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EFFECTS OF TRACE ELEMENTS ON NITROGEN MINERALISATION IN SOILS

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Studies to evaluate the effects on nitrogen [illegible] that all 19 inhibit mineral nitrogen production [illegible] relative effectiveness of the trace elements [illegible] depends on the soil. When the trace elements were [illegible] soil, Ag(I) and Hg(II) were the most effective [illegible] As(III), Se(IV), As(V), and W(VI) the least effective in inhibiting [illegible] sation. Other trace elements that inhibited nitrogen mineralisation [illegible] Cu(II), Cd(II), Pb(II), Mn(II), Fe(II), Zn(II), Ni(II), Sn(II), [illegible] B(III), [illegible] and Mo(VI); their degrees of effectiveness were [illegible] studied. [illegible] Hg(II), Cd(II), Ni(II), Cr(III), Fe(III), Al(III), Be(II) [illegible] inhibited nitrification causing accumulation of ammonium-N in some of the [illegible]

INTRODUCTION

Trace element content of soils may be substantially increased by the application of sewage sludge and industrial and mining wastes. Many such materials contain large quantities of various trace elements that could be retained and thus accumulate in soil (Berrow & Webber, 1972; Dean & Smith, 1973; Lindsay, 1973). Also, soil pollution by heavy metals is one of the major environmental problems associated with industries involved in processing such metals. In a review of the literature on the fate and effects of trace elements in sewage sludge applied to agricultural lands, Page (1974) concluded that surface horizons of sludge-amended soils are enriched in trace elements. The extent of this enrichment depends upon the amount of sludge applied and the trace element composition of sewage sludge. Page also concluded that applications of any sludge equal to 400 tonnes/ha, if mixed uniformly through the top 15 cm, will add more Cd, Cu, Hg, and Zn to this zone than is normally present in natural soils.

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Research dealing with the chemistry of trace elements in soils and the toxicity of the various elements to biological systems, including accumulation in plants, is extensive (Kubota & Allaway, 1972; Lagerwerff, 1972; Chaney, 1973; Page, 1974), but little is known about the relative effects of trace elements on the biochemical processes in soils. Addition of trace elements to soils may affect microbial proliferation and enzymatic activities, possibly leading to a decrease in the rates of the biochemical processes in the soil environment. In the few studies reporting on the effects of selected trace elements on nitrogen mineralisation in, or carbon dioxide evolution from, soils (Turk, 1939; Javillier, 1941; Quraishi & Cornfield, 1971; Bhuiya & Cornfield, 1972), the trace elements were added to soils on a ppm basis rather than on an equimolar basis, which makes the comparison of their effectiveness in inhibition of nitrogen mineralisation difficult. The effect of any trace element on biochemical reactions in soils may vary with soil pH, organic matter content, and texture. We studied the effects of 19 trace elements commonly found in sludge samples on nitrogen mineralisation in soils. In this study, the amounts of ammonium-N, nitrate-N, and nitrite-N produced were determined in four soils incubated with either a trace element solution (5 μmole of trace element/g of soil) or water

MATERIALS AND METHODS

The soils used were surface soils (0–15 cm) selected to obtain a range in pH (5·8–7·8), organic matter content (2·58–5·45% organic C), and texture (23–45% clay, 39–54% silt, and 1–38% sand). Before use, each soil was air-dried and crushed to pass a 2-mm screen. In the analyses reported in Table 1, pH was determined with a glass electrode (soil/water ratio, 1:2·5), organic C by the method of Mebius (1960), total N by a semimicro-Kjeldahl procedure (Bremner, 1965), ammonium-N and nitrate-N by a steam distillation method (Bremner & Keeney, 1966), and particle-size distribution by the pipette analysis described by Kilmer & Alexander (1949).

The analyses for organic C and total N were performed on subsamples that had been ground to pass a 100-mesh sieve. The other analyses were performed on the coarser, <2 mm, soil samples. All soil analyses reported are on an oven-dry basis, moisture being determined from loss in weight after drying at 105°C for 24 h.

TABLE 1
PROPERTIES OF SOILS USED

Soil	*pH*	*Organic C* %	*Total N* %	*Inorganic N, ppm* NH_4-*N*	NO_3-*N*	*Clay* %	*Silt* %
Webster	5·8	2·58	0·210	3	5	23	39
Judson	6·6	2·95	0·245	3	1	45	54
Harps	7·8	3·74	0·305	2	1	30	44
Okoboji	7·4	5·45	0·463	4	2	34	50

The trace elements used were Fisher certified reagent-grade chemicals. Of these, Ag(I), Cu(II), Cd(II), Zn(II), Fe(II), Co(II), and V(IV) were added as the sulphate; Hg(II), Sn(II), Mn(II), Ni(II), Fe(III), Cr(III), and Al(III) as the chloride; Pb(II) as the acetate; and As(III), B(III), Se(IV), As(V), Mo(VI), and W(VI) as $NaAsO_2$, $Na_2B_4O_7$, H_2SeO_3, Na_2HAsO_4, H_2MoO_4, and Na_2WO_4, respectively.

