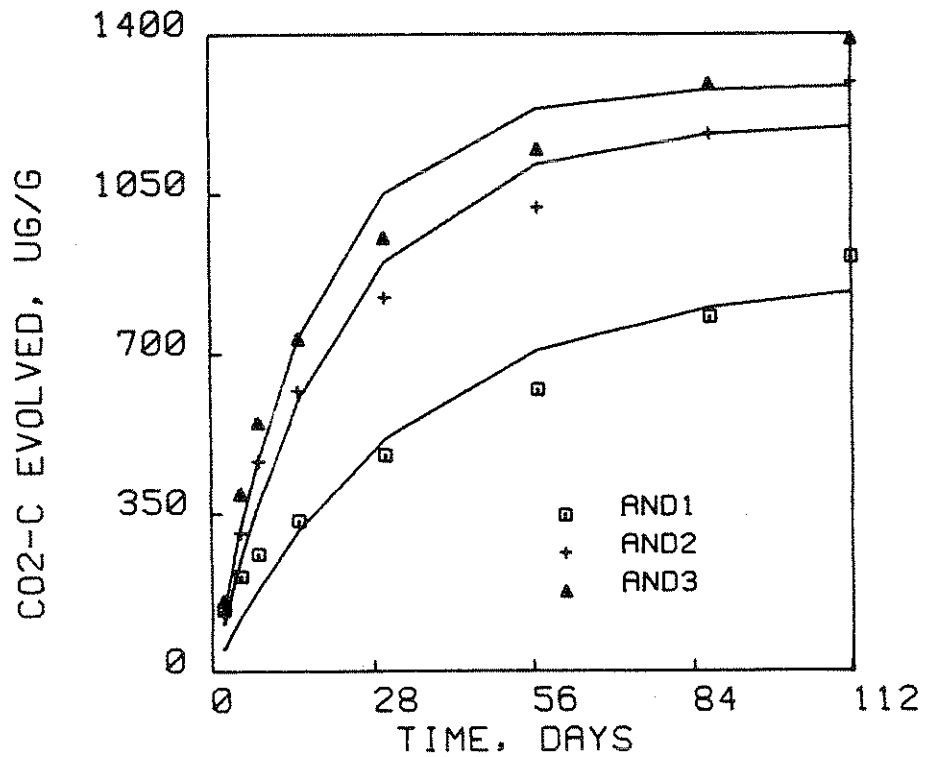
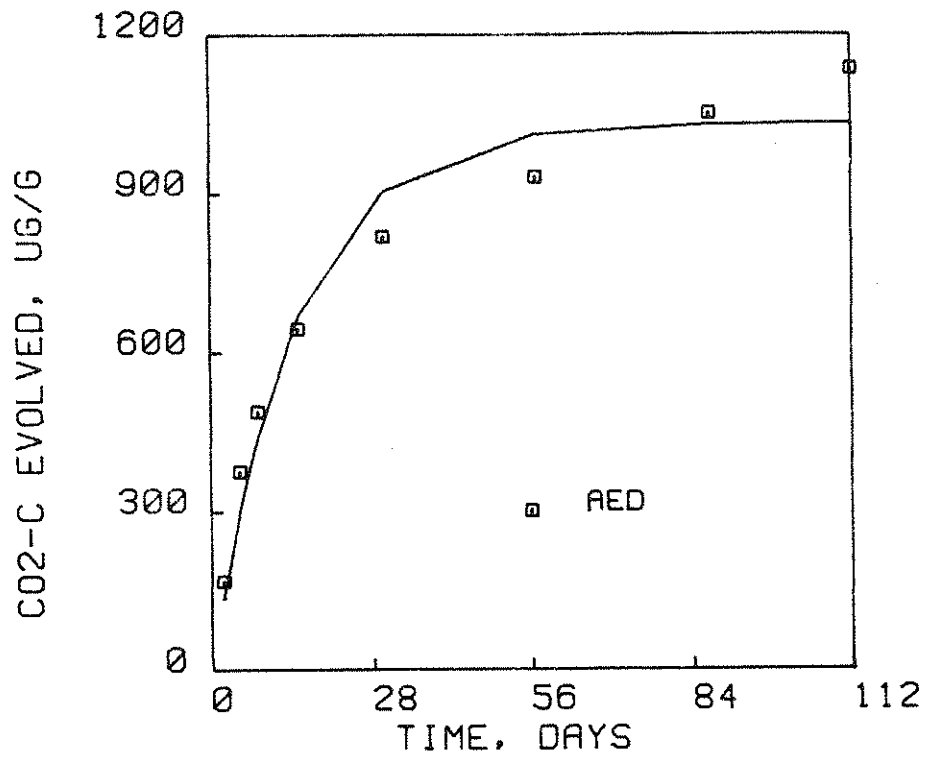


