

Accumulation of heavy metals in the soil due to annual dressings with sewage sludge

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Accepted: 3 September 1980

Key words: heavy metals, sewage sludge, soil, leaching

Summary

In a long-term fertilizing experiment on permanent grassland, dressings of sewage sludge were applied at different rates. In 5 successive years 0, 6, 12 and 18 tonnes of sludge per hectare per year were applied on a dry matter basis. The accumulation of a number of heavy metals in the soil was measured to obtain a better understanding of the relation plant-soil. To gain some idea of the translocation of heavy metals to deeper layers, the soil was sampled to depths of 55 cm. The contents of Cd, Cu and Mo had distinctly increased into the 15-25 cm layer. Some heavy metals showed a slight increase in the 45-55 cm layer, but only at the highest sludge level.

Introduction

To limit as much as possible the pollution of surface waters various countries have paid much attention to the treatment of sewage. The number of sewage treatment plants is still growing and consequently the amount of sewage sludge. In the Netherlands 86 500 tonnes of sludge, on a dry matter basis, was produced in 1970. This had grown to 137 000 tonnes in 1974 (Brouwer, 1977) and to about 200 000 tonnes in 1978 (van Engers, 1980).

Sewage sludge, besides being a valuable fertilizer, is a good product for soil improvement, because of its high content of organic material (de Haan, 1976). It is therefore not surprising that the sewage treatment boards try to find markets for this sludge in agriculture and horticulture. However, transport costs limit its use to the direct neighbourhood of the treatment plants.

According to the most recent data (van Engers, 1980), in 1978 about half of the sludge produced, on a dry matter basis, was profitably used, for example in agriculture and horticulture, in public gardens and for the raising of areas. The remaining half was dumped.

The usefulness of sewage sludge is determined by its origin. Normally, sludge of purely domestic origin can be used without drawbacks, although even then only restricted use – as in the Netherlands – would be advisable. The contents of heavy metals in the sludge of industrial origin may be so high that use in agriculture and horticulture is not advisable. When used as a dressing or as a soil improver, the

crops grown on this sludge may show such high contents of heavy metals that consumption of these products may be hazardous to the health of man and animals.

Although sewage sludge is also used on grassland, little is known about the uptake of heavy metals by grassland plants and about the effect a nitrogen fertilizer application might have on this. Only few data are available on the translocation of the different heavy metals to lower soil layers.

This paper will only deal with the effect of annual dressings of sewage sludge on the contents of a number of heavy metals at various depths in the soil. In a subsequent paper a detailed study will be made of the uptake of a number of heavy metals by grassland plants.

Experimental design

In 1973, a long-term field experiment was laid out in permanent grassland on sandy soil (ca. 5 % organic matter, pH-KCl 5.9 in the layer 0-5 cm) on the experimental farm 'Droevendaal' at Wageningen. Each February, four different sewage-sludge dressings were applied, viz 0, 6, 12 and 18 tonnes/ha on a dry matter basis. In the tables and frequently also in the text the sludge treatments are indicated with S0, S1, S2 and S3, respectively.

Soil samples were taken every year before the sludge dressings. Initially, sampling was limited to the layers 0-5 and 5-15 cm. In view of the soil intake of grazing animals, the content of heavy metals in the top soil layer is important. From 1975 onwards the layer 0-5 cm was therefore divided into the layers 0-2.5 and 2.5-5 cm.

In Table 2 the contents for 1974 in the layers 0-2.5 and 2.5-5 cm have been estimated on the basis of these contents in the same layers in more recent years.

When based on the analyses higher contents were to be expected in deeper soil layers, these layers were included in the next sampling. Ultimately, the soil was sampled to a depth of 55 cm.

In the first two years only the contents of cadmium, lead, zinc and copper were determined in the soil samples and in the sewage sludge samples. From 1975 onwards the contents of nickel, chromium, cobalt, molybdenum, manganese and iron were included in the analyses.

Methods of analysis

After drying at 105 °C the sludge and soil samples were pulverized with a hammer mill with a 1-mm sieve. Except for molybdenum all the metals were analysed by atomic absorption (AAS). The Mo content was determined by a colorimetric method (Perrin, 1946) after destruction with nitric acid and sulphuric acid. The lower limit of this determination is 0.3 mg Mo per kg, proceeding from 3 g of sample.

