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ROLE OF TRANSITION METALS IN  
NITRITE DECOMPOSITION IN SOIL

by

J. S. Bajwa

A thesis submitted in partial fulfillment  
of the requirements for the degree

of

MASTER OF SCIENCE

in

Soils and Meteorology

Approved:

UTAH STATE UNIVERSITY  
Logan, Utah

1971

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Finally, I express my appreciation to my wife, Amarjit for her encouragement to pursue my higher studies in the United States.

*J. S. Bajwa*  
J. S. Bajwa

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ABSTRACT

Role of Transition Metals in Nitrite Decomposition in Soils

by

J. S. Bajwa, Master of Science

Utah State University, 1971

Major Professor: Dr. R. L. Smith  
Department: Soils and Meteorology

Iron and copper increased the decomposition of nitrite significantly during the first two hours of reaction when 150 parts per million (ppm) of nitrite nitrogen was added to an acidic soil. Manganese was found to have a slight effect. There was no additional effect of the added metals after two hours reaction time.

The higher concentration of metals was not effective in catalyzing the decomposition of the added nitrite nitrogen. All the added nitrite nitrogen was not recovered and the deficit could be due to the formation of nitrogen gas.

(52 pages)

## INTRODUCTION

An appreciable loss of soil nitrogen occurs through the process of denitrification. Although most workers have assumed this process is biological, it may in fact be strictly chemical in some instances. Nitrite ion ( $\text{NO}_2^-$ ) is considered to be the seat of a number of chemical reactions which leads to the loss of nitrogen. Nitrites may be accumulated in the soils for a temporary period as transitory intermediates of the process of nitrification and denitrification. Nitrogen deficits ranging up to 55 percent of the nitrogen applied have been reported from acid soils which accumulate nitrite (Clark, Beard, and Smith, 1960; Hauck and Stephenson, 1965).

The decomposition of nitrite in acid soils to various end products like nitrate nitrogen ( $\text{NO}_3^-$ ), oxides of nitrogen ( $\text{NO}$  and  $\text{NO}_2$ ), and elemental nitrogen ( $\text{N}_2$ ) has been confirmed by several workers (Reuss and Smith, 1965; Kuratti, 1969; and Rashid, 1966). Several mechanisms have been proposed to account for the possible loss of nitrogen from nitrite in the soil.

Wullstein and Gilmour (1964) postulated that metallic cations play an important role in nitrite decomposition in soils and this theory has received considerable attention in recent discussions of the mechanisms of nitrite decomposition and chemodenitrification in soils (Broadbent and Clark, 1965; Allison, 1966; Wullstein, 1967; Hauck, 1968; Woldendorp, 1968). The experimental basis for this theory was work indicating that extraction of kaolinite and an Oregon soil with



1 M NaCl reduced the amount of nitric oxide (NO) formed when these materials were treated with nitrite under mildly acidic conditions and that 1M NaCl extracts of these materials contain metal ions that promoted  $\text{NO}_2^-$  decomposition. Chao and Kroontje (1963) also found that NO was formed by reaction of ferrous iron ( $\text{Fe}^{++}$ ) with  $\text{NO}_2^-$  under acidic conditions but they were unable to detect the formation of any  $\text{N}_2$  in this reaction.

Chao and Bartholomew (1964) studied the reaction of  $\text{NO}_2^-$  with Al-saturated bentonite under acidic conditions and were unable to detect the formation of either NO or  $\text{N}_2$  in this reaction.

Recently Nelson and Bremner (1970) indicated that soil minerals and metallic cations do not promote chemical decomposition of  $\text{NO}_2^-$  in soils and do not play a significant role in the processes leading to gaseous loss of nitrogen through chemodenitrification.

The work reported here was undertaken to study the role of transition metals like copper, manganese, and iron on the chemical decomposition of nitrite resulting in the loss of nitrogen.

## REVIEW OF LITERATURE

Nitrites may accumulate in the soils for a temporary period as transitory intermediates of the process of nitrification and denitrification. Recent work has provided indirect evidence that significant gaseous losses of nitrogen occur through chemodenitrification, i.e., chemical decomposition of nitrite accumulated in the soil. In view of the importance of nitrite in connection with possible nitrogen losses, it is considered necessary to find out under what conditions does nitrite accumulation take place in soils.

Factors Influencing Nitrite AccumulationSoil pH

Soil pH is considered to be the most important factor governing the accumulation of nitrite. Under alkaline soil conditions greater nitrite accumulation takes place than in acid soils. Kelley (1916) found large quantities of  $\text{NO}_2^-$  when small amounts of sodium carbonates were incorporated with soils to which dried blood or ammonium sulphate was added. In some cases the nitrite content greatly exceeded the nitrate content. He noted distinct increase in nitrite content and suppression in nitrate formation with the addition of the alkali salts. Robinson (1923) reported rapid loss of nitrite in all acid soils without any nitrate formation. He observed longer retention of nitrite when calcium carbonate was incorporated into an acid soil receiving sodium nitrite.

Midgley (1932), in his studies of nitrification in heavily limed soils, noticed nitrite accumulation sixteen times greater than in the

same soils receiving light doses of lime. Albrecht and McCalla (1937) also found that soils with lime had seven times more nitrite than soils receiving no lime. Similar results have been reported by Fraps and Sterges (1939).

Martin, Buehrer, and Caster (1942) made a comparative study of nitrification of ammonium sulphate and urea in six typical Arizona desert soils. They observed an accumulation of nitrite in well aerated alkaline soils and concluded that alkaline pH hindered the nitrite oxidation phase of nitrification until other natural (biological) processes reduce the pH value to a point where nitrite oxidation could take place. In case the pH was not lowered, the formation of nitrites was greatly retarded. There are evidences, however, to show that nitrification occurs at much higher pH values, though at slower rates, and the threshold pH of  $7.7 \pm 0.2$  suggested by them is not of much importance.

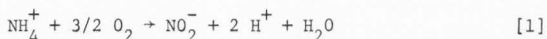
Chapman and Liebig (1952) found substantial amounts of nitrite accumulation following the application of urea, anhydrous ammonia, ammonium or other ammonia-forming fertilizers to neutral or alkaline soils under both field and laboratory conditions. From this observation they concluded that in neutral and alkaline soils of the arid and semi-arid regions heavy applications of ammonia and ammonia-forming fertilizers are likely to lead to nitrite accumulation. Nitrites may persist or disappear depending upon the resistance of the soil to pH changes.

Wahhab and Uddin (1954) reported accumulation and persistence of large quantities of nitrite in soils of Punjab with pH 8.0 to 8.3 that had been fertilized with ammonium sulphate. Duisberg and Buehrer (1954), Martin and Cox (1956), Broadbent, Tyler, and Hill (1958), and Stojanovic

and Alexander (1958) found high accumulation of nitrite in alkaline soils treated with large quantities of ammonium hydroxide, ammonium sulphate, and ammonium nitrate.

From the foregoing discussions it is clear that alkaline soil conditions favor large accumulations of nitrite. Soil reaction seems to influence nitrite accumulation directly and indirectly.

Nitrification takes place in two stages, each stage being brought about by a different set of organisms. In the first stage, the nitrite bacteria, *Nitrosomonas*, convert ammonium ion to nitrate.



In the second stage, nitrate bacteria, *Nitrobacter*, convert nitrite to nitrate.



Kelley (1916) and Martin, Buehrer, and Caster (1942) were of the view that alkaline conditions are not conducive to the activity of *Nitrobacter* whereas they do not affect *Nitrosomonas*.

