LAND DISPOSAL OF SEWAGE SLUDGE

A SUMMARY OF RESEARCH RESULTS

1972 - 1980

REPORT COMPILED UNDER
PROVINCIAL LOTTERY PROJECT No. 80-046-11

This Report records the Research Results
of Provincial Lottery Project No. 78-012-31
and Canada-Ontario Agreement on
Great Lakes Water Quality
Research Project No. 72-5-17

Ministry
of the
Environment
Ontario

The Honourable
Keith C. Norton, Q.C.,
Minister

Gérard J. M. Raymond
Deputy Minister

LAND DISPOSAL OF SEWAGE SLUDGE

A summary of research conducted by the Departments of Land Resource Science and Microbiology, the University of Guelph, from 1972 to 1981. This summary was prepared from detailed annual reports by:

Y.K. Soon, Research Scientist

and

T.E. Bates, Professor

Department of Land Resource Science
University of Guelph
Guelph, Ontario

The research was funded under project No. 72-5-17 of the Canada-Ontario Agreement by Environment Canada and the Ontario Ministry of the Environment from 1972 to 1978, and by the Ontario Provincial Lottery Funds through the Ontario Ministry of the Environment from 1978 to 1981.

YKSoon

Y.K. Soon

T.E. Bates,
Professor

ABSTRACT

This report summarizes the results of a research program, conducted between 1972 and 1980, on land application of fluid sewage sludge. The sludges used resulted from the chemical treatment of sewage with calcium hydroxide, ferric chloride and aluminum sulphate for P removal. The objective was to determine safe rates of sludges which may be applied to agricultural soils without polluting ground and surface waters with elements or micro-organisms pathogenic to humans and animals, and without reducing the quantity or quality of the crops produced.

The various phases of the research involved (i) runoff studies with fall, winter and spring applied sewage sludge, (ii) rate and source of sludge field studies with corn and bromegrass, (iii) nitrogen studies, (iv) microbial studies, (v) pedological examination and characterization of soils treated with sewage sludges, and (vi) a greenhouse study on metal uptake with sewage sludges. One other study involved a greenhouse and laboratory experiment for the selection of a chemical extractant for plant available heavy metals in polluted soils.

Runoff studies

Runoff losses of nutrients and metals can be restricted to acceptable levels if sludges are (i) applied at low rates (not exceeding 1.5 cm per application), (ii) are applied not less than 48h before heavy rains are predicted, and (iii) are not applied on steep slopes or near waterways. In winter, sludge should not be applied on ice or frozen soil, or on snow-covered ground if a significant thaw is predicted within 48h.

Source and rate of sludge field studies

Low rates of sludges produced as high yields of corn and bromegrass as ammonium nitrate plus phosphate fertilizers. High rates of sludge may result in nitrate-N concentrations in plant tissues which are hazardous to livestock consuming them. Sludge application increased sodium bicarbonate soluble P in soil. Cadmium, Cu, Ni, Zn and Mo concentrations in plants are increased by high rates of sewage sludges high in metals. The Ca-treated sludge increased soil pH and this reduced the effects of metals in sludge on plant uptake. Chromium concentration in corn increased slightly

but significantly with one sludge high in Cr after about 7 years of sludge application. Boron, Co, Hg, Pb and Se concentrations in plants were not increased by sludge application.

Nitrogen studies

About 60% of ammonium-N in sludge applied on the soil surface was lost by volatilization. Organic N in sludge was capable of being rapdily mineralized and nitrified in soil. The chemicals used in sewage treatment had no apparent effect on N mineralization and nitrification. Sludge application in excess of the crop's N requirement resulted in accumulation of excess N in the soil. Total N in sludge was approximately half as available as N contained in ammonium nitrate fertilizer.

Microbial studies

Fluid digested sewage sludges contained considerable numbers of total and faecal coliforms and faecal streptococci. Sewage sludge application on crop land did not result, however, in greatly increased numbers of the indicator micro-organisms in runoff waters. Salmonella was detected in 20 of 54 sludge samples, in one of 484 runoff samples and in six of 207 plant samples examined.

Soil characterization

There was some movement of heavy metals applied in sludge into the soil as sludge components decomposed. The heavy metals appeared to be associated mainly with soil organic matter, amorphous hydrous iron and aluminum oxides, and dilute acid-soluble components (such as carbonates and sulphides). Sludge application increased soil CEC, organic matter and iron and aluminum oxide content.

Greenhouse experiment with sewage sludges

Ryegrass was the crop grown. Nine sludges were used in five cycles of sludge application and cropping; six high metal sludges were retained and used for nine further cycles of sludge application and cropping. Yields were reduced by a high Cu sludge from Fergus. High Cu concentrations in the ryegrass shoots and roots from this treatment indicated Cu as the main cause of toxicity. Boron, Cd, Cu, Ni and Zn concentrations in ryegrass were increased by high sludge application rates, especially by sludges high in these elements. Sludges which reduced soil pH increased the Mn concentration in ryegrass. There were slight but significant

sludge source and rate effects on Cr and Pb concentrations, but not on Co, Hg and Se concentrations. Two sludges with relatively high Mo content increased Mo concentration in ryegrass. In those pots to which no sludge was applied after the fifth crop, the B and Ni concentrations in ryegrass decreased. No apparent decrease in Cd, Cu and Zn concentrations occurred, however, when sludge was not applied after the fifth crop.

Greenhouse experiment with metal-polluted soils

Swiss chard was grown on 46 Ontario surface mineral soils contaminated with metals. Nine chemical extractants were used to extract Cd, Cu, Ni, Pb and Zn, and the extractable metals and some common soil properties were used in multiple regression analysis with plant metal content. The most suitable extractant was DTPA, being effective for Cd, Ni and Zn. Acetic acid was also an effetive extractant for Cd and Ni when soil pH was the only other independent variable. Of the common soil properties, CEC, pH, clay and organic matter content, soil pH was apparently the most important factor determining metal concentration in Swiss chard.

TABLE OF CONTENTS

Page

Page

Page

Page

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

Sewage and sewage sludges have been applied to agricultural land for many years, but until recently there has been little concern about the quality of the crops produced and the effects on surface and groundwater quality.

In Ontario, sewage plants whose capacity exceed one million gallons per day and which are located in the Lake Erie and Lake Ontario drainage basins are required by law to have phosphorus removal programs. The chemicals most commonly used when the phosphorus removal program was initiated were calcium hydroxide, aluminum sulphate and ferric chloride. There was little, if any, information published on land utilization of sludges resulting from these chemical treatments. This research program was initiated in 1972 to fill the gap. The objectives of this project were to determine safe rates of sludges, resulting from chemical treatment of sewage for phosphorus removal, which may be applied to agricultural soils in southern Ontario without polluting ground and surface waters with elements or micro-organisms pathogenic to humans and animals, and without reducing the quantity or quality of the crops produced. Up to March 31, 1978 the project was financed jointly by Environment Canada and the Ontario Ministry of the Environment under project No 72-5-17 of the Canada-Ontario Agreement on Great Lakes Water Quality. From April 1, 1978 to March 31, 1980, funding for the project was from the Ontario Provincial Lottery Research Funds through the Ontario Ministry of the Environment. Annual reports and scientific publications resulting from this project are listed in a bibliography at the end of this report.

The various phases or sections of the research project and the research leaders responsible were:

Project Co-ordinator - T.E. Bates
Runoff Studies - J.W. Ketcheson[1]
Field rate and source of sludge studies - T.E. Bates[1]
Nitrogen studies - E.G. Beauchamp[1]
Soil characterization - R. Protz[1]
Microbial studies - R.A. Johnston[2]
Greenhouse studies - T.E. Bates[1]

---

[1] Dept. of Land Resource Science
[2] Dept. of Microbiology

J.R. Moyer was the scientist supervising the detailed operations of the project from 1972 to 1975 followed by Y.K. Soon from 1975 to 1981.

This report is a summary of the results obtained between 1972 and 1980.

2. RUNOFF STUDIES

2.1 Objective

The aim of the runoff studies was to determine rates of fluid sewage sludge which may be safely applied to sloping land at specified times of the year.

2.2 Experimental

Field plots, 0.01 ha in size [22.25 with the slope x 4.5 m] were situated on 2% and 6% slopes of an imperfectly drained silty clay loam soil at the Elora Research Station about 24 km north of Guelph. The land on which the plots were situated was systematically tile-drained. The surface soil has a pH of 7.3 (in soil-water paste) and an organic matter content of 4%. Wooden boards were used as edgings around each plot, and runoff was collected in a covered concrete tank at the bottom of the slope. Three hundred gallon tanks were used for the plots on the 2% slope and 500 gallon tanks on the 6% slope. Fluid, anaerobically digested sewage sludge from the North Toronto treatment plant was applied once a year to separate plots in November, January and May. Rates of application, based on the N content of the sludge, were 200 and 800 kg N/ha applied to the 2% slope, and 200 kg N/ha to the 6% slope. The 200 kg N/ha rate resulted in a loading of less 1 cm of fluid sludge and the 800 kg N/ha rate in about 3 cm of sludge. On each slope a control or check treatment received no sludge but 112 kg N/ha from NH_4NO_3 applied in the spring. There were two replicates of each treatment. After the sludge applied in the spring had dried, the plots were plowed and cropped to corn (Zea mays L.), with a final stand of 50,000 plants/ha. Corn rows ran up and down the slope and were 76 cm apart.

After each runoff event, the volumes of runoff were measured, samples taken for analysis and the tanks emptied. The first sludge application was in November, 1972. Following the 1976 winter period, the 2% slope treatments were discontinued; the study continued on the 6% slope until November 1977.

All runoff samples collected from each plot between sludge application in January, May and November were bulked to constitute one composite sample each for winter, summer and fall. For example, all samples of runoff between January and May sludge applications were combined to constitute the winter runoff sample.

Water-soluble N and P were determined in the water after filtering through a 0.45 µm filter. Total N and P in the unfiltered water sample were analysed after digestion with H_2SO_4 and H_2O_2 (Thomas, et al. 1967).

Soluble Cd, Cu, Ni, Pb and Zn were also determined in the filtered water samples. If necessary, the samples were preconcentrated by solvent extraction, using APDC (ammonium pyrrolidine dithiocarbonate) as the chelating agent and MlBK (methyl isobutylketone) as the solvent. Acid-extractable metals were determined after digestion of the unfiltered runoff samples with aqua regia (1:3 HNO_3:HCl). The metal concentrations were determined by atomic absorption.

Mercury was determined on separate subsamples. The water samples passing through 0.45 µm filter were reacted with acid potassium permanganate and potassium persulphate to oxidize organic material. The water soluble Hg (free and organic) was determined by flameless atomic absorption using a cold vapour generation technique (Hamm and Stewart, 1973). The sediments remaining on the filters were digested with aqua regia at 60°C and acid-soluble Hg was determined as described above for the water soluble Hg.

Chemical oxygen demand (COD) was also determined in the runoff waters to estimate the amount of oxidizable organic material present.

2.3 Results and Discussion

There was no measurable difference in corn yield between the times of sludge application. Therefore only the effects of rate of application and of slope of land are presented in Table 2.1. Only in 1973 did the higher rate of sludge cause a higher grain yield than the lower application rate. At the 200 kg N rate, yield was similar to the check.

The chemical composition of the North Toronto sludge was quite consistent from application to application. Typical loadings of nutrients and metals at a rate supplying 200 kg N/ha are presented in Table 2.2. The sludge is not considered to be unusually high in any one metal.

The number of runoff events by season of year between 1973 through 1977 is presented in Table 2.3. Several of the runoff events in the winter period (ie. mid-Jan. to April) were the result of snow melt. The winters of 1976 and 1977 were without a significant thaw period with temperatures generally below freezing. The snow depth was about 90 cm and the underlying soil was not frozen to a depth of at least 45 cm. This facilitated infiltration of subsequent snow melt and reduced runoff. The other winters had a January thaw during which the snow depth was reduced, and subsequent to which the underlying soil froze to a minimum depth of 30 cm. This reduced infiltration and increased runoff. The only two fall runoff events were due to rain immediately following sludge application: 1.63 cm and 2.79 cm in 1973 and 1974 respectively. The fall application in 1973 was preceded by 1.67 cm of rain the day before.

Runoff losses of N and P are presented for 1974 and 1975 in Table 2.4. Runoff loss of total N generally ranged from < 1% to about 8% of the total added in sludge each year, and was greater with the higher application rate and the steeper slope of land. Although similar amounts of N and P were added in sludge, P losses were considerably smaller, < 1% to about 2%. The effects of rate and slope on P losses were less pronounced than the effects on N losses. The high runoff losses of N and P in 1974 from the 2% slope receiving 800 kg N/ha from sludge in the fall were due mainly to the runoff caused by rain immediately following sludge application. Runoff losses of total N and P were greater from the steeper slope in summer than in winter, although runoff volume was about four-fold greater in winter (Table 2.5). Summer runoff was more dependent on the slope of land than winter runoff. Generally more than 50% of the total N loss in winter runoff was soluble while at least 90% of N loss in summer was associated with the suspended material[1] (Table 2.5). A higher percentage of P loss in the summer was also associated with the sediment fraction. The important role of sediment in runoff losses in the summer is even more significant

---

[1] Total minus soluble fraction = suspended or sediment fraction.

when the volumes of runoff in the winter and summer are compared. Average sediment loss in the summer was estimated to be about 4-8 tonnes/ha for the 6% slope and 1-2 tonnes/ha for the 2% slope.

Total runoff losses of Cu, Ni, Pb and Zn are presented in Table 2.6. In general, the higher application rate and greater slope of land increased metal losses in runoff. Total Cd and Hg losses were 2-14 g/ha and 1-10 g/ha, respectively, and were not affected by treatment. Runoff losses of the soluble fractions were generally < 5% of the total: Cu, 2-23 g/ha; Ni, 1-5 g/ha; Pb, 7-25 g/ha; and Zn, 20-90 g/ha. Runoff losses, therefore, appear to be associated with the sediments. Metal loss tended to be greater in summer, especially from the steeper slope because of greater sediment loss (not shown). In winter, however, metal losses were greater in the soluble fraction than in the sediment fraction.

Increased losses of Cu, Ni, Pb, and Zn occurred with the fall application of sludge applied at the higher rate and on the steeper slope in 1974 (Table 2.6) and in 1973 (not shown). The contribution to metal losses of the one fall runoff event in the fall of 1974 immediately following sludge application is presented in Table 2.7. Up to 90% of the total metal loss during the year was due to this runoff event.

The variability in the chemical oxygen demand (COD) makes it difficult to establish trends (Table 2.8). However, it is worth noting that the fall application of sludge in 1974, particularly at the 800 kg N/ha rate, made a significant contribution to the total COD in runoff during that period. When there was no immediate runoff following sludge application, the contribution of sludge to COD in runoff appears not to be a serious problem when the rate of application is kept low.

2.4 Conclusions

Runoff losses of nutrients and metals can be restricted to acceptable levels if the following management practices are followed when applying sludge on land:-

1. The rate of fluid sludge should not exceed 1.5 cm per application.

2. Fluid sludge should not be applied on steep slopes or near waterways.

3. Sludge application should be avoided when heavy rains are predicted within 48 h.

4. Sludge may be applied in winter if the following precautions are taken. Sludge application on ice or frozen soil should be avoided. Sludge should not be applied on snow covered ground if a significant thaw is predicted within 48 h.

Table 2.1: Yield of corn grain from runoff plots.

Treatment	1973	1974	1975	1976	1977
		kg/ha*			
6% slope					
200 kg N/ha	4700	5060	7700	6210	6590
Check	4690	5200	7620	6810	7020
2% slope					
200 kg N/ha	4660	6580	8950		
800 kg N/ha	6520	5770	8930		
Check	4780	5490	8530		

* 15% moisture, averaged over time of application.

Table 2.2: Typical nutrient and metal loading by the Fe-treated sludge applied at a rate supplying 200 kg N/ha.

Constituent	kg/ha	Constituent	kg/ha
Solids (dry wt)	4420	Fe	274
Soluble and		Cd	0.10
exchangeable NH_4^+-N	68	Cr	3.1
P	204	Cu	6.0
K	17	Ni	0.2
Mg	30	Pb	7.5
Ca	160	Zn	13.3
Na	14	Hg	0.06

Table 2.3: Number of runoff events by time of year and by year.

Year	Total precipitation	Winter (mid Jan-April)	Summer (May-mid Nov)	Fall (mid Nov-mid Jan)
	cm		No. of runoff events	
1973	91.3§	7	2	1†
1974	79.4	8	2	1†
1975	92.2§	12	3	0
1976	97.1§	1	1	0
1977*	75.0	5	2	-

* Experiment terminated in mid Nov.

† Runoff event resulting from rain immediately after sludge application.

§ indicates higher than 30-year average of 85.8 cm.

Table 2.4: Runoff losses and total and soluble N and P losses in runoff in 1974 and in 1975.

Slope and Treatment	Runoff		Total N		Total P		Soluble N		Soluble P	
	1974	1975	1974	1975	1974	1975	1974	1975	1974	1975
	----cm-----		----------kg/ha----------							
6% slope										
200 kg N Fall	18.9	19.3	7.5	15.8	1.6	5.0	3.0	3.0	0.6	0.6
Winter	17.3	20.2	8.5	18.9	2.3	4.5	3.6	9.3	0.6	1.1
Spring	17.3	20.5	3.8	12.8	1.1	4.6	0.6	1.5	0.2	0.3
Check	16.5	17.6	5.5	10.5	1.8	3.3	0.9	1.3	0.3	0.3
2% slope										
200 kg N Fall	15.8	17.2	4.0	4.0	1.3	0.8	1.6	2.6	0.5	0.3
Winter	12.2	13.0	3.3	4.8	0.9	1.3	1.7	2.2	0.3	0.3
Spring	12.8	14.0	2.8	4.9	0.9	1.3	0.8	1.5	0.3	0.3
800 kg N Fall	18.7	18.5	19.9	9.7	4.4	2.0	16.8	6.0	3.3	0.3
Winter	15.0	17.0	10.5	10.3	1.5	2.1	7.0	6.3	0.5	0.4
Spring	15.7	18.2	3.7	6.6	1.1	2.1	1.0	2.0	0.3	0.2
Check	12.5	13.5	2.9	5.8	0.7	1.6	0.8	1.4	0.2	0.3

Table 2.5: Runoff losses of total and soluble N and P in the summer and winter periods*.

Slope and rate of N	Runoff	Total		Soluble	
		N	P	N	P
	cm	kg/ha			
6% slope		Winter period			
Sludge, 200 kg N/ha†	15.5	4.8	1.0	3.2	0.4
Check	13.6	2.3	0.7	0.9	0.3
2% slope					
Sludge, 200 kg N/ha	11.9	2.5	0.6	1.6	0.2
Sludge, 800 kg N/ha	14.1	5.2	0.7	4.2	0.2
Check	10.5	1.9	0.3	1.0	0.2
6% slope		Summer period			
Sludge, 200 kg N/ha	3.3	6.3	2.1	0.2	0.1
Check	3.4	5.2	1.8	0.2	0.1
2% slope					
Sludge, 200 kg N/ha	2.3	1.5	0.5	0.1	0.1
Sludge, 800 kg N/ha	2.7	2.7	1.0	0.2	0.1
Check	2.5	2.4	0.8	0.1	0.1

* The winter period was from mid-January to April, and the summer period was from May to mid-November, ie. the periods following the winter and spring applications of sludge respectively. The data presented are average of the 1974 and 1975 data.

† The sludge treatment represents the average of the winter, spring and fall applications.

Table 2.6: Total Cu, Ni, Pb and Zn losses in runoff in 1974 and in 1975.

Slope and Treatment	Cu		Ni		Pb		Zn	
	1974	1975	1974	1975	1974	1975	1974	1975
				g/ha				
<u>6% slope</u>								
200 kg Fall	200	100	150	90	410	210	760	420
Winter	110	80	110	100	290	250	450	460
Spring	50	50	70	80	140	190	270	260
Check	100	80	120	70	240	150	380	340
<u>2% slope</u>								
200 kg N Fall	30	20	40	50	90	80	140	170
Winter	20	20	20	30	70	70	90	90
Spring	20	20	30	50	110	120	120	130
800 kg N Fall	420	40	110	70	730	130	880	230
Winter	50	60	40	50	110	130	210	240
Spring	40	50	70	80	120	140	230	250
Check	30	20	50	40	130	80	180	140

Table 2.7: Total metal lost in one runoff event resulting from 2.79 cm of rainfall immediately after the fall sludge application on 20th Nov. 1974.

Slope and Treatment	Runoff	Cu	Cd	Hg	Ni	Pb	Zn
	cm	----------------g/ha----------------					
6% slope, 200 kg N Fall	0.38	88	3.2	1.0	8.6	126	147
2% slope, 200 kg N Fall	0.13	5.5	0.2	0.6	1.3	19	11
2% slope, 800 kg N Fall	1.52	376	11.5	7.7	35	601	661
Check	0.08	<0.1	<0.1	<0.1	0.4	1.7	2.8

Table 2.8: Chemical oxygen demand in runoff in the winter, summer, and fall periods, 1974 and 1975.

Slope and Treatment	Winter		Summer		Fall
	1974	1975	1974	1975	1974
			kg/ha		
6% slope					
200 kg N Fall	89	136	349	255	81
Winter	182	225	421	276	
Spring	97	42	344	203	
Check	180	114	273	279	
2% slope					
200 kg N Fall	103	179	103	42	30
Winter	71	51	55	175	
Spring	74	59	267	85	
800 kg N Fall	121	126	232	123	678
Winter	113	118	225	101	
Spring	120	130	177	97	
Check	68	73	103	187	1.4

3. RATE AND SOURCE FIELD EXPERIMENTS

3.1 Objectives

The objective of the field studies was to determine the rate of chemically-treated sewage sludges which may be safely used on agricultural soils in southern Ontario without adversely affecting crop yields, and nitrate and metal contents.

