

EFFECT OF AMMONIUM AND PHOSPHOROUS FERTILIZERS
ON
SOIL ORGANIC MATTER AND REACTION

by

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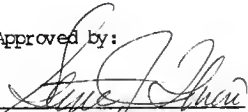
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INTRODUCTION

Ample evidence exists of the beneficial effects of nitrogenous and phosphorous fertilizers on plant growth and crop production, but little is known about the effects of these fertilizers on soil properties.

Farmers often remark that anhydrous-ammonia application makes soil tillage more difficult, but published investigations do not presently support such a theory. Intrawech *et al.* (1982) found no significant change in soil structure or compactability resulting from NH_3 application. However some experimental work has shown anhydrous ammonia capable of apparently dissolving soil organic matter (SOM). After application of anhydrous ammonia to soil in Czechoslovakia, Nemeč and Vopenka (1971) noted an increase in extracted humic substances.

Less is known about the comparable effect of phosphorous fertilizers on soil. Bell and Black (1970) reported that MAP and DAP solubilized SOM.

In the present experiment we treated soil samples in the laboratory with various formulations of ammonium hydroxide and either ammonium ortho- or pyrophosphate. After various incubation periods, we leached the treated soil with water. The pH of the leached soil and leachate were determined, then the leachate was analyzed for organic matter to determine whether any of the fertilizer formulations increased water-extractable humic substances. Color photographs of leachate samples recorded any visual differences due to dissolved humic substances.

The results showed that N and P treatments dissolved SOM, and that the dissolved OM colored aqueous leachate yellow, amber, brown, and black.

LITERATURE REVIEW

ORGANIC MATTER: GENESIS

Following the semantics of Waksman (1936) and more recently Stevenson (1982), in the present paper I'm using 'humus' and 'soil organic matter' synonymously to include decomposed organic residues and synthesized microbial products but to exclude undecomposed plant residues. Such usage of 'humus' and 'SOM' does not necessarily receive universal acceptance. Kononova (1966) aptly pointed out the need for an "ordered and unified terminology of organic substances".

Soil organic matter links present plant and animal life with past plant and animal life by carbon cycling. The break down of the composition of plant residues added to soil after green plants die is shown in Fig. 1. Paths residues undergo during microbial-action synthesis of humus are outlined in Fig. 2. At the same time new humus is being formed, microbial enzymes also accelerate mineralization of existing humus which frees nutrients for growing plants.

Kononova (1966) has given one of the clearest descriptions of humus formation:

Humus formation is a complex two-stage process in which organic residues of plant and animal origin undergo profound transformations involving:

- (1.) The decomposition of the original components of tissues and their conversion by micro-organisms into simpler chemical compounds and partially to products of complete mineralization (CO_2 , NO_2^- , NO_3^- , NH_3 , CH_4 , H_2O , etc.).
- (2.) The synthesis of organic compounds with the formation of high-molecular-weight humus substances of specific nature. For example, the humic-acid molecule is formed during the condensation of aromatic compounds with amino acids or peptides, with the possible participation of reducing substances.

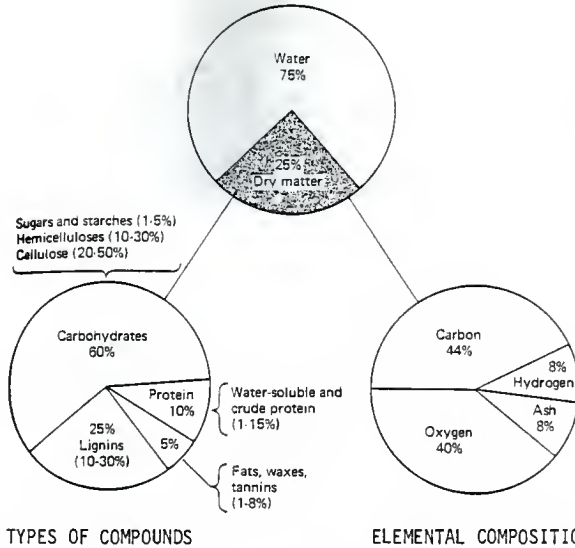


Figure 1. Composition of representative green plant materials added to soils. All inorganic elements, including nitrogen, are represented in the ash. Common ranges in the percentage of compounds present are shown in parentheses. (Data from Waksman, 1948. Cited by Brady, 1974).

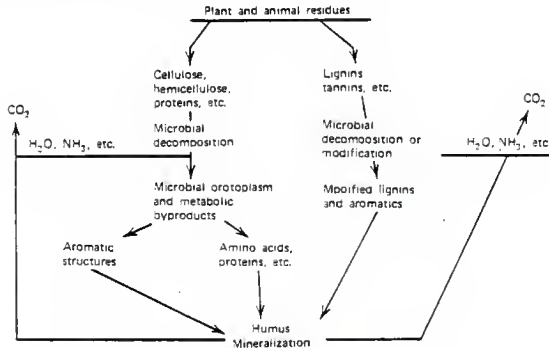


Figure 2. Decomposition of plant and animal residues and subsequent formation of humus. (From Bear, F. E. (Ed.). 1964. *Chemistry of the Soil*, ACS Monograph Series No. 160. Cited by Bohn et al., 1979).

In recent years the agricultural faculty at Nagoya University in Japan has made extensive studies on humus. Tsutsuki et al. (1979) briefly summarized their findings:

To clarify the relationship existing between the chemical structure of humic acids and the degree of humification or soil characteristics, we have investigated the elementary composition, the functional groups, and the products of acid hydrolysis and the degradation with KOH of various humic acids. From the results, it was presumed that humic acids are formed by the contribution of various natural polymers such as lignin, polysaccharides, and protein, and thereafter undergo oxidation, polymerization and the degradation of easily degradable fraction, to form dark-colored amorphous polymers.

Stevenson (1982) expressed humus formation in soils as a function of all soil-forming factors.

$$O.M. = f(\text{time, climate, vegetation, parent material, topography}).$$

Over periods of geological time such an equation probably describes soil-forming processes adequately, but since the advent of human civilization on the earth, man has played an increasing role in soil formation. Bidwell and Hole (1964) clearly explain man's role in soil formation.

With intensive agricultural systems such as grain-growing monocultures of today we need some additional terms to describe the effect of cultural practices on soil-forming processes. Continued cultivation of virgin soil can cause gradual decrease in SOM (Fig. 3). When soil-air contact increases, oxidative losses occur more rapidly, at least partially explaining why SOM levels decrease in tilled soil. Any expression describing the rate of OM formation should include a tillage factor.

Ellis (1982) noted that when fertilizers containing ammoniacal nitrogen undergo nitrification in soil, hydrogen ions are released and soil

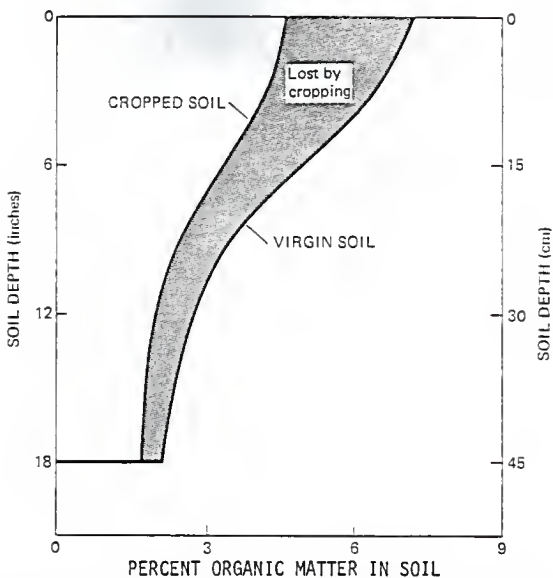
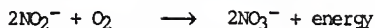
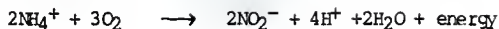


Figure 3. Average organic matter content of three North Dakota soils before and after an average of 43 years of cropping. About 25 percent of the organic matter was lost from the 0 to 15 cm layer as a result of cropping. (Haas, H. J. et al. 1957. Cited by Brady, 1974).

acidity increases.



Since soil microbes show sensitivity to soil pH levels, a change in soil pH may change the natural distribution of microbial populations. According to Brady (1974), fungi, including molds, adapt to a wide range of pH levels from acid to basic, whereas actinomycetes and bacteria populations need neutral or basic pH for optimum activity. pH levels below 5.5 sharply curtail actinomycete and bacteria activity. Therefore as soil pH falls below 6 we would expect actinomycete and bacteria populations to decrease, and conversely expect fungi populations and their activities to increase due to lack of competition from other microbial populations. Since microbial populations actively participate in SOM formation, any equation attempting to describe the process also needs a soil-reaction factor.

HUMUS: COMPOSITION AND STRUCTURE

Brady (1974) described humus as:

A complex and rather resistant mixture of brown or dark brown amorphous and colloidal substances modified from the original tissues or synthesized by various soil organisms. It is a natural body with properties that distinguish it sharply from the original parent tissues and from the simple products that develop during its synthesis.

Schnitzer (1978) characterized humic substances according to their various properties:

Humus substances are dark-coloured, acidic, predominantly aromatic, hydrophilic, chemically complex, poly-electrolyte like materials that range in molecular weights from a few hundred to several thousand.

Kononova (1961) explained that humus substances consist of only two

groups: humic acids (HAs) and fulvic acids (FAs). Humins, the author believed, are simply types of humic acids which are bound to the mineral fraction of the soil. Another compound often known as humatmelanic acid, the author suggested, is another form of humic acid, the alcohol-soluble fraction of humic acid and perhaps some resin acids.

The structural framework of humic substances is believed to consist of integrated structures made up of various building blocks with phenolic and carboxylic groups comprising two of the most prominent structural components. See Fig. 4 and 5.

Schnitzer (1978) pointed out that the structures of HA and FA may be flexible:

At pH levels prevailing in agricultural soils, HAs and FAs behave like flexible, linear synthetic polyelectrolytes largely or exclusively composed of condensed rings, but there must be present numerous linkages about which relatively free rotation can occur. It becomes thus more apparent that humic substances are not single molecules but rather associations or aggregates of molecules of microbiological, polyphenolic, lignin and condensed lignin origins.

Decomposition products of humic substances consist primarily of phenolic and benzenecarboxylic acids. (Schnitzer and Khan, 1978)

As shown by a wide variety of chemical-degradation experiments on HAs and FAs extracted from soils differing widely in locations and pedological histories, the major HA and FA degradation products are phenolic and benzenecarboxylic acids.

That consistency of composition from soils of different locations and pedological histories gives evidence to the theory of uniformity in organic matter. Further findings by the above authors showed that humic materials from widely differing pedological and geochemical environments, geographically 3000 miles apart contained almost identical amounts of fatty acids per unit weight.

Carbon-to-nitrogen ratios in humus range from about 8:1 to 15:1 with a

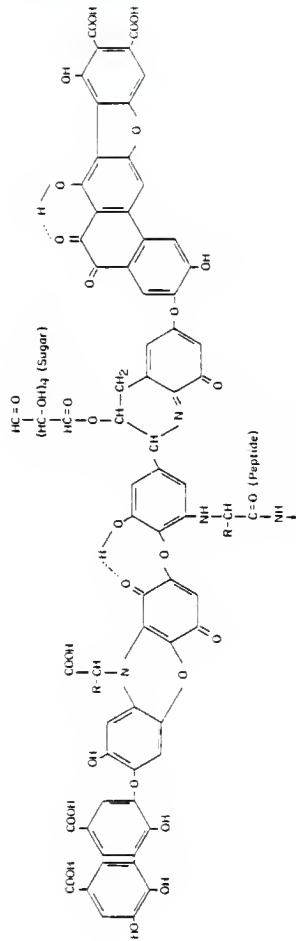


Figure 4. Hypothetical structure of humic acid. (Stevenson and Ardakani, 1972).

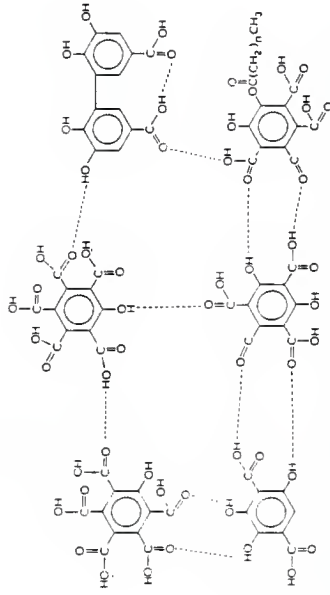


Figure 5. A partial chemical structure of FA. (Schmitzer and Khan, 1978).

median of 10:1 to 12:1. Calculating empirical formulas for fulvic acid, Felbeck (1970) found a ratio of H/C approximately equal to one. Such a ratio indicates a substantial degree of unsaturation. He explained:

This (unsaturation) is borne out by the dark color of the humic acid which is usually ascribed to a variety of conjugated double bonds. Depending upon the assumptions that one wishes to accept, approximately 50 to 55 percent of the total humic molecule has been identified as being made up of the following fragments: amino acids, hexosamines, polycyclic aromatics, aliphatic structures and single-ring aromatics may be included.

The remaining unknown fractions appear to consist of easily oxidized heterocyclic compounds that have a degree of unsaturation sufficient to cause the dark color characteristic of almost all humic compounds.

Morrison and Boyd (1974) have also associated color with unsaturation in the form of conjugated bonds: "Because they are highly conjugated, quinones are colored. P-berzoquinone is yellow". See Fig. 6.

Associating color with quinone structures becomes increasingly fascinating in soil chemistry because some soil scientists believe quinone-type structures constitute an intrinsic link in SOM formation. Senesi and Schnitzer (1977) suggested that humic acid is a mixture of free radicals of the semiquinone type. Using IR spectra to study the structure of humic acids, Eltantawy and Baverez (1978) confirmed the presence of aromatic and aliphatic fractions associated with various other functional groups including quinone groups. The authors also suggested that paramagnetism of humic compounds may arise from a variety of sources such as a semiquinone polymer, hydroxyquinone, polynuclear hydrocarbon and/or a trapped radical.

In uneroded Mollisols the dark black color of the A horizon results from a covering of humus on soil peds. The characteristic dark black color of humus results from the brilliant black color of humic acid (Fig. 7); the color of humic acid may result from conjugated bonds in the humus

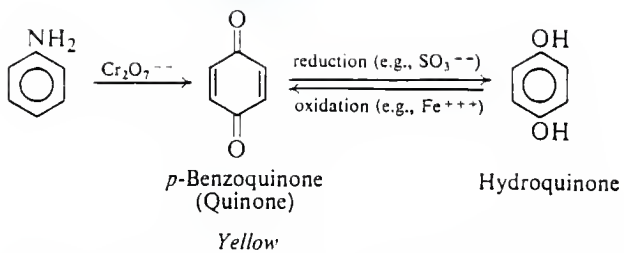


Figure 6. Quinone structures. (Morrison and Boyd, 1974).



Figure 7. Fulvic acid and humic acid extracted from 12 g of Kennebec silt loam.

structure.

Fulvic acid is an amber or orange color (Fig. 7). In a solution of humus, black humic acid masks fulvic acid. The color of FA may also result from conjugated bonds. It should be noted here that the color of HA and FA may vary in different soils.

Because of the complexity of humus, its precise structure and composition are not well understood. Kuwatsuka *et al.* (1978), making reference to our incomplete knowledge on the structure of humic components, stated:

Humic acids, which account for about one third of soil humus, are dark colored, amorphous, and high molecular materials. Though many studies on the chemical nature of humic acids have been accomplished since the early 18th century, little is known about their chemical structures and compositions because they are very complicated, diverse and high molecular.

Studies indicate that up to 50% of the aliphatic structures in HAs and FAs consist of n-fatty acids esterified to phenolic-OH groups. In making a quantitative analysis of HA and FA, Schnitzer and Khan (1978) found a phenolic to fatty acid molar ratio of 0.76 for HA and 1.90 for FA. "This suggests that in humic substances fatty acids react with phenolic-OH groups to form esters."

If the formation of esters from phenols and organic acids does occur, it raises the question of whether humic substances increase cation-exchange capacity uniformly during their entire life cycle or only during certain phases. The ionizable-hydrogen ions of phenolic and carboxylic groups give organic matter a high CEC, but during esterification dehydration would remove some of those hydrogen ions. As a result, the segment of organic matter undergoing esterification could lose at least a portion of its CEC.

Esterification would contribute to the structural magnitude and

complexity of humus aggregates. Like polymerization, esterification would increase the molecular weight of humic substances.

A number of workers have studied molecular weights of humic components. Orlov *et al.* (1971) found the structural nuclei of humic acids and fulvic acids as 1490-3885 and 5430-7000, respectively, but the average molecular weights of fulvic acid and humic acid were much higher at 10 000-12 000 and 50 000-90 000. Those figures indicate polymerization, and perhaps some esterification, occur during the formation of fulvic acid, with much more occurring during the formation of humic acid.

Cameron *et al.* (1972) found molecular weights of humic acid which ranged from 2×10^3 to 1.5×10^6 with the higher figure not necessarily representing the upper limit. They proposed that the molecule adopts a randomly coiled polymer in which branching may be significant, particularly at higher molecular weights.

Glebova (1972) found round molecular associates of humic acid with calculated molecular weights of 10^5 - 10^6 . Fulvic acid formed a relatively small percentage of the large molecular associates.

Rashid and King (1968) determined the molecular-weight distribution of humic and fulvic acids extracted from marine clays and found a range of less than 700 to over 2 000 000.

In studying the structural characteristics of humic acids with electron microscopy, Orlov and Glebova (1972) suggested that humic-acid molecules are disk-shaped molecules or flat ellipsoids. The authors estimated molecular weights of aggregates of Na-humates to range from several hundreds of thousands to several million with the diameters of some aggregates exceeding 13 nm.

EFFECT OF CHEMICAL TREATMENTS ON SOIL

It has been shown for nearly two centuries that some chemicals can affect SOM. Kononova (1961) credits Achard in 1786 with the discovery that alkali solutions extract SOM. That basic method of SOM extraction is still used. In 1961 Kononova stated that extraction of SOM with alkali solutions remained the usual method for SOM analysis. More recently Schnitzer and Khan (1978) similarly wrote:

The most efficient and most widely used extractant for humic substances from soils is dilute NaOH (either 0.1 N or 0.5 N) solution.

Investigating the effect of different pH levels on humic acids, Ritchie and Posner (1982) used sedimentation and diffusion measurements to determine the molecular weight, shape and size of fractionated humic acids and their metal complexes. For all the species studied the molecular weight and size decreased as the pH became more alkaline. However, the shape of the molecule, approximately spherical, was unaffected by pH. The authors also observed molecular weight and size of the metal humates depended not only on the type of cation but also on the degree of dissociation of the humic acid and the hydrolysis of the metal ion.

In discussing the effect of pH on humus, Schnitzer and Khan (1978) made the following observations.

At low pH, HA and FA tend to aggregate, forming elongated fibers and bundles of fibers. The aggregation appears to be brought about by hydrogen bonding, Van der Waal's forces and inter-actions between pi-electrons of adjacent aromatic rings, as well as by homolytic reactions between free radicals.

Hydrogen bonding in FA and HA is illustrated in Fig. 4 and 5.

The authors believed the molecular forces holding the humic components of HA and FA are similar in both acids with the higher molecular-weight

fractions (HAs) having greater complexity simply because of an additional amount of bonding.

Schnitzer (1978) explained why bonding in humus weakens as pH increases.

Increasing ionization of COOH and phenolic-OH groups induces the particles to separate and repel each other electrostatically so the molecular arrangements become smaller and smaller but better orientated.

Bonding becomes weaker in both humic and fulvic acid as pH increases, probably because increased concentrations of hydroxide ions pull hydrogen ions from the aggregating organic structures, resulting in separation of like-charged particles which repel each other electrostatically.

The molecular arrangements (at elevated pH levels) become smaller and smaller but better orientated. Thus one witnesses aggregation at low pH and dispersion at high pH, which is also the basis for separating humic substances into HA's and FA's. (Schnitzer and Khan, 1978).

The authors may have explained here what Achard had observed and demonstrated nearly two centuries previously in 1786 when he extracted soil with an alkali solution. After acidification of the extract Achard noted that humic substances precipitated out in the form of a dark amorphous precipitate (Kononova, 1961). Schnitzer and Khan believed that high pH weakens bonding forces in humic substances.

If high pH values have a degrading effect on humus the question arises: at precisely what pH value does that degradation begin? Davis and Mott (1981) investigated the solution stabilities of a polycarboxylic-acid fraction and a polysaccharide fraction of fulvic acid by pH titrations. They found that at pH 8.0 alkali-consuming reactions occurred on the polycarboxylic acid fraction. Such results present evidence that at pH 8 chemical changes occur on the polycarboxylic acid functional groups of humus.

Research by Saiz-Jimenez *et al.* (1978) on humic and fulvic acids showed the prominence of polysaccharide-like substances in the humus structure. Using pyrolysis mass spectrometry to study the composition of humic and fulvic acids they found that polysaccharide-like materials in soil and its humic fractions "are more important than presumed till now." They found the polysaccharide-like materials in the humic, fulvic, and humin fractions.

If high pH values degrade fractions of humus, then what effect do highly basic fertilizers, such as anhydrous ammonia, have on soil? The literature contains only a limited amount of material on that topic.

In Czechoslovakia, Nemec and Vopenka (1971) investigated the effect of a number of nitrogen fertilizers on soil and found anhydrous ammonia most aggressively "released humus substances". Extracted humic substances expressed as a percent of the control were 188, 139, 129, and 117 for NH_3 , NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, and NH_4NO_3 , respectively. The authors observed:

The general comparison of the effect of anhydrous ammonia in gaseous state and that of ammonium hydroxide in solution indicate that gaseous ammonia always exerts a more pronounced effect on the releasing of humus substances and cations than a solution of ammonium hydroxide.

The authors did not postulate why NH_3 exerts a "more pronounced effect".

Parr and Khasawneh (1968) investigated drying patterns in soil after application of NH_3 . They found a more rapid rate of water evaporation from soil in the NH_3 -retention zone, and the NH_3 -induced drying effect could persist at least 100 days, even where systems were subjected to alternate wetting and drying. The authors found similar drying patterns due to NH_3 application in both field conditions and closed containers.

Immediately after application of NH_3 , Parr and Khasawneh (1968) noted that in many soils the pH at the center of the retention zone often

exceeded 9.5.

Khasawneh and Parr (1968) studied the thermal effects of anhydrous ammonia injected into soil, but did not feel the exothermic reactions caused moisture gradients observed in differential drying patterns. The authors suggested that dissolved and redistributed SOM could have an effect on drying patterns.

Treating soil with anhydrous ammonia, McDowell and Smith (1958) found that high concentrations of ammonia resulted in the partial breakdown of OM. The authors also investigated rates of nitrification and found little nitrification occurred the first two weeks after NH_3 treatment. The authors suggested that nitrifying bacteria may have suffered from the sterilizing effects of NH_3 during the initial two weeks.

Stanley and Smith (1956) found soil pH four inches from the injection point still abnormally high 2 months after anhydrous-ammonia application.

Normic and Nilsson (1964a) found that soil treatments of $\text{NH}_4\text{Cl} + \text{NaOH}$ or NH_4OH dissolved increasing amounts of SOM as pH increased. They also showed that leaching with CaCl_2 extracted substantially less SOM than leaching with water. They related ammonia-fixing capacity of soils directly to SOM and pH. Soils with highest OM content and highest pH fixed largest amounts of ammonia.

Brinton (1979) published results comparing the use of inorganic NPK fertilizer with organic fertilizers. For compost, farmyard manure, farmyard manure + NPK, control, and NPK alone, he found that the combined humic and fulvic acid amounts in the soil expressed as percentage change after 19 years were +42, +40, -29, 0 -14, respectively. Both treatments that included inorganic NPK decreased organic-acid levels in the soil; whereas compost and manure treatments increased organic acids.

Intrawech et al. (1982) compared the physical and chemical effects of various nitrogen fertilizers on soil after 10 years of regular applications. They found NH_3 , NH_4NO_3 , and UAN all significantly reduced pH. No significant differences in SOM were observed.

Fox et al. (1952) broadcast NH_4NO_3 on the surface of an eroded Sharpsburg soil with low SOM and acid pH. The NH_4^+ ions mostly remained in the surface 1.75 cm when sampled 4 to 5 months later. The authors attributed soil dispersion to the continued presence of high concentrations of the NH_4^+ ions still persisting due to lack of climatic and soil conditions conducive for nitrification of the ammonium ions.

On irrigated soils in California, Aldrich et al. (1945) observed structural deterioration following annual fertilizer treatments for 16 years.

The poor physical condition of the ammonium-sulfate plots is apparently due to the dispersing action of the ammonium ion which builds up in the exchange complex as a result of reduced ability of soil organisms to nitrify the ammonium at low pH produced by continued application of ammonium sulfate.

Bell and Black (1970) observed that MAP and DAP dissolved soil organic matter to the extent that the extract stained paper fibers brown. The staining by DAP exceeded that with MAP. Since their experiment was not designed to investigate the effect of treatments on SOM, they didn't attempt to quantify such an effect, but did note that "direct visual examination of the soils showed no effect on the soil organic matter" from MAP and DAP treatments.

Giordano et al. (1971) found as much as 10 percent of total SOM dissolved by treatments of triammonium pyrophosphate, but only about half as much was dissolved by MAP. The authors considered the degradation of SOM by pyrophosphate as "considerable". In commenting on the degrading

effect of MAP and triammonium pyrophosphate on SOM, Sample et al. (1980) suggested that ammonium ions may replace divalent and trivalent ions in stable metallic-organic matter complexes resulting in increased solubility of the OM.

Fraps and Starges (1939) found that addition of phosphate to soil increased the rate of nitrification. Reports by Brown and Gawda (1924) showed similar results, however Robison and Bullis (1922) found phosphate had a beneficial effect on nitrification in one soil, but a depressing effect on nitrification in three other soils.

Studying the effect of anhydrous ammonia on nitrification in soil, Nommik and Nilsson (1964b) found high ammonia concentration near the line of injection raised pH to 9.4, inhibited nitrification, and severely depressed oxidation of nitrite to nitrates.

After applying various rates of anhydrous ammonia to soil, Eno and Blue (1954) studied the effect on microorganisms. The authors found the high concentration of NH_3 in the retention zone toxic to both fungi and bacteria. After nitrification lowered pH and ammonium levels, the numbers of bacteria and fungi again returned to normal. The authors noted:

From a total population standpoint none of the changes noted are likely to permanently disturb the ecological balance in the soil.

In a subsequent study, Eno et al. (1955) observed similar results indicating that high NH_3 levels severely depressed fungi and bacteria activity, but expressed uncertainty about the agronomic effects of such a phenomenon. The authors explained:

Nitrification would probably be inhibited within the retention zone but would occur at the periphery and therefore, gradually reduce the concentration of ammonia by nitrification. This may or may not be desirable, depending upon the crop requirements and the environmental conditions.

Sohn and Peech (1958) investigated the OM fraction of the soil after applications of NH_3 and found that OM sorbed significant amounts of ammonia. The authors also noted that the presence of SOM is "known to hinder the fixation of NH_4^+ , presumably by blocking the entrance of the ammonium ions between the clay plates". (Note here that the authors indicated SOM blocked fixation of ammonium ions.)

However Sohn and Peech (1958) also estimated that at least 50% of the ammonia fixed by some mineral surface soils may result from some reaction of ammonia with SOM. (Note here the authors indicated SOM increased molecular NH_3 fixation in mineral soils.)

The exact nature of the ammonia-organic matter complex is not well understood presently. Mortland (1958) mentioned some possible compounds in SOM which might enter into a reaction with ammonia.

The fact that ammonia will react with carboxyl, phenol, aldehyde, ketone, and alcohol groups to form amines, amides, and imides of various kinds suggests that possibility of a variety of reactions with soil organic matter.

Junker (1941) found that ammonia combined with lignin in three different stages. He suggested that two of the stages correspond to the combination with phenolic-hydroxyl groups and the third with an aldehyde or alcoholic-hydroxyl group.

Mattson and Knoutler-Anderson (1954) concluded lignin to be the primary constituent involved in auto-oxidation of OM in the presence of ammonia and that lignin is also responsible for the fixation of ammonia.

REACTIONS OF HAS AND FAS WITH METALS AND MINERALS

Humic substances are capable of interacting with metallic ions,

metallic oxides, metallic hydroxides and minerals to form metal-organic associations and organo-mineral associations of widely differing chemical and biological stabilities and characteristics.

With oxygen-containing functional groups such as aldehydes, hydroxides, and acid groups, humic substances can attack and degrade soil minerals by complexing and dissolving metals. The dissolved metals can be transported throughout the soil profile by mass flow and diffusion.

Discussing different humic-acid fractions in soil, Anderson *et al.* (1981) described one fraction as a conventional humic-acid fraction and a second fraction as a clay-associated humic acid. Kononova (1966) expressed a similar opinion that humin consisted of a complex of minerals bonded to humic acid.

Stevenson (1976a) found that metal complexing by humic substances involves carboxylic- and phenolic-OH groups. Similarly, Schnitzer, and Skinner (1965) found that either one organic-acid and one phenolic-OH group, or two organic-acid groups reacted simultaneously with metallic ions and hydrous oxides.

Schnitzer (1969) confirmed that divalent metallic ions formed complexes with fulvic acid, and that at pH 5, the stability of those complexes increased in the order Cu, Pb, Fe, Ni, Mn, Co, Ca, Zn, and Mg. (Note that the stability of the zinc complex at pH 5 appears next to the highest.)

After oxidizing organic matter with peroxide, Himes and Barber (1957) showed that soil lost its ability to complex zinc. If soil loses its ability to complex zinc after the oxidation of OM, that gives a strong indication that organic matter provides the only viable complexing agent present in soil with respect to zinc. Tests have shown that after the

surface horizons are removed by erosion or land-leveling, zinc deficiencies often occur in plants grown on such land. Zinc deficiencies occur after excavation or erosion of top soil because zinc is associated closely with SOM, and the top soil holds the major portion of SOM. Zinc may be primarily associated with SOM because of the unique complexing relationship between the two.

Beckwith (1959) reported that metals of the first transition series of the periodic table formed complexes with humic substances. Adhikari *et al.* (1972) identified complexes of fulvic acid with Fe, Al, Cu, Zn, and Ni.

MacCarthy and Cinneide (1974) studied the interaction of metallic ions of the first transition series with fulvic acid. Results indicated the non-cationic fraction of fulvic acid and the metallic ions formed both stable soluble complexes and highly insoluble complexes over the entire pH range. The soluble complexes formed under alkali conditions carried a negative charge. The fulvic material "vigorously competed" with other ligands for metal ions. The expression, "vigorously competed", suggests FA has a strong propensity for complexing with metallic ions.

In studying the interaction between humic acids and various metallic cations, Orlov and Eroshicheva (1967) found the reactions followed different mechanisms, but primarily between the metallic ions and the H⁺ of the carboxyl groups. That gives strong indications that pH affects reactions between OM and metallic ions.

Investigating the molecular-weight distribution of various humic acids and metallic humates, Sipos *et al.* (1974) found that molecular aggregates were present in aqueous solutions at low pH but absent at high pH. During the same study the authors observed that average molecular weight increased to a greater degree with trivalent ions (Fe, Al) than with divalent ions

(Cu, Co, Fe).

Work by Sinha (1971a,b) indicated that the amount of iron and aluminum complexed by organic matter also affected amounts of soluble organo-metallic phosphates present in the soil.

Schnitzer and Kodama (1969) used thermal analysis to study fulvic acid-montmorillonite complexes. The differential thermal analysis curve at 670°C indicated the presence of an interlamellar complex with fulvic acid. Almost all the externally adsorbed acid decomposed before the combustion of the interlamellar retained acid. About half of the adsorbed fulvic acid was held externally on montmorillonite; the remainder was held in the interlamellar spaces. The amounts of fulvic acids adsorbed decreased with increasing pH.

The amount and type of complexing between organic matter and minerals depends greatly on the type of minerals present as well as upon the amount of organic matter available. Emerson *et al.* (1959) proposed a model in which SOM stabilized quartz as well as clay during the formation of soil crumbs. SOM formed a bridging bond between the quartz and clay. Anderson *et al.* (1978) proposed similar complexes of clay-associated humic acids. Kononova (1966) suggested an analogous theory, that complexed minerals bound to humic-acid structures compose humin.

Materials and Methods

SOIL

Kennebec silt loam, a fine-silty, mixed, mesic Cumulic Hapludoll from Mosquito Creek bottom land 4.8 km southwest of Netawaka in northeastern Kansas was used throughout the experiment. The field had been in cultivation about 25 years, planted to soybeans most years, but occasionally to wheat or corn. The year previous to taking the soil samples, the field was in wheat. The three previous years soybeans were raised in the field. No fertilizer of any kind had been applied to the field for 3 or 4 years previous to taking the samples. The land is subject to flooding during rainy seasons.

Immediately before collecting soil in August, 1982, the field was plowed about 20 cm deep, then soil was collected from that 20 cm layer. The soil had a pH of 7.0, bulk density of 1.5 g/cm^3 in its natural state, and an organic-matter content of 19 g/kg. The soil was screened to 2 mm and then air-dried.

INCUBATION CHAMBERS

Individual incubation chambers 30.5 cm in height were made by taping together 6 sections of Lucite tubing with an inside diameter of 7 cm and height of 5.08 cm. The bottom of the chamber was covered with filter paper and nylon screen secured by a heavy rubber band. A 0.15 cm hole was drilled through the tubing wall in the middle of the third section from the bottom and a serum stopper inserted (Fig. 8).

SOIL COLUMNS



Figure 8. From left to right: soil chamber with inserted serum stopper, Buchner funnel in a 250 ml graduated filter flask, and soil column.

Individual soil columns were made by adding a 5 cm layer of sieved and air-dried soil to the incubation chamber. A 1.0 kg tamper was dropped from 25 cm three times on the added soil, then the soil around the edges was tamped firmly. The tamped soil had a bulk density of 1.1 g/cm^3 . Before adding more soil, the tamped surface was roughened to prevent increased density at the interface. The column height was built to 25.4 cm, then moistened to about 20% w/w by adding 210 ml deionized water. A 5 cm layer of glass wool was added on top of the column to retard drying. To insure uniform distribution of moisture throughout the columns, they were left setting at room temperature for 6 days, then incubated at 35°C for 12 h before injecting fertilizers.

SOIL TREATMENT

Fertilizer treatments (Appendix A) were prepared by combining required amounts of either monobasic ammonium orthophosphate (MAP) or triammonium pyrophosphate (APP) with the amounts of ammonium hydroxide ($\text{NH}_4^+\text{-N}$) and water shown in Table 1. Before applying the orthophosphate treatments with the highest rates of $\text{NH}_4^+\text{-N}$, the mixtures were warmed to 35°C in a warm water bath to dissolve the ammonium phosphate formed upon the introduction of ammonium ions from ammonium hydroxide.

Treatment Method for 0 d incubation

The appropriate treatment solution shown in Table 1 was mixed with about 75 ml of deionized water. The 5 cm section of soil, the third section from the bottom of the soil column, was transferred to a Buchner funnel according to the directions in the section below on 'Leaching the Soil'. After the soil was transferred to the funnel, the treatment

Table 1. Treatment rates and formulations for individual soil samples.

Treatment †		Treatment solution					H ₂ O
MAP	APP	NH ₄ ⁺ -N [‡] (mg/kg)	1.55 M NH ₄ H ₂ PO ₄ ml	0.78 M (NH ₄) ₃ HP ₂ O ₇ ml	13.8 M NH ₄ OH ml	ml	
0	0	0	0	0	0	20	
0	0	600	0	0	2.0	18	
0	0	1200	0	0	4.0	16	
0	0	2400	0	0	8.0	12	
300	0	0	4.0	0	0	16	
300	0	600	4.0	0	2.0	14	
300	0	1200	4.0	0	4.0	12	
300	0	2400	4.0	0	8.0	8	
0	300	0	0	4.0	0	16	
0	300	600	0	4.0	2.0	14	
0	300	1200	0	4.0	4.0	12	
0	300	2400	0	4.0	8.0	8	
600	0	0	8.0	0	0	12	
600	0	600	8.0	0	2.0	10	
600	0	1200	8.0	0	4.0	8	
600	0	2400	8.0	0	8.0	4	
0	600	0	0	8.0	0	12	
0	600	600	0	8.0	2.0	10	
0	600	1200	0	8.0	4.0	8	
0	600	2400	0	8.0	8.0	4	

†Treatment rates of 600 mg/kg in a zone 7.0 cm in diameter at 61 cm spacings equate to 25 mg/kg uniform application. Rates were computed on the basis that treatments diffuse 7.6 cm both above and below the point of application.

‡Ammonium hydroxide furnishes the nitrogen. In addition to that nitrogen, orthophosphate adds 135 mg/kg N using 300 mg/kg P and twice that at the higher P rate, and pyrophosphate adds 203 mg/kg N at the 300 mg/kg P rate and twice that at the higher P rate.

solution was poured uniformly over the soil, so that all the soil came in contact with the treatment.

Treatment Method for 0.5 through 16 d incubation

A syringe and needle was used to inject the treatment solution (Table 1) through the serum stopper into the center of the respective soil column.

