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Effect of soil pH and ammonium and nitrate treatments on heavy metals in ryegrass from sludge-amended soil

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Summary

Ryegrass was grown, in pots, on sludge-amended soil which was adjusted to different pH levels and supplied with either ammonium sulphate or calcium nitrate.

The chemical form in which nitrogen was applied influenced the grass accumulations of Mn, Ni, Zn and Cd only when the difference in soil pH between the treatments, resulting from soil and plant factors, had developed to a sufficient extent to affect the availability of the contaminating metals for uptake by grass.

Introduction

Soil accumulations of heavy metals resulting from sewage sludge applications have been examined by Hemkes et al. (1980). Annual applications were, on a dry weight basis, nil (S0), 6 tonnes (S1) and 18 tonnes (S3) per ha of a metalliferous sludge, spread on established grassland plots.

After six years bulk samples of the 0-15 cm surface soils were collected for glasshouse studies. First, the effect of pH manipulation on grass accumulations of Mn, Zn, Ni, Cd, Pb, Cu, and Cr was examined (Dijkshoorn et al., 1981). In a second study (Dijkshoorn et al., 1982) the soil from the control plots (S0) was enriched with the pure salts of these metals in order to be independent of their particular abundance in the sludge. Treatments with ammonium and nitrate were then compared at different soil-pH levels.

This third study is concerned with the influence of pH in combination with either ammonium sulphate or calcium nitrate as the nitrogen fertilizer on heavy-metal concentrations in ryegrass from the sludge-amended soil S3. Attention was given to the elements Mn, Zn, Ni and Cd with concentrations well above the detection limit of the available procedure. Concentrations of Pb, Cu and Cr were either too low or too little responsive to changes in soil pH to yield instructive results.

New aspects were the higher buffering capacity occurring with the sludge-amended soil (S3) than the soil from the control plots, and sewage sludge as the source of polluting metals.

Material and methods

Design and execution were exactly similar to those of the preceding experiment (Dijkshoorn et al., 1982), but supplementary heavy metals were omitted in order to maintain their levels in the soil S3 as they were in the field plots with the highest loading rate of sludge.

The 16 treatments consisted of eight pH levels (including pH 6.5 of the original soil), ranging from about pH 4 to pH 7, for each form in which N was applied. Nitrogen was added as either ammonium sulphate or calcium nitrate at a constant rate of 10 mmol N per kg humid soil.

Each portion of the treated soils was evenly divided into 10 pots of 2 kg capacity of which eight were planted with perennial ryegrass, and two were kept bare. The transplants were defoliated (harvest 0 at zero time), and the ten pots per treatment were divided into two groups A and B. Group A yielded the successive harvests 1, 3 and 5 of grass 10, 20 and 20 days old respectively, and group B the successive harvests 2, 4 and 6 of 20-day old grass.

After each harvest the grass planted soils were sampled for analysis and then surface-fertilized with the nutrients in solutions containing the proper form of nitrogen, always at the rate of 10 mmol N per kg humid soil. The bare soils were also sampled but received no further dressings.

The pots were planted at the end of July. With the harvests 1 through 6 alternating between groups A and B, the whole experiment was sampled at 10-day intervals over a period of 60 days.

Soil pH adjustement and change with time

In Fig. 1 the initial pH values as measured at zero time are plotted against the amount of sulphuric acid solution or solid calcium carbonate (expressed as their equivalents of H ions or OH ions) used for pH adjustment. Where the curve is linear, the slope indicates that about 80 mmol H ions per kg were needed to decrease pH by one unit.

The sign of subsequent changes in pH depends on the form in which N is applied, its extent on the rate of nitrification of added ammonium, plant uptake of nitrogen, and the buffering capacity of the soil. Superimposed is a general alkaline drift after the initial pH adjustments.

Complete nitrification of the 30 mmol N per kg soil, given as ammonium sulphate in the three successive dressings, would liberate 60 mmol H ions per kg in balance with the sulphate anions and the generated nitrate anions as strong acids.

Added as calcium nitrate, its complete assimilation by the plants would release into the soil about 20 mmol OH ions per kg soil (Dijkshoorn, 1962).

On this basis, the balance in terms of H-ions would create a difference between the ammonium and the nitrate soils under grass of the order of 80 mmol per kg. This would account for a final difference in pH of 1 unit.

