Soil Biol. Biochem. Vol. 9, pp. 277 to 280. Pergamon Press 1977. Printed in Great Britain.

Ref 160 0071

NITRIFICATION IN THREE SOILS AMENDED WITH ZINC SULFATE

D. O. WILSON

Department of Agronomy, University of Georgia, Georgia Station, Experiment, GA 30212

(Accepted 22 November 1976)

Summary—Zinc as $ZnSO_4$ was added to three soils at rates of 0, 10, 100 and 1000 μg Zn g^{-1} soil. The soils were uniformly treated with 100 μg N g^{-1} as NH_4Cl, incubated at 30°C and NH_4^+-N and (NO_3^- + NO_2^-)-N determined weekly for 7 weeks. Nitrification in all three soils was totally inhibited by 1000 μg Zn g^{-1}. At the 100 μg Zn g^{-1} rate, nitrification was significantly reduced in two of the three soils during some part of the incubation. This differential effect on nitrification at the 100 μg Zn g^{-1} rate was related to differences in soil properties. These results imply that, with respect to nitrification, care should be taken not to apply Zn-containing materials indiscriminately to soils.

INTRODUCTION

The introduction of metals into soils by such routes as land application of sewage sludge and the deposition of airborne particulates from mining operations can significantly increase the native soil concentration of these metals. Heavy metals are commonly present in domestic sewage sludge at rather high concentrations and often at extremely high concentrations in industrial sludges. Elevation of the metal content of agricultural soils is of particular concern because of possible toxic effects on plant growth and other biological processes. Zinc is considered one of the metals most likely to produce phytotoxicity as a result of sludge application to soil (Webber, 1972).

Since soils exhibit a wide range of physical and chemical properties, it is difficult to compare and extrapolate results of various workers with respect to the effects of Zn on soil N mineralization processes. Reported here are the results of a study relating nitrification to various rates of Zn added to three agriculturally important soils.

MATERIALS AND METHODS

Some of the physical and chemical properties of the soils used in these experiments are shown in Table 1. The values given are for the soils as they were collected from the field. The Decatur soil is a clayey, kaolinitic, thermic member of Rhodic Paleudults; Cecil is a clayey, kaolinitic thermic member of Typic Hapludults; and Leefield is a loamy, siliceous, thermic member of Arenic Plinthaquic Paleudults.

The soils were air-dried, ground, and passed through 2-mm mesh. Additions of P and K were made to bring the soils to adequate amounts for plant growth. A mixture of MgO and $CaCO_3$ was added to the Decatur and Leefield soils to bring the pH to 6.8 and 7.4, respectively. Nitrogen as NH_4Cl was added to all soils at a concentration of 100 μg N g^{-1} dry soil. Solutions of $ZnSO_4$ were added to each soil to give rates of 10, 100 and 1000 μg Zn g^{-1} dry soil. Each soil was brought to a moisture content which approximated its field capacity; these values being 18, 12 and 7% (oven-dry basis) for the Decatur, Cecil

Table 1. Characteristics of Decatur, Cecil and Leefield soils

Characteristic	Soil Series		
	Decatur	Cecil	Leefield
pH	5.5	6.2	5.1
Cation exchange capacity (m-equiv/100 g)*	12.43	4.44	3.13
Organic matter (%)*	2.37	1.60	1.14
Clay (%)*	28.1	7.6	2.4
Sand (%)*	21.7	75.0	84.4
Textural class*	Clay loam	Sandly loam	Loamy sand
N (%)†	0.105	0.059	0.044
Fe (%)	2.89	1.27	0.13
K ($\mu g\ g^{-1}$)	5673	4673	180
P ($\mu g\ g^{-1}$)	488	342	179
Ca ($\mu g\ g^{-1}$)	846	873	105
Mg ($\mu g\ g^{-1}$)	1940	806	103
Mn ($\mu g\ g^{-1}$)	3600	490	21
Zn ($\mu g\ g^{-1}$)	136	24	7
Cu ($\mu g\ g^{-1}$)	24	5.4	2.6

* Values of Shuman, 1975.

† All elemental values are from total analyses.