INCUBATION

After treating the soil samples, they were incubated at 35°C. For various samples, seven different incubation periods of 0, 0.5, 1, 2, 4, 8, and 16 d were used to complete the following design.

DESIGN

A randomized split-plot design was prepared in the following way. 21 sets of 20 random numbers were prepared for soil columns and 3 sets of 7 random numbers for incubation periods. The former were randomly assigned to the latter. The incubation periods constituted the whole plot of the randomized design, and the treatments the subplots. 20 soil columns were prepared at one time according to the random numbers for one time period. The 20 columns were treated according to treatments shown in Table 1. One replicate over all incubation periods was completed before beginning the second replicate. A total of three replicates were completed.

LEACHING THE SOIL

A 250 ml graduated filtering flask was fitted with a 9-cm Buchner funnel fitted with a SPECTRA/MESH filter having mesh openings of 111 μ m. (Filter porosity was critical because a fine filter clogged with OM and

clay particles.) At the end of each incubation period, the tape was removed at the top and bottom of the 5 cm soil section into which fertilizer had been injected. A knife was used to slice through the soil column at those two places. The section of soil was removed intact and transferred to the prepared Buchner funnel by shaving the soil particles into the funnel.

Deionized water was added to the soil in the funnel, and the funnel was bumped a few times on each side to settle the soil. Suction equal to 5.3×10^4 Pa was applied for about 5 seconds, then stopped. The 250-ml filter flask was emptied back into the funnel, then fitted again to the funnel before filtration with the same suction was begun again. The funnel was kept nearly filled with deionized water at all times. Filtration times were recorded when the leachate reached the following graduations on the flask: 0, 75, 100, 150, 200, and 250 ml. After 250 ml of leachate was collected, suction was turned off. The leachate was transferred to polyethylene storage bottles and refrigerated.

THE LEACHED SOIL

After decanting excess water from soil in the filter funnel, pH of the wet soil was recorded, then the free water was suctioned from the soil. The soil was then transferred to open containers and dried at room temperature. After the soil dried sufficiently to crumble, it was transferred to polyethylene bags and thoroughly mixed, then transferred back to drying containers to complete drying before storing in polyethylene bags. The soil was saved to make analyses of exchangeable cations and micronutrients.

ANALYSES

pH of the leachate and leached soil was determined using a pH meter with a glass electrode. Leachate was analyzed for total organic matter, then quantitatively fractionated into fulvic and humic acids.

ORGANIC MATTER ANALYSES

To determine the total oxidizable organic matter in soil, the Walkley-Black method described by Jackson (1958) was used with two exceptions. When analyzing leachate, 10 ml of leachate was used instead of 0.5 g soil, and the 0.77 recovery factor Jackson used in the denominator of his equation on p. 221 was deleted because in the leachate the organic carbon was probably all or nearly all oxidized by the action of the acid and dichromate.

To fractionate the organic matter, the basic procedure outlined by Mortensen and Himes (1964) was used. To 100 ml centrifuge tubes 40-ml samples of leachate were transferred and acidified to 1.25-2.0 with 10 ml of 1.0 M HNO_3 . Tubes were closed with rubber stoppers covered with parafilm, then shaken vigorously. Tubes with the acidified leachate were left setting in a rack for 30 minutes before centrifuging at medium speed. The humic acid fraction of OM precipitated in the acid solution. The supernatant was analyzed for oxidizable organic matter using the method described above. The resulting amount of OM, when corrected for dilution with acid, gave the amount of fulvic acid in the leachate. The initial amount of OM in the leachate, minus the fulvic acid, gave the amount of humic acid.

STATISTICAL ANALYSIS

Analysis of variance (ANOVA), using Duncan's Multiple Range Test, was made using the Statistical Analysis Systems computer program (SAS Institute Staff, 1982). Regression analyses were made using the General Linear Models (GLM) procedure of the SAS program.

Least significant difference (LSD) analyses, to show differences in means between different incubation periods, were computed using the method set forth for split-plot designs by Cochran and Cox (1957).

PHOTOGRAPHING LEACHATE SAMPLES

Photographic procedures may be designed to fit the particular needs of the researcher, however the following method gave satisfactory results.

Placing 20 Petri dishes, 5.5 cm diameter and about 1.3 cm deep, in 5 rows of 4 on a white poster board, the left row was separated from the next two rows to the right by a 2.5 cm strip of light yellow poster paper, and those two rows were separated from the last 2 rows on the right by a 2.5 cm strip of light yellow poster paper. Then the area above, below, and on each side of the rows of dishes was made solid with the yellow poster paper, making the boundaries immediately adjacent to the dishes straight lines rather than in contour with the dishes. The 4 rates of $\text{NH}_4^+\text{-N}$ were labelled on the y-axis top to bottom, and the P rates were labelled below the x-axis, with a title 'EXTRACTED HUMIC SUBSTANCES' placed above the sample dishes. For an example see Fig. 52.

We placed the poster board with labels on a copy-stand and covered them with a piece of glareless glass 45 by 55 cm before putting the sample dishes in place. After filling the dishes nearly full of leachate from each of the 20 treatment combinations for one incubation period, we photographed the samples together, and followed similar procedure to get

photos of samples from each of the 7 incubation periods.

We did not attempt to mix leachate samples from corresponding formulations from the three replicates. Some variation in leachate colors did occur between samples with corresponding formulations from different replicates, but those color differences appeared insufficient to warrant a display of each leachate sample from every replicate.

For 2 by 2 slides, we used tungsten balanced color film and 3200 K Tungsten lighting with two 500 watt bulbs on each side of the copy-stand and two more bulbs on stands directly in front. Without the bulbs in front, dark shadows appeared in the alleys between the sample dishes, especially when photographing the black samples of leachate.

Settings on the camera needed adjusting according to the color of the leachate samples being photographed. Leachate samples from 0- and 16-d incubation periods needed greater exposure settings on the camera because the samples from those time periods were lighter in color than from some of the other time periods. For example, many of the leachate samples from the 1-d incubation period were black.

Meisel's photographic services in Dallas, Texas reproduced high quality color prints from our color slides. We were unable to obtain satisfactory prints from slides any place else.

We made photos of the prints from Meisel's using Kodacolor film with a film speed ISO 100. In this way we could obtain any number of reprints for only 40 cents each. The quality of the reprints did not match the original custom finished prints from Meisel's, however the reprints adequately showed the differences in the leachate samples. For an example see Fig. 52.

In order to get a composite photo of all 140 samples of leachate for

one representative replicate, we photographed the original color prints of leachate samples from each of the 7 incubation periods, including them all in one photo (Appendix C, Fig. 1).

When using Kodacolor film with Tungsten lighting, our film required the use of an 80A blue filter on the camera. When using the Kodacolor film, we used only two 500 watt tungsten bulbs on stands set at corners of the copy-stand.

RESULTS: Part I

A. Effect of N- and P-treatment rates on pH.

Increasing rates of NH_4^+ -N increased pH in both leachate and soil (Fig. 9-22) during all incubation periods 0-16 d. The rise in pH occurred because of the hydroxide ion content of NH_4OH .

On agricultural land today, analogous conditions occur after knifing anhydrous ammonia into the soil; ammonia dissolves in water to form NH_4OH . One difference between anhydrous-ammonia treatment and ammonium-hydroxide treatment lies in the extreme hygroscopicity of anhydrous ammonia. It interacts with more moisture from the surrounding microenvironment than NH_4OH .

pH consistently rose with increasing rates of NH_4^+ -N (Tables 2 and 3) regardless of P source or P rates. Increasing N rates usually caused significant increases in both leachate- and soil-reaction.

Immediately after treatment, leachate- and soil-pH may appear disproportionately high. We computed treatment rates on the basis that diffusion of applied chemicals extended uniformly 7.5 cm both above and below the point of application. At time 0, only 33.3% of that volume of soil was exposed to treatment; consequently, the soil received a triple treatment at time 0.

However such a situation also has a close analogue in field applications where farmers knife anhydrous ammonia into soil in localized bands across the field. Initial injection of NH_3 in the soil is restricted to a line, whereas application rates are computed on the basis that the ammonia diffuses uniform distances each direction from the line of application. The theory of uniform diffusion is a hypothetical situation

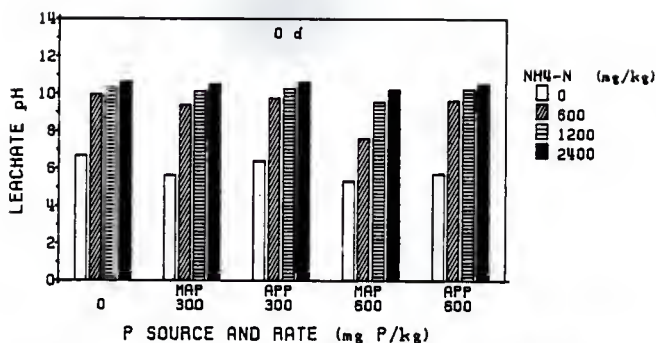


Figure 9. Leachate pH from Kennebec silt loam immediately after treatment.

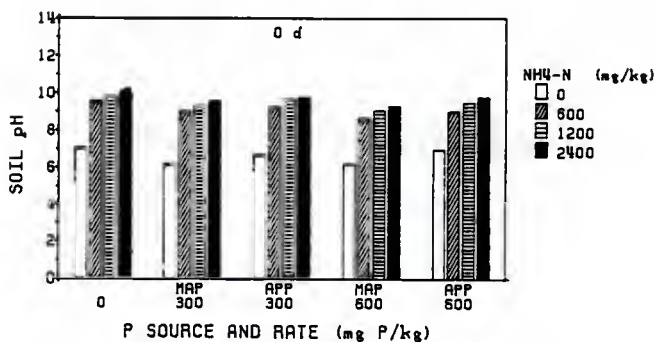


Figure 10. Soil pH of Kennebec silt loam immediately after treatment.

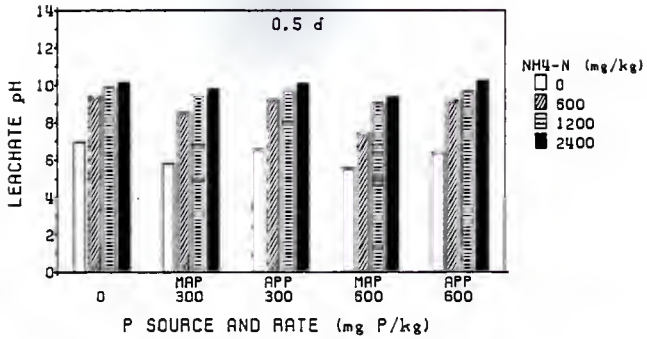


Figure 11. Leachate pH from Kennebec silt loam 0.5 d after treatment.

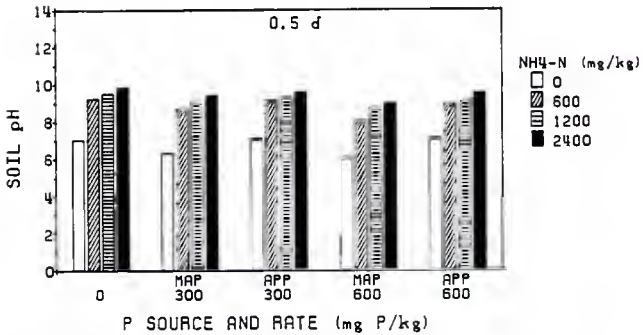


Figure 12. Soil pH of Kennebec silt loam 0.5 d after treatment.

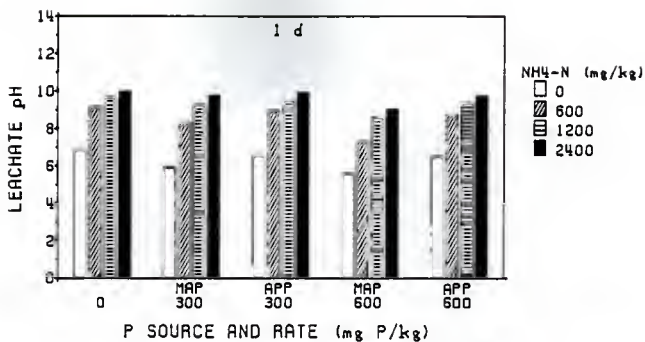


Figure 13. Leachate pH from Kennebec silt loam 1 d after treatment.

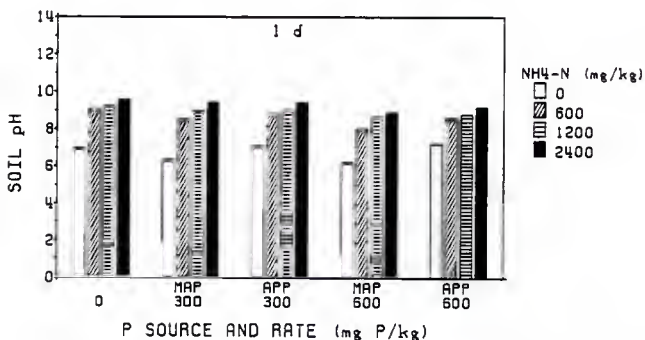


Figure 14. Soil pH of Kennebec silt loam 1 d after treatment.

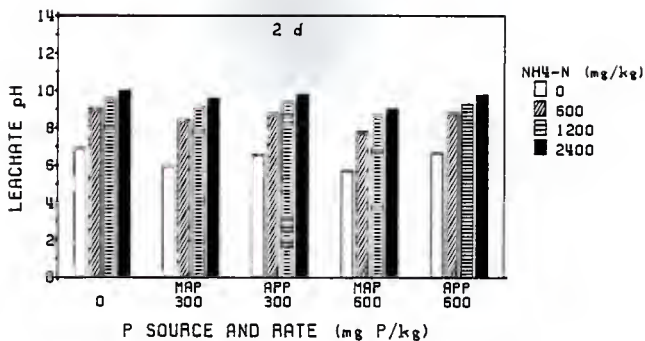


Figure 15. Leachate pH from Kennebec silt loam 2 d after treatment.

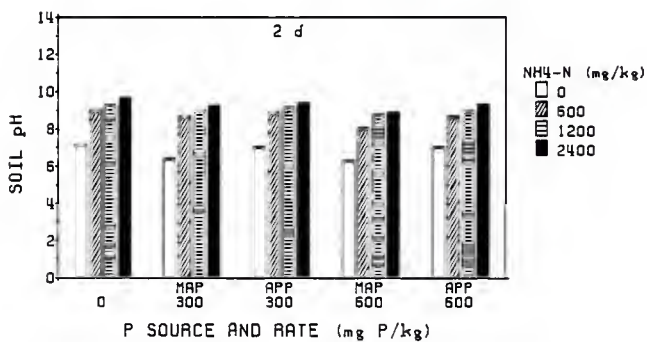


Figure 16. Soil pH of Kennebec silt loam 2 d after treatment.

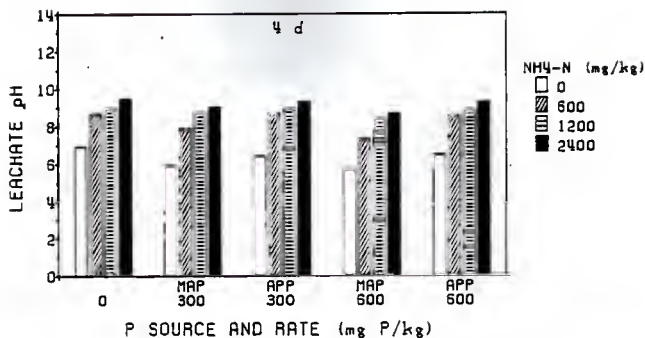


Figure 17. Leachate pH from Kennebec silt loam 4 d after treatment.

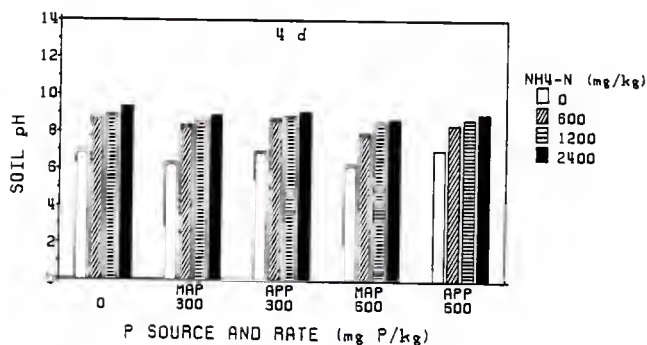


Figure 18. Soil pH of Kennebec silt loam 4 d after treatment.

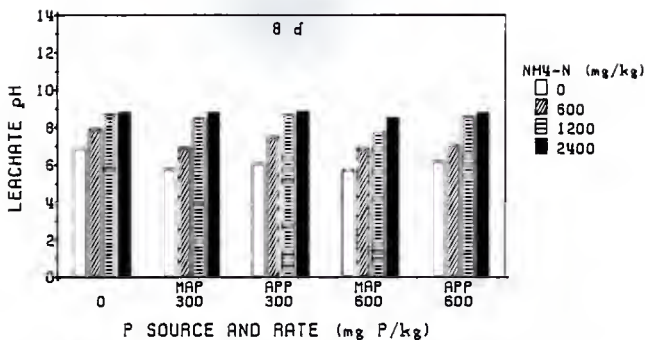


Figure 19. Leachate pH from Kennebec silt loam 8 d after treatment.

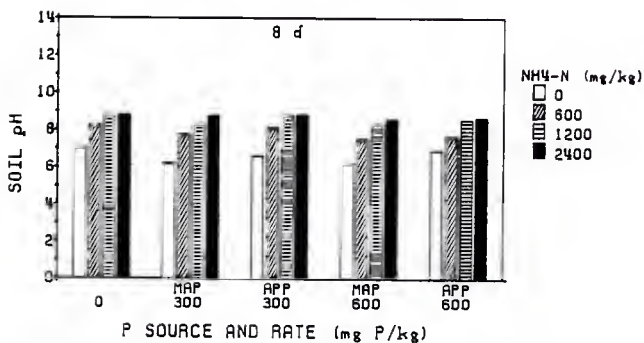


Figure 20. Soil pH of Kennebec silt loam 8 d after treatment.

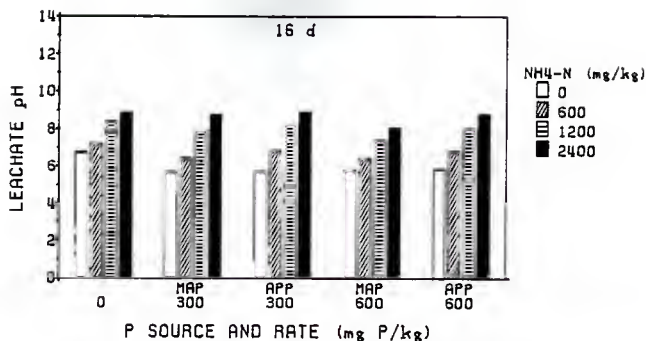


Figure 21. Leachate pH from Kennebec silt loam 16 d after treatment.

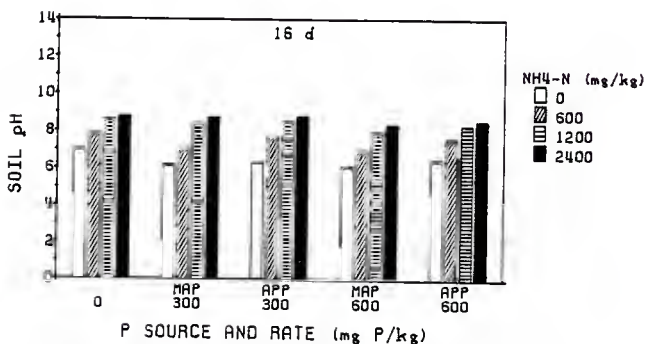


Figure 22. Soil pH of Kennebec silt loam 16 d after treatment.

Table 2. pH of leachate from Kennebec silt loam after treatment with various rates of orthophosphate, hydrophosphate, and nitrogen.

Treatment	Leachate pH*							Mean
	Incubation period (d)							
MAP APP NH ₄ -N (mg P/kg)	0	0.5	1	2	4	8	16	
0	6.7 i	7.0 k	6.9 k	6.9 l	6.9 i	6.9 h	6.7 f	6.9
0	10.0 de	9.4 ef	9.2 ef	9.0 efg	8.7 de	7.9 d	7.2 e	8.8
0	10.3 bc	9.9 b	9.7 bc	9.6 bc	9.0 b	8.7 ab	8.4 b	9.4
0	10.6 a	10.1 a	10.0 a	10.0 a	9.5 a	8.8 a	8.8 a	9.7
300	5.6 k	5.8 m	5.9 m	6.0 n	5.9 k	5.8 j	5.7 h	5.8
300	9.4 g	8.5 i	8.3 i	8.4 j	7.9 g	6.9 gh	6.4 g	8.0
300	10.1 cd	9.5 de	9.3 de	9.1 def	8.7 cde	8.5 c	7.9 d	9.0
300	10.5 ab	9.8 bc	9.8 b	9.6 bc	9.0 b	8.8 a	8.7 a	9.5
0	6.4 j	6.5 l	6.6 l	6.6 m	6.4 j	6.1 i	5.7 h	6.3
0	9.8 ef	9.2 fgh	9.0 g	8.8 hl	8.7 de	7.5 f	6.8 f	8.5
0	10.3 bc	9.7 bc	9.5 c	9.4 cd	8.9 bc	8.7 ab	8.2 bc	9.2
0	10.6 a	10.1 a	9.9 a	9.8 ab	9.3 a	8.8 a	8.9 a	9.6
600	5.3 l	5.5 n	5.6 n	5.7 o	5.7 l	5.7 j	5.8 h	5.6
600	7.6 h	7.4 j	7.3 j	7.5 i	7.3 h	7.0 h	7.2	7.2
600	9.6 fg	9.0 h	8.6 h	8.7 i	8.4 f	7.8 e	7.4 e	8.5
600	10.2 cd	9.3 efg	9.0 fg	9.0 fgh	8.7 de	8.5 c	8.0 cd	9.0
0	5.7 k	6.4 l	6.5 l	6.6 m	6.5 j	6.2 i	5.8 h	6.2
0	9.5 fg	9.2 gh	8.7 h	8.8 hkl	8.5 ef	7.1 j	6.8 f	8.4
0	10.2 cd	9.6 cd	9.4 d	9.3 de	8.8 bcd	8.6 bc	8.0 cd	9.1
0	10.5 ab	10.2 a	9.7 b	9.8 ab	9.3 a	8.8 a	8.8 a	9.6

*Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Table 3. Soil pH of Kennebec silt loam after treatment with various rates of orthophosphate, Pyrophosphate, and nitrogen.

Treatment		Soil pH*							Mean
		Incubation period (d)							
MAP	APF N ₄ -N (mg P/kg)	0	0.5	1	2	4	8	16	
0	0	7.0 h	7.0 k	6.9 k	7.1 i	6.9 h	7.0 e	7.0 h	7.0
0	600	9.5 a-d	9.2 cde	9.0 cd	9.0 de	8.8 cd	8.2 c	7.8 ef	8.8
0	1200	9.8 ab	9.5 b	9.2 bc	9.2 bc	8.8 bcd	8.8 a	8.6 abc	9.1
0	2400	9.9 a	9.8 a	9.5 a	9.6 a	9.3 a	8.8 a	8.7 a	9.4
300	0	6.1 i	6.3 l	6.3 l	6.4 j	6.3 i	6.2 g	6.1 j	6.2
300	600	9.0 fg	8.7 i	8.5 h	8.7 g	8.3 f	7.7 d	7.0 h	8.3
300	1200	9.3 def	9.1 ef	8.9 de	9.0 de	8.6 de	8.3 bc	8.4 cd	8.8
300	2400	9.5 a-d	9.4 bc	9.4 ab	9.2 bc	8.8 bcd	8.7 a	8.7 ab	9.1
0	300	6.6 h	7.1 k	7.0 jk	7.0 i	6.9 h	6.6 f	6.3 ij	6.8
0	600	9.2 def	9.1 def	8.8 efg	8.9 efg	8.7 de	8.1 c	7.7 fg	8.6
0	1200	9.6 a-d	9.3 cd	9.0 cde	9.1 cd	8.8 cd	8.8 a	8.5 bcd	9.0
0	2400	9.7 abc	9.5 b	9.4 ab	9.4 b	9.0 b	8.8 a	8.8 a	9.2
600	0	6.1 i	6.0 m	6.2 l	6.3 j	6.2 i	6.2 g	6.1 j	6.2
600	600	8.6 g	8.0 h	8.0 h	8.0 h	7.9 g	7.5 d	7.0 h	7.9
600	1200	9.1 ef	8.7 j	8.6 fgh	8.7 fg	8.5 ef	8.3 bc	7.9 e	8.5
600	2400	9.3 c-f	9.0 fg	8.8 de	8.9 efg	8.6 de	8.6 ab	8.3 cd	8.8
0	600	7.0 h	7.1 k	7.2 j	7.0 i	7.0 h	6.9 e	6.4 l	6.9
0	600	9.0 f	8.9 gh	8.6 gh	8.7 g	8.4 f	7.6 d	7.6 g	8.4
0	1200	9.5 b-e	9.1 de	8.8 def	8.9 def	8.7 de	8.6 ab	8.3 d	8.8
0	2400	9.8 ab	9.5 b	9.2 bc	9.3 bc	9.0 bc	8.7 a	8.6 abc	9.2

*Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

at the initial time of application because diffusion cannot occur until, or after, placement of fertilizer. In the present experiment we used a point charge in comparison to the line charge used in field application.

How quickly does diffusion of NH_3 cause uniform pH throughout the entire treatment zone? In some preliminary tests, we treated soil samples with high rates of $\text{NH}_4^+\text{-N}$ and P. At the end of a 24-hour incubation period, we checked the pH of the soil at different points throughout the entire volume of treated soil and found pH nearly uniform at all points 7.5 cm both above and below the point of treatment. Some diffusion of P, above and below the point of application, had occurred at the end of the 24-hour period, but to a lesser degree than that of NH_3 .

When pH values were averaged across all MAP and APP treatments, leachate- and soil-pH were dependent on $\text{NH}_4^+\text{-N}$ rates (Tables 4 and 5). In each time period significant pH increases occurred with increments of $\text{NH}_4^+\text{-N}$.

Phosphate, unlike nitrogen, depressed pH. Tables 6 and 7 show soil- and leachate-pH averaged across all N treatments. MAP depressed pH more than APP, probably because the pH of 1.55 M MAP is about 4.5, whereas the pH of 0.78 M APP is 6.75.

Comparing the pH (Tables 6 and 7) for 0-16 d shows a consistent drop in pH from 0 to 300 units of MAP. A greater drop in pH occurred when 600 units of MAP was used. The effect held true for both leachate and soil.

The comparative effects of MAP, APP, and N on soil and leachate pH for incubation periods 0 through 16 d can be seen graphically in Figures 9-22. pH increased as N rates increased. pH decreased with increased MAP rates. pH decreased with increasing APP rates, but the decreases were less than when using MAP.

Table 4. Effect of various rates of NH_4^+ -N on leachate pH.

Treatment	Leachate pH*						
	Incubation period (d)						
	0	0.5	1	2	4	8	16
NH_4^+ -N (mg/kg)							
0	6.0 d	6.2 d	6.3 d	6.4 d	6.2 d	6.1 d	5.9 d
600	9.3 c	8.7 c	8.5 c	8.6 c	8.8 c	7.3 c	6.7 c
1200	10.1 b	9.6 b	9.3 b	9.2 b	9.5 b	8.4 b	8.0 b
2400	10.5 a	9.9 a	9.7 a	9.6 a	9.9 a	8.7 a	8.6 a

*Values are means of all P treatments. Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Table 5. Effect of various rates of $\text{NH}_4^+\text{-N}$ on soil pH.

Treatment	Soil pH*						
	Incubation period (d)						
$\text{NH}_4^+\text{-N}$ (mg/kg)	0	0.5	1	2	4	8	16
0	6.6 d	6.7 d	6.7 d	6.7 d	6.7 d	6.6 d	6.4 d
600	9.1 c	8.8 c	8.6 c	8.6 c	8.8 c	7.8 c	7.4 c
1200	9.4 b	9.1 b	8.9 b	9.0 b	9.1 b	8.5 b	8.3 b
2400	9.6 a	9.4 a	9.2 a	9.3 a	9.4 a	8.7 a	8.6 a

*Values are means of all P treatments. Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Table 6. Effect of various rates of P on leachate pH.

Treatment		Leachate pH*						
		Incubation period (d)						
MAP (mg P/kg)	APP (mg P/kg)	0	0.5	1	2	4	8	16
0	0	9.4 a	9.1 a	8.9 a	8.9 a	8.5 a	8.1 a	7.8 a
300	0	8.9 c	8.4 c	8.3 d	8.3 c	7.9 c	7.5 d	7.2 c
0	300	9.3 b	8.8 b	8.8 b	8.6 b	8.3 b	7.8 b	7.4 b
600	0	8.2 d	7.8 d	7.6 c	7.8 d	7.5 d	7.2 e	6.9 d
0	600	9.0 c	8.8 b	8.6 c	8.6 b	8.3 b	7.6 c	7.4 b

*Values are means of all NH_4^+ -N treatments. Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Table 7. Effect of various rates of P on soil pH.

Treatment		Soil pH*						
		Incubation period (d)						
MAP	APP (mg P/kg)	0	0.5	1	2	4	8	16
0	0	9.1 a	8.9 a	8.6 a	8.7 a	8.4 a	8.2 a	8.0 a
300	0	8.5 c	8.3 d	8.3 d	8.3 d	8.0 c	7.7 d	7.6 c
0	300	8.8 b	8.7 b	8.5 b	8.6 b	8.4 ab	8.1 b	7.8 b
600	0	8.3 d	7.9 e	7.9 e	8.0 e	7.8 d	7.6 d	7.3 d
0	600	8.8 b	8.6 c	8.4 c	8.5 c	8.3 b	7.9 c	7.7 b

*Values are means of all NH_4^+ -N treatments. Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

B. Effect of incubation time and N- and P-treatment rates on pH.

With increasing incubation time the high pH of leachate and soil resulting from N treatments began to gradually fall (Tables 8 and 9). pH continued to drop through 16 d. The only major departure from such a trend appeared in the 2-d period with 600 units of MAP and 600 units of N. An increase in leachate pH from 7.3 to 7.8 occurred between day 1 and day 2. The value of 7.8 on day 2 may have resulted from contamination of a sample because the soil pH for those given samples did not show a comparable increase in pH between day 1 and 2.

Some of the samples receiving no N showed a significant decrease in pH during the 2- to 16-d period in both leachate and soil (Tables 10 and 11). Ammonium ions present in MAP and APP can nitrify to nitrates releasing H^+ ions. That nitrification process may have begun between 2 and 16 days, and could account for the slow decrease in pH.

The trend of soil- and leachate-pH decreasing with increasing incubation time continued throughout 16 d (Tables 10 and 11).

With the 3 highest N rates, a sharp drop in pH between day 4 and day 8 occurred in both soil and leachate. Nitrification rates may have increased in the 4- to 8-d interval, accounting for the sharp drop in pH. The general trend toward reduced pH with increasing incubation time (Tables 10 and 11) probably resulted from two factors:

1. Diffusion of NH_3 and NH_4OH from the localized point of application would, in time, reduce the concentration of OH^- ions and cause a subsequent drop in pH.
2. As nitrification of NH_4^+ to NO_3^- began occurring, H^+ ions from the reaction would neutralize the OH^- ions and cause a subsequent drop in pH.

Diffusion and nitrification, in some measure, likely occurred

Table 8. Effect of incubation time and N and P treatments on leachate pH.

Treatment	Leachate pH*							Mean
	Incubation period (d)							
	0	0.5	1	2	4	8	16	
MRP APP NH ₄ ⁺ -N (mg P/kg) (mg/kg)								
0 0	6.7 a	7.0 a	6.9 a	6.9 a	6.9 a	6.9 a	6.7 a	6.9
0 0 600	10.0 f	9.4 e	9.2 de	9.0 cd	8.7 c	7.9 b	7.2 a	8.8
0 0 1200	10.3 d	9.9 c	9.7 c	9.6 c	9.0 b	8.7 ab	8.4 a	9.4
0 0 2400	10.6 d	10.1 c	10.0 c	10.0 c	9.5 b	8.8 a	8.8 a	9.7
300 0	5.6 a	5.8 ab	5.9 ab	6.0 b	5.9 ab	5.8 ab	5.7 ab	5.8
300 0 600	9.4 e	8.5 d	8.3 d	8.4 d	7.9 c	6.9 b	6.4 a	8.0
300 0 1200	10.1 e	9.5 d	9.3 cd	9.1 c	8.7 b	8.5 b	7.9 a	9.0
300 0 2400	10.5 c	9.8 b	9.8 b	9.6 b	9.0 a	8.8 a	8.7 a	9.5
0 300 0	6.4 c	6.5 c	6.6 c	6.6 c	6.4 c	6.1 b	5.7 a	6.3
0 300 600	9.8 e	9.2 d	9.0 cd	8.8 c	8.7 c	7.5 b	6.8 a	8.5
0 300 1200	10.3 d	9.7 c	9.5 c	9.4 c	8.9 b	8.7 b	8.2 a	9.2
0 300 2400	10.6 d	10.1 c	9.9 c	9.8 c	9.3 b	8.8 a	8.9 a	9.6
600 0	5.3 a	5.5 ab	5.6 abc	5.7 bc	5.7 bc	5.7 bc	5.8 c	5.6
600 0 600	7.6 cd	7.4 c	7.3 c	7.8 d	7.3 c	6.9 b	6.4 a	7.2
600 0 1200	9.6 e	9.0 d	8.6 c	8.7 cd	8.4 c	7.8 b	7.4 a	8.5
600 0 2400	10.2 e	9.3 d	9.0 cd	9.0 cd	8.7 bc	8.5 b	8.0 a	9.0
0 600 0	5.7 a	6.4 bc	6.5 bc	6.6 c	6.5 bc	6.2 b	5.8 a	6.2
0 600 600	9.6 d	9.2 c	8.7 b	8.8 b	8.5 b	7.1 a	6.8 a	8.4
0 600 1200	10.2 d	9.6 c	9.4 c	9.3 c	8.8 b	8.6 b	8.0 a	9.1
0 600 2400	10.5 d	10.2 d	9.7 c	9.8 c	9.3 b	8.8 a	8.8 a	9.6
Mean	9.0	8.6	8.4	8.4	8.1	7.7	7.3	

*Means within a row followed by the same letter do not differ significantly at the 0.05 level. LSD = 0.3.

Table 9. Effect of incubation time and N and P treatments on soil pH.

Treatment	Soil pH*							
	Incubation period (d)							
MAP, DFP, NH ₄ ⁺ -N (mg P/kg) (mg/kg)	0	0.5	1	2	4	8	16	Mean
0 0 0	7.0 a	7.0 a	6.9 a	7.1 a	6.9 a	7.0 a	7.0 a	7.0
0 0 600	9.5 e	9.2 de	9.0 cd	9.0 cd	8.8 c	8.2 b	7.8 a	8.8
0 0 1200	9.8 c	9.5 bc	9.2 b	9.2 b	8.8 a	8.8 a	8.6 a	9.1
0 0 2400	9.9 d	9.8 cd	9.5 bc	9.6 bcd	9.3 b	8.8 a	8.7 a	9.4
300 0 0	6.1 a	6.3 a	6.3 a	6.4 a	6.3 a	6.2 a	6.1 a	6.2
300 0 600	9.0 e	8.7 de	8.5 cd	8.7 de	8.3 c	7.7 b	7.0 a	8.3
300 0 1200	9.3 d	9.1 cd	8.9 bc	9.0 cd	8.6 ab	8.3 a	8.4 a	8.8
300 0 2400	9.5 b	9.4 b	9.4 b	9.2 b	8.8 a	8.7 a	8.7 a	9.1
0 300 0	6.6 ab	7.1 c	7.0 c	7.0 c	6.9 bc	6.6 ab	6.3 a	6.8
0 300 600	9.2 d	9.1 d	8.8 c	8.9 cd	8.7 c	8.1 b	7.7 a	8.6
0 300 1200	9.6 d	9.3 cd	9.0 b	9.1 bc	8.8 ab	8.8 ab	8.5 a	9.0
0 300 2400	9.7 b	9.5 b	9.4 b	9.4 b	9.0 a	8.8 a	8.8 a	9.2
600 0 0	6.1 a	6.0 a	6.2 a	6.3 a	6.2 a	6.2 a	6.1 a	6.2
600 0 600	8.6 d	8.0 c	8.0 c	8.0 c	7.9 c	7.5 b	7.0 a	7.9
600 0 1200	9.1 d	8.7 c	8.6 bc	8.7 c	8.5 bc	8.3 b	7.9 a	8.5
600 0 2400	9.3 d	9.0 cd	8.8 bc	8.9 bc	8.6 ab	8.6 ab	8.3 a	8.8
0 600 0	6.00	7.1 b	7.2 b	7.0 b	7.0 b	6.9 b	6.4 a	6.9
0 600 600	9.0 d	8.9 cd	8.6 bc	8.7 bcd	8.4 b	7.6 a	7.6 a	8.4
0 600 1200	9.5 d	9.1 c	8.8 bc	8.9 bc	8.7 b	8.6 ab	8.3 a	8.8
0 600 2400	9.8 d	9.5 cd	9.2 bc	9.3 bc	9.0 b	8.7 a	8.6 a	9.2
Mean	8.7	8.5	8.4	8.4	8.2	7.9	7.7	

*Means within a row followed by the same letter do not differ significantly at the 0.05 level.
LSD = 0.3.