Lees and Quastel (1946) reported that high concentrations of ammonium ion inhibit the growth and metabolism of *Nitrobacter* and hence the oxidation of nitrite. It was further pointed out that the degree of inhibition increases as the pH of the medium increases. This may be because at pH greater than 7.0, the free ammonia concentration, known to be injurious to the cells in general, rises sharply. Broadbent, Tyler, and Hill (1957) and Stojanovic and Alexander (1958) have supported this viewpoint suggesting that at high pH, free ammonia is present in the soil in large quantities and this free ammonia is selective as an

inhibitor of the *Nitrobacter* species. Aleem and Alexander (1960) have also suggested a selective inhibitory effect of free ammonia on *Nitrobacter agilis*. Under similar conditions they have noticed only slight inhibition in the activity of *Nitrosomonas*.

Acid soil conditions do not favor the accumulation of nitrite. The inhibitory effects do not exist under these conditions and hence the biological oxidation of nitrite to nitrate is rapid. In addition, under acid soil conditions, the accumulated nitrite may rapidly decompose, resulting in a loss of nitrogen. There are, however, some instances to show that nitrite may accumulate even under acidic conditions. Wagner and Smith (1958) reported that a soil having an initial pH of 5.6, treated with 500 ppm N as urea, accumulated nitrite to the extent of 94 ppm after two weeks. Patil (1963) has reported large accumulation of nitrite in acid Walla Walla soil (pH 6.5) when treated with 1000 ppm N as urea. With the application of urea, the pH shifted to alkaline condition.

#### Nitrogen fertilizers

It is pointed out in the foregoing discussion that ammonia is probably toxic to *Nitrobacter* at higher pH values, and, as such, applications of ammonia or ammonia-yielding fertilizers give rise to large amounts of nitrite accumulation.

#### Organic matter

Smith and Burns (1965) reported higher nitrite accumulation in regions of active organic matter decomposition.

### Soil temperature

*Nitrobacter* organisms are sensitive to soil temperature; their function seems to be inhibited at both the extremes. *Nitrosomonas* on the other hand are susceptible to fluctuations. Chapman and Liebig (1952) stated that nitrites would likely persist for several months if the temperature is not conducive to the activity of *Nitrobacter*. Tyler and Broadbent (1960) reported that *Nitrobacter* are sensitive to low temperature. Justice and Smith (1962) have found high accumulation of nitrite both at high and low temperatures.

### Chemical Decomposition of Nitrite

In the foregoing discussions, ample evidence has been presented to show that nitrite may accumulate as transitory intermediate of the process of nitrification. The nitrite ions are not stable in acid soils and undergo rapid transformations giving rise to various end products like nitrate nitrogen, oxides of nitrogen, and elemental nitrogen. In recent years, evidence has been shown regarding losses of nitrogen arising due to nitrite reactivity. There is good agreement among workers that acid soil conditions aggravate the problem but considerable disagreement exists with regard to the mechanism and end products of the various possible nitrite reactions. The various mechanisms are discussed under the following groupings.

1. Self decomposition of nitrite under acid conditions.
2. Reactions with organic matter.
3. Reactions involving hyponitrous acid.

Self decomposition of nitrite  
under acid conditions

The spontaneous or self decomposition of nitrite under acid soil conditions, resulting in the possible loss of nitrogen, is one of the accepted mechanisms. Temple (1914) was probably the first person to suggest the possibility of self decomposition of nitrous acid ( $\text{HNO}_2$ ) when he added sodium nitrite ( $\text{NaNO}_2$ ) to either an acid soil or an acidic solution. He proposed the following possible pathway of nitrite decomposition



Summing up the above equations



Robinson (1923) noticed a rapid loss of nitrite from acid soils with the addition of  $\text{NaNO}_2$ . Such loss was considered to be greater in acid soils than in neutral or alkaline soils. The loss of nitrogen was attributed to the instability of nitrous acid formed in acid soils as



Nitrous acid is very unstable and escapes rapidly after decomposition depending on the degree of acidity.

Fraps and Sterges (1939) added 100 ppm of nitrite nitrogen to acidic soils that ranged in pH from 4.4 to 6.9. They observed a loss of 10 to 95 ppm over an 8-day period. They were of the opinion that the loss had occurred through the formation of nitrogen oxides according to Equation [6].

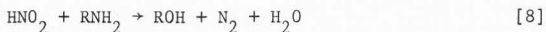
Wagner and Smith (1958) studied the various forms in which added nitrogen could be lost from acid soils. The oxides of nitrogen were found to be produced during the decomposition of nitrite.

Tyler and Broadbent (1960), using sterile and non-sterile soils, found no more than trace amounts of the oxides of nitrogen when nitrite was added to acid soils. Thorne (1961) studied the decomposition of nitrous acid in solution media. Equation [6] was believed to explain most of his results.

Reuss and Smith (1965), while studying the reaction of nitrite in acid media, concluded that nitric oxide and nitrogen dioxide (NO and NO<sub>2</sub>) were the products of decomposition. They further concluded that the evolution of these oxides in the absence of adequate moisture may lead to considerable losses of added nitrogen.

Reactions of nitrite  
with organic matter

The Van Slyke type reaction, which involves NO<sub>2</sub><sup>-</sup> or nitrous acid in acid media, has been extensively studied in attempts to explain losses of gaseous nitrogen compounds from acid soils.



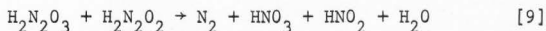


Most notable among those who favor the occurrence of the Van Slyke type of reaction in soils are Gerretsen and De Hoop (1957). They observed nitrogen losses up to 74 percent of added ammonium sulphate which were attributed to the reaction of ammonium sulphate with nitrite. They suggested that during the process of microbial decay of organic matter a great variety of amino acids are produced in the soil which can react with  $\text{HNO}_2$  resulting in the loss of nitrogen.

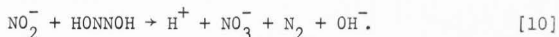
Allison and Doetsch (1951) did not find any reaction of amino acids or ammonia with nitrite to form nitrogen gas in dilute solutions under conditions commonly occurring in nature. Other workers (Jones, 1951, and Smith and Clark, 1960) are also of the view that Van Slyke type of reaction is of minor importance in soils. Allison (1963) has suggested that the Van Slyke reaction cannot be legitimately generalized to include the reaction of  $\text{HNO}_2$  with compounds such as urea or  $\text{NH}_4^+$  and that it is applicable only to compounds containing  $\alpha$  amino groups. A reaction, comparable to the Van Slyke reaction, occurs between  $\text{NO}_2^-$  or  $\text{HNO}_2$  and either  $\text{NH}_4^+$  or urea, however, and in all cases results in the formation of  $\text{N}_2$ .

#### Reactions of nitrite with hyponitrous acid

Thorne (1961) has postulated hyponitrous and hyponitric acids as intermediates during nitrous acid decomposition. The reaction between hyponitrous acid and hyponitric acid is supposed to give rise to elemental nitrogen.



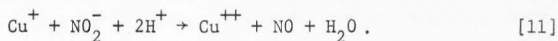
Buchholz (1963) has presented evidence to show that by adding sodium nitrite to acidified solution of hyponitrous acid, nitrogen and nitrate, small amounts of nitric oxide and nitrous oxide evolve. He has proposed the following reaction



Nitric oxide and nitrous oxide may be the product of decomposition of nitrous acid and hyponitrous acid ( $\text{H}_2\text{N}_2\text{O}_2$ ), respectively.

