LIMING EFFECTS ON THE YIELD AND COMPOSITION OF PERENNIAL RYEGRASS TREATED WITH SEWAGE SLUDGE CONTAMINATED WITH HEAVY METALS [1]

by

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Summary

Up to 12% of the dry matter of a sewage containing 0.65% Zn, 0.20% of Ni, 0.5% Cu, and 0.41% Cr was mixed with an acid loamy sand limed to give a pH range from 4.6 to 7.0 and cropped with ryegrass in pots. The results obtained were similar to a previous experiment (2). Yields of three cuts of grass were reduced by the largest amo unts of sludge at soil pH's less than 6. However, grass yields were increased by medium amounts (8%) of sludge at soil pH more than 6. The increases in yield were caused by increased supplies of N, P, Mg, and S from the sludge.

Concentrations of more than 300 ug/g Zn, and 200 ug/g Ni in the grass dry matter were associated with lowest yields. The treatments had only small effects on Cu concentrations.

Acetic acid-extractable metals in the cropped air-dried soils were increased by the maximum sludge addition to 300 mg/Kg Zn, 100 mg/Kg Cu, 67 mg/Kg Ni, equivalent to 30% of the total applied Zn, 17% of Cu, and 28% of Ni.

The pH of the sludge (5.0) significantly affected soil pH. Sludge used on agricultural land should be adjust to pH 7.0 before spreading so as to minimize any possible heavy metal toxicities to crops.

Introduction

Sewage sludges produced in Britain usually contain 40 per cent organic matter, 2.4 per cent N, 1.3 per cent P along with a wide range in concentrations of trace elements. There is a disposal problem for the sludge and increasing pressure on farmers to use the sludge as a fertilizer on agricultural land. However, a serious disadvantage is that it often contains toxic metals which, if allowed to accumulate to a dangerous level in the soil, have a permanent harmful effect.

Berrow and Webber (1) analysed 42 sewage sludges from representative areas throughout Englagd and Wales and showed that Zn, Cu, and Ni appeared to be the elements most likely to give rise to a toxicity problem.

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*All the experimental work was conducted in the Department of Chemistry, Rothamsted Experimental Station, England.

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The toxicity of metals in sewage sludge to crops depends very greatly on the pH value of the soil. Recently results showed that sludge used on agricultural land should be adjusted to pH 7.0 before spreading, otherwise, the yield of perennial ryegrass reduced by large applications of sewage sludge contaminated with zinc, copper, nickle, and chromium (2).

This pot experiment was set up to obtain further information on toxic levels of heavy metals in grass when yields are reduced and to test the effect of liming and large application of a heavily contaminated sludge on perennial ryegrass yield and composition. A more sandy soil from Woburn Experimental Station was used as a contrast to the clay-loam from Rothamsted Experimental Station used in the previous work.

The pot experiment

The design of this experiment was the same as in the previous report (2), but an acid loamy sand from Woburn was used (Table 1.). 400 g of sieved ($<$2mm) soil was mixed with appropriate amounts of sludge, calcium hydroxide, and poly-ethylene chips (see below), in a mechanical mixer, the mixture was then placed in 12 cm diameter pots whose weights had been equalized with quarts. Different amounts of polyethylene chips ($>$3mm) were added according to the amounts of sludge used so that the volumes of the contents were equal for all pots.

The treatments were as follows:

	Sludge (wet) g/pot	Polyethylene chips g/pot	Dry sludge additions % soil
S_0	0	120	0
S_1	40	80	4
S_2	80	40	8
S_3	120	0	12

The sludge treatments were combined factorially with none, 25, 50, and 100 mg/pot Ca (L_0 to L_3). There were 3 replicates of each treatments, two were cropped, one was left uncropped.

All 48 pots were given 50 mg P and 65 mg K in solution as KH_2PO_4 to the surface, than 250 mg of S23 perennial ryegrass (Lolium perenne) seed was planted. To avoid dust contamination, the pots were kept in a controlled environment (Saxcil) cabinet and watered (by weighing) with deionized water twice daily to 80% of water holding capacity. A 16 h day was used with day/night temperature of 20°C/15°C and 70/90% relative humidities.

