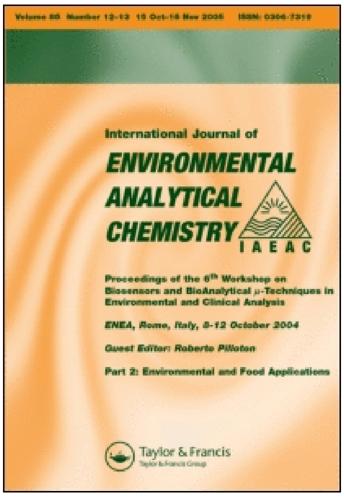

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M. L. Berrow[a]; J. C. Burridge[a]
[a] The Macaulay Land Use Research Institute, Aberdeen, Scotland, UK

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PERSISTENCE OF METAL RESIDUES IN SEWAGE SLUDGE TREATED SOILS OVER SEVENTEEN YEARS

M. L. BERROW and J. C. BURRIDGE

The Macaulay Land Use Research Institute, Aberdeen, Scotland, AB9 2QJ, UK

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Results from two long-term sewage sludge experiments conducted on different soil types are presented. Sewage sludges highly contaminated with Cr, Cu, Ni or Zn and a relatively uncontaminated sludge were applied at both sites at the same rates and metal contents in 1968. The Cr-rich sludge also had a high Cd content. Plot soils were sampled in 1972, 1976 or 1977, 1981 and 1985 and total and extractable metal contents determined. Metals added in sewage sludge may change their form but persist in soils in an extractable and plant available form for many years. There is little difference in soil extractable contents or plant uptake of Cu and Zn whether sludge is applied as one single application or as its equivalent in four separate annual applications of one quarter the amount. The percentages of the total chromium contents extractable by both EDTA and acetic acid were small and this was reflected in a low uptake of this element by pasture herbage species (<0.3 mg Cr/kg DM).

KEYWORDS: Sewage sludges, heavy metals, persistence, extractable forms, metal residues.

INTRODUCTION

Two long-term sewage sludge experiments conducted at Luddington and Lee Valley Experimental Horticulture Stations, about 100 km apart and on different soil types, have been monitored in conjunction with the Agricultural Development and Advisory Service. In 1968 the same sewage sludges, highly contaminated with Cr, Cu, Ni or Zn and a "relatively uncontaminated sludge" were applied at both sites at the same rates and metal contents. Treatments were replicated four times. The Cr-rich sludge also had a high Cd content of 75 mg/kg. Plot soils were sampled in 1972, 1976 or 1977, 1981 and 1985 and their contents of total and extractable metals determined. Horticultural crops were grown annually for the first 4 years and since 1972 the plots have been maintained under a grass/clover ley. Herbage was sampled in 1976 or 1977 with special care to avoid soil contamination. Details of the experimental design, treatments and some earlier results have been reported for Luddington by Berrow and Burridge (1980)[1] and for Lee Valley by Burridge and Berrow (1984).[2] Uptake of metals by grass and clover species and amounts of metals extractable from the soils by a range of extractants have also been reported by Berrow and Burridge (1985).[3]

MATERIALS AND METHODS

Soil samples were taken to a depth of 15 cm from the field plots (2x4 m) using a

Table 1 Persistent effects of applying 125 t/ha of four contaminated sewage sludges in 1968 on 0.05 M EDTA-extractable metal contents in soils at Luddington and Lee Valley, as mg/kg in dry soil (0–15 cm)

	Zn	*Cu*	*Ni*	*Cr*	*Cd*[b]
LUDDINGTON					
1968[a]	7.6	5.8	2.5	0.12	0.18
1972	510	360	84	3.4	3.2
1976	370	240	77	4.4	3.0
1981	320	280	53	3.4	2.5
1985	250	220	42	4.3	1.8
LEEVALLEY					
1968[a]	4.7	6.9	3.3	0.28	<0.10
1972	690	220	105	4.7	4.7
1977	620	200	140	5.2	4.6
1981	630	230	105	4.2	4.3