Table 10. Effect of incubation time and various rates of $\text{NH}_4^+\text{-N}$ on leachate pH.

Treatment	Leachate pH*							Mean
	Incubation period (d)							
$\text{NH}_4^+\text{-N}$ (mg/kg)	0	0.5	1	2	4	8	16	
0	6.0 ab	6.2 cd	6.3 de	6.4 d	6.2 de	6.1 bc	5.9 a	6.2
600	9.3 f	8.7 e	8.5 d	8.6 de	8.8 c	7.3 b	6.7 a	8.3
1200	10.1 f	9.6 e	9.3 d	9.2 d	9.5 c	8.4 b	8.0 a	9.2
2400	10.5 e	9.9 d	9.7 c	9.6 c	9.9 b	8.7 a	8.6 a	9.6

*Values are means of all P treatments. Means within a row followed by the same letter do not differ significantly at the 0.05 level.
LSD = 0.1.

Table 11. Effect of incubation time and various rates of $\text{NH}_4^+\text{-N}$ on soil pH.

Treatment	Soil pH*							Mean
	0	0.5	1	2	4	8	16	
$\text{NH}_4^+\text{-N}$ (mg/kg)								
0	6.6 b	6.7 b	6.7 b	6.7 b	6.7 b	6.6 b	6.4 a	6.6
600	9.1 f	8.8 e	8.6 d	8.6 d	8.8 c	7.8 b	7.4 a	8.4
1200	9.4 f	9.1 e	8.9 d	9.0 de	9.1 c	8.5 b	8.3 a	8.9
2400	9.6 e	9.4 d	9.2 c	9.3 cd	9.4 b	8.7 a	8.6 a	9.2

*Values are means of all P treatments. Means within a row followed by the same letter do not differ significantly at the 0.05 level.
LSD = 0.1.

simultaneously during the interval of incubation from 0 to 16 d. We did not make quantitative analyses for NH_4^+ ions and NO_3^- ions to determine at exactly what time and at what rates nitrification occurred.

The high pH and high NH_3 concentrations near the point of injection of N treatments probably initially suppressed nitrifying microbial activity in that area; therefore diffusion of NH_3 and NH_4OH away from the point of injection would have been primarily responsible for initially reducing the pH level in the treated zone. Nitrification more likely began at the periphery of the diffused treatment in the buffer zone of neutral soil above and below the treated zone. Nitrification at the periphery would lower the pH and the NH_3 concentration at that point, and increase the pH gradient and the NH_3 concentration gradient from the point of injection to the periphery.

Those increased gradients would increase the rate of diffusion away from the point of injection. Therefore, pH was probably initially lowered in the treated zone as diffusion reduced NH_3 and NH_4OH concentrations, but nitrification at the periphery probably increased rates of diffusion by increasing the pH and NH_3 gradients from the point of injection to the periphery of the treated zone. Additional tests would be needed to determine the relative importance of diffusion and nitrification in lowering pH levels at the different incubation times.

Effects of incubation time and P on pH (Tables 12 and 13) were similar to results of Tables 10 and 11. With increasing incubation time, pH continued decreasing for 16 d in leachate and soil. The reasons for that decrease in pH would be the same as those explained for the results of Tables 10 and 11.

Table 12. Effect of incubation time and various rates of P on leachate pH.

Treatment	Leachate pH*								
	Incubation period (d)								
MAP APP (mg P/kg)	0	0.5	1	2	4	8	16	Mean	
0	0	9.4 f	9.1 e	8.9 d	8.9 d	8.5 c	8.1 b	7.8 a	8.7
300	0	8.9 e	8.4 d	8.3 d	8.3 d	7.9 c	7.5 b	7.2 a	8.1
0	300	9.3 f	8.8 e	8.8 e	8.6 d	8.3 c	7.8 b	7.4 a	8.4
600	0	8.2 e	7.8 d	7.6 d	7.8 d	7.5 c	7.2 b	6.9 a	7.6
0	600	9.0 f	8.8 e	8.6 e	8.6 d	8.3 c	7.6 b	7.4 a	8.3

*Values are means of all $\text{NH}_4^+\text{-N}$ treatments. Means within a row followed by the same letter do not differ significantly at the 0.05 level. LSD = 0.1.

Table 13. Effect of incubation time and various rates of P on soil pH.

Treatment	Soil pH*								
	Incubation period (d)								
MAP APP (mg P/kg)	0	0.5	1	2	4	8	16	Mean	
0	0	9.1 f	8.9 e	8.6 d	8.7 d	8.4 c	8.2 b	8.0 a	8.6
300	0	8.5 d	8.3 c	8.3 c	8.3 c	8.0 b	7.7 a	7.6 a	8.1
0	300	8.8 f	8.7 ef	8.5 d	8.6 de	8.4 c	8.1 b	7.8 a	8.4
600	0	8.3 e	7.9 cd	7.9 cd	8.0 d	7.8 c	7.6 b	7.3 a	7.8
0	600	8.8 f	8.6 e	8.4 cd	8.5 de	8.3 c	7.9 b	7.7 a	8.3

*values are means of all $\text{NH}_4^+\text{-N}$ treatments. Means within a row followed by the same letter do not differ significantly at the 0.05 level.
LSD = 0.1.

C. Regression analyses for leachate- and soil-pH.

R^2 values from ANOVA show the maximum portion of variation between observations of different replicates which the best model of any type, such as a linear or polynomial model, would explain.

R^2 values from regression analysis show the portion of variation between observations of different replicates explained by the linear regression model which we used.

R^2 regression/ R^2 ANOVA = the portion of variation which the linear regression model accounts for, in comparison to the variation which the best model would explain.

R^2 values for leachate pH, 0 through 16 d

Table 14. R^2 values for leachate pH, 0 through 16 d.

	Incubation period (d)						
	0	0.5	1	2	4	8	16
R^2 Regression	.678	.731	.766	.750	.749	.820	.896
R^2 ANOVA	.996	.996	.997	.993	.994	.995	.989
R^2 Reg./ R^2 ANOVA	.681	.734	.768	.755	.754	.824	.906

Since we are primarily interested in major trends in pH rather than highly precise values at all levels of N and P, we have not calculated a regression equation to determine the pH because 5 different regression equations would be required for each time period. With 7 time periods, 35 different regression equations would be required for leachate pH alone. Such a list of equations would likely serve no useful purpose for the reader.

R^2 values for soil pH, 0 through 16 d.Table 15. R^2 values for soil pH, 0 through 16 d.

	Incubation period (d)						
	0	0.5	1	2	4	8	16
R^2 Regression	.624	.690	.706	.692	.677	.741	.819
R^2 ANOVA	.981	.994	.992	.993	.989	.980	.987
R^2 Reg./ R^2 ANOVA	.636	.694	.712	.697	.684	.756	.930

The R^2 regression values are lower for soil than those for the corresponding leachate samples. Experimental error in determining soil pH of leached soil may have exceeded the experimental error in determining leachate pH. Repeated pH readings of the same leachate sample were always nearly identical, but probing the leached soil in different locations often gave different readings of as much as 0.1 to 0.3 units on the pH scale. We averaged the different readings to record the soil pH.

D. Probability of interactions between N and P treatments affecting pH

Leachate pH

Table 16. Probability of an interaction between $\text{NH}_4^+\text{-N}$ and MAP affecting pH of aqueous leachate from Kennebec silt loam.

	Incubation period (d)						
	0	0.5	1	2	4	8	16
F value	30.34	21.99	19.86	2.89	11.01	30.35	7.89
Pr > F	0.0001	0.0001	0.0001	0.0204	0.0001	0.0001	0.0001

All interactions between N and MAP affecting leachate pH (Table 16) were significant at the 0.05 level.

Table 17. Probability of an interaction between $\text{NH}_4^+\text{-N}$ and APP affecting pH of aqueous leachate from Kennebec silt loam.

	Incubation period (d)						
	0	0.5	1	2	4	8	16
F value	5.80	4.19	1.41	0.28	3.47	20.73	8.63
Pr > F	0.0002	0.0025	0.2356	0.9408	0.0078	0.0001	0.0001

Interactions between N and APP (Table 17) were significant at the 0.05 level except for the 1- and 2-d periods.

Interactions of N and P treatments affecting leachate pH probably resulted primarily from the opposing effect the N and P treatments had on pH.

MAP had a greater pH depressing effect than APP. Similarly, F values were higher and Pr values were lower for MAP-N interactions than for APP-N interactions.

The interaction response of leachate pH to various rates of $\text{NH}_4^+\text{-N}$ and P is illustrated (Fig. 23-36). Increasing rates of $\text{NH}_4^+\text{-N}$ increased pH. Both MAP and APP depressed pH, but MAP had the greatest depressing effect, probably because the pH of the MAP treatment formulation was lower than that of the APP formulation, 4.5 and 6.7, respectively.

Soil pH

Table 18. Probability of an interaction between $\text{NH}_4^+\text{-N}$ and MAP affecting soil pH of Kennebec silt loam.

	Incubation period (d)						
	0	0.5	1	2	4	8	16
F value	0.82	4.17	4.45	5.19	3.37	3.55	7.67
Pr > F	0.5621	0.0026	0.0017	0.0006	0.0093	0.0069	0.0001

N-MAP interactions (Table 18) were all significant at the 0.05 level except for the 0-d period.

Table 19. Probability of an interaction between $\text{NH}_4^+\text{-N}$ and APP affecting soil pH of Kennebec silt loam.

	Incubation period (d)						
	0	0.5	1	2	4	8	16
F value	1.10	2.93	5.74	1.12	3.10	3.66	4.79
Pr > F	0.3809	0.0190	0.0003	0.3671	0.0144	0.0057	0.0010

N-APP interactions were all significant at the 0.05 level (Table 19) except for the 0- and 2-d periods.

The interaction response of soil pH to various rates of $\text{NH}_4^+\text{-N}$ and P is illustrated (Fig. 37-50). Increasing N rates increased pH. Both MAP and APP treatments depressed soil pH, but MAP depressed pH more than APP.

The reason for that was explained under the section for leachate pH.

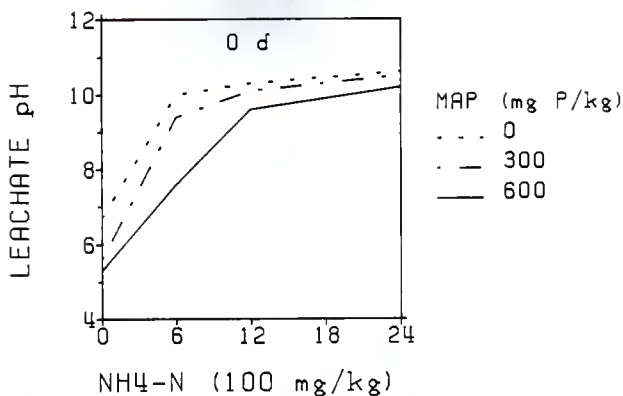


Figure 23. Response of leachate pH to various rates of MAP and N, immediately after treatment.

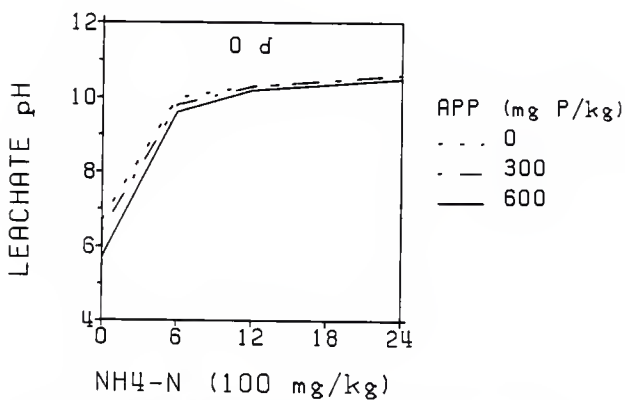


Figure 24. Response of leachate pH to various rates of APP and N, immediately after treatment.

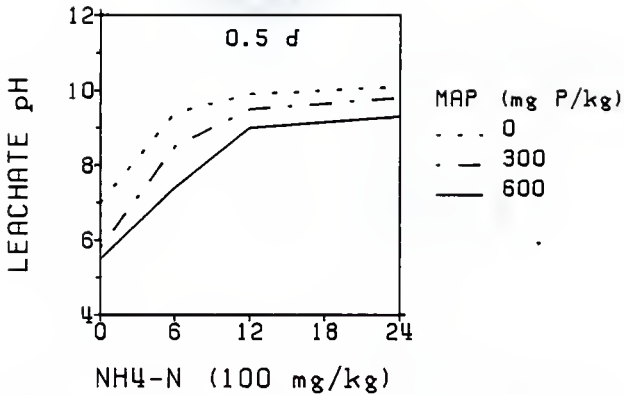


Figure 25. Response of leachate pH to various rates of MAP and N, 0.5 d after treatment.

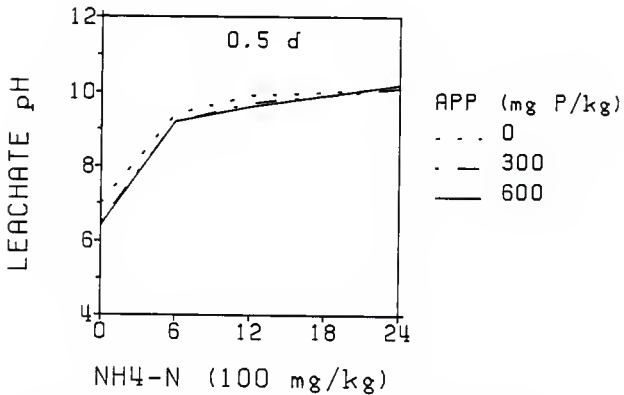


Figure 26. Response of leachate pH to various rates of APP and N, 0.5 d after treatment.

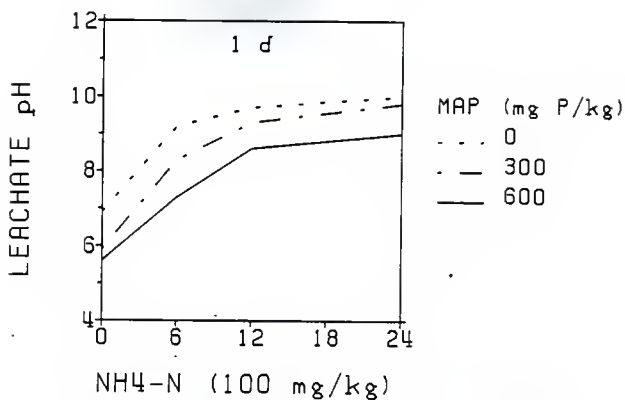


Figure 27. Response of leachate pH to various rates of MAP and N, 1 d after treatment.

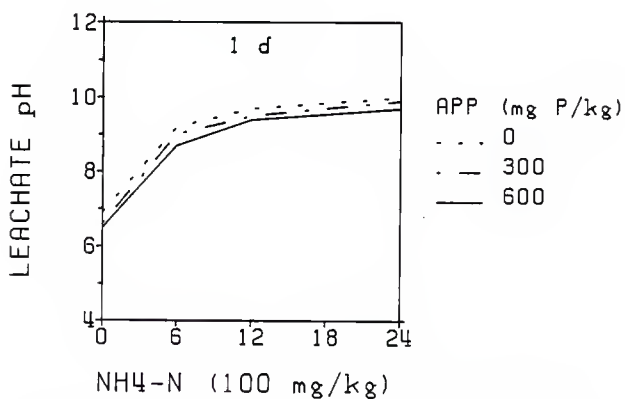


Figure 28. Response of leachate pH to various rates of APP and N, 1 d after treatment.

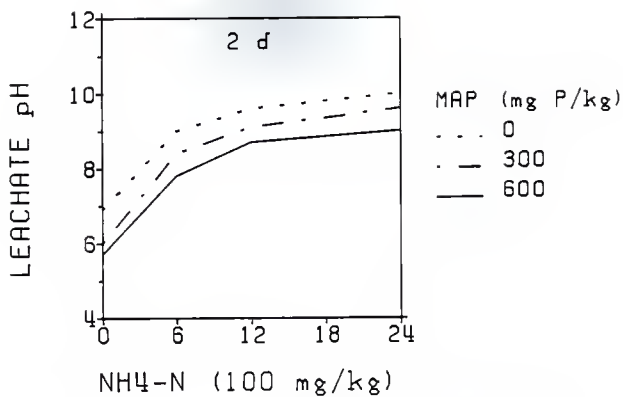


Figure 29. Response of leachate pH to various rates of MAP and N, 2 d after treatment.

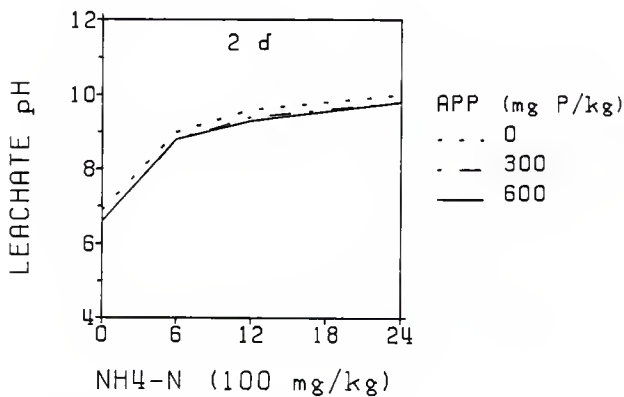


Figure 30. Response of leachate pH to various rates of APP and N, 2 d after treatment.

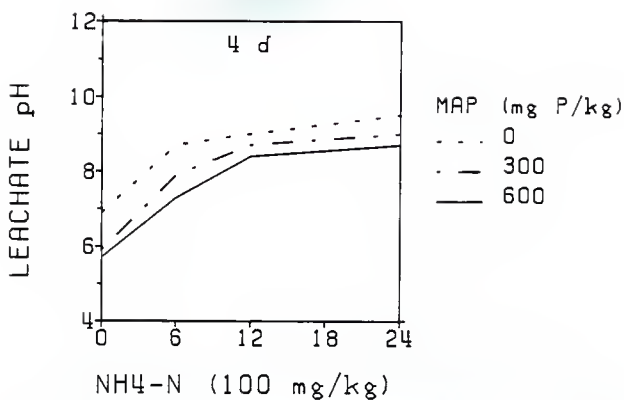


Figure 31. Response of leachate pH to various rates of MAP and N, 4 d after treatment.

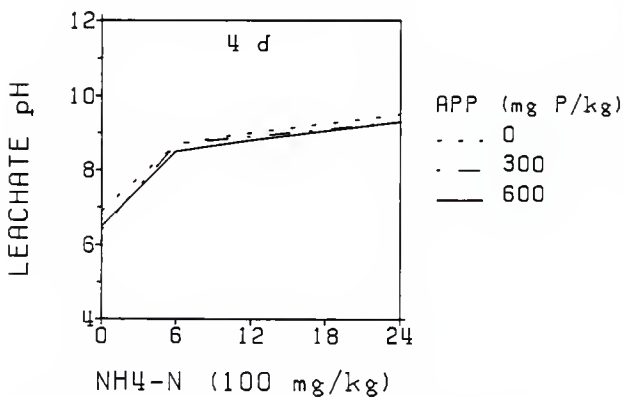


Figure 32. Response of leachate pH to various rates of APP and N, 4 d after treatment.

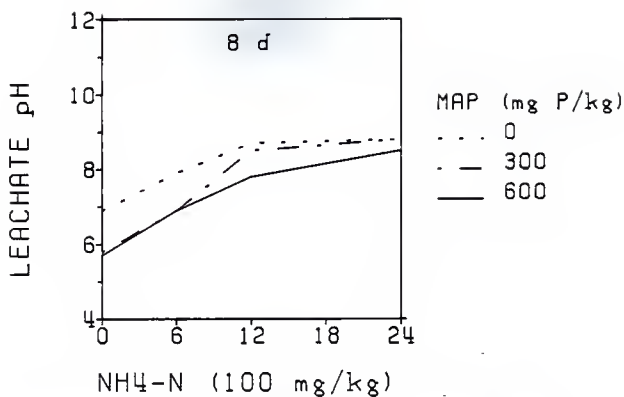


Figure 33. Response of leachate pH to various rates of MAP and N, 8 d after treatment.

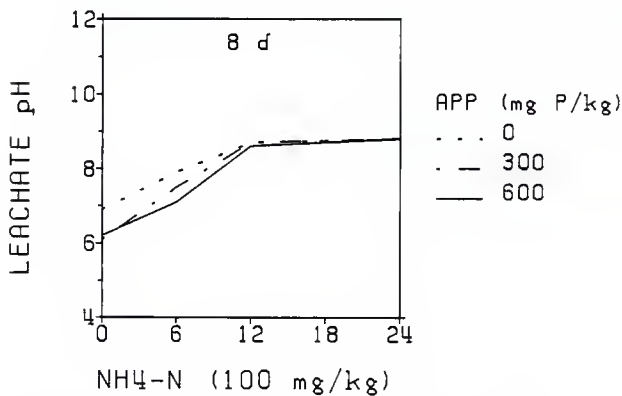


Figure 34. Response of leachate pH to various rates of APP and N, 8 d after treatment.

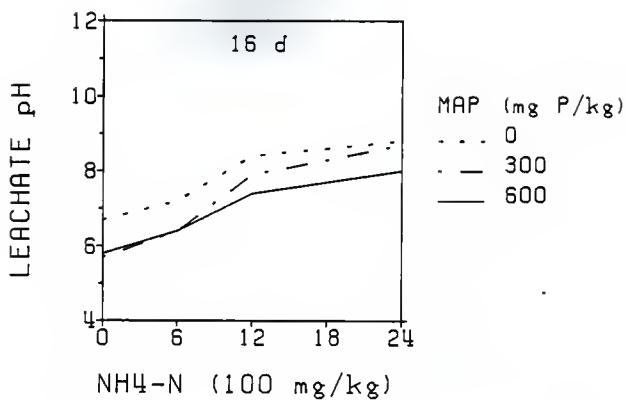


Figure 35. Response of leachate pH to various rates of MAP and N, 16 d after treatment.

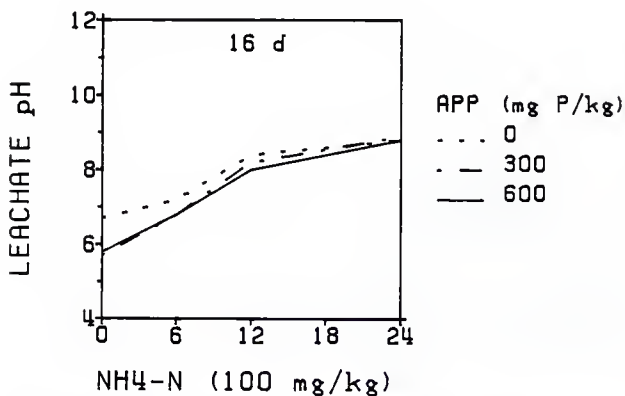


Figure 36. Response of leachate pH to various rates of APP and N, 16 d after treatment.

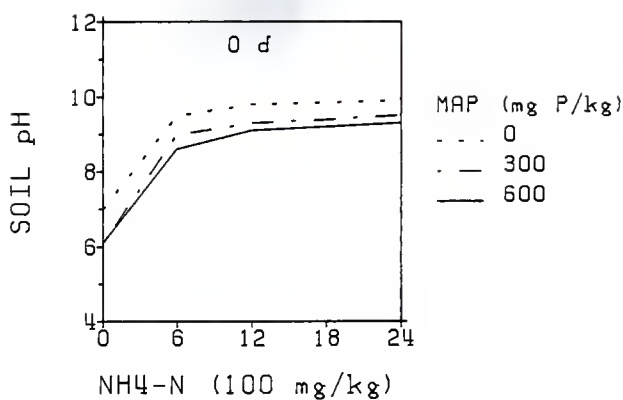


Figure 37. Response of soil pH to various rates of MAP and N, immediately after treatment.

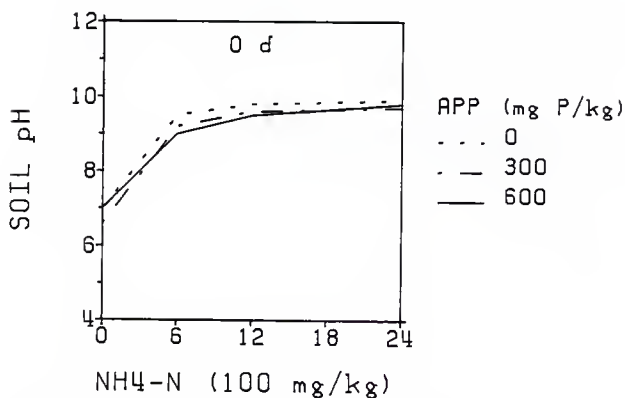


Figure 38. Response of soil pH to various rates of APP and N, immediately after treatment.

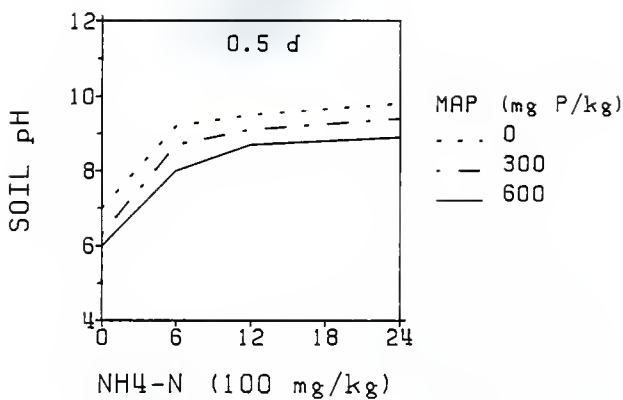


Figure 39. Response of soil pH to various rates of MAP and N, 0.5 d after treatment.

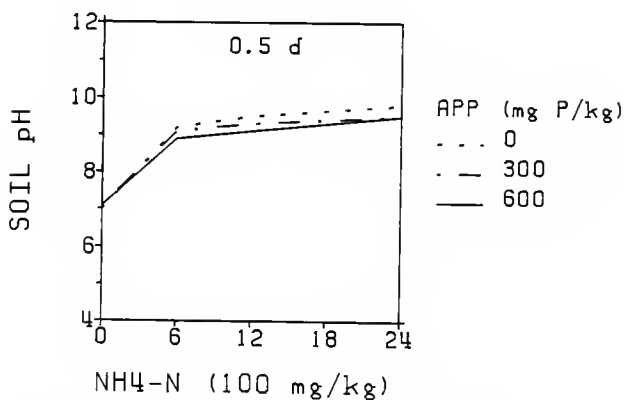


Figure 40. Response of soil pH to various rates of APP and N, 0.5 d after treatment.

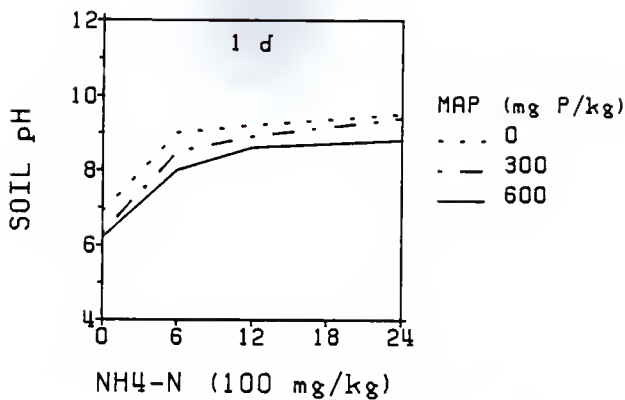


Figure 41. Response of soil pH to various rates of MAP and N, 1 d after treatment.

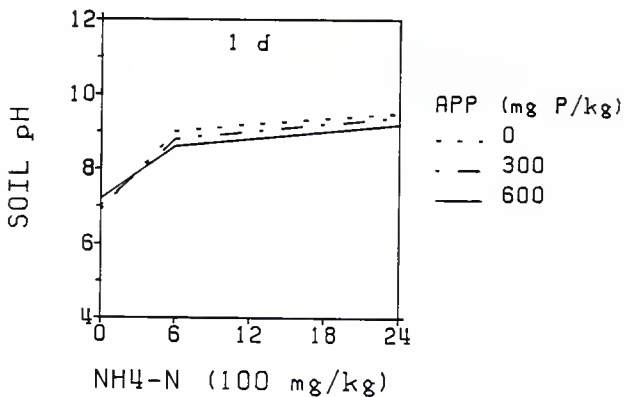


Figure 42. Response of soil pH to various rates of APP and N, 1 d after treatment.

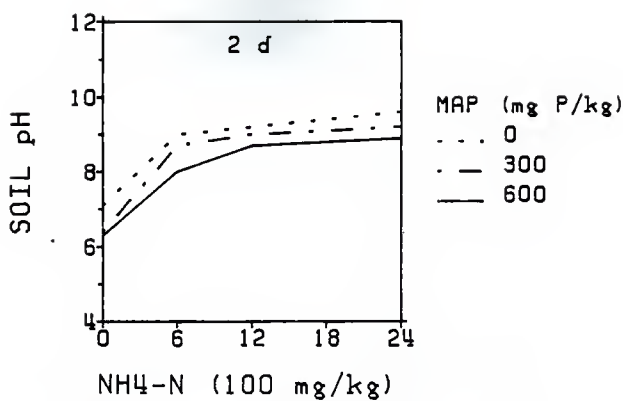


Figure 43. Response of soil pH to various rates of MAP and N, 2 d after treatment.

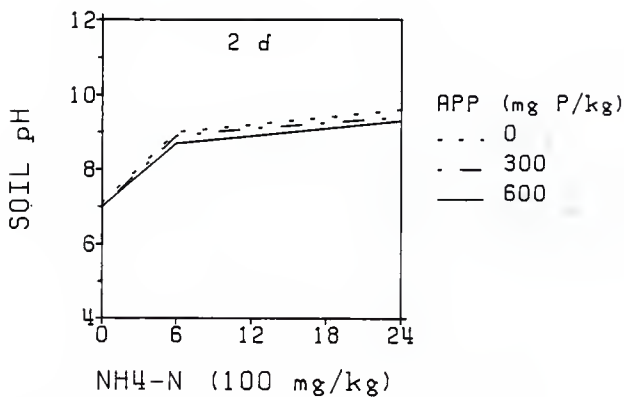


Figure 44. Response of soil pH to various rates of APP and N, 2 d after treatment.

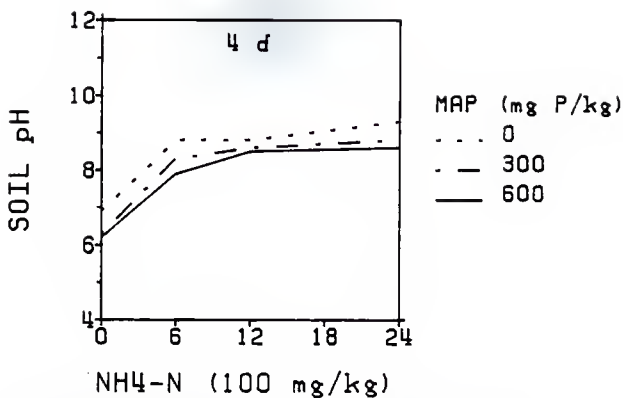


Figure 45. Response of soil pH to various rates of MAP and N, 4 d after treatment.

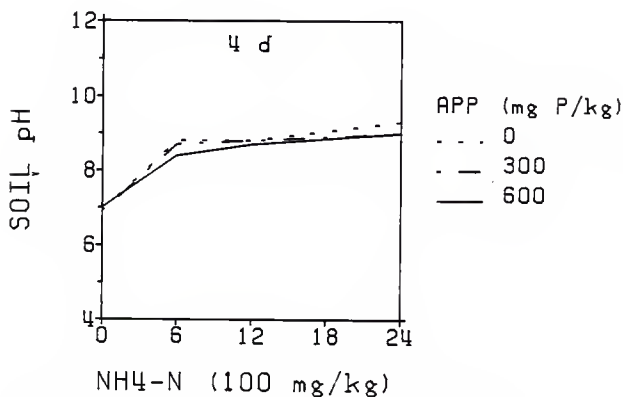


Figure 46. Response of soil pH to various rates of APP and N, 4 d after treatment.

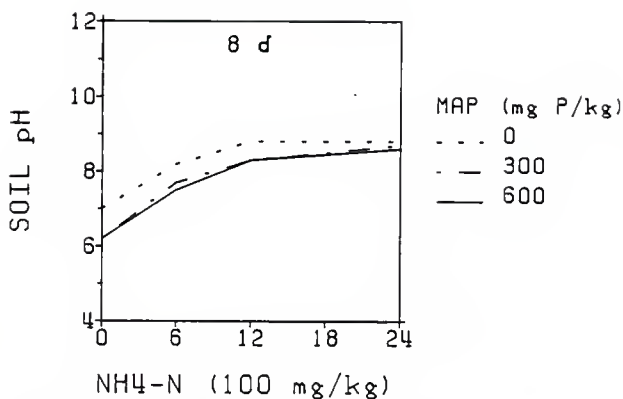


Figure 47. Response of soil pH to various rates of MAP and N, 8 d after treatment.

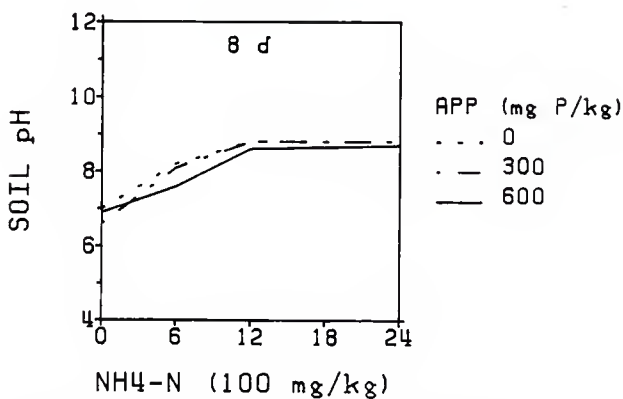


Figure 48. Response of soil pH to various rates of APP and N, 8 d after treatment.

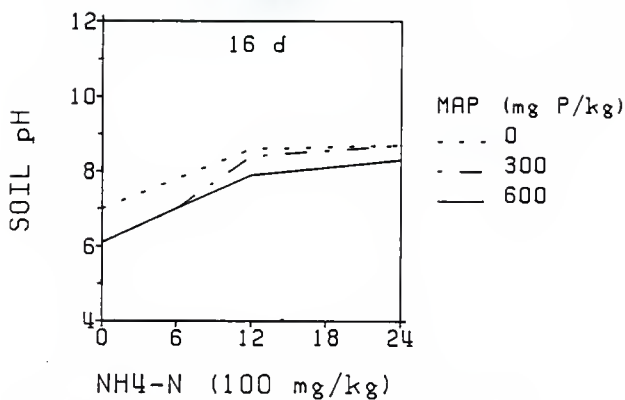


Figure 49. Response of soil pH to various rates of MAP and N, 16 d after treatment.

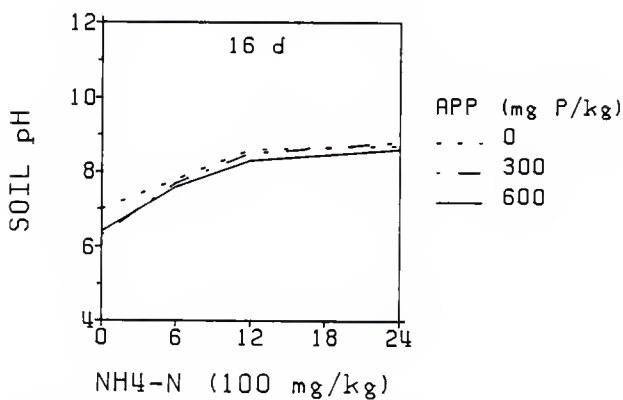


Figure 50. Response of soil pH to various rates of APP and N, 16 d after treatment.

RESULTS: PART II

EFFECT OF N AND P TREATMENTS ON HUMIC SUBSTANCES

N and P treatments apparently dissolved soil organic matter in varying amounts depending upon the treatment. We did not make a physical analysis of the humic substances in the leachate samples to determine their exact physical nature, so the terms 'dissolved' and 'solubilized' used in explaining the nature of the extracted humic substances are based upon visual observations.

Following treatments with any combination of N and MAP, the leachate samples had the appearance of a homogenous solution. Following some of the treatments of N and APP, a major portion of each leachate sample appeared a homogenous solution, but a smaller portion in some of the samples settled to the lower part of the flask. That portion which settled had the appearance of a colloidal dispersion rather than a distinct precipitate.

Sometime in the future we plan to make a physical analysis of leachate samples to determine the particle-size distribution of any dispersed colloids of the extracted humic substances.

A. Extractable humic substances immediately after treatment

Total extracted humic substances (0 d)

Total extracted humic substances varied from 0 from the untreated soil to 321 mg/kg for the 0-600-2400 treatment (Table 20). Extracted humic substances usually increased as N rates increased. Increasing N rates from 0 to 1200 mg N/kg caused significant increases in extracted humic substances when P rates were either 300 or 600 mg P/kg, regardless of P

Table 20. Humic substances extracted from Kennebec silt loam immediately after treatment with various rates of orthophosphate, pyrophosphate, and nitrogen.