During growth, the following additions were made to each pot:

Date	Days after planting/cutting	Chemical mixture $Ca(NO_3)_2+NH_4NO_3$	KNO_3+MgSO_4
9/May	8 days after planting	40 mg N/pot	
13/May	12 days after planting	60 mg N/pot	
29/may	On the same day of 1st cutting	40 mg N/pot	
3/June	5 days after 1st cutting	60 mg N/pot	
9/June	11 days after 1st cutting		30 mg N+20 mg Mg+80 mg K
19/June	On the same day of 2nd cutting	100 mg N/pot	

The sewage sludge was an anaerobically digested sludge as used in the previous experiment. Some analyses of the sludge are given in Table 1.

Table 1. Analyses of the soil and sewage sludge

Soil		
Texture	pH (water)	pH ($CaCl_2$)
Loamy sand	4.50	4.05

Sewage sludge							
Dry matter %	pH (water)	Ni	Cu % in D. M.	Zn	Pb	Cr	Mn
39	5.0	0.20	0.50	0.65	0.1	0.42	0.05

N	P	K	Ca	Mg	S
2.78%	1.80%	0.09%	2.96%	0.31%	1.24%

Analytical methods

The ryegrass samples were dried overnight at 80°C and ground <1 mm. For the zinc, copper and nickel and sulphur analyses, sub-samples were mixed with known amounts of cellulose powder and further ground in a tungsten carbide disc mill. Pellets of the mixtures made in a 31 mm die, using 10 tonnes pressure were analysed in a Philips 1540 X-ray fluorescence spectrometer (XRF). In the ryegrass and sludge dry matter, nitrogen was determined colorimetrically by the indol phenol-blue methcd after digesting with concentrated H_2SO_4 and catalyst ($K_2SO_4+CuSO_4$), phosphorus by a molybdenum blue method, K by flame photometry, Ca, and Mg by atomic absorption spectrophotometry on HCl extracts of the plant ash.

Soil and sludge pH's were measured in 1:2.5 soil water or soil:0.01 M $CaCl_2$ suspension using a combined calomel/glass electrode. Zn, Ni, and Cu in the soil after cropping were measured by extracting 5.0 gm samples with 200 ml of M acetic acid, shaking for 30 min. at 25°C, filtering and determining the metals in the extracts by atomic absorption spectrophotometry using standards made up in acetic acid.

Results

Grass yields

The dry matter yields of tops of the three cuts are shown in Figure 1. In all cases, without liming, the yields of ryegrass decreased as the rate of sludge increased. With most lime, yields were also reduced by maximum rate of sludge (S_3), probably partly because the addition of more sludge decreased the soil pH and reduced the liming effect. Incorporation of 4% sludge dry matter (S_1) in the soil increased yield at all levels of liming except at the first cut where yield showed a slight decrease at the lowest liming level (L_1). It seems to be due to the releases of major nutrients from the sludge during crop growth as shown in Table 2.

Grass analyses

1. Heavy metals (Zn, Ni, and Cu)

Concentrations of Zn, Ni, and Cu in the grass dry matter from the differently treated pots are shown in Figure 2.

Zn concentrations decreased as the rate of lime increased. These decreases were from about 60 to 20 ug/g in grass grown in soil alone and from 1000 to 300 ug/g in grass given the maximum rate of sludge. In most cases, concentrations of Zn were increased about fifteen fold by the sludge additions. The relationship between dry matter yields of ryegrass and Zn concentrations in the tops (Figure 3) showed that lower yield of grass usually associated with Zn concentrations of more than 300-350 ug/g dry matter.

The Ni determinations showed a similar pattern to those for Zn except that the concentrations in the dry matter of ryegrass was somewhat lower than those of zinc at successive cuts. The Ni content of the grass was increased by sludge addition from 20 to 700 ug/g in the soil without liming and from about 10 to 170 ug/g in the soil received the maximum rate of lime. It was about thirty-five fold for the former and seventeen fold for the latter. The relationship betwean yield of grass and its Ni concentration in the tops was also negatively correlated (Fig. 3). The higher yield of ryegrass usually contained less than 200-250 ug/g dry matter.