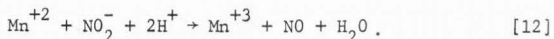
#### Role of transition metals

Yost and Russel (1944) suggested that cuprous ion ( $\text{Cu}^+$ ) catalyzed nitrite decomposition to nitric oxide according to the following equation



Wullstein and Gilmour (1964) postulated that metallic cations play an important role in nitrite decomposition in soils and this theory has received considerable attention in recent discussions of nitrite decomposition and chemodenitrification in soils. The experimental basis for this theory was work indicating that extracting of kaolinite and an Oregon soil with 1 M NaCl reduced the amount of nitric oxide formed from these materials which were treated with nitrite under mildly acidic conditions and the M NaCl extracts of these materials contained metal ions that promoted nitrite decomposition. They concluded that copper ions ( $\text{Cu}^+$ ) in the kaolinite extract and manganese ions ( $\text{Mn}^{++}$ ) in the soil extract were primarily responsible for the observed effects of nitrite

decomposition. They also reported that the solution studies demonstrate that the reduced state of the transition metals, copper, iron, and manganese and certain aluminium salts, can be quite active in promoting  $\text{NO}_2^-$  loss. They postulated that these metal ions can reduce  $\text{NO}_2^-$  to NO as indicated by the following equation



More recently, Wullstein and Gilmour (1966) reported that both nitrogen and nitric oxide are formed by reaction of  $\text{Fe}^{+2}$  with nitrite under acidic conditions in a helium atmosphere. They concluded that this reaction may be an important mechanism of nitrogen loss from soils under conditions that promote microbial reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$ .

Sneed and Brasted (1956) established that acidic conditions generally favor the reduced state of transition like metals which is more active than the oxidized form with respect of nitric oxide formation.

Cotton and Wilkinson (1966) indicated that nitrite ion and nitric oxide are reactive with metal solutions and commonly form complexes with them such as  $[\text{Fe NO}(\text{H}_2\text{O}_5)]^{++}$  formed from nitric oxide and aqueous ferrous sulphate. These complexes may be stable or reactive depending upon the condition of the total system.

Chao and Bartholomew (1964) found that Al saturated bentonite and ferrous iron influenced the transformation of nitrite and the reaction rates were directly proportional to the concentration of aluminium and ferrous ions. They were able to recover the theoretical quantity of NO by aeration but with Al bentonite no NO or  $\text{NO}_2$  was removed by aeration.

In case of iron partial recovery of NO was affected, as a nitric oxide--ferrous iron complex may have been formed.

Chao and Kroontje (1963) also found that nitric oxide was formed by reaction of ferrous ions with nitrite under acidic conditions.

Mortland (1965) found that nitric oxide was chemically adsorbed on montmorillonite and nontronite in the absence of air when exchange complexes of these minerals were saturated with certain transition metal ions and that  $N_2O$  was formed when NO was adsorbed by  $Fe^{+++}$  saturated nontronite.

Recently, Nelson and Bremner (1970) pointed out that soil mineral and metallic cations do not promote chemical decomposition of  $NO_2^-$  in soils and do not play a significant role in the process leading to gaseous loss of nitrogen through chemodenitrification. Of the various metallic cations tested, they found that only ferrous, cuprous, and stannous ions promote nitrite decomposition.

## MATERIALS AND METHODS

The present investigation consisted of adding sodium nitrite and two different concentrations of copper, manganese, and iron to the soil and then removing all the oxides of nitrogen, by passing air through the system. The oxides of nitrogen were trapped in an alkaline permanganate solution and the nitrite nitrogen left over in the soil and nitrate nitrogen formed were determined. An air flow of 100 ml per minute was maintained throughout the experiment to sweep out the oxides of nitrogen produced and to avoid the oxidation of the nitrogen oxides to nitrate nitrogen.

Soils Used

Two acid soils, Miami silt loam and Olympic silty clay loam, were used in this study. Some of the properties of the soils used are given in Table 1.

Table 1. Some chemical and physical properties of the two soils used

Soils <sup>a</sup>	pH paste	CEC meq/100 g	Fe ppm	Cu ppm	Mn ppm	Organic matter %	Moisture Content	
							0.3 bars %	Air- dry %
Miami silt loam	5.2	11.2	525	50	153	2.0	24.0	1.26
Olympic silty clay loam	4.6	31.4	525	50	182	6.98	32.0	3.8

<sup>a</sup>The Olympic silty clay loam soil was supplied by Dr. T. Jackson, Department of Soils, Oregon State University. The Miami silt loam was supplied by Dr. R. B. Clark, Ohio State Experiment Station, Wooster.

### Metals Used

Three metals, copper, manganese, and iron were used in the form of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , respectively. Two different concentrations, 1000 ppm and 2000 ppm, were used for the investigation.

### Preparation of Soil

Soils, taken from a depth of six inches, were air-dried, ground, passed through a 200 mesh sieve, and stored in air-tight bins.

Fifty grams of oven dry soil was put in 250 cc Erlenmeyer flask. An appropriate amount of water was added (taking into consideration the amount of water added while adding the sodium nitrite and the metal solution) to bring the soil to one-third bar moisture tension. Five ml of the metal solution of appropriate concentration and 5 ml of the sodium nitrite solution was then added. The flasks were corked tightly and the air flow regulated to 100 ml per minute. The oxides of nitrogen produced were trapped in the alkaline permanganate solutions for two, four, and eight hours from the start of the experiment.

### Apparatus Used

Air from the line was controlled by a one-stage pressure regulator and measured in a rotometer. A safety valve system was introduced in order to permit the excess air to escape. The safety valve consisted of the vertical arm of the "T" tapering down dipped into water contained in a 1000 ml cylinder. The air, regulated at 100 ml per minute, was saturated with moisture by bubbling it through water contained in an

Erlenmeyer flask. The moisture-saturated air was then directed to the reaction flask which consisted of a 200 ml Erlenmeyer flask.

Three tubes containing the alkaline permanganate were connected in series with the reaction vessel. The air carrying the nitrogen oxides was forced through the alkaline permanganate tubes. All the connections were air-tight.

#### Analysis of the Different Forms of Nitrogen

##### Nitrate and nitrite in soil

About 100 ml of 2 normal KCl solution was added to the reaction flask after the end of the experiment. The reaction flask was shaken for about five minutes on a mechanical shaker and allowed to stand for about 20 minutes. The solution was removed by filtration with the help of suction pump into a 250 ml Erlenmeyer flask. The total volume was 250 ml in order to insure the complete extraction of the nitrite. Five ml of the extract was taken to determine the nitrite nitrogen by the method described by Shinn (1941), employing a diazo coupling of sulfanilic acid (N-(1-naphthyl)-ethylenediamine dihydrochloride) as a coupling reagent. A standard phenol disulfonic acid method, similar to that of Jackson (1958), was used to determine nitrate after destroying nitrite with sulfamic acid. The complete analytical procedures are included in the Appendix.

##### Oxides of nitrogen

The alkaline permanganate solution (20 ml) held in each of the tubes was used to trap the nitric oxide and nitrogen dioxide gases swept out of the system during the course of the reaction. The

permanganate solutions were analyzed at the end of each reaction period. The solution was washed into beakers and the excess potassium permanganate solution destroyed by adding about 20 ml oxalic acid ( $0.6 \text{ M Na}_2\text{C}_2\text{O}_4$  in  $7 \text{ N H}_2\text{SO}_4$ ). The solution was made alkaline by adding  $5 \text{ N}$  sodium hydroxide and then digested on a hot plate for about 30 minutes. After filtering, the manganous hydroxide precipitate on the filter paper was washed several times with hot distilled water and the volume made up to 250 ml. Aliquots from this filtrate were analyzed for nitrate by the phenol disulfonic acid method. The method was calibrated by adding known amounts of potassium nitrate to the alkaline permanganate trapping solution. Calibration curves, using either sodium nitrite or potassium nitrate, were identical. The complete procedure is included in the Appendix.



## EXPERIMENTAL RESULTS AND DISCUSSION

Results

The amount of the nitrogen that was found in the permanganate trapping solution when the nitrogen (150 ppm N) was allowed to react in the two soils with various levels of added metals is found in Table 2. The amount remaining in the soil is given in Table 3. The data are graphed in Figures 1 through 6.