Treatment			Extracted humic substances*			
			Total		Acids	
MAP (mg P/kg)	APP (mg/kg)	NH ₄ ⁺ -N (mg/kg)	(mg/kg)	%	FULVIC (mg/kg)	HUMIC (mg/kg)
0	0	0	0 g	0.0	0 g	0 e
0	0	600	55 fg	0.3	32 efg	22 de
0	0	1200	100 ef	0.5	58 c-g	42 cde
0	0	2400	100 ef	0.5	59 b-g	41 cde
300	0	0	5 g	0.0	5 g	0 e
300	0	600	60 fg	0.3	22 efg	37 cde
300	0	1200	115 def	0.6	49 d-g	66 cde
300	0	2400	165 b-e	0.9	67 b-f	98 bc
0	300	0	50 fg	0.3	35 efg	15 de
0	300	600	120 d-f	0.6	70 b-f	50 cde
0	300	1200	160 b-e	0.9	82 a-e	78 bcd
0	300	2400	196 bcd	1.0	112 abc	83 bcd
600	0	0	40 fg	0.2	17 fg	23 de
600	0	600	60 fg	0.3	39 efg	21 de
600	0	1200	100 ef	0.5	68 b-f	32 cde
600	0	2400	205 bc	1.1	107 a-d	99 bc
0	600	0	60 fg	0.3	29 efg	31 cde
0	600	600	220 b	1.2	78 a-f	143 ab
0	600	1200	306 a	1.6	118 ab	188 a
0	600	2400	321 a	1.7	131 a	190 a

*Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

source.

Increasing APP rates from 0 to 300, or 300 to 600 mg P/kg with N rates of either 1200 or 2400 mg N/kg significantly increased total extracted humic substances. The effect of MAP was less than the effect of APP at the 0-d incubation period.

Apparently SOM began dissolving immediately upon contact with the treatments, and that reaction is the most striking feature shown by the data from the 0-d incubation period. We do not know the nature of the chemical reaction which caused SOM to dissolve.

Increasing amounts of extracted humic substances caused by increasing N rates are shown in Fig. 51. Increasing color intensities (Fig. 52) of leachate samples reflect increasing amounts of extracted humic substances. In comparing the color of leachate samples, most samples from various N and P treatments have observably greater coloration than the control in the upper left.

It is worth noting that the results from the 0-d incubation period showed slightly less consistency than from other periods. One inconsistent result appears in Figure 51 between the 0-0-1200 and 0-0-2400 treatments. The total extracted humic substances were the same for those two treatments (Table 20). Another inconsistent result appears in Figure 52 with treatment 0-600-600 where the leachate sample has a darker color than the samples below from the 0-600-1200 and 0-600-2400 treatments.

Percentages of total humic substances leached from the soil varied from 0 for the control to 1.7 for the 0-600-2400 treatment (Table 20). Although the percentage of 1.7 appears low, still when 1.7% of SOM in a given volume of soil dissolves every year for several decades, the cumulative effects could be significant.

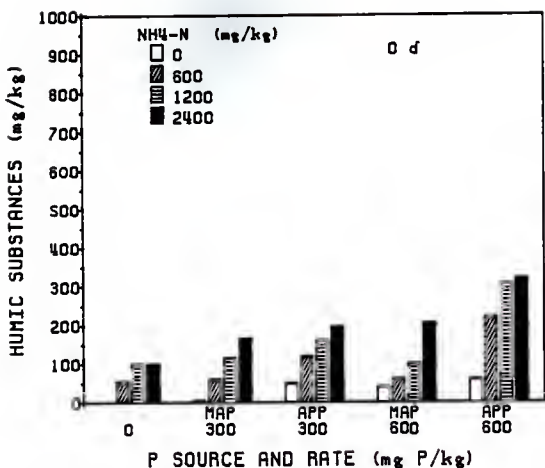


Figure 51. Total humic substances extracted from Kennebec silt loam immediately after treatment.

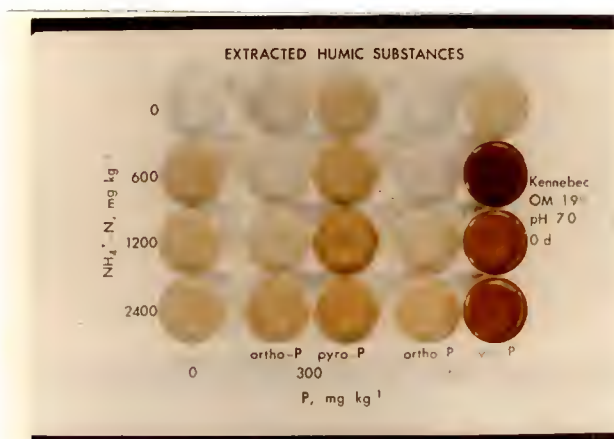


Figure 52. Solution colors due to dissolved humic substances in aqueous leachate from Kennebec silt loam immediately after treatment.

Extracted acids (0 d)

Total extracted humic substances were separated into fulvic acid and humic acid (Table 20). Slightly more fulvic than humic acid was extracted when only N treatments were applied. For further discussion on FA/HA ratios see section H.

Amounts of FA increased significantly when N rates were increased from 0 to 2400 mg N/kg with 300 or 600 mg P/kg of either MAP or APP. The same results held true for HA except for the 300 mg P/kg rate of APP where there were no significant differences.

Fig. 53 and 54 illustrate how increments of N and P usually increased amounts of extracted FA and HA.

For statistical data on FA and HA refer to Table 20.

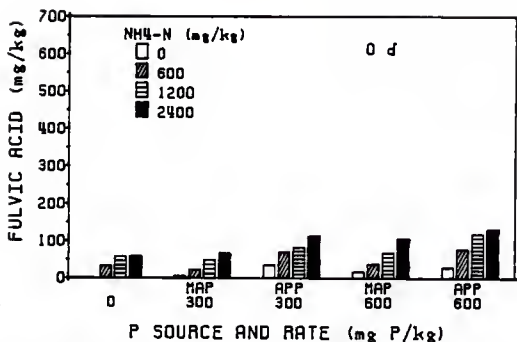


Figure 53. Fulvic acid extracted from Kennebec silt loam immediately after treatment.

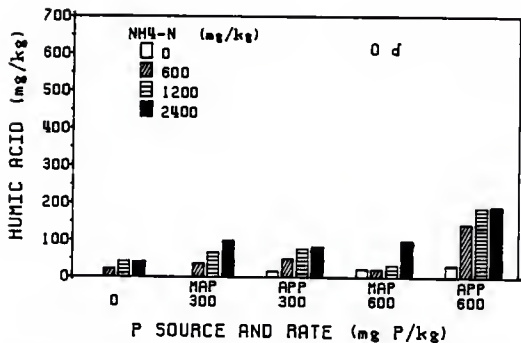


Figure 54. Humic acid extracted from Kennebec silt loam immediately after treatment.

B. Extractable humic substances 0.5 d after treatment

Total extracted humic substances (0.5 d)

Total extracted humic substances varied from 0 for the control to 914 mg/kg for treatment 0-600-2400 (Table 21). Increments of N caused significant increases in extracted humic substances. Addition of P to N treatments usually caused greater amounts of extracted humic substances than when only N treatments were used.

Amounts of extracted humic substances (Fig. 55) rose to their highest level with the highest rate of N. Amounts were usually greater when both P and N were included in the treatment than when only N was included, indicating P as well as N contributed to the degradation of SOM.

A close correlation between amounts of extracted humic substances and color intensities in leachate samples can be observed in Figures 55 and 56. Increased amounts of extracted humic substances resulted in increased color of leachate samples. In comparing the 300-0-600 and 600-0-600 treatments (Fig. 56) where MAP rates were increased, the leachate from the higher MAP rate has a lighter color than the leachate from the lower MAP rate. The higher rate of MAP depressed pH more than the lower MAP rate. The lower pH was probably the reason for less extracted humic substances coloring the leachate from the 600-0-600 treatment. Quantitative amounts of extracted humic substances (Table 21 and Fig. 55) also show decreases when MAP rates were increased in the 600-0-600 treatment, compared to the 300-0-600 treatment.

Percentages of total humic substances extracted from the soil ranged from 0 for the control to 4.8 for the 0-600-2400 treatment (Table 21).

Table 21. Humic substances extracted from Kennebec silt loam 0.5 d after treatment with various rates of orthophosphate, pyrophosphate, and nitrogen.

Treatment			Extracted humic substances*			
			Total		Acids	
MAP (mg P/kg)	APP (mg/kg)	NH ₄ ⁺ -N (mg/kg)	(mg/kg)	%	Fulvic (mg/kg)	Humic (mg/kg)
0	0	0	0 j	0.0	0 j	0 h
0	0	600	139 gh	0.7	106 gh	33 gh
0	0	1200	239 f	1.3	195 def	45 gh
0	0	2400	359 e	1.9	288 c	71 gh
300	0	0	35 ij	0.2	16 j	19 gh
300	0	600	210 fg	1.1	116 gh	93 fgh
300	0	1200	459 d	2.4	208 de	251 de
300	0	2400	708 b	3.7	303 c	405 ab
0	300	0	95 hi	0.5	49 ij	45 gh
0	300	600	269 f	1.4	157 efg	113 fg
0	300	1200	399 de	2.1	229 d	170 ef
0	300	2400	564 c	3.0	323 bc	241 de
600	0	0	40 ij	0.2	38 j	2 h
600	0	600	120 h	0.6	93 hi	26 gh
600	0	1200	564 c	3.0	214 d	350 bc
600	0	2400	699 b	3.7	294 c	405 ab
0	600	0	144 gh	0.7	144 fgh	0 h
0	600	600	459 d	2.4	232 d	227 de
0	600	1200	674 b	3.5	372 b	302 cd
0	600	2400	914 a	4.8	436 a	478 a

*Means within a column followed by the same letter are not significantly different at the 0.05 level according Duncan's Multiple Range Test.

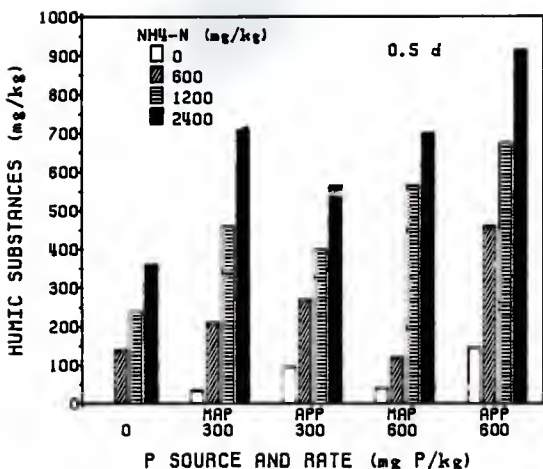


Figure 55. Total humic substances extracted from Kennebec silt loam 0.5 d after treatment.

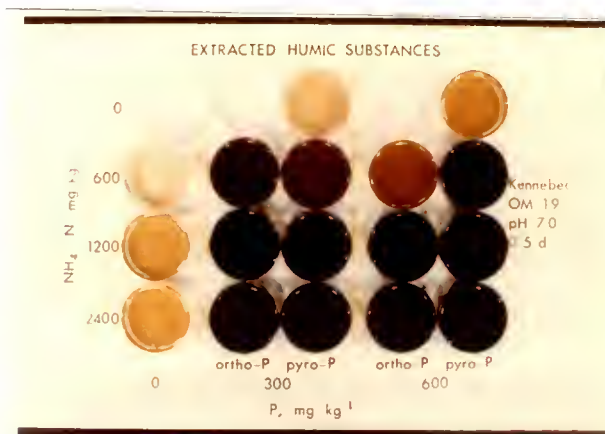


Figure 56. Solution colors due to dissolved humic substances in aqueous leachate from Kennebec silt loam 0.5 d after treatment.

Extracted acids (0.5 d)

When only NH_4CH was used, more FA than HA dissolved (Table 21). For further discussion of FA/HA ratios see section H.

Increments of N caused some significant increases in FA and HA. The addition of MAP and APP caused a greater number of significant increases in amounts of humic acid than fulvic acid, but that was at least partly due to the lower values of humic acid when only N was used.

Fig. 57 and 58 illustrate how increments of N increased amounts of extracted fulvic and humic acid. The addition of P to N treatments caused greater amounts of extracted FA and HA than N treatments alone.

For statistical data on FA and HA refer to Table 21.

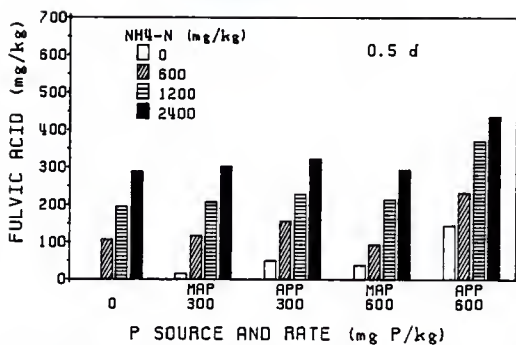


Figure 57. Fulvic acid extracted from Kennebec silt loam 0.5 d after treatment.

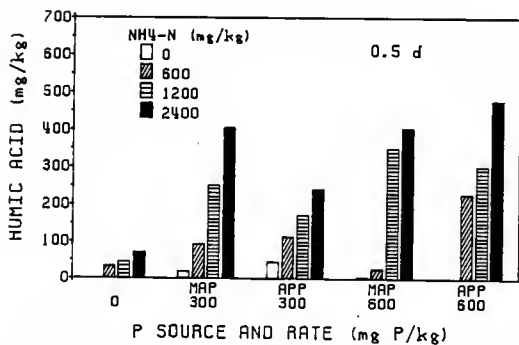


Figure 58. Humic acid extracted from Kennebec silt loam 0.5 d after treatment.

C. Extractable humic substances 1 d after treatment

Total extracted humic substances (1 d)

Total extracted humic substances varied from 5 mg/kg for the control to 798 mg/kg for treatment 0-600-2400 (Table 22). Increasing rates of N usually caused significant increases in extracted humic substances when the P source and rate remained constant.

An increase in MAP from 0 to 300 mg P/kg gave some significant increases in extracted humic substances. There were no significant differences between treatments of 300 and 600 mg P/kg using MAP. Some of the values were slightly less for 600 mg P/kg of MAP than for 300. That was probably due to the lower pH caused by the higher MAP rate.

An increase in APP rates from 0 to 300 or from 300 to 600 mg P/kg caused significant increases in extracted humic substances when the N rates were 1200 or 2400 mg N/kg.

Including P with N treatments usually caused greater amounts of extracted humic substances than when only N treatments were used (Fig. 59).

Color intensities of leachate samples (Fig. 60) closely correlate with quantitative values (Figure 59). Greater amounts of extracted humic substances resulted in greater color intensity in leachate samples. In comparing the 300-0-600 and 600-0-600 treatments, the leachate from the higher MAP rate has a lighter color than the leachate from the lower MAP rate. The apparent reason for that is the same as that explained for the 0.5-d period. The higher rate of MAP depressed pH more than the lower rate. The lower pH in the 600-0-600 treatment probably caused less extracted humic substances in the leachate, therefore the leachate from

Table 22. Humic substances extracted from Kennebec silt loam 1 d after treatment with various rates of orthophosphate, pyrophosphate, and nitrogen.

Treatment			Extracted humic substances*			
			Total		Acids	
MAP (mg P/kg)	APP (mg/kg)	NH ₄ ⁺ -N (mg/kg)	Total (mg/kg)	%	Fulvic (mg/kg)	Humic (mg/kg)
0	0	0	5 j	0.0	0 k	5 g
0	0	600	130 hi	0.7	88 hij	42 g
0	0	1200	259 fg	1.4	200 d-g	59 fg
0	0	2400	352 ef	1.8	287 bc	66 fg
300	0	0	57 ij	0.3	40 jk	17 g
300	0	600	200 gh	1.0	84 hij	115 efg
300	0	1200	452 de	2.4	185 efg	267 bcd
300	0	2400	670 b	3.5	310 abc	360 ab
0	300	0	81 ij	0.4	53 ijk	28 g
0	300	600	210 gh	1.1	123 ghi	87 efg
0	300	1200	413 e	2.2	243 cde	170 def
0	300	2400	546 cd	2.9	346 ab	200 cde
600	0	0	61 ij	0.3	40 jk	21 g
600	0	600	150 hi	0.8	96 hij	54 fg
600	0	1200	447 de	2.4	208 def	240 bcd
600	0	2400	645 bc	3.4	334 ab	311 abc
0	600	0	150 hi	0.8	138 fgh	12 g
0	600	600	422 e	2.2	160 fgh	262 bcd
0	600	1200	561 c	3.0	274 bcd	287 bcd
0	600	2400	798 a	4.2	386 a	412 a

*Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

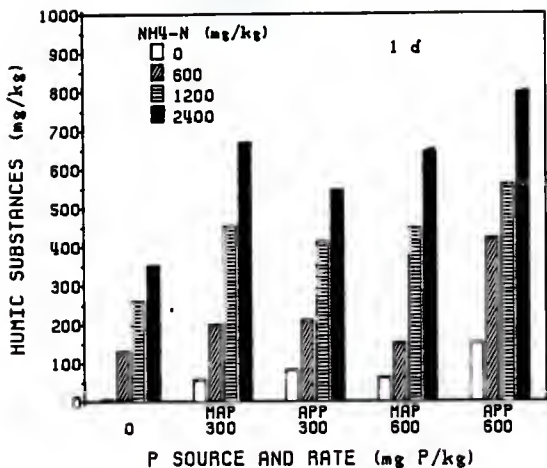


Figure 59. Total humic substances extracted from Kennebec silt loam 1 d after treatment.

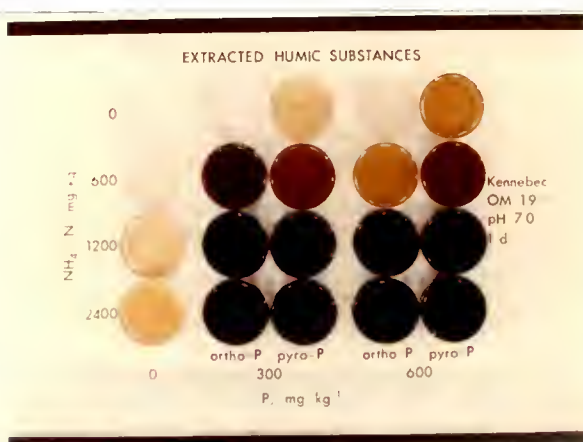


Figure 60. Solution colors due to dissolved humic substances in aqueous leachate from Kennebec silt loam 1 d after treatment.

that treatment had a lighter color.

Extracted acids (1 d)

N treatments, without P, dissolved more fulvic than humic acid (Table 22). Treatments with 300 units of MAP released greater amounts of humic acid than fulvic acid, except for 0 mg N/kg. The higher rate of MAP did not selectively remove more fulvic than humic acid. For further discussion of FA/HA ratios see section H.

Some significant increases in amounts of FA and HA occurred with increments of N. Some significant increases resulted from increments of P.

Fig. 61 and 62 illustrate how increments of N increased amounts of extracted fulvic and humic acids. Inclusion of P with N treatments usually resulted in greater amounts of extracted FA and HA than when only N treatments were used.

For statistical data on FA and HA refer to Table 22.

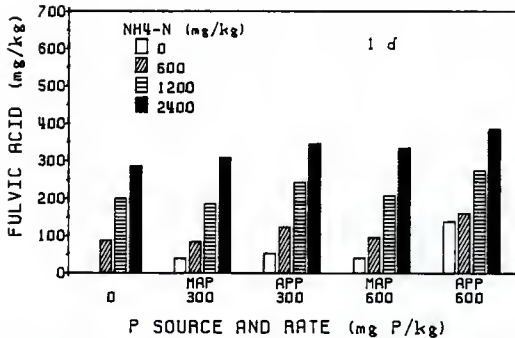


Figure 61. Fulvic acid extracted from Kennebec silt loam 1 d after treatment.

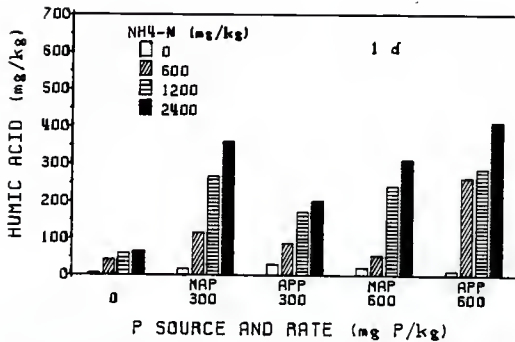


Figure 62. Humic acid extracted from Kennebec silt loam 1 d after treatment.

D. Extractable humic substances 2 d after treatment

Total extracted humic substances (2 d)

Total extracted humic substances in leachate ranged from 0 for the control to 865 mg/kg for the 0-600-2400 treatment (Table 23). Increased rates of N always significantly increased amounts of extracted humic substances.

Increasing MAP and APP rates from 0 to 300 mg P/kg caused numerical increases in amounts of extracted humic substances, but the increases were not all significant. Raising APP rates from 300 to 600 mg P/kg resulted in significant increases. However, when MAP rates increased from 300 to 600 mg P/kg, significantly greater levels of extracted humic substances were observed only at the 1200 mg N/kg rate. The pH depressing effect of high MAP rates probably also depressed increases in amounts of extracted humic substances.

Increments of N quantitatively increased amounts of extracted humic substances (Fig. 63), and addition of P to N treatments caused greater amounts of extracted humic substances than when only N treatments were used.

Color intensities of leachate samples (Fig. 64) correlate closely with amounts of extracted humic substances (Figure 63). Greater quantitative amounts resulted in greater coloration in leachate samples. In comparing the 300-0-600 and 600-0-600 treatments (Fig. 64), the higher MAP treatment caused a lighter colored leachate. The apparent reason for that occurrence was explained for the 0.5- and 1-d periods.

Percentages of total extracted humic substances ranged from 0 for the

control to a high of 4.6 for the 0-600-2400 treatment (Table 23).

Table 23. Humic substances extracted from Kennebec silt loam 2 d after treatment with various rates of orthophosphate, pyrophosphate, and nitrogen.

			Extracted humic substances*			
Treatment			Total		Acids	
MAP (mg P/kg)	APP (mg/kg)	NH ₄ ⁺ -N (mg/kg)	(mg/kg)	%	Fulvic (mg/kg)	Humic (mg/kg)
0	0	0	0 k	0.0	0 j	0 h
0	0	600	131 ij	0.7	104 g-j	27 fgh
0	0	1200	298 gh	1.6	212 d-g	86 e-h
0	0	2400	417 ef	2.2	365 abc	53 fgh
300	0	0	32 jk	0.2	23 ij	10 h
300	0	600	261 h	1.4	175 e-h	86 e-h
300	0	1200	512 de	2.7	256 cde	256 c
300	0	2400	755 b	4.0	359 abc	396 a
0	300	0	84 jk	0.5	52 ij	33 fgh
0	300	600	214 hi	1.1	111 g-j	103 e-h
0	300	1200	442 ef	2.3	229 de	213 cd
0	300	2400	686 bc	3.6	399 ab	287 bc
600	0	0	80 jk	0.4	64 hij	16 gh
600	0	600	248 h	1.3	117 f-i	132 def
600	0	1200	606 cd	3.2	224 def	382 ab
600	0	2400	746 b	3.9	285 cde	461 a
0	600	0	194 hi	1.0	69 hij	124 d-g
0	600	600	383 fg	2.0	192 efg	191 cde
0	600	1200	586 cd	3.1	318 bcd	269 c
0	600	2400	865 a	4.6	430 a	436 a

*Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

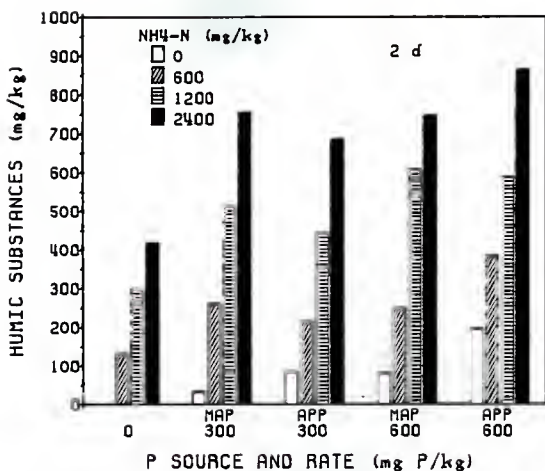


Figure 63. Total humic substances extracted from Kennebec silt loam 2 d after treatment.

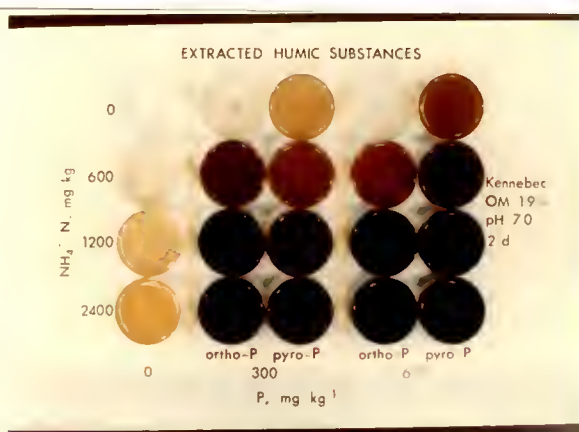


Figure 64. Solution colors due to dissolved humic substances in aqueous leachate from Kennebec silt loam 2 d after treatment.

Extracted acids (2 d)

When only NH_4OH was applied, amounts of fulvic acid exceeded amounts of humic acid in leachate samples (Table 23). Amounts of fulvic acid continued to exceed amounts of humic acid when treatments included 300 mg P/kg of APP with all rates of N. For further discussion of FA/HA ratios, see section H.

An increase in N rates caused some significant increases in extracted FA and HA.

Increments of APP caused quantitative increases in extracted FA and HA. An increase in MAP rates from 300 to 600 mg P/kg with the 3 highest rates of N consistently decreased quantitative amounts of FA. That was probably due to the pH depressing effect of the higher rate of MAP, indicating amounts of extracted FA were pH dependent.

Fig. 65 and 66 illustrate how increments of N increased amounts of extracted fulvic and humic acid. Addition of P to N treatments usually resulted in greater amounts of extracted FA and HA than when only N treatments were used.

For statistical data on FA and HA refer to Table 23.

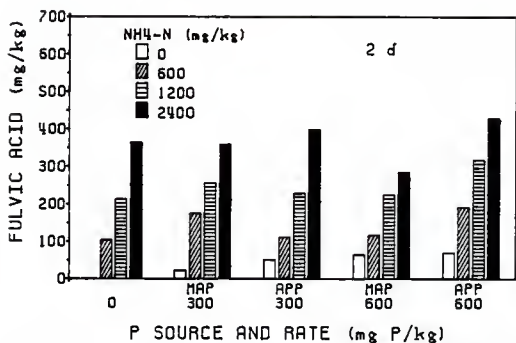


Figure 65. Fulvic acid extracted from Kennebec silt loam 2 d after treatment.

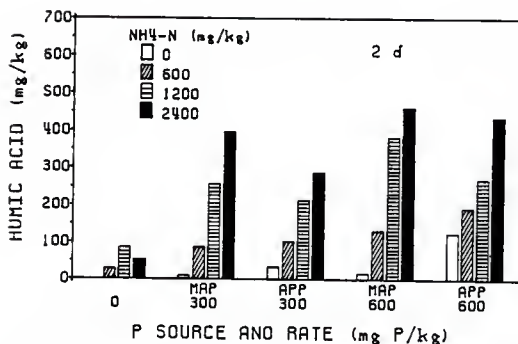


Figure 66. Humic acid extracted from Kennebec silt loam 2 d after treatment.

E. Extractable humic substances 4 d after treatment

Total extracted humic substances (4 d)

Total extracted humic substances varied from 0 for the control to 688 mg/kg for the 600-0-2400 treatment (Table 24). Increments of N always significantly increased amounts of extracted humic substances.

Increasing MAP from 0 to 300, or 300 to 600 mg P/kg significantly increased extracted humic substances when N rates were either 1200 or 2400 mg N/kg. Significant increases in extracted humic substances resulted when APP rates were increased from 300 to 600 mg P/kg, when N rates were either 600, 1200, or 2400 mg N/kg.

Amounts of extracted humic substances increased with increments of N (Fig. 67). As APP and MAP rates increased extracted humic substances also increased.

The color intensities of the leachate samples (Fig. 68) closely correlate with the quantitative values (Fig. 67). Greater amounts of extracted humic substances resulted in more intense colors in leachate samples.

Percentages of total extracted humic substances ranged from 0 for the control to a high of 3.7 for the 600-0-2400 treatment (Table 24).

Extracted acids (4 d)

When no P was added, N treatments dissolved greater amounts of fulvic than humic acid (Table 24). FA/HA ratios at the 600, 1200, and 2400 mg N/kg, were about 3, 4, and 7, when no P was added. For further discussion of FA/HA ratios see section H.

Table 24. Humic substances extracted from Kennebec silt loam 4 d after treatment with various rates of orthophosphate, pyrophosphate, and nitrogen.

			Extracted humic substances*			
Treatment			Total		Acids	
MAP (mg P/kg)	APP (mg/kg)	NH ₄ ⁺ -N (mg/kg)	(mg/kg)	%	FULVIC (mg/kg)	HUMIC (mg/kg)
0	0	0	0 i	0.0	0 j	0 i
0	0	600	80 ghi	0.4	61 ghi	18 i
0	0	1200	195 ef	1.0	155 ef	40 hi
0	0	2400	334 c	1.8	292 b	42 hi
300	0	0	20 i	0.1	11 ij	9 i
300	0	600	165 efg	0.9	88 gh	77 f-i
300	0	1200	374 c	2.0	168 ef	206 de
300	0	2400	504 b	2.7	245 bcd	259 bcd
0	300	0	65 hi	0.4	42 hij	23 hi
0	300	600	225 de	1.2	113 fg	112 fgh
0	300	1200	354 c	1.9	199 de	156 ef
0	300	2400	514 b	2.7	301 b	213 cde
600	0	0	85 ghi	0.4	51 hij	33 hi
600	0	600	180 ef	1.0	113 fg	67 ghi
600	0	1200	514 b	2.7	173 e	340 b
600	0	2400	688 a	3.7	267 bc	421 a
0	600	0	119 fgh	0.7	80 gh	39 hi
0	600	600	289 cd	1.5	161 ef	129 efg
0	600	1200	494 b	2.6	230 cd	264 bcd
0	600	2400	653 a	3.4	359 a	294 bc

*Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

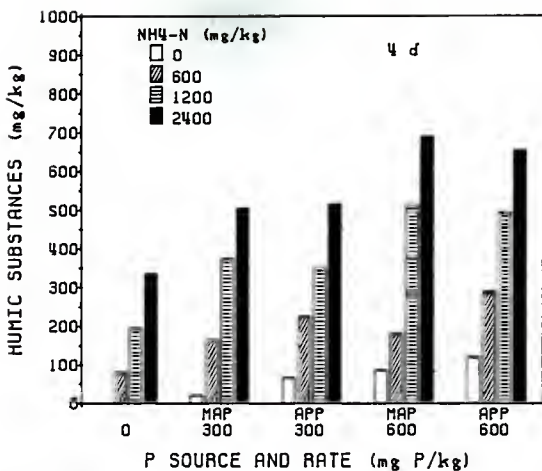


Figure 67. Total humic substances extracted from Kennebec silt loam 4 d after treatment.

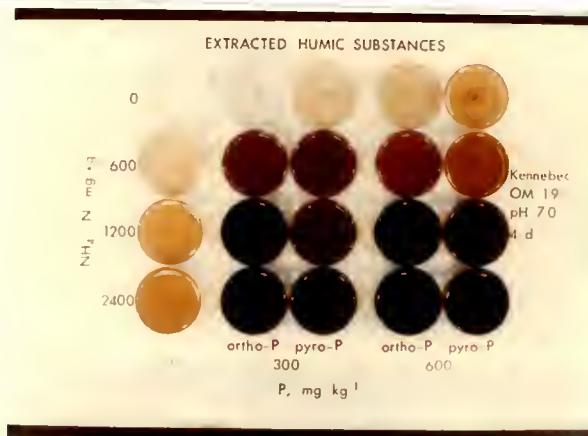


Figure 68. Solution colors due to dissolved humic substances in aqueous leachate from Kennebec silt loam 4 d after treatment.

Increases in N rates caused significant increases in extracted FA. Significant increases in FA resulted from increasing APP rates from 0 to 600 mg P/kg, with all levels of N. At those P rates numerical increases in FA resulted from increased rates of MAP, but the increases in amounts of extracted FA were not significant.

Increasing either MAP or APP, from 0 to 300 or 0 to 600 mg P/kg, caused significant increases in extracted HA with N rates of 1200 or 2400 mg N/kg.

Increments of N increased amounts of extracted fulvic and humic acids (Fig. 69 and 70). The addition of P to N treatments did not greatly affect amounts of extracted FA (Fig. 69), but did usually increase amounts of HA (Fig. 70).

For statistical data on FA and HA refer to Table 24.

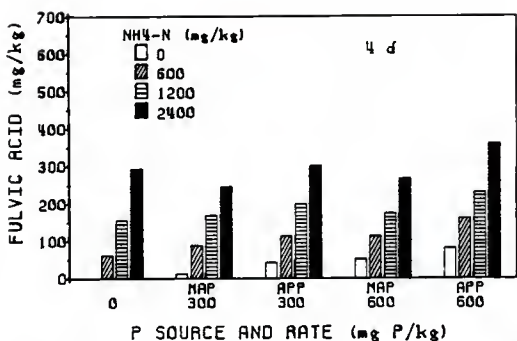


Figure 69. Fulvic acid extracted from Kennebec silt loam 4 d after treatment.

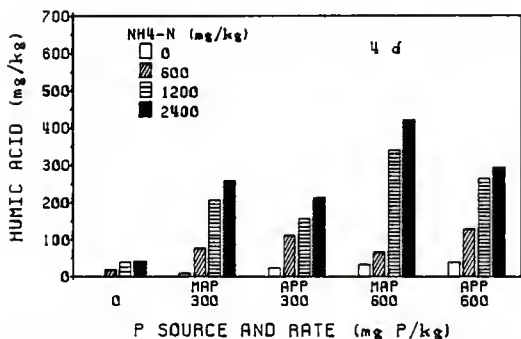


Figure 70. Humic acid extracted from Kennebec silt loam 4 d after treatment.

F. Extractable humic substances after 8 d after treatment

Total extracted humic substances (8 d)

Total extracted humic substances varied from 0 for the control to 682 mg/kg for the 600-0-2400 treatment (Table 25), and showed significant increases with increments of N.

Increasing rates of either MAP or APP from 0 to 300 or from 300 to 600 mg P/kg significantly increased extracted humic substances when using either 1200 or 2400 mg N/kg.

Increasing amounts of extracted humic substances resulted from increasing rates of N and P (Fig. 71).

Color intensities of leachate samples (Fig. 72) closely correlate with the quantitative amounts of extracted humic substances shown (Fig. 71). Increased amounts of extracted humic substances resulted in increased coloration of leachate samples.

Percentages of total extracted humic substances (Table 25) ranged from 0 for the control to a high of 3.6 for the 600-0-2400 treatment.

Extracted acids (8 d)

Using treatments with only N (Table 25), ratios of FA/HA were 1.6, 1, and 1.5 for the 3 highest values of N. For a further discussion of ratios of FA/HA see section H.

Significant increases in amounts of extracted FA resulted from increments of N, except in the 0-0-600 and 0-0-1200 treatments.

Increasing rates of either MAP or APP from 0 to 300 mg P/kg caused significant increases in extracted FA with N treatments of 1200 and 2400 mg

Table 25. Humic substances extracted from Kennebec silt loam 8 d after treatment with various rates of orthophosphate, pyrophosphate, and nitrogen.

			Extracted humic substances*			
Treatment			Total		Acids	
MAP (mg P/kg)	APP (mg/kg)	NH ₄ ⁺ -N (mg/kg)	(mg/kg)	%	Fulvic (mg/kg)	Humic (mg/kg)
0	0	0	0 i	0.0	0 h	0 i
0	0	600	105 h	0.6	64 ef	41 e-i
0	0	1200	181 g	1.0	88 cde	92 d-g
0	0	2400	261 ef	1.3	156 b	105 def
300	0	0	40 hi	0.2	12 gh	28 ghi
300	0	600	191 g	1.0	87 cde	103 def
300	0	1200	356 d	1.9	156 b	200 c
300	0	2400	567 b	3.0	219 a	348 b
0	300	0	55 hi	0.3	18 gh	37 f-i
0	300	600	191 g	1.0	75 de	116 de
0	300	1200	286 e	1.5	175 b	111 def
0	300	2400	396 d	2.1	232 a	165 cd
600	0	0	50 hi	0.2	35 fg	15 hi
600	0	600	176 g	0.9	107 cd	68 e-i
600	0	1200	460 c	2.4	168 b	292 b
600	0	2400	682 a	3.6	226 a	456 a
0	600	0	95 h	0.5	19 gh	76 e-h
0	600	600	201 fg	1.1	113 c	88 e-h
0	600	1200	386 d	2.0	168 b	218 c
0	600	2400	527 b	2.8	233 a	294 b

*Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

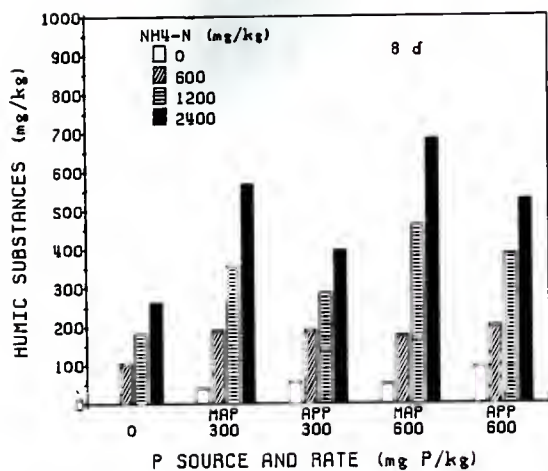


Figure 71. Total humic substances extracted from Kennebec silt loam 8 d after treatment.