Concentrations of Cu in the grass were less affected by the treatments than Ni or Zn, but they do shown somewhat increase in Cu concentration from the sludge addition at all cuts in most cases. The correlation coefficient (−0.1714) between yield and Cu concentration in the tops was negative and insignificant.

2. Major nutrient concentrations (N, P , K, Ca, Mg, & S)

Mean analyses for all three cuts in Table 2 showed that major nutrient concentrations in ryegrass treated without sludge were fairly constant and un-affected by liming. However, with sludge they were significantly decreased by liming, particularly N, K, Ca, and S.

Concentrations of major nutrients in ryegrass treated with sludge but without lime were always significantly higher than those without any sludge additions, probably because toxic heavy metals in the sludge retarded the production of dry matter and consequently increased the concentrations of major nutrients.

The total uptake of major nutrients by ryegrass treated without sludge was not affected by liming, but when given sludge (S_1) were much increased except for K, probably because the sludge contained negligible amounts of K (Table 1).

The uptake of nutrients in mg/pot by ryegrass treated with sludge in comparison with that without sludge were 118.2 and 82.8 for N, 9.71 and 6.97 for P, 80.1 and 40.1 for Ca, 7.85 and 4.01 for Mg and 16.33 and 9.71 for S. All the differences were statistically significant. This suggests that the additional dry matter yields from sludge additions with proper liming adjustment could be attributed to the major nutrients supplied from the sludge during growth.

Soil analyses

After the final harvest of grass, the soil, sludge and polyethylene chips mixtures in each pot were air-dried, sieved (<2 mm) and the roots and the polyethylene chip removed as far as possible. pH measurements on the air-dried soil (Table 3) show that sludge additions decreased pH in both limed and unlimed soil. At constant rate sludge, soil pH increased by increasing rate of liming, but at maximum rate of sludge addition (S_3), the final pH tended to attain a pH of 4.7 rather lower than the pH of the original sludge (pH 5.0). The pH of uncropped soil/sludge mixtures was about 0.85 pH units less than when cropped with ryegrass (nitrogen was also added to these pots).

pH values measured in water suspensions were consistently 0.2 units higher without sludge additions (S_0) but only 0.05 units higher with the highest rate of sludge (S_3).

The analyses of soil mixtures extracted with M acetic acid are given in Table 4. Liming had no effect on Zn, Cu, and Ni contents of the soil. The concentrations of Zn, Cu, and Ni in the uncropped soil were higher than those in the cropped soil. It is especially significant in the case where soil had been given sludge treatment. The acetic acid extracts contained about 40% of the total Zn, 17% of total Cu and 28% of total Ni added in the sludge at all rates.

Table 2. Sewage sludge and liming effects on the major nutrient concentrations and uptake of ryegrass

Major nutrient	Sludge added	Liming level				
		L_0	L_1	L_2	L_3	SE±
N %	None	3.44	3.37	3.34	3.15	0.3030
	S_1	4.20	3.43	3.15	2.94	—
Uptake mg/pot	None	83.0	83.3	85.2	82.8	25.0783
	S_1	66.2	109.9	120.0	118.2	—
P %	None	0.28	0.28	0.27	0.26	0.0265
	S_1	0.26	0.25	0.25	0.24	—
Uptake mg/pot	None	6.74	6.95	6.94	6.97	0.8102
	S_1	3.65	8.55	10.19	9.71	—
K %	None	1.72	1.71	1.75	1.66	0.1965
	S_1	2.64	1.49	1.25	1.11	—
Uptake mg/pot	None	42.4	43.2	44.7	43.1	6.2103
	S_1	37.3	45.0	46.3	46.9	—
Ca %	None	1.22	1.33	1.37	1.50	0.1371
	S_1	2.10	1.74	1.45	1.49	—
Uptake mg/pot	None	29.3	32.9	35.2	49.1	4.4507
	S_1	30.8	55.1	55.9	60.1	—
Mg %	None	0.19	0.19	0.17	0.15	0.0265
	S_1	0.22	0.22	0.20	0.20	—
Uptake mg/pot	None	4.65	4.58	4.42	4.01	0.7645
	S_1	3.22	6.91	7.75	7.86	—
S %	None	0.40	0.38	0.37	0.38	0.0787
	S_1	0.84	0.59	0.46	0.41	—
Uptake mg/pot	None	9.87	9.47	9.26	9.71	1.7203
	S_1	10.03	17.29	17.03	16.33	—