Table 2. Amount of NO + NO<sub>2</sub> evolved at various reaction periods when 50 g of soil was treated with 150 ppm NO<sub>2</sub>-N

Soil	NO + NO <sub>2</sub> evolved		
	2 hours	4 hours	8 hours
	ppm		
Miami only	28	17	10
+ 1000 ppm Fe	52 <sup>a</sup>	15	13
+ 2000 ppm Fe	73 <sup>a</sup>	13	13
+ 1000 ppm Mn	34	12	17
+ 2000 ppm Mn	32	15	16
+ 1000 ppm Cu	46 <sup>a</sup>	15	16
+ 2000 ppm Cu	44 <sup>a</sup>	15	13
Olympic only	25	15	10
+ 1000 ppm Fe	60 <sup>a</sup>	17	15
+ 2000 ppm Fe	61 <sup>a</sup>	15	10
+ 1000 ppm Mn	28	17	20
+ 2000 ppm Mn	28	21	18
+ 1000 ppm Cu	41 <sup>a</sup>	13	17
+ 2000 ppm Cu	41 <sup>a</sup>	13	15

<sup>a</sup>Significant from the check by Least Significant Difference (LSD) test at .01 level

Table 3. Amount of various forms of nitrogen found after an 8-hour reaction period when 50 g of soil was treated with 150 ppm  $\text{NO}_2^-$ -N

Soil	$\text{NO} + \text{NO}_2$ evolved	$\text{NO}_2^-$ -N in soil	$\text{NO}_3^-$ -N in soil	Total
Miami only	55	63	4	122
+ 1000 ppm Fe	80	15	5	100
+ 2000 ppm Fe	99	0	5	104
+ 1000 ppm Mn	63	40	5	108
+ 2000 ppm Mn	63	40	5	108
+ 1000 ppm Cu	77	25	5	107
+ 2000 ppm Cu	72	28	5	105
Olympic only	50	60	5	115
+ 1000 ppm Fe	92	10	5	107
+ 2000 ppm Fe	86	8	5	99
+ 1000 ppm Mn	65	35	5	105
+ 2000 ppm Mn	67	35	5	107
+ 1000 ppm Cu	71	30	5	106
+ 2000 ppm Cu	69	30	5	104

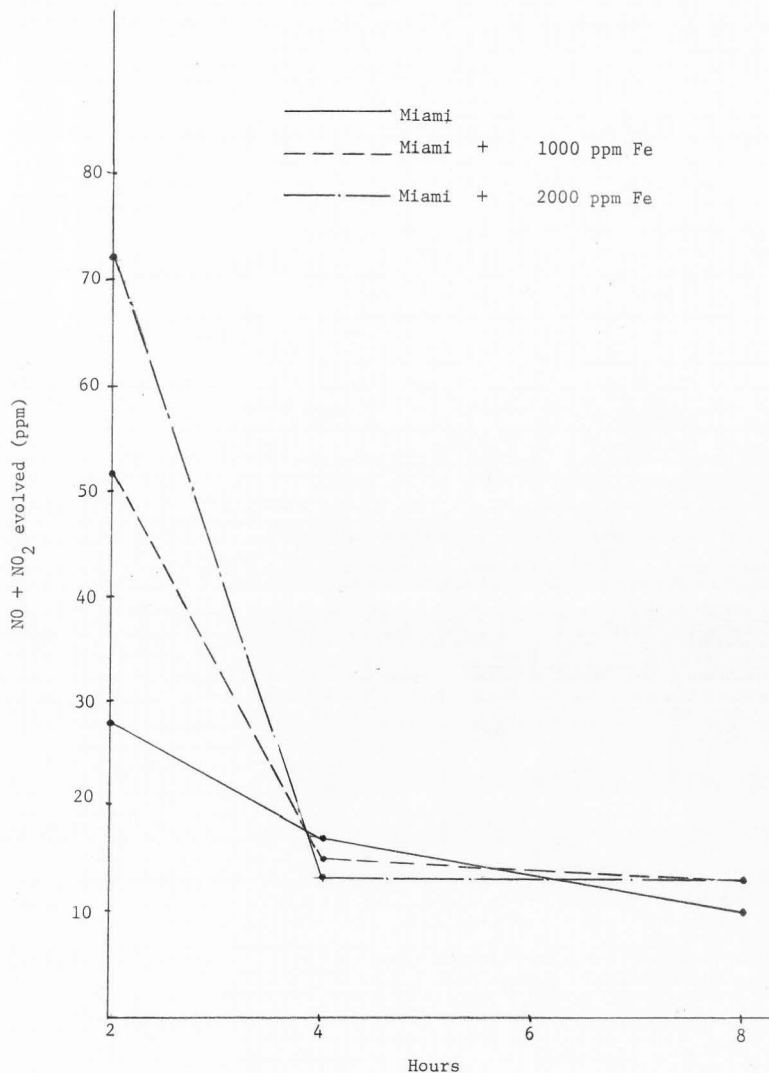


Figure 1. Comparison of NO + NO<sub>2</sub> evolved at various time periods in Miami soil with and without the addition of iron (Fe<sup>++</sup>), treated with 150 ppm NO<sub>2</sub>-N.

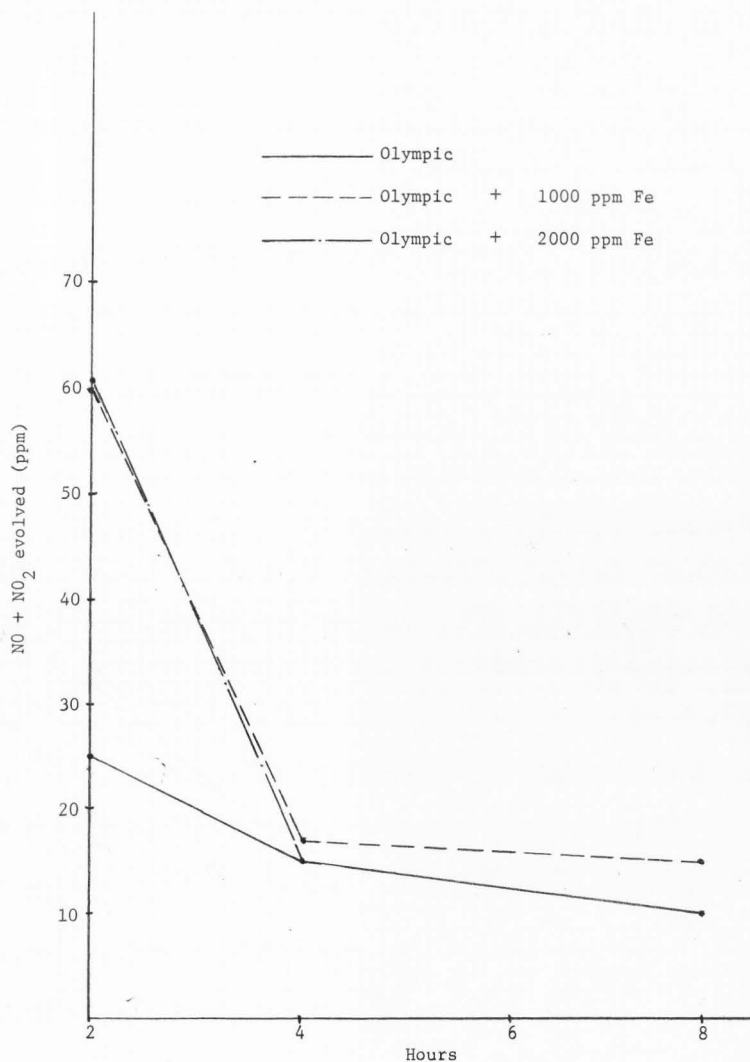


Figure 2. Comparison of NO + NO<sub>2</sub> evolved at various time periods in Olympic soil with and without the addition of iron (Fe<sup>++</sup>), treated with 150 ppm NO<sub>2</sub><sup>-</sup>-N.