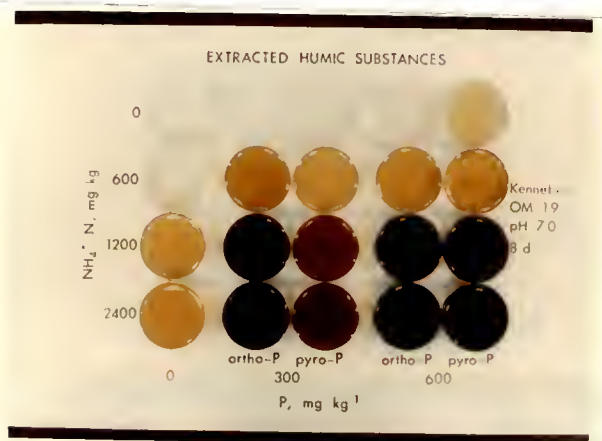


Figure 72. Solution colors due to dissolved humic substances in aqueous leachate from Kennebec silt loam 8 d after treatment.

N/kg. Increasing either MAP or APP rates from 300 to 600 mg P/kg caused significant increases in means of FA when N rates were 600, 1200, or 2400 mg N/kg.

Significant increases in extracted HA occurred when N rates were increased from 600 to 1200 or 1200 to 2400 mg N/kg, except for samples receiving no P treatments, and for samples with 300 mg P/kg APP.

At the two highest rates of N combined with the 2 highest rates of P, increments of either MAP or APP resulted in significant increases in extracted HA when the P source remained constant.

Increments of N and P usually increased amounts of extracted FA and HA (Fig 73 and 74).

For statistical data on FA and HA refer to Table 25.

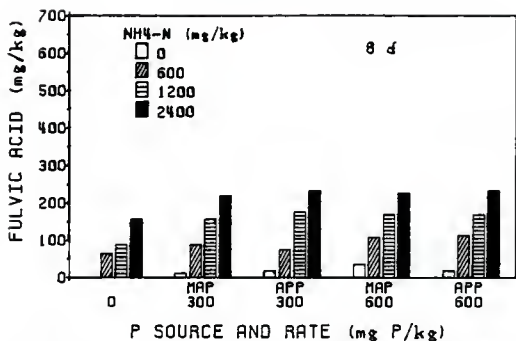


Figure 73. Fulvic acid extracted from Kennebec silt loam 8 d after treatment.

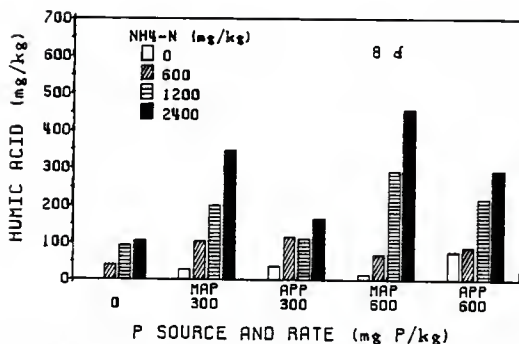


Figure 74. Humic acid extracted from Kennebec silt loam 8 d after treatment.

G. Extractable humic substances after 16 d incubation

Total humic substances (16 d)

Extracted humic substances varied in amounts from 0 for the control to 497 mg/kg for the 0-600-2400 treatment (Table 26). Increasing rates of N always caused numerical increases in amounts of total extracted humic substances, and some of the increases were significant. Using APP, increases resulting from increments of N were always significant. Using MAP, significant increases resulting from increments of N occurred with the 3 highest N rates.

Significant increases in extracted humic substances resulting from either MAP or APP treatments occurred with an increase in rates from 0 to 300 and 0 to 600 mg P/kg when N rates were 1200 or 2400 mg N/kg.

Increments of N caused quantitative increases in extracted humic substances (Fig. 75), and placement of P with N usually resulted in greater amounts of extracted humic substances than when only N treatments were used.

Color intensities (Fig. 76) closely correlate with quantitative amounts in Fig. 75. Greater amounts of extracted humic substances usually resulted in greater color intensity in leachate samples.

Percentages of total extracted humic substances (Table 26) ranged from 0 for the control to a high of 2.6 for treatment 0-600-2400.

Extracted acids (16 d)

For a discussion of FA/HA ratios see section H.

Extracted FA and HA (Table 26) usually quantitatively increased with

Table 26. Humic substances extracted from Kennebec silt loam 16 d after treatment with various rates of orthophosphate, pyrophosphate, and nitrogen.

Treatment			Extracted humic substances*			
			Total		Acids	
MAP (mg P/kg)	APP (mg/kg)	NH ₄ ⁺ -N (mg/kg)	(mg/kg)	%	Fulvic (mg/kg)	Humic (mg/kg)
0	0	0	0 i	0.0	0 j	0 h
0	0	600	105 efg	0.5	36 ghi	68 efg
0	0	1200	149 e	0.8	67 fg	82 def
0	0	2400	274 cd	1.4	150 cde	124 cd
300	0	0	32 hi	0.2	16 ij	16 gh
300	0	600	90 e-h	0.5	50 gh	40 fgh
300	0	1200	239 d	1.3	141 cde	96 cde
300	0	2400	453 ab	2.4	168 c	285 a
0	300	0	65 fgh	0.4	29 hij	37 fgh
0	300	600	134 e	0.7	69 fg	66 efg
0	300	1200	229 d	1.2	86 f	142 c
0	300	2400	412 b	2.2	205 b	208 b
600	0	0	104 efg	0.6	49 gh	55 efg
600	0	600	129 ef	0.7	49 gh	80 def
600	0	1200	323 c	1.7	130 de	193 b
600	0	2400	443 ab	2.3	155 cd	288 a
0	600	0	60 ghi	0.3	42 ghi	17 gh
0	600	600	149 e	0.8	62 fg	87 def
0	600	1200	219 d	1.1	118 e	101 cde
0	600	2400	497 a	2.6	235 a	262 a

*Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

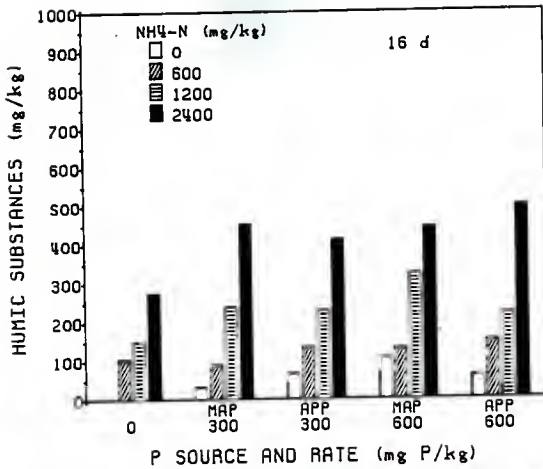


Figure 75. Total humic substances extracted from Kennebec silt loam 16 d after treatment.

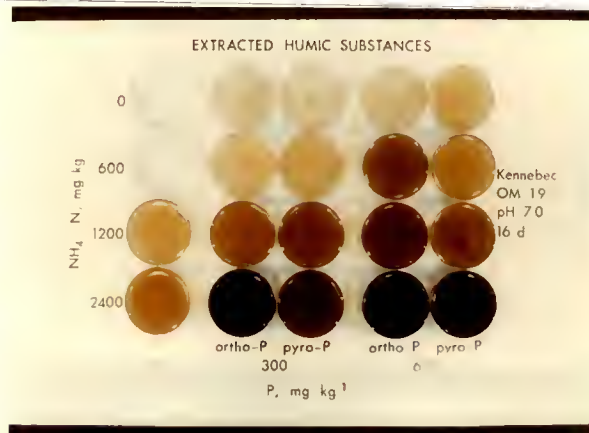


Figure 76. Solution colors due to dissolved humic substances in aqueous leachate from Kennebec silt loam 16 d after treatment.

increasing N rates.

Increases in either MAP or APP rates usually increased extracted HA and FA, except for the 600 mg P/kg rate of MAP with the 3 highest rates of N which gave lower amounts of extracted FA than the 300 mg P/kg rates. That may have been at least partially due to the pH depressing effect of the high rate of MAP.

Increments of N increased amounts of extracted FA and HA (Fig. 77 and 78). Addition of MAP or APP with the 2 highest rates of N resulted in increases in amounts of extracted FA and HA compared to treatments when only N was used.

For statistical data on FA and HA refer to Table 26.

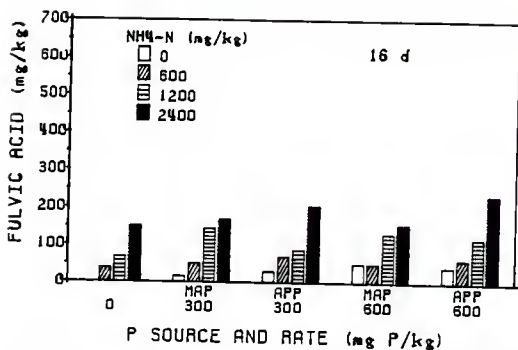


Figure 77. Fulvic acid extracted from Kennebec silt loam 16 d after treatment.

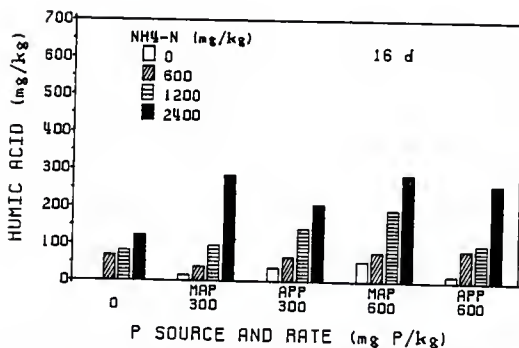


Figure 78. Humic acid extracted from Kennebec silt loam 16 d after treatment.

H. Ratios of extractable FA and HA

Ratios of FA/HA

Though not necessarily precise, the ratios (Table 27) still merit consideration because they show selective extraction of FA and HA due to various treatments. With treatments including only N, the ratios were higher than when N and P were both used. The higher ratios show that omitting P from treatments resulted in less extracted HA compared to extracted FA. For treatments with only N, the ratios were nearer to 1 by the 8- and 16-d periods than on the previous 4 periods, indicating selectivity of extracted FA and HA was virtually absent by the 8- and 16-d periods.

A comparison of the ratios from the 0 mg P/kg rate (the top four rows of data in Table 27) with the ratios from samples where P was added (the bottom 16 rows of data in Table 27), show lower ratios where P was included. That indicates that P increased amounts of extracted HA in relation to extracted FA. The photos of leachate samples also clearly showed darker solution colors, indicating increased extracted HA, when P was included in treatments.

The FA/HA ratios in Table 27 show a tendency to center around 1. Quantitative amounts confirmed that indication showing that total amounts of FA and HA, over all time periods and all treatments, were nearly equal with about 51% FA and 49% HA.

A word of caution should be mentioned here regarding interpretation of the FA/HA ratios. In the original soil those ratios may have been different than ascertained by our analyses because of the degrading action

of the fertilizer treatments on SOM.

Table 27. Effect of incubation time and N and P treatments on ratios of extracted fulvic acid and extracted humic acid.

Treatment			FA/HA						
			Incubation period (d)						
MAP (mg P/kg)	APP (mg/kg)	NH ₄ ⁺ -N (mg/kg)	0	0.5	1	2	4	8	16
0	0	0	#	#	#	#	#	#	#
0	0	600	1.4	3.2	2.1	3.8	3.4	1.6	0.5
0	0	1200	1.4	4.3	3.4	2.5	3.9	1.0	0.8
0	0	2400	1.4	4.1	4.3	6.9	7.0	1.5	1.2
300	0	0	#	0.8	2.4	2.3	1.2	0.4	1.0
300	0	600	0.6	1.2	0.7	2.0	1.1	0.8	1.2
300	0	1200	0.7	0.8	0.7	1.0	0.8	0.8	1.5
300	0	2400	0.7	0.8	0.9	0.9	0.9	0.6	0.6
0	300	0	2.3	1.1	1.9	1.6	1.8	0.2	0.8
0	300	600	1.4	1.4	1.4	1.1	1.0	0.6	1.0
0	300	1200	1.0	1.3	1.4	1.1	1.3	1.6	0.6
0	300	2400	1.4	1.3	1.7	1.4	1.4	1.4	1.0
600	0	0	0.7	19.0	1.9	4.0	1.5	2.3	0.9
600	0	600	1.8	3.6	1.8	0.9	1.7	1.6	0.6
600	0	1200	2.1	0.6	0.9	0.6	0.5	0.6	0.7
600	0	2400	1.1	0.7	1.1	0.6	0.6	0.5	0.5
0	600	0	0.9	0.0	11.5	0.6	2.0	0.2	2.5
0	600	600	0.5	1.0	0.6	1.0	1.2	1.3	0.7
0	600	1200	0.6	1.2	1.0	1.2	0.9	0.8	1.2
0	600	2400	0.7	0.9	0.9	1.0	1.2	0.8	0.9

#Not valid numerical ratios.

I. Effect of N- and P-treatment rates on extractable humic substances

Tables 28, 29, 30, and 31 show the effect of NH_4^+ -N rates on humic substances when means were averaged over all APP and MAP treatments. Increasing rates of N caused significant increases in extracted humic substances in all 7 incubation periods (Table 28). Corresponding percentages of total extracted humic substances showed the same increases (Table 29). The percentages differed from the total mg/kg only by a common factor.

Similar trends occurred for extracted FA (Table 30); consistent numerical increases in extracted FA occurred when N rates were increased. The increases were all significant except for the 0-d incubation period.

The effects of N rates on extracted HA (Table 31) showed similar results as the effects of N rates on FA (Table 30). Increasing N rates significantly increased extracted HA except for the 2 highest N rates in the 0-d incubation period.

Tables 32, 33, 34, and 35 show the effect of P rates on humic substances when averaged over all N treatments. Increasing MAP or APP from 0 to 300 mg P/kg (Table 32), significantly increased extracted humic substances except in the case of MAP at the 0-d incubation period.

Increasing MAP from 300 to 600 mg P/kg caused numerical increases in extracted humic substances for all incubation periods except 1 d, however the differences were significant for only the 4-, 8-, and 16-d periods. Increasing APP from 300 to 600 mg P/kg caused numerical increases in extracted humic substances for all incubation periods, and the differences were all significant except for the 16-d period.

Table 28. Effect of various rates of $\text{NH}_4^+\text{-N}$ on total amounts of extracted humic substances.

Treatment	Total extracted humic substances (mg/kg)*						
	Incubation period (d)						
$\text{NH}_4^+\text{-N}$ (mg/kg)	0	0.5	1	2	4	8	16
0	31 d	63 d	71 d	78 d	58 d	48 d	52 d
600	103 c	240 c	222 c	248 c	188 c	173 c	121 c
1200	156 b	467 b	426 b	489 b	386 b	334 b	232 b
2400	198 a	649 a	602 a	694 a	539 a	487 a	416 a

*Values are means of all P treatments. Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Table 29. Effect of various rates of $\text{NH}_4^+\text{-N}$ on total amounts of extracted humic substances.

Treatment	Total extracted humic substances (%)*						
	Incubation period (d)						
$\text{NH}_4^+\text{-N}$ (mg/kg)	0	0.5	1	2	4	8	16
0	0.2	0.3	0.4	0.4	0.3	0.2	0.3
600	0.6	1.2	1.2	1.3	1.0	0.9	0.6
1200	0.8	2.4	2.2	2.6	2.0	1.8	1.2
2400	1.0	3.4	3.2	3.6	2.8	2.6	2.2

*Values are means of all P treatments.

Table 30. Effect of various rates of $\text{NH}_4^+\text{-N}$ on amounts of extracted fulvic acid.

Treatment	Fulvic acid (mg/kg)*						
	Incubation period (d)						
$\text{NH}_4^+\text{-N}$ (mg/kg)	0	0.5	1	2	4	8	16
0	17 c	49 d	54 d	41 d	37 d	17 d	27 d
600	48 b	141 c	110 c	140 c	107 c	89 c	53 c
1200	75 a	243 b	222 b	248 b	185 b	151 b	109 b
2400	95 a	329 a	333 a	368 a	293 a	213 a	182 a

*Values are means of all P treatments. Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Table 31. Effect of various rates of $\text{NH}_4^+\text{-N}$ on amounts of extracted humic acid.

Treatment	Humic acid (mg/kg) *						
	Incubation period (d)						
	0	0.5	1	2	4	8	16
$\text{NH}_4^+\text{-N}$ (mg/kg)							
0	14 c	13 d	17 d	37 d	21 d	31 d	25 d
600	55 b	98 c	112 c	108 c	81 c	83 c	68 c
1200	81 a	224 b	205 b	241 b	201 b	182 b	123 b
2400	102 a	320 a	270 a	326 a	246 a	273 a	233 a

*Values are means of all P treatments. Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Table 32. Effect of various rates of P on total amounts of extracted humic substances.

Treatment		Total extracted humic substances (mg/kg)*						
		Incubation period (d)						
MAP (mg P/kg)	APP (mg P/kg)	0	0.5	1	2	4	8	16
0	0	64 c	184 c	187 c	212 d	152 c	137 d	132 c
300	0	86 c	353 b	345 b	390 bc	266 b	288 b	203 b
0	300	131 b	332 b	313 b	357 c	290 b	232 c	210 b
600	0	101 bc	356 b	326 b	420 b	367 a	342 a	250 a
0	600	226 a	548 a	483 a	507 a	389 a	302 b	231 ab

*Values are means of all NH_4^+ -N treatments. Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Table 33. Effect of various rates of P on total amounts of extracted humic substances.

Treatment		Total extracted humic substances (%) *						
		Incubation period (d)						
MAP (mg P/kg)	APP (mg P/kg)	0	0.5	1	2.0	4.0	8.0	16
0	0	0.3	1.0	1.0	1.1	0.8	0.7	0.7
300	0	0.5	1.8	1.8	2.1	1.4	1.5	1.1
0	300	0.7	1.7	1.6	1.9	1.5	1.2	1.1
600	0	0.5	1.9	1.7	2.2	1.9	1.8	1.3
0	600	1.2	2.9	2.6	2.7	2.0	1.6	1.2

*Values are means of all NH_4^+ -N treatments.

Table 34. Effect of various rates of P on amounts of extracted fulvic acid.

Treatment		Extracted fulvic acid (mg/kg)*						
		Incubation period (d)						
MAP	APP	0	0.5	1	2	4	8	16
0	0	37 c	147 c	144 d	170 b	127 c	77 b	63 c
300	0	36 c	161 c	155 bc	203 ab	128 c	119 a	94 b
0	300	75 ab	189 b	191 b	198 b	164 b	125 a	97 b
600	0	58 bc	160 c	170 bc	172 b	151 bc	134 a	96 b
0	600	89 a	296 a	239 a	252 a	208 a	133 a	115 a

*Values are means of all $\text{NH}_4^+\text{-N}$ treatments. Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Table 35. Effect of various rates of P on amounts of extracted humic acid.

Treatment		Extracted humic acid (mg/kg)*						
		Incubation period (d)						
MAP	APP	0	0.5	1	2	4	8	16
0	0	26 b	37 d	43 d	41 c	25 c	60 d	69 c
300	0	50 b	192 b	190 ab	187 b	138 b	170 b	109 b
0	300	56 b	142 c	121 c	159 b	126 b	107 c	113 b
600	0	44 b	196 b	157 bc	248 a	216 a	208 a	154 a
0	600	138 a	252 a	243 a	255 a	181 a	169 b	117 b

*Values are means of all NH_4^+ -N treatments. Means within a column followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test .

For periods 0, 0.5, 1, and 2 d (Table 32), at the 600 mg P/kg rate, APP caused significantly greater amounts of extracted humic substances than MAP. That can be explained by noting that at the 600 mg P/kg rate MAP had a greater depressing effect on pH than did APP. Since pH, apparently to some extent, determines the amounts of humic substances extracted, those samples receiving high treatments of MAP had lower amounts of extracted humic substances on the given time periods 0 through 2 d because of depressed pH levels.

Percentages of total extracted humic substances varied with different rates of P (Table 33), proportionately to quantitative amounts of extracted humic substances (Table 32).

APP (Table 34) caused greater numerical increases in amounts of FA than MAP caused, except at the 2-d period at the 300 mg P/kg rate, and at the 8-d period at the 600 mg P/kg rate.

Increasing either MAP or APP from 0 to 300 mg P/kg caused significant increases in extracted humic acid (Table 35) in all time periods, except 0 d. At the 0.5-, 1-, and 8-d periods MAP treatments resulted in significantly greater amounts of HA than from APP treatment.

At the 600 mg P/kg rate, APP caused significantly greater amounts of extracted HA than did MAP for incubation periods 0, 0.5, and 1 d.

Increasing MAP rates from 300 to 600 mg P/kg significantly increased amounts of extracted HA at the 2-, 4-, and 16-d periods. Increasing APP rates from 300 to 600 mg P/kg significantly increased amounts of extracted HA at all periods except for 16 d.

J. Effect of incubation time and N- and P-treatment rates on extractable humic substances

With no N in the treatment, incubation time had no significant effect on total extracted humic substances (Table 36), except when the high rate of APP was used. When the high rate of APP was used a significant increase from the 0- to the 2-period occurred, then a significant decrease in extracted humic substances occurred between the 2- and 16-d periods.

At the 600, 1200, or 2400 mg N/kg rates, however, an observable pattern developed. Values began increasing from 0 to 0.5 d, slightly dropped at 1 d, then continued to rise again at 2 d before beginning a decline which continued through days 4, 8, and 16. We don't have an explanation for that slight drop in amounts at day 1.

Table 37 shows total extracted humic substances expressed as percentages of the SOM contained in the soil samples.

Fulvic acid

Effect of incubation time, N, and P treatments on FA (Table 38) show results similar to those just described for total extracted humic substances in Table 36. When 600, 1200, or 2400 mg N/kg were used, amounts of extracted FA reached a peak at the 0.5-, 1-, or 2-d periods, before beginning a decline which continued through the 4-, 8-, and 16-d periods (Table 38).

Humic acid

Trends over different incubation periods for amounts of extracted HA

(Table 39) were quite similar to those just described for FA (Table 38). Amounts of extracted HA reached a peak at the 0.5- or 1-d period, then began levelling off or dropping through the 4- and 8-d periods. From 8 to 16 d, 5 values numerically increased and the remainder numerically decreased or remained the same.

Table 36. Effect of incubation time and N and P treatments on total amounts of extracted humic substances.

Treatment	Total extracted humic substances (mg/kg)*									
	Incubation period (d)									
	0	0.5	1	2	4	8	16	Mean		
MAP	0	0 a	5 a	0 a	0 a	0 a	0 a	0 a	1	
ANP	0	55 a	130 a	131 a	80 a	105 a	105 a	105 a	106	
N ₄	0	100 a	239 bcd	259 cd	298 d	195 abc	181 abc	149 ab	203	
-N	0	100 a	359 cd	352 bcd	418 d	334 bcd	261 b	274 bc	300	
0	0	0	0	0	0	0	0	0	0	
300	0	5 a	35 a	32 a	20 a	40 a	32 a	32 a	32	
0	600	60 a	210 c	200 c	261 c	165 bc	191 c	90 ab	168	
300	0	115 a	459 de	452 cde	512 d	374 cd	356 c	239 b	358	
0	2400	165 a	708 d	670 d	755 d	504 bc	567 c	453 b	546	
0	300	0	50 a	81 a	84 a	65 a	55 a	65 a	71	
0	300	120 a	269 c	210 abc	214 abc	225 bc	191 abc	134 ab	195	
0	300	1200	160 a	399 cd	413 d	354 cd	286 bc	229 ab	326	
0	300	2400	196 a	564 c	546 c	686 d	396 b	412 b	473	
600	0	40 a	40 a	61 a	80 a	85 a	50 a	104 a	66	
0	600	60 a	120 ab	130 ab	248 c	180 bc	176 bc	129 ab	152	
600	0	1200	102 a	564 d	447 c	606 d	514 cd	460 c	431	
0	2400	205 a	639 cd	645 c	746 d	688 cd	682 cd	442 b	587	
0	600	0	60 a	144 ab	150 ab	194 b	119 ab	95 a	117	
0	600	600	220 ab	459 d	422 d	383 cd	289 bc	201 ab	303	
0	600	1200	306 ab	674 d	561 c	586 cd	494 c	386 b	461	
0	600	2400	321 a	914 e	798 d	665 d	653 c	527 b	654	
Mean	122	355	330	377	293	260	205			

*Means within a row followed by the same letter do not differ significantly at the 0.05 level. LSD = 96.

Table 37. Effect of incubation time and N and P treatments on total amounts of extracted humic substances.

Treatment	Total extracted humic substances (t)									
	Incubation period (d)									
MAP APF NH ₄ ⁺ -N (mg P/kg)	0	0.5	1	2	4	8	16	Mean		
0 0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0 0 600	0.3	0.7	0.7	0.7	0.4	0.6	0.5	0.5	0.6	0.6
0 0 1200	0.5	1.3	1.4	1.6	1.0	1.6	0.8	1.1	1.1	1.1
0 0 2400	0.5	1.9	1.8	2.2	1.8	1.3	1.4	1.6	1.6	1.6
300 0	0.0	0.2	0.3	0.2	0.1	0.2	0.2	0.2	0.2	0.2
300 0 600	0.3	1.1	1.0	1.4	0.9	1.0	0.4	0.9	0.9	0.9
300 0 1200	0.6	2.4	2.4	2.7	2.0	1.9	1.3	1.9	1.9	1.9
300 0 2400	0.9	3.7	3.5	4.0	2.7	3.0	2.4	2.9	2.9	2.9
0 300 0	0.3	0.5	0.4	0.5	0.4	0.3	0.4	0.4	0.4	0.4
0 300 600	0.6	1.4	1.1	1.1	1.2	1.0	0.7	1.0	1.0	1.0
0 300 1200	0.9	2.1	2.2	2.3	1.9	1.5	1.2	1.7	1.7	1.7
0 300 2400	1.0	3.0	2.9	3.6	2.7	2.1	2.2	2.5	2.5	2.5
600 0	0.2	0.2	0.3	0.4	0.4	0.2	0.6	0.3	0.3	0.3
600 0 600	0.3	0.5	0.8	1.3	1.0	0.9	0.7	0.8	0.8	0.8
600 0 1200	0.5	3.0	2.4	3.2	2.7	2.4	1.7	2.3	2.3	2.3
600 0 2400	1.1	3.7	3.4	3.9	3.7	3.6	2.3	3.1	3.1	3.1
0 600 0	0.3	0.7	0.8	1.0	0.7	0.5	0.3	0.6	0.6	0.6
0 600 600	1.2	2.4	2.2	2.0	1.5	1.1	0.8	1.6	1.6	1.6
0 600 1200	1.6	3.5	3.0	3.1	2.6	2.0	1.1	2.4	2.4	2.4
0 600 2400	1.7	4.8	4.2	4.6	3.4	2.8	2.6	3.4	3.4	3.4
Mean	0.6	1.9	1.7	2.0	1.6	1.4	1.1	1.1	1.1	1.1

Table 38. Effect of incubation time and N and P treatments on amounts of extracted fulvic acid.

Treatment	Incubation period (d)								Mean
	0	0.5	1	2	4	8	16	16	
MAP APF NH ₄ ⁺ -N (mg P/kg) (mg/kg)									
0 0 600	0 a	0 a	0 a	0 a	0 a	0 a	0 a	0 a	0
0 0 1200	32 a	106 c	88 abc	104 bc	61 abc	64 abc	96 ab	70	
0 0 2400	58 a	195 c	209 c	212 c	155 bc	88 ab	67 a	139	
0 0 2400	59 a	288 c	287 c	365 d	292 c	156 b	150 b	228	
300 0 0	5 a	16 a	40 a	23 a	11 a	12 a	16 a	18	
300 0 600	22 a	116 bc	84 ab	175 c	88 ab	27 a	56 ab	89	
300 0 1200	49 a	208 bc	185 b	256 c	168 b	157 b	143 b	166	
300 0 2400	67 a	303 de	310 de	359 e	245 cd	219 bc	168 b	239	
0 300 0	35 a	49 a	53 a	52 a	42 a	18 a	29 a	40	
0 300 600	70 a	157 b	123 ab	111 ab	113 ab	75 a	69 a	103	
0 300 1200	82 a	229 b	243 b	229 b	199 b	175 b	86 a	176	
0 300 2400	112 a	323 c	346 cd	399 d	301 c	232 b	205 b	274	
600 0 0	17 a	38 a	40 a	64 a	51 a	35 a	49 a	42	
600 0 600	39 a	93 ab	96 ab	117 b	113 b	107 ab	49 ab	86	
600 0 1200	68 a	214 c	208 c	224 c	173 bc	168 bc	130 ab	169	
600 0 2400	107 a	294 bc	334 c	285 bc	267 bc	226 b	155 a	238	
0 600 0	29 a	144 b	138 b	69 a	80 ab	19 a	42 a	74	
0 600 600	78 a	232 d	159 bc	192 cd	161 bc	113 ab	62 a	142	
0 600 1200	118 a	372 e	274 cd	318 de	230 bc	168 ab	118 a	228	
0 600 2400	131 a	436 d	386 cd	430 d	359 c	233 b	236 b	316	
Mean	59	191	180	199	155	118	93		

*Means within a row followed by the same letter do not differ significantly at the 0.05 level.
LSD = 68.

Table 39. Effect of Incubation time and N and P treatments on amounts of extracted humic acid.

Treatment	Extracted humic acid (mg/kg)*										Mean	
	Incubation period (d)											
	0	0.5	1	2	4	8	16					
MAP APN N ₄ P ₄ N												
(mg P/kg) (mg/kg)												
0 0 0	0 a	0 a	5 a	0 a	0 a	0 a	0 a	0 a	0 a	0 a	1	
0 0 600	22 a	33 a	42 a	27 a	18 a	41 a	66 a	66 a	41 a	66 a	36	
0 0 1200	43 a	45 a	59 a	86 a	40 a	92 a	82 a	82 a	92 a	82 a	64	
0 0 2400	41 a	71 a	66 a	53 a	42 a	105 a	124 a	124 a	105 a	124 a	72	
300 0 0	0 a	19 a	17 a	10 a	9 a	28 a	16 a	16 a	28 a	16 a	14	
300 0 600	37 a	83 a	115 a	86 a	77 a	103 a	40 a	40 a	103 a	40 a	79	
300 0 1200	66 a	251 b	267 b	256 b	206 b	200 b	96 a	96 a	200 b	96 a	192	
300 0 2400	98 a	405 d	360 cd	396 d	259 b	348 cd	285 bc	285 bc	348 cd	285 bc	307	
0 300 0	15 a	45 a	28 a	33 a	23 a	37 a	37 a	37 a	37 a	37 a	31	
0 300 600	50 a	113 a	87 a	103 a	112 a	116 a	66 a	66 a	116 a	66 a	92	
0 300 1200	78 a	170 bc	170 bc	213 c	156 ab	111 ab	142 ab	142 ab	156 ab	142 ab	149	
0 300 2400	83 a	241 bc	200 b	287 c	213 bc	165 ab	208 bc	208 bc	213 bc	165 ab	200	
600 0 0	23 a	2 a	21 a	16 a	33 a	15 a	55 a	55 a	33 a	15 a	24	
600 0 600	21 a	26 a	54 ab	132 b	67 ab	68 ab	80 ab	80 ab	67 ab	68 ab	64	
600 0 1200	32 a	350 de	240 bc	382 d	340 de	292 cd	193 b	193 b	340 de	292 cd	261	
600 0 2400	99 a	405 c	311 b	461 c	421 c	456 c	288 b	288 b	421 c	456 c	349	
0 600 0	31 a	0 a	12 a	124 a	39 a	76 a	17 a	17 a	39 a	76 a	43	
0 600 600	143 abc	227 cd	262 d	191 bcd	129 ab	88 a	87 a	87 a	129 ab	88 a	161	
0 600 1200	188 a	302 c	287 c	269 bc	264 bc	218 bc	101 a	101 a	264 bc	218 bc	233	
0 600 2400	190 a	478 c	412 c	436 c	294 b	294 b	262 ab	262 ab	436 c	294 b	338	
Mean	63	164	151	178	137	143	112	112	137	143		

*Means within a row followed by the same letter do not differ significantly at the 0.05 level.

LSD = 85.

K. Effect of incubation time and NH_4^+ -N treatment rates on extractable humic substances

At rates of 600, 1200, and 2400 mg N/kg, amounts of total extracted humic substances (Table 40) numerically increased from the 0- to the to 0.5-d period, then dropped slightly at the 1-d period before peaking at the 2-d period. From 2 to 16 days, a gradual decline occurred.

The percentage of total humic substances extracted (Table 41) show trends identical to those in Table 40 because percentages differ from quantitative amounts only by a factor.

Fulvic acid

Amounts of extracted FA (Table 42) numerically increased until the 0.5-, 1-, or 2-d periods and then began a steady decrease through the 16-d period. The 0 mg N/kg rate showed a slight quantitative rise from the 8- to 16-d period.

Humic acid

A similar pattern of increasing and decreasing amounts held true for HA (Table 43) as for FA in Table 42.

Table 40. Effect of incubation time and various rates of $\text{NH}_4^+\text{-N}$ on total amounts of extracted humic substances.

Treatment $\text{NH}_4^+\text{-N}$ (mg/kg)	Total extracted humic substances(mg/kg) *							Mean
	0	0.5	1	2	4	8	16	
0	31 a	63 a	71 a	78 a	58 a	48 a	52 a	57
600	103 a	240 c	222 c	248 c	188 b	173 b	121 a	185
1200	156 a	467 ef	426 e	489 f	386 d	334 c	232 b	356
2400	198 a	649 f	602 e	694 g	539 d	487 c	416 b	512

*Values are means of all P treatments. Means within a row followed by the same letter do not differ significantly at the 0.05 level. LSD = 43.

Table 41. Effect of incubation time and various rates of $\text{NH}_4^+\text{-N}$ on total amounts of extracted humic substances.

Treatment	Total extracted humic substances (%) *							Mean
	Incubation period (d)							
$\text{NH}_4^+\text{-N}$ (mg/kg)	0	0.5	1	2	4	8	16	
0	0.2	0.3	0.4	0.4	0.3	0.2	0.3	0.3
600	0.6	1.2	1.2	1.3	1.0	0.9	0.6	1.0
1200	0.8	2.4	2.2	2.6	2.0	1.8	1.2	1.9
2400	1.0	3.4	3.2	3.6	2.8	2.6	2.2	2.7

*Values are means of all P treatments.

TABLE 42. Effect of incubation time and various rates of $\text{NH}_4^+\text{-N}$ on amounts of extracted fulvic acid.

Treatment	Fulvic acid (mg/kg)*							Mean
	Incubation period (d)							
$\text{NH}_4^+\text{-N}$ (mg/kg)	0	0.5	1	2	4	8	16	
0	17 a	49 b	54 b	41 ab	37 ab	17 a	27 ab	35
600	48 a	141 d	110 bc	140 cd	107 b	89 b	53 a	95
1200	75 a	243 e	222 e	248 e	185 d	151 c	109 b	176
2400	95 a	329 e	333 e	368 f	293 d	213 c	182 b	259

*Values are means of all P treatments. Means within a row followed by the same letter do not differ significantly at the 0.05 level. LSD = 30.

Table 43. Effect of incubation time and various rates of $\text{NH}_4^+\text{-N}$ on amounts of extracted humic acid.

Treatment	Humic acid (mg/kg)*							Mean
	Incubation period (d)							
$\text{NH}_4^+\text{-N}$ (mg/kg)	0	0.5	1	2	4	8	16	
0	14 a	13 a	17 a	37 a	21 a	31 a	25 a	23
600	55 a	98 bc	112 c	108 c	81 abc	83 abc	68 ab	86
1200	81 a	224 de	205 cd	241 d	201 cd	182 c	123 b	180
2400	102 a	320 d	270 bc	326 d	246 bc	273 c	233 b	253

*Values are means of all P treatments. Means within a row followed by the same letter do not differ significantly at the 0.05 level. LSD = 38.

L. Effect of incubation time and P-treatment rates on extractable humic substances

Amounts of total extracted humic substances, averaged over all N treatments, numerically increased until the 0.5-, 1-, or 2-d periods (Table 44), then decreased through the 16-d period. The increases between 0 and 0.5 d were always significant.

Percentages in Table 45 differ only by a factor from quantitative values in Table 44.