Table 3. pH ($CaCl_2$) and pH (water) of the soil/sludge mixture after cropping

		S_0	S_1	S_2	S_3
L_0	$CaCl_2$	5.25	4.60	4.58	4.60
	Water	5.60	4.65	4.60	4.65
L_1	$CaCl_2$	5.93	5.64	4.65	4.69
	Water	6.15	5.73	4.70	4.73
L_2	$CaCl_2$	6.28	6.20	5.05	4.80
	Water	6.45	6.30	5.09	4.85
L_3	$CaCl_2$	6.80	6.60	6.45	5.63
	Water	7.00	6.70	6.53	5.70

Standard error ±0.292 ($CaCl_2$), ±0.324 (water)

Table 4. Acetic acid soluble metals in soil/sludge mixture after cropping

Sludge level	Cropped soil* mg/kg				Uncropped soil** mg/kg			
	Zn	Cu	Ni	Zn-equivalent***	Zn	Cu	Ni	Zn-equivalent***
S_0	6.3	1.3	1.7	22.5	8.2	1.4	1.5	23.0
S_1	105.3	35.7	23.5	364.8	137.8	40.9	29.5	455.6
S_2	211.8	73.1	46.7	731.6	247.3	80.3	53.8	838.3
S_3	298.2	104.6	67.1	1044.2	413.5	133.3	89.3	1394.5
SE±	18.8	6.3	4.6					

*Each value is the mean of 8 pots, **each value is the mean of 4 pots.

***the recommended limit is 250 mg/kg (Zn-equivalent=Zn+2Cu+8Ni) (3)

Discussion

The results from this pot experiment are the similar to the previous experiment (2) and provide further evidence that applications of a sewage sludge containing more than twenty times the heavy metal limits proposed by A. D. A. S. had no deleterious effects on ryegrass yields providing the soil pH was increased to 6.5. However, this in no way invalidates these limits, because the chemistry of heavy metals in different soils and the susceptibility of plant species are not fully understood. To avoid permanent hazard, it is necessary, therefore, to advise strict limit on heavy metal applications to agricultural land.

The sludge contained several potentially toxic metals and it is impossible to determine which element was responsible for the growth reduction and the liming effects. When the grass yields were related to their Ni, Zn, and Cu concentrations, both the Ni, and Zn relationships showed distinct depressions in yields when the dry matter contained more than 200 ug/g Ni, and 300 ug/g Zn. There was no indication of a similar relationship for Cu.

Similar amounts of heavy metals were extracted by acetic acid from both the limed and unlimed soil/sludge mixture, yet their toxicities were markedly dependent on soil pH. With 120 ug/g Zn, 37 ug/g Cu, and 27 ug/g Ni in the soils extractable with acetic acid, grass yields were significantly reduced at pH 4.5 as compared with those without sludge addition, yet at pH 6.5, grass yield was increased even with 200 ug/g Zn, 70 ug/g Cu, and 40 ug/g Ni extractable with acetic acid in the growing medium. The increased grass yield was mainly caused by the supplies of major nutrients from the sludge. The soil analyses must, therefore, be interpreted in conjunction with the soil pH.

When sludges are to be used on agricultural land, the supplier should always ensure that the pH is near neutral, if necessary, by adding lime before the sludge is spread.