9222

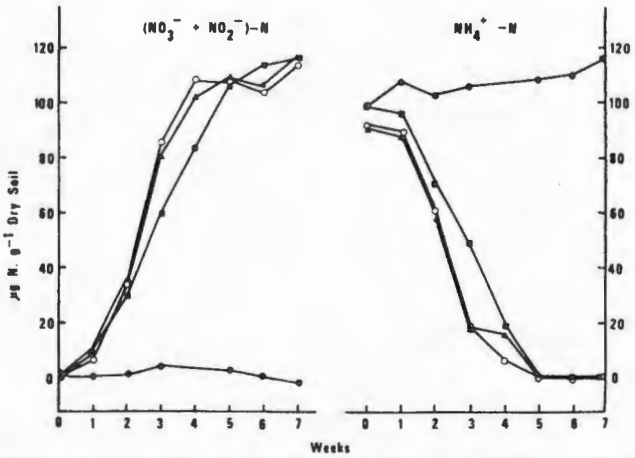

Fig. 1. Effect of Zn on inorganic N values in Decatur soil during nitrification of 100 μg NH_4^+-N g^{-1} soil. ○——○ control; ▲——▲ 10 μg Zn g^{-1}; ■——■ 100 μg Zn g^{-1}; ●——● 1,000 μg Zn g^{-1}.

and Leefield soils, respectively. Ten-gram (oven-dry weight) portions of the moist, treated soil were weighed into 250-ml glass bottles and capped with a lid having a 1-mm hole in the center. The bottles were placed in an incubator and maintained at 30 ± 0.5°C. The soil in the bottles was brought back to its original moisture value by twice-weekly additions of water. At weekly intervals for 7 weeks, samples of each treatment were extracted with 100 ml 2 M KCl on a rotary shaker for 30 min, filtered, and analyzed for NH_4^+-N and $(NO_3^- + NO_2^-)$-N.

Organic matter was determined by the Walkley–Black method (Allison, 1965) and soil N by the microKjeldahl method (Bremner, 1965a). Analysis of the soil for the remaining elements was performed using total digestion and analytical techniques (Wilson, 1977). The amounts of NH_4^+-N and $(NO_3^- + NO_2^-)$-N in the 2 M KCl soil extracts were determined by steam distillation (Bremner, 1965b). All pH values are for a 1:2 soil:water suspension. The treatments were replicated four times and mean values are plotted.

RESULTS

The effect of Zn concentration on NH_4^+-N and $(NO_3^- + NO_2^-)$-N values for all three soils are presented in Figs. 1, 2 and 3. For each of the soils, the $(NO_3^- + NO_2^-)$-N values have been corrected by subtracting the average initial $(NO_3^- + NO_2^-)$-N concentration in that particular soil. The NH_4^+-N values were not corrected since the initial NH_4^+-N concentration in all soils was nearly zero. The addition of 1000 μg Zn g^{-1} completely eliminated nitrification in all three soils, whereas the 100 μg Zn g^{-1} rate had a variable effect depending on the soil. In the Decatur soil (Fig. 1), nitrification at the three lowest Zn rates followed the same pattern, but in the Cecil and Leefield soils (Figs. 2 and 3), nitrification at the 100 μg Zn g^{-1} rate did not follow a pattern similar to the two lower rates. A statistical analysis of the data indicated that for the Cecil soil, both NH_4^+-N and $(NO_3^- + NO_2^-)$-N values for the 100 μg Zn g^{-1} rate were statistically lower ($P = 0.05$) than those for the two lowest Zn rates at the second and third weeks of incubation. A similar comparison for the Leefield soil shows significant effects at the third, fourth, fifth and seventh weeks of incubation.

In nitrification studies of this nature, there is always a question as to whether the treatment might not be affecting nitrification by altering the soil pH since it is known that the addition of metal salts generally lowers soil pH (Premi and Cornfield, 1969; Wilson,

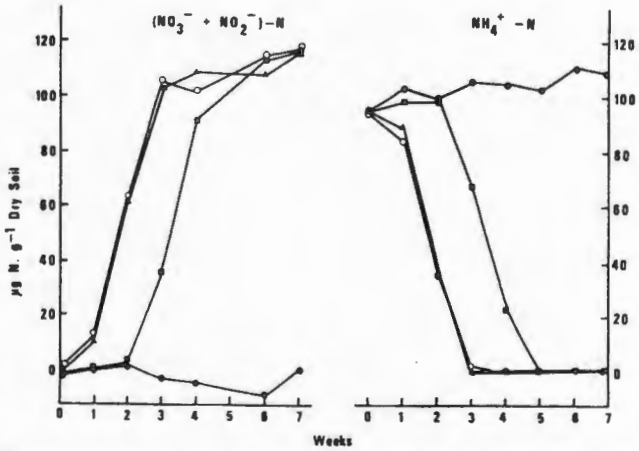

Fig. 2. Effect of Zn on inorganic N values in Cecil soil during nitrification of 100 μg NH_4^+-N g^{-1} soil. ○——○ control; ▲——▲ 10 μg Zn g^{-1}; ■——■ 100 μg Zn g^{-1}; ●——● 1,000 μg Zn g^{-1}.

