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EFFECTS OF COPPER, ZINC, AND CHROMIUM ON IMMOBILIZATION AND SUBSEQUENT RE-MOBILIZATION OF NITROGEN DURING INCUBATION OF SOIL TREATED WITH SUCROSE

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SUMMARY

The effects of adding 100 and 1,000 p.p.m. of Cu^{2+}, Zn^{2+}, and Cr^{3+} (sulphates) on mineral-nitrogen levels after 1 and 8 weeks of aerobic incubation of a sandy loam (pH 7.6) treated with ammonium nitrate (50 p.p.m. N) and 0.2% sucrose were studied. During the nitrogen immobilization phase (1 week of incubation) 1,000 p.p.m. Cu was the only treatment which increased immobilization of nitrogen, whilst 1,000 p.p.m. Cu and Cr altered somewhat the normal preference of nitrate over ammonia by the immobilizing organisms. During subsequent re-mobilization (further 7 weeks of incubation) both levels of Cu and Zn and the higher level of Cr increased nitrogen mineralization. Nitrification was decreased by the higher level of Cu and by both levels of Zn. Nitrite was not detected at any stage. Results are discussed in relation to the amounts of Cu, Zn, and Cr extracted by 0.1 N-EDTA (pH 4.0).

INTRODUCTION

Soils may receive metallic trace elements through application of mining and industrial wastes, sewage sludges, and pesticides. The accumulation of trace elements resulting from prolonged use of such materials may affect soil microbial activity and plant and animal performance. Work has been reported (Eno, 1953; Lees and Meiklejohn, 1948; Lipman and Burgess, 1914; Sedova, 1958) on the effects of adding various trace elements on ammonification and nitrification of native organic nitrogen and added organic materials of narrow C/N ratio. No work appears to have been done on the effects of added trace elements on the whole process of immobilization followed by remobilization of nitrogen during the decompostion of easily decomposable carbohydrate material.

This paper reports on the effects of adding Cu, Zn, and Cr (as sulphates) at levels of 100 and 1,000 p.p.m. on ammonium and nitrate content during incubation of soil treated with sucrose and ammonium nitrate.

MATERIALS AND METHODS

The soil used was an alluvial sandy loam topsoil (12.1% clay) from a

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cultivated area and was air-dried and ground to pass a 2 mm sieve. The soil had pH 7.6 and contained 0.16% total nitrogen and 2.0% organic carbon. The soil contained 33 p.p.m. Cu, 57 p.p.m. Zn and less than 0.1 p.p.m. Cr as determined by extraction with boiling 6N-hydrochloric acid and analysis using the Unicam SP90 atomic absorption spectrophotometer.

Copper, zinc and chromium were mixed as finely ground sulphates to give levels of 100 and 1,000 p.p.m. of each cation on the air-dry soil basis. Samples of 10 g of treated and control soils were placed in flat-bottomed vials. 0.2% sucrose and 50 p.p.m. nitrogen, as ammonium nitrate, (air-dry soil basis) were then added in the water used to bring the soil moisture contnet to 50% of the maximum water-holding capacity. Sucrose was used becau of its rapid rate of decomposition and ammonium nitrate was added so that mineral nitrogen was not limiting sucrose decomposition. The vials were clo ed with rubber bungs and the barium peroxide method (Cornfield, 1961) was used to absorb carbon dioxide and supply oxygen during incubation. Sufficient replicates of each treatment were prepared to allow for duplicate determinations after incubation at 30°C for 1 and 8 weeks. Previous tests with this soil showed that maximum decomposition of sucrose and immobilization of nitrogen occurred during the first week, and a further 7 weeks of incubation was required for virtually complete re-mobilization of an equivalent amount of nitrogen.

After each incubation period 10 ml water was added to each tube and the pH measured after shaking. Then 10 ml 0.2 N-Na-EDTA (diaminoethanetetracetic acid) at pH 4.0 was added, the tubes were shaken for 2 minutes and the contents filtered. Suitable aliquots of the extracts were analysed for ammonia- and nitrate-nitrogen by the microdiffusion method of Bremner and Shaw (1955) and for nitrite-nitrogen by a colorimetric α-naphthylamine-sulphanilic acid method. The EDTA reagent was also used as a measure of extractable trace elements. Pizer et al. (1966) used 0.1 N-NH_4-EDTA (ph 4.0 for assessing the copper status of soils with respect to plant growth. Since ammonia-nitrogen was determined in the present study the reagent was altered by replacing ammonium by sodium. Preliminary tests showed that the extractability of Cu, Zn and Cr was very similar irrespective of whether the sodium or ammonium form of the reagent was used. In addition, the EDTA reagent was as effective as N-sodium chloride in extracting the mineral forms of nitrogen.

RESULTS AND DISCUSSION

The levels of mineral-nitrogen (ammonia- and nitrate-nitrogen) in p.p.m. on the air-dry soil basis, initially and after 1 and 8 weeks of incubation, are presented in Table I. Nitrite could not be detected ($<$ 0.02 p.p.m. nitrogen) after either period of incubation in any of the samples.