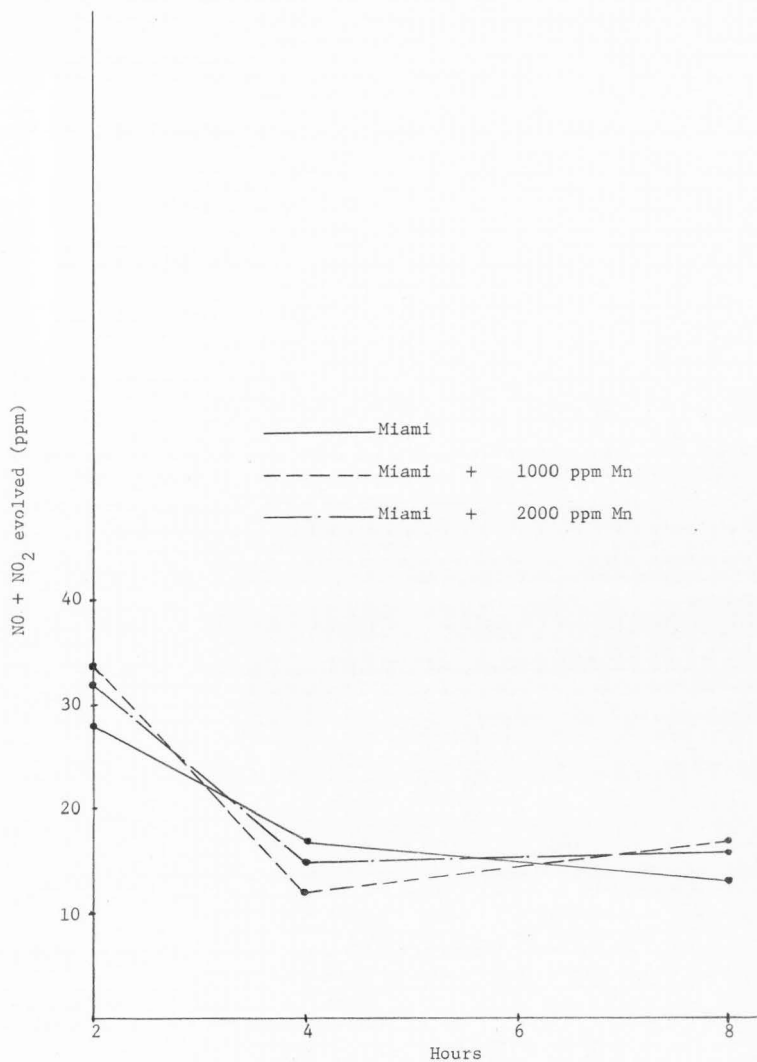


Figure 3. Comparison of  $\text{NO} + \text{NO}_2$  evolved at various time periods in Miami soil, with and without the addition of manganese ( $\text{Mn}^{++}$ ), treated with  $150 \text{ ppm NO}_2^- \text{-N}$ .

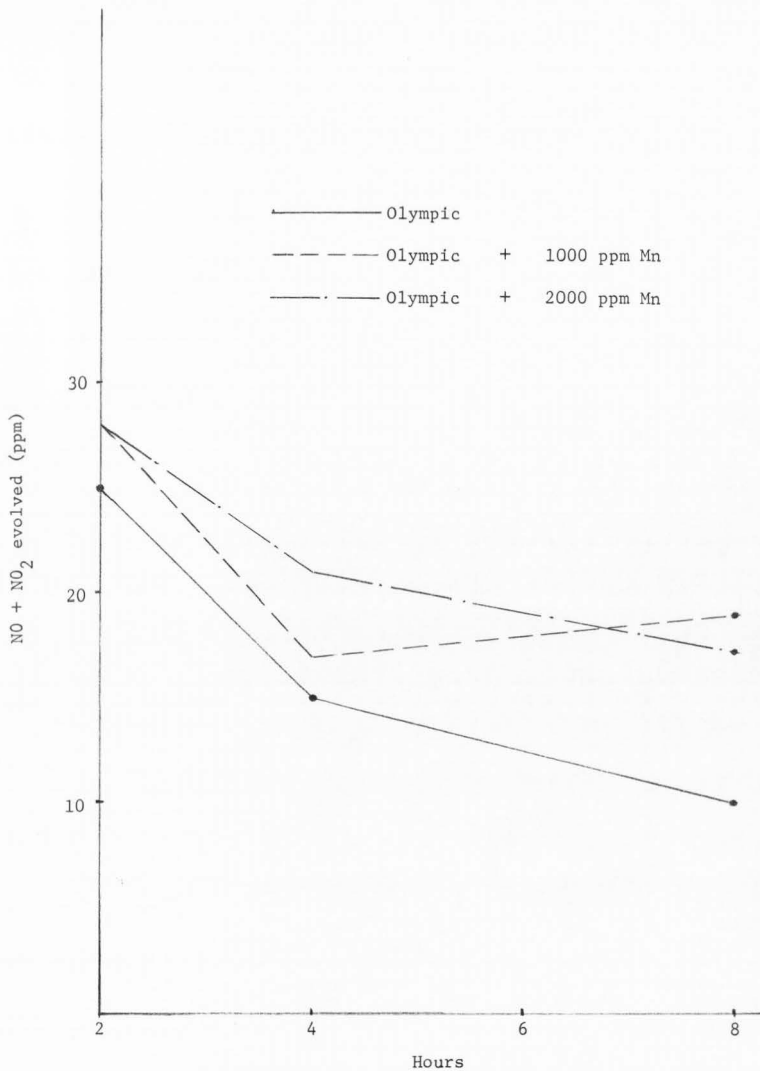


Figure 4. Comparison of NO + NO<sub>2</sub> evolved at various time periods in Olympic soil, with and without the addition of manganese (Mn<sup>++</sup>) treated with 150 ppm NO<sub>2</sub><sup>-</sup>-N.

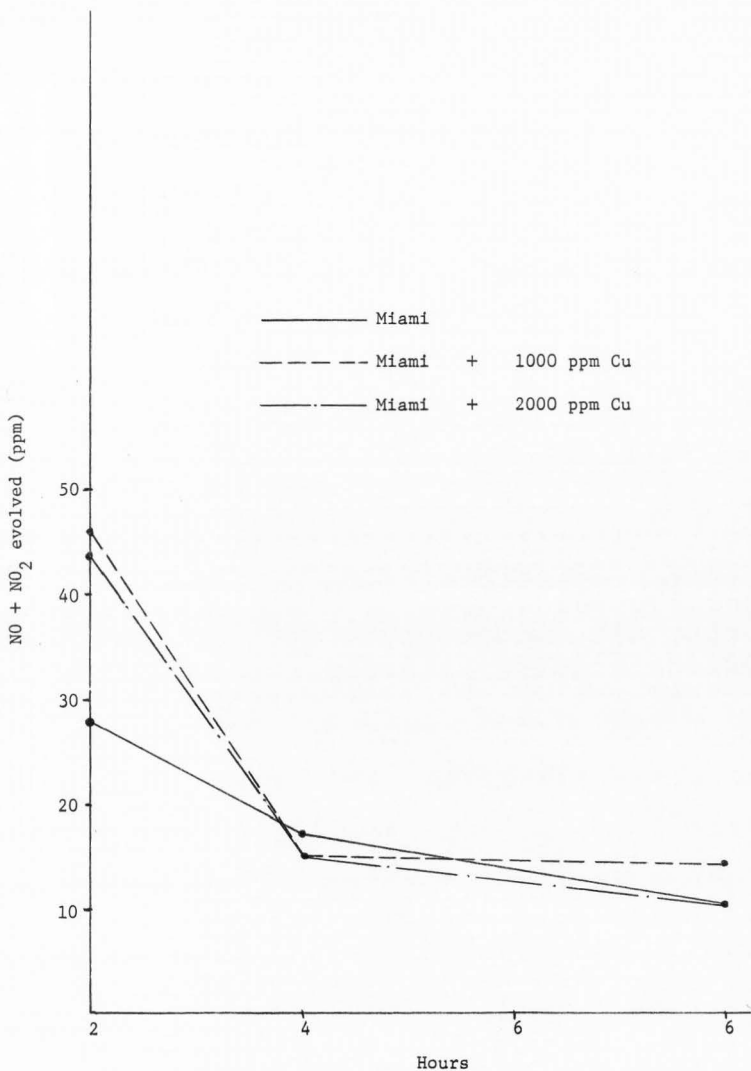


Figure 5. Comparison of NO + NO<sub>2</sub> evolved at various time periods in Miami soil with and without the addition of copper (Cu<sup>++</sup>) treated with 150 ppm NO<sub>2</sub><sup>-</sup>-N.