[a]Before sludge application
[b]Cd in Cr-rich sludge

pot auger. At least 25 cores were taken from each plot and bulked to provide a representative sample, Berrow (1988).[4] Total metal contents in the finely ground soils were determined by boiling under reflux with aqua regia for two hours and analysis of the filtrate by atomic absorption spectrophotometry as described by Berrow and Stein (1983).[5] Metals extractable by 0.05 M EDTA from the <2 mm fine soils were determined following extraction for 1 h (15 g soil + 75 ml extractant) as described by Ure and Berrow (1970).[6] The soils were also extracted overnight with 0.43 M (2.5%) acetic acid (20 g soil + 800 ml extractant), filtered, evaporated to dryness, oxidised with conc HNO_3 and the residue taken up in hydrochloric acid before filtration and making up to volume (200 ml) in 0.1 M HCl. The metals were then determined by atomic absorption spectrophotometry using the procedure and analysis lines quoted by Berrow and Stein (1983).[5]

RESULTS

High levels of both 0.05 M EDTA and 0.43 M acetic acid-extractable Cd, Cr, Cu, Ni and Zn persist in the soils at both sites for at least 13 years and at Luddington for at least 17 years. This is shown in Table 1 and Figure 1 which report the data for EDTA-extractable metals in soils treated with 125 t/ha of the sludges having the higher metal contents. The 1968 values in Figure 1 for the year of sludge application are calculated from the sludge analyses reported in references 1 and 2, and not by soil analysis. For each element there are similar changes with time at both sites and these are relatively small particularly from 1976 onwards. The differences in extractable levels for any one element in the same year of sampling at the two sites are probably related to differences in soil characteristics. The acetic acid-extractable metal contents show similar effects (Table 2) and confirm the striking persistence of metals in extractable form over 17 years.

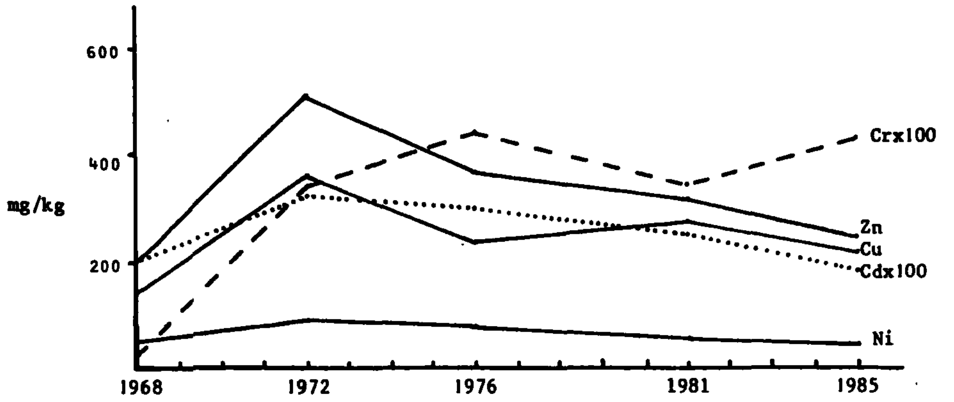

Figure 1 0.05 M EDTA-extractable metals—LUDDINGTON

Table 2 Effect on topsoil contents of adding 125 t/ha of four contaminated sewage sludges at Luddington in 1968, as mg/kg in dry soil (0–15 cm)

	Zn	*Cu*	*Ni*	*Cr*	*Cd*[b]
TOTAL CONTENT					
1968[a]	50	20	15	30	0.5
1972	650	420	285	350	3.9
1981	420	320	110	255	2.5
ACETIC ACID-EXTRACTABLE					
1968[a]	8.2	1.7	2.2	0.14	0.18
1972	460	180	80	5.1	3.8
1976	450	180	83	4.9	3.1
1981	330	140	46	3.0	2.1
1985	250	105	43	2.1	1.4