During the *immobilization phase* (first week of incubation) 1,000 p.p.m. Cu was the only treatment which significantly increased immobilization of nitrogen (the differences in results between the control and treated soils), whilst the other treatments had no effect. This indicates that the activity of the heterotrophic organisms responsible for decomposition of sucrose was stimulated by 1,000 p.p.m. Cu. In the control soil nitrate was completely immobilized, whilst ammonia was hardly affected, indicating that in this

TABLE I

Effect of addition of copper, zinc, and chromium (as sulphates) on mineral-N contents after 1 and 8 weeks of incubation of soil receiving 0.2% sucrose and 50 p.p.m. nitrogen (ammonium nitrate)[1]

Added trace element (p.p.m.)		After 1 week of incubation				After 8 weeks of incubation			
		NH_4-N (p.p.m.)	NO_3-N (p.p.m.)	min-N (p.p.m.)	pH	NH_4-N (p.p.m.)	NO_3-N (p.p.m.)	min-N (p.p.m.)	pH
nil		32	0	32	7.6	0	53	53	7.8
Cu^{2+}	100	36	30	36	7.6	0	72*	72*	7.5
Zn^{2+}	100	32	0	32	7.5	30*	40*	70*	7.8
Cr^{3+}	100	31	0	31	7.0	0	58	58	7.7
Cu^{2+}	1,000	15*	5*	20*	6.9	32*	52	84*	7.4
Zn^{2+}	1,000	32	0	32	6.8	33*	45	78*	6.7
Cr^{3+}	1,000	34	5*	39	6.7	0	67*	67*	6.8
L.S.D. ($P < 0.05$)		8.4	3.7	8.8		11.0	11.2	12.6	

[1]Samples contained initially 64 p.p.m. mineral-N (24 p.p.m. ammonium- and 40 p.p.m. nitrate-N).
*Significantly different ($P < 0.05$) from nil treatment.

soil the immobilizing organisms preferred to utilize nitrate to ammonia. 1,000 p.p.m. Cu and Cr were the only treatments which did not prevent the complete immobilization of nitrate during the immobilization phase, but the extent of this effect, though significant, was small. This indicates that these two treatments have altered somewhat the normal preference for nitrate over ammonia by the immobilizing organisms, either by modifying the nature or directly affecting the nitrogen-metabolizing properties of the microbial population.

During the re-mobilization phase (a further 7 weeks of incubation) 100 and 1,000 p.p.m. Cu and Zn and 1,000 p.p.m. Cr significantly stimulated nitrogen mineralization in comparison with the control. The higher levels of Cu and Zn also caused significantly greater mineral nitrogen accumulation by the end of incubation than that originally present (initial mineral N). These treatments appeared to have stimulated mineralization of native organic nitrogen during the re-mobilization phase.

Although none of the treatments decreased nitrogen mineralization during the re-mobilization phase, there were differences due to type and level of trace elements added on the proportion of ammonia and nitrate which accumulated. The accumulation of mineralized nitrogen entirely as nitrate in the control soil as well as where 100 and 1,000 p.p.m. Cr and 100 p.p.m. Cu were applied indicates that these treatments were not decreasing nitrification. In fact they may have been stimulating nitrification, but since no ammonia accumulated, nitrification rate was being limited by ammonification rate. The significant accumulation of ammonia where 1,000 p.p.m. Cu and 100 and 1,000 p.p.m. Zn were added indicates that these treatments decreased nitrification.

The treatments decreased soil pH by 0.1–1.1 units compared with the control soil (pH 7.8), with the higher levels of added salts having the

greater effect in this respect. The decrease in pH was presumably due to the acid residues of the sulphate salts used. It may be argued that where decrease in nitrification occurred, this may have been due to the normal effect of lowered pH in decreasing nitrification. However, the lowest pH attained was 6.7 (1,000 p.p.m. Zn treatment) and previous tests with this soil had shown that variation in pH over the range 6.5 to 8.0 had negligible effects on nitrification rate. In addition the possibility that changes in nitrogen metabolism may have been due to the sulphate portion of the added salts is unlikely since it had been found previously for this soil (Sindhu, 1967) that the addition of even 5 times the amounts of sulphate (as calcium sulphate) as compared with that added in the present study had negligible effects on nitrogen metabolism. It appears therefore that the changes in ammonification and nitrification rates due to the treatments used in this study arise from the effects of the trace elements and not from changes in pH or sulphate content of the soil.

After 8 weeks of incubation EDTA (pH 4.0) extracted 74, 80 and 1 p.p.m. of Cu, Zn, and Cr respectively where 100 p.p.m., and 584, 700, and 3 p.p.m. respectively where 1,000 p.p.m. of these cations had been added. Extractable levels of all elements after 1 week of incubation were very similar to those after 8 weeks of incubation. It is interesting to note that the only element, viz. Cr, which did not decrease nitrification during the re-mobilization phase even at the 1,000 p.p.m. level was the only element which was converted by the soil to a form which was virtually non-extractable by EDTA. Nitrification was more sensitive to low levels of EDTA-extractable Zn than of extractable Cu, but at the higher extractable levels of both these elements nitrification was decreased by about the same extent. Increase in ammonification rate during the re-mobilization phase was correlated roughly with the logarithm of the increase in EDTA-extractable Cu and Zn.

CONCLUSIONS

This study has shown that the presence of certain trace elements in soil in amounts greater than found normally may exert some effects on nitrogen metabolism during both the nitrogen immobilization stage of decomposition of carbohydrates and also during the subsequent nitrogen mobilization phase. The effects produced include stimulation of immobilization of nitrogen, alteration of the normal preference by micro-organisms of one form of mineral nitrogen over another during the immobilization phase, and, during the re-mobilization phase, stimulation of mineralization and decrease in nitrification. Thus, apart from the direct effects (toxic or stimulating) which high levels of trace elements may have on plants, their ability to alter nitrogen changes arising from microbial activity in soil may also have an indirect effect on plant performance.

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