Reprinted from SOIL SCIENCE SOCIETY OF AMERICA PROCEEDINGS
Vol. 29, No. 2, March–April 1965, pages 179–181
677 South Segoe Road, Madison, Wisconsin 53711 USA

Ion Gradients and Nitrification Associated with Decomposition of a Plant Material Layer in Soil[1]

J. H. Smith and G. R. Burns[2]

ABSTRACT

Changes in the pH and in concentrations of ammonia, NO_2^-, NO_3^-, and K^+ with distance from layers of decomposing leguminous plant material in Red Bay sandy loam soil were measured after 16 days' incubation. High concentrations of ammonia (2.7 meq/100 g) and of K^+ (1.4 meq/100 g) were found near the plant material layer. Nitrification was inhibited and NO_2^- was found in this zone. Farther away, NO_3^- accumulated. A change in pH from 8.9, near the layer, to 5.6, about 4 cm away, was observed. Treatment with $CaCO_3$ decreased the pH range and increased nitrification. When the decomposing plant material layer was separated from the soil on one side by an air space, NH_3 diffused across the air space. This resulted in segregation of some of the NH_3 from the cations and other potentially toxic substances and lowered the overall toxicity to nitrification. Besides the toxicity observed, the availability of plant nutrients as well as growth of microorganisms and plant roots could be drastically affected by pH and cation concentration changes found near layers of decomposing plant material.

In modern agricultural practice, crop residues high in N content are often plowed into the soil in layers. The decomposition of these layers of plant material releases ions that affect surrounding soil and plants. Under certain conditions decomposition products may accumulate that are toxic to higher plants and to nitrifying organisms (6). Ammonia accumulation can be toxic to nitrification (3, 4, 5, 9). In a previous paper (8) the toxicity of ammonia from particles of plant material in soil was related to the cation-exchange capacity (CEC) of the soil. A decrease in CEC by sand dilution of the soil decreased the capacity of the soil to adsorb ammonia and increased ammonia toxicity. The postulation was made that at high ammonia adsorbing capacity, ammonia was confined largely to the volume of soil immediately surrounding the plant material particle, thus leaving zones of soil relatively unaffected by it where nitrification could proceed. At lower ammonia-adsorbing capacity these nitrification zones were eliminated.

The objectives of the present study were to determine the distribution of ions in soil associated with a decomposing plant material layer of high N content and to relate these ion distribution gradients to inhibition of nitrification by ammonia. In this paper ammonia is used as a general term to indicate NH_3 gas and both NH_3 and NH_4^+ in solution. Specific forms are designated as NH_3 for nonionized ammonia and NH_4^+ for ammonium ions.

MATERIALS AND METHODS

Red Bay sandy loam soil diluted with glass beads was incubated with layers of alfalfa in plastic boxes. The boxes had an open end, 26 by 76 mm and were 66 or 117 mm long with a screw-driven plunger at the opposite end for extruding the contents. After incubating the layers of plant material with soil, the soil was extruded from the box with the plunger and sliced into 0.5-cm layers parallel to the plant material. The soil slices were analyzed for pH, ammonia, NO_2^-, NO_3^-, and K^+.

The soil was prepared in batches as follows: 220 g of the A horizon of a Red Bay sandy loam soil from Wedgefield, South Carolina, was screened through a 0.5-mm sieve. The weight of particles that did not pass the sieve was replaced with glass beads of 0.2-mm average diameter. An additional 44 g of glass beads were added to the soil. This resulted in a synthetic soil (Table 1) with CEC of 7.2 meq/100 g of such texture that it could be easily sliced into segments for chemical analyses. These batches of soil were the experimental units for treatment application.

Calcium carbonate treatments equivalent to 0, 0.66, 2.66 and 5.33 meq of Ca^{2+} and a $Ca(OH)_2$ treatment equivalent to 7.2 meq of Ca^{2+} per 100 g of soil were applied. Two grams of 149- to 250-micron alfalfa meal (Table 1) was wetted with 2 ml of water and packed into a layer in the bottom of a plastic box. Soil containing approximately 10% of water was then packed on top of the plant material until the box was full. The open end of the box was covered with aluminum foil and the box was then incubated for 16 days at 27C in a high-humidity chamber.

Three additional treatments were set up and conducted similarly to the 2.66 meq of $CaCO_3$ treatment. The principal difference was the physical arrangement of the soil and the plant material. The various arrangements are illustrated in Fig. 1. In these treatments the plant material was inoculated with 2 ml of soil suspension rather than with water because in certain cases there was no soil contact.