3.2 Materials and Methods

3.2.1 Soil and site description

The experiments were started in 1973 on three soils: a Conestoga loam[1] (Gleyed Orthic Melanic Brunisol) at the Elora Research Station, a Caledon loamy sand[2] (Brunisolic Gray Brown Luvisol) at the Cambridge Research Station, and an Oneida clay loam (Brunisolic Gray Brown Luvisol) on a farm near Milton. Some properties of the surface soil are shown in Table 3.1. These three sites were cropped to corn (*Zea mays* L.). An experiment with bromegrass (*Bromus inermiss* Leyess) as the crop was conducted on the Conestoga loam adjacent to the corn experiment at the Elora Research Station. The plots on the Conestoga loam were tile-drained.

The bromegrass experiment was conducted on an established stand. The site for the adjacent corn experiment was also previously cropped to bromegrass which was plowed down in November 1972 in preparation for the experiment. The site on Caledon loamy sand was acquired for field research in 1972; a crop of oats (*Avena sativa* L.) was grown and plowed down in the fall of 1972. The previous history of the field is uncertain. The site on the Oneida clay loam had been in grain corn for at least four years before the experiment started.

---

[1] The soil texture varied from loam to silt loam within the experimental area. For convenience, the soil will be referred to as a loam.

[2] The texture was sandy loam to loamy sand. For convenience, the soil will be referred to as a loamy sand since this applies over a larger area.

3.2.2 Sludge description

The sources and typical chemical analyses of the fluid sludges used are presented in Table 3.2 (a and b). All sludge samples except the Caledonia sludge were anaerobically digested, were taken direclty from the anaerobic digestor outlet and all sludges were transported from the treatment plants by tank trucks. Subsamples were taken immediately for total N analysis by Kjeldahl digestion. In addition to normal secondary treatment, the sewage was chemically treated with either lime [$Ca(OH)_2$], alum [$Al_2(SO_4)_3$] or $FeCl_3$, to precipitate P from effluent waters. These sludges will be referred to as Ca-sludge, Al-sludge and Fe-sludge, respectively, for brevity.

The Newmarket sewage treatment plant switched from lime to $FeCl_3$ treatment for P removal in 1976; as a result the Fe-treated Newmarket sludge was used in error on Ca-sludge treatments of the Elora corn experiment and for the first 1976 application of the bromegrass trial. Subsequently and until 1978, and for the 1976 application on the corn experiment at Cambridge, a Ca-sludge from Midland was used. In 1977 the Midland treatment plant used $FeCl_3$ in addition to lime to precipitate P in sewage. In 1978, the Midland plant switched completely to $FeCl_3$ to remove P. Therefore from 1978 on, the Ca-sludge treatments of the grass experiment received no further sludge application. From 1979 onwards, all the Ca-sludge treatment of the grass experiment received 400 kg N/ha from NH_4NO_3 as N source. In 1978, the corn experiments received as Ca-sludge, a lime-treated primary (and not anaerobically digested) sludge from Caledonia. The source of the Ca-sludge in 1979 was the Vauxhall treatment plant in London. Chemical analysis showed its Ca content to be 0.11% and the pH 5.5. It appears lime was used to reduce the acidity of the sewage, but it was not a Ca-sludge in the normal sense. This Ca-sludge was applied only to the corn experiment at Elora, and only up to the 800 kg N/ha rate so as not to further delay the planting of corn. No Ca-sludge was used at Elora in 1980 and at Cambridge in 1979 and 1980. When this experiment started lime treatment of sewage looked promising. As the trials progressed it became more difficult and finally impossible to obtain a Ca-sludge as sewage plants switched from the lime treatment. The Fe-sludge used through the experiments was from the North Toronto treatment plant.

3.2.3 Experimental design

The sludges were applied to the corn experiments in the spring before planting at rates supplying 200, 400, 800 and 1600 kg N/ha, and worked in with a disk after the plots had dried (usually in 1 to 2 weeks). At the high rates of application, diking was necessary to retain the sludges in the plots. Treatments with 0, 100, 200 and 400 kg N/ha from NH_4NO_3 were included for comparison. Ammonium nitrate was applied just before seeding. Each treatment was applied to the same plots each year. There were four nitrogen sources, four rates of application per source and three replications resulting in a total of 48 plots for each trial laid out in a completely randomized block design. The corn plot size ws 4.57 x 7.62 m. On the grass experiment, sludges and ammonium nitrate were applied in three equal portions: at the beginning of growth in late April or early May, and after harvest of the first and second cuts in the first week of June and late July. The grass plots were 2.4 x 6.1m.

In 1973, the Al-sludge at the 1,600 kg N/ha rate was not applied to the corn experiments on the Caledon loamy sand and Oneida clay loam because the lengthy period required for drying of sludge with this heavy application would have delayed planting. Neither sludge nor ammonium nitrate was applied on the Oneida clay loam in 1975 at the farmer's request and the site was abandoned after crop harvest. In this summary, only data from Elora and Cambridge will be presented.

3.2.4 Field operations

All plots on the Conestoga loam and Caledon loamy sand were fertilized with KCl (averaging about 90 and 40 kg K/ha, respectively) each spring, and all plots on the Conestoga loam not receiving sludge were fertilized with superphosphate (43 to 50 kg P/ha) as suggested by the Ontario Ministry of Agriculture and Food's soil testing service. Phosphate was not required on the loamy sand, and neither phosphate nor potash was required on the clay loam. About 60 kg/ha of 6-18-6 liquid fertilizer were banded with the seed during seeding.

Corn was seeded at twice the rate required and thinned at the 4- to 6-leaf stage to 55,000 plants/ha on the Conestoga loam and Oneida clay loam, and to 40,000 plants/ha on the Caledon loamy sand. Several corn hybrids have been used in these trials through the years: UH106 (1973 to 1976), Stewarts 2501 (1977), and PAG SX111 (1978 to 1980).

At harvest of both grass and corn, moist weight of harvested material was obtained. A subsample was taken for dry matter determination (70°C) and a second subsample was dried and ground for subsequent chemical analyses. Grass samples for chemical analysis were immediately washed before drying but not the corn samples. Yields of corn grain are reported based on 15.5% moisture.

3.2.5 Chemical analysis of plant and sludge samples

For the analysis of the major nutrients (N, P, K, Ca, Mg), plant and fluid sludge samples were digested in H_2SO_4 and H_2O_2 according to Thomas, et al (1969). The digest was analysed for N and P by an automated colorimetric procedure, and for K, Ca and Mg by atomic absorption. Nitrate-N in plant samples was extracted in distilled water and determined by an automated cadmium-reduction method. For metal analysis, sludge samples were dried at 70°C, finely ground and digested in aqua regia (van Loon and Lichwa, 1972). Soluble and exchangeable NH_4^+-N in fluid sludges were extracted in 2M KCl and analysed by an automated procedure using NH_3 distillation and subsequent colour development. For metal analysis, 1 g of plant material was ashed at 450°C in a muffle furnace and the ash dissolved in 3 ml of 25% (v/v) HNO_3, heated to 90°C and made up to 10 ml for analysis by atomic absorption. Mercury in sludge and plant samples was analysed by cold vapour generation and atomic absorption following digestion at 60°C with aqua regia (Hamm and Stewart, 1972). Selenium in sludge and plant material was analysed by flurometry from 1973 to 1977 and by atomic absorption through hydride generation from 1978 to 1980 following digestion with $HClO_4$ and HNO_3.

3.2.6 Soil sampling and analysis

Soil from 0 to 15 cm depth was sampled each fall and routinely analysed for available nutrients and pH by the Ontario Ministry of Agriculture and Food's soil testing service. The soils were analysed for the heavy metals Cd, Cu, Ni and Zu in some years by extraction with NTA[1] (Haq et al. 1980) and DTPA[2] (Lindsay and Norvall, 1978). Only the NTA data are reported in this summary because they are available for five years while the DTPA data are available only for 1979 and 1980.

3.3 Results and Discussion

The results for the corn experiment on the Oneida clay loam (Milton site) have been omitted from this report because of the short duration (3 years) and absence of any interesting effects due to metals. Low metal sludges were used on the experiment. In 1974 the corn yields at Milton were low due to late planting and drought. The Ca-sludge did increase the water-stability of soil aggregates (33% of water-stable aggregates in the 0.5 to 4 mm size range compared to 19% for the control); this may have resulted in slightly higher yields of corn from the treatment. The soil structure at this site is believed to be a serious problem. The total amounts of various constituents added to the bromegrass and the Elora and Cambridge corn experiments are presented in Tables 3.3, 3.4 and 3.5.

3.3.1 Bromegrass yields

Annual yields of bromegrass from 1973 through 1980 are presented in Fig. 3.1. Yields were significantly higher with ammonium nitrate than with the same total N in sludge in 1973 and 1974. In subsequent years, however, sludges and ammonium nitrate produced similar yields. The low yields with the 1973 Al-sludge from Point Edward are believed to be due to high petroleum hydrocarbon content (7.6 g/L) and a high lipid content (10 g/L) resulting from abnormal contamination of the sludge (Chawla et al. 1974). In 1974, a switch was made to the Al-sludge from Kitchener, and the yield was rather similar for the three sludges. There appears to be some residual effects of sludge on bromegrass yields. For example, in 1974, 200 kg N/ha from sludge produced a yield of 3150 kg/ha. This increased through the years until 1979 when a high average yield of 8180 kg/ha was obtained. Relatively low yields were obtained in 1978 because of drought.

Generally, the first cutting of bromegrass produced about

---

[1] Nitrilotriacetic acid

[2] Diethylenetriaminepentaacetic acid

60% of the annual yield of dry matter, with the second and third cuttings producing about 20% each. A satisfactory rate of sludge application appears to be 400 kg N/ha/annum.

3.3.2 Corn yields

Both ammonium nitrate and sludge tended to increase corn yields. Corn grain and stover yields were, however, little affected by rates of ammonium nitrate higher than 100 kg N/ha and rates of sludge higher than 200 kg N/ha. Therefore only the averaged effects of sludge and of ammonium nitrate are presented and compared to the no-nitrogen treatment in Figs. 3.2 and 3.3. Sources of sludge were not significantly different in their effects. A satisfactory rate of sludge application for corn is 200 kg N/ha.

3.3.3 Chemical composition of crop tissue and soil analysis

3.3.3.1 Nitrogen concentration in bromegrass was increased by sludge or ammonium nitrate application, and was greater in cuts 2 and 3 than it was in cut 1 (Table 3.6). This resulted in the N uptake by cuts 2 and 3 combined exceeding 50% of the total annual N uptake (Fig. 3.4), although dry matter production in cuts 2 and 3 was only about 40% of the annual total.

The effect of sludge and ammonium nitrate on N concentration in corn grain and stover was somewhat variable. In some years, ammonium nitrate or sludge increased the N concentration but not in other years (Table 3.7). The effect on N removal in stover and grain is summarized in Table 3.8 for 1974 and 1975. It is apparent that corn is not as efficient as bromegrass in utilizing the applied N.

Nitrogen in the soil is discussed separately in section 4. Nitrate-N concentration in bromegrass was increased by high application rates of sludge and ammonium nitrate, and increased from cut 1 through cut 3 (Table 3.9). The pattern was the same in most years. Levels of NO_3^--N in forage > 3 mg/g may be hazardous to livestock consuming them (Webber and Lane, 1969).

Nitrate-N concentration in corn stover approached levels considered hazardous to livestock consuming them at the Cambridge site in 1975 only. The data shown in Table 3.10 represent two extreme years with respect to stover NO_3^--N concentration. In most years the concentration ranges were more similar to those of 1975 at Elora.

3.3.3.2 Phosphorus concentration in bromegrass was higher with sludge than with ammonium nitrate and phosphorus fertilizer application (Table 3.11). Rates of application greater than 100 kg N/ha from ammonium nitrate and 200 kg N/ha from sludge had little or no effect on P concentration. The P concentration tended to be higher with the Ca-sludge than with the other sludges, and to be higher in the second and third cuts than in the first. Phosphorus removal by bromegrass is presented in Table 3.12, the 1975 data being quite typical of values obtained in subsequent years.

Sludge application had only small effects on P concentration in corn grain and stover (Table 3.13) when compared to ammonium nitrate accompanied by phosphate fertilizer. This is reflected in the rather similar P removal in corn grain and stover presented in Table 3.14. It is apparent from comparing the amount of P added in sludges (Tables 3.3, 3.4 and 3.5) that P is accumulating in the soil.

Soil phosphorus extractable by sodium bicarbonate (a measure of plant-available P) increased rapidly in the soil from sludge application, and appeared to have reached a plateau in and after 1976 (Tables 3.15 and 3.16). Although the three sludges supplied approximately similar amounts of P, the amount of sodium bicarbonate-soluble P was: Ca-sludge > Fe-sludge > Al-sludge. A plot of bicarbonate-soluble P vs. total P added (not shown) for the corn experiment on Conestoga loam showed that about 450 kg of Ca-sludge P and about 1100 kg of Fe- or Al-sludge P may be applied before exceeding the limit set by the Ontario sludge guideline of 60 μg/g soil. The P levels reported for sludge soils in Tables 3.15 and 3.16 represent levels for beyond those where a crop response might be expected.

3.3.3.3 Potassium concentration in bromegrass tended to be reduced by medium to high rates of sludge but the effect was no greater than those of ammonium nitrate. The data in Table 3.17 for 1975 are quite typical. Amongst the sludges, the effect was greatest with the Ca-sludge probably because of K/Ca antagonism.

The rate and source of N had no measurable effect on K concentration in corn grain at Elora and Cambridge (Table 3.18) or in corn stover at Cambridge (Table 3.19). Potassium concentration in corn stover from Elora tended to be increased slightly but significantly by the Al- and Fe-sludges (Table 3.20).

The amount of K added by sludge was low (Tables 3.3, 3.4 and 3.5). Extractable soil K was reduced by ammonium nitrate and sludge in the bromegrass trial in spite of potash fertilization but not in the corn trials (Table 3.21). This may be because K removal by bromegrass was greater than removal by corn (average of 100 vs. 72 kg K/ha at the Elora site in 1973). Potash fertilization was similar in the two trials. Although no more K was added by the Al- and Fe-sludges than the Ca-sludge, extractable soil K in the corn trials was increased by high rates of the Al- and Fe-sludges.

3.3.3.4 Calcium concentration in bromegrass and corn stover was increased by sludge and to a lesser extent by ammonium nitrate (Table 3.22 and 3.23). There was no apparent effect of sludge on Ca concentration in corn grain (average concentration of 0.01 to 0.02%).

Soil calcium extracted by ammonium acetate was increased by the Ca-sludge (Table 3.24). However, extractable soil Ca concentrations were not apparently higher in 1979 than in 1975 (not shown).

3.3.3.5 Soil pH was increased by the Ca-sludge and decreased by the Fe-sludge. The pH was also reduced slightly by high application of the Al-sludge at Elora (Table 3.25). The acidifying effect of the Fe- and Al-sludges is believed to be due to the higher N/base (K + Ca + Mg + Na) ratio of these sludges, particularly the Fe-sludge.

3.3.3.6 Magnesium concentration in bromegrass was increased by ammonium nitrate or sludge application (Table 3.26) and followed for the different cuttings the trend: cut 1 < cut 2 < cut 3 (Table 3.27). Magnesium concentration in corn stover tended to be increased by ammonium nitrate or sludge application, but not the concentration in the grain (Table 3.28).

Soil magnesium extracted by ammonium acetate is presented in Table 3.29. The treatment effects were variable from site to site. On the grass plots, extractable soil Mg was increased by ammonium nitrate and decreased by the Ca- and Al-sludges. There was no apparent treatment effect on extractable soil Mg in the corn experiment at Elora. Ammonium nitrate and the Fe-sludge appeared to increase soil Mg at Cambridge.

3.3.3.7 Boron concentration in bromegrass was not affected by source or rate of nitrogen. It increased, however, from cut 1 through cut 3 (Table 3.30). Boron concentration in corn grain and stover varied somewhat from site to site and from year to year, but was in general, not affected by source or rate of nitrogen (Table 3.31).

3.3.3.8 Cadmium concentration in bromegrass was increased by the Al- and Fe-sludges (Table 3.32), and appears to increase each year with the Al-sludge and to have reached a plateau of about 0.3 μg/g with the Fe-sludge. The concentrations tended not to be measurably different in the three cuttings obtained per year. With the Ca-sludge, Cd addition exceeded the maximum set by the Ontario sludge guidelines without affecting Cd concentration in bromegrass.

Cadmium concentration in corn stover was increased by the Al-sludge and high application rates of the Fe-sludge (Table 3.33). Three different hybrids were used in the corn trials with the change in hybrids occurring in 1976, 1977 and 1978. The three hybrids appeared to have some effect on Cd concentration in corn stover. When the hybrid effect is minimized by plotting the deviation in Cd concentration from the treatment receiving 100 kg N/ha from ammonium nitrate (i.e. as Δ Cd) against year (not shown), the trend in Cd concentration from year to year becomes more apparent. The Al-sludge resulted in increasing Cd concentration from 1973 through 1980. The Fe-sludge resulted in increasing Cd concentration to 1975 at Elora and to 1974 at Cambridge; thereafter the Cd concentration declined slightly or remained fairly constant. The Ca-sludge had no significant effect on Cd concentration in corn stover. The effect of sludge applied at the low rate (200 kg N/ha) was smaller. Even when the Ontario sludge guideline for Cd was exceeded at the low application rate of the Al-sludge, the Cd concentration was appreciably lower than when the guideline was exceeded with the high rate. The Al-sludge added the most Cd of the three sludges and this may be the reason for the strong cumulative effect observed. The Fe-sludge did not have a strong cumculative effect, while the higher pH with the Ca-sludge may have limited Cd uptake and solubility.

There was no significant treatment effect on Cd concentration in corn grain which was about 0.1 μg/g, usually less. An exception was in 1978 and 1979 when the high rate of the Al-sludge did increase the Cd concentration slightly but significantly.

The effect of sludge application on NTA extractable soil Cd is presented in Table 3.34. Cadmium solubility was apparently limited with the Ca-sludge.

3.3.3.9 Chromium concentration in bromegrass was little affected by treatment or cutting (Table 3.35). The Al-sludge tended to increase Cr concentration in corn stover, particularly at the high application rates. Only the average effect of N source on Cr concentration in corn stover is presented in Table 3.36. Chromium concentration in corn grain was low, generally close to or below the detection limit of 0.3 μg/g. There appears to be no cumulative effect of sludge on Cr concentration in any of the field experiments. By 1977, both the Ca- and Al-sludges at the highest application rate had exceeded the maximum Cr addition set by the Ontario sludge guidelines (210 kg/ha).

3.3.3.10 Cobalt concentrations in bromegrass and corn stover and grain do not appear to be influenced by sludge applications.

3.3.3.11 Copper concentration in bromegrass was increased by sludge, with the Al-sludge having the greatest effect and the Ca-sludge the least (Table 3.37). The Cu concentrations tended to increase with the rate of sludge, to be higher in the third cut than in the first or second cuts, and to vary somewhat from year to year, but there was no apparent cumulative effect.

Sludge did not result in significantly higher Cu concentration in corn stover than ammonium nitrate, with the exception of the high rate of the Al-sludge in 1978 through 1980 at Elora and in 1978 at Cambridge (Table 3.38). As with bromegrass, the Al-sludge tended to produce higher Cu concentrations than the other sludges, possibly because the Al-sludge added the most Cu. There was no apparent increase in Cu concentration from one year to the next. It has been reported by several workers that there is a close correlation between the Cu and N concentrations in plant tops, and this has led to the suggestion that Cu forms strong protein complexes in plants and that these influence the concentration and behaviour of Cu in plants.

There was no treatment effect on Cu concentration in corn grain which was usually in the range of 1.5 to 3 μg/g.

3.3.3.12 Lead concentration in bromegrass and in corn grain and stover was unaffected by sewage sludge (Tables 3.39 and 3.40). Lead concentration in corn grain (not shown) was usually less than 1 μg/g. By 1977, the maximum Pb addition of 90 kg/ha set by the Ontario sludge guidelines had been exceeded by the highest application of all sludges in the field studies.

3.3.3.13 Manganese concentration in bromegrass tended to be reduced by the Ca- and Al-sludges, and by the Fe-sludge to a lesser extent (Table 3.41). The concentrations increased from cut 1 through cut 3. The data for corn stover are somewhat more variable but there was no significant effect of sludge (Table 3.42). There was no treatment effect on Mn in corn grain (not shown) which varied about a mean of 4 to 5 μg/g. The sludges added only small amounts of Mn (Tables 3.3, 3.4 and 3.5).

3.3.3.14 Mercury concentrations in bromegrass and corn grain and stover were unaffected by sludge application. By 1978, the highest application of all three sludges used had added more Hg than the maximum set by the Ontario sludge guidelines (0.8 kg/ha).

3.3.3.15 Molybdenum concentration in bromegrass was increased by the Ca-sludge, and to a lesser extent by the Al- and Fe-sludges (Table 3.43). The concentrations tended to be higher in the third cut than in the first. Molybdenum concentrations in corn grain and stover were increased by the Ca-sludge (Table 3.43). A pH increase due to the liming effect of the Ca-sludge probably increased Mo availability since the other sludges added at least as much Mo as the Ca-sludge.

3.3.3.16 Nickel concentration in bromegrass was increased after a high Ni-containing sludge from Midland was used following the first harvest in 1976 (Table 3.44). No Ca-sludge was applied after 1977. The Ni concentration subsequently dropped and remained steady. The Al-sludge also increased Ni concentration in bromegrass and at the highest rate of application exceeded the Ontario sludge guidelines for Ni addition in 1977. The Fe-sludge had low Ni content and no effect on the concentration in bromegrass.

Nickel concentration in corn stover was increased by the Ca-sludge when the Midland sludge was used on the Cambridge site in 1976 and on the Elora site in 1977 (Table 3.45). In 1978 the Midland treatment plant stopped using lime in the chemical treatment and the sludge was dropped from the field experiments. Other sludges low in Ni were used until 1979. The Al- and the Fe-sludges had no significant effect on Ni concentration in the stover even though the highest application of the Al-sludge added more than the maximum Ni recommended by the Ontario sludge guidelines.

Nickel concentration in corn grain was about 0.2 to 0.3 μg Ni/g. In 1977, 1978 and 1979, the highest application rate of the Ca-sludge increased Ni concentration in the grain to about 0.4 to 0.9 μg/g. The highest level was attained in 1977.