Amounts of extracted FA (Table 46) averaged over all N treatments, numerically increased until the 0.5 or 2 d period, then decreased through the 16-d period. The increases between 0 and 0.5 d were always significant.

Amounts of extracted HA, averaged over all N treatments (Table 47), numerically increased until the 0.5- or 2-d period, then numerically decreased through the 16 d period. The increases between 0 and 0.5 d were always significant except for the 0 mg P/kg rate of both MAP and APP.

Table 44. Effect of incubation time and various rates of P on total amounts of extracted humic substances.

Treatment	Total extracted humic substances (mg/kg)*							Mean
	0	0.5	1	2	4	8	16	
MAP APP (mg P/kg)								
0	64 a	184 cde	187 de	212 e	152 bcd	137 bc	132 b	152
300	86 a	353 d	345 d	390 d	266 c	288 c	203 b	276
0 300	131 a	332 cd	313 cd	357 d	290 c	232 b	210 b	266
600	101 a	356 c	326 c	420 d	367 c	342 c	250 b	309
0 600	226 a	548 e	483 d	507 de	389 c	302 b	231 a	384

*Values are means of all $\text{NH}_4^+\text{-N}$ treatments. Means within a row followed by the same letter do not differ significantly at the 0.05 level. LSD = 48.

Table 45. Effect of incubation time and various rates of P on total amounts of extracted humic substances.

Treatment	Total extracted humic substances (%) *							Mean	
	Incubation period (d)								
MAP APP (mg P/kg)	0	0.5	1	2.0	4.0	8.0	16		
0	0	0.3	1.0	1.0	1.1	0.8	0.7	0.7	0.8
300	0	0.5	1.8	1.8	2.1	1.4	1.5	1.1	1.5
0	300	0.7	1.7	1.6	1.9	1.5	1.2	1.1	1.4
600	0	0.5	1.9	1.7	2.2	1.9	1.8	1.3	1.6
0	600	1.2	2.9	2.6	2.7	2.0	1.6	1.2	2.0

*Values are means of all $\text{NH}_4^+\text{-N}$ treatments.

Table 46. Effect of incubation time and various rates of P on amounts of extracted fulvic acid.

Treatment		Extracted fulvic acid (mg/kg) *							Mean
		Incubation period (d)							
MAP	APP (mg P/kg)	0	0.5	1	2	4	8	16	
0	0	37 a	147 cd	144 cd	170 d	127 c	77 b	63 ab	109
300	0	36 a	161 c	155 c	203 d	128 bc	119 b	94 b	123
0	300	75 a	189 c	191 c	198 c	164 c	125 b	97 ab	149
600	0	58 a	160 cd	170 d	172 d	151 cd	134 c	96 b	134
0	600	89 a	296 e	239 cd	252 d	208 c	133 b	115 ab	190

*Values are means of all $\text{NH}_4^+\text{-N}$ treatments. Means within a row followed by the same letter do not differ significantly at the 0.05 level. LSD = 34.

Table 47. Effect of incubation time and various rates of P on amounts of extracted humic acid.

Treatment	Extracted humic acid (mg/kg) *							Mean
	Incubation period (d)							
MAP APP (mg P/kg)	0	0.5	1	2	4	8	16	
0 0	26 a	37 a	43 a	41 a	25 a	60 a	69 a	43
300 0	50 a	192 d	190 d	187 d	138 bc	170 cd	109 b	148
0 300	56 a	142 bc	121 bc	159 c	126 bc	107 bc	113 bc	118
600 0	44 a	196 bc	157 b	248 d	216 cd	208 cd	154 b	174
0 600	138 ab	252 c	243 c	255 c	181 b	169 b	117 a	194

*Values are means of all $\text{NH}_4^+\text{-N}$ treatments. Means within a row followed by the same letter do not differ significantly at the 0.05 level. LSD = 43.

M. Regression analyses for extractable humic substances.

R^2 values from ANOVA show the maximum portion of variation between observations of different replicates which the best model of any type, such as a linear or polynomial model, would explain.

R^2 values from regression analyses show the portion of variation between observations of different replicates explained by the linear-regression model which we used.

$R^2 \text{ reg.} / R^2 \text{ ANOVA}$ = the portion of variation which the linear-regression model accounts for, in comparison to the variation which the best model would explain.

Since we are primarily interested in major trends of amounts of extracted humic substances resulting from various N and P treatments rather than precise quantitative amounts at some specific treatment rate, we have not calculated linear regression equations. Each dependent variable would require 5 different regression equations for each of 7 different incubation periods. Such a list of equations would probably not help enlighten the reader's understanding.

R² values for total extracted humic substanceTable 48. R² values for total extracted humic substances.

	Incubation period (d)						
	0	0.5	1	2	4	8	16
R ² Regression	.773	.865	.870	.903	.893	.865	.910
R ² ANOVA	.873	.980	.960	.970	.966	.977	.965
R ² Reg./R ² ANOVA	.885	.883	.906	.931	.924	.885	.943

R² values for extracted fulvic acidTable 49. R² values for extracted fulvic acid.

	Incubation period (d)						
	0	0.5	1	2	4	8	16
R ² Regression	.710	.906	.892	.827	.917	.895	.869
R ² ANOVA	.775	.957	.916	.882	.939	.967	.954
R ² Reg./R ² ANOVA	.916	.947	.974	.938	.977	.926	.911

R² values for extracted humic acidTable 50. R² values for extracted humic acid.

	Incubation period (d)						
	0	0.5	1	2	4	8	16
R ² Regression	.632	.701	.621	.747	.698	.725	.828
R ² ANOVA	.796	.927	.854	.911	.914	.938	.934
R ² Reg./R ² ANOVA	.794	.756	.727	.820	.764	.773	.886

The R² regression values in Tables 48, 49, and 50 are relatively high, but that does not justify an inference that lower values in another experiment would be less satisfactory.

N. Effect of interactions between N and P treatments on extractable humic substances

Total extracted humic substances

Table 51. Probability of an interaction between NH_4^+ -N and MAP affecting amounts of total humic substances extracted from Kennebec silt loam.

	Incubation period (d)						
	0	0.5	1	2	4	8	16
F value	0.89	16.21	4.59	5.26	6.69	18.34	5.47
Pr > F	0.5113	0.0001	0.0014	0.0005	0.0001	0.0001	0.0004

N-MAP interactions were significant for all incubation periods (Table 51), except for 0 d.

The probability level held significant throughout the interaction studies was 0.05.

Table 52. Probability of an interaction between NH_4^+ -N and APP affecting amounts of total humic substances extracted from Kennebec silt loam.

	Incubation period (d)						
	0	0.5	1	2	4	8	16
F value	2.11	12.76	3.60	3.00	2.77	4.20	4.40
Pr > F	0.0744	0.0001	0.0063	0.0170	0.0246	0.0024	0.0018

N-APP interactions (Table 52) were significant at all incubation periods except 0 d.

The interaction response of total extractable humic substances to various rates of NH_4^+ -N used with either MAP or APP is illustrated (Fig.

79-92). Slopes are only slightly unequal immediately after N and MAP treatment (Fig. 79), indicating a minimum of N-MAP interaction. In contrast, Fig. 80-92 show highly unequal slopes, indicating significant N-MAP and N-APP interactions.

The widely diverging slopes (Fig. 80-92) show that greater amounts of humic substances were extracted when N and P treatments were used in combination than when they were used separately.

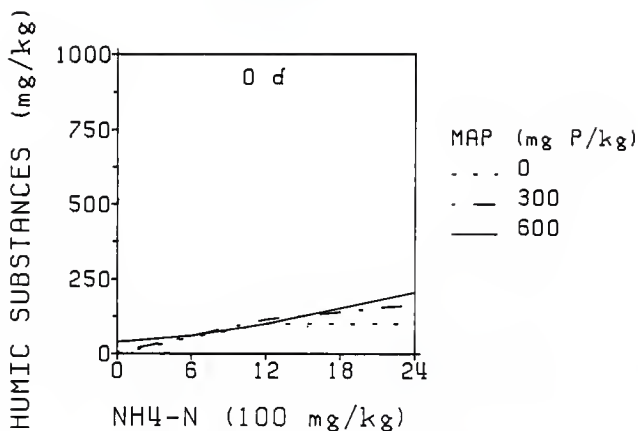


Figure 79. Interaction response of total extractable humic substances to various rates of MAP and N, immediately after treatment.

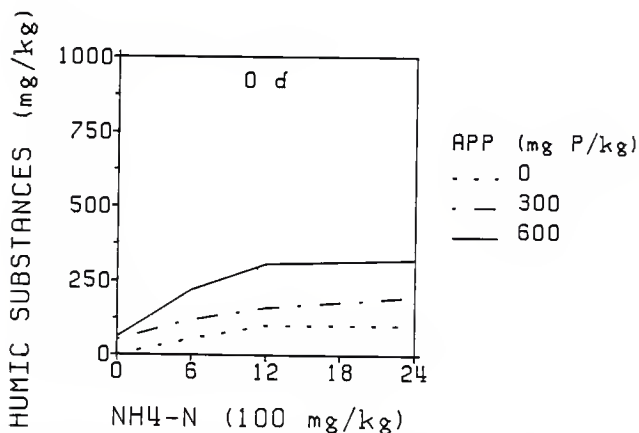


Figure 80. Interaction response of total extractable humic substances to various rates of APP and N, immediately after treatment.

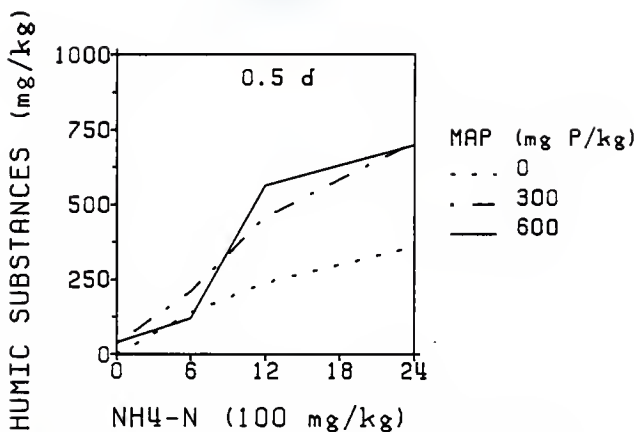


Figure 81. Interaction response of total extractable humic substances to various rates of MAP and N, 0.5 d after treatment.

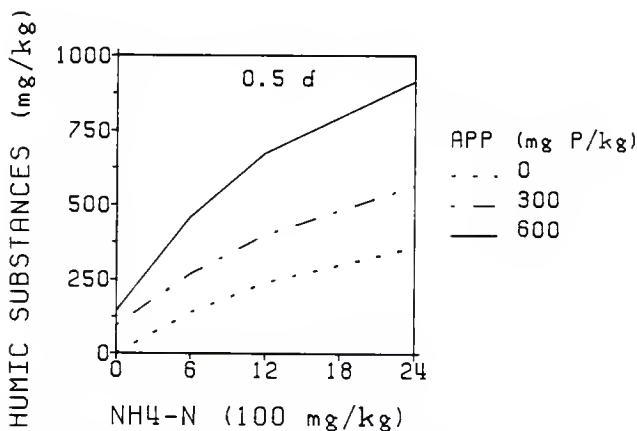


Figure 82. Interaction response of total extractable humic substances to various rates of APP and N, 0.5 d after treatment.

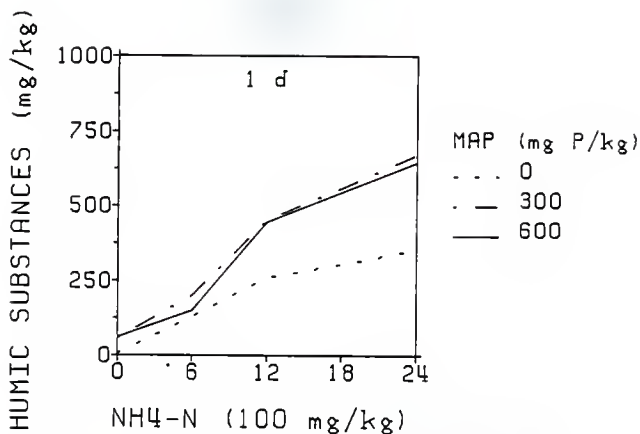


Figure 83. Interaction response of total extractable humic substances to various rates of MAP and N, 1 d after treatment.

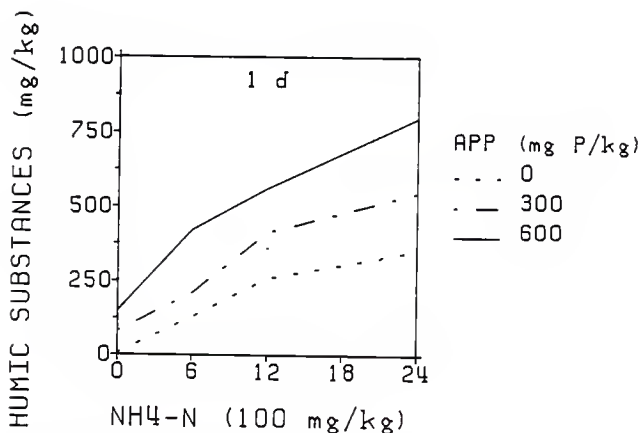


Figure 84. Interaction response of total extractable humic substances to various rates of APP and N, 1 d after treatment.

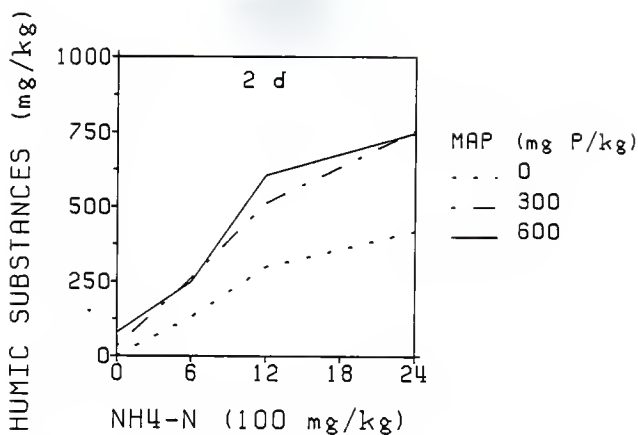


Figure 85. Interaction response of total extractable humic substances to various rates of MAP and N, 2 d after treatment.

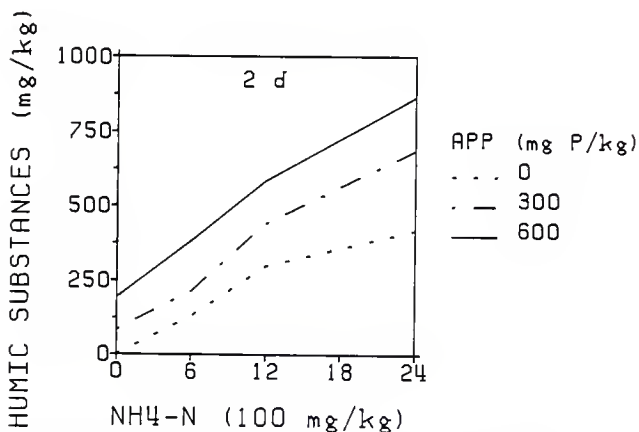


Figure 86. Interaction response of total extractable humic substances to various rates of APP and N, 2 d after treatment.

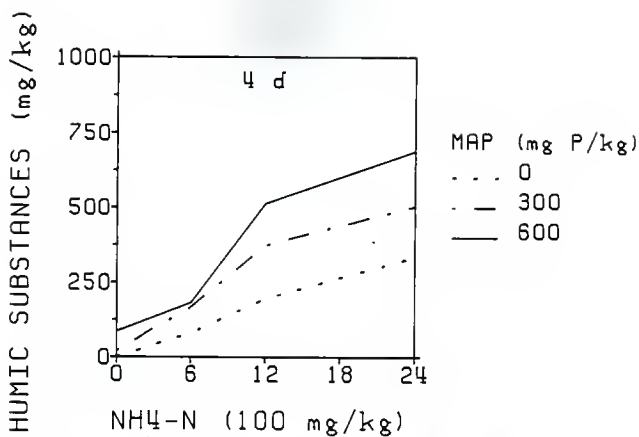


Figure 87. Interaction response of total extractable humic substances to various rates of MAP and N, 4 d after treatment.

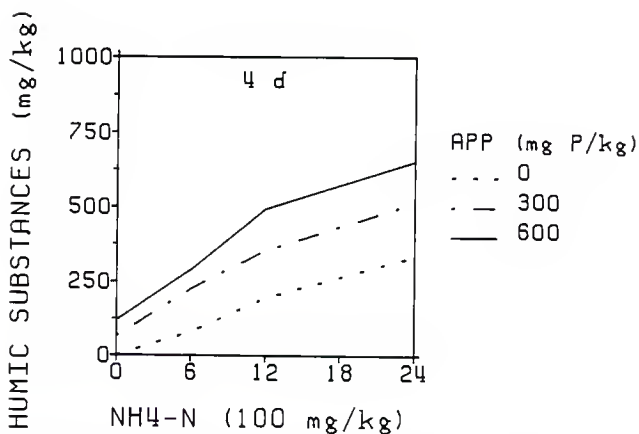


Figure 88. Interaction response of total extractable humic substances to various rates of APP and N, 4 d after treatment.

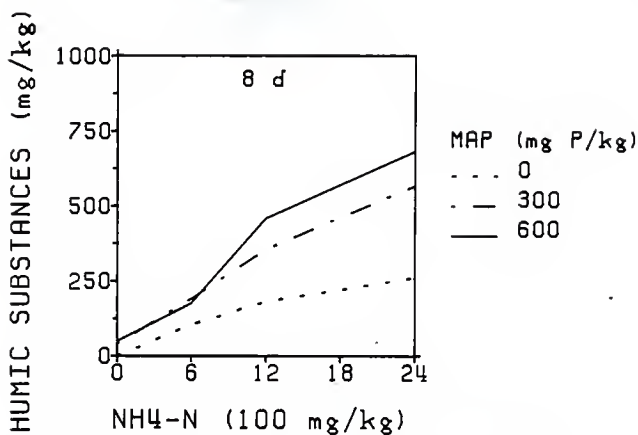


Figure 89. Interaction response of total extractable humic substances to various rates of MAP and N, 8 d after treatment.

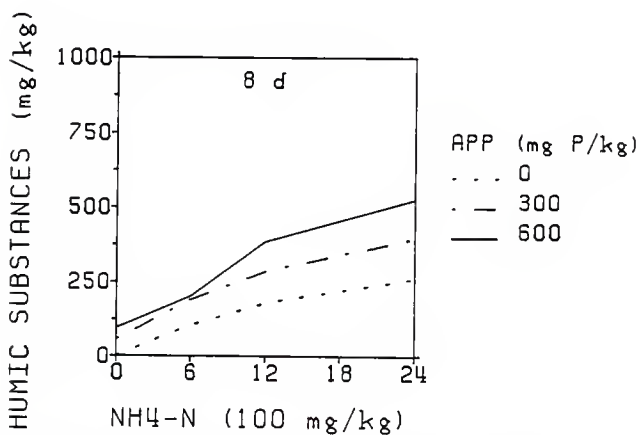


Figure 90. Interaction response of total extractable humic substances to various rates of APP and N, 8 d after treatment.

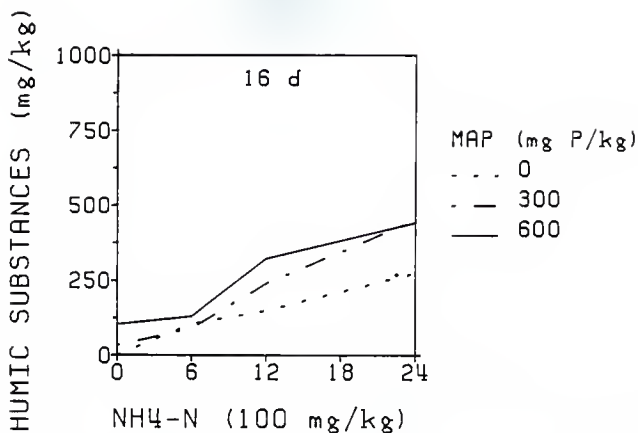


Figure 91. Interaction response of total extractable humic substances to various rates of MAP and N, 16 d after treatment.

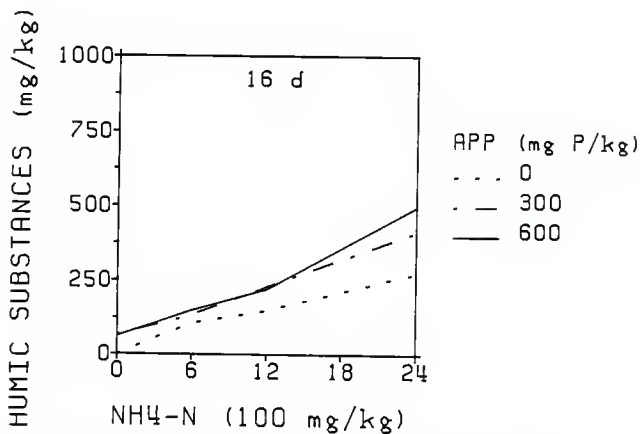


Figure 92. Interaction response of total extractable humic substances to various rates of APP and N, 16 d after treatment.

Fulvic acid and humic acid

Table 53. Probability of an interaction between $\text{NH}_4^+\text{-N}$ and MAP affecting amounts of fulvic acid extracted from Kennebec silt loam.

	Incubation period (d)						
	0	0.5	1	2	4	8	16
F value	0.31	0.42	0.32	1.00	1.25	1.97	3.40
Pr > F	0.9300	0.8638	0.9244	0.4406	0.3048	0.0938	0.0087

N-MAP interactions significantly affected amounts of extracted FA at only the 16-d period (Table 53).

Table 54. Probability of an interaction between $\text{NH}_4^+\text{-N}$ and APP affecting amounts of fulvic acid extracted from Kennebec silt loam.

	Incubation period (d)						
	0	0.5	1	2	4	8	16
F value	0.42	0.67	0.45	0.28	0.33	4.18	1.89
Pr > F	0.861	0.6725	0.8407	0.9451	0.9179	0.0026	0.1075

N-APP interactions significantly affected amounts of extracted FA at only the 8-d period (Table 54).

Table 55. Probability of an interaction between $\text{NH}_4^+\text{-N}$ and MAP affecting amounts of humic acid extracted from Kennebec silt loam.

	Incubation period (d)						
	0	0.5	1	2	4	8	16
F value	0.80	10.21	3.46	8.20	10.52	13.00	7.48
Pr > F	0.5774	0.0001	0.0079	0.0001	0.0001	0.0001	0.0001

N-MAP interactions significantly affected amounts of extracted HA at all periods except 0 d (Table 55).

Table 56. Probability of an interaction between $\text{NH}_4^+\text{-N}$ and APP affecting amounts of humic acid extracted from Kennebec silt loam.

	Incubation period (d)						
	0	0.5	1	2	4	8	16
F values	1.97	7.60	3.65	3.26	3.54	3.14	3.954
Pr > F	0.0945	0.0001	0.0058	0.0109	0.0070	0.0134	0.0036

N-APP interactions significantly affected amounts of extracted HA at all periods except 0 d (Table 56).

The interaction response of fulvic acid and humic acid to various rates of $\text{NH}_4^+\text{-N}$ and P is illustrated (Fig. 93-120). Extractable fulvic acid shows little interaction response to various rates of N and P treatments. The fulvic acid slopes for each of the respective periods are nearly enough equal to show that N-P interactions do not significantly affect amounts of extracted FA.

Extractable humic acid showed much interaction response to various

rates of N and P treatments. The widely diverging humic acid slopes at each of the respective periods, except for 0 d with the N-MAP treatment, indicate significant N-P interactions affecting amounts of extracted humic acid. The widely diverging humic acid slopes show that N and P used in combination extracted greater amounts of humic acid than when used separately.

The lack of significant N-P interactions affecting FA and the marked significance of N-P interactions affecting HA show a distinct difference in the way FA and HA react with N and P treatments. We have not determined the cause of that difference.

The lack of N-P interactions affecting FA compared with the highly significant N-P interactions affecting HA indicate that HA is the primary component of total humic substances responsible for the significant N-P interaction effect on total humic substances.

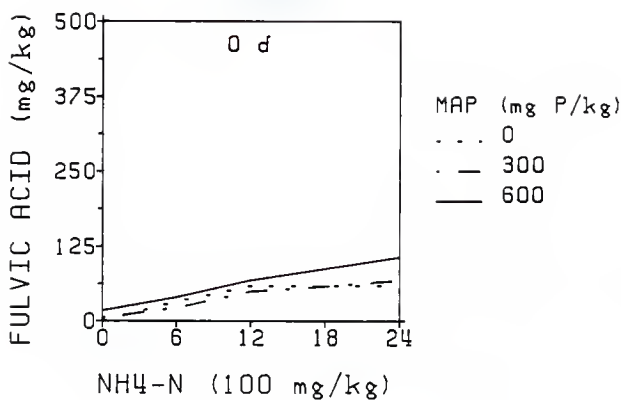


Figure 93. Interaction response of extractable fulvic acid to various rates of MAP and N, immediately after treatment.

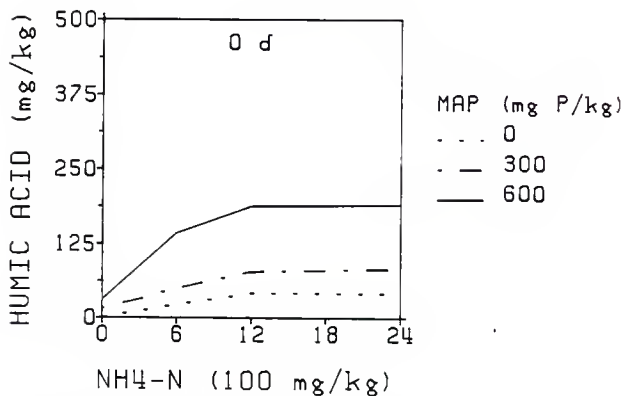


Figure 94. Interaction response of extractable humic acid to various rates of MAP and N, immediately after treatment.

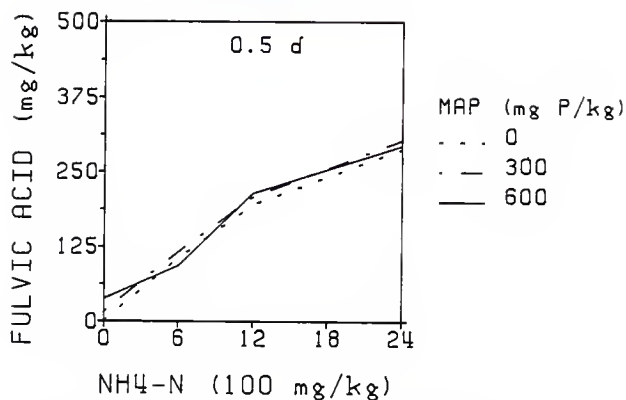


Figure 95. Interaction response of extractable fulvic acid to various rates of MAP and N, 0.5 d after treatment.

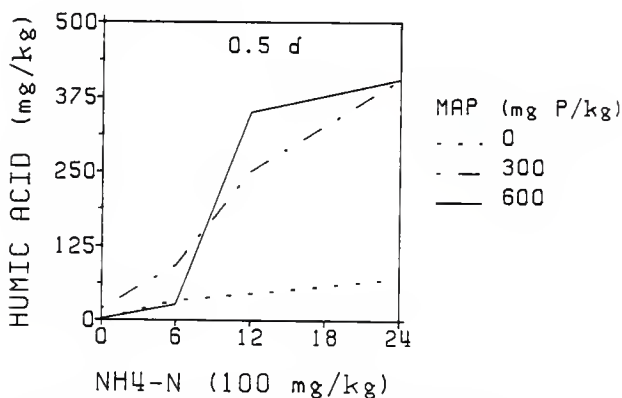


Figure 96. Interaction response of extractable humic acid to various rates of MAP and N, 0.5 d after treatment.

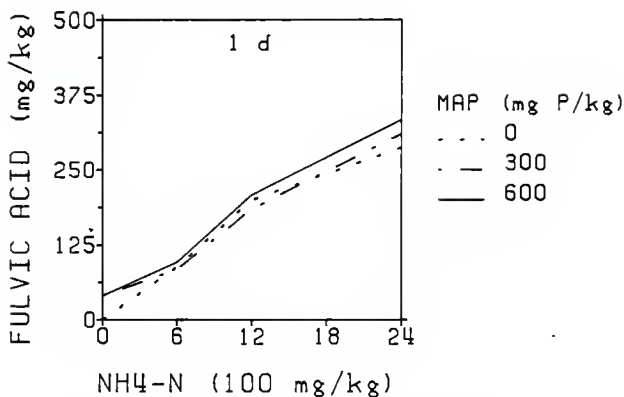


Figure 97. Interaction response of extractable fulvic acid to various rates of MAP and N, 1 d after treatment.

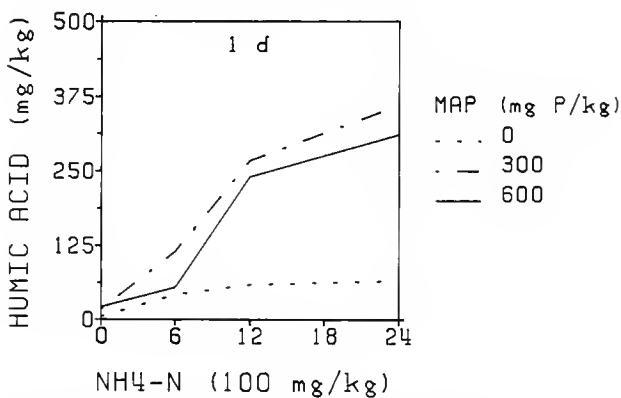


Figure 98. Interaction response of extractable humic acid to various rates of MAP and N, 1 d after treatment.

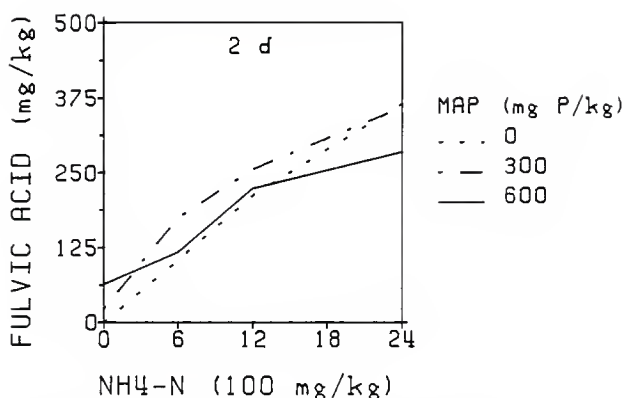


Figure 99. Interaction response of extractable fulvic acid to various rates of MAP and N, 2 d after treatment.

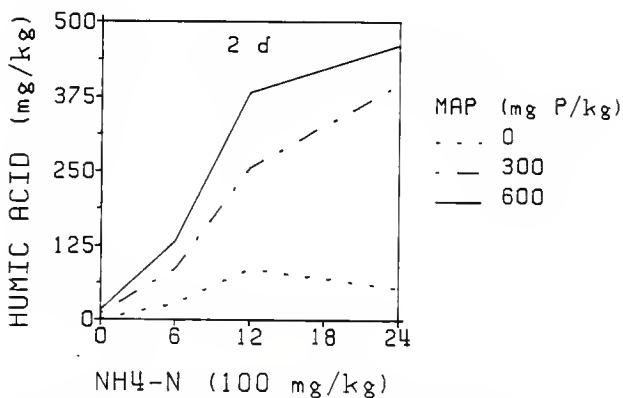


Figure 100. Interaction response of extractable humic acid to various rates of MAP and N, 2 d after treatment.

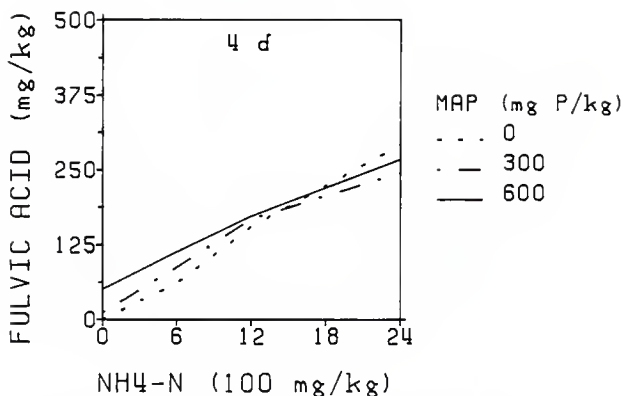


Figure 101. Interaction response of extractable fulvic acid to various rates of MAP and N, 4 d after treatment.

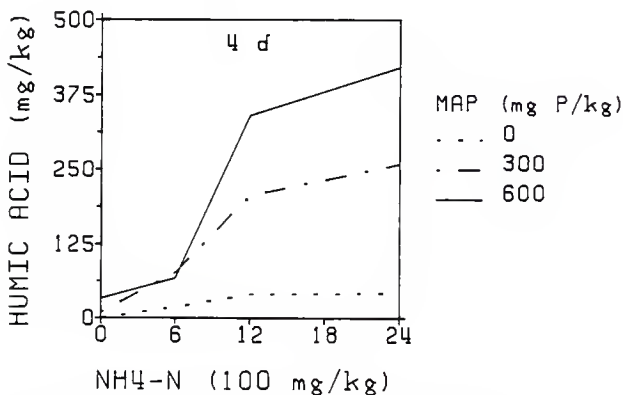


Figure 102. Interaction response of extractable humic acid to various rates of MAP and N, 4 d after treatment.

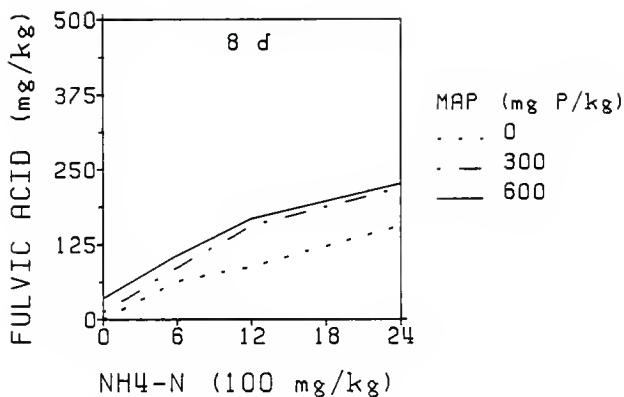


Figure 103. Interaction response of extractable fulvic acid to various rates of MAP and N, 8 d after treatment.

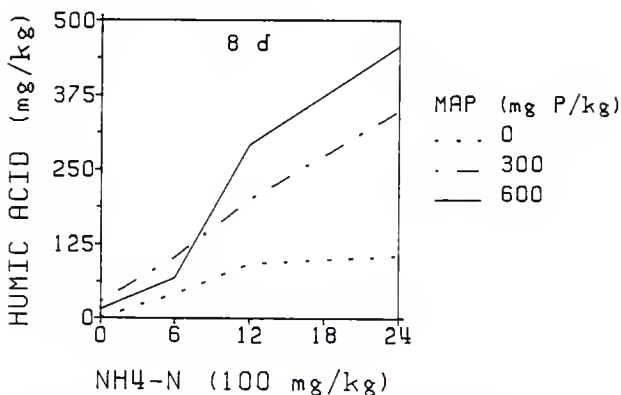


Figure 104. Interaction response of extractable humic acid to various rates of MAP and N, 8 d after treatment.

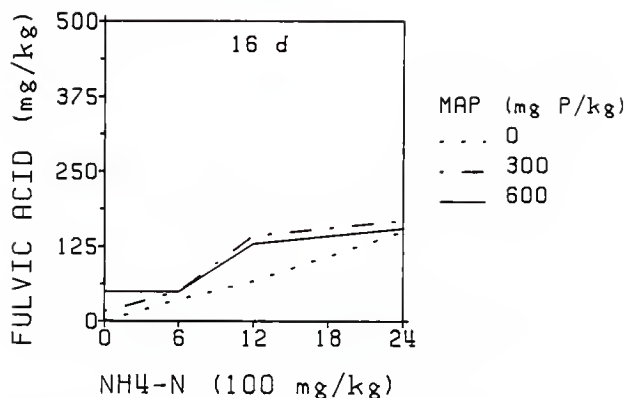


Figure 105. Interaction response of extractable fulvic acid to various rates of MAP and N, 16 d after treatment.

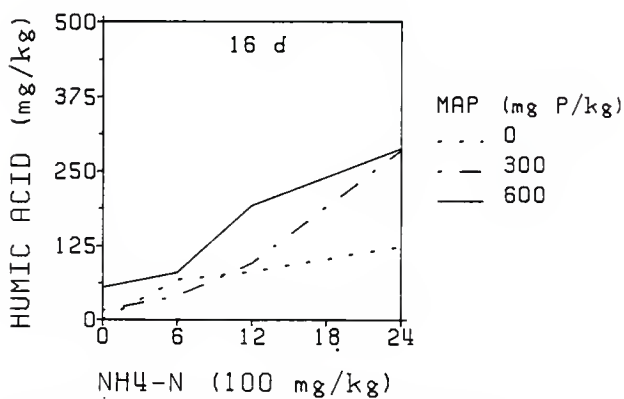


Figure 106. Interaction response of extractable humic acid to various rates of MAP and N, 16 d after treatment.