In determining the other metals by AAS an extraction with nitric acid was used. The glassware was rinsed beforehand with nitric acid (4 mol/litre). The acids used (HNO₃ and HCl) were obtained from Merck (Suprapur). The salts required for the calibration curves were from BDH (AR). Double-demineralized water was used and in each series of determinations a blank was included. Of the samples 3 g were

weighed in a volumetric flask of 100 ml, adding 25 ml of 7 mol/litre HNO_3 . The mixture was left overnight and then heated and kept at 130 °C for four hours. After cooling, the solution was made up with water to 100 ml. The solution was filtered through an ash-free filter and 50 ml of the filtrate were transferred to a 100-ml beaker. This liquid was evaporated to dryness over a heating plate and the residue was treated twice with 2 ml of concentrated nitric acid and after this twice with 2 ml of concentrated hydrochloric acid. After each treatment the liquid was evaporated to dryness at 135 °C.

The residue was solved in 20 ml of 1 mol/litre HCl after which the solution was centrifuged and next analysed by atomic absorption. If necessary, the liquid was diluted to a concentration suitable for measurement. All these solutions were measured by a Varian AA-4 or a Varian AA-6 spectrophotometer. The AA-6 was equipped with a simultane background correction, with the AA-4 the background correction was carried out separately with a H_2 lamp.

A mixture of acetylene and air was used as a calibration flame. The flame (height, temperature and such) was adjusted to the various metals in such a way that no inter-element interference could occur.

Experiments with additions of possibly interfering metals to calibration lines did not show deviations.

In general the values measured were far above the determination limit under the prevailing conditions. The values below this limit have been indicated as smaller than (<) this limit value. When interpreting the values, it should be realized that those near the determination limit are less accurate than the higher values. The hammer mill almost certainly contributed to contamination of the soil samples. Measurements have shown that especially iron will cause some contamination due to pulverization. Determinations of the organic matter fraction (wet method) and the pH value of the soil were carried out according to standard specifications (Hofstee & Fien, 1971).

Results and discussion

The chemical composition of the sewage sludge used in the years 1973-1977 is shown in Table 1. The sludge used in 1973 and 1974 came from the same sewage treatment plant. In 1975 sludge of another plant was obtained for a number of succeeding years, therefore the contents of the various heavy metals in this sludge varied only slightly during the following experimental years.

Striking is that the Pb content in the sludge of the second plant was 3 to 5 times higher than that in the sludge used in the first two experimental years. The contents of cadmium, zinc and copper were at the same level in both sludge types.

Table 1 also gives the average composition of sewage sludge of domestic origin according to de Haan (1976). The contents of heavy metals in this sludge are distinctly lower than in the sludge used in this experiment. The Cd content, for example, was a factor 40 lower in the domestic sludge than the average Cd content in the sludge used in the field experiment. Table 2 shows the effect of the various sludge applications in 5 succeeding years, on the contents of heavy metals at various depths in the

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Table 1. Chemical composition of sewage sludge of different origins.

	Domestic + industrial (this trial)					Domestic (de Haan, 1976)
	1973	1974	1975	1976	1977	
Dry matter (g/kg)	300		252	245	262	
Organic matter (g/kg DM)	468	395	448	503	467	480
Nitrogen (g/kg DM)	22.5	17.7	24.1	24.4	23.4	30.8
Ca (g/kg DM)					40.7	33.0
pH-KCl	5.5	6.9	6.5	6.6	6.8	
<i>Metals (mg/kg)</i>						
Cd	370	215	316	349	327	8
Pb	450	333	1561	1693	1616	250
Zn	4941	3149	3953	4353	4055	1650
Cu	1446	722	1594	1724	1661	420
Ni			497	573	630	30
Cr			2274	2487	2086	130
Co			62	80	91	
Mo			144	168	117	
Mn			1071	1186	1151	830
Fe			36500	42200	43100	28700

soil. Of course, the contents in the top 2.5 cm have increased more considerably than in the deeper layers. This is important, because with animals grazing under adverse conditions upwards 10 % of the dry matter intake may consist of soil (Field & Purvis, 1964).

The increase in the contents of the different heavy metals in the topsoil layer is primarily dependent on the contents in the sludge in proportion to the initial contents in the soil. The mobility of the metal ion is also important, because this will determine the rate of penetration to the subsoil. A possible decrease in the contents in the topsoil is closely related to this. The S0 values mentioned in Table 2 are averages of the experimental years. To a depth of 15 cm this is an average of the initial situation in 1973 and of the S0 values found during the subsequent years. Because deeper layers were included in soil sampling during the experiment, the S0 values of these layers are based on fewer observations.