Soil Ni extracted by NTA may be used to measure "plant available Ni". The data presented in Table 3.46 showed that when application of the high Ni-containing Ca-sludge was stopped in 1977, the NTA-extractable Ni level dropped. There appears to be no cumulative effect of the Al-sludge on NTA-extractable Ni, and this is also reflected in the plant Ni concentration.

3.3.3.17 Selenium concentrations in bromegrass and in corn grain and stover were not affected by sludge application. The concentrations generally varied somewhat about a mean of 0.04 to 0.05 μg/g. In none of the experiments were the Ontario sludge guidelines for Se (NH_4^+-N/Se ratio and maximum Se added) exceeded.

3.3.3.18 Zinc concentration in bromegrass and in corn stover in both corn experiments increased with increasing rates of sludge application (Tables 3.47 and 3.48). The Ca-sludge increased Zn concentration least and the Al-sludge the most. The effect of sludge source was greater on corn stover than it was on broemgrass. The Al-sludge supplied the highest cumulative amount of Zn and the Fe-sludge the least (Tables 3.3, 3.4 and 3.5). The higher Zn concentration in plant resulting from the Fe-sludge was compared to the Ca-sludge may be explained by the soil pH differences between the two sludge treatments (Table 3.25). A lower soil pH induced by the Fe-sludge tends to increase plant available Zn. In the bromegrass, Zn concentration was increased slightly but significantly by ammonium nitrate. This may be due partly to the acidifying effect of ammonium nitrate in the soil. Zinc concentration tended to be greater in the second and third cuts of bromegrass than in the first.

The year-to-year increase in Zn concentration in broemgrass resulting from the highest application of the Al-sludge is apparent but is relatively small compared to that observed in corn stover (Tables 3.47 and 3.48). Termination of Ca-sludge application in 1978 and continued application of the Fe-sludge caused little or no change in Zn concentration in bromegrass.

In the corn experiments, the data for the Ca- and Fe-sludges are somewhat variable, but do not show the year-to-year increase apparent with the Al-sludge. Part of the variability may be due to the change in the corn hybrid grown. When Zn concentration in corn stover is plotted as ΔZn (i.e. Zn conc. in stover resulting from sludge application minus Zn conc. in stover resulting from 100 kg N/ha from NH_4NO_3) to minimize the differential hybrid effect against years (not shown), the Fe-sludge applied at the 1600 kg N/ha rate resulted in a maximum ΔZn at Elora in 1975, and ΔZn subsequently and gradually decreased. At Cambridge, the Fe sludge application at 1600 kg N/ha gradually increased ΔZn from 1974 through 1980. At the 200 kg N/ha rate, the Fe- and Ca-sludges resulted in no apparent increase in ΔZn at both sites. The cumulative effect of the Al-sludge at the low rates of sludge application is apparent but small. The Zn concentration may have reached a plateau at Cambridge with the high rate of application of the Al-sludge.

The Ca-sludge application at the 1600 kg N/ha rate resulted in decreasing ΔZn at Cambridge, and increased ΔZn to a maximum in 1977 at Elora and subsequently decreased it. Discontinuing the Ca-sludge application in 1979 and in 1980 may have contributed to the observed decline in Zn concentration in 1979 and 1980. It is apparent that the trend in Zn concentration is quite complex and varies to some extent with the soil and sludge used.

The Al- and Fe-sludges, particularly at the highest application rate, increased Zn concentration in corn grain (Table 3.49).

Soil Zn extracted by NTA to estimate "plant-available" Zn is presented in Table 3.50. The amount of Zn added in sludge was Al-sludge >> Ca-sludge > Fe-sludge. Zinc extracted from soil was Al-sludge >> Fe-sludge > Ca-sludge, most probably because the Ca-sludge increased soil pH while the Fe-sludge decreased it. Zinc is more soluble at lower soil pH.

3.4 Conclusions

The sewage sludges used in the field experiments, with the exception of the Point Edward sludge in 1973, produced as high and frequently higher yields of bromegrass and corn than ammonium nitrate. A satisfactory sludge application rate on the basis of crop yield is 400 kg N/ha for bromegrass and not more than 200 kg N/ha for corn. High sludge application rates may result in nitrate-N concentrations in plant tissues which are hazardous to livestock consuming them. Sodium bicarbonate soluble P accumulates rapidly in soil from sewage sludge application, particularly Ca-treated sludges. The Al- and Fe-sludges supplied rather similar amounts of total P as the Ca-sludge, but less of the P added was extracted from the soil by sodium bicarbonate. The Ca-sludge also increased ammonium acetate-extractable soil Ca and soil pH. The Fe-sludge had a high N/base cation ratio and this resulted in decreasing soil pH.

Cadmium, Cu, Ni, Zn and Mo concentrations in bromegrass and corn stover were increased by high application rates of sludge. The increase in metal concentration in plant tissue was generally higher with sludges containing high concentrations of metals. An exception was Mo. The Ca-sludge increased Mo concentration in the plant tissues analysed, but added no more Mo than the other sludges. The availability of Mo is believed to be increased by the liming effect of the Ca-sludge. Zinc concentration in corn grain was increased by high application rates of sludges high in Zn content. The Al-sludge added the most Cr to the soil, and appeared to increase the Cr concentration in corn stover particularly at the Cambridge site.

The Al-sludge containing high Cd and Zn concentrations increased Cd and Zn concentrations in corn stover and in bromegrass from one year to the next. The results suggest that several light sludge applications resulted in lower metal availability and concentration in the plant than fewer but heavier sludge applications supplying an equivalent amount of metal. The source of the sludge appears to be quite important. Two sludges having approximately equal amounts of a metal may be quite different in terms of availability of the metal to a crop. The Ca- and Fe-sludges did not increase Cd and Zn concentrations from one year to the next over the experimental period, i.e. from 1973 to 1980.

The application in 1976 and 1977 of a Ca-sludge containing large amounts of Ni increased Ni concentrations in bromegrass and corn stover and grain. The residual effect of this sludge was strong enough to maintain elevated Ni concentrations in bromegrass and corn stover in 1978 through 1980.

Copper added in sludge appears to have no cumulative effects on the plant tissues analysed. The effect of rate of sludge was also not as apparent as for Cd or Zn.

Sludge application had little effect on Mn concentration in corn grain and stover. However, the Ca- and Al-sludges tended to decrease Mn concentration in bromegrass.

Boron, Co, Hg, Pb and Se concentrations were not significantly affected by sludge application.

Table 3.1: Chemical properties of experimental soils (0-15 cm depth).

Site	Soil	pH	Exchangeable cations				Organic matter	Total N
			Ca	Mg	K	Na		
			------meq/100 g-----				%	%
Elora	Conestoga loam	7.3	16	3.6	0.2	0.1	4.9	0.23
Cambridge	Caledon loamy sand	7.4	10	0.5	0.1	0.1	2.2	0.15
Milton	Oneida clay loam	6.9	11	2.0	0.3	0.2	2.5	0.24

Table 3.2a: Typical chemical composition of sludges used (fluid weight basis).

Sludge (Treatment and Source)	Year Used	pH	D.M.*	Total N	Sol. & Exch. NH_4-N	P	K	Ca	Mg	Na	Al	Fe
			------	------	------	------	------	-%-	------	------	------	------
Calcium												
Newmarket	(1973-75)	7.0	8.8	0.15	0.036	0.09	0.01	1.88	0.04	0.02	0.025	0.054
Midland	(1976-77)	7.1	6.9	0.10	0.016	0.26	0.01	0.69	0.05	0.01	0.083	0.66
Caledonia	(1978)	9.7	10.1	0.07	0.011	0.06	0.01	1.84	0.10	0.05	0.011	0.022
Aluminum												
Pt. Edward	(1973)	7.2	4.2	0.11	0.031	0.14	0.01	0.14	0.02	-	0.53	0.037
Kitchener	(1974-75)	7.5	5.3	0.28	0.112	0.19	0.02	0.41	0.04	0.03	0.18	0.055
Guelph	(1976-80)	7.3	4.5	0.19	0.060	0.17	0.01	0.25	0.03	0.02	0.11	0.17
Iron												
North Toronto	(1973-76)	7.3	6.1	0.28	0.096	0.27	0.02	0.24	0.04	0.02	0.068	0.39
	(1977-80)	7.2	5.3	0.25	0.085	0.25	0.01	0.18	0.03	0.02	0.058	0.36

* after drying at 65°C.

Table 3.2b: Typical micronutrient and metal content of sludges used (fluid weight basis).

Sludge	Year used	B	Cd	Cr	Co	Cu	Hg	Mn	Mo	Ni	Pb	Se	Zn
		----	----	----	----	---μg/g---	----	----	----	----	----	----	----
Calcium													
Newmarket	(1973-75)	1.3	0.32	3.3	-	18	0.17	31	0.6	2.1	23	0.10	70
Midland	(1976-77)	2.1	0.45*	108*	2.2	38*	0.59*	32	1.3*	209*	33*	0.06	175*
Caledonia	(1978)	2.0	0.20	2.0	1.7	21	0.13*	8.9	3.0*	1.0	5.6	<.01	22
Aluminum													
Pt. Edward	(1973)	-	0.37	16	-	26	0.14	4.6	-	1.8	11	-	40
Kitchener	(1974-75)	1.5	0.45	450*	-	34	0.16	13	0.7	21	23	0.11	276
Guelph	(1976-80)	1.6	4.80*	135*	0.5	105*	0.32	10	2.6	3.6	70*	<0.01	640*
Iron													
North Toronto	(1973-76)	1.1	1.41	32	-	82	1.25*	26	2.0	2.4	107*	<0.01	189
	(1977-80)	1.9	1.22	44	0.6	80	1.28*	36	2.7	1.2	89*	<0.01	100

* indicates that the NH_4-N plus NO_3-N/metal ratio was below the minimum set by the Ontario sludge guidelines.

Table 3.3: Total amount of various constituents added to bromegrass by annual application of sludge at 200 kg N/ha rate from 1973 to 1980.

Constituent	Calcium Sludge*	Aluminum Sludge	Iron Sludge
		kg/ha	
Dry matter	58,900	38,200	34,500
Total N	1,000	1,600	1,600
Soluble & Exch. NH_4-N	225	541	521
P	1,240	1,390	1,470
K	90	98	116
Ca	10,020	2,100	1,270
Mg	374	247	192
Na	130	175	104
Al	377	1,260	423
Fe	1,560	994	2,090
Mn	25	7.8	18.1
Cd	0.31	2.73	0.76
Cr	41	138	22.1
Cu	21	63	49
Ni	78	5.4	0.99
Pb	16	42	57
Zn	94	385	84
B	1.5	1.3	1.0
Hg	0.30	0.20	0.72
Mo	0.51	1.35	1.18
Co†	-	0.21	0.21
Se	0.032	0.070	0.003

* No calcium sludge was added from 1978 to 1980. The amounts added from 1973 to 1977 are presented instead.

† Amount added in 1977 to 1980 only. No Co analyses were done prior to 1977.

Table 3.4: Total amount of various constituents added to Elora corn experiment by annual application of sludge at 200 kg N/ha rate from 1973 to 1980.

Constituent	Calcium Sludge*	Aluminum Sludge	Iron Sludge
		kg/ha	
Dry matter	73,000	37,400	26,400
Total N	1,400	1,600	1,600
Soluble & Exch. NH_4-N	394	545	525
P	1,230	1,390	1,420
K	146	94	112
Ca	11,640	1,910	1,220
Mg	534	260	185
Na	207	140	99
Al	369	1,070	312
Fe	1,690	967	1,980
Mn	27.9	8.1	17.3
Cd	0.32	2.37	0.68
Cr	41	126	18.9
Cu	26.4	61.8	44.2
Ni	63.4	4.8	0.84
Pb	17.4	40.0	54.3
Zn	92.7	361	76.8
B	1.98	0.88	0.93
Hg	0.21	0.20	0.67
Mo	1.21	1.52	1.25
Co†	0.87	0.22	0.18
Se	0.26	0.038	0.003

* Ca sludge not applied in 1980. The total amount added is for 1973 to 1979.

† Amount added in 1977 to 1980 only.

Table 3.5: Total amount of various constituents added to Cambridge corn experiment by annual application of sludge at 200 kg N/ha rate from 1973 to 1980.

Constituent	Calcium Sludge*	Aluminum Sludge	Iron Sludge
		kg/ha	
Dry matter	73,100	39,500	29,900
Total N	1,200	1,600	1,600
Soluble & Exch. NH_4-N	248	549	532
P	1,220	1,440	1,470
K	101	83	101
Ca	19,200	2,190	1,120
Mg	348	276	181
Na	134	152	109
Al	397	1,990	328
Fe	1,780	1,070	1,920
Mn	28.7	8.4	17.2
Cd	0.35	2.58	0.63
Cr	42.4	141	24.9
Cu	23.9	66.6	42.5
Ni	67.2	4.7	1.31
Pb	19.4	44.3	50.7
Zn	100	369	79.5
B	1.24	1.15	0.74
Hg	0.27	0.22	0.61
Mo	0.76	1.60	1.49
Co†	0.38	0.21	0.17
Se	0.018	0.036	0.003

* Ca sludge not applied in 1979 and 1980. The total amount added is for 1973 to 1978.

† Amount added in 1977 to 1980 only.

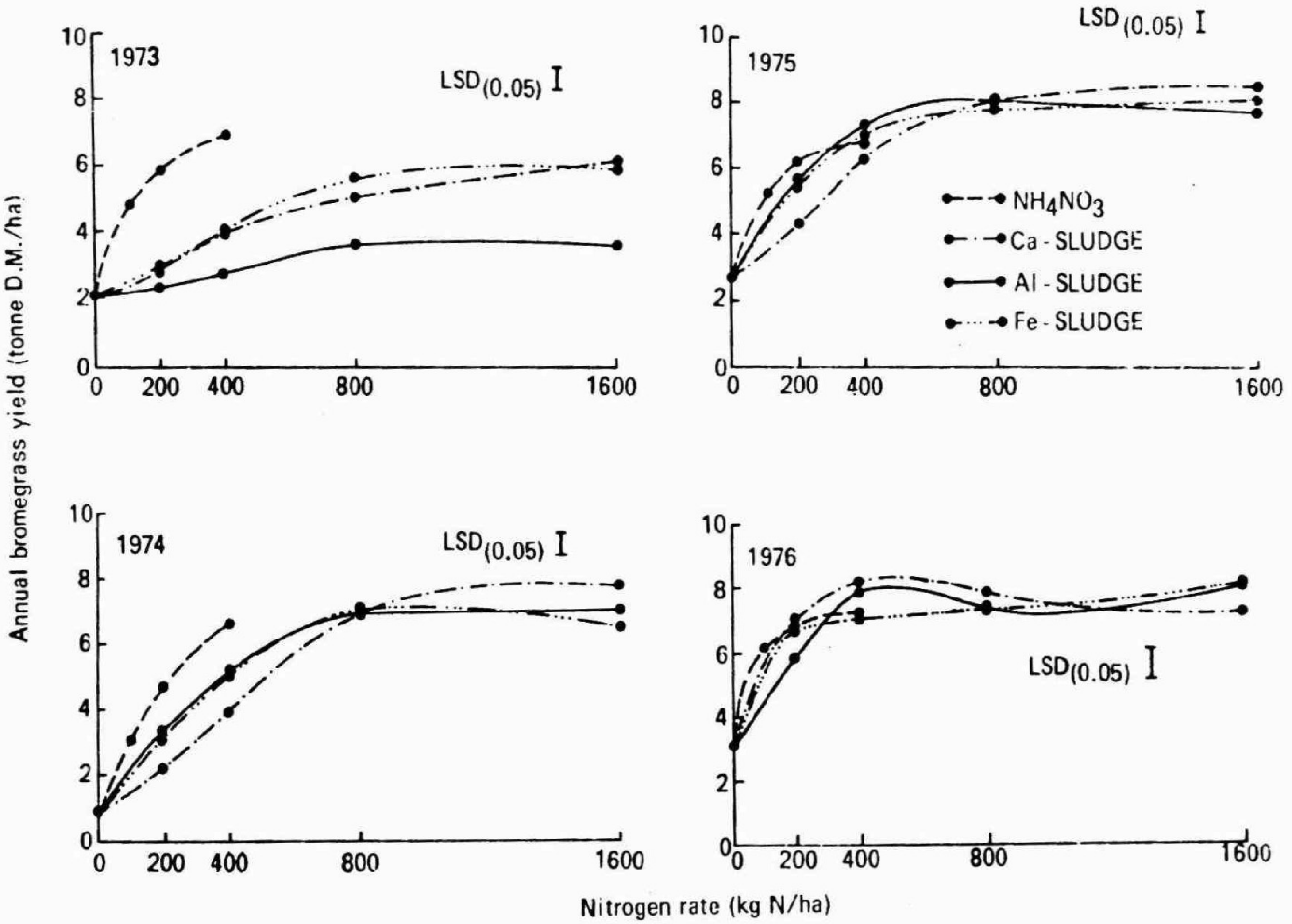


Figure 3.1 The effect of rate and source of N on bromegrass yield.

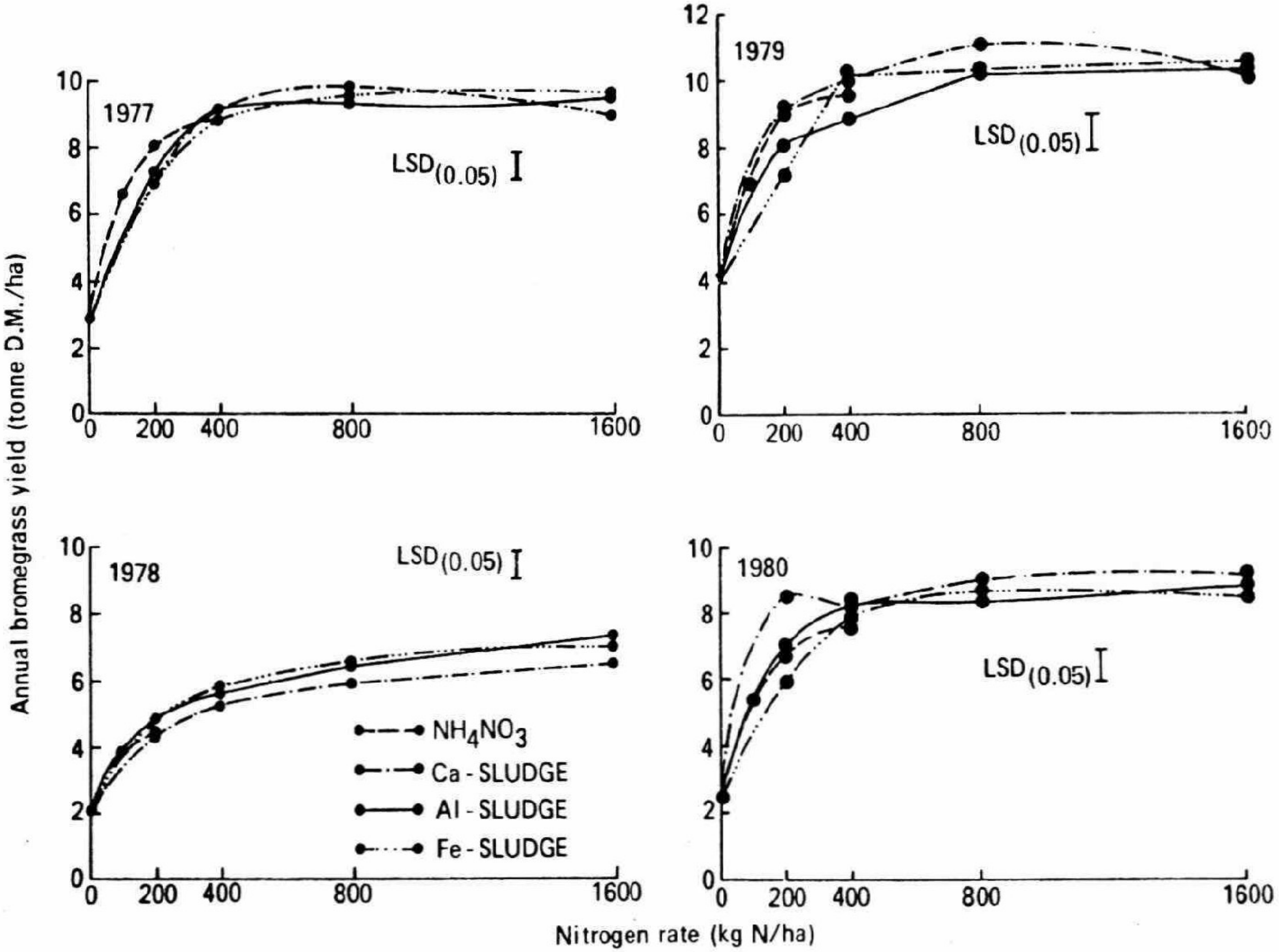


Figure3.1(cont.). The effect of rate and source of N on bromegrass yield.