In Fig. 2 the final pH readings, made at harvest 6, are plotted as ordinates against the initial values. In the zone below pH 6 where the titration curve of the soil is lin-

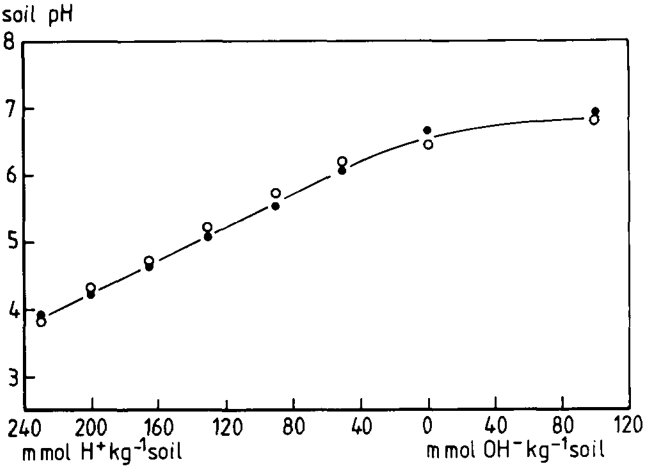

Fig. 1. Initial soil pH(H_2O) values at the time of planting. Abscissas: added sulphuric acid or calcium carbonate expressed as the equivalent amounts of H-ions or OH-ions per kg humid soil. Form of added N indicated by solid (nitrate) or open (ammonium) dots.

ear, the distance between the curves for nitrate and ammonium along the final pH axis is of the order of 1 unit indeed.

The plant and soil factors operate in a more complex manner when either mineral nitrogen is in excess of the plant requirements, or more advanced starvation of nitrogen developes between one harvest and the next (Dijkshoorn, 1973). Agreement with the present simplification can only be expected if the total supply equals its requirements for the growth. As will be shown below this came out to be approximately true.

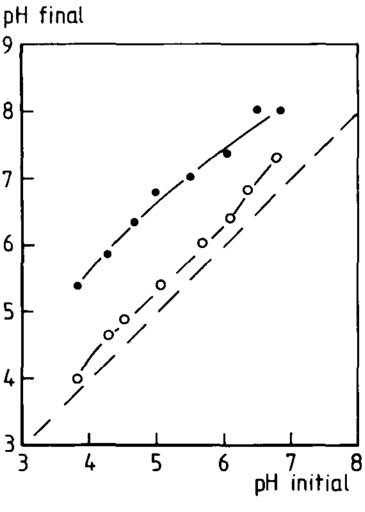

Fig. 2. Final pH(H_2O) in the grass-planted soils treated with calcium nitrate (solid dots) or ammonium sulphate (open dots), measured at harvest 6, 60 days after planting. Abscissas are the initial values of the eight pH treatments. The interrupted line is the diagonal between the axes.

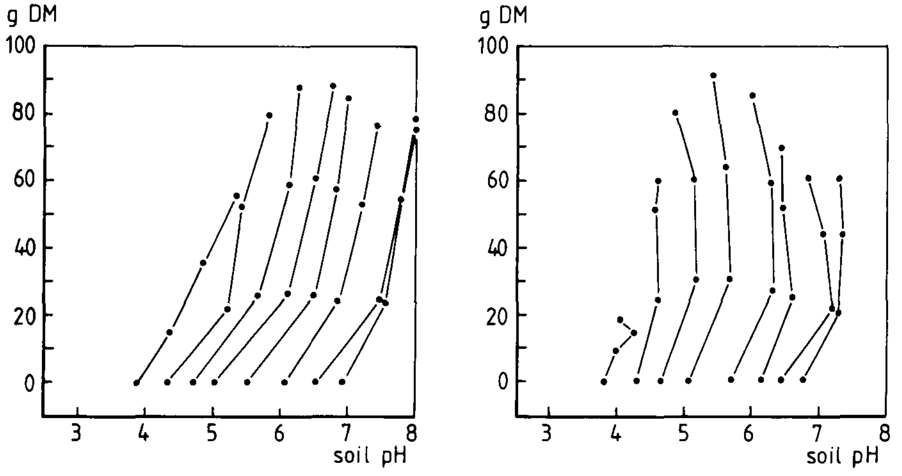

Fig. 3. Cumulative yields of successive harvests 0, 2, 4, and 6 from group B (g dry matter per 4 replicate pots) in relation to pH at harvest in the soil under grass. Graph on the left: nitrate series. Graph on the right: ammonium series.