Table 2 shows that under the influence of the various sludge applications the Cd content in the soil increased considerably. In the 0-2.5 cm layer this value is already 7 times higher after one sludge dressing at a rate of 6 tonnes of dry matter per hectare per year. After 5 annual applications at the same rate the Cd content in this layer increased from 0.7 to upwards 15 mg per kg of dry soil. This is roughly 20 times the initial value. When the soil intake by grazing cattle is 5 % of the total dry matter intake, the Cd content in the ration would be some 0.3 mg per kg of dry matter higher after applying 6 tonnes of such sludge, only once. After 5 annual dressings at a rate of 6 tonnes of dry sludge this increase would be about 0.8 mg per kg of dry matter. The sludge dressings at rates of 12 and 18 tonnes of dry matter per year (in the table

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Cr (2.0)	0 - 2.5	21.3	79.5	90.7	103	131	137	151	193	231	230	222	290	399
	2.5- 5	16.8	32.4	56.3	55.7	92.9	45.4	102	96.4	168	68.5	142	156	256
	5 -15	13.5	18.3	21.1	20.6	27.2	17.7	25.7	26.2	48.6	18.0	31.3	32.9	52.6
	15 -25	11.9	12.4	12.2	12.0	13.4	15.9	15.9	12.3	13.4	17.6	17.6	13.0	14.1
	25 -35	7.2	9.3	9.3	7.3	7.3	7.6	7.8	7.6	7.8	8.4	8.4	8.4	7.7
35 -45	6.5	7.5	7.5	6.8	6.8	7.8	7.8	7.8	7.8	7.7	7.7	7.7	7.7	
45 -55	6.6	6.6	6.6	6.8	6.8	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.5	
Co (2.0)	0 - 2.5	<2.0	<2.0	<2.0	3.6	3.3	<2.0	2.2	5.5	6.5	<2.0	2.3	8.6	12.4
	2.5- 5	<2.0	<2.0	<2.0	2.2	2.2	<2.0	<2.0	2.7	3.8	<2.0	<2.0	3.3	5.2
	5 -15	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	2.2
	15 -25	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
	25 -35	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
35 -45	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	
45 -55	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	
Mo (0.3)	0 - 2.5	0.3	0.6	1.3	2.3	2.8	0.4	2.1	4.2	5.4	0.7	3.2	7.5	7.4
	2.5- 5	<0.3	<0.3	0.8	1.5	1.9	0.5	1.4	2.2	3.5	0.3	1.9	3.6	5.0
	5 -15	<0.3	<0.3	0.5	0.5	0.6	<0.3	0.7	0.9	1.7	<0.3	1.2	1.5	2.0
	15 -25	<0.3	<0.3	0.7	<0.3	<0.3	<0.3	0.9	0.3	0.5	<0.3	0.8	0.4	0.8
	25 -35	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	0.3
35 -45	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	0.4	
45 -55	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	
Mn (1.0)	0 - 2.5	243	220	198	307	374	216	212	335	422	242	243	421	555
	2.5- 5	169	133	160	178	242	139	172	188	278	133	188	206	302
	5 -15	138	168	142	140	154	151	133	136	158	138	133	134	152
	15 -25	119	112	112	114	131	118	118	116	123	131	131	125	128
	25 -35	50.6	50.1	53.7	50.1	53.7	49.6	49.6	57.2	50.1	50.1	50.1	60.0	60.0
35 -45	37.6	35.4	35.4	35.4	35.4	41.4	41.4	41.4	41.4	40.8	40.8	40.8	40.8	
45 -55	27.6	30.8	30.8	30.8	30.8	30.4	30.4	30.4	30.4	33.3	33.3	33.3	33.3	
Fe** (0.001)	0 - 2.5	4.31	4.31	4.52	6.04	6.70	4.64	4.93	7.34	8.34	5.49	5.82	9.41	11.1
	2.5- 5	4.26	3.88	4.27	4.73	5.75	4.04	4.53	5.74	6.77	3.80	5.18	6.19	7.52
	5 -15	4.06	4.37	4.39	4.31	5.01	4.17	3.98	4.45	5.05	3.80	3.93	4.62	4.75
	15 -25	4.57	3.83	3.83	4.58	4.82	4.14	4.14	4.64	4.44	4.14	4.14	4.68	5.00
	25 -35	4.73	5.17	5.17	5.17	4.41	5.58	5.58	4.74	4.74	4.98	4.98	5.08	5.08
35 -45	4.07	4.10	4.10	4.10	4.10	4.12	4.12	4.12	4.12	4.36	4.36	4.36	4.36	
45 -55	4.28	4.10	4.10	4.10	4.10	4.35	4.35	4.35	4.35	5.01	5.01	5.01	5.01	

* S0, S1, S2, S3: 0, 6, 12 and 16 tonnes of dry matter of sludge applied per ha per year, respectively.