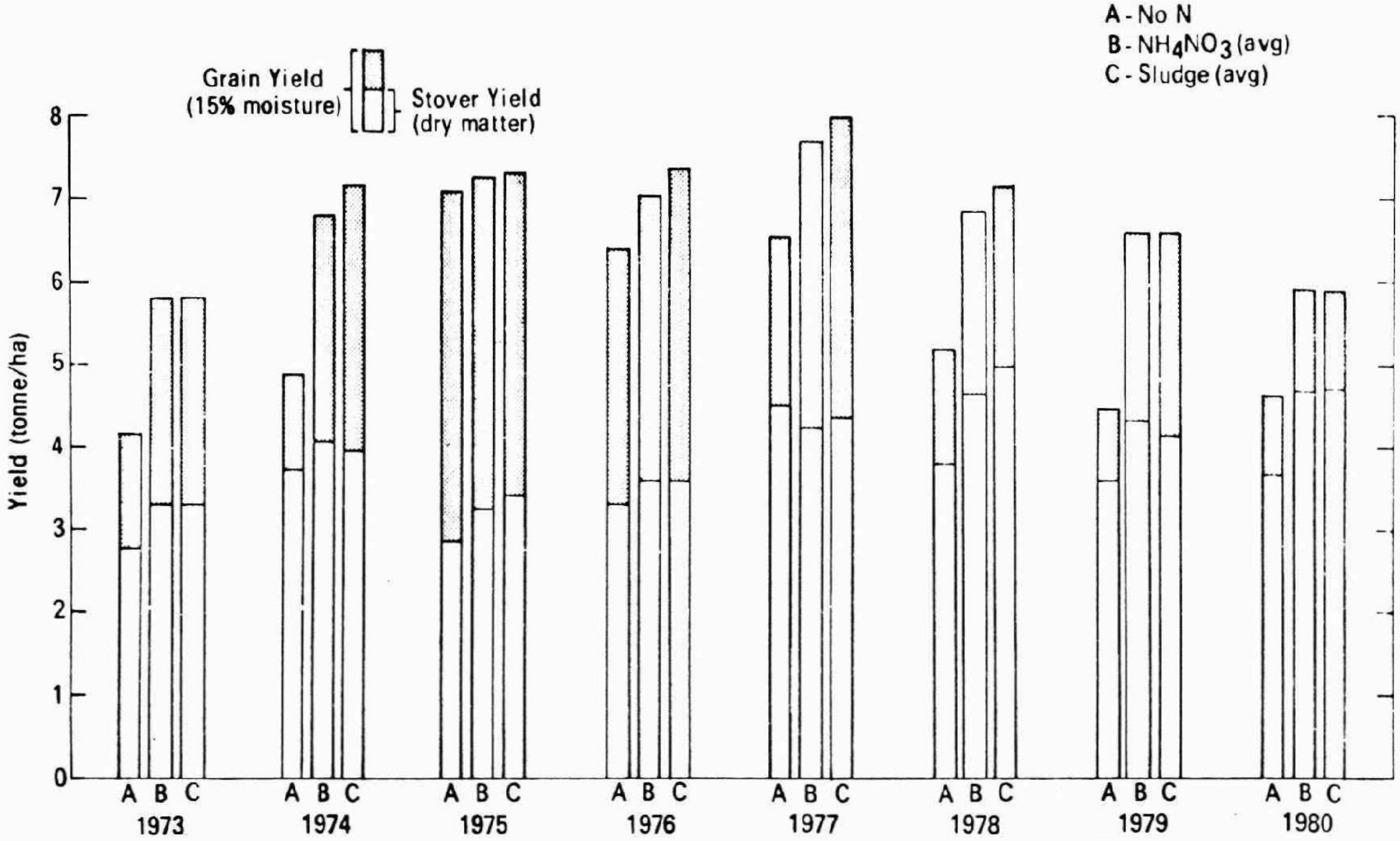


Figure 3.2 Effect of nitrogen source on yield of corn grain and stover, Elora Site.

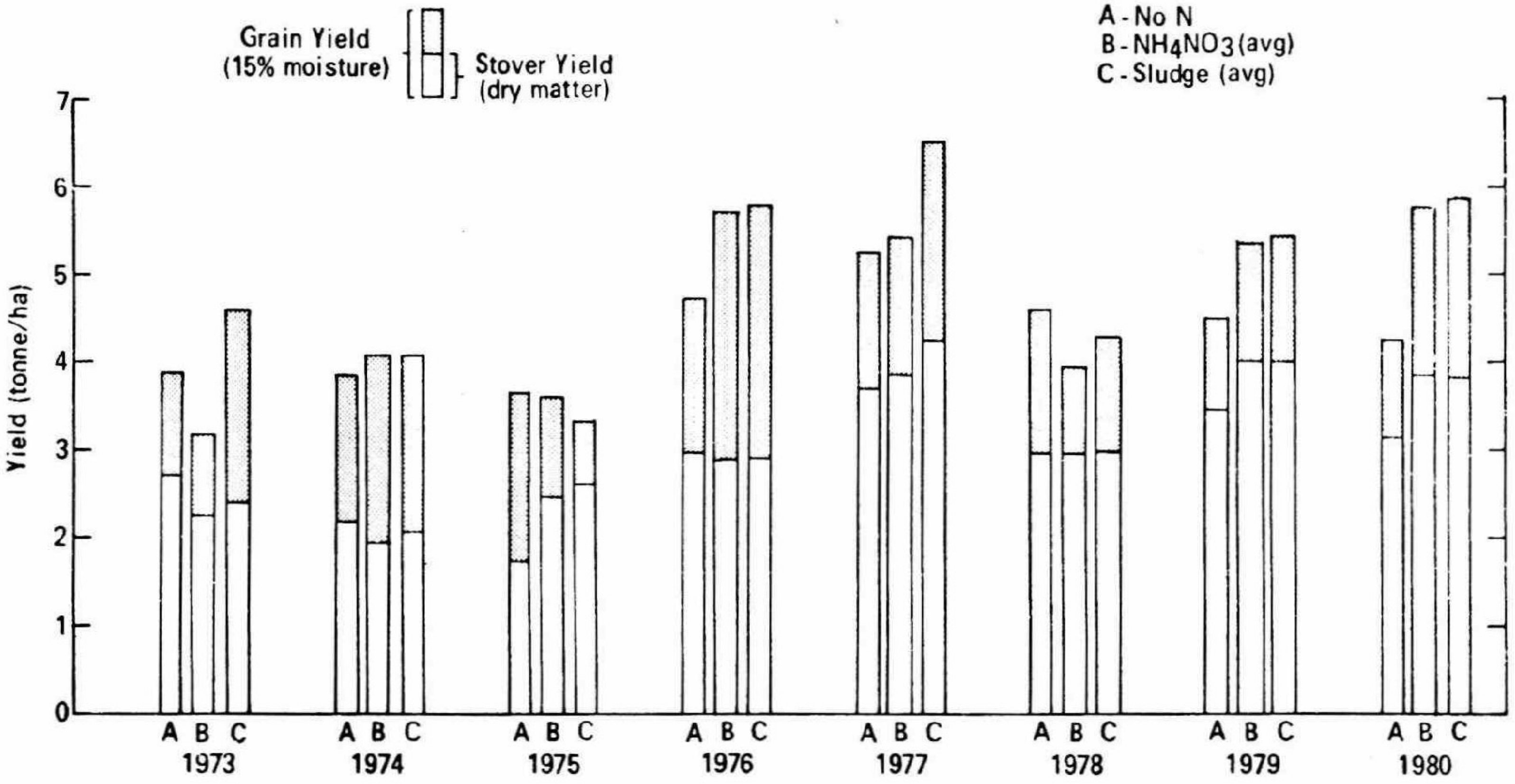


Figure 3.3 **Effect of nitrogen source on yield of corn grain and stover, Cambridge site.**

Table 3.6: Effect of source and rate of N on N concentration in bromegrass. First cut (June 6) and third cut (Sept. 7), 1975.

N Rate	N source				Sludge Avg.
	NH_4NO_3	Ca-sludge	Al-sludge	Fe-sludge	
kg/ha		%N			
		First cut			
0	2.07ef*				
100	1.78g				
200	2.52e	1.93efg	2.18de	1.93efg	2.02
400	3.13a	1.87fg	2.43cd	2.45c	2.25
800		2.52e	2.83b	3.12a	2.82
1600		3.10a	3.07ab	3.18a	3.12
		Third cut			
0	2.90de*				
100	2.82e				
200	3.42bc	3.05cde	3.17cde	3.25cd	3.14
400	3.85a	3.28c	3.72ab	3.73ab	3.58
800		3.80ab	3.77ab	3.97a	3.90
1600		3.75ab	3.92a	4.03a	3.62

* Treatment means in any cut not followed by a common letter are signficantly different at 0.05 probability by Duncan's Multiple Range test.

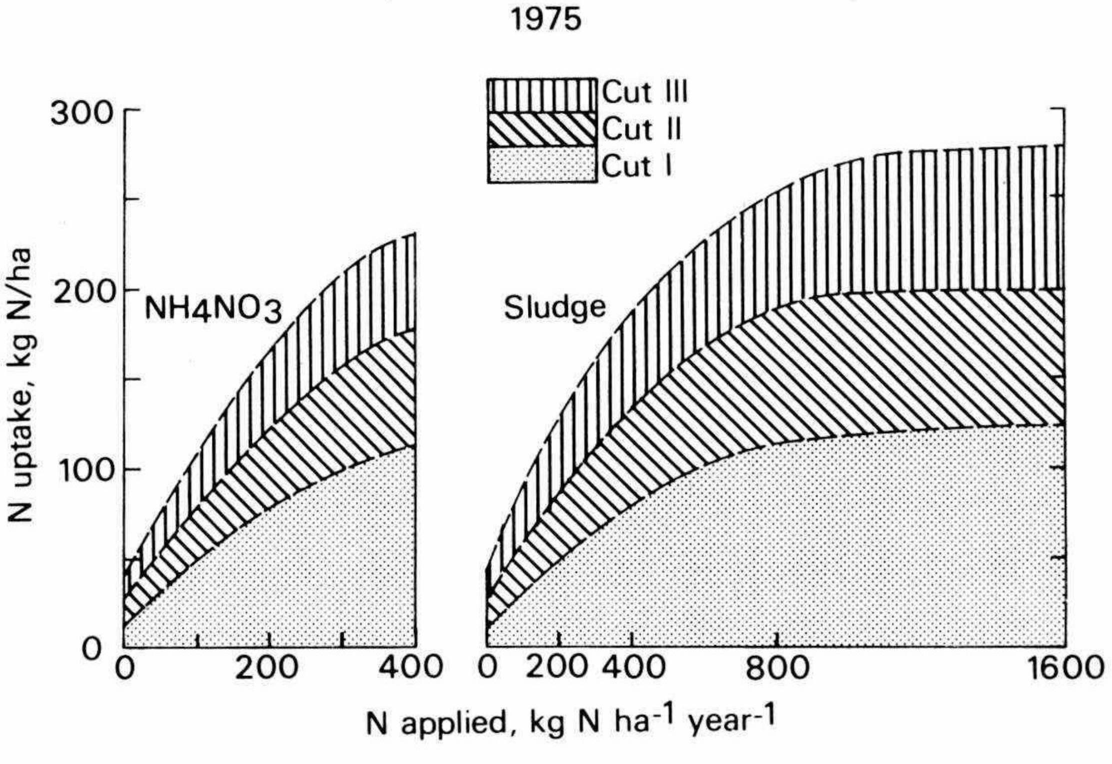


Figure 3.4 Effect of sludge (average of 3 sludges) and ammonium nitrate on total N removal by the first, second and third cut of bromegrass in 1975.

Table 3.7: Nitrogen concentration in corn stover and grain from the Elora and Cambridge sites in 1974 and 1975.

			N rate kg N/ha					
Tissue	Year	N Source	0	100	200	400	800	1600
			%N					
					Elora			
Stover	1974	NH_4NO_3	1.6	1.1	1.1	1.2		
		sludge*			1.1	1.1	1.1	1.2
	1975	NH_4NO_3	0.8	0.9	1.1	1.0		
		sludge			0.9	1.1	1.1	1.1
Grain	1974	NH_4NO_3	1.0	1.4	1.6	1.5		
		sludge			1.4	1.5	1.5	1.6
	1975	NH_4NO_3	1.3	1.6	1.4	1.4		
		sludge			1.4	1.4	1.5	1.5
					Cambridge			
Stover	1974	NH_4NO_3	0.7	0.8	0.9	1.1		
		sludge			1.1	1.1	1.0	1.1
	1975	NH_4NO_3	1.6	1.3	1.3	1.7		
		sludge			1.4	1.5	1.7	1.5
Grain	1974	NH_4NO_3	1.6	1.7	1.9	1.5		
		sludge			1.8	1.9	1.8	1.9
	1975	NH_4NO_3	1.4	1.6	1.6	1.7		
		sludge			1.5	1.7	1.7	1.7

* Average of three sludges.

Table 3.8: Nitrogen removal in corn grain and stover.

Experimental Site	Tissue	Year	N source No N	 NH_4NO_3*	 Sludge†
				kg N/ha	
Elora	Stover	1974	59	45	44
		1975	24	33	36
	Grain	1974	42	83	92
		1975	78	93	93
Cambridge	Stover	1974	15	18	20
		1975	27	35	40
	Grain	1974	53	60	66
		1975	43	50	46

* Averaged over rate.

† Averaged over rate and source.

Table 3.9: Effect of rate of NH_4NO_3 and sludge on nitrate-N concentration in bromegrass, 1975.

N rate	Cut 1 (June 6)		Cut 2 (July 17)		Cut 3 (Sept. 2)	
	NH_4NO_3	Sludge*	NH_4NO_3	Sludge	NH_4NO_3	Sludge
kg/ha			mg NO_3^--N/g			
0	<.01		0.01		0.07	
100	0.03		<.01		0.09	
200	0.08	<.01	0.07	0.01	0.74	0.48
400	1.48	0.21	1.00	0.21	2.22	1.72
800		1.01		1.30		2.69
1600		2.03		2.09		3.94

Table 3.10: Effect of rate of NH_4NO_3 and sludge on nitrate-N concentration in corn stover, 1974 and 1975.

N rate	1974		1975	
	NH_4NO_3	Sludge*	NH_4NO_3	Sludge
kg/ha		mg NO_3^--N/g		
		Elora		
0	<0.01		0.07	
100	0.03		0.42	
200	0.05	0.03	0.69	0.55
400	0.10	0.06	0.82	0.80
800		0.08		0.99
1600		0.12		1.18
		Cambridge		
0	0.04		1.61	
100	0.04		2.03	
200	0.11	0.07	3.78	1.81
400	0.15	0.11	3.82	2.85
800		0.13		2.91
1600		0.13		3.08

* Average of three sludges.

Table 3.11: Effect of N source* on P concentration in bromegrass in cuts 1, 2 and 3.

Year/cut	No N	NH_4NO_3	Ca-sludge	Al-sludge	Fe-sludge
			%P		
1974/1	0.30	0.25	0.29	0.26	0.28
1974/2	0.36	0.31	0.38	0.36	0.36
1974/3	0.29	0.27	0.33	0.30	0.31
1975/1	0.33	0.28	0.32	0.29	0.31
1975/2	0.36	0.31	0.37	0.33	0.33
1975/3	0.34	0.38	0.45	0.40	0.48

* Averaged over rates.

Table 3.12: Effect of sludge and ammonium nitrate on annual P removal by bromegrass.

	1974		1975	
N rate	NH_4NO_3	Sludge*	NH_4NO_3	Sludge
kg/ha		kg P/ha		
0	3.1		5.9	
100	8.6		15.0	
200	12.5	10.6	19.4	20.2
400	18.2	17.1	21.8	24.5
800		20.3		26.6
1600		20.4		30.8

* Average of the three sludges used.

Table 3.13: Phosphorus concentration in corn grain and stover.

		N source*				
Year	Tissue	No N	NH_4NO_3	Ca-sludge	Al-sludge	Fe-sludge
				%P		
				Elora		
1974	Grain	0.26	0.27	0.30	0.27	0.28
	Stover	0.08	0.10	0.11	0.10	0.10
1975	Grain	0.34	0.36	0.34	0.33	0.33
	Stover	0.13	0.11	0.11	0.10	0.10
				Cambridge		
1974	Grain	0.34	0.33	0.34	0.32	0.34
	Stover	0.11	0.12	0.13	0.13	0.12
1975	Grain	0.41	0.34	0.35	0.34	0.35
	Stover	0.22	0.15	0.18	0.17	0.18

* Averaged over rates of N which were not significantly different.

Table 3.14: Phosphorus removal in corn grain and stover.

Experimental Site	Tissue	Year	N source No N	 NH_4NO_3*	 Sludge†
				kg P/ha	
Elora	Stover	1974	2.8	3.8	4.1
		1975	3.6	3.5	3.6
	Grain	1974	10.7	15.4	17.0
		1975	20.0	23.0	21.0
Cambridge	Stover	1974	2.6	2.2	2.6
		1975	3.8	3.8	4.6
	Grain	1974	11.1	11.6	11.6
		1975	12.4	10.4	9.8

* Averaged over rate

† Averaged over rate and source

Table 3.15: Sodium bicarbonate extractable P in surface soil (0-15 cm) from the bromegrass experiment, 1973 to 1980.

Year	Source and rate of N (kg N/ha)						
	NH_4NO_3	Ca-sludge		Al-sludge		Fe-sludge	
	200	400	1600	400	1600	400	1600
			µg P/g				
1973	6b*	14b	108a	8b	12b	6b	12b
1974	9e	27cd	150a	13e	26cd	16de	32c
1975	13f	72b	147a	16ef	40cd	31cde	62b
1976	40f	182c	560a	73efg	97def	90ef	150cd
1977	30gh	148c	423a	53e-h	85de	68efg	108d
1978	13hi	158cd	605a	63e-h	105e	73efg	178c
1979	12i	160cd	533a	64g	128e	81fg	193e
1980	30ij	137d	438a	77fgh	97ef	80fgh	168c

* Treatment means in any one row not followed by a common letter are significantly different at 0.05 probability by Duncan's Multiple Range test.

Table 3.16: Sodium bicarbonate extractable P in surface soil (0-15 cm) of the corn experiments, 1974 to 1980.

Year	Source and rate of N (kg N/ha)						
	NH_4NO_3	Ca-sludge		Al-sludge		Fe-sludge	
	100	200	1600	200	1600	200	1600
			µg P/g				
			Conestoga loam, Elora				
1974	11de*	33b-e	83a	17b-e	40b	14cde	69a
1975	28fg	56cde	147a	31fg	76b	27fg	84b
1976	30f	87c-f	290a	57ef	117de	53ef	160bc
1977	53efg	73def	227a	57efg	97d	60efg	148c
1978	27g	112de	297a	50fg	112de	47fg	173c
1979	34f	118cd	300a	53e	123c	60e	202b
1980	40f	102d	285a	68e	125cd	70e	188b
			Caledon loamy sand, Cambridge				
1974	70ef	90c-f	143a	77def	90def	82def	112bc
1975	66b	114b	304a	83b	92b	72b	150b
1976	73f	150de	397a	113ef	123def	103ef	170cd
1977	73gh	127de	228a	92fgh	113ef	92fgh	150cd
1978	63i	137de	350a	110efg	133de	90gh	187c
1979	82fg	140d	325a	104def	132de	99ef	192e
1980	78gh	145d	322a	100efg	125de	105efg	198c

* Treatment means in any one row not followed by a common letter are significantly different at 0.05 probability by Duncan's Multiple Range test.

Table 3.17: Effect of rate and source of N on K concentration in bromegrass, 1975.

	N source			
N Rate	NH_4NO_3	Ca-sludge	Al-sludge	Fe-sludge
kg/ha		%K†		
0	2.63abc*			
100	2.48a-f			
200	2.28d-h	2.73ab	2.57a-d	2.40c-g
400	2.11gh	2.38c-g	2.43b-f	2.25e-h
800		2.02h	2.44b-f	2.19fgh
1600		2.22fgh	2.77a	2.54a-e

† Weighted average of three cuts i.e. $\frac{\Sigma \text{ (conc. X dry matter yields)}}{\text{total dry matter yields}}$

* Treatment means not followed by a common letter are significantly different at 0.05 probability level by Duncan's Multiple Range test.

Table 3.18: Potassium concentration in corn grain.

		N source		
Experimental Site	Year	No N	NH_4NO_3*	Sludge†
			% K	
Elora	1974	0.50	0.50	0.49
	1975	0.50	0.53	0.50
Cambridge	1974	0.50	0.50	0.49
	1975	0.54	0.44	0.46

* Averaged over rate.

† Averaged over rate and source.

Table 3.19: Potassium concentration in corn stover, Cambridge.

Year	No N	NH_4NO_3*	Sludge†
		%K	
1974	1.04	1.13	1.11
1975	1.81	1.91	1.73

* Averaged over rate.
† Averaged over rate and source.

Table 3.20: Effect of rate and source of N on K concentration in corn stover, Elora, 1974.

	N source				Sludge
N Rate	NH_4NO_3	Ca-sludge	Al-sludge	Fe-sludge	Avg.
kg/ha			%K		
0	0.72ab*				
100	0.79ab				
200	0.64a	0.62a	0.66a	0.81abc	0.69
400	0.86abc	0.66ab	0.77ab	0.78ab	0.74
800		0.68ab	0.80abc	0.85a-d	0.78
1600		0.95abc	1.08cd	1.12d	1.05
Avg.		0.73	0.83	0.89	

* Treatment means not followed by a common letter are significantly different at 0.05 probability level by Duncan's Multiple range test.

Sources and rates of sludge are significantly different by "F" test at 0.05 and 0.01 probability levels respectively.

Table 3.21: Ammonium acetate extractable K from surface soil (0-15 cm) October, 1980.

	N source			
N Rate	NH_4NO_3	Ca-sludge	Al-sludge	Fe-sludge
kg/ha		μg K/g		
		Bromegrass Expt. Elora		
0	113a*			
200	62c-g	67c	67cd	75b
400	63c-f	59e-h	58e-h	59d-h
1600		54h	64cde	67cd
		Corn Expt. Elora		
0	111de*			
200	117cde	111de	113cde	105e
400	119cde	124cd	120cde	127c
1600		117cde	148b	170a
		Corn Expt. Cambridge		
0	75de*			
200	82cde	76de	81de	79de
400	78de	81de	85b-e	90a-d
1600		69e	101a	97ab

* For any one site, treatment means not followed by a common letter are significantly at 0.05 probability by Duncan's multiple range test.

Table 3.22: Calcium concentration in selected treatments of first, second and third cuts bromegrass, 1980.

N source	N rate	Cut 1	Cut 2	Cut 3
	kg/ha		%Ca	
NH_4NO_3	200	0.47d-g*	0.50c	0.69b
Ca-sludge	400	0.64abc	0.72a	1.05a
	1600	0.61abc	0.79a	1.05a
Al-sludge	400	0.46d-g	0.62b	0.79b
	1600	0.70a	0.81a	1.08a
Fe-sludge	400	0.54c-f	0.54bc	0.77b
	1600	0.57cd	0.81a	1.02a

* Treatment means in any one cut not followed by a common letter are significantly different at 0.05 probability level by Duncan's multiple range test.

Table 3.23: Calcium concentration in corn stover as affected by source of nitrogen§, Elora and Cambridge.

Experimental Site	Year	No N	NH_4NO_3	Calcium sludge	Aluminum sludge	Iron sludge
			%Ca			
Elora	1979	0.38	0.42	0.44*	0.45*	0.44*
	1980	0.21	0.29	0.38**	0.38**	0.36*
Cambridge	1979	0.50	0.66*	0.64*	0.64*	0.57
	1980	0.56	0.72**	0.78**	0.68*	0.66

*, ** in any one row denote that N source effect is significantly different from no N treatment by L.S.D. test at 0.05 and 0.01 probability levels respectively.