Soil pH in relation to plant growth

In Fig. 3 the cumulative yields of the successive 20-day harvests 2, 4 and 6 from group B are plotted against pH of the grass planted soils as measured at harvest. The yield of harvest 0 was set at zero to symbolize the beginning of the new growth under the experimental conditions.

The alkaline effect of nitrate uptake is evident from the increase in pH between each harvest and the next.

The acidic effect of ammonium sulphate is masked by a small increase in pH during the first 20 days, followed by minor changes between harvests 2 and 4, until it appears between harvests 4 and 6. A more pronounced alkaline drift occurred with soil S3 than the soil from the control plots, the net result being here that also with ammonium sulphate the final pH was higher than the initial value (compare Fig. 2). Despite this complexity, the difference in final pH between the ammonium and the nitrate soils remained of the expected order of 1 unit.

The state in which N was absorbed

In many of the grass-planted soils ammonium and nitrate had disappeared at harvest. Only at the early harvest 1, and in the acid soil treated with ammonium sulphate which yielded little grass for uptake, mineral N remained residually in the soil.

In general about half the N supplied in the three successive dressings returned as herbage nitrogen in the three successive harvests of the shoots. This suggests that mineralization, summated over the duration of the experiment, contributed to a mi-

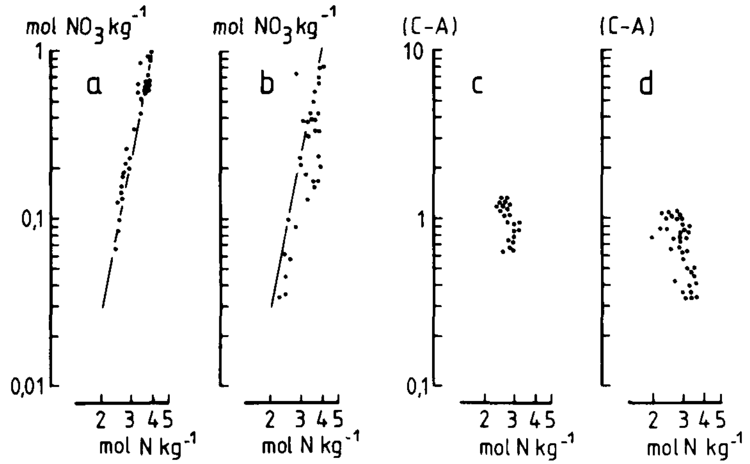

Fig. 4. Relation between nitrate-N and total N in the grass samples from the nitrate series (a) and from the ammonium series (b), and between the nutrient index (C-A) and the organic-N content in the grass from the nitrate series (c) and the ammonium series (d). Concentrations in mol N per kg dry matter (1 mol N = 14 g N). (C-A) in ion equivalents per kg dry matter.

nor proportion to fertilizer nitrogen. It should be recalled that grass fed with nitrate nitrogen always contains nitrate in the tops unless prolonged starvation leads to its complete metabolic consumption. When ammonium is applied, nitrate may accumulate in the tissue either as a result of nitrification in the soil or through the sparing action of ammonium consumption on pre-existing nitrate reserves in the tissue. So long as the tests for tissue nitrate are positive, no serious deficiency of nitrogen can have developed between one harvest and the next.

The slower the rate of nitrification, the greater is the likelyhood of plant uptake of applied ammonium. Following the arguments outlined earlier (Dijkshoorn et al., 1982), evidence of this was obtained from plant analysis.

The straight line relating nitrate in the grass to total nitrogen in the double log graph for the nitrate series (Fig. 4a) is redrawn in Fig. 4b, together with the data from the ammonium series. In the dot diagrams of Figs. 4c and 4d the nutrient index (C – A) in the grass samples is plotted against their organic-N content. Lower ratios of nitrate to total N, and of (C – A) to organic N among the individuals of the ammonium series indicated that, where nitrification was slow relative to the growth of the grass, more ammonium had contributed to the formation of plant nitrogen (Dijkshoorn, 1973).