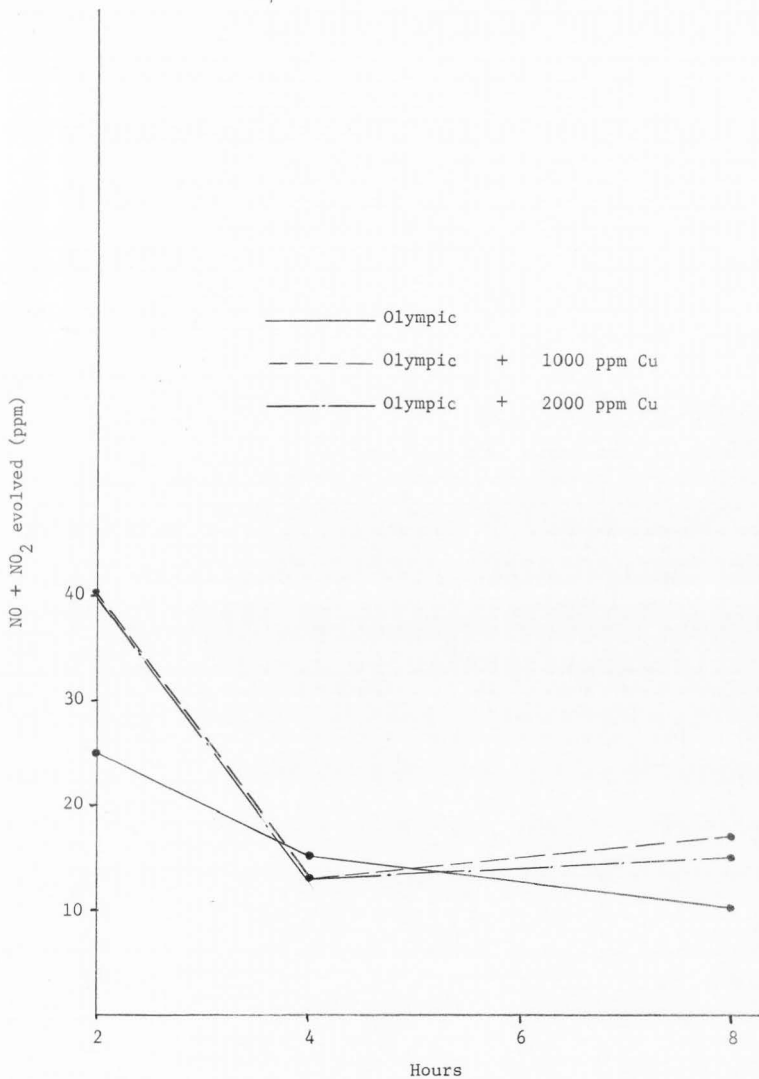


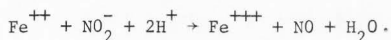
Figure 6. Comparison of NO + NO<sub>2</sub> evolved at various time periods in Olympic soil with and without the addition of copper (Cu<sup>++</sup>) treated with 150 ppm NO<sub>2</sub>-N.



## Discussion

### Role of iron

It is evident from Figures 1 and 2 that iron at both levels (1000 and 2000 ppm) promoted the chemical decomposition of nitrite during the first two hours of reaction. Although it did not have any effect in the later stages of reaction, the reaction of nitrite with metal seemed to be active immediately after the addition of the metal. In case of Miami soil, after two hours of reaction, 1000 ppm of Fe produced 52 ppm of  $\text{NO} + \text{NO}_2$  as compared to 28 ppm  $\text{NO} + \text{NO}_2$  in the same soil with no addition of iron, whereas 2000 ppm of Fe produced 73 ppm of the oxides of nitrogen. The amount of  $\text{NO} + \text{NO}_2$  are 60 and 61 ppm, at 1000 ppm and 2000 ppm of added iron, respectively, after two hours reaction time compared to 25 ppm of oxides of nitrogen with no addition of iron in Olympic soil. Iron at 2000 ppm seemed to be more effective in case of Miami soil whereas there was no significant difference between levels of iron in the case of Olympic soil. This is in agreement with Wullstein and Gilmour (1964) who postulated that iron catalyze the decomposition of nitrite according to the following equation



The metal is oxidized and nitrite is reduced to nitric oxide with the formation of water (half cell reaction). It is implied that hydrogen ions are necessary for such a reaction, so the reaction can take place only under acidic conditions. Chao and Bartholomew (1964) also found that  $\text{Al}^{+++}$  and  $\text{Fe}^{++}$  catalyze the decomposition of nitrite and the reaction rates were directly proportional to the concentration of aluminium

and iron ions. The reduced form of the metals which are active in catalyzing the decomposition of nitrite are generally favored by acidic conditions.

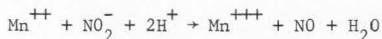
The various forms of nitrogen that were found with and without the addition of metal are presented in Table 3. In the Miami soil, the various forms of nitrogen recovered after eight hours were totalled and were found to be 100 ppm and 104 ppm at 1000 ppm and 2000 ppm of added iron level, respectively, compared to 122 ppm with no addition of iron. In the Olympic soil, the total nitrogen recovered after eight hours of reaction time was found to be 107 ppm and 99 ppm at two levels of iron compared to 115 ppm without the addition of iron. These differences of the nitrogen recovered with and without the addition of iron were found to be significant by the LSD test at .05 level. It is clear that addition of iron resulted in a greater production of the oxides of nitrogen.

The amount of nitrogen recovered in all cases was found to be less than the added amount of nitrogen (150 ppm of N as  $\text{NO}_2^-$ ). The deficit could be attributed to some loss of nitrogen in the form of nitrogen gas during the reaction, which was not measured. Wullstein and Gilmour (1966) reported that both  $\text{N}_2$  and  $\text{NO}$  are formed by reaction of  $\text{Fe}^{++}$  with nitrite under acidic conditions in a helium atmosphere. They concluded that this reaction may be an important mechanism of nitrogen loss from soils under conditions that promote microbial reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$ .

#### Role of manganese

The two levels of added manganese were reacted with the added amount of nitrite nitrogen in the soil and the results are presented in Table 2. The amount of  $\text{NO} + \text{NO}_2$  evolved at various reaction periods in the Miami

and Olympic soils are presented in Figures 3 and 4, respectively. Manganese seems to catalyze the reaction only slightly during the first two hours and did not have any significant effect after that period. The amount of  $\text{NO} + \text{NO}_2$  that was evolved was considerably less during the two hours of reaction time than was found for the same level of added iron. This may mean that manganese is not as effective in catalyzing this particular reaction as is iron. The reaction between manganese and nitrite nitrogen could be explained according to the following equation in which manganese is oxidized from two valence to three valence and nitrite is reduced to nitric oxide with the formation of water.

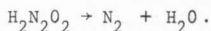


This type of reaction is favored under acidic conditions where sufficient number of hydrogen ions and the reduced form of manganese is present. Wullstein and Gilmour (1964) found manganese to catalyze the decomposition of nitrite according to the above equation.