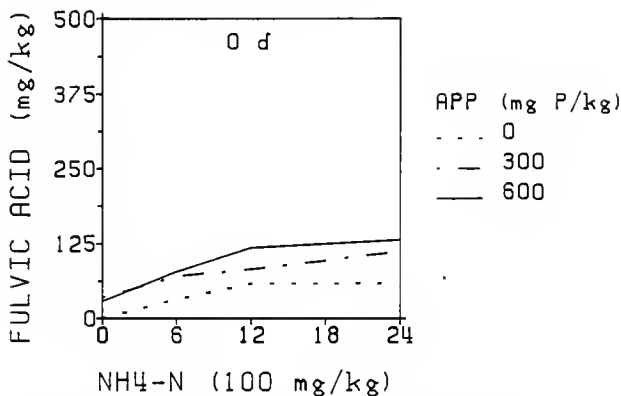


Figure 107. Interaction response of extractable fulvic acid to various rates of APP and N, immediately after treatment.

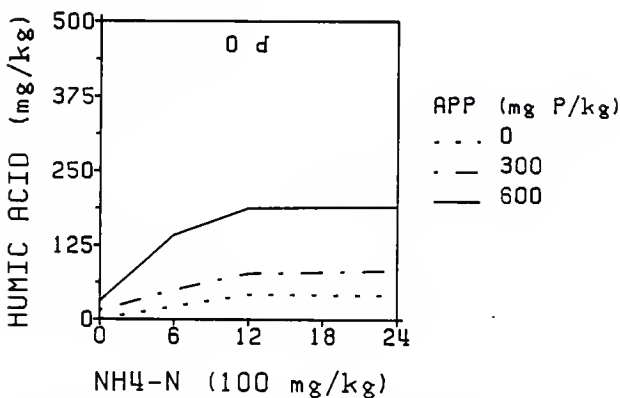


Figure 108. Interaction response of extractable humic acid to various rates of APP and N, immediately after treatment.

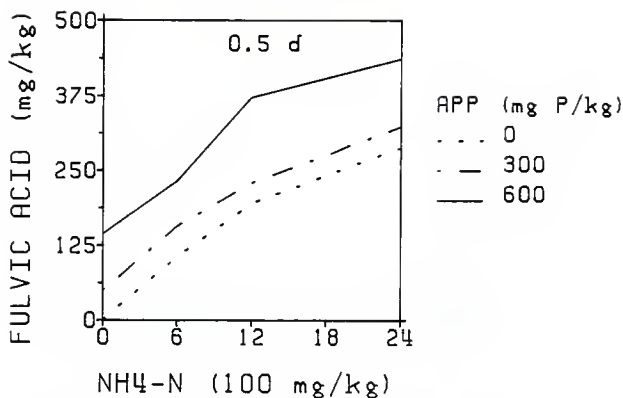


Figure 109. Interaction response of extractable fulvic acid to various rates of APP and N, 0.5 d after treatment.

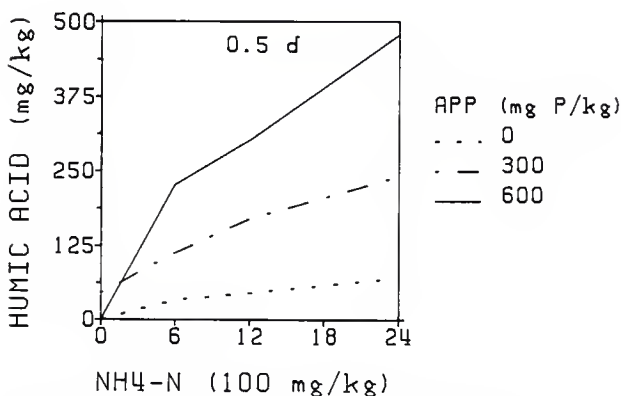


Figure 110. Interaction response of extractable humic acid to various rates of APP and N, 0.5 d after treatment.

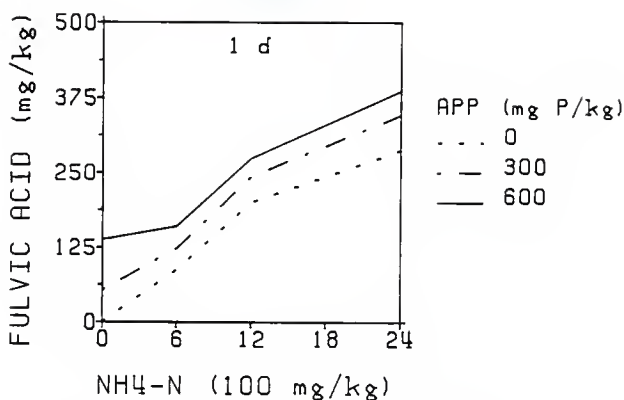


Figure 111. Interaction response of extractable fulvic acid to various rates of APP and N, 1 d after treatment.

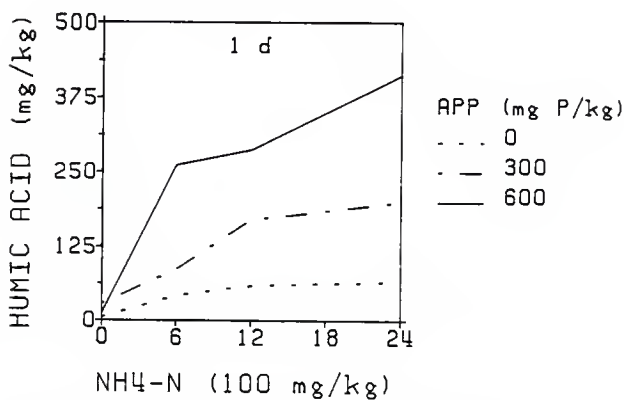


Figure 112. Interaction response of extractable humic acid to various rates of APP and N, 1 d after treatment.

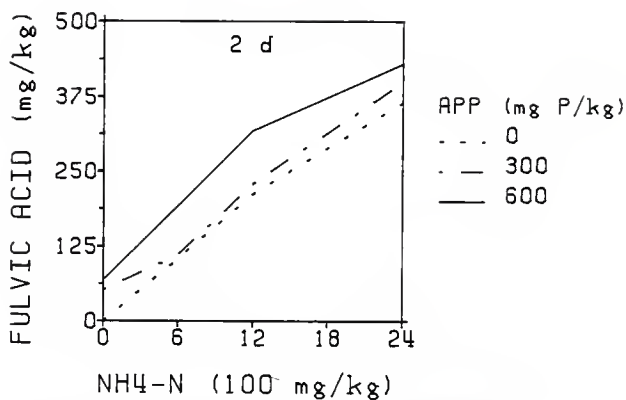


Figure 113. Interaction response of extractable fulvic acid to various rates of APP and N, 2 d after treatment.

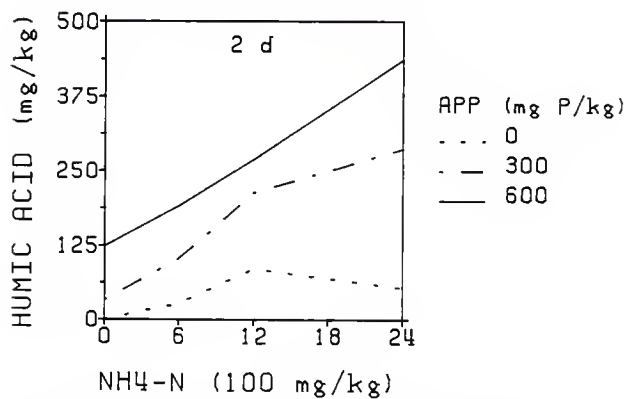


Figure 114. Interaction response of extractable humic acid to various rates of APP and N, 2 d after treatment.

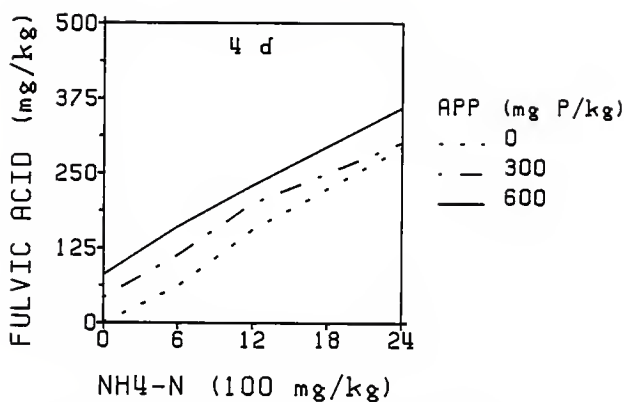


Figure 115. Interaction response of extractable fulvic acid to various rates of APP and N, 4 d after treatment.

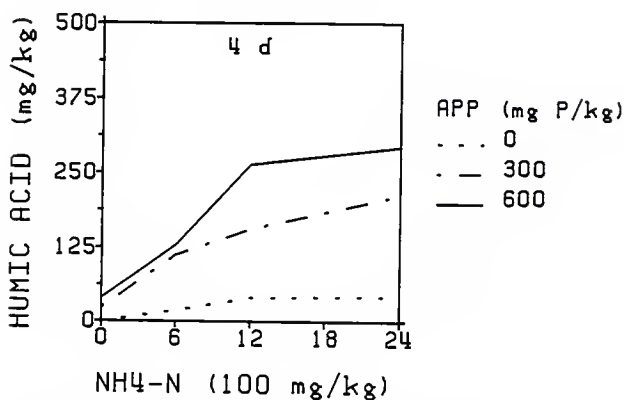


Figure 116. Interaction response of extractable humic acid to various rates of APP and N, 4 d after treatment.

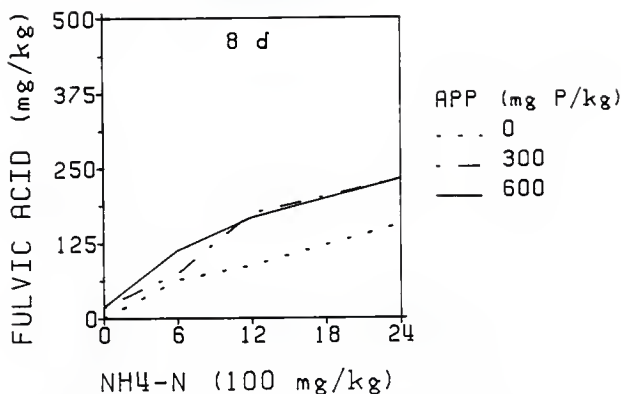


Figure 117. Interaction response of extractable fulvic acid to various rates of APP and N, 8 d after treatment.

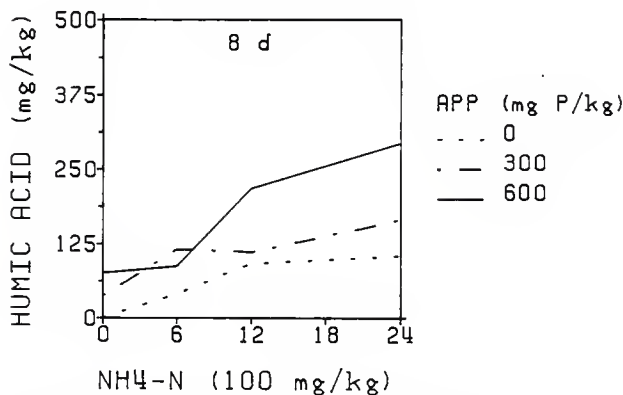


Figure 118. Interaction response of extractable humic acid to various rates of APP and N, 8 d after treatment.

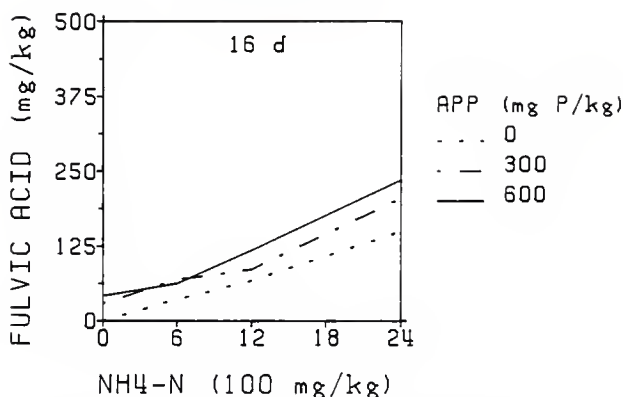


Figure 119. Interaction response of extractable fulvic acid to various rates of APP and N, 16 d after treatment.

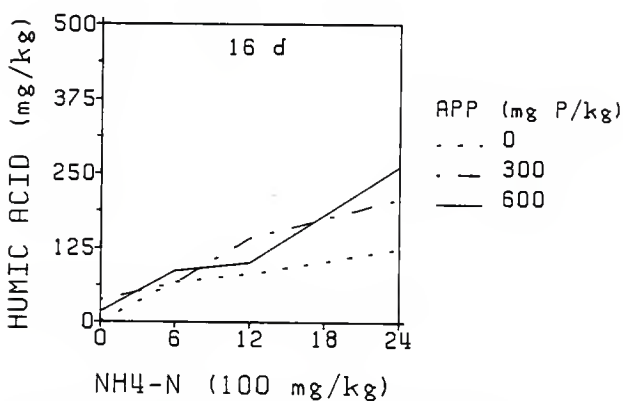


Figure 120. Interaction response of extractable humic acid to various rates of APP and N, 16 d after treatment.

DISCUSSION

pH

Increases in soil- and leachate-pH following increments of $\text{NH}_4^{+}\text{-N}$ result from the OH^{-} ion effect. Nommic and Nilsson (1963), and Parr and Khasawneh (1968) observed sharp pH rises in the retention zone immediately following soil treatment with NH_3 .

Intrawech *et al.* (1982) noted a decrease in soil pH following annual anhydrous NH_3 applications for 10 years, but nitrification was complete or nearly complete when they determined soil pH in the fall of the year after early spring application. That decrease in pH resulted at least partially from nitrification of ammonium ions which release H^{+} ions. In our experiment, the incubation period of 16 d was not long enough for nitrification to reach completion. This view is supported by noting that high pH values resulting from N treatments in our experiment never dropped to initial levels or below.

McDowell and Smith (1958) observed little nitrification during the first 2 weeks after soil treatment with anhydrous ammonia; however in making tests for nitrification they took samples 0-2.5 cm from the center of the retention zone where soil pH and NH_3 concentrations would have been the highest. The high pH and high NH_3 concentrations would have depressed activity of nitrifying microorganisms. That could explain why they observed little nitrification the first 2 weeks after treatment. At the periphery of the zone more nitrification may have occurred the first two weeks.

Parr and Khasawneh (1968) observed that pH in the NH_3 -retention zone began falling the first week after treatment and continued falling for 8 weeks. The authors found that nitrification began around the periphery of

the zone where the NH_3 concentration and pH levels were favorable for nitrifying microorganisms. The authors attributed the decrease in pH to nitrification of the NH_4^+ ion accompanied by the release of H^+ ions which often reduced pH to levels that inhibited activity of nitrifying microorganisms. During the last few weeks of that 8-week period, pH fell at a slower rate than the first 4 or 5 weeks.

Nommic and Nilsson (1963a) found that in the earliest stages, nitrification proceeded most rapidly in the peripheral parts of the retention zone where the NH_3 concentration was least.

In our experiment a number of varying conditions may have affected rates of nitrification in the retention zone. High concentrations of NH_3 are toxic to nitrifying bacteria (McDowell and Smith, 1958), so nitrification was likely depressed in the retention zone while NH_3 concentrations remained high. Since we did not have a buffer zone of soil outside the 7 cm diameter retention zone, nitrification in our soil columns probably first began in the 5-cm buffer zone of soil above and below the 15 cm column of treated soil. Even though nitrification may not have initially begun occurring at the injection point because of the high pH and high NH_3 concentrations, still nitrification occurring at the top and bottom of the columns may have lowered the pH and NH_3 concentration at the periphery. The lowered pH and lowered NH_3 concentration at the periphery would have increased the pH- and NH_3 -gradients from the injection point to the periphery causing an increase in NH_3 diffusion away from the injection point.

Therefore even though diffusion was probably initially the primary cause of pH reduction in the treated zone, nitrification likely increased the rate of diffusion by increasing the pH- and NH_3 -gradients from the

center of the treated zone to the periphery.

Soil treatment with phosphate has shown varying effects on nitrification in different studies. Some authors (Fraps and Starges, 1939, and Brown and Gawda, 1924) found addition of phosphate to soil increased the rate of nitrification; however Robison and Bullis (1922) found phosphate had a beneficial effect on nitrification in one soil, but a depressing effect on nitrification in three other soils.

Ammonia concentrations, soil pH, and phosphate addition probably all had some effect on rates of nitrification in our experiment. We did not make any specific tests to determine their relative importance.

The depressing effect MAP and APP had on pH was at least partially due to the lower pH of the treatment formulations, especially MAP. The pH of 1.56 M MAP was about 4.5 compared to about 6.75 for 0.78 M APP. Accordingly, MAP depressed pH more than APP.

Extracted Humic Substances

Results of SOM extraction from our soil samples treated with N and P agree with other experimental reports. We observed that N and P treatments both dissolved SOM. In 1786 Achard (Kononova, 1966) observed a dark colored precipitate after treating soil with alkali solutions and acidifying the extract. After treating soil with MAP and DAP, Bell and Black (1970) noted dissolution and precipitation of SOM which colored paper strips. Nemeč and Vopenka (1971) showed that NH_4OH and anhydrous ammonia extracted humic substances from soil. Giordano *et al.* (1971) found that both monoammonium orthophosphate and triammonium pyrophosphate solubilized

SOM.

After treating soil with anhydrous ammonia, Papendick and Parr (1966) observed darkened areas of soil which they believed resulted from solubilized SOM. We did not observe either darkened areas of soil or dark colored extracts after treating soil with only ammonium hydroxide. The extracts were predominantly an amber color. The explanation for the difference in our results and the results of Papendick and Parr may rest in the fact that SOM is degraded either more quickly or more completely by anhydrous ammonia than by ammonium hydroxide. Nemeč and Vopenka (1971) found that gaseous ammonia more aggressively released humic substances from soil than did the aqueous form of ammonia.

The reason for the more aggressive nature of anhydrous NH_3 over NH_4OH in extracting humic substances from soil is not readily apparent, but some differences are worth noting. Anhydrous NH_3 , being highly hygroscopic, vigorously withdraws moisture from the surrounding environment, including SOM, while ammonium hydroxide does not. A higher soil pH level and higher NH_3 concentration at the injection point would result when using anhydrous ammonia than when using ammonium hydroxide.

A competitive interaction between NH_3 and water for sorption sites and reaction sites in soils has been reported by James and Harward (1964) and Parr and Papenick (1966). That could provide one explanation for the more aggressive nature of anhydrous NH_3 over NH_4OH in dissolving SOM. Anhydrous NH_3 may withdraw water molecules from the SOM structure or surface and leave the SOM more exposed to attack from other NH_3 molecules; whereas NH_4OH would only furnish NH_3 molecules to attack initially exposed sites. The hygroscopicity of anhydrous NH_3 may act as a catalyst in increasing the rate of reaction between NH_3 and SOM by removing H_2O molecules from SOM

resulting in a greater surface area and more reaction sites on the SOM structure for NH_3 molecules to attack.

Molecular NH_3 would be present even in aqueous ammonia. The amount of molecular NH_3 in solution depends upon the pH of the solution and the dissociation constant (Parr and Khasawneh, 1968). According to Warren (1962), with a pKa of 9 the respective percentages of nonionic NH_3 at pH 6, 7, 8, and 9 would be 0.1, 1.0, 10, and 50% of total NH_3 . Little NH_4^+ would exist in an aqueous ammonia system at any one time (Khasawneh and Parr, 1968). A 13.6 M NH_4OH solution would be only about 0.016 M in NH_4^+ ions.

Sohn and Peech (1958) noted that SOM hinders fixation of ammonium ions, presumably by blocking accessibility between clay lattices. The same authors found that SOM is responsible for the fixation of up to 50% of molecular NH_3 in mineral soils. They noted that a substantial portion of the fixed ammonia was in nonexchangeable form resistant to decomposition. Mattson and Koutler-Andersson (1954) noted that lignin has been found to be the constituent which possesses the ability to fix ammonia in a purely chemical oxidation reaction.

Mortland (1958) mentioned various organic groups including carboxyl, phenol, aldehyde, ketone, and alcohol which might combine with NH_3 to form an ammonia-organic matter complex. Mattson and Koutler-Andersson (1954) proposed that lignin is the component in SOM involved in both the fixation of NH_3 , and the auto-oxidation of OM in the presence of NH_3 .

There may be some relation between ammonia-organic matter complexes, the auto-oxidation of SOM in the presence of NH_3 , and the degradation of SOM resulting in extracted humic substances which we observed in leachate samples.

It is not clear exactly what occurs during the auto-oxidation of SOM

when NH_3 complexes with SOM. Bennett (1949) performed methylation studies with lignin and results supported Mattson and Koutler-Andersson's idea that simultaneous oxidation of lignin and ammonia fixation takes place by way of the phenolic-OH groups. However, Stevenson (1982) did not believe that a sound basis for choosing any one particular mechanism for the fixation of NH_3 by SOM exists at this time. He noted that ammonia will react with a wide variety of organic compounds present in SOM.

It is known that at high pH levels the ionizable hydrogen on the carboxylic-OH and phenolic-OH groups can be easily removed from the OM molecule making it more reactive and less stable. Though not necessarily related to the NH_3 fixation reaction, the replacement of the hydrogen ion with an amine group from ammonia could have a destabilizing steric effect upon the SOM structure since the size of the amine ion is greater than that of the hydrogen ion. Any destabilizing steric effect upon the SOM structure could cause a concurrent disruption of hydrogen bonding and van der Waal's forces which help maintain the structural integrity.

It is believed that hydrogen bonding plays an important role in contributing to the stability of SOM. At high pH values, the high hydroxide concentrations may disrupt the hydrogen bonds resulting in SOM degradation and extraction.

Schnitzer (1978) pointed out that at high pH ionization of carboxyl-OH and phenolic-OH groups induces SOM particles to separate and become smaller in size causing the soil aggregates to disperse.

The cause of the effect of P treatments on SOM is not well established. Sample *et al.* (1980) suggested that monovalent ammonium ions from ammonium phosphate formulations may replace divalent and trivalent cations from stable organo-metallic complexes resulting in increased

solubility of SOM. A similar theory could be proposed that phosphate ions from P formulations pull Ca^{++} ions from the stable organo-metallic complexes destroying the integrity of the complex structure, and resulting in dispersion of SOM.

Since SOM is a highly complex substance partially stabilized by hydrogen bonding and van der Waals forces, any effect upon the OM structure which results in disruption of those bonding forces will reduce stability.

High soil pH, high NH_3 concentrations, NH_3 fixation by OM, auto-oxidation of OM, an excess of phosphate ions, and high concentrations of monovalent cations may all independently, or in combination, have an adverse effect upon bonding forces in SOM.

Until the exact chemical structure and bonding forces of SOM are better understood, it will be difficult if not impossible to define exactly how that structure and those bonding forces are changed by destabilizing effects of N and P soil treatments.

However the present data indicate that subjecting Kennebec silt loam to high pH, high NH_3 concentrations, and high P concentrations resulting from N and P treatments had an adverse effect upon structural stability of SOM resulting in a potential for SOM extraction and translocation. We observed the adverse effects on SOM when N and P were used separately as well as when they were placed together. When placed together in the soil, N and P treatments significantly interacted resulting in greater amounts of extracted humic substances than when the treatments were used separately.

SUMMARY

Increasing application rates of ammonium hydroxide caused soil pH and leachate pH to rise sharply to levels of 8 to 10, depending on the rates of N and the length of incubation period. Adding P treatments depressed pH in both soil and leachate. MAP depressed pH more than APP, probably because the pH of the MAP formulations, 4.5, was much lower than the pH of the APP formulation, 6.75. Increasing the length of incubation period caused pH to decrease in both soil and leachate. Nitrification and diffusion may have both contributed to decreased pH as incubation time increased. Diffusion of NH_3 away from the point of injection was probably the primary cause for decreasing pH with increasing incubation time, however nitrification at the periphery probably increased the pH- and NH_3 -gradients from the point of injection to the periphery, thereby increasing rates of diffusion.

The presence of humic substances in leachate from soil samples treated with various rates of $\text{NH}_4^+\text{-N}$ and MAP or APP showed that the treatments degraded SOM. Amounts of extracted humic substances increased until the 0.5-, 1-, or 2-d incubation period, then usually decreased gradually through the the remainder of the 16-d incubation period.

Colors of extracted humic substances ranged from yellow, amber, and orange to brown and black.

N-P interactions significantly increased amounts of total extractable humic substances and extractable HA, but did not significantly affect amounts of extractable FA. Those results indicate that the humic-acid component of SOM was responsible for the significant N-P interactions affecting total extractable humic substances, since N-P interactions affecting extractable FA were not usually significant.

Only about the equivalency of 4% of the total volume of soil 15 cm

deep in the field was treated with N and P. That was based upon calculations that the retention zone was 7 cm in diameter with 61 cm spacings between each individual zone. The 7 cm diameter is an arbitrary figure which may vary with soil type, moisture content, and fertilizer concentration. The question may arise whether the treated soil constitutes a significant volume of soil.

What happens to soil below the zone of treatment when leachate with a high pH moves downward? We don't know. We define the secondary zone of soil affected by N and P treatments as the zone of soil through which leaching and diffusion move the aqueous leachate from the primary zone of treated soil. That secondary zone of soil affected by leaching and diffusion from the primary zone may be much greater in volume than the primary zone. Therefore an inference that the treated zone of soil lacks sufficient volume for N and P treatments to cause significant adverse effects to an entire upper horizon of soil may not be sustainable because the total volume of soil affected by treatment may be much greater than the initial retention zone.

When SOM dissolves, the potential for its translocation arises. Results showed SOM remained dissolved, in some degree, up to at least 32 d (Appendix D) following treatment. In most grain-growing regions of the world where fertilizer is applied to agricultural land, substantial moisture often falls within a 32 d period. If substantial moisture falls on soil with dissolved SOM in the upper horizons of the soil, then translocation of that SOM is highly probable.

The specific effects of translocation of SOM from one soil horizon to a lower horizon are not well documented; however in the horizon of eluviation, reduced CEC, reduced permeability, degraded soil structure,

increased compactability, lighter soil color, and decreased fertility would be expected. We are presently completing analyses on exchangeable cations of leachate and leached soil samples after treating soil with N and P. Those results may provide information on the effects of N and P treatments on CEC.

Because of the potential for adverse soil effects arising from the eluviation of SOM to lower horizons after N and P treatments, the results raise a serious question of whether farmers should apply anhydrous ammonia or ammonium phosphates in highly concentrated zones in soil, as is often done at the present time. The significant interactions between N and P treatments affecting total humic substances raises a second question whether N and P treatments should be placed together in the soil since they dissolved greater amounts of SOM when placed together than when placed separately.

A number of different soil types from different geographical locations should be tested to determine how they react to N and P treatments. If the results of those tests indicate that high concentrations of N and P fertilizers in localized soil zones dissolve SOM in a significant number of different soils from different geographical locations, then alternate methods for applying N and P fertilizers may be needed. Methods will be needed which will not have a degrading effect on SOM as we observed in this study.

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APPENDIX

APPENDIX A

Calculation of Fertilizer Rates

1. Find the mass of soil in the retention zone of one hectare of soil.

Assume the diameter 6.985 cm with spacings of 61 cm.

$$M_{\text{soil}} = \pi(3.4925 \text{ cm})^2 \times (100\,000\,000 \text{ cm}^2 \text{ ha}^{-1}/61 \text{ cm}) \times 1.5 \text{ g cm}^{-3} = 94\,228\,900 \text{ g ha}^{-1} \\ = 94\,228.900 \text{ kg ha}^{-1}$$

2. Find mass of soil sample. Assume diffusion of fertilizer occurs uniformly 7.62 cm above and below the point of application in the soil column.

$$M_{\text{soil}} = \pi(3.4925 \text{ cm})^2 \times 15.24 \text{ cm} \times 1.1 \text{ g cm}^{-3} = 642.4 \text{ g} \\ = 0.6424 \text{ kg}$$

3. Nitrogen rates using NH_4OH as the N source. Assume the fertilizer is concentrated entirely in the given zone.

$$\text{*Example: } (113.1 \text{ kg N ha}^{-1}/94\,228\,900 \text{ kg ha}^{-1}) \times 1\,000\,000 = 1200 \text{ mg kg}^{-1} \text{ N} \\ 0.001\,200 \times 642.4 \text{ g} = 0.770\,880 \text{ g N per soil sample} \\ = 0.055\,062\,9 \text{ moles N} \\ = 3.72 \text{ ml of } 14.8 \text{ M NH}_4\text{OH}$$

To prepare N solution add 232.5 ml of 14.8 M NH_4OH to a 250 ml volumetric flask. Add water to correct volume. The solution is 13.8 M NH_4OH . Then to each respective soil sample add the following amounts of N solution.

$$2.0 \text{ ml for } 600 \text{ mg kg}^{-1} \text{ N } (56.5 \text{ kg ha}^{-1}) \\ 4.0 \text{ ml for } 1200 \text{ mg kg}^{-1} \text{ N } (113.1 \text{ kg ha}^{-1}) \\ 8.0 \text{ ml for } 2400 \text{ mg kg}^{-1} \text{ N } (226.1 \text{ kg ha}^{-1})$$

4. Orthophosphate rates using $\text{NH}_4\text{H}_2\text{PO}_4$ as the P source.

$$\text{Ratio of } \text{NH}_4\text{H}_2\text{PO}_4/\text{P} = 115.03/31 = 3.7106$$

$$\text{Example: } (56.5 \text{ kg P ha}^{-1}/94\,228.900 \text{ kg soil ha}^{-1}) \times 1\,000\,000 = 600 \text{ mg kg}^{-1} \text{ P} \\ 0.000\,600 \times 642.4 \text{ g} \times 3.7106 = 1.430\,2 \text{ g NH}_4\text{H}_2\text{PO}_4 \text{ per soil sample}$$

To prepare an orthophosphate solution weigh exactly

$$25 \times 1.430\,2 \text{ g NH}_4\text{H}_2\text{PO}_4 = 35.755\,0 \text{ g and dissolve it in about } 125 \text{ ml water.}$$

* 1200 mg kg^{-1} concentrated in a zone 7.00 cm in diameter at 61 cm spacings equates to 50 mg kg^{-1} uniform application.

Calculation of Fertilizer Rates

Transfer to a 200 ml volumetric flask and complete volume with water.

The solution is 1.55 M $\text{NH}_4\text{H}_2\text{PO}_4$. To each respective soil sample add the following amounts of P solution.

4.0 ml for 300 mg kg^{-1} P

8.0 ml for 600 mg kg^{-1} P

5. Pyrophosphate rates using $(\text{NH}_4)_3\text{HP}_2\text{O}_7$ as the P source.

Ratio of $(\text{NH}_4)_3\text{HP}_2\text{O}_7/\text{P}_2 = 229.0/62 = 3.6936$

Example: $0.000600 \times 642.4 \text{ g} \times 3.6936 = 1.4237 \text{ g } (\text{NH}_4)_3\text{HP}_2\text{O}_7$

To prepare a solution, weigh exactly 8.8981 g $(\text{NH}_4)_3\text{HP}_2\text{O}_7$, then transfer it to a graduated beaker and add water to make a total volume of about 40 ml.

After dissolving the mixture by stirring, transfer the solution to a 50 ml volumetric flask and complete volume with water. The solution is 0.78 M $(\text{NH}_4)_3\text{HP}_2\text{O}_7$. Make fresh immediately before using. To each respective soil sample add the following amounts of P solution.

4.0 ml for 300 mg kg^{-1} P

8.0 ml for 600 mg kg^{-1} P

APPENDIX B

Data from individual observations

Data lines on the following pages present data in the following order, moving left to right within a row: total observations, replicate, MAP, APP, $\text{NH}_4^+\text{-N}$, incubation period, total extracted humic substances (mg/kg), total extracted humic substances (%), extracted FA (mg/kg), extracted HA (mg/kg), leachate pH, and soil pH.