[a]Before sludge application
[b]Cd in Cr-rich sludge

The proportions of the total metal contents extractable by EDTA and by acetic acid in the soils sampled in 1972 and 1981 were calculated for each treatment and these show a remarkable consistency. Acetic acid extracts water soluble and hydrogen ion-exchangeable forms at pH 2.5. The 0.05 M EDTA extracts both water soluble and exchangeable and also organically complexed forms. There is little or no carbonate-bound fraction present as the pH's of the soils are 5.8 and 6.5, respectively, with no free carbonate present. The percentage extractability for each metal varied with the amount of metal added and was generally greatest for the most highly contaminated soils. The percentage extractabilities averaged over the 14 sludge treatments at each site are shown in Table 3. These data show:

i) That there has been little or no change in the extractable forms of these five metals between 1972 and 1981. Any changes in total metal contents (Table 2) have been closely reflected in corresponding changes in extractable contents.

Table 3 Relative extractability. Percentage of total metal contents extractable by EDTA and by acetic acid in soils sampled in 1972 and 1981 averaged over 14 sludge treatments at each site

	Cr	*Cu*	*Ni*	*Pb*	*Zn*
1972					
EDTA Luddington	1.1	66	33	52	49
EDTA Lee Valley	2.4	65	40	37	58
HOAc Luddington	1.5	25	34	6.2	54
HOAc Lee Valley	1.5	22	35	4.5	54
1981					
EDTA Luddington	1.8	64	34	62	54
EDTA Lee Valley	2.4	80	38	51	61
HOAc Luddington	1.3	22	30	6.8	54
HOAc Lee Valley	1.1	17	31	3.9	57

ii) That EDTA extracts approximately the same percentages of the total contents from both soils in 1972 and 1981 for each individual element.

iii) That EDTA extracts much more Cu and Pb from the soils than acetic acid indicating that these two elements remain largely in organically complexed form.

iv) That the percentages of the total Cr contents extractable by both extractants are similar and small (1 to 2%).

Total carbon contents determined in the soils 8 years after sludge application showed that at Luddington 62% and at Lee Valley 90% of the organic matter added in the sludge had been lost. The data suggested that following the decomposition of the sludge organic matter the metals have taken up other organic forms, possibly similar in the two soils. The amounts of metals extracted by EDTA remained as high as 80 to 90% for Cd, Cu and Zn, around 50 to 60% for Ni and Pb but only up to 2 to 3% for Cr.

It has already been demonstrated that the Ni and Zn contents of pasture species are approximately linearly related to the amounts of these elements extractable from the soils, Berrow and Burridge (1980)[1] and Burridge and Berrow (1984).[2]

Table 4 compares the effects of single applications of 125 t/ha with those of four annual applications of 31 t/ha on the EDTA-extractable metal contents at Luddington. The values for sludges applied at 125 t/ha but with only half the metal contents are also shown. There was little difference in EDTA-extractable values over the years 1972 to 1985 resulting from the different methods of application of the same amount of sludge and this was reflected in the Cu and Zn contents of timothy grass sampled in 1976, Berrow and Burridge (1980).[1]

CONCLUSIONS

Metals added in sewage sludge persist in soils in an extractable and plant-available form for many years.

Table 4 Effect of single applications of 125 t/ha or four annual applications of 31 t/ha at Luddington as mg/kg extractable by 0.05 M EDTA

	ZINC			*COPPER*		
	single		*annual*	*single*		*annual*
	H	*L*		*H*	*L*	
1968	7.6			5.8		
1972	510	230	510	360	150	280
1976	370	140	410	240	115	180
1981	316	150	410	280	135	220
1985	250	96	305	220	91	180

	NICKEL			*CHROMIUM*		
	single		*annual*	*single*		*annual*
	H	*L*		*H*	*L*	
1968	2.5			0.12		
1972	84	41	50	3.4	1.3	2.7
1976	77	50	62	4.4	2.0	3.3
1981	53	32	39	3.4	2.0	2.2
1985	42	29	33	4.3	2.3	3.1

H = Higher content of principal contaminant
L = Lower content (L = 0.5H)

There is little difference in soil extractable contents or plant uptake of Cu and Zn whether sludge is applied as one single application or as its equivalent in four separate annual applications of one quarter the amount.

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