Figure 3.15. Carbon dioxide evolution from Fincastle soil amended with aerobically digested sludge from Medina, OH (AeD) and anaerobically digested sludges from Anderson, IN(AND 1), Baltimore, MD(AND 2), and Chicago, IL(AND 3). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

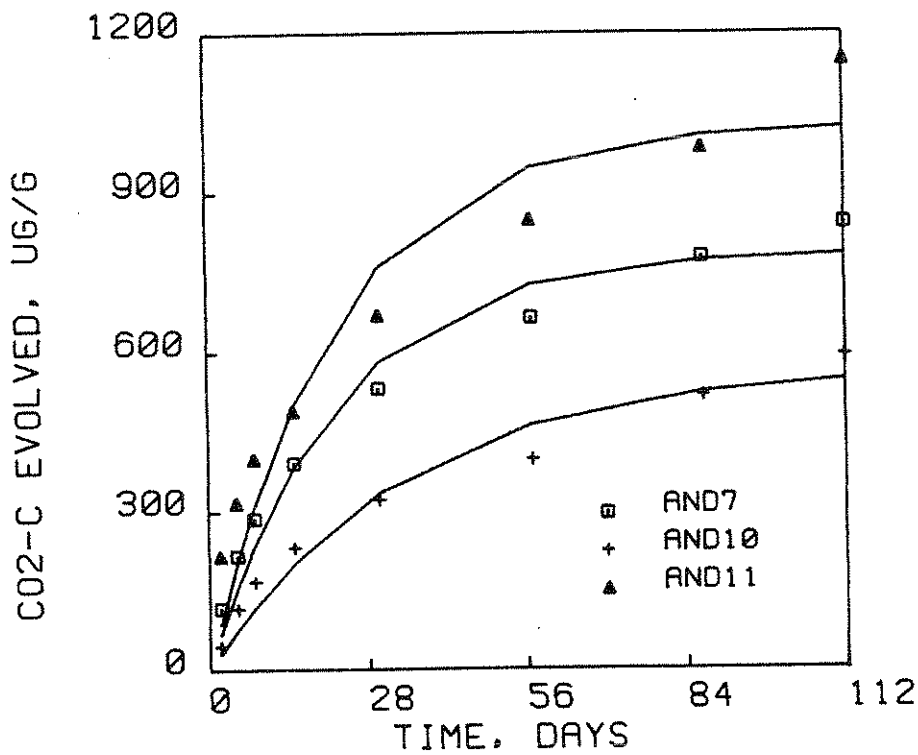
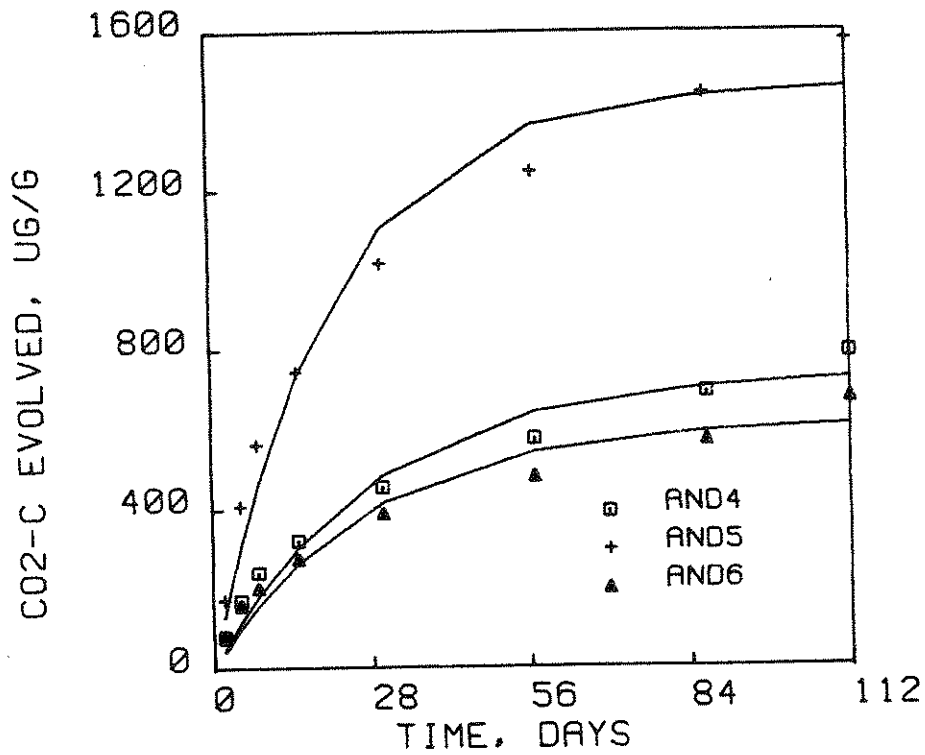