Heavy metals in the soil

The tested soil S3 contained 158 mg Mn, 165 mg Zn, 31 mg Ni, 10 mg Cd, 63 mg Pb, 57 mg Cu, and 100 mg Cr per kg dry soil (Dijkshoorn et al., 1981). Repeated analysis gave similar values. The degree of contamination caused by the sludge can be judged by comparing the values under S3 and S0 in Table 1 of the reference.

Heavy metals in the grass

The results were similar in nature to those of the preceding experiment, and little would be gained by reproducing them all.

Cu was little responsive to pH. The Cr values were low and erratic because Cr in the soil was still below the high level needed for its breakthrough in the grass tops (Dijkshoorn et al., 1979). Cr in the grass remained near to the detection limit of the employed method. The same occurred with Pb.

The metals Mn, Ni, Zn and Cd produced reliable data and were highly responsive to soil pH. Therefore, these metals were chosen for presentation of the main effects.

Another selection is concerned with the harvests. Results will be presented for harvest 1 (first cut of group A, 10-day old grass), 2 (first cut of group B, 20-day old grass), 4 and 6 (second and third cut of group B, both 20-day old grass), under maintenance of the harvest numbers allocated to them in the sampling schedule (Dijkshoorn et al., 1982).

In Figs. 5, 6 and 7 the element concentrations in the grass in mg of the element per kg dry matter (DM) are plotted against pH in the soil under grass as measured at the time the harvest was made. Increases with the decrease in pH over the tested range were of the order of 25-fold for Mn, 20-fold for Ni, and 10-fold for Zn and Cd.

In the instance of harvest 1 soil pH was on the average only 0.1 unit higher with

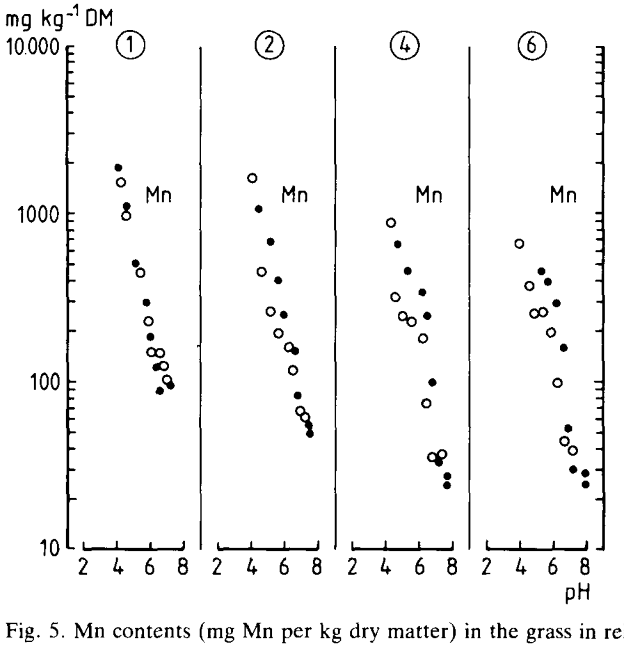

Fig. 5. Mn contents (mg Mn per kg dry matter) in the grass in relation to soil pH at harvest. The encircled figures are harvest numbers. Solid dots: with calcium nitrate. Open dots: with ammonium sulphate as the fertilizer.

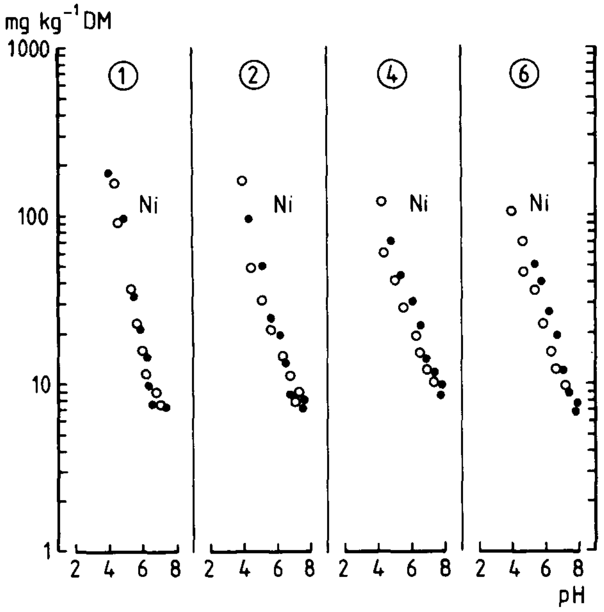

Fig. 6. As Fig. 5, but for Ni.