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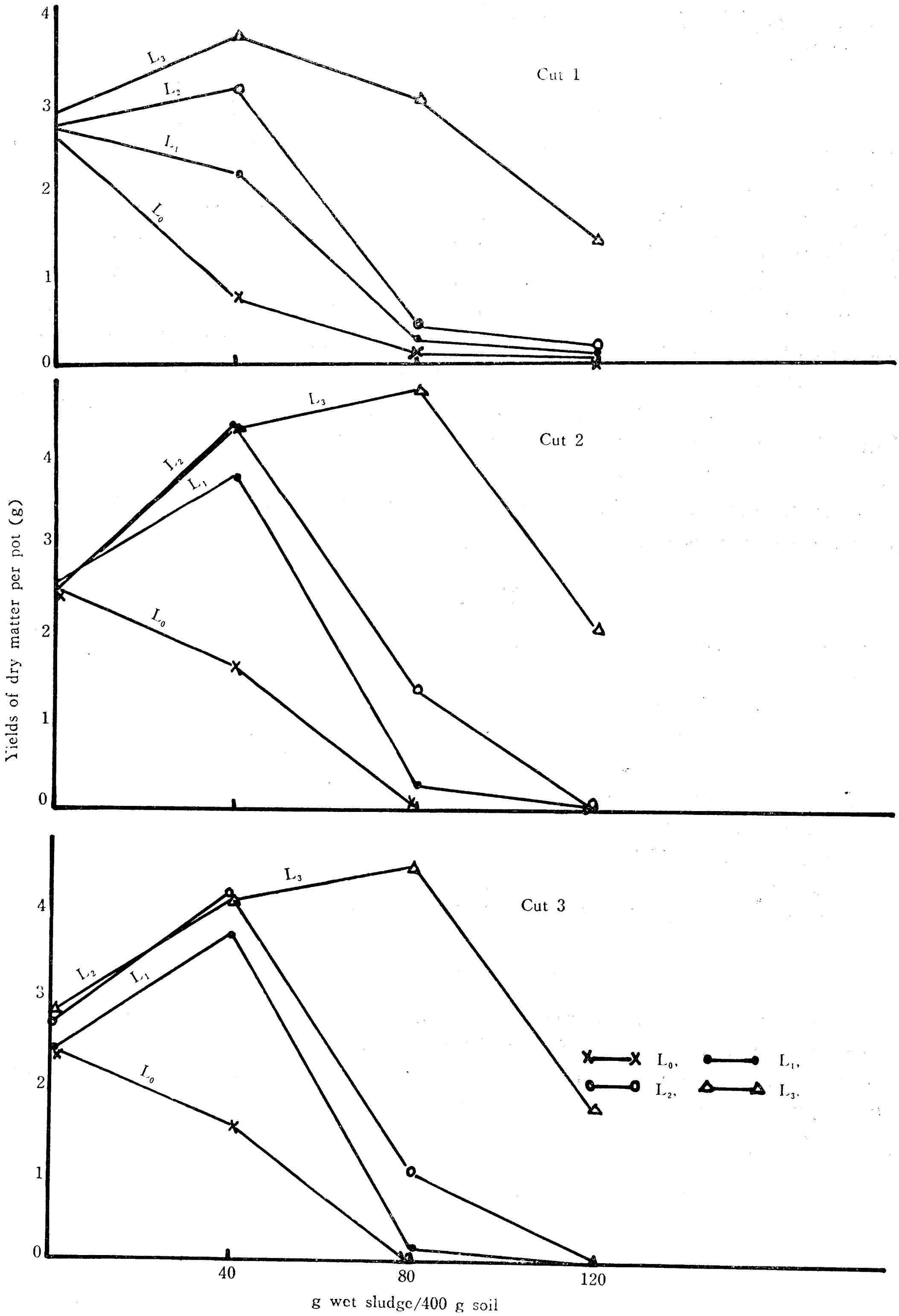


Figure 1. Sewage sludge and liming effects on the dry matter yields of three cuts of ryegrass