Figure 3.16. Carbon dioxide evolution from Fincastle soil amended with anaerobically digested sludges from Chicago, IL(AND 4), Columbus, OH(AND 5), Frankfort, IN(AND 6), Glenwood Springs, CO(AND 7), Tucson, AZ(AND 10), and Waukesha, WI(AND 11). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

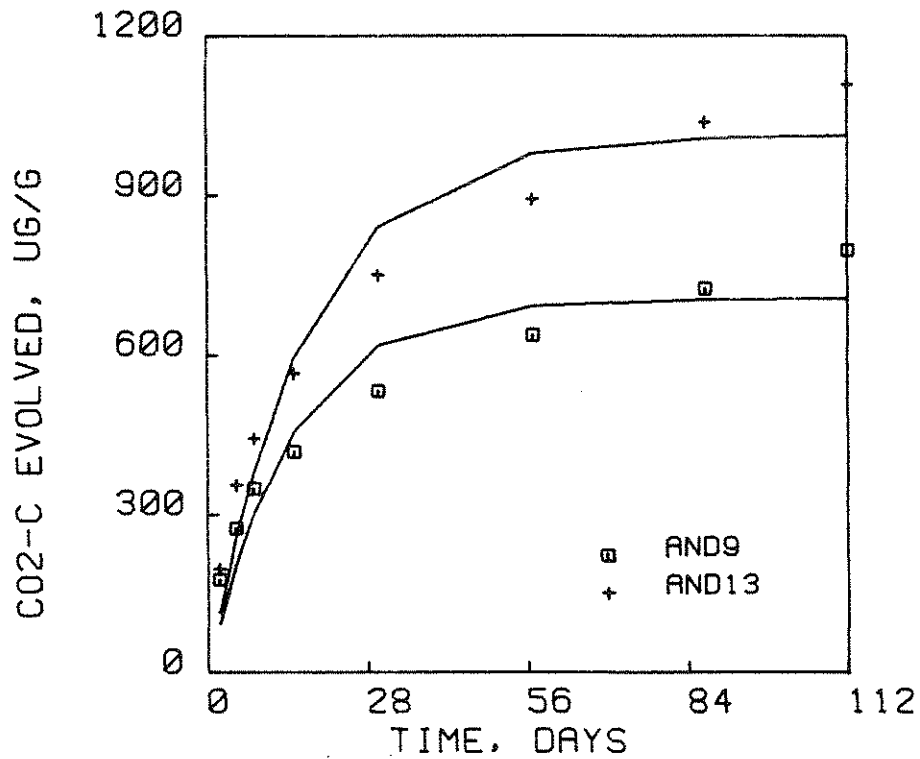
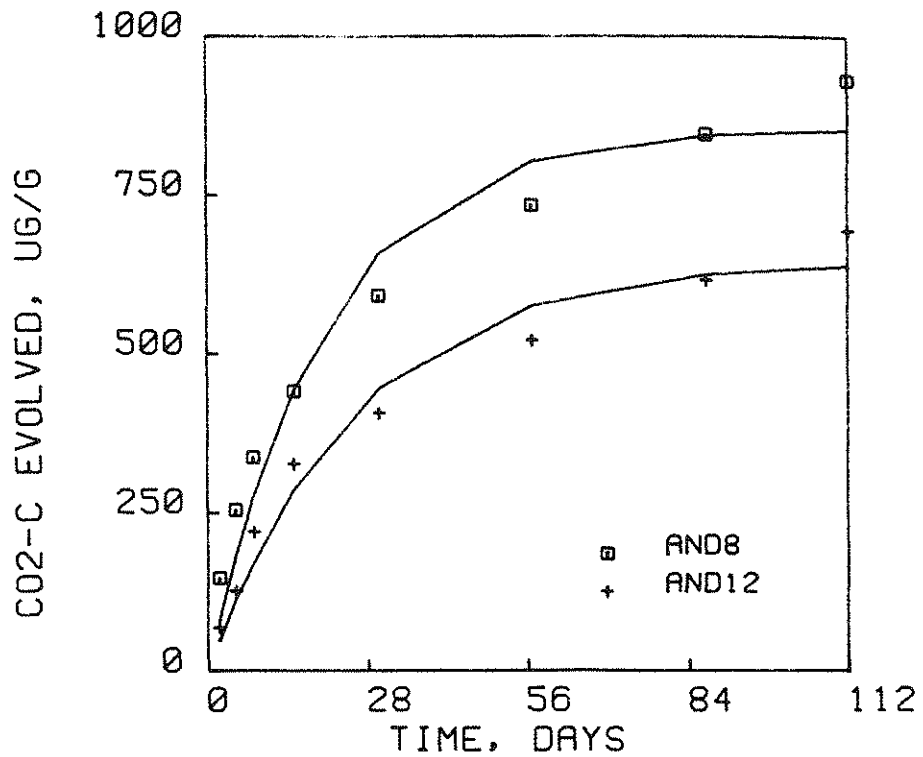