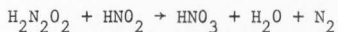
There were no differences in the amount of nitrogen recovered in the form of  $\text{NO} + \text{NO}_2$  at the two levels of added manganese in both the soils (Table 2). Also the total amount of nitrogen recovered in the various forms comes out the same at both levels of added manganese (Table 3). So the higher concentration of added manganese does not have greater effect on the decomposition of nitrite as compared to lower concentration of added manganese.

The total amount of nitrogen recovered at both levels of manganese after eight hours of reaction period differ significantly from that found for the soil without the addition of manganese. The total amount of

nitrogen recovered is less than the amount of nitrogen (150 ppm) added as nitrite nitrogen. This deficit could possibly be due to the loss of nitrogen in the gaseous form when manganese reacted with nitrite nitrogen. Gaseous loss of nitrogen was not verified during the investigation. Chao and Kroontje (1963) have suggested the formation of hyponitrous acid as an intermediate product during the course of reaction. They suggested that hyponitrous acid may decompose according to the following reaction



Hyponitrous acid may also react with nitrous acid resulting in the formation of nitrogen gas.

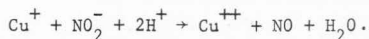


#### Role of copper

The results of the reaction between added copper and added nitrite nitrogen in the soils are presented in Table 2. The amount of NO + NO<sub>2</sub> evolved as a result of the reaction of nitrite nitrogen and copper at various reaction periods in Miami and Olympic soil are presented in Figures 5 and 6, respectively. Copper, like iron and manganese, also catalyzed the decomposition of nitrite during the first two hours of reaction and did not have any effect afterwards. This suggests that all these metals react with nitrite nitrogen immediately after the addition of metal.

There is no difference in the production of NO + NO<sub>2</sub> between the two levels of added copper. The production of NO + NO<sub>2</sub> is about 60 percent greater with the addition of copper in case of Miami soil and

50 percent greater in case of Olympic soil during the first two hours of reaction. Wullstein and Gilmour (1964) also found that copper catalyzes the decomposition of nitrite under acidic conditions. Nelson and Bremner (1970) found that cuprous ions promote nitrite decomposition in soil. Yost and Russel (1944) were of the opinion that copper catalyzes nitrite decomposition according to the following reaction



The various form of nitrogen recovered after eight hours reaction period are presented in Table 3. The total amount of nitrogen recovered with and without the addition of copper differ significantly from each other. At both levels of added copper, the total amount of nitrogen recovered does not differ much (107 and 105 ppm in the case of Miami soil and 106 and 104 ppm in the case of Olympic soil). The amount of nitrogen recovered without the addition of metal was 122 ppm in the case of Miami soil and 115 ppm in the case of Olympic soil which is less than the amount (150 ppm) added. There is a greater deficit in the Olympic soil than in the Miami soil. The deficit could possibly be due to the gaseous loss of nitrogen during the reaction.

Copper was found to be more effective than manganese in promoting nitrite decomposition during the first two hours of reaction but less effective than iron.

## SUMMARY AND CONCLUSIONS

An investigation was carried to study the role of iron, manganese, and copper in catalyzing the decomposition of nitrite resulting in the loss of nitrogen in acidic soil. The metals were added at two levels, 1000 ppm and 2000 ppm, respectively, and were allowed to react with nitrite nitrogen for various reaction periods (two, four, and eight hours). The nitrite nitrogen remaining after eight hours, the nitrate nitrogen formed, and the oxides of nitrogen ( $\text{NO} + \text{NO}_2$ ) produced and trapped in an alkaline permanganate system were analyzed and the deficits calculated.

Iron, copper, and manganese were found to catalyze the decomposition of nitrite in two acidic soils during the first two hours of reaction with nitrite nitrogen. By the four hour reaction time, there was no additional effect of the added metals.

Iron was found to be most effective in promoting the nitrite decomposition. Copper was more effective than manganese.

The higher concentration (2000 ppm) of metals were as effective as low concentration (1000 ppm) in catalyzing the decomposition of nitrite except iron which was more effective at the higher concentration in the case of the Miami soil.

Nitrate nitrogen was not formed in the reaction as the oxides of nitrogen ( $\text{NO} + \text{NO}_2$ ) were swept by air flowing at a high rate which reduced any contact time with the soil.

Under most field conditions, the transition metals do not play a significant role, because soils do not contain significant amounts of these metals under the aerobic conditions required for microbial oxidation of ammonium to nitrite. However, the role of ferrous ions in promoting nitrite decomposition deserves serious consideration, because significant amounts of ferrous iron have been detected in water-logged soils under conditions that promote microbial reduction of nitrate to nitrite.

## IMPROVEMENTS AND FUTURE LINE OF WORK

1. The role of transition metals as influenced by the solution system and soil texture should be studied.
2. A system, where  $N_2$  liberated and oxides of nitrogen ( $NO + NO_2$ ) determination is possible, needs to be worked out to describe completely the nitrite transformation.
3. An effort should be made to identify the intermediate products and various pathways of reactions leading to nitrite decomposition in acid media.
4. More levels of the metals should be tried in order to find the best concentration of metal promoting maximum nitrite decomposition.



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## APPENDIX

Nitrate Nitrogen DeterminationExtraction of soil for  
nitrite and nitrate

1. Weigh out 10 or 20 g soil into 250 ml Erlenmeyer flask.
2. Add 100 ml 2 N KCl solution.
3. Place flasks on mechanical shaker and shake for five minutes.
4. Let stand for 20 minutes.
5. Filter into numbered 125 ml Erlenmeyer flasks, using small funnels. Mix the last portion of soil and extract by swirling the flask quickly and pour the soil and liquid onto the filter paper. Let stand until extract has stopped dripping from the funnels.
6. Retain filtrate for  $\text{NO}_2$  and  $\text{NO}_3$  determination.

Reagents

Phenodisulfonic acid:  $(\text{C}_6\text{H}_5\text{OH}(\text{HSO}_3)_2)$ . Dissolve 200 g pure white phenol in 1200 ml concentrated  $\text{H}_2\text{SO}_4$  (avoid Dupont  $\text{H}_2\text{SO}_4$ ). Add 600 ml fuming  $\text{H}_2\text{SO}_4$  (15 percent free  $\text{SO}_3$ ); stir well, heat for two hours on hot water bath.

Acetic acid solution. One part glacial acetic acid and three parts distilled water.

Ammonium sulfamate: 0.5 percent solution in water. Dissolve 5 g ammonium sulfamate in distilled water and dilute to 1 liter.

Ammonium hydroxide. One part concentrated  $\text{NH}_4\text{OH}$  to one part distilled water.

Standard KNO<sub>3</sub> solution

Stock. Dissolve 0.722 g anhydrous KNO<sub>3</sub> and dilute to 1 liter with distilled water. Contains 0.1 mg N/ml.

Standard. Evaporate 50 ml stock KNO<sub>3</sub> solution to dryness; dissolve residue by rubbing with 2 ml phenodisulfonic acid, dilute to 500 ml with distilled water: 1 ml = 0.01 mg N. For preparation of standard curve use 0, 0.5, 1.0, 2.0, 3.5, 8.0, 10.0, 15.0, and 20.0 ml of standard KNO<sub>3</sub> solution (1 ml = 0.01 mg N).

Treat and evaporate as outlined in "Procedure."