The effects of trace elements on nitrogen mineralisation in soils were studied by comparing the amounts of nitrogen mineralised (under aerobic conditions) by trace element-amended soils and by unamended soils. In this work, a 10-g sample of soil in an 8 oz (250 ml) French square bottle was treated with 3 ml of a solution containing 50 μmole of trace element (or, in the control, 3 ml of water), added dropwise to moisten the whole soil (*ca.* 60% of WHC). The bottle was stoppered and incubated at 30°C. The stopper was removed and the bottle aerated every three days. After 20 days, the ammonium-, nitrate-, and nitrite-N produced were extracted with 50 ml of 2M KCl. Ammonium-N and (nitrate + nitrite)-N were determined by a steam distillation method (Bremner & Keeney, 1966), and nitrite-N by the diazotisation and coupling reaction method described by Barnes & Folkard (1951). Percentage inhibition of nitrogen mineralisation by each trace element was calculated from (A-B/A)100, where A is the amount of N mineralised in unamended soil and B is the amount of N mineralised in trace element-amended soil. All results reported are averages of duplicate determinations.

RESULTS AND DISCUSSION

Table 2 shows the amounts of NH_4-N and NO_3-N produced in unamended and trace element treated soils. The results are those obtained after 20 days of incubation minus those present initially. Nitrite was not detected in any of the soils studied. The amounts of mineral N produced in unamended soils ranged from 46 ppm in Harps soil to 71 ppm in Okoboji soil. With the exception of Judson soil, virtually all the mineral N produced in the untreated soils studied was nitrified. Judson soil evidently did not have enough nitrifying microorganisms, which resulted in accumulation of NH_4-N; 40% of the mineral N produced in this soil during 20 days of incubation remained in the NH_4-N form (this soil was stored under air-dry conditions for several weeks longer than the other soils).

The effects of the trace elements on nitrogen mineralisation varied considerably, however, Ag(I) and Hg(II) were the most effective [with Ag(I) $\geq$ Hg(II)] and Co(II), As(III), Se(IV), As(V), and W(VI) the least effective inhibitors of nitrogen mineralisation in the four soils studied (Table 3). Other trace elements that inhibited nitrogen mineralisation were Cu(II), Cd(II), Pb(II), Mn(II), Fe(II), Zn(II), Ni(II), Sn(II), Cr(III), Fe(III), Al(III), B(III), V(IV), and Mo(VI); their degrees of effectiveness varied among the four soils. It seems that the chemical and physical properties of the soils used, and perhaps the nature of N in these soils, have a marked effect

TABLE 2

EFFECTS OF TRACE ELEMENTS ON THE AMOUNT OF NITROGEN MINERALISED BY FOUR SOILS DURING A 20-DAY INCUBATION

Trace element		Webster		Judson		Harps		Okoboji	
Element	*Oxidation state*	NH_4-N	NO_3-N	NH_4-N	NO_3-N	NH_4-N	NO_3-N	NH_4-N	NO_3-N
		Nitrogen mineralised, μg of N/g of soil							
None		2	57	27	32	2	44	3	68
Ag	I	6	10	29	6	5	14	11	23
Hg	II	11	5	33	3	26	4	44	4
Cu		1	46	23	36	1	42	2	11
Cd		16	33	29	14	11	17	5	53
Pb		0	49	24	24	2	31	1	63
Mn		1	51	20	30	1	33	1	57
Fe		1	53	28	21	1	36	1	59
Zn		1	50	21	31	1	38	1	60
Ni		3	46	25	30	2	36	1	60
Sn		1	53	27	26	2	35	1	62
Co		1	51	25	33	1	42	2	65
Cr	III	19	28	28	22	0	40	1	53
Fe		19	34	28	21	1	35	1	56
Al		7	47	25	24	1	36	1	58
B		3	48	31	24	1	42	1	60
As		0	58	23	33	1	43	2	68
V	IV	1	53	16	35	1	40	1	60
Se		35	23	47	10	2	40	1	64
As	V	1	56	21	34	1	43	2	64
Mo	VI	1	52	5	41	1	35	2	31
W		1	53	7	50	1	41	1	64
LSD	($P < 0.05$)	2·0	1·1	0·8	3·6	0·8	1·2	1·0	1·2
	($P < 0.01$)	2·8	1·5	1·0	4·9	1·0	1·6	1·4	1·7

on inhibition of nitrogen mineralisation by trace elements. However, the average percentage inhibition by the mono- and di-valent ions of the four soils studied in decreasing order were Ag(I) > Hg(II) > Cu(II) > Cd(II) > Pb(II) ≥ Mn(II) > Fe(II) > Zn(II) = Ni(II) > Sn(II) > Co(II), and by the tri-valent ions were Cr(III) > Fe(III) > Al(III) > B(III) > As(III). Results obtained with Judson soil (Table 2) suggest that Mo(VI) and W(VI) enhanced nitrification, as is evident from the amounts of NH_4-N and NO_3-N produced in Mo- and W-treated samples compared with those obtained for the controls.