Figure 3.17. Carbon dioxide evolution from Fincastle soil amended with anaerobically digested sludges from Grand Rapids, MI (AND 8), Wisconsin Rapids, MI(AND 12), Marion, IN (AND 9), and Zanesville, OH(AND 13). Solid line was calculated from non-linear least squares regression assuming first order kinetics.

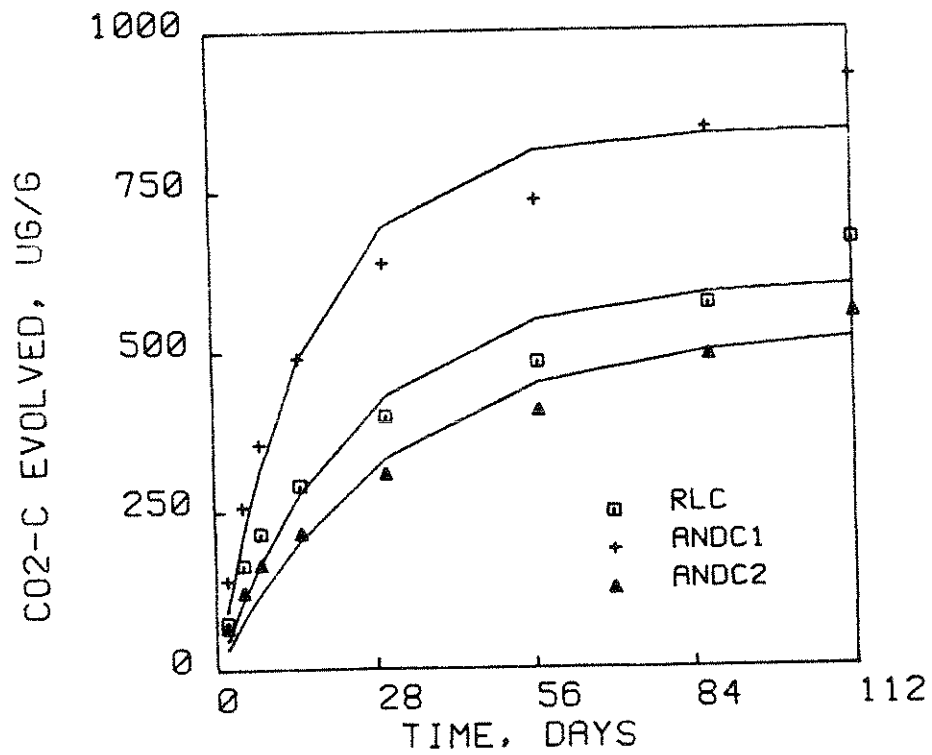


Figure 3.18. Carbon dioxide evolution from Fincastle soil amended with raw plus CaO and composted sludge from Blue Plains, DC (RLC) and anaerobically digested and composted sludges from Baltimore, MD (ANDC 1), and Los Angeles, CA (ANDC 2). Solid line was calculated from non-linear least squares regression assuming first-order kinetics.

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