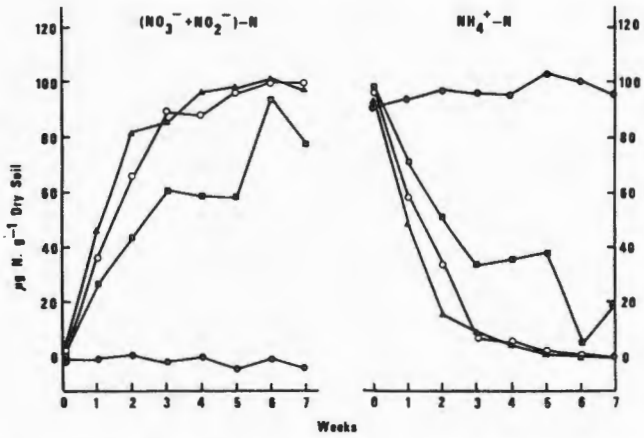

Fig. 3. Effect of Zn on inorganic N values in Leefield soil during nitrification of 100 μg NH_4^+-N g^{-1} soil. ○——○ control; ▲——▲ 10 μg Zn g^{-1}; ■——■ 100 μg Zn g^{-1}; ●——● 1,000 μg Zn g^{-1}.

1977). This question is particularly pertinent when considering soils with very low cation exchange capacities, as such soils usually have generally low pH buffering capacities. Table 2 shows the soil pH after 7 weeks incubation for all treatments. The acidity produced from nitrification of the added NH_4^+-N was sufficient to lower the pH to 5.5, 5.4 and 6.1 in the Decatur, Cecil and Leefield soils, respectively. Addition of the Zn treatments did not substantially reduce pH below the control value in any of the soils. In all three soils, the highest pH value was associated with the highest added Zn concentration which is not surprising since nitrification was not occurring in these treatments.

There was a general and gradual increase in total mineral N with time for nearly all treatments in all soils (Figs. 1, 2 and 3), indicating that mineralization of organic N was occurring. This increase was more apparent in the Decatur and Cecil soils than the Leefield soil, suggesting a relationship to soil organic matter content. In the Decatur and Cecil soils, after 7 weeks incubation, N accumulated as $(NO_3^- + NO_2^-)$-N in the 0, 10 and 100 μg Zn g^{-1} treatments but as NH_4^+-N in the 1000 μg Zn g^{-1} treatment.

Table 2. pH values of treated soils after incubation for 7 weeks

Soil	Zn added μg g^{-1}	pH value
Decatur	0	5.5
	10	5.6
	100	5.6
	1000	6.1
Cecil	0	5.4
	10	5.5
	100	5.3
	1000	5.8
Leefield	0	6.1
	10	6.0
	100	6.1
	1000	6.2

DISCUSSION

Reports on the effects of Zn on nitrification are limited. Lees and Meiklejohn (1948) could find no substantial stimulatory effect from the addition of Mn, Zn or Cu to liquid cultures of nitrifying bacteria. Their work was designed to determine whether the omission of any of the micronutrients from the culture media would suppress nitrification. Using non-purified salts they were able to establish that, of the micronutrients, only the omission of Fe significantly reduced growth. Using a strain of *Nitrosomonas europaea* isolated from sludge, Loveless and Painter (1968) found that nitrite production was sensitive to low concentrations of Zn, showing inhibition at 0.08 to 0.5 μg Zn ml^{-1} of nutrient solution. Tyler (1975) concluded that a combined Cu and Zn concentration of three times the background value was sufficient to measurably reduce N mineralization in a Swedish forest soil. Premi and Cornfield (1969) reported that soil Zn concentrations of 100, 1000, and 10,000 μg Zn g^{-1} (as $ZnSO_4$) showed no, partial, and complete inhibition of nitrification, respectively. These observations are in contrast to the results of the present study where partial inhibition of nitrification was observed on some soils at 100 μg Zn g^{-1} with total inhibition being produced in all soils at 1000 μg Zn g^{-1}. However, the soils used in these various studies were so dissimilar any observed differences in response were certainly due to differences between the soils investigated.