§ Averaged over rates of N.

Table 3.24: Ammonium acetate extractable Ca in surface soil (0-15 cm), October 1979.

N Rate	N source			
	NH_4NO_3	Ca-sludge	Al-sludge	Fe-sludge
kg/ha	mg Ca/g			
	Bromegrass Expt, Elora			
0	2.44g*			
200	2.43g	3.63c	2.61fg	2.56gh
400	2.36g	3.57cd	2.70fg	2.49fg
1600		5.67a	3.16de	2.30g
	Corn Expt, Elora			
0	2.95de*			
200	2.88de	5.02bc	3.04de	3.03de
400	3.03de	4.77c	3.47d	3.15de
1600		6.28a	3.08de	2.79c
	Corn Expt. Cambridge,			
0	2.19d*			
200	1.69d	3.11c	2.07d	1.85d
400	1.88d	3.18c	2.17d	1.70d
1600		5.37a	2.05d	1.77d

* For any one site, treatment means not followed by a common letter are significantly at 0.05 probability by Duncan's multiple range test.

Table 3.25: Soil pH§ every second year, 1973 to 1979*.

	Source and rate of N (kg/ha)							
	NH_4NO_3		Ca-sludge		Al-sludge		Fe-sludge	
Year	100	400	200[400]†	1600	200[400]	1600	200[400]	1600
				Bromegrass expt, Elora				
1973	7.1ab*	7.3abc	7.4bc	7.6c	7.3abc	7.1ab	7.3bc	6.9a
1975	7.5bc	7.4c	7.9a	7.8a	7.5bc	7.6b	7.4b	7.0b
1977	7.5ab	7.1d	7.8a	7.8a	7.3bcd	7.3bcd	7.4bcd	6.7e
1979	7.7cde	7.4fg	7.9bc	8.1a	7.5ef	7.4fg	7.4fg	6.8h
				Corn expt. Elora				
1973	7.1def	6.7a	7.3f	7.3f	7.0bcd	7.0cd	7.1cde	6.8ab
1975	7.8ab	7.6c	8.0a	8.0a	7.5c	7.5c	7.6bc	7.1cd
1977	7.7a	7.5bc	7.9a	7.9a	7.5bc	7.3bc	7.5b	6.8e
1979	7.9b	7.6c	8.1a	8.1ab	7.5def	7.2g	7.7c	6.9h
				Corn expt. Cambridge				
1973	7.3ab	7.2a	7.6a-d	7.6bcd	7.6a-d	7.5a-d	7.4a-d	7.3ab
1975	7.3bc	7.4b	8.0a	8.0a	7.5b	7.4b	7.4b	7.1c
1977	7.4bc	7.4b	7.9a	7.9a	7.5b	7.3bc	7.3bc	6.9d
1979	7.7bc	7.6bc	8.0a	8.0a	7.6bc	7.4cde	7.6bc	6.9f

§ measured in soil-water paste.

† 200 kg N/ha for corn, and 400 kg N/ha for the grass.

* Treatment means in any one row followed by a common letter are not significantly different at 0.05 probability level by Duncan's multiple range test.

Table 3.26: Magnesium concentration in first cut bromegrass, 1979.

Nitrogen Rate	Nitrogen Source: Ammonium Nitrate	Calcium Sludge	Aluminum Sludge	Iron Sludge	Sludge Mean
kg/ha	% Mg				
0	0.11i*				
100	0.13gh				
200	0.15fgh	0.15fgh	0.13hi	0.13gh	0.14
400	0.20b	0.15fgh	0.14fgh	0.16efg	0.15
800		0.16def	0.18cde	0.19bc	0.18
1600		0.18cd	0.20b	0.23a	0.20
Mean		0.16	0.16	0.18	0.17

* Treatment means not followed by a common letter are significantly different at 0.05 probability level by Duncan's Multiple Range test.

Sources and rates of sludge, rates of NH_4NO_3 and source x rate of sludge interactions are significant at 0.01 probability level by "F" test.

Table 3.27: Magnesium concentration in selected first, second and third cut bromegrass, 1979.

N source	N rate	Cut 1	Cut 2	Cut 3	Mean
	kg/ha	%Mg			
NH_4NO_3	200	0.15	0.24	0.38	0.26
NH_4NO_3	400	0.20	0.33	0.43	0.32
Ca-sludge	1600	0.18	0.32	0.36	0.29
Al-sludge	1600	0.20	0.32	0.37	0.30
Fe-sludge	1600	0.23	0.35	0.39	0.32
Mean		0.19	0.31	0.39	0.30

Table 3.28: Effect of N source on Mg concentration in corn grain and stover.

Year	Tissue	No N	NH_4NO_3	Ca-sludge	Al-sludge	Fe-sludge
		N source*				
			% Mg			
			Elora			
1974	Grain	0.12	0.13	0.14	0.12	0.13
	Stover	0.23	0.37	0.36	0.35	0.33
1975	Grain	0.12	0.13	0.12	0.12	0.12
	Stover	0.30	0.33	0.32	0.31	0.30
			Cambridge			
1974	Grain	0.15	0.14	0.15	0.14	0.14
	Stover	0.21	0.25	0.23	0.24	0.23
1975	Grain	0.17	0.14	0.15	0.15	0.15
	Stover	0.27	0.26	0.27	0.29	0.28

* Averaged over rates of N which were not significantly different.

Table 3.29: Effect of N source on ammonium acetate extractable soil Mg from surface soil (0-15 cm) in the fall, 1978 and 1979.

Experimental Site	Year	No N	NH_4NO_3	Ca-sludge	Al-sludge	Fe-sludge
		N source*				
			µg Mg/g			
Bromegrass,	1978	345	400	289	297	351
Elora	1979	389	444	282	315	394
Corn,	1978	334	338	398	310	353
Elora	1979	397	403	373	346	400
Corn,	1978	96	139	131	122	124
Cambridge	1979	90	139	101	109	136

* Averaged over rates of N.

Table 3.30: Boron concentration in selected first, second and third cut bromegrass, 1980.

N source	N rate	Cut 1	Cut 2	Cut 3
	kg/ha		%Ca	
NH_4NO_3	200	6.3ab*	10.7b	17.3ab
NH_4NO_3	400	6.7ab	11.7b	16.3ab
Ca-sludge	1600	6.7ab	12.7ab	19.0a
Al-sludge	1600	7.0ab	11.7ab	14.0b
Fe-sludge	1600	7.0ab	12.3ab	17.0ab

* Treatment means in any one cut not followed by a common letter are significantly different at 0.05 probability level by Duncan's multiple range test.

Table 3.31: Boron concentration* in corn grain and stover at the Elora and Cambridge sites in 1979 and in 1980.

Tissue	Year	No N	NH_4NO_3	Calcium sludge	Aluminum sludge	Iron sludge
			µg B/g			
			Elora			
Grain	1979	-	5.3	6.2	6.2	6.2
	1980	-	3.4	3.5	3.8	3.2
Stover	1979	12	12	12	13	12
	1980	5.7	5.7	6.7	6.5	6.2
			Cambridge			
Grain	1979	-	5.3	5.5	6.0	6.2
	1980	-	2.8	2.8	2.8	2.5
Stover	1979	15	15	16	16	15
	1980	10	10	10	9	9

* Averaged over rates of N which had no significant effects.

Table 3.32: Cadmium concentration in first cut bromegrass from selected treatments from 1974 to 1980 and in the second and third cuts of 1980.

Year	N source and rate (kg N/ha)							
	Ammonium Nitrate		Calcium Sludge		Aluminum Sludge		Iron Sludge	
	200	400	400	1600	400	1600	400	1600
				µg Cd/g				
1974	0.05c-f*	0.08ab	0.03f	0.06b-e	0.04ef	0.07a-d	0.04ef	0.09a
1975	0.11c	0.13c	0.11c	0.10c	0.06c	0.14bc	0.16bc	0.37a†
1976	0.05efg	0.09c	0.05efg	0.07c-f	0.05efg	0.08cd†	0.08cd	0.23a
1977	0.07de	0.10cde	0.05e	0.08cde†	0.08cde	0.18a	0.12cd	0.20a
1978	0.09de	0.16b	0.04e	0.08de	0.17b†	0.27a	0.11cd	0.28a
1979	0.04d	0.09d	0.07d	0.06d	0.23bc	0.35a	0.08d	0.27a
1980	0.06ef	0.11def	0.10ef	0.07ef	0.31c	0.56a	0.12de	0.30c
1980 (cut 2)	0.07cd	0.12d	0.10d	0.09d	0.29c	0.61a	0.11d	0.45b
1980 (cut 3)	0.08d	0.12d	0.13d	0.10d	0.28c	0.60a	0.13d	0.37b

* Individual treatments for a given cut not followed by a common letter are significantly different at 0.05 probability level by Duncan's Multiple Range Test.

† Indicates that the maximum Cd addition (1.6 kg/ha) recommended by the Ontario sludge guidelines was exceeded.

Table 3.33: Cadmium concentration in corn stover from Elora and Cambridge from 1973 to 1980.

Year	N source and rate (kg N/ha)							
	NH_4NO_3		Ca-sludge		Al-sludge		Fe-sludge	
	100	400	200	1600	200	1600	200	1600
	µg Cd/g							
	Conestoga loam, Elora							
1973	0.23b*	0.28ab	--	0.30ab	--	0.40ab	--	0.38a
1974	0.28abc	0.31abc	0.26bc	0.37abc	0.38abc	0.46ab	0.30ab	0.54a†
1975	0.24d	0.43cd	0.32cd	0.43cd	0.35cd	0.67ab	0.29cd	0.80a
1976	0.30def	0.33def	0.30def	0.43cde	0.33def	0.67a†	0.27ef	0.70a
1977	0.21ef	0.23def	0.23def	0.35de†	0.34cde	0.77a	0.25def	0.53b
1978	0.13g	0.15g	0.15g	0.25de	0.24def	0.71a	0.17fg	0.36c
1979	0.16e	0.15e	0.15e	0.16e	0.31cd†	0.97a	0.16e	0.39c
1980	0.11g	0.16efg	0.14fg	0.18efg	0.29de	1.41a	0.18efg	0.57c
	Caledon loamy sand, Cambridge							
1973	0.38b	0.58a	--	0.60a	--	--	--	0.64a
1974	0.36bc	0.48bc	0.37bc	0.86ab	0.42bc	0.67abc	0.62abc	1.09a†
1975	0.43ab	0.56ab	0.41ab	0.55ab	0.33ab	0.47ab	0.56ab	0.36ab
1976	0.43fg	0.70c-f	0.40f	0.63c-g†	0.53d-g	1.03ab†	0.63c-g	1.13a
1977	0.37de	0.43c	0.36de	0.44cde	0.44cde	0.90ab	0.68bcd	0.72bc
1978	0.24e	0.36de	0.26e	0.35de	0.44cd	1.29a	0.38bc	0.91bc
1979	0.31ef	0.38ef	0.27f	0.26f	0.54de†	1.33a	0.40ef	0.88bc
1980	0.23fg	0.34d-g	0.26efg	0.24fg	0.43cde	1.49h	0.36d-g	0.70a

* Individual treatments in any one row not followed by a common letter are significantly different at 0.05 probability level by Duncan's Multiple Range Test.

† Indicates that the Ontario sludge guideline for maximum Cd addition to the soil was exceeded.

Table 3.34: NTA-extractable Cd in surface soil from the corn experiments at Elora and Cambridge.

Year‡	N sourcce and rate (kg N/ha)						
	NH_4NO_3	Ca-sludge		Al-sludge		Fe-sludge	
	100	200	1600	200	1600	200	1600
	µg Cd/g						
			Elora				
1976	0.24c*	--	0.30c	--	0.43b	--	0.90a†
1977	0.27de	0.19e	0.28e†	0.69c	1.61a†	0.37d	1.13b
1978	0.38de	0.30e	0.28e	0.97c	2.63a	0.50d	1.27b
1979	0.33f	0.40ef	0.53e	1.28d†	3.83a	0.58e	1.72c
1980	0.28e	0.28e	0.38e	1.20d	4.30a	0.48e	1.63c
			Cambridge				
1976	0.40b	-	0.47b	--	0.49b	--	0.90a†
1977	0.41d	0.29d	0.21e†	0.69c	2.01a†	0.75c	1.23b
1978	0.42de	0.32e	0.33e	0.82c	2.58a	0.72cd	1.23b
1979	0.50d	0.56d	0.63d	1.58c†	5.07a	0.82d	1.75c
1980	0.42fg	0.37fg	0.40fg	1.10d	3.85a	0.72ef	1.47c

‡ With the exception of the 1976 soil sampling which was done in April before the sludge application for that year, all other soil samplings were done in October.

* Treatment means in any one row not followed by a common letter are significantly different at 0.05 probability by Duncan's multiple range test.

† Indicates that the Ontario sludge guidelines for maximum Cd addition to the soil had been exceeded, i.e. total Cd addition was > 1.6 kg/ha.

Table 3.35: Chromium concentration in selected treatments of first, second and third cut bromegrass, 1980.

N source	N rate	Cut 1	Cut 2	Cut 3	Mean
	kg/ha		μg Cr/g		
NH_4NO_3	200	0.6c*	1.8a	1.5a	1.3
NH_4NO_3	400	0.8abc	1.2a	1.9a	1.3
Ca-sludge	1600	1.4a	1.5a	1.6a	1.5
Al-sludge	1600	1.0abc	1.0a	1.9a	1.3
Fe-sludge	1600	1.0abc	1.1a	2.0a	1.0

* Treatment means in any one cut not followed by a common letter are significantly different at 0.05 probability by Duncan's Multiple Range test.

Table 3.36: Chromium concentration† in corn stover, 1979 and 1980.

Experimental Site	Year	No N	NH_4NO_3	Calcium sludge	Aluminum sludge	Iron sludge
			μg Cr/g			
Elora	1979	0.8	1.8	0.8	1.1	1.2
	1980	1.1	1.1	1.5	2.2*	1.2
Cambridge	1979	2.5	1.9	3.0	4.2**	2.3
	1980	2.0	1.7	2.3	3.3*	2.5

† Averaged over rates of N.

*, ** denote effect of N source is significantly different from No N treatment at 0.05 and 0.01 level, respectively, by LSD test.

Table 3.37: Copper concentration in first cut bromegrass from selected treatments from 1974 to 1980 and in the second and third cuts of 1980.

Year	N source and rate (kg N/ha)							
	Ammonium Nitrate		Calcium Sludge		Aluminum Sludge		Iron Sludge	
	200	400	400	1600	400	1600	400	1600
				μg Cu/g				
1974	7.8def*	9.1c	7.6def	10.2b	8.8cd	11.6a	7.9c-f	10.5b
1975	9.0d-g	11.3bc	7.0fgh	13.3ab	10.3b-e	15.0a	10.3b-e	14.7a
1976	8.3ef	8.7def	9.0abc	12.0ab	7.7ab	12.3ab	9.0abc	13.7a†
1977	7.3ghi	9.3e-h	7.7f-i	10.0bcd	9.0c-f	11.7a†	9.7b-e	10.3abc
1978	8.7fgh	9.3efg	8.3fgh	13.3ab†	11.3cd	13.3ab	10.3de	14.7a
1979	6.4ij	6.7hij	8.8efg	11.2cd	8.4e-h	14.5a	7.3f-j	13.6ab
1980 (cut 1)	7.1hij	7.1hij	9.3def	11.0c	10.1cd	15.4a	8.0gh	13.7b
1980 (cut 2)	8.3d	10.2bcd	10.2bcd	11.9b	11.8bc	14.5a	9.9cd	14.4a
1980 (cut 3)	10.9f	12.5ef	12.9de	14.6c	14.3cd	19.2a	11.3ef	16.8b

* Individual treatments for a given cut not followed by a common letter are significantly different at 0.05 probability level by Duncan's Multiple Range Test.

† Indicates that the maximum Cu addition (150 kg/ha) recommended by the Ontario sludge guidelines was exceeded.

Table 3.38: Copper concentration in corn stover from Elora and Cambridge, 1974 to 1980.

	N source and rate (kg N/ha)							
	Ammonium Nitrate		Ca-sludge		Al-sludge		Fe-sludge	
Year	100	400	200	1600	200	1600	200	1600
	µg Cu/g							
				Elora				
1974	6.7e*	9.0b-e	9.0b-e	11.3a-d	13.7a	10.3a-e	8.0cde	11.7abc
1975	9.7ab	9.6ab	12.4a	8.9abc	9.5abc	8.5bc	8.1bc	9.9ab
1976	5.3a	6.7a	5.7ab	6.3ab	6.3a	7.0a	6.0ab	6.7a†
1977	8.7ab	8.7ab	9.3ab	9.2ab	8.8ab	10.4ab†	8.8ab	10.5a
1978	5.2fgh	6.3def	5.8efg	7.5bc†	5.0gh	9.5a	5.9efg	8.3b
1979	6.3de	7.5b-e	7.3cde	6.9de	7.3cde	10.1a	6.1e	8.6bc
1980	5.6de	7.6bcd	7.2bcd	7.6bcd	6.8bcd	10.0a	6.4bcd	7.7bcd
				Cambridge				
1974	8.3b*	10.7ab	9.0ab	11.0ab	10.0ab	12.0ab	10.0ab	12.3ab
1975	8.5ab	10.5ab	8.5ab	10.1ab	8.5ab	10.4ab	10.0ab	10.7ab
1976	7.7bc	8.3bc	7.0cd	8.0bc	8.0bc	9.3ab†	7.7bc	11.0a†
1977	11.7abc	12.0abc	10.7bc	10.5bc†	12.8abc	12.3abc	10.2c	11.5abc
1978	8.5cd	10.3bcd	8.7cd	9.7cd	11.5abc	14.5a	10.5bcd	10.8bc
1979	10.1abc	12.0ab	9.0bc	11.6ab	14.2a	13.6a	12.4ab	10.8abc
1980	10.4b	12.1ab	11.6ab	11.5ab	11.2ab	14.1a	11.7ab	13.2ab

* Treatment means in any one row not followed by a common letter are significantly different at 0.05 probability level by Duncan's multiple range test.

† Indicates total Cu addition had exceeded Ontario sludge guideline maximum of 150 kg/ha.

Table 3.39: Lead concentration in selected first, second and third cut bromegrass, 1980.

N source	N rate	Cut 1	Cut 2	Cut 3	Mean
	kg/ha		μg Pb/g		
NH_4NO_3	200	1.3	1.3	1.2	1.3
NH_4NO_3	400	1.2	1.6	1.1	1.3
Ca-sludge	1600	1.7	1.5	0.9	1.0
Al-sludge	1600	1.7	0.8	0.9	1.1
Fe-sludge	1600	1.4	1.4	1.2	1.3

Table 3.40: Lead concentration* in corn stover, 1979 and 1980.

Experimental Site	Year	No N	NH_4NO_3	Calcium sludge	Aluminum sludge	Iron sludge
			μg Pb/g			
Elora	1979	2.1	2.6	2.7	2.8	2.4
	1980	3.3	2.5	2.9	3.5	3.1
Cambridge	1979	6.5	6.3	5.9	6.4	4.8
	1980	3.2	4.0	3.9	3.8	4.1

* Averaged over rates of N.

Table 3.41: Manganese concentration in bromegrass, 1974 and 1980.

Year	Cut	N source and rate (kg N/ha)						
		NH_4NO_3	Ca-sludge		Al-sludge		Fe-sludge	
		200	400	1600	400	1600	400	1600
				µg Mn/g				
1974	1	51gh*	40cde	30a	42c-f	37bc	48fg	42c-f
	2	57cd	50abc	45ab	50abc	50abc	52bcd	60de
	3	119i	75cde	49a	79de	61abc	80de	75cde
1980	1	50bc	36def	36def	35ef	29f	43b-e	41b-e
	2	68ab	53bc	49c	50c	43c	56bc	69ab
	3	64bc	59bc	53c	58bc	53c	61bc	87ab

Table 3.42: Manganese concentration in corn stover, 1974 and 1980.

Experimental Site and Year	N source and rate (kg N/ha)						
	NH_4NO_3	Ca-sludge		Al-sludge		Fe-sludge	
	100	200	1600	200	1600	200	1600
			µg Mn/g				
Elora 1974	49a*	53a	52a	50a	57a	51a	58a
1980	37cde	38b-e	45abc	36cde	31de	39b-e	41a-d
Cambridge 1974	86a	58a	68a	85a	96a	77a	78a
1980	67ab	65ab	51ab	47b	54ab	60ab	55ab

* Treatment means in any one row not followed by a common letter are significantly different at 0.05 probability level by Duncan's Multiple Range Test.

Table 3.43: Molybdenum concentration in bromegrass, and corn grain and stover from selected treatments, 1977-1980.

	Source and rate of N (kg N/ha)				
	Ammonium nitrate		Ca-sludge	Al-sludge	Fe-sludge
Year	100[200]*	400	1600	1600	1600
	µg Mo/g				
			Bromegrass		
1977	0.33c**	0.33c	1.03a	0.74b	0.50bc
1978	0.51b	0.45b	0.84†a	0.61†ab	0.48†b
1979	0.16d	0.17d	0.97a	0.75b	0.38c
1980(cut 1)	0.17c	0.17c	1.78a	0.67b	0.48bc
1980(cut 3)	0.59b	0.47b	1.92a	1.64a	0.92ab
			Elora, grain		
1977	0.10bc	0.05c	0.24†A	0.14†b	0.10†bc
1978	0.16b	0.16b	0.21ab	0.22ab	0.29a
1979	0.07b	0.08b	0.20a	0.09b	0.11b
1980	0.13b	0.12b	0.25a	0.18b	0.17b
Mean	0.12	0.10	0.23	0.16	0.17
			Elora, stover		
1977	0.17b	0.20ab	0.24†a	0.20†ab	0.15†b
1978	0.21c	0.21c	0.58a	0.44b	0.39b
1979	0.19b	0.24b	0.39a	0.23b	0.24b
1980	0.24b	0.16b	0.67a	0.28b	0.28b
Mean	0.20	0.20	0.47	0.29	0.27
			Cambridge, grain		
1977	0.28a	0.28a	0.25†A	0.21†a	0.26†a
1978	0.42a	0.42a	0.61a	0.49	0.57a
1979	0.33ab	0.36ab	0.48a	0.27b	0.29b
1980	0.25c	0.32b	0.73a	0.29bc	0.25c
Mean	0.32	0.35	0.52	0.31	0.34
			Cambridge, stover		
1977	0.35b	0.46b	0.79†a	0.28†b	0.54†ab
1978	0.47a	0.45a	0.53a	0.57a	0.41a
1979	0.85b	0.78b	2.83a	0.52b	0.38b
1980	1.01b	1.40b	3.67a	0.72b	0.65b
Mean	0.67	0.77	1.96	0.52	0.50

* 100 kg N/ha for corn and 200 kg N/ha for bromegrass.