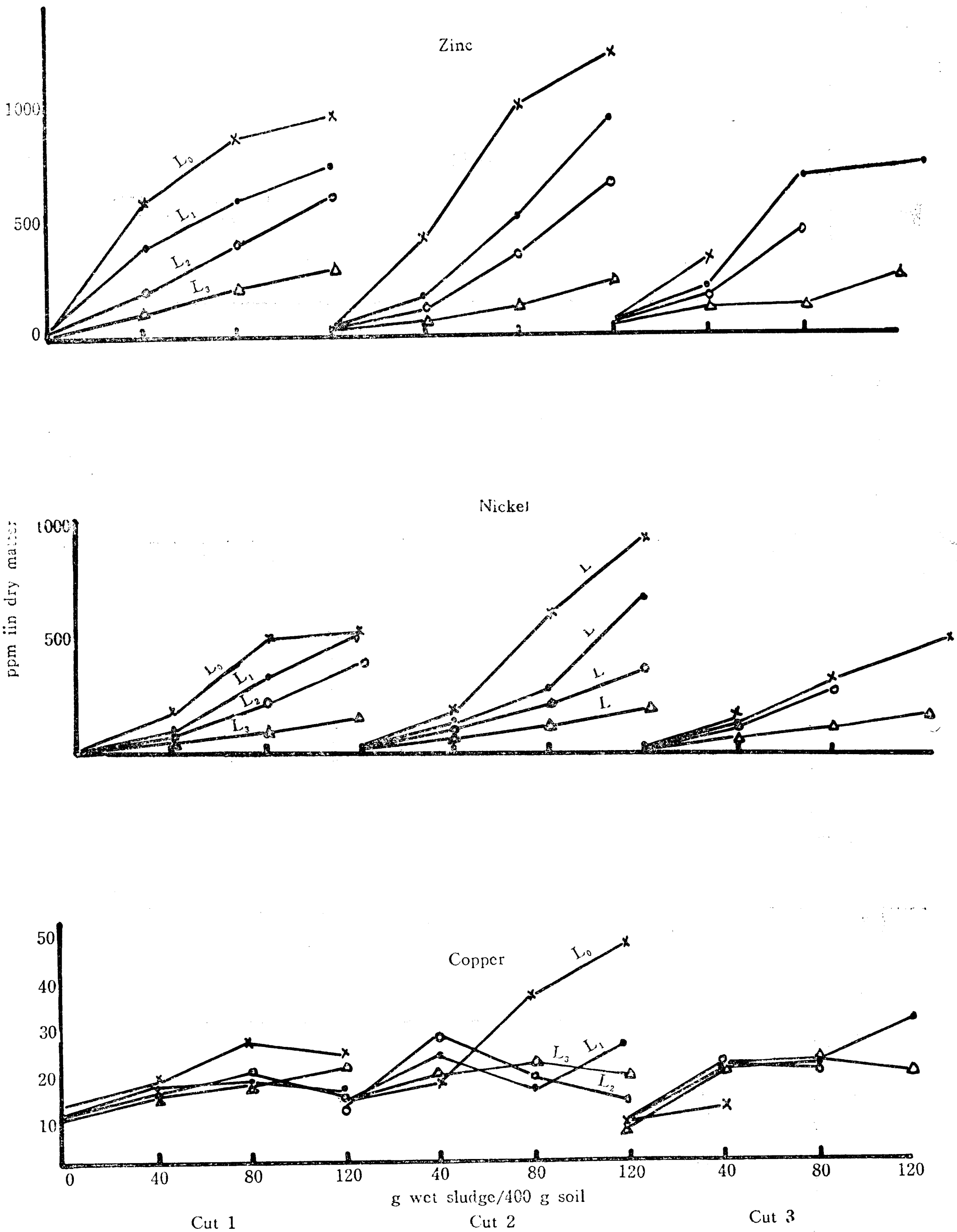
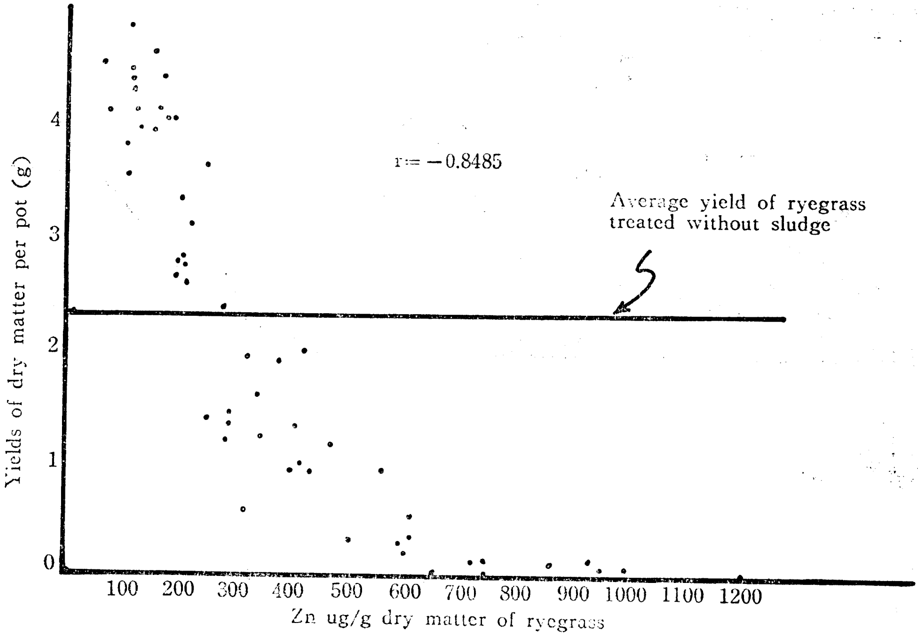