The form and amount of native soil Zn, the form in which Zn is added to the soil, and the capacity of the soil to adsorb and fix Zn are all factors which will greatly influence biological responses. The availability of native soil Zn to participate in biological processes is determined by both physical and chemical factors. Zinc that is located within crystal and clay lattices and chemical forms of Zn that are highly insoluble have low biological availabilities, whereas soluble and exchangeable forms of the element have high availabilities. The distribution of these forms of Zn may vary greatly between soils. For this reason, total Zn in a soil may not be a good indicator of its biological availability.

Soils also vary in their ability to adsorb and inactivate Zn that is added to them. Thus, the probable reason for the Decatur soil showing the least (Fig. 1) and Leefield the greatest (Fig. 3) reduction in nitrification with the addition of 100 μg Zn g^{-1} is greater adsorption and inactivation of the element by the Decatur soil. Shuman (1975) has shown that the Decatur soil has a much greater Zn adsorptive capacity than Leefield due, in large part, to its greater clay and organic matter content.

The form in which Zn is added to soils also has a bearing on whether or not the Zn is inhibitory to nitrification. Premi and Cornfield (1969) found that, in contrast to their previously discussed results with Zn as the sulfate, the addition of up to 10,000 μg Zn or Cu g^{-1} soil as carbonates had no inhibitory effect on nitrification. Zinc is being added to soils in ever increasing amounts as sewage sludge. Wilson (1977) reported temporary reductions in nitrification from the addition of 16 mg of industrial sewage sludge g^{-1} Cecil soil. This amount of sludge resulted in the addition of approximately 150 μg Zn g^{-1} soil. Based on the current findings, it seems likely that the inhibitory effect of the sludge was due, in large part, to the Zn which it contained.

The direct results of the present study, as well as its relation to other work, demonstrate that the type of soil to which Zn is added is an important factor in determining the soil concentration at which Zn will inhibit nitrification. These findings have important implications relative to site selection for land disposal sewage sludge and other wastes containing appreciable amounts of Zn.

Acknowledgements—The author wishes to express appre ciation to Mrs. Helen Piercy for technical assistance, Mis E. Vicki Berryman for soil chemical analyses, Dr. J. R Allison for statistical methods and Mr. J. C. Elrod for sta tistical analyses.

REFERENCES

ALLISON L. E. (1965) Organic carbon. In *Methods of So Analysis, Part 2*. (C. A. Black, Ed.) pp. 1367–1378, Ameri can Society of Agronomy, Madison, Wisconsin.

BREMNER J. M. (1965a) Total nitrogen. In *Methods of So Analysis, Part 2*. (C. A. Black, Ed.) pp. 1149–1178. Ameri can Society of Agronomy, Madison, Wisconsin.

BREMNER J. M. (1965b) Inorganic forms of nitrogen. I *Methods of Soil Analysis, Part 2*. (C. A. Black, Ed.) pp 1179–1237, American Society of Agronomy, Madison Wisconsin.

LEES H. and MEIKLEJOHN J. (1948) Trace elements an nitrification. *Nature* **161**, 398–399.

LOVELESS J. E. and PAINTER H. A. (1968) The influenc of metal ion concentrations and pH value on the growt of a Nitrosomonas strain isolated from activated sludge *J. gen. Microbiol.* **52**, 1–14.

MURPHY J. and RILEY J. P. (1962) A modified single solu tion method for the determination of phosphate i natural waters. *Anal. chim. Acta* **27**, 31–36.

PREMI P. R. and CORNFIELD A. H. (1969) Effects of addi tions of copper, manganese, zinc and chromium com pounds on ammonification and nitrification during incu bation of soil. *Pl. Soil* **31**, 345–352.

SHUMAN L. M. (1975) The effect of soil properties on zin adsorption by soils. *Proc. Soil Sci. Soc. Am.* **39**, 454–458

TYLER G. (1975) Heavy-metal pollution and mineralizatio of nitrogen in forest soils. *Nature* **255**, 701–702.

WEBBER J. (1972) Effects of toxic metals in sewage on crops *Wat. Pollut. Control* **71**, 404–413.

WILSON D. O. (1977) Nitrification in soil treated wit domestic and industrial sewage sludge. *Environ. Pollut* **12**, 73–82.