The results showed that Ag(I), Hg(II), and Cd(II) inhibited nitrification in the four soils studied, causing accumulation of NH_4-N (Table 2). It is interesting to note that while Ni(II), Cr(III), Fe(III), Al(III), B(III), and Se(IV) inhibited nitrification in the most acid (Weller) soil, only B(III) and Se(IV) inhibited nitrification in the Judson soil. No such inhibition by these elements was observed in the two calcareous soils (Harps and Okoboji).

TABLE 3
PERCENTAGE INHIBITION OF NITROGEN MINERALISATION IN SOILS BY TRACE ELEMENTS

Trace element		*Percentage inhibition of nitrogen mineralisation in soil specified*				
Element	*Oxidation state*	*Webster*	*Judson*	*Harps % Inhibition*	*Okoboji*	*Average*
Ag	I	73	41	59	52	56·3
Hg	II	73	39	35	32	44·8
Cu		20	0	7	82	27·3
Cd		17	27	39	18	25·3
Pb		17	19	28	10	18·5
Mn		12	15	26	18	17·8
Fe		8	17	20	15	15·0
Zn		14	12	15	14	13·8
Ni		17	7	17	14	13·8
Sn		8	10	20	11	12·3
Co		12	2	7	6	6·8
Cr	III	20	15	13	24	18·0
Fe		10	17	22	20	17·3
Al		8	17	20	17	15·5
B		14	7	7	14	10·5
As		2	5	4	1	3·0
V	IV	8	14	11	14	11·8
Se		2	3	9	8	5·5
As	V	3	7	4	7	5·3
Mo	VI	10	22	22	54	27·0
W		8	3	9	8	7·0

Quraishi & Cornfield (1971) studied the effects of 100 and 1000 ppm Cu(II) as CuO or $CuHPO_4$ on nitrogen mineralisation in a calcareous soil treated with 200 ppm N as dried blood and showed that Cu(II) caused 30% and 100% increases, respectively, in the amount of nitrogen mineralised during 21 days at 30°C. Our results indicated (Table 3) that the addition of 5 μmole Cu(II)/g of soil (300 ppm on a soil basis) as $CuSO_4$ inhibited nitrogen mineralisation in amounts ranging from 0% in the acid Judson soil to 82% in the calcareous Okoboji soil. None of the 19 trace elements studied stimulated nitrogen mineralisation in any of the four soils used.

Previous studies on the toxicity of arsenate and arsenite on nitrification in soils enriched with nitrifying organisms and perfused with NH_4Cl showed that $2{\cdot}5 \times 10^{-3}$M of arsenate is less effective than the same amount of arsenite (Quastel & Scholefield, 1951). Results obtained in the present work (Table 3) indicated that both As(III) and As(V) have very similar effects on nitrogen mineralisation, presumably because arsenite is oxidised to arsenate within the first few days of incubation.

The toxicity of Ag(I), Hg(II), Cu(II), and Cd(III) could be due to reaction of these ions with sulphydryl groups of the enzyme systems of the microorganisms

involved in nitrogen mineralisation of soils. Because no nitrite-N could be detected in any of the soils after 20 days of incubation, it seems that none of the trace elements studied inhibited *Nitrobacter* (the organism responsible for conversion of NO_2^- to NO_3^-), under the conditions of this experiment.

The small amounts of chloride and sulphate ions associated with the trace elements are unlikely to have stimulated or depressed nitrogen mineralisation in our experiments. Sindhu & Cornfield (1967) studied the effects of chlorides and sulphates of Na, K, Ca, and Mg, added to soils in amounts ranging from 0·1 to 2% (NaCl-equivalent), on nitrogen mineralisation in soils during three weeks of incubation at 30°C. They found that mineral N production was not affected when soils were treated with up to 1% of the different salts. The amounts of these anions added to the soils in the present study ranged from 0·018% for chloride to 0·048% for sulphate.

Our results indicate that accumulation of trace elements, such as the ones we tested, in soils could lead to a reduction in the amount of plant-available nitrogen derived from soil organic-matter.

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