All treatments were set up one at a time to allow immediate chemical analysis of the soil after incubation. The soil was extruded from the box by the screw-driven plunger and sliced into layers approximately 0.5 cm thick. The second layer was used for the determination of the final moisture content of the soil. All the other soil layers were divided into two parts. Ammonia was extracted from the first with 20 ml of acidic K_2SO_4 (8) and analyzed by the Conway microdiffusion technique in a manner similar to that described by Bremner and Shaw (2). The second part was used for pH, NO_2^-, NO_3^-, and nonwater-extractable K^+ determinations. Twenty milliliters of water was added to the soil sample and the pH determined with a Beckman Model G pH meter. The filtrate was analyzed for NO_2^- by the method of Rider and Melon (7), and NO_3^- by the phenoldisulfonic acid method. The residual soil was then extracted with 1N ammonium acetate for K^+ determination by flame photometry. All analyses were made on moist samples and the results were converted to dry soil equivalent values.

Table 1—Composition of plant material and exchangeable ions in experimental soil

	N	Ca^{2+}	Mg^{2+}	K^+	$(H_2PO_4)^-$	H^+
	meq/100 g					
Alfalfa particles (149 to 250 μ)	271	53.6	28.1	68.2	12.2	--
Experimental soil	--	4.39	0.31	0.34	--	2.18

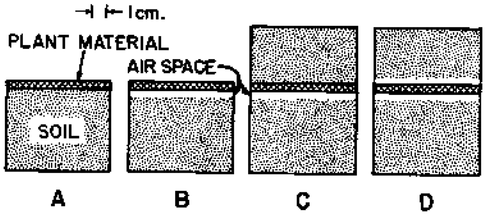

Fig. 1—Schematic diagram illustrating the physical arrangements of soil, plant material, and air space in ion diffusion and nitrification experiments.

---

[1] Contribution from the U. S. Soils Laboratory, Soil and Water Conservation Research Division, ARS, USDA, Beltsville, Md. Received Sept. 11, 1964. Approved Nov. 3, 1964.

[2] Research Soil Scientists.

RESULTS

Typical concentration gradients of ammonia, NO_2^-, NO_3^-, K^+, and H^+ resulting from decomposition of layers of plant material are illustrated in Fig. 2. Generally, these gradients extended as far as 4.5 cm into the soil away from the plant material. The ranges in concentrations of ammonia and those of K^+ were similar in the limed and unlimed soils. In the first 0.5-cm layer of soil, adjacent to the plant material, ammonia concentration approached 3 meq/100 g of soil in contrast to a level of 0.05 meq in the unaffected soil. Comparable figures for K^+ were 1.4 meq and 0.3 meq, respectively. The pH ranged from 8.9, near the layer, to 5.6, about 4 cm away, in the soil that was not limed, and from 8.6 to 7.2 in the limed soil. In both cases the range included the pH of the unaffected soil.

Nitrification was inhibited for a distance of about 3 cm in the soil that was not limed and for about 2 cm in the limed soil. In both soils NO_2^- accumulated in the first 2 cm. Nitrification was stimulated in the limed soil between 2 and 4 cm and was associated with a dip in the pH curve.

Ion concentration gradients in soil separated from a layer of plant material by an air space are shown in Fig. 3. The movement of gaseous NH_3 across the air space resulted in ammonia concentrations in the soil that ranged from 1.3 meq/100 g of soil in the layer of soil nearest the air space to 0.002 meq at a distance of about 4 cm. However, because K^+ is not volatile, the K^+ released by the decomposition of the plant material did not cross the air space. Therefore, the K^+ concentration in the soil was not directly affected and remained almost constant with distance at the concentration of the control soil. The pH ranged from 7.5 to 6.7 in a distance of about 3 cm. Nitrification was not noticeably inhibited and only a trace of NO_2^- was found near the air space. The NO_3^- content ranged from 0.52 meq to 0.30 meq in a distance of about 5.5 cm.

Ion concentration gradients were determined in soil contacting a layer of plant material and in soil that was separated from the layer of plant material by an air space (see Fig. 1-C). These concentration gradients are reported in Fig. 4. Gaseous NH_3 moved across the air space, and both NH_3 and NH_4^+ moved into the soil contacting the plant material. Ammonia concentration in both soils was about the same, however, it was considerably lower than the concentration shown in Fig. 2 and 3. The pH curves in both soils were cup-shaped with a range in pH from 6.6 to 5.7 in the soil on the air space side and 7.0 to 6.0 in the soil contacting the plant material. The lower pH of the soil across the air space is probably related to the fact that K^+ from the decomposing plant material did not diffuse across the air space.