1	1	0	0	0	0.0	0	0.0	0	0	6.6	7.0
2	1	0	0	1	0.0	60	0.3	60	0	10.1	9.6
3	1	0	0	2	0.0	136	0.7	136	0	10.4	9.9
4	1	0	0	4	0.0	136	0.7	121	15	10.7	10.2
5	1	1	0	0	0.0	15	0.1	15	0	5.7	6.0
6	1	1	0	1	0.0	91	0.5	30	60	9.5	9.1
7	1	1	0	2	0.0	166	0.9	91	76	10.2	9.4
8	1	1	0	4	0.0	227	1.2	91	136	10.5	9.7
9	1	0	1	0	0.0	30	0.2	30	0	7.0	6.4
10	1	0	1	1	0.0	91	0.5	60	30	9.7	9.7
11	1	0	1	2	0.0	166	0.9	60	106	10.3	10.0
12	1	0	1	4	0.0	227	1.2	76	151	10.7	10.0
13	1	2	0	0	0.0	45	0.2	15	30	5.2	6.0
14	1	2	0	1	0.0	76	0.4	60	15	7.5	8.7
15	1	2	0	2	0.0	136	0.7	91	45	9.6	9.2
16	1	2	0	4	0.0	287	1.5	151	136	10.3	9.2
17	1	0	2	0	0.0	30	0.2	30	0	6.0	7.0
18	1	0	2	1	0.0	302	1.6	121	182	9.8	9.4
19	1	0	2	2	0.0	438	2.3	166	272	10.4	9.7
20	1	0	2	4	0.0	438	2.3	151	287	10.5	10.2
21	2	0	0	0	0.0	0	0.0	0	0	6.7	7.1
22	2	0	0	1	0.0	89	0.5	37	52	10.0	9.7
23	2	0	0	2	0.0	119	0.6	37	82	10.3	9.8
24	2	0	0	4	0.0	119	0.6	56	63	10.6	9.8
25	2	1	0	0	0.0	0	0.0	0	0	5.6	6.2
26	2	1	0	1	0.0	74	0.4	37	37	9.4	9.0
27	2	1	0	2	0.0	134	0.7	56	78	10.2	9.2
28	2	1	0	4	0.0	194	1.0	92	102	10.6	9.4
29	2	0	1	0	0.0	74	0.4	56	20	6.3	6.8
30	2	0	1	1	0.0	194	1.0	112	82	9.9	9.3
31	2	0	1	2	0.0	209	1.1	131	78	10.3	9.4
32	2	0	1	4	0.0	224	1.2	186	38	10.6	9.5
33	2	2	0	0	0.0	45	0.2	18	27	5.4	6.3
34	2	2	0	1	0.0	74	0.4	56	18	7.9	8.6
35	2	2	0	2	0.0	104	0.5	74	30	9.6	9.0
36	2	2	0	4	0.0	224	1.2	131	93	10.2	9.4
37	2	0	2	0	0.0	149	0.8	56	93	5.8	7.0
38	2	0	2	1	0.0	268	1.4	112	156	9.7	9.0
39	2	0	2	2	0.0	313	1.6	131	182	10.2	9.7
40	2	0	2	4	0.0	343	1.8	186	157	10.6	10.0
41	3	0	0	0	0.0	0	0.0	0	0	6.8	6.9
42	3	0	0	1	0.0	15	0.1	0	15	9.8	9.3
43	3	0	0	2	0.0	45	0.2	0	45	10.2	9.6
44	3	0	0	4	0.0	45	0.2	0	45	10.5	9.8
45	3	1	0	0	0.0	0	0.0	0	0	5.6	6.2
46	3	1	0	1	0.0	15	0.1	0	15	9.3	8.8
47	3	1	0	2	0.0	45	0.2	0	45	10.0	9.2
48	3	1	0	4	0.0	75	0.4	19	56	10.4	9.5
49	3	0	1	0	0.0	45	0.2	19	26	5.9	6.7
50	3	0	1	1	0.0	75	0.4	38	37	9.7	8.6
51	3	0	1	2	0.0	105	0.6	56	49	10.2	9.4
52	3	0	1	4	0.0	136	0.7	75	61	10.5	9.6
53	3	2	0	0	0.0	30	0.2	19	11	5.4	6.1
54	3	2	0	1	0.0	30	0.2	0	30	7.4	8.5
55	3	2	0	2	0.0	60	0.3	38	22	9.5	9.0
56	3	2	0	4	0.0	105	0.6	38	67	10.1	9.3

57	3	0	2	0	0.0	0	0.0	0	0	5.4	6.9
58	3	0	2	1	0.0	90	0.5	0	90	9.4	8.6
59	3	0	2	2	0.0	166	0.9	56	110	10.1	9.0
60	3	0	2	4	0.0	181	1.0	56	125	10.4	9.1
61	1	0	0	0	0.5	0	0.0	0	0	7.1	7.1
62	1	0	0	1	0.5	106	0.6	76	30	9.4	9.4
63	1	0	0	2	0.5	227	1.2	191	36	9.8	9.5
64	1	0	0	4	0.5	378	2.0	287	91	10.0	10.1
65	1	1	0	0	0.5	30	0.2	15	15	5.9	6.5
66	1	1	0	1	0.5	167	0.9	76	91	8.4	8.9
67	1	1	0	2	0.5	423	2.2	190	233	9.4	9.1
68	1	1	0	4	0.5	648	3.4	323	325	9.8	9.4
69	1	0	1	0	0.5	91	0.5	36	54	6.6	7.3
70	1	0	1	1	0.5	227	1.2	190	37	9.0	9.1
71	1	0	1	2	0.5	348	1.8	227	121	9.7	9.4
72	1	0	1	4	0.5	529	2.8	333	197	10.0	9.8
73	1	2	0	0	0.5	30	0.2	30	0	5.6	6.0
74	1	2	0	1	0.5	121	0.6	76	45	7.4	8.0
75	1	2	0	2	0.5	544	2.9	121	424	9.1	8.7
76	1	2	0	4	0.5	756	4.0	266	490	9.4	9.0
77	1	0	2	0	0.5	121	0.6	121	0	6.4	7.3
78	1	0	2	1	0.5	378	2.0	227	151	9.2	9.0
79	1	0	2	2	0.5	726	3.8	333	393	9.6	9.4
80	1	0	2	4	0.5	907	4.8	469	438	10.6	9.6
81	2	0	0	0	0.5	0	0.0	0	0	7.0	7.0
82	2	0	0	1	0.5	135	0.7	114	21	9.4	9.1
83	2	0	0	2	0.5	196	1.0	190	6	9.9	9.5
84	2	0	0	4	0.5	271	1.4	265	6	10.2	9.7
85	2	1	0	0	0.5	15	0.1	15	0	5.8	6.2
86	2	1	0	1	0.5	196	1.0	144	52	8.6	8.6
87	2	1	0	2	0.5	452	2.4	208	244	9.4	9.1
88	2	1	0	4	0.5	752	4.0	340	412	9.8	9.4
89	2	0	1	0	0.5	75	0.4	75	0	6.5	6.9
90	2	0	1	1	0.5	271	1.4	114	157	9.3	9.2
91	2	0	1	2	0.5	406	2.1	208	198	9.7	9.2
92	2	0	1	4	0.5	497	2.6	340	157	10.1	9.3
93	2	2	0	0	0.5	30	0.2	30	0	5.5	6.1
94	2	2	0	1	0.5	120	0.6	93	27	7.5	8.0
95	2	2	0	2	0.5	542	2.8	283	259	9.0	8.7
96	2	2	0	4	0.5	647	3.4	340	307	9.4	8.9
97	2	0	2	0	0.5	135	0.7	135	0	6.4	6.9
98	2	0	2	1	0.5	557	2.9	244	313	9.2	8.8
99	2	0	2	2	0.5	572	3.0	376	196	9.7	9.0
100	2	0	2	4	0.5	918	4.8	433	485	10.0	9.4
101	3	0	0	0	0.5	0	0.0	0	0	6.8	7.0
102	3	0	0	1	0.5	177	0.9	129	48	9.4	9.2
103	3	0	0	2	0.5	295	1.6	203	92	9.9	9.5
104	3	0	0	4	0.5	428	2.2	313	115	10.2	9.6
105	3	1	0	0	0.5	59	0.3	18	41	5.7	6.1
106	3	1	0	1	0.5	266	1.4	129	137	8.6	8.5
107	3	1	0	2	0.5	502	2.6	226	276	9.6	9.0
108	3	1	0	4	0.5	724	3.8	245	479	9.8	9.3
109	3	0	1	0	0.5	118	0.6	37	81	6.5	7.0
110	3	0	1	1	0.5	310	1.6	166	144	9.3	9.0
111	3	0	1	2	0.5	443	2.3	251	192	9.7	9.2
112	3	0	1	4	0.5	665	3.5	295	370	10.1	9.5

113	3	2	0	0	0.5	59	0.3	53	6	5.5	6.0
114	3	2	0	1	0.5	118	0.6	111	7	7.4	8.0
115	3	2	0	2	0.5	606	3.2	239	367	9.0	8.7
116	3	2	0	4	0.5	694	3.6	277	417	9.2	8.9
117	3	2	2	1	0.5	177	0.9	177	0	6.3	7.0
118	3	0	2	1	0.5	443	2.3	226	217	9.1	8.8
119	3	0	2	2	0.5	724	3.8	406	318	9.6	9.0
120	3	0	2	4	0.5	916	4.8	406	510	10.0	9.4
121	1	0	0	0	1.0	0	0.0	0	0	6.7	6.8
122	1	0	0	1	1.0	149	0.8	149	0	9.2	9.0
123	1	0	0	2	1.0	254	1.3	254	0	9.7	9.2
124	1	0	0	4	1.0	328	1.7	298	30	10.0	9.5
125	1	1	0	1	1.0	60	0.3	60	0	6.0	6.3
126	1	1	0	1	1.0	194	1.0	119	74	8.4	8.6
127	1	1	0	2	1.0	477	2.5	209	268	9.4	9.0
128	1	1	0	4	1.0	700	3.7	298	402	9.7	9.4
129	1	0	1	0	1.0	60	0.3	60	0	6.6	7.0
130	1	0	1	1	1.0	179	0.9	164	15	9.0	8.8
131	1	0	1	2	1.0	328	1.7	313	15	9.6	9.0
132	1	0	1	4	1.0	418	2.2	358	60	10.0	9.6
133	1	2	0	0	1.0	30	0.2	30	0	5.7	6.1
134	1	2	0	1	1.0	164	0.9	119	45	7.5	8.1
135	1	2	0	2	1.0	462	2.4	209	254	8.8	8.8
136	1	2	0	4	1.0	760	4.0	320	440	9.3	8.9
137	1	0	2	0	1.0	164	0.9	149	15	6.5	7.2
138	1	0	2	1	1.0	372	2.0	149	224	8.8	8.7
139	1	0	2	2	1.0	507	2.7	283	223	9.4	8.9
140	1	0	2	4	1.0	760	4.0	298	462	9.8	9.1
141	2	0	0	0	1.0	0	0.0	0	0	7.1	7.0
142	2	0	0	1	1.0	123	0.6	41	82	9.2	9.0
143	2	0	0	2	1.0	285	1.5	197	88	9.7	9.2
144	2	0	0	4	1.0	404	2.1	282	122	10.0	9.6
145	2	1	0	0	1.0	50	0.3	41	9	6.0	6.4
146	2	1	0	1	1.0	197	1.0	59	138	8.3	8.4
147	2	1	0	2	1.0	432	2.3	179	253	9.3	8.9
148	2	1	0	4	1.0	697	3.7	353	345	9.8	9.4
149	2	0	1	0	1.0	65	0.3	24	41	6.6	7.1
150	2	0	1	1	1.0	182	1.0	94	88	9.0	8.8
151	2	0	1	2	1.0	462	2.4	229	233	9.6	8.8
152	2	0	1	4	1.0	594	3.1	382	212	10.0	9.2
153	2	2	0	0	1.0	35	0.2	35	0	5.6	6.2
154	2	2	0	1	1.0	123	0.6	94	29	7.4	8.2
155	2	2	0	2	1.0	506	2.7	265	241	8.7	8.6
156	2	2	0	4	1.0	609	3.2	441	168	9.0	8.9
157	2	0	2	0	1.0	153	0.8	153	0	6.5	7.1
158	2	0	2	1	1.0	565	3.0	162	403	8.8	8.6
159	2	0	2	2	1.0	594	3.1	297	297	9.4	8.7
160	2	0	2	4	1.0	888	4.7	506	382	9.8	9.2
161	3	0	0	0	1.0	15	0.1	0	15	6.8	6.9
162	3	0	0	1	1.0	119	0.6	75	44	9.1	9.0
163	3	0	0	2	1.0	239	1.3	149	90	9.6	9.1
164	3	0	0	4	1.0	325	1.7	280	45	9.9	9.4
165	3	1	0	0	1.0	60	0.3	18	42	5.8	6.2
166	3	1	0	1	1.0	209	1.1	75	134	8.3	8.4
167	3	1	0	2	1.0	448	2.4	168	280	9.1	8.8
168	3	1	0	4	1.0	612	3.2	280	332	9.8	9.3

169	3	0	1	0	1.0	119	0.6	75	44	6.5	7.0
170	3	0	1	1	1.0	269	1.4	112	157	8.9	8.7
171	3	0	1	2	1.0	448	2.4	186	262	9.4	9.1
172	3	0	1	4	1.0	627	3.3	298	329	9.8	9.3
173	3	2	0	0	1.0	119	0.6	56	63	5.5	6.2
174	3	2	0	1	1.0	164	0.9	75	89	7.1	7.6
175	3	2	0	2	1.0	373	2.0	149	224	8.3	8.4
176	3	2	0	4	1.0	567	3.0	242	325	8.8	8.7
177	3	0	2	0	1.0	134	0.7	112	22	6.5	7.2
178	3	0	2	1	1.0	328	1.7	168	160	8.6	8.4
179	3	0	2	2	1.0	582	3.1	242	340	9.3	8.8
180	3	0	2	4	1.0	746	3.9	354	392	9.6	9.2
181	1	0	0	0	2.0	0	0.0	0	0	6.8	7.0
182	1	0	0	1	2.0	207	1.1	133	74	9.2	9.1
183	1	0	0	2	2.0	355	1.9	281	74	9.8	9.3
184	1	0	0	4	2.0	473	2.5	384	89	10.1	9.7
185	1	1	0	0	2.0	29	0.2	0	29	6.1	6.4
186	1	1	0	1	2.0	325	1.7	148	177	8.7	8.8
187	1	1	0	2	2.0	621	3.3	355	266	9.5	9.2
188	1	1	0	4	2.0	917	4.8	532	385	9.9	9.3
189	1	0	1	0	2.0	59	0.3	44	15	6.5	7.0
190	1	0	1	1	2.0	178	0.9	89	89	8.7	9.0
191	1	0	1	2	2.0	517	2.7	237	280	9.6	9.2
192	1	0	1	4	2.0	828	4.4	503	325	10.0	9.5
193	1	2	0	0	2.0	104	0.5	59	45	5.7	6.3
194	1	2	0	1	2.0	370	2.0	89	281	8.1	8.5
195	1	2	0	2	2.0	754	4.0	222	532	9.0	8.9
196	1	2	0	4	2.0	784	4.1	281	503	9.1	8.9
197	1	0	2	0	2.0	281	1.5	59	222	6.6	7.0
198	1	0	2	1	2.0	414	2.2	237	177	9.0	8.8
199	1	0	2	2	2.0	739	3.9	503	236	9.6	9.0
200	1	0	2	4	2.0	917	4.8	503	414	10.0	9.4
201	2	0	0	0	2.0	0	0.0	0	0	7.0	7.0
202	2	0	0	1	2.0	74	0.4	66	8	8.9	8.8
203	2	0	0	2	2.0	238	1.2	167	71	9.4	9.2
204	2	0	0	4	2.0	358	1.9	316	42	9.8	9.4
205	2	1	0	0	2.0	30	0.2	30	0	5.9	6.2
206	2	1	0	1	2.0	194	1.0	113	81	8.2	8.5
207	2	1	0	2	2.0	447	2.4	167	280	8.9	8.7
208	2	1	0	4	2.0	670	3.5	262	408	9.3	9.0
209	2	0	1	0	2.0	104	0.6	36	68	6.6	6.9
210	2	0	1	1	2.0	238	1.2	131	107	8.7	8.7
211	2	0	1	2	2.0	417	2.2	224	193	9.2	9.0
212	2	0	1	4	2.0	626	3.3	316	310	9.6	9.1
213	2	2	0	0	2.0	60	0.3	57	3	5.7	6.1
214	2	2	0	1	2.0	179	0.9	92	87	7.5	7.7
215	2	2	0	2	2.0	507	2.7	167	340	8.4	8.6
216	2	2	0	4	2.0	656	3.4	298	358	8.8	8.8
217	2	0	2	0	2.0	164	0.9	74	90	6.6	6.9
218	2	0	2	1	2.0	358	1.9	131	227	8.7	8.6
219	2	0	2	2	2.0	432	2.3	224	208	9.0	8.8
220	2	0	2	4	2.0	775	4.1	372	403	9.6	9.2
221	3	0	0	0	2.0	0	0.0	0	0	6.9	7.3
222	3	0	0	1	2.0	113	0.6	113	0	9.0	9.0
223	3	0	0	2	2.0	301	1.6	189	112	9.5	9.2
224	3	0	0	4	2.0	422	2.2	395	27	10.0	9.8

225	3	1	0	0	2.0	38	0.2	38	0	5.9	6.5
226	3	1	0	1	2.0	264	1.4	264	0	8.4	8.7
227	3	1	0	2	2.0	467	2.5	245	222	9.0	9.0
228	3	1	0	4	2.0	678	3.6	283	395	9.5	9.3
229	3	0	1	0	2.0	90	0.5	75	15	6.6	7.1
230	3	0	1	1	2.0	226	1.2	113	113	8.9	8.9
231	3	0	1	2	2.0	392	2.1	226	166	9.3	9.2
232	3	0	1	4	2.0	603	3.2	377	226	9.7	9.5
233	3	2	0	0	2.0	75	0.4	75	0	5.7	6.4
234	3	2	0	1	2.0	196	1.0	169	27	7.8	7.9
235	3	2	0	2	2.0	558	2.9	283	275	8.6	8.7
236	3	2	0	4	2.0	799	4.2	277	522	9.1	8.9
237	3	0	2	0	2.0	136	0.7	75	61	6.7	7.1
238	3	0	2	1	2.0	377	2.0	207	170	8.7	8.6
239	3	0	2	2	2.0	588	3.1	226	362	9.2	9.0
240	3	0	2	4	2.0	904	4.8	414	490	9.7	9.3
241	1	0	0	0	4.0	0	0.0	0	0	7.0	6.9
242	1	0	0	1	4.0	89	0.5	89	0	8.9	8.8
243	1	0	0	2	4.0	163	0.9	163	0	9.2	9.0
244	1	0	0	4	4.0	327	1.7	277	50	9.7	9.4
245	1	1	0	0	4.0	15	0.1	15	0	6.0	6.2
246	1	1	0	1	4.0	148	0.8	131	17	8.2	8.5
247	1	1	0	2	4.0	342	1.8	204	138	9.0	8.7
248	1	1	0	4	4.0	564	3.0	321	243	9.4	8.9
249	1	0	1	0	4.0	30	0.2	30	0	6.6	7.0
250	1	0	1	1	4.0	193	1.0	131	62	8.8	8.8
251	1	0	1	2	4.0	297	1.6	146	151	9.2	9.1
252	1	0	1	4	4.0	535	2.8	321	214	9.7	9.3
253	1	2	0	0	4.0	59	0.3	59	0	5.8	6.3
254	1	2	0	1	4.0	134	0.7	134	0	7.4	8.4
255	1	2	0	2	4.0	549	2.9	219	330	8.6	8.7
256	1	2	0	4	4.0	713	3.8	292	421	8.9	8.8
257	1	0	2	0	4.0	148	0.8	73	75	6.6	7.2
258	1	0	2	1	4.0	327	1.7	219	108	8.7	8.6
259	1	0	2	2	4.0	535	2.8	277	258	9.0	9.0
260	1	0	2	4	4.0	802	4.2	365	437	9.6	9.2
261	2	0	0	0	4.0	0	0.0	0	0	6.9	6.9
262	2	0	0	1	4.0	60	0.3	57	3	8.5	8.7
263	2	0	0	2	4.0	166	0.9	114	52	8.8	8.7
264	2	0	0	4	4.0	301	1.6	244	57	9.2	9.2
265	2	1	0	0	4.0	15	0.1	0	15	5.8	6.3
266	2	1	0	1	4.0	166	0.9	57	109	7.7	8.2
267	2	1	0	2	4.0	391	2.1	169	222	8.6	8.6
268	2	1	0	4	4.0	467	2.5	208	259	9.0	8.8
269	2	0	1	0	4.0	90	0.5	57	33	6.2	6.9
270	2	0	1	1	4.0	196	1.0	114	82	8.7	8.6
271	2	0	1	2	4.0	346	1.8	244	102	8.8	8.7
272	2	0	1	4	4.0	497	2.6	301	196	9.1	8.9
273	2	2	0	0	4.0	75	0.4	57	18	5.6	6.2
274	2	2	0	1	4.0	181	1.0	93	88	7.2	7.8
275	2	2	0	2	4.0	497	2.6	151	346	8.3	8.4
276	2	2	0	4	4.0	752	4.0	265	487	8.7	8.6
277	2	0	2	0	4.0	105	0.6	93	12	6.4	7.0
278	2	0	2	1	4.0	286	1.5	132	154	8.3	8.3
279	2	0	2	2	4.0	452	2.4	169	283	8.8	8.5
280	2	0	2	4	4.0	572	3.0	337	235	9.1	8.9

281	3	0	0	0	4.0	0	0.0	0	0	6.9	6.9
282	3	0	0	1	4.0	90	0.5	38	52	8.7	8.8
283	3	0	0	2	4.0	255	1.3	188	67	8.9	8.8
284	3	0	0	4	4.0	375	2.0	356	19	9.5	9.3
285	3	1	0	0	4.0	30	0.2	19	11	5.9	6.4
286	3	1	0	1	4.0	180	1.0	75	105	7.8	8.3
287	3	1	0	2	4.0	390	2.0	131	259	8.6	8.6
288	3	1	0	4	4.0	480	2.5	206	274	8.7	8.8
289	3	0	1	0	4.0	75	0.4	38	37	6.4	6.8
290	3	0	1	1	4.0	285	1.5	94	191	8.6	8.6
291	3	0	1	2	4.0	420	2.2	206	214	8.8	8.6
292	3	0	1	4	4.0	510	2.7	281	229	9.1	8.9
293	3	2	0	0	4.0	120	0.6	38	82	5.7	6.2
294	3	2	0	1	4.0	225	1.2	112	113	7.3	7.5
295	3	2	0	2	4.0	495	2.6	150	345	8.2	8.4
296	3	2	0	4	4.0	600	3.2	244	356	8.4	8.5
297	3	0	2	0	4.0	105	0.6	75	30	6.4	6.9
298	3	0	2	1	4.0	255	1.3	131	124	8.6	8.3
299	3	0	2	2	4.0	495	2.6	244	251	8.7	8.6
300	3	0	2	4	4.0	585	3.1	375	210	9.1	8.8
301	1	0	0	0	8.0	0	0.0	0	0	7.0	7.0
302	1	0	0	1	8.0	105	0.6	60	45	7.9	8.3
303	1	0	0	2	8.0	195	1.0	114	81	8.8	8.9
304	1	0	0	4	8.0	255	1.3	168	87	8.9	8.9
305	1	1	0	0	8.0	45	0.2	36	9	5.9	6.2
306	1	1	0	1	8.0	165	0.9	93	72	7.0	7.8
307	1	1	0	2	8.0	345	1.8	186	159	8.4	8.6
308	1	1	0	4	8.0	600	3.2	243	357	8.8	8.8
309	1	0	1	0	8.0	60	0.3	18	42	6.1	6.6
310	1	0	1	1	8.0	195	1.0	93	102	7.6	8.1
311	1	0	1	2	8.0	270	1.4	225	45	8.7	8.8
312	1	0	1	4	8.0	405	2.1	243	162	8.9	8.8
313	1	2	0	0	8.0	45	0.2	30	15	5.8	6.2
314	1	2	0	1	8.0	195	1.0	132	63	6.9	7.8
315	1	2	0	2	8.0	475	2.5	186	289	7.8	8.4
316	1	2	0	4	8.0	795	4.2	243	552	8.5	8.6
317	1	0	2	0	8.0	120	0.6	18	102	6.1	7.0
318	1	0	2	1	8.0	210	1.1	132	78	7.0	7.6
319	1	0	2	2	8.0	420	2.2	207	213	8.6	8.6
320	1	0	2	4	8.0	585	3.1	264	321	8.8	8.6
321	2	0	0	0	8.0	0	0.0	0	0	6.7	7.0
322	2	0	0	1	8.0	90	0.5	57	33	7.9	8.2
323	2	0	0	2	8.0	166	0.9	75	91	8.6	8.7
324	2	0	0	4	8.0	256	1.3	150	106	8.7	8.7
325	2	1	0	0	8.0	45	0.2	0	45	5.6	6.2
326	2	1	0	1	8.0	211	1.1	93	118	6.8	7.7
327	2	1	0	2	8.0	376	2.0	132	244	8.5	7.6
328	2	1	0	4	8.0	587	3.1	188	399	8.8	8.7
329	2	0	1	0	8.0	60	0.3	18	42	5.9	6.5
330	2	0	1	1	8.0	196	1.0	38	158	7.3	7.9
331	2	0	1	2	8.0	301	1.6	150	151	8.6	8.7
332	2	0	1	4	8.0	391	2.1	226	165	8.8	8.8
333	2	2	0	0	8.0	45	0.2	38	7	5.7	6.2
334	2	2	0	1	8.0	196	1.0	114	82	6.9	7.4
335	2	2	0	2	8.0	527	2.8	150	377	7.9	8.3
336	2	2	0	4	8.0	707	3.7	226	481	8.5	8.5

337	2	0	2	0	8.0	105	0.6	0	105	6.2	6.8
338	2	0	2	1	8.0	211	1.1	75	136	6.9	7.5
339	2	0	2	2	8.0	361	1.9	129	232	8.5	8.5
340	2	0	2	4	8.0	497	2.6	226	271	8.7	8.6
341	3	0	0	0	8.0	0	0.0	0	0	6.9	7.0
342	3	0	0	1	8.0	121	0.6	76	45	8.0	8.2
343	3	0	0	2	8.0	181	1.0	76	105	8.7	8.7
244	3	0	0	4	8.0	272	1.4	151	121	8.8	8.8
345	3	1	0	0	8.0	30	0.2	0	30	5.8	6.2
346	3	1	0	1	8.0	196	1.0	76	120	7.0	7.7
347	3	1	0	2	8.0	347	1.8	151	196	8.5	8.7
348	3	1	0	4	8.0	513	2.7	226	287	8.8	8.7
349	3	0	1	0	8.0	45	0.2	19	26	6.2	6.7
350	3	0	1	1	8.0	181	1.0	94	87	7.6	8.3
351	3	0	1	2	8.0	287	1.5	151	136	8.7	8.8
352	3	0	1	4	8.0	393	2.1	226	167	8.8	8.8
353	3	2	0	0	8.0	60	0.3	38	22	5.7	6.2
354	3	2	0	1	8.0	136	0.7	76	60	6.8	7.3
355	3	2	0	2	8.0	378	2.0	169	209	7.6	8.2
356	3	2	0	4	8.0	544	2.9	208	336	8.5	8.6
337	3	0	2	0	8.0	60	0.3	38	22	6.2	6.8
358	3	0	2	1	8.0	181	1.0	132	49	7.3	7.8
359	3	0	2	2	8.0	378	2.0	169	209	8.6	8.6
360	3	0	2	4	8.0	498	2.6	208	290	8.8	8.8
361	1	0	0	0	16.0	0	0.0	0	0	6.4	6.9
362	1	0	0	1	16.0	74	0.4	15	59	7.0	7.8
363	1	0	0	2	16.0	133	0.7	56	77	8.3	8.5
364	1	0	0	4	16.0	280	1.5	130	150	8.8	8.6
365	1	1	0	0	16.0	15	0.1	0	15	5.5	6.1
366	1	1	0	1	19.0	74	0.4	56	18	6.5	7.2
367	1	1	0	2	16.0	221	1.2	112	109	7.9	8.4
368	1	1	0	4	16.0	427	2.2	148	279	8.7	8.5
369	1	0	1	0	16.0	30	0.2	30	0	5.6	6.2
370	1	0	1	1	16.0	103	0.5	56	47	6.8	7.7
371	1	0	1	2	16.0	221	1.2	91	130	8.4	8.5
372	1	0	1	4	16.0	442	2.3	183	259	8.8	8.8
373	1	2	0	0	16.0	88	0.5	35	53	5.7	6.0
374	1	2	0	1	16.0	103	0.5	35	68	6.4	6.9
375	1	2	0	2	16.0	339	1.8	148	191	7.5	8.1
376	1	2	0	4	16.0	472	2.5	165	307	8.2	8.5
377	1	0	2	0	16.0	15	0.1	15	0	5.8	6.3
378	1	0	2	1	16.0	118	0.6	56	62	6.8	7.8
379	1	0	2	2	16.0	236	1.2	130	106	8.1	8.3
380	1	0	2	4	16.0	472	2.5	239	233	8.7	8.5
381	2	0	0	0	16.0	0	0.0	0	0	7.0	7.1
382	2	0	0	1	16.0	119	0.6	37	82	7.4	7.9
383	2	0	0	2	16.0	164	0.9	89	75	8.6	8.8
384	2	0	0	4	16.0	269	1.4	149	120	8.9	8.8
385	2	1	0	0	16.0	30	0.2	30	0	5.7	6.2
386	2	1	0	1	16.0	104	0.5	56	48	6.4	7.2
387	2	1	0	2	16.0	254	1.3	166	88	8.1	8.4
388	2	1	0	4	16.0	388	2.0	166	222	8.7	8.8
389	2	0	1	0	16.0	90	0.5	37	53	5.8	6.4
390	2	0	1	1	16.0	149	0.8	74	75	6.9	7.8
391	2	0	1	2	16.0	239	1.3	74	165	8.2	8.5
392	2	0	1	4	16.0	433	2.3	223	210	8.8	8.8

393	2	2	0	0	16.0	104	0.6	56	48	5.8	6.1
394	2	2	0	1	16.0	149	0.8	56	93	6.5	7.0
395	2	2	0	2	16.0	343	1.8	111	232	7.4	7.9
396	2	2	0	4	16.0	358	1.9	111	247	7.8	8.2
397	2	0	2	0	16.0	119	0.6	74	45	6.0	6.6
398	2	0	2	1	16.0	209	1.1	74	135	7.0	7.5
399	2	0	2	2	16.0	224	1.2	111	113	8.1	8.4
400	2	0	2	4	16.0	507	2.7	222	285	8.8	8.6
401	3	0	0	0	16.0	0	0.0	0	0	6.8	6.9
402	3	0	0	1	16.0	121	0.6	57	64	7.2	7.7
403	3	0	0	2	16.0	151	0.8	57	94	8.2	8.4
404	3	0	0	4	16.0	272	1.4	170	102	8.8	8.8
405	3	1	0	0	16.0	51	0.3	19	32	5.8	6.1
406	3	1	0	1	16.0	91	0.5	38	53	6.4	6.6
407	3	1	0	2	16.0	242	1.3	151	91	7.7	8.3
408	3	1	0	4	16.0	544	2.9	189	355	8.8	8.8
409	3	0	1	0	16.0	76	0.4	19	57	5.7	6.2
410	3	0	1	1	16.0	151	0.8	76	75	6.8	7.6
411	3	0	1	2	16.0	226	1.2	94	132	8.1	8.4
412	3	0	1	4	16.0	362	1.9	208	154	9.0	8.7
413	3	2	0	0	16.0	121	0.6	57	64	5.8	6.2
414	3	2	0	1	16.0	136	0.7	57	79	6.3	7.0
415	3	2	0	2	16.0	287	1.5	131	156	7.2	7.8
416	3	2	0	4	16.0	498	2.6	189	309	8.1	8.3
417	3	0	2	0	16.0	45	0.2	38	7	5.7	6.4
418	3	0	2	1	16.0	121	0.6	57	64	6.6	7.4
419	3	0	2	2	16.0	196	1.0	113	83	7.8	8.2
420	3	0	2	4	16.0	513	2.7	245	268	8.8	8.6

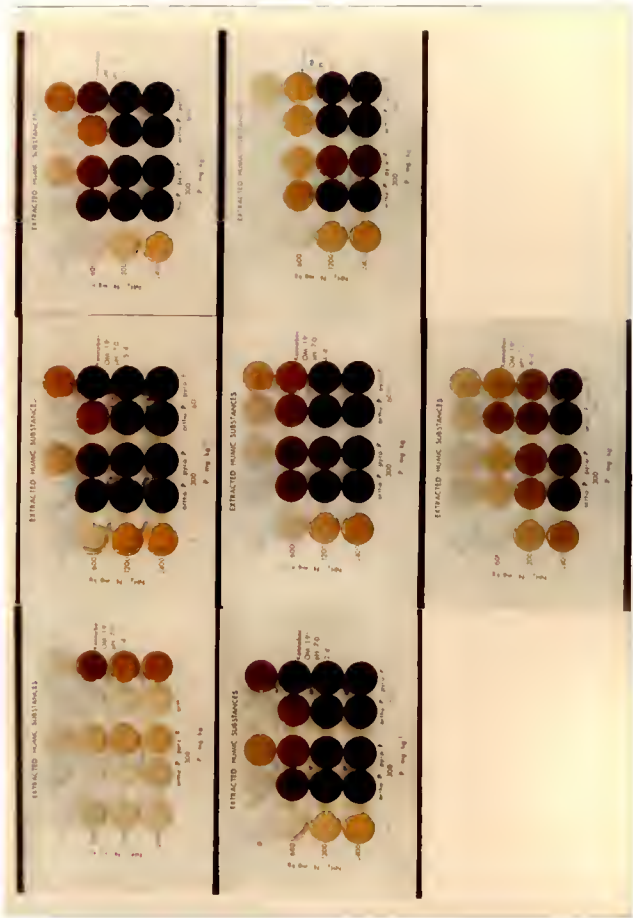


Figure 1. Solution colors from dissolved humic substances in aqueous leachate from Kennebec silt loam. Sets of samples in the top row, from left to right: 0, 0.5, and 1 d after treatment. Middle row, from left to right: 2, 4, and 8 d after treatment. Bottom row, 16 d after treatment.

APPENDIX D

Effects of N- and P-treatments on Kennebec silt loam 32 d after treatment

Some SOM apparently remained dissolved 32 d after N and P treatments (Tables 1 and 2), indicating that some of the effects of N and P treatments on soil still persisted after 32 d.

Samples in Table 1 were incubated, but samples in Table 2 were not. Incubation had some drying effect on the soil samples. That drying effect was visually observable when working with the samples. The samples in Table 2 which set at ambient room temperature for 32 d retained original moisture content better than samples in Table 1 which were incubated at 35°C.

Most of the samples in Table 2 contained more water-extractable humic substances than samples in Table 1. That indicates that as soil drying occurred the dissolved humic substances may have either precipitated from solution or were adsorbed onto the soil colloids.

Leachate samples (Figure 2) were taken from samples of Table 2. The samples show how increasing rates of N caused increased color in the solutions, and how the four columns of samples on the right, where P treatments were added, had greater color intensity than the column on the left where only N treatments were used.

Quantitative amounts (Tables 1 and 2) also indicated that increasing rates of N increased amounts of extracted humic substances, and that the addition of P to N treatments resulted in greater amounts of extracted humic substances than when only N treatments were used.

The soil pH for all treatments with 600 mg N/kg (Tables 1 and 2) was

APPENDIX D

Table 1. Soil pH and humic substances extracted from Kennebec silt loam incubated at 35°C for 32 d after treatment with various rates of orthophosphate, pyrophosphate, and nitrogen.

Treatment	Extracted humic substances				Soil pH
	Total		Acids		
	(mg/kg)	%	Fulvic (mg/kg)	Humic (mg/kg)	
0 0 0	15	0.1	0	15	6.8
0 0 600	30	0.2	30	0	7.1
0 0 1200	60	0.3	36	24	8.0
0 0 2400	120	0.6	93	27	8.6
300 0 0	15	0.1	15	0	5.5
300 0 600	30	0.2	0	30	6.0
300 0 1200	105	0.6	36	69	7.4
300 0 2400	240	1.3	72	168	8.4
0 300 0	0	0.0	0	0	5.7
0 300 600	75	0.4	36	39	6.8
0 300 1200	120	0.6	72	48	7.8
0 300 2400	210	1.1	72	138	8.4
600 0 0	45	0.2	21	24	6.0
600 0 600	60	0.3	21	39	6.4
600 0 1200	105	0.6	36	69	6.8
600 0 2400	195	1.0	72	123	7.5
0 600 0	30	0.2	30	0	5.9
0 600 600	45	0.2	36	9	6.8
0 600 1200	90	0.5	57	33	7.7
0 600 2400	135	0.7	72	63	8.3

APPENDIX D

Table 2. Soil pH and humic substances extracted from Kennebec silt loam 32 d after treatment with various rates of orthophosphate, pyrophosphate, and nitrogen. (Samples were not incubated, but left setting at ambient room temperature.)

Treatment	Extracted humic substances				Soil pH		
	Total		Acids				
	MAP (mg P/kg)	APP NH ₄ ⁺ -N (mg/kg)	(mg/kg)	%		Fulvic (mg/kg)	Humic (mg/kg)
0	0	0	30	0.1	18	12	6.8
0	0	600	45	0.2	38	7	6.0
0	0	1200	150	0.8	26	124	7.6
0	0	2400	166	0.9	75	91	8.4
300	0	0	30	0.2	18	12	5.7
300	0	600	45	0.2	38	7	5.8
300	0	1200	105	0.6	75	30	7.4
300	0	2400	241	1.3	113	128	8.5
0	300	0	30	0.2	18	12	5.5
0	300	600	45	0.2	26	19	6.3
0	300	1200	135	0.7	26	109	7.8
0	300	2400	241	1.3	113	128	8.6
600	0	0	60	0.3	18	42	5.6
600	0	600	60	0.3	26	34	6.3
600	0	1200	105	0.6	26	79	6.6
600	0	2400	211	1.1	113	987	7.4
0	600	0	60	0.3	38	22	5.9
0	600	600	60	0.3	38	22	6.0
0	600	1200	150	0.8	75	75	7.7
0	600	2400	181	1.0	132	49	8.3

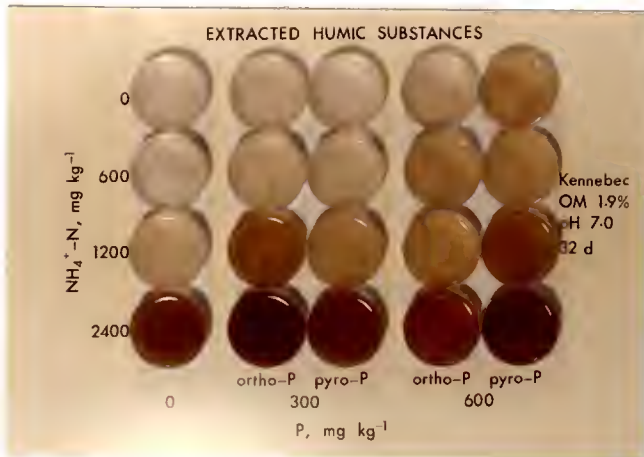


Figure 2. Solution colors from dissolved humic substances in aqueous leachate from Kennebec silt loam 32 d after treatment.

lower for samples which were not incubated. That may indicate that the more moist soil provided a better environment for nitrifying bacteria resulting in their increased activity. An increase in nitrification would result in decreased pH.

EFFECT OF AMMONIUM AND PHOSPHOROUS FERTILIZERS
ON
SOIL ORGANIC MATTER AND REACTION

by

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B. A., Washburn University, 1967

AN ABSTRACT OF A MASTER'S THESIS

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ABSTRACT

Using Kennebec silt loam, we investigated the effect of ammonium and phosphorous fertilizers on soil organic matter and reaction. After moistening soil samples to about 20% w/w moisture, we treated various samples with rates of 0, 600, 1200, and 2400 mg N/kg from NH_4OH , and 0, 300, and 600 mg P/kg from either $\text{NH}_4\text{H}_2\text{PO}_4$ (MAP) or $(\text{NH}_4)_3\text{HP}_2\text{O}_7$ (APP). Various samples were incubated at 35°C for 0, 0.5, 1, 2, 4, 8, and 16 d. We leached the samples with water, then determined pH of leachate and soil, and analyzed the leachate for organic matter.

Averaged over all incubation periods, pH values resulting from various treatments ranged from 5.6 to 9.7 in the leachate, and from 6.2 to 9.4 in the soil. Increasing $\text{NH}_4^+\text{-N}$ rates increased pH, but increasing P rates depressed pH. With treatments of 0, 300, and 600 mg P/kg, averaged over all N rates and over all incubation periods, pH values after using MAP were 8.7, 8.1, and 7.6 for leachate, and 8.6, 8.1, and 7.8 for soil. Those pH values after using APP were 8.7, 8.4, and 8.3 for leachate, and 8.6, 8.4, and 8.3 for soil.

Average extracted humic substances for various treatments over all incubation periods ranged from 1 to 654 mg/kg. Increments of N increased extracted humic substances. Addition of P to N treatments usually resulted in greater amounts of extracted humic substances than when only N treatments were used.

Total extracted humic substances, averaged over all MAP and APP rates and all incubation periods, were 57, 185, 356, and 512 mg/kg when $\text{NH}_4^+\text{-N}$ rates were 0, 600, 1200, and 2400 mg N/kg. Total extracted humic substances averaged over all $\text{NH}_4^+\text{-N}$ rates and all incubation periods were

152, 276, and 309 mg/kg using MAP, and 152, 266, and 384 mg/kg using APP, when the 3 rates 0, 300, and 600 mg P/kg, respectively, were used.

Total extracted humic substances were fractionated into fulvic acid and humic acid. Total amounts of fulvic acid and humic acid over all incubation periods and all treatments consisted of 51.2% fulvic acid and 48.8% humic acid.

Photos of leachate samples showed intensity of yellow, amber, brown, and black colors increased as extracted humic substances increased.