** Expressed in g/kg dry soil.

S2 and S3, respectively) will increase the Cd contents in the 0-2.5 cm layer to 31.4 and 57.2 mg per kg of soil by the end of the experiment. At the lowest sludge dressing cadmium penetrated to a depth of 25 cm in the soil profile. In the other two sludge treatments the penetration of cadmium was somewhat deeper, although this was hardly demonstrable.

The Pb contents in the 0-2.5 cm layer showed a relatively smaller increase than that of cadmium. The supply of Cd with the sludge was the highest with respect to its content in the soil. After the fifth sludge dressing in 1977, the Pb contents in the treatments S1, S2 and S3 roughly were 80, 140 and 250 mg kg of soil. This is 3.5, 6 and 11 times the initial content in the soil, respectively. During the experimental period the lead did not penetrate deeper into the soil profile than 20-25 cm, neither at the highest sludge dressings.

The Zn contents in the top 2.5 cm of soil, after one dressing of sludge at the three rates, increased from 26.4 to 91.9, 141 and 230 mg per kg of dry soil, respectively. By the end of the experiment the Zn contents in the same soil layer had increased to 234, 439 and 757 mg per kg of soil. The table shows that a distinct effect of the three sewage sludge dressings could be observed on the Zn content in the 15-25 cm layer. Although there is a slight difference between the 0 treatment and the three sludge levels in deeper layers, the difference in the effect between these sludge dressings is less distinct.

After one year the Cu content at the lowest sludge dressing in the 0-2.5 cm layer was more than 3 times the initial content to almost 20 mg per kg of soil. After 5 years the content in the top 2.5 cm of soil of the same treatment had increased to almost 70 mg per kg of soil. In the treatments S2 and S3 in the same period the Cu contents in the same layer increased to 138 and 265 mg per kg of dry soil. In the 2.5-5 cm layer the Cu contents in the treatments S1, S2 and S3 had increased to approximately 50, 100 and 150 mg per kg of soil, respectively. In the 0-5 cm layer, normally sampled in grassland, the Cu contents at the different sludge levels had increased to almost 60, 120 and 200 mg per kg of soil. Up to a depth of 25 cm the Cu contents increased distinctly. This applies to all the sludge treatments. In the deeper layers the difference between sludge dressings or no sludge is still observable, but the difference between the rates applied is only slight.

The contents of chromium, cobalt, molybdenum, manganese and iron were not determined in the years 1973 and 1974. The content of nickel could only be assessed reliably in 1978.

After 5 years the Ni contents in the 0-2.5 cm layer were in the sludge treatments S1, S2 and S3 30.5, 56.8 and 101 mg per kg of dry soil, respectively. This is almost 8.5, 16 and 28 times the initial content which was 3.6 mg Ni per kg of soil. Table 2 shows that sludge application increased the Ni contents down to the 15-25 cm layer. A distinct difference between the various sludge treatments with respect to the Ni content does not extend beyond the 5-15 cm layer.

A distinct increase in the Cr contents due to the different sewage sludge treatments can be seen down to the 15-25 cm layer. Although even at greater depth there seems to be a slight effect of the sludge dressings on the Cr content, the differences between the sludge levels are not distinct. The effect of the sludge dressings on the

Co content is only observable in the top 5 cm layer of the soil.

The effect of the different sludge dressings on the Mo content still shows variation down to a depth of approximately 25 cm. Only the highest sewage sludge rate seems to have a demonstrable effect on the Mo content at greater depth. However, this is not beyond 45 cm.

With respect to the heavy metals previously discussed, the contents of manganese and iron in the 0-2.5 cm layer only show a slight rise due to the sludge dressings. This is not surprising, because the differences between the contents of these metals in the sludge used and those in the soil are much smaller than for the other metals discussed in this paper. Due to the sewage sludge dressings the pH value in the top 5 cm layer of the soil increased to 7 and even somewhat higher, depending on the rate of the dressing. In the S1 treatment the contents of cadmium, zinc and copper in the 0-5 cm layer already attained such high values that decreasing the pH to a more normal value for grassland might be accompanied by a growth retardation in grasses and clover (Dijkshoorn et al., 1979).