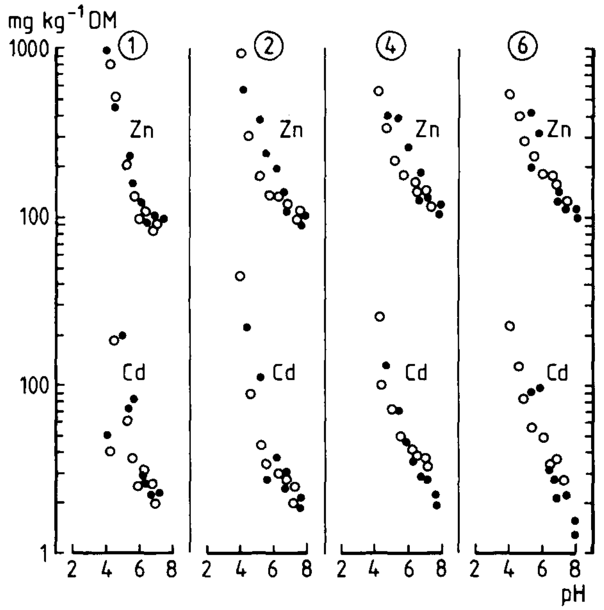

Fig. 7. As Fig. 5, but for Zn and Cd.

nitrate than with ammonium in the fertilizer. This divergence is negligible, and the data are consistent with a single curve for the relationship between grass metal and soil pH, irrespective of the form in which nitrogen was applied to and consumed by the plants.

At the time of harvest 2 the divergence in pH had developed to 0.4 units higher values with calcium nitrate, and at harvests 4 and 6 to 0.8 and 1.2 units higher pH values with calcium nitrate instead of ammonium sulphate in the fertilizer. Compared with some half-way state attained after the preceding harvests, the pH readings made at these harvests were larger overestimates with nitrate than ammonium fertilizer.

Again, this uncertainty in coordinating pH of the treatment is the cause of a systematic scattering. Where this occurs, the points for the nitrate series (solid dots) are situated a little higher along the pH scale than those for the ammonium series (open dots).

In the present experiment the deviation of the data from a single curve is smaller than in the preceding experiment, not exceeding 0.5 units along the pH scale. This is in line with the greater buffering capacity of soil S3 as a result of the sludge addition. Supplies and uptakes of N were of the same order, but the sludge-amended soil was more resistant to pH changes after the release or neutralization of similar amounts of acid by soil and plant factors than the control soil S0 employed in the preceding experiment.

The data support the conclusion that the change in soil pH is the sole source of the variance in grass accumulation of heavy metals associated with the form in which nitrogen is applied.

References

Dijkshoorn, W, 1962. Metabolic regulation of the alkaline effect of nitrate utilization in plants. *Nature, London* 194: 165-167.

Dijkshoorn, W., 1973. The role of organic acids in ion uptake. In: G. W. Butler & R. W. Bailey (Eds.), Chemistry and biochemistry of herbage, Vol. 2, pp. 163-187. London, New York, Academic Press.

Dijkshoorn, W., L. W. van Broekhoven & J. E. M. Lampe, 1979. Phytotoxicity of Zn, Ni, Cd, Pb, Cu, and Cr in three pasture plant species supplied with graduated amounts from the soil. *Neth. J. agric. Sci.* 27: 2411-253.

Dijkshoorn, W., J. E. M. Lampe & L. W. van Broekhoven, 1981. Influence of soil pH on heavy metals in ryegrass from sludge-amended soil. *Plant and Soil* 61: 277-284.

Dijkshoorn, W., J. E. M. Lampe & L. W. van Broekhoven, 1983. The effect of soil pH and chemical form of nitrogen fertilizer on heavy-metal contents in ryegrass. *Fert. Res.* 4: 63-74.

Hemkes, O. J., A. Kemp & L. W. van Broekhoven, 1980. Accumulation of heavy metals in the soil due to annual dressings of sewage sludge. *Neth. J. agric. Sci.* 28: 228-237.

Obituary

We are sad to report the death of Dr W. Dijkshoorn on 4 March 1983.

Since 1957, he has regularly contributed to our Journal. With this paper, a life active in plant nutrition comes to a close.

We have lost too an amiable colleague. The Editors