Figure 2. Sewage sludge and liming effects on the zinc, nickel and copper concentrations of three cuts of ryegrass (symbols as in figure 1)



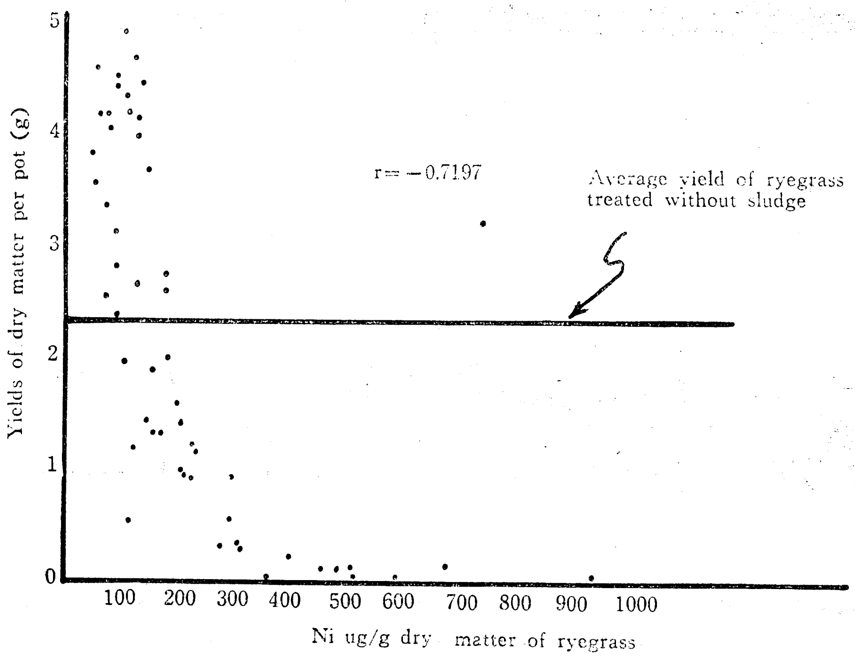


Figure 3. Relationship between dry matter yield and Zn/Cu concentration in the grass

施用石灰於污染重金屬之腐泥（Sewage sludge）後對於裸麥草收量與成分之影響

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摘　要

為瞭解施用石灰對於污染重金屬腐泥肥效之改進，特在人工氣象室內舉行盆栽試驗，所用土壤為酸性壤砂土，腐泥用量分為 4 平準，最高達土壤用量的 12%，石灰用量亦為 4 平準，土壤 pH 從4.6調整至 7.0 ，並以裸麥草（Rye grass）為指示作物， 三次收割後，裸麥草乾物及栽培後土壤經用 X-ray fluorescence spectrometer 原子吸光儀及 Technicon 自動分析儀測定結果， 摘要於後。

1.施用大量腐泥，使土壤 pH 降至6.0以下時，顯然因重金屬為害，降低裸麥草收量；若施用中量腐泥，保持土壤 pH 在 6.0 以上，則可提高裸麥草收量，此乃由於重金屬為害減弱，腐泥供應主要營養素如氮、磷、鎂及硫等所致。

2.裸麥草乾物中鋅濃度超過 300ppm，鎳濃度超過 200ppm時，將降低裸麥草收量。

3.栽培後土壤中醋酸可抽出鋅、銅、及鎳濃度隨腐泥用量而提高，鋅高達300ppm，銅100ppm，鎳 67ppm ，均超出英國農部規定標準。

4.酸性腐泥可影響土壤 pH ，施用農田之前，必須先調整 pH 為 7.0，藉可減少重金屬為害的可能性。

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