Fig. 1 shows the relation between the contents of heavy metals at various depths in the soil after 5 annual sludge dressings at a rate of 18 tonnes of dry matter per

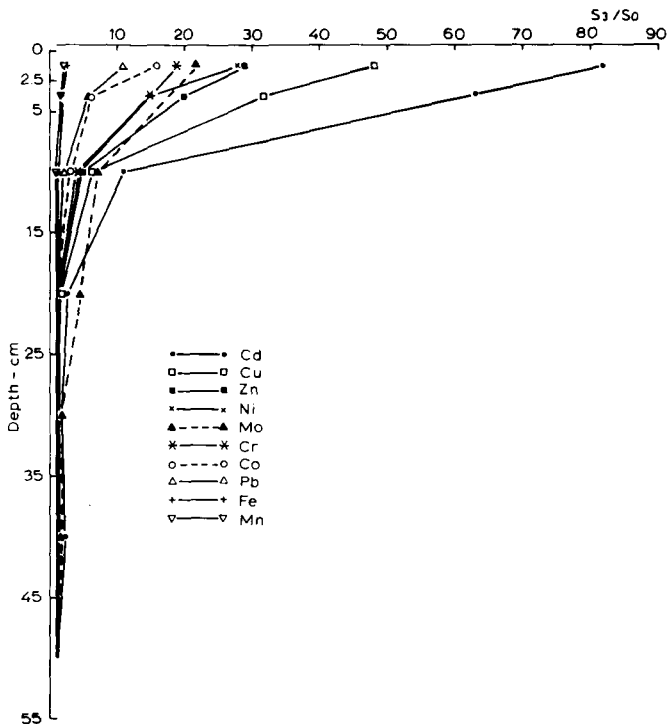


Fig. 1. Relation between the content of heavy metals in the treatment with the highest sludge dressing (S3) and the 0 treatment (S0) at various depths in the soil after 5 annual sludge dressings of 18 tonnes of dry matter per ha.

hectare per year and the 0 treatment (S3/S0). The great scatter in the S3/S0 ratio of the various heavy metals in the top 2.5 cm layer of the soil is evidently due to the great differences in the supply of heavy metals with the sewage sludge with respect to their initial contents in this soil layer, before the sewage sludge dressings. It was to be expected that the scatter would remain great in the next 2.5 cm layer. It is striking that the S3/S0 values for most of the heavy metals discussed have already dropped to the lowest possible value (= 1) in the 15-25 cm layer. This indicates only a slight translocation of the metal ions from the top layer, which may have been caused by the pH value which increased under influence of the sewage sludge dressings. It is also in agreement with the findings of many other authors reporting decreased uptake of heavy metals by the crop and so a lower mobility of these metals with a neutral pH value than with a low pH value of the soil.

The contents of cadmium and copper show the sharpest rise in the top soil layer. Both metals have also penetrated to a greater extent to deeper layers of the soil profile. Whether the trend in the Cd curve at greater depth reflects the actual situation is not quite clear. It is in accordance with Harmsen (1977) who assumed on the basis of differences in the contents of heavy metals in the soil profile that the mobility of cadmium ions might be greater than those of zinc and lead.

Since for molybdenum and cobalt the trend in the S3/S0 values from the 2.5 cm soil layer to deeper layers could not be determined reliably, they are indicated by an interrupted line in the figure. However, apparently the contents of molybdenum have increased more sharply than those of the other metals between 15 and 45 cm. This could mean greater mobility of the molybdenum ions in the top soil, brought about by the almost neutral pH value in this layer. The following argument may also indicate greater mobility. The actual increase in the contents of the heavy metals cadmium, lead, zinc, copper and molybdenum in the 0-5 cm soil layer of the S3 treatment was compared with the increase expected on the basis of their contents in the sewage sludge used. Proceeding from these contents and the initial contents in the soil, the metals were arranged according to the decrease in their increasing contents in the 0-5 cm layer: Mo, Cd, Cu, Zn, Pb. However, the actual order was: Cd, Cu, Mo, Zn, Pb. The increase in the Mo content in the 0-5 cm layer was lower than expected on the basis of the supply with the sludge. In view of the greater mobility of the molybdenum ions assumed before, probably more molybdenum than other metals penetrated to deeper layers. The trend in the Mo curve in Fig. 1 also reflects this to some extent. Moreover, more molybdenum was supplied with the sludge in a period of 5 years than could roughly be calculated on the basis of the increased Mo contents in the 0-55 cm layer of the soil profile. For the other heavy metals in the series the reverse was found. At the depth to which the soil was sampled ground water was present, which could imply that a part of the molybdenum supplied with the sewage sludge leached to the ground water.

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