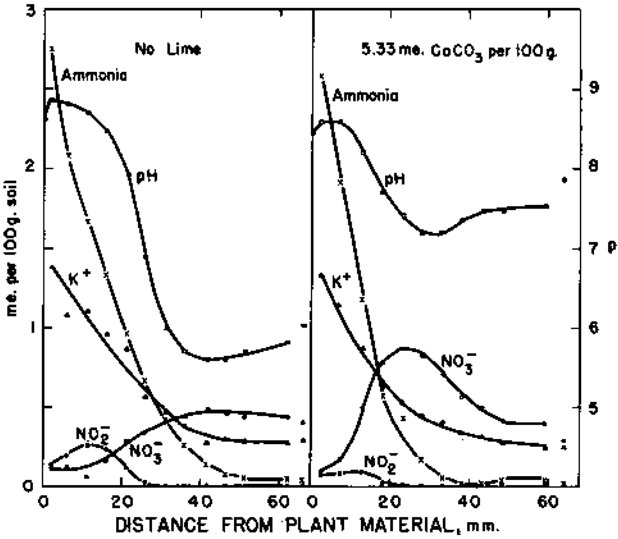

Fig. 2—The distribution of ions and nitrification away from a layer of decomposing plant material in contact with soil as influenced by lime. (The unconnected points beyond the ends of the curves are for control samples.)

Nitrification, as shown in Fig. 4, proceeded rapidly and did not appear to be appreciably inhibited in the soil on the air space side, although some NO_2^- accumulated. There was some inhibition of nitrification in the soil contacting the plant material and a slightly higher NO_2^- content was found there. The nitrification rates in both cases were the most rapid of any of the treatments; on the air space side NO_3^- reached 1.6 meq/100 g of soil, but was much lower in the soil contacting the plant material. It is especially interesting to note that more N moved across the air space into the soil than into the soil contacting the plant material layer. When the soil was separated from the plant material by an air space on each side as shown in Fig. 1-D, the ion concentration gradients were almost identical to those shown on the air space side of Fig. 4.

DISCUSSION

Concentrations of ammonia, NO_2^-, NO_3^-, K^+, and H^+ found in soil at various distances from a layer of decomposing leguminous plant material were determined after 16 days' incubation and describe the situation at that time only. Nevertheless, these results, obtained at only one sampling time, can be used to predict the development of the ion concentration gradients because of the systematic order of the reactions involved. At zero time there would be little, if any, ammonia, NO_2^-, or NO_3^-, and K^+ and pH would be constant with distance from the decomposing plant material layer. At some time later, the maximum concentration gradients would be found. Under the experimental conditions used in this study, maximum gradient development was probably reached about the time of sampling.

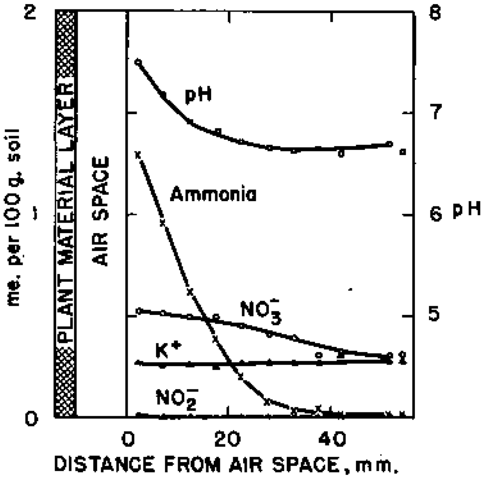

Fig. 3—The distribution of ions and nitrification in soil separated from a layer of decomposing plant material by an air space. (The unconnected points beyond the ends of the curves are for control samples.)

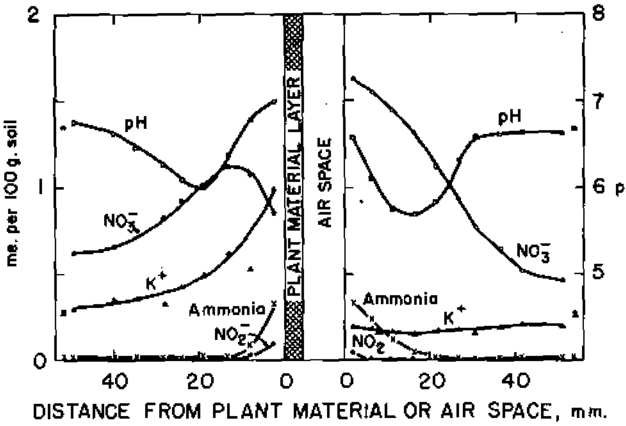

Fig. 4—The distribution of ions and nitrification in soil in contact with a layer of decomposing plant material and in soil separated from the same layer by an air space. (The unconnected points beyond the ends of the curves are for control samples.)

Ammonia released during the decomposition of plant material in soil is usually nitrified rather rapidly. The oxidation steps, NH_3 to NO_2^- to NO_3^- can be inhibited by very high concentrations of nonionized NH_3. The oxidation of NO_2^- to NO_3^-, however, appears to be the most sensitive; in fact, NH_3 has been reported to be specifically toxic to *Nitrobacter,* the organism that performs this step (1). The toxicity of ammonia is largely pH dependent because the proportion of the total ammonia in an aqueous system that exists as NH_3 depends on the pH (10).

The curves in Fig. 2 show that there was a toxic zone, in which nitrification was inhibited, apparently by NH_3, near the layers of decomposing plant material. The ammonia concentration was high, NO_3^- concentration was low, and NO_2^- accumulated. This zone of NO_2^- accumulation extended about 2 cm from the plant material. At greater distances nitrification was apparently not inhibited by NH_3. Beyond the zone of inhibition, the liming treatment stimulated nitrification. However, when $Ca(OH)_2$ equivalent to the CEC of the soil was applied, nitrification was completely inhibited; that is, neither NO_2^- nor NO_3^- accumulated. In this case the pH of the soil was much higher than in the $CaCO_3$-treated soil.

The data in Fig. 2 support the hypothesis made in a previous paper (8) concerning the effect of CEC on the toxicity of ammonia from decomposing particles of plant material in soil. The presence of extensive toxic zones associated with ammonia released from decomposing layers of plant material make it reasonable to assume that toxic zones may also exist around individual particles of decomposing plant material in soil. Under certain conditions, when the particles are close together or the exchange capacity of the soil is low, the toxic zones may overlap and eliminate nitrification.

The ion gradients can be modified by the extent of contact between the plant material and the soil. When air spaces exist between the plant material and the soil, NH_3 can diffuse across, but the nongaseous ions arising from decomposition can not. This segregation of decomposition products can affect the toxicity patterns in soil. In Fig. 3, ammonia concentration in the soil was highest near the air space and decreased rapidly with distance. The air space prevented the diffusion of nongaseous ions and resulted in their accumulation in the layer of plant material. The accumulation of these nongaseous products may have contributed to the decreased decomposition of the plant material. When the plant material contacted both soil and an air space, decomposition was much greater than it was without soil contact, presumably because the nongaseous ions diffused from the plant material into the soil.

The distribution of ions away from a decomposing layer of plant material illustrates the drastic chemical changes that can occur when layers of plant material decompose in soil. For example, in the no-lime treatment the pH varied with distance from the plant material layer from 8.9 to 5.6. This alone would change the relative proportions of NH_3 in solution from almost 50% of the total ammonia to $< 0.1\%$ (8, 10) and could thereby change an extremely toxic condition near the plant material layer to a nontoxic condition at a greater distance. The same pH change could also markedly alter the availability of essential plant nutrients. Although such pH changes are transitory, they may be especially important in terms of minor element availability because the changes occur in an environment where complexing substances are available.

The approach used in these experiments where plant material was placed in a single layer reveals a heterogeneity that would not be measured by making similar analyses of soil with which the plant material was thoroughly mixed. The influence of the plant material layer extended as far as 5 cm into the soil and was modified by the degree of soil contact with the layer. The results imply that there can be a local zone adjacent to layers of leguminous residues plowed into the soil in which conditions are toxic to nitrification and possibly even to plant roots. Whether these zones are agriculturally important or not depends on the physical distribution of the plant material in the soil as well as the amount and N content of the material.

LITERATURE CITED

1. Aleem, M. I. H., and Alexander, M. 1960. Nutrition and physiology of *Nitrobacter agilis.* Appl. Microbiol. 8:80–84.
2. Bremner, J. M., and Shaw, K. 1955. Determination of ammonia and nitrate in soil. J. Agr. Sci. 46(3):320–328.
3. Broadbent, F. E., Tyler, K. B., and Hill, G. N. 1957. Nitrification of ammoniacal fertilizers in some California soils. Hilgardia 27:247–267.
4. Chapman, H. D., and Liebig, G. F., Jr. 1952. Field and laboratory studies of nitrite accumulation in soils. Soil Sci. Soc. Amer. Proc. 16:267–282.
5. Fuller, W. H., Martin, W. P., and McGeorge, W. T. 1950. Behavior of nitrogenous fertilizers in alkaline calcareous soils. II. Field experiments with organic and inorganic nitrogenous compounds. Ariz. Agr. Exp. Sta. Tech. Bull. No. 121.: 471-500.
6. McCalla, T. M., and Haskins, F. A. 1964. Phytotoxic substances from soil microorganisms and crop residues. Bacteriol. Rev. 28(2):181–207.
7. Rider, B. F., and Melon, M. G. 1946. Colorimetric determination of nitrites. J. Ind. Eng. Chem. 18(2):96–99.
8. Smith, J. H. 1964. Relationships between cation-exchange capacity and the toxicity of ammonia to the nitrification process. Soil Sci. Soc. Amer. Proc. 28:640–644.
9. Stojanovic, B. J., and Alexander, M. 1958. Effect of inorganic nitrogen on nitrification. Soil Sci. 86:208–215.
10. Warren, K. S. 1962. Ammonia toxicity and pH. Nature 195: 47–49.