† Indicates total Mo addition had exceeded the Ontario sludge guideline maximum of 4 kg/ha.

** Treatment means in any one row not followed by a common letter are significantly different at 0.05 probability by Duncan's Multiple Range test.

Table 3.44: Nickel concentration in first cut bromegrass from selected treatments from 1974 to 1980 and in the second and third cut bromegrass, 1980.

Year	N source and rate (kg N/ha)							
	Ammonium Nitrate		Calcium Sludge		Aluminum Sludge		Iron Sludge	
	200	400	400	1600	400	1600	400	1600
	µg Ni/g							
1974	0.3bc*	0.3bc	0.3bc	0.2c	0.3bc	1.0a	0.2bc	0.4bc
1975	1.4a	2.1a	1.6a	1.2a	1.7a	1.9a	1.6a	1.6a
1976	0.5b	0.5b	0.5b	0.6b	0.5b	1.1ab	0.5b	0.5b
1977	0.8e	0.7e	3.5c†	6.0a†	0.8e	1.7b†	0.8e	1.1de
1978	0.4e	0.4e	2.0c	4.3a	0.5e	1.1de	0.5e	0.7e
1979	0.1h	0.3gh	2.2c	4.2a	0.3gh	1.2e	0.3gh	0.9ef
1980 (cut 1)	0.2f	0.2f	1.9c	4.8a	0.4f	1.1de	0.2f	0.5f
1980 (cut 2)	0.5c	0.6c	1.7b	2.9a	0.4c	0.9c	0.4c	0.7c
1980 (cut 3)	0.2d	0.5d	2.1b	2.8a	0.3d	1.3c	0.2d	1.3c

* Individual treatments for a given cut not followed by a common letter are significantly different at 0.05 probability level by Duncan's Multiple Range Test.

† Indicates that the maximum Ni addition (32 kg/ha) recommended by the Ontario sludge guidelines had been exceeded.

Table 3.45: Nickel concentration in corn stover from Elora and Cambridge from 1973 to 1980.

Year	N sourcce and rate (kg N/ha)							
	NH_4NO_3		Ca-sludge		Al-sludge		Fe-sludge	
	100	400	200	1600	200	1600	200	1600
	µg Ni/g							
	Conestoga loam, Elora							
1974	0.9+	1.3	1.0	1.5	1.7	1.3	1.1	1.1
1975	1.5ab*	1.1ab	1.6ab	1.5ab	1.3ab	1.0ab	0.9b	0.9b
1976	0.6abc	0.6abc	0.4bc	0.5abc	0.5abc	0.7ab	0.4bc	0.6abc
1977	0.8c	0.8c	1.9bc†	2.3b†	0.8c	0.8c	0.7c	0.9c
1978	0.6bc	0.5c	0.7bc	1.0ab	0.5c	0.7bc†	0.7bc	0.6bc
1979	0.5bc	0.5bc	0.6bc	1.2a	0.4bc	0.5bc	0.4bc	0.4bc
1980	0.5c	0.4c	0.7bc	1.9a	0.5c	0.5c	0.4c	0.5c
	Caledon loamy sand, Cambridge							
1974	0.9a	0.9a	0.9a	0.6a	1.1a	1.5a	0.7a	0.8a
1975	0.5bc	0.6ab	0.4bc	0.4bc	0.4bc	0.5bc	0.5bc	0.5bc
1976	0.9bcd	0.7d	1.5abc	2.0a†	0.8d	1.2bcd†	0.8d	0.8d
1977	1.1cde	1.0cde	1.9ab†	2.5a	1.0cde	1.0cde	1.0cde	0.8e
1978	1.0d	1.5bcd	3.0ab	3.9a	1.3cd	1.5bcd	1.1d	0.9d
1979	0.7c	0.8c	1.4ac	2.1a	0.9c	0.9c	0.9c	0.5c
1980	0.6c	0.8c	1.6b	2.5a	0.7c	0.8c	0.8c	0.5c

+ No statistical anlaysis was done because several samples believed to have been contaminated were discarded.

* Individual treatments in any one row not followed by a common letter are significantly different at 0.05 probability level by Duncan's Multiple Range Test.

† Indicates that the maximum Ni addition (32 kg/ha) recommended by the Ontario sludge guidelines had been exceeded.

Table 3.46: NTA-extractable Ni from surface soil of the corn experiments at Elora and Cambridge.

Year‡	N sourcce and rate (kg N/ha)						
	NH_4NO_3	Ca-sludge		Al-sludge		Fe-sludge	
	100	200	1600	200	1600	200	1600
	μg Ni/g						
			Elora				
1976	0.8bc*	-	0.6c	-	3.4a	-	1.1b
1977	0.9d	5.4b†	28.8a†	1.2d	2.7c	1.7d	1.5d
1978	1.6c	4.8b	16.5a	1.4c	3.3bc†	1.8c	1.9c
1979	2.1c	4.7b	15.9a	1.7b	3.5b	2.5bc	2.4c
1980	1.2e	3.9c	13.1a	1.2e	3.0cd	1.7de	1.7de
			Cambridge				
1976	0.8bc	-	0.7c	-	3.6a	-	1.4b
1977	1.2d	7.1b†	16.1a†	1.1d	3.3c†	0.9d	1.8d
1978	1.4d	5.1b	18.7a	1.5d	3.2c	1.4d	2.8c
1979	1.2d	4.4c	15.0a	1.2d	3.2cd	1.2d	2.6cd
1980	1.1fg	4.8c	13.4a	1.3fg	3.3d	1.0g	2.4e

‡ With the exception of the 1976 soil sampling which was done in April before the sludge application for that year, all other soil samplings were done in October.

* Treatment means in any one row not followed by a common letter are significantly different at 0.05 probability by Duncan's multiple range test.

† Indicates that the Ontario sludge guidelines for maximum Cd addition to the soil had been exceeded, i.e. total Ni addition was > 32 kg/ha.

Table 3.47: Zinc concentration in first cut bromegrass from selected treatments from 1974 to 1980 and in the second and third cuts of 1980.

Year	N source and rate (kg N/ha)							
	Ammonium Nitrate		Calcium Sludge		Aluminum Sludge		Iron Sludge	
	200	400	400	1600	400	1600	400	1600
				µg Zn/g				
1974	21def*	24cd	21ab	28ab	22ab	28ab	20ab	28ab
1975	19efg	30bc	20efg	30bc	23de	33b	24de	41a
1976	17e	20cde	20abc	25bc	19ab	24bcd†	25cd	39a†
1977	18f	22de	19f	25cd†	23de	30b	23de	34a
1978	19ij	24e-h	22ghi	28cde	30bcd	40a	27def	40a
1979	18h	21gh	24fg	29def	32de†	48a	24fg	42b
1980	18k	23ij	29efg	33d	38c	57a	25ghi	44b
1980 (cut 2)	23d	32cd	36bc	43b	40bc	68a	32cd	65a
1980 (cut 3)	25e	30de	35cd	36cd	41c	63a	31de	52b

* Individual treatments for a given cut not followed by a common letter are significantly different at 0.05 probability level by Duncan's Multiple Range Test.

† Indicates that the maximum Zn addition (330 kg/ha) recommended by the Ontario sludge guidelines had been exceeded.

Table 3.48: Zinc concentration in corn stover from Elora and Cambridge from 1973 to 1980.

Year	N source and rate (kg N/ha)							
	NH_4NO_3		Ca-sludge		Al-sludge		Fe-sludge	
	100	400	200	1600	200	1600	200	1600
	µg Zn/g							
	Conestoga loam, Elora							
1973	19e*	18e	28b-e	30b-e	37a-e	37a-d	26cde	41ab
1974	15i	22f-i	23f-i	36cde	19ghi	54b	23f-i	69a
1975	18f	23f	36def	54bc	33def	72b	35def	103a
1976	15f	20ef	28def	62b	34def	72ab†	30def	88a†
1977	18e	22e	36e	71bcd†	40e	115a	31e	85abc
1978	21e	22e	29de	66b	37cde†	124a	30cde	77b
1979	20h	21h	37fg	50e	53de	144a	29gh	74c
1980	14h	21fgh	26fg	42d	51d	175a	27f	65c
	Caledon loamy sand, Cambridge							
1974	53ef	72c-f	47f	128a	57def	100bc	63def	112ab
1976	45f	65def	43f	76cde†	62def	124ab†	58def	135a†
1977	49fg	66def	50efg	100bc	72def	161a	60efg	109b
1978	52f	58f	57f	95cde	80c-f†	229a	68ef	139b
1979	40e	52de	41e	67de	87cd	219a	57de	147b
1980	41f	52f	44f	58ef	79de	220a	48f	118bc

* Individual treatments in any one row not followed by a common letter are significantly different at 0.05 probability level by Duncan's Multiple Range Test.

+ Data for 1973 and 1975 are not presented because of contaminated samples.

† Indicates that the maximum Zn addition (330 kg/ha) recommended by the Ontario sludge guidelines had been exceeded.

Table 3.49: Zinc concentration in corn grain from Elora and Cambridge in 1974, 1979 and 1980.

Year	N source and rate (kg N/ha)							
	NH_4NO_3		Ca-sludge		Al-sludge		Fe-sludge	
	100	400	200	1600	200	1600	200	1600
	µg Zn/g							
	Conestoga loam, Elora							
1974	19e*	20de	22b-e	24bcd	20de	27ab	25a-d	30a
1979	16c	18bc	19bc	22ab	22ab	26a	22ab	24a
1980	16c	17c	18bc	20bc	23b	28a	17bc	23b
	Caledon loamy sand, Cambridge							
1974	27c	31abc	28bc	35abc	31abc	34ab	32abc	36a
1979	26c	26c	24c	22c	27c	51a	26c	41b
1980	20c	22c	19c	22c	26b	32a	19c	26b

* Treatment means in any one row not followed by a common letter are significantly different at 0.05 probability by Duncan's Multiple Range Test.

Table 3.50: NTA-extractable Zn from surface soil of the corn experiments at Elora and Cambridge.

Year‡	N sourcce and rate (kg N/ha)						
	NH_4NO_3	Ca-sludge		Al-sludge		Fe-sludge	
	100	200	1600	200	1600	200	1600
	-------------------------------μg Zn/g-------------------------------						
			Elora				
1976	5c*	-	32b	-	66a	-	63a
1977	9e	25d	89b†	44c	156a†	24d	92b†
1978	9d	18d	46c	63bc†	246a	19d	86b
1979	7g	23f	56e	87cd	370a	24f	112c
1980	8h	21fg	48e	84d	387a	24f	110c
			Cambridge				
1976	20c	-	51b	-	78a	-	63ab
1977	23d	42c	57c†	58c	218a†	40c	92b†
1978	23e	30e	62cd	72bc†	238a	40de	94b
1979	24g	33fg	55def	78cd	324a	37efg	98c
1980	24g	35fg	53de	99c	390a	39ef	97c

‡ With the exception of the 1976 soil sampling which was done in April before the sludge application for that year, all other soil samplings were done in October.

* Treatment means in any one row not followed by a common letter are significantly different at 0.05 probability by Duncan's multiple range test.

† Indicates that the maximum Zn addition (330 kg/ha) recommended by the Ontario sludge guidelines had been exceeded.

4. NITROGEN STUDIES

4.1 Objectives

The objectives of this research program were to determine (i) the availability in the soil of N contained in sewage sludges, and (ii) the movement of N, especially NO_3-N, in the soil profile following sludge application.

Three separate studies were conducted: (i) field studies on N availability and movement, (ii) ammonia loss by volatilization after field application of sewage sludge, and (iii) laboratory studies of sludge N mineralization and nitrification in soil.

4.2 Field studies on N availability and movement

4.2.1 Materials and Methods

These studies were conducted on the field rate and source of sludge experiments with corn and with bromegrass described in Section 3.2. The soils were: Conestoga loam (under corn and bromegrass at Elora), Caledon loamy sand (under corn at Cambridge) and Oneida clay loam (under corn at Milton). Surface soil (0-15 cm) of treatments receiving 100 and 400 kg N/ha from NH_4NO_3, and 200 and 800 kg N/ha from sludge was sampled in June of 1974 and 1975 for NO_3^- and NH_4^+ determination.

Soil from 0-15, 15-30, 30-45, 45-60 and 60-90 cm was sampled in April before the spring sludge application, and in June, October and November from the following treatments: 0, 400 and 800 kg N/ha from the Fe-sludge. Soil NH_4^+ was extracted with 1M K_2SO_4 and NO_3^- was extracted with 0.5 M $NaHCO_3$.

4.2.2 Results and Discussion

The effect of sludge and NH_4NO_3 application on NH_4^+-N and NO_3^- in the surface soil is presented in Tables 4.1 and 4.2. Soil nitrate was increased by the rate of N application. The sources of sludge were not appreciably different in their effects on NH_4^+-N and NO_3^--N in the loamy sand (Cambridge site) or in the clay loam (Oneida site); therefore only the averages for the three sludges used are presented in Table 4.1. On the loam soil at Elora, the effect of source of sludge on NO_3^--N concentration was, in general, Al-sludge > Fe-sludge > Ca-sludge (Table 4.2). The amount of readily available N (i.e. soluble plus exchangeable NH_4^+-N) applied for each 100 kg of total sludge N/ha for the three sites were: Ca-sludge, 19 to 21 kg;

Al-sludge, 41 to 44 kg; and Fe-sludge, 29 to 36 kg. Thus the amount of readily available N supplied and its subsequent nitrification explains, at least partly, the different levels of NO_3^- in the sludge treated soils.

The NO_3^--N concentrations in the soil to 90 cm depth at different times of the year are presented in Figs. 4.1 through 4.4. The NO_3^--N concentrations are shown as deviation from the no N treatment. It is apparent that in early spring prior to sludge application, NO_3^--N concentrations in the loamy sand profile (Fig. 4.1) and in the loam profile under grass (Fig. 4.4) were no different from the no N treatment. In the loam soil under corn at Elora (Fig. 4.3) the sludge treatment may have up to 10 μg/g more NO_3^--N than the no N treatment. Following sludge application, the NO_3^--N in the soil profles under corn increased rapidly. This is a reflection of the rapid conversion of sludge N by mineralization and/or nitrification since the anaerobically digested sludges contained no measureable NO_3^- initially. Nitrite-N (NO_2^--N) was detected only in the soil samples obtained in the June samplings of 1973, and then only in concentrations generally < 1 μg/g soil although a few samples had concentrations of about 2.5 μg/g soil. The occurrence of NO_2^- in the June samples coincided with the high nitrification rate which would normally occur at about that time if NH_4^+ was available. The limiting step in the nitrification process in soil is usually considered to be the conversion of NH_4^+ to NO_2^-; the subsequent step from NO_2^- to NO_3^- is normally relatively rapid. Nitrite was consequently not analysed in the 1974 and 1975 samples.

High NO_3^- concentration was confined mainly to the top 15cm of soil in the clay loam profile (Fig. 4.2). In the loamy sand (Cambridge) and loam (Elora) profiles (Figs. 4.1 and 4.3), high NO_3^- levels may be found down to about 60 cm. The elevated soil NO_3^- level may persist until about October or November, especially in the loamy soil. The peak NO_3^- concentration appeared to move deeper into the soil profile in the fall. By the next sampling date in the following April, the NO_3^- had declined to a level or concentration similar to that of the previous spring. Thus the excess NO_3^- may have been lost by denitrification and/or leaching.

In the loamy sand and clay loam profiles, NO_3^- concentration at the 400 kg N/ha rate was appreciably below that resulting from the 800 kg N/ha rate. In the loamy soil profile, however, the NO_3^- concentration resulting from 400 kg N/ha from sludge was often not proportionally lower than the 800 kg N/ha rate, especially in 1975.

At comparable annual sludge application rate to the same soil, NO_3^- in the soil profile under grass (Fig. 4.4) was considerably lower than that in the soil under corn (Fig. 4.3). Part of the reason for this may be that in the corn experiment the sludge was applied in one application in April, whereas in the grass experiment the sludge was applied in three applications in April, June and July. Part of the reason may be the inhibition of nitrification under grass reported by several investigators. The cause of the inhibition has been attributed to toxins secreted by the grass, but this claim has been disputed by other workers. The NO_3^- in the soil under grass appeared to increase from 1973 to 1975, indicating some residual effects of N from sludge.

The concentrations of NH_4^+-N were relatively low, rarely exceeding 10 μg/g even in the surface soil (Table 4.1). The concentrations below the 15 cm soil depth were generally lower and showed little or no effect of rate of sludge application. It therefore appears that NH_4^+ is rapidly nitrified in the surface soil and there was little or no movement of NH_4^+-N into the profile.

4.3 Ammonia loss by volatilization

4.3.1 Materials and Methods

A circular plot of 0.405 ha was set up in 1975 to measure ammonia loss by volatilization following surface application of fluid sewage sludge to soil in the spring (May 8) and in the fall (Oct. 8). The application rate was 116 t/ha in May and 134 t/ha in October. A mast holding gas collection flasks at 10, 50, and 100, and 150 cm heights above the soil surface was set up in the centre of the plot. The flasks contained 3% (v/v) H_3PO_4 solution. Air was pulled in by suction, and the ammonia trapped in the acid was subsequently determined. The air flow rate and wind speed were monitored. The air collection period was 8-13 May and 8-15 October. A diffusion model was used to predict the normalized product (wind speed x NH_3-N conc.) as a function of height, from which the NH_3- N flux was estimated. A detailed description of the experimental procedure is given by Beauchamp et al., (1978).

4.3.2 Results and Discussion

The daily and total losses of NH_3 by volatilization during the May and October experiments are presented in Table 4.3. The total NH_4^+-N added was 150 kg/ha in May and 89 kg/ha in October. Therefore 60% and 56% of the applied NH_4^+-N was volatilized during the May and October experiments respectively. The rate of decrease in NH_3- N by volatilization closely followed an exponential pattern. Half of the applied NH_4^+-N was lost in 3.6 days in May and in 5.0 days in October. The difference probably reflects the less favourable conditions (cooler days and more days with rain) for volatilization during the October experimental period.

4.4 Laboratory studies of sludge N mineralization and nitrification

It has been estimated that from 15 to 40% of the organic N applied in sludge may be mineralized in the year of application, with less quantities mineralized in the succeeding years (Keeney, et al. 1975; Pratt, et al. 1973). A preliminary incubation study showed that NO_3^- production was inhibited when an Al-sludge from Point Edward was mixed with soil (Beauchamp and Moyer, 1974). The studies reported in this section were conducted to determine if the chemical treatment of sewage affected the mineralization and nitrification of sludge N in soil.

4.4.1 Materials and Methods

Experiment 1 was performed with six whole sludges to determine if chemical treatment of sewage with $Al_2(SO_4)_3$ or $FeCl_3$ had any effect on N mineralization and nitrification in soil. A mixture of 15g quartz sand and 15g soil (a silt loam with 4% O.M. and a pH of 7.6 in 0.01M $CaCl_2$) was mixed with a quantity of sludge containing 12 mg of total N. The mixture was spread on a glass-fibre filter paper in a No. 2 Buchner funnel, and immediately leached with 125 ml of distilled water to 0.3 bar moisture content. The soil was then incubated at 23-25°C for 31 weeks. Moisture loss was minimized by a black plastic film held in place over the Buchner funnel. Filtrates were collected weekly following leaching with 125 ml of distilled water and analysed for NH_4^+ and NO_3^-. The treatments were set up in triplicate.

Experiment 2 was conducted in the same manner as experiment 1 with five sludges from which soluble and exchangeable NH_4^+ and soluble organic N had been removed by leaching with 2M KCl. The leached sludges were then analysed for total N content by Kjeldahl digestion and mixed and treated in the same manner as the whole sludges in experiment 1. The experiment was terminated after 49 weeks and the total N in the soil/sand mixture was analysed following Kjeldahl digestion. In this experiment, the rate of mineralization and nitrification of insoluble organic sludge N was studied. More details of the two experiments are provided by Beauchamp et al. (1979).

4.4.2 Results and Discussion

Some chemical characteristics of the sludges used are presented in Table 4.4

The NO_3^- production for the six whole sludges differed in a manner unrelated to the chemical treatment of the sewage (Fig. 4.5). Nitrate production was severely inhibited with the Point Edward sludges. Apparent nitrification of the Point Edward (1973) sludge did not commence until the ninth week. Although chemical treatment of sewage at Point Edward changed from $Al_2(SO_4)_3$ in 1973 to $FeCl_3$ in 1974, NO_3^- production was still relatively low with the 1974 sludge, and was not apparent until the eighth week. The Point Edward sludges produced during this period were found to have about 16 times more petroleum hydrocarbons and lipids than other "normal" sludges (Chawla et al., 1974). It is possible that the apparent inhibition of nitrification in this study was related to the relatively high contents of these substances.

The reasons for the difference in NO_3^- production between the other sludges are not so apparent. It is believed that the heavy metals such as Cu, Cr and Zn are not factors, since none of the sludges used resulted in an addition of > 33 μg Cu, 88 μg Cr and 75 μg Zn per g of soil/sand mixture. Premi and Cornfield (1971) reported that addition of 100 μg Cu, Zn or Mn per g soil did not depress N mineralization and nitrification. They also suggested that relatively high NH_4^+ concentrations delayed nitrification. This possibility cannot be ruled out in this study since the amount of

NH_4^+ added in sludge was Kitchener > Guelph > Tillsonburg > North Toronto. Apparent nitrification was less with the Kitchener and Guelph sludges than with the N. Toronto or Tillsonburg sludges (Fig. 4.5).

Apparent nitrification amounted to, 17 to 30% of the applied N within 16 weeks of incubation except with the Point Edward sludges.

When sludges from which soluble and exchangeable NH_4^+ and soluble organic N had been removed were incubated, a lag in NO_3^- production was not apparent (Fig. 4.6). Since leaching was done at weekly intervals, a lag period of less than a week would not be detected. Mineralization and nitrification with four of the sludges (N. Toronto, Guelph, Kitchener and Newmarket) did not differ appreciably. The apparent absence of a lag period lend support to the observation in the first experiment that high NH_4^+ in the sludges inhibited nitrification.

With the Point Edward (1974) sludge, nitrification lagged behind the control treatment until the 10th week, but after that the rate of NO_3^- production was similar to those of the other sludges. The factor or factors retarding mineralization and nitrification in this sludge appeared, therefore, to slowly dissipate with time, and appeared not to have been removed in the liquid sludge fraction.

With the exception of the abnormal Point Edward sludge, 29-32% of the insoluble organic N in the other sludges was recovered as NO_3^- in 16 weeks, and 41 to 46% in 49 weeks.

The sand/soil mixture used in the incubation contained 31.5 mg N as determined by Kjeldahl digestion, while 12 mg of insoluble organic N was added in sludge. As shown in Fig. 4.6 and Table 4.5, sludge N was more readily mineralized and nitrified than soil N. It is possible, however, that sludge may have accelerated soil N mineralization somewhat.

These experiments demonstrate that (i) with whole sludges there appears to be a lag period of two to three weeks before rapid nitrification begins; (ii) the lag period appears to be attributable partly to the high NH_4^+ concentration in the sludges; and (iii) when the soluble and exchangeable NH_4^+ was removed the organic N fraction can become a significant source of N to crops through rapid mineralization and nitrification.

4.5 Summary and conclusions

About 60% of NH_4^+-N in sludge applied on soil surface was lost by volatilization. The NH_3 loss decreased in an exponential manner with time, with about half of the loss occurring within 4 to 5 days. Following a lag period, N in anaerobically digested sludges applied to soil in the laboratory was rapidly nitrified. In a laboratory study (Expt. 2) in which soluble and exchangeable NH_4^+ and soluble organic N were removed from sludge before mixing with soil, the organic N was rapidly mineralized and nitrified. About 30% of the organic N was recovered as NO_3^- in 16 weeks. In the field, during the growing season, NO_3^- in sludge-treated soil was confined mainly to the top 30 cm. Considerable NO_3^- remained in the soil after harvest if sludge N was applied in excess of crop requirements. This excess NO_3^- was lost by leaching and possibly by denitrification by the following spring. To prevent NO_3^- leaching, sludge application rates should be limited to the N requirements of the crops grown.

Table 4.1: Effect of sludge and NH_4NO_3 on NH_4^+-N and NO_3^--N concentrations in surface soil (0-15 cm) in June 1974 and 1975 at Cambridge and Milton.

N application rate	Cambridge (Caledon ls)				Milton (Oneida cl)			
	1974		1975		1974		1975	
	NH_4NO_3	sludge	NH_4NO_3	sludge	NH_4NO_3	sludge	NH_4NO_3	sludge*
kg N/ha	µg NH_4^+-N/g							
0	5		6		9		-	
100	9		4		9		6	
400	6	8	4	6	39	12	6	7
800		11		7		21		7
	µg NO_3^--N/g							
0	15		16		28		-	
100	29		50		49		50	
400	64	26	89	52	103	36	139	87
800		33		83		63		127

* No sludge applied in 1975.

Table 4.2: Effect of N source on NH_4^+-N and NO_3^--N concentrations in surface soil (0-15 cm) in June 1974 and 1975 at Elora.

N application rate	1974				1975			
	NH_4NO_3	Ca-sludge	Al-sludge	Fe-sludge	NH_4NO_3	Ca-sludge	Al-sludge	Fe-sludge
kg N/ha	µg NH_4^+-N/g							
0	8				5			
100	13				5			
400	12	17	16	9	5	7	7	6
800		15	29	10		8	8	12
	µg NO_3^--N/g							
0	13				34			
100	33				50			
400	116	31	78	48	139	79	87	96
800		69	167	70		106	139	126

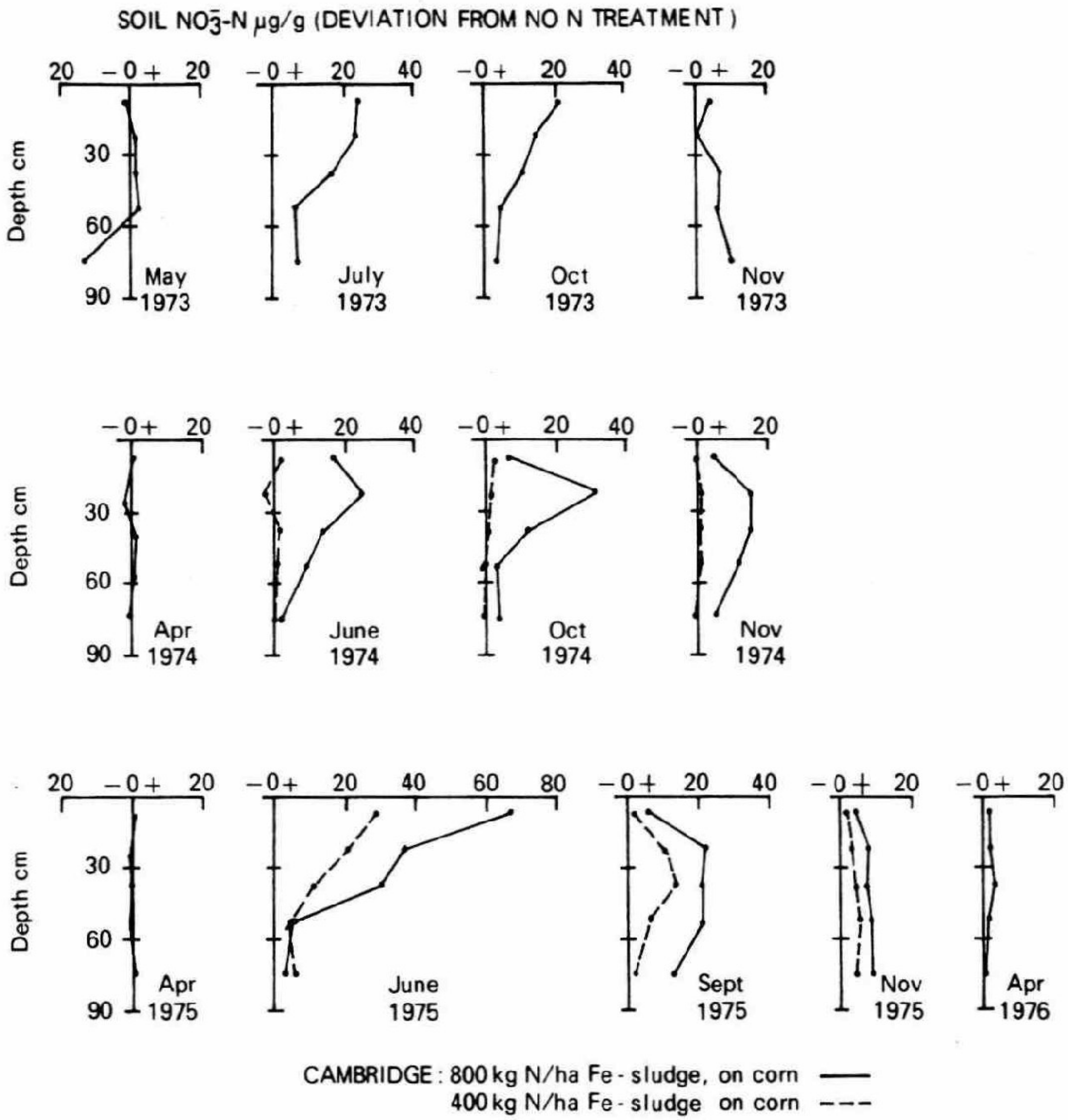


Figure 4.1 Movement of NO$_3^-$ in Caledon loamy sand treated with Fe - sludge.

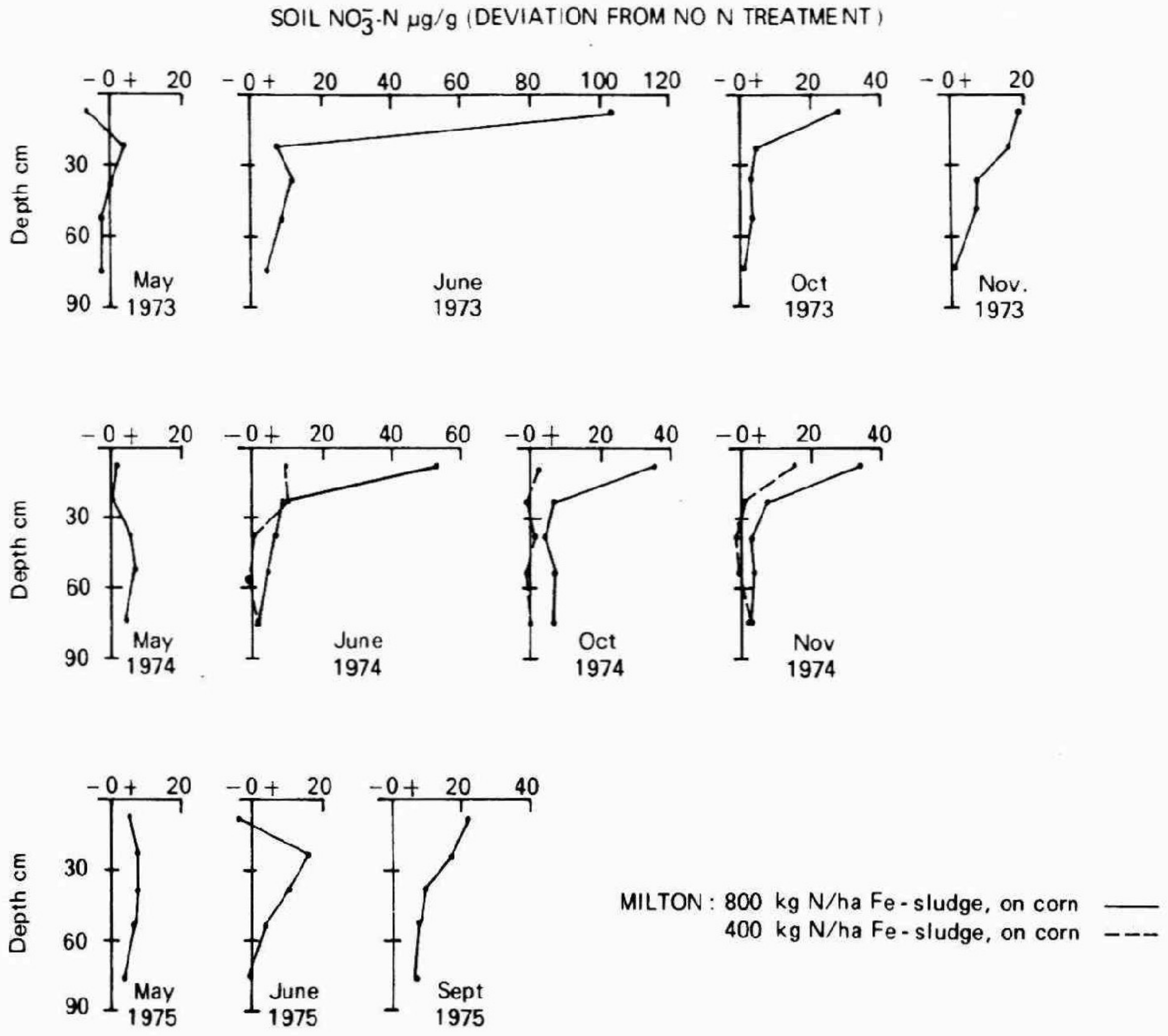


Figure 4.2 ***Movement of NO$_3^-$ in Oneida clay loam treated with Fe-sludge.***

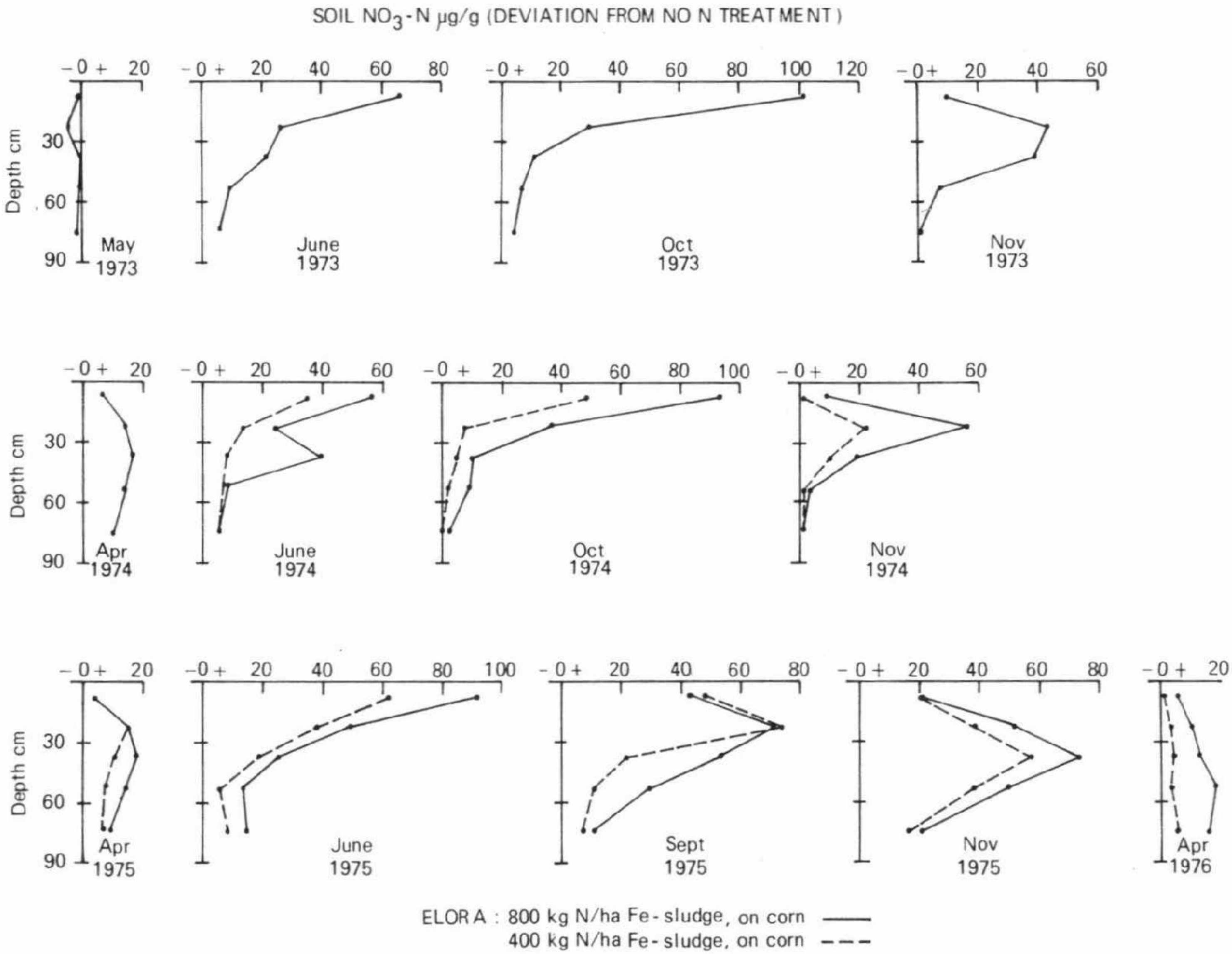
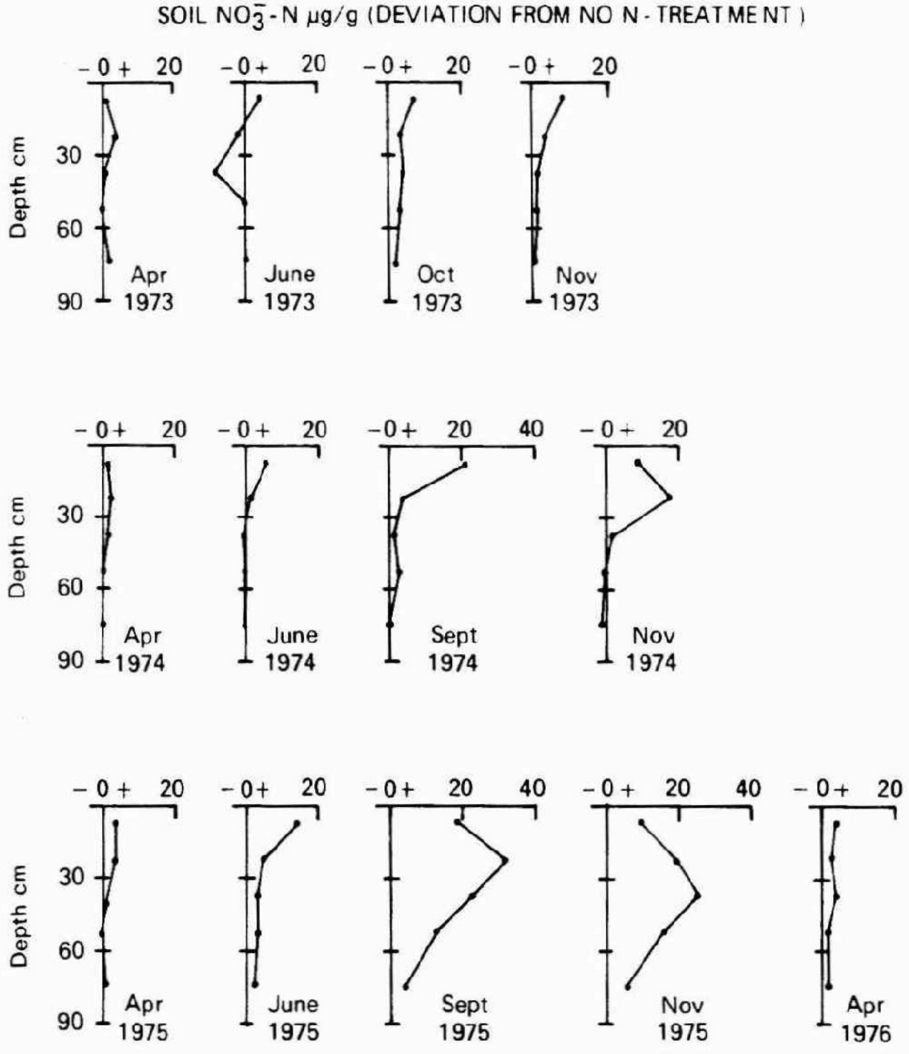


Figure 4.3 Movement of NO_3^- in Conestoga loam under corn, treated with Fe-sludge.



ELORA : 800 kg N/ha Fe-sludge, on grass

Figure 4.4 Movement of NO_3^- in Conestoga loam under bromegrass, treated with Fe-sludge.

Table 4.3: Daily losses of ammonia volatilized during the May and October experimental periods.

May Experiment		October Experiment	
Date	NH_3-N volatilized	Date	NH_3-N volatilized
	kg/ha		kg/ha
8*	22.2	8+	16.4
9	36.5	9	14.5
10	14.5	10	4.2
11	8.9	11	4.5
12	5.4	12	3.9
13	3.5	13	2.0
		14	3.2
Total	90.9	15	1.6
		Total	50.3

* measurements began at 1300h.

\+ measurements began at 1200h.

Table 4.4: Some chemical properties of liquid sludges used in laboratory incubation experiments 1 and 2.

Sludge		Properties						
Source	Treatment	pH	D.M.	Al	Fe	Ca	Total N	Sol. + Exch. NH_4^+-N
			(%)	----------μg/ml----------				
Experiment 1								
North Toronto	$FeCl_3$	7.1	6.8	1000	5400	3800	3000	973
Point Edward (1973)	$Al_2(SO_4)_3$	7.2	3.9	6900	750	1100	1000	425
Point Edward (1974)	$FeCl_3$	7.1	19.4	563	22300	19400	3100	658
Kitchener	$Al_2(SO_4)_3$	7.3	6.5	1600	700	6500	2800	1334
Guelph	$Al_2(SO_4)_3$	7.2	4.7	2070	940	2800	1700	648
Tillsonburg	$Al_2(SO_4)_3$	--	--	--	--	--	1700	621
Experiment 2								
Kitchener	$Al_2(SO_4)_3$	7.2	6.7	1900	700	6500	--	--
North Toronto	$FeCl_3$	7.2	5.4	750	4530	3000	--	--
Point Edward	$FeCl_3$	7.1	6.4	170	9280	4100	--	--
Newmarket	$Ca(OH)_2$	7.1	10.0	190	470	43900	--	--
Guelph	$Al_2(SO_4)_3$	7.2	2.4	720	630	2000	--	--

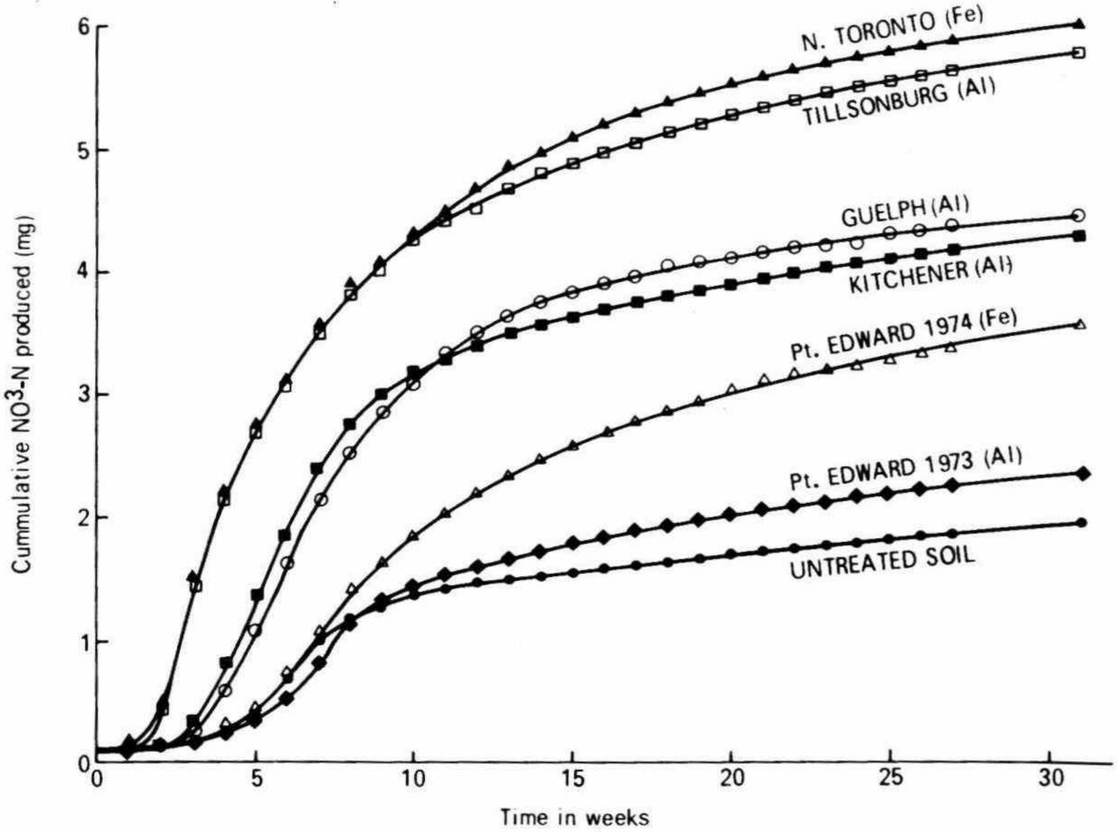


Figure 4.5 Nitrate production during incubation of soil/sand mixtures treated with sludges supplying 12 mg N per incubation unit.

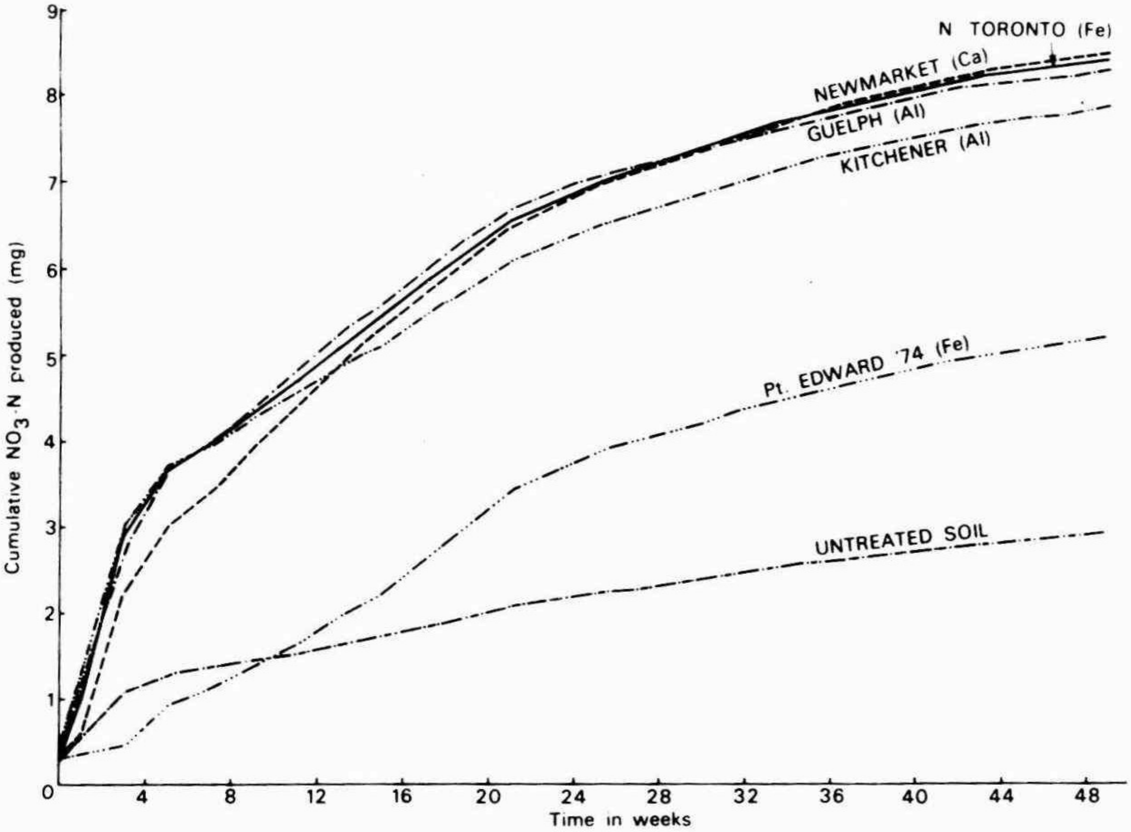


Figure 4.6 Nitrate production during incubation of soil/sand mixtures treated with sludges supplying 12 mg of organic N per incubation unit. Soluble and exchangeable NH_4^+ and soluble organic N were removed from the sludge by leaching before mixing with the soil/sand.

Table 4.5: Total N in untreated and treated soil/sand mixtures, and calculated N losses and NO_3^--N recoveries at the end of the 49-week period in Experiment 2.

Sludge Treatment	Total N	Calculated§ N loss	Calculated† NO_3^--N Recovery
	------------ mg N/incubation unit		-----------
Control*	28.8 ± 1.3**	2.7	2.6
Kitchener	32.6 ± 3.3	10.9	7.5
North Toronto	32.1 ± 1.0	11.4	8.1
Point Edward '74	30.7 ± 2.5	12.8	4.8
Newmarket	32.7 ± 2.4	10.8	8.1
Guelph	31.4 ± 0.9	12.1	8.0

† From Fig. 4.6.

* Soil/sand mixture in each incubation unit initially contained 31.5 ± 0.6 mg N.

** ± standard deviation.

§ By difference between total N at the beginning and at the end of experiment.

5. MICROBIOLOGICAL STUDIES

5.1 Objective

The objective of this phase of the program was to establish the number of some groups of indicator bacteria in runoff waters and in sludges, and to determine the presence or absence of such human pathogenic types as members of the genera Salmonella and Shigella in sludges and runoff waters and on plant material harvested from plots receiving sludges. The program was terminated in early 1976.

5.2 Materials and Methods

(a) Sludges and runoff waters: Samples of these were examined as soon as possible following application or collection. For the detection of Salmonella and Shigella, 250 g of sludge or 250 ml of runoff were added to duplicate flasks of the following enrichment media:

Tetrathionate Broth (Difco #0491)
Selenite Brilliant Green Sulfa Broth (Difco #0715)
GN Broth (Difco #0486)

A flow diagram of the procedure is presented in Fig 5.1. The primary plating media were:

MacConkey Agar (Difco #0075)
Br. Green Sulfa Agar (Difco #0717)
Hektoen Enteric Agar (Difco #0853)
SS Agar (Difco #0074)

The most probable numbers of coliforms and faecal coliforms were established by a multiple tube dilution procedure using Lauryl Typtose Broth and Brilliant Green Bile Broth at 37°C and EC Broth at 44.5°C. The most probable numbers of faecal streptococci were estimated by a multiple tube procedure with KF Streptococcus Broth.

(b) Corn and grass samples: Corn plant samples were obtained from the field studies when the plants were at the four-to six-leaf stage, ie. at the time of thinning, from plots receiving 1600 kg N/ha from sludge or 200 kg N/ha from NH_4NO_3. Some corn plant samples were also obtained from an Elgin county farm which had not received sludge but had received animal manure and chemical fertilizers.

The grass samples were obtained from each of three cuttings per year from the bromegrass experiment from plots receiving 1600 kg N/ha from sludge or 200 kg N/ha from NH_4NO_3.

The plant samples were stored refrigerated or frozen in plastic bags until examined. The plant materials were cut into short lengths and mixed with buffered water in a blender jar. The culturing, isolation and identification follows the flow diagram in Fig. 5.1.

5.3 Results and Discussion

5.3.1 Sludges

During the period May 1973 to March 1976, Salmonella species were detected in 20 of 54 sludge samples. This was found in all three sources of sludge used in the field studies. The numbers of indicator organisms in the North Toronto sludge samples are presented in Table 5.1. Similar values were obtained for the Newmarket and Kitchener sludges.

5.3.2 Runoff Waters

The North Toronto sludge was applied to the runoff plots. Microbial studies of runoff waters produced rather variable results, with the sludge treatments not consistently higher in faecal coliforms or faecal streptococci than the treatments receiving chemical fertilizers (Table 5.2). Therefore the value of these indicator bacteria as indicators of quality of runoff water is questionable. Of 484 samples studied, Salmonella was detected in one. The lack of faecal coliforms is consistent with the absence of Salmonella-Shigella types.

5.3.3 Corn and grass tissue samples

Salmonella was detected in two out of 96 samples of grass and four out of 111 corn samples. One of the grass samples was from the Ca-sludge and the other from the Fe-sludge treatment. Both were from the third cutting in 1974. Of the four corn seedling samples found to contain Salmonella, three were from the Cambridge site and involved the Ca-sludge. The fourth sample, also involving the Ca-sludge, was from Elora. These were 1975 samples.

5.4 Conclusions

The fluid digested sewage sludges used contain appreciable numbers of total and faecal coliforms and faecal streptocci. Sewage sludge application did not result, however, in measurably increased numbers of indicator organisms in runoff waters.

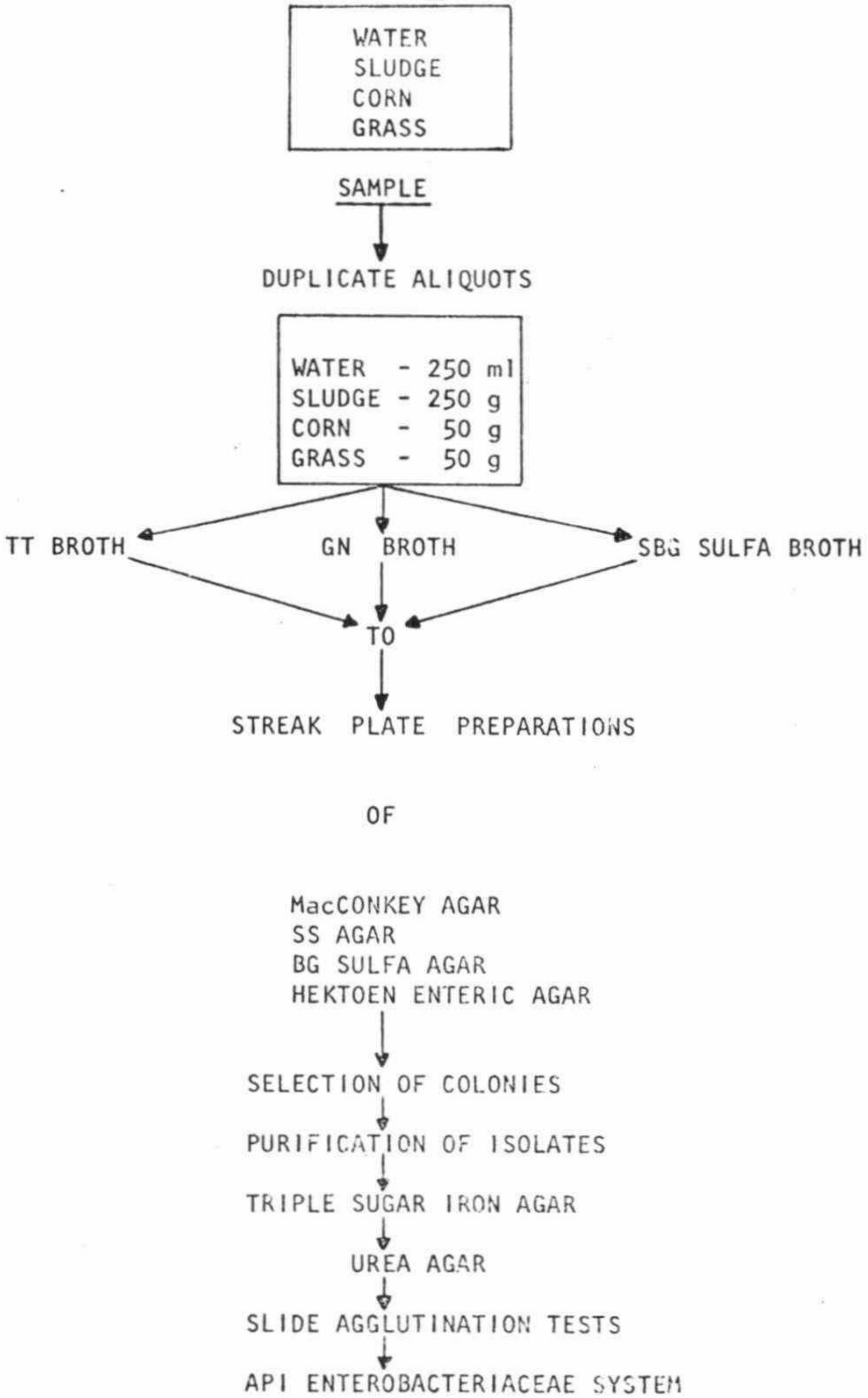


Figure 5.1 Procedure for the detection of Salmonella-Shigella

Table 5.1: Number of some indicator organisms* in North Toronto (iron-treated) sludge.

				Samples of:		
Microorganisms	May 9/73	May 19/73	May 25/73	May 29/73	June 23/73	July 26/73
Total Coliforms	155,000	480,000	795,000	19,500,000	165,000	1,900,000
Faecal Coliforms	20,000	12,500	80,000	2,400,000	80,000	24,000
Faecal Steptococci	2,300,000	445,000	895,000	6,000,000	295,000	7,300,000

	April 30/74	May 2/74	May 24/74	June 20/74	July 25/74	Nov. 19/74	Jan 15/75
Total Coliforms	200,000	12,500	45,000	1,200,000	1,550 000	1,260,000	260,000
Faecal Coliforms	37,000	200	0	500,000	550,000	107,000	126,000
Faecal Steptococci	16,000,000	1,900,000	1,600,000	11,000,000	8,320,000	73,000	24,000

* Most probable number/100 ml

Table 5.2: Average numbers of indicator organisms in runoff waters.

Indicator Microorganisms	Time* and rate of sludge application (kg N/ha)										
	None		F(200)		W(200)		S(200)		F(800)	W(800)	S(800)
	Slope of land (%)										
	2	6	2	6	2	6	2	6	2	2	2
	Most probable number/100ml										
	Runoff event of April 2, 1974										
Total coliforms	65,000	805,000	2,300	455,000	130,000	417,000	19,000	51,000	58,000	104,000	12,000
Faecal coliforms	2	1	4	1	0	0	2	3	2	0	1
Faecal Streptococci	2,400	9,100	2,300	27,000	32,000	37,000	16,000	140,000	3,000	5,000	2,100
	Runoff event of May 17, 1974†										
Total Coliforms	100	93	60	1,200	1,650	2,500	200	795	90	340	220
Faecal coliforms	0	0	0	10	0	0	0	32	0	0	0
Faecal Streptococci	1,100	790	250	28,500	1,300	8,000	700	2,400	650	4,450	1,600

* Fall, winter and spring applications are denoted by F, W, and S respectively.
† The spring 1974 application was on May 3.

6 SOIL CHARACTERIZATION

6.1 Objectives

The main objectives of the pedochemical studies were to (a) determine the nature of sludge-soil interaction, and (b) determine the extent of movement and distribution in the soil of chemical elements added in sludge.

6.2 Characterization of sludge samples by X-ray diffraction

The aim of this study was to identify the inorganic and/or crystalline components in some sewage sludges.

6.2.1 Materials and Methods

The sludges were plated on 2.5 x 7.5 cm glass slides, and X-ray diffraction patterns were collected after each of four pretreatments (air drying, heating to 100°C, to 350°C and to 550°C).

6.2.2 Results and Discussion

The X-ray diffraction information is summarized in Table 6.1. Quartz, feldspar, silicate clays and calcite were soil minerals found in the sludges. Some forms of iron and aluminum phosphate and aluminum sulphate hydrate were present in some sludges. As the diffraction patterns were taken on the total sludge, definite identification of the complex iron and aluminum phosphate hydrates was not possible.

6.3 Characterization of soil from the greenhouse experiment

The objective of this study was to examine the nature of sludge-soil interaction products and to determine the location of heavy metals in soils receiving sludge.

6.3.1 Materials and Methods

All analyses were done on soil samples from the control and the 1600 kg N/ha rate of each sludge after the fourth crop of ryegrass. The surface peds and deposits were examined by an Etec-Autoscan scanning electron microscope.

Specially cut thin sections of blocks of soils were examined with an Acton electron microprobe at the University of Waterloo. The sections were carbon-coated using standard high vacuum techniques.

Bulk soil samples were ground to 100 mesh size and subsamples extracted with sodium pyrophosphate and acid ammonium oxalate, and the metal concentrations determined by atomic absorption.

6.3.2 Results and Discussion

Coloured deposits on the soil surface were found under the microscope to be accumulations of microorganisms and evaporites. Generally, white-coloured deposits overlie green and red deposits. Under the scanning electron microscope, the coloured "ped" or surface deposits were found to be composed mainly of collapsed cellular structure or organic matter. The white deposits were needle-like or plate-like particles and were probably evaporites.

During investigation with the electron microprobe analyser, one detector had a high background, resulting in concentrations of Fe, Ca, Cu, Zn, Ni and Cr in the non-soil part of the sections that were too high. However, P appeared to be associated with Fe accumulation in the soil treated with the Sarnia sludge. In the soil treated with the Midland sludge, P appeared to be associated mainly with Ca accumulation.

Generally, sodium pyrophosphate extracts soil Fe and Al associated with organic matter as complexes, and ammonium oxalate extracts Fe and Al associated with organic matter and dissolves amorphous soil Fe_2O_3 and Al_2O_3. The results of the chemical extractions are presented in Table 6.2. It is evident that the Fe-treated sludges increased the soil Fe content, and the Al-sludges increased the soil Al content.

6.4 Characterization of soil profiles in the field corn experiments

The objective of this study was to determine the extent of movement of some main sludge chemical constituents in the soil.

6.4.1 Materials and Methods

One soil profile from one replicate of the 1600 kg N/ha treatment of each of the three sludge treatments was taken in the fall of 1975. Two profiles from check plots, taken in 1972, were used as a basis for comparison. The low number of profiles was chosen so as to disturb the soil to a minimum. It did make comparison somewhat difficult. Extraction and analysis were done as described in Section 6.3.1. The profiles were described according to "The System of Soil Classification for Canada" (Canada Department of Agriculture, 1974).

6.4.2 Results and Discussion

The Fe-sludge caused the biggest increase in oxalate-extractable Fe in the plow layer (0 to ≈ 15 cm depth). The Fe-sludge added considerably more Fe than the other sludges, and the Al-sludge more Al (Table 6.3). Sludge application also increased the oxalate-extractable Al in the plow layer. In these experiments, the surface applied sludge was incorporated into the top 15 cm of soil during seedbed preparation. Thus movement can only be inferred if the added sludge constituents are found below the plow layer. There appears to be some movement below the 15 cm depth at the Elora site. The maximum Al and Fe content were found at about 30 cm depth with the Ca-sludge. However, because of a lack of replicaton, the results could have been due to soil variability. As was the case with the Elora site, the results of the profile analyses of the Cambridge site suggest that there may have been some movement of Al and Fe from sludge application. There is, however, even greater profile variation at this site. Thus the higher Fe and Al contents in the Bt horizon of the Fe-sludge treated soil may have been due to movement and accumulation, or to previous pedogenetic accumulation. The high Fe content of the III Ck and V Ck horizons of the Ca-sludge soil profile is believed to be due to pedogenetic effects.

6.5 Characterization of soil from the bromegrass experiment

In the grass experiment, the sludge was surface applied and not incorporated into the soil by tillage. As such it presented the best opportunity to study the distribution and movement of sludge components added to the soil surface. Additionally, the effects of sewage sludge on some soil chemical properties are also determined.

6.5.1 Materials and Methods

In September, 1974, after the third cut of bromegrass, soil was sampled in increments of 2.5 cm to a depth of 30 cm. Extraction and analysis for Fe and Al were done as described in Section 6.3.1. Surface layers of one plot of each sludge treatment at the 1600 kg N/ha and 200 kg N/ha rates were sampled for thin section preparation.

In 1979, it was decided to broaden the study of chemical changes and distribution with depth. Soil receiving 400 kg N/ha from sludge or from NH_4NO_3 and 1600 kg N/ha from sludge were sampled in October 1979 from the 0-5, 5-10, 10-15 and 15-20 cm depths. Twenty-four soil cores were sampled from each of three replications, and bulked to constitute a composite sample. The air-dried samples were ground to pass through 2 mm sieve. The soil was analysed in triplicate for carbonates, organic-C using a modification of the Tinsley method (Kalembasa and Jenkinson, 1973), and pH. Iron and Al were extracted by 0.1M sodium pyrophosphate ($Na_4P_2O_7$), 0.2M ammonium oxalate (pH 3), and 0.2M sodium citrate-citric acid containing 5% (w/v) sodium dithionite ($Na_2S_2O_4$). The pyrophosphate and oxalate extractions are those described by McKeague et al.(1971). The dithionite extraction is described by Coffin (1963). In addition, extractable Cd, Cu, Cr, Ni, Pb and Zn were characterized by the following extraction procedure. Half a gram of sludge-amended soil or 1 g of untreated soil was shaken sequentially with 25 ml of the following extractants: 1M KNO_3 for 3 hrs; 0.1M $Na_4P_2O_7$ for 16 hrs; 0.2M ammonium oxalate (pH 3) for 4 hrs in darkness; 0.2M sodium citrate-citric acid containing 5% (w/v) $Na_2S_2O_4$ (precleaned by solvent extraction in APDC-MIBK to remove trace contaminants) for 30 minutes at 50°C in a hot water bath; and in 1M HNO_3 for 24 hrs. The extractants provide a measure of the amount of metal that is exchangeable, is associated with organic matter, with amorphous iron and aluminum oxides, with crystalline iron and aluminum oxides, and with carbonate and/or sulfide fractions respectively. After each extraction, the suspension was centrifuged and filtered