Procedure

1. a. Pipette 5 ml of the filtered KCl extract into 100 ml tall beakers.
- b. Pipette into extra beaker 5 ml of KCl extracting solution.
2. Add five drops of acetic acid; swirl to mix.
3. Add 0.5 ml of ammonium sulfamate solution, swirl to mix. (Add 1 ml to those samples having high NO<sub>2</sub><sup>-</sup> content.)
4. Place on hot plate.
5. When warmed to 60-80 C, add five drops of 10 percent NaOH solution; swirl to mix.
6. Let contents evaporate to dryness.
7. Remove beakers from hot plate.
8. Add 2 ml of phenodisulfonic acid to the beaker in such a way that the residue will be moistened quickly and thoroughly.
9. Rub sides of beaker with a stirring rod to bring the phenodisulfonic acid in contact with any of the nitrates that may have spattered onto the wall while drying.

10. Let stand about 20 minutes (or longer) or until the residue is dissolved.
11. Add 34 ml of distilled water to beaker.
12. Add  $\text{NH}_4\text{OH}$  solution (1:1) to beaker until a permanent yellow color remains (about 14 ml). Perform this step under the fume hood.
13. Let cool. Make further dilution if color is too intense. Record final volume.
14. Mix contents by stirring with stirring rod or swirling carefully and read on spectrophotometer after adjusting with blank KCl solution.

#### Nitrite Nitrogen Determination

##### Reagents

Sulfanilamide: 0.2 percent solution in water. Dissolve 4 g p-amino-benzenesulfanilamide in distilled water in 2000 ml volumetric flask. Dilute to mark, then transfer to storage bottle. Keep tightly stoppered in refrigerator. Prepare a new solution one or two days before required or at least every month.

Hydrochloric acid. One to one dilution of concentrated acid with distilled water.

Coupling reagent. Dissolve 1 g N-(1-naphthyl)-ethylenediamine dihydrochloride in 1 liter distilled water. Store in dark bottle.

##### Sodium nitrite standard

1. Employing assayed  $\text{NaNO}_2$ , prepare an accurately known solution containing about 0.005 mg of N per ml (solution A).



2. Dilute 50 ml of above solution to 100 ml in volumetric flask (solution B).
3. With a volumetric pipette measure 0.5, 1.0, 1.5, and 1.8 ml of A and 1, 2, 4, ml of B into 50 ml volumetric flasks.
4. Add 20 ml of 2 N KCl solution to each.
5. Treat as outlined in Steps 2 through 7 of "Procedure."
6. Keep standard sodium nitrite solution tightly stoppered in refrigerator.

#### Procedure

1. a. Pipette 20 ml of KCl soil extract into 50 ml volumetric flasks. Use smaller aliquot (2 to 5 ml) if  $\text{NO}_2^-$  content of sample is high. Make up to 20 ml with KCl solution.  
b. Pipette 20 ml of KCl extracting solution into an extra 50 ml volumetric flask.  
c. Fill burettes with 50 percent HCl, 0.2 percent sulfanilamide, and coupling reagent.
2. From a burette add 1 ml of 50 percent HCl.
3. From a burette add 5 ml of 0.2 percent sulfanilamide solution.
4. Wait three minutes.

NOTE: Steps 2 and 3 can be performed on 10 samples within three minutes as follows. Add the HCl and sulfanilamide to the first sample, then set the time clock for three minutes. Then quickly add HCl and sulfanilamide to the other nine samples in succession.

5. At the end of the three minute interval, begin adding 1 ml of the coupling reagent to each sample, timing the additions so that each sample will have remained at three minutes after the addition of sulfanilamide.

6. Make up to volume with distilled water.
7. If the color is too dark, take smaller quantities of aliquot and develop color.
8. Read on spectrophotometer at 550 m $\mu$  wave length.

Analysis of Alkaline Permanganate  
Traps for Oxides of Nitrogen

The oxides of nitrogen that dissolve in the traps will be oxidized to nitrate by  $\text{KMnO}_4$ . Thus this procedure is designed to destroy the color of the  $\text{KMnO}_4$  and permit colorimetric nitrate determination.

Reagents

1. Trapping solution of alkaline permanganate 0.2 M  $\text{KMnO}_4$  in 2N KOH. Dissolve 112.2 g reagent-grade KOH in about 800 ml of distilled water. Add 31.7 g  $\text{KMnO}_4$ , warm and stir until solution is complete. Transfer to 1 liter volumetric flask and make up to volume. Store in brown bottle away from direct light.
2. Oxalate sulphuric acid solution 0.6 M  $\text{Na}_2\text{C}_2\text{O}_4$  in 7 N  $\text{H}_2\text{SO}_4$ . Place about 1200 ml distilled water in a 2 liter beaker. Add carefully 390 ml concentrated  $\text{H}_2\text{SO}_4$ . Weigh out and add 160.6 g  $\text{Na}_2\text{C}_2\text{O}_4$ . Stir until oxalate is completely dissolved, transfer to 2 liter volumetric flask and make up to volume. Store in brown plastic bottle, the oxalate will attack glass.
3. 5 N NaOH. Weigh out 200 g reagent-grade NaOH and dissolve in about 800 ml distilled water. Allow to cool; transfer to 1 liter volumetric flask and make to volume.

### Procedure

Wash the entire contents (20 ml) of trap into 125 ml beaker. Avoid using excess water. A blank of unused trap solution should be included. Add 20 ml of reagent 2 (acid and oxalate). In a few minutes, the reaction should be complete and the material should be colorless. Warming on a hot plate will facilitate reaction. Incomplete reaction may be the result of insufficient acidity or insufficient oxalate.

After slight warming add 30 ml of 5 N NaOH to each beaker. Precipitation will occur at this point and the base must be in sufficient quantities to make the solution alkaline. Upon standing a slight brown scum of  $MnO_2$  should form on the surface. Failure of this formation may be due to insufficient base.

The precipitate should be digested with gentle warming for at least one-half hour. The material is then filtered into 250 ml volumetric flask. This filtration must be quantitative and the residue washed several times with small portions of warm water. The volume is then made up to 250 ml and an aliquot (5 ml) taken for standard phenoldisuphonic acid nitrate determination. The addition of ammonium sulfamate to destroy nitrites is unnecessary. The blank carried through the entire procedure is used to set the zero on spectrophotometer.

NOTE: Do not use excess water to wash the trap solution into the beaker or for washing the precipitate as the total volume must be less than 1000 ml. The destruction of  $KMnO_4$  by  $C_2O_4^{=}$  requires high acidity and incomplete reaction at this point is often the result of insufficient acidity. If the traps are to be exposed to large amounts of  $CO_2$  evolution, it may be necessary to use 4 N KOH and/or 10 ml trapping

solution per trap. If more trapping solution is used, the amounts of reagents 2 and 3 may be increased accordingly. If 3 N KOH is used in the trap solution, the acidity of reagent 2 should be increased to 9 N. After the residue from filtration is exposed to the air; it should assume a dark brown color. If it remains grey, add a ml or two of NaOH to the filtrate. If any precipitate occurs, refilter.

## VITA

Jaswant Singh Bajwa

Candidate for the Degree of

Master of Science

Thesis: Role of Transition Metals in Nitrite Decomposition in Soil

Major Field: Soil Science

## Biographical Information:

Personal Data: Born in Dhode, Punjab State, India, January 11, 1944, son of Sardar Mota Singh Bajwa and Balwant Kaur Bajwa; married Amarjit Kaur July 2, 1967; two children--Jaspreet Kaur and Gurpreet Singh.

Education: Attended elementary school, graduated from High School in 1959; received the Bachelor of Science degree in 1963 from Punjab Agricultural University, Ludhiana, India with a major in soil chemistry. Received the Master of Science degree in soil science from Punjab Agricultural University, Ludhiana, India in 1965; completed requirements for the Master of Science degree, at Utah State University in 1971.

Professional Experience: November 1965 to July 1966, Lecturer in Soils, Agricultural College, Sangrur, Punjab, India; July 1966 to September 1969, Lecturer in Soils, Punjab Agri. Univ. Ludhiana, Punjab, India; September 1969 to date, Graduate Research Assistant, Department of Soils and Meteorology, Utah State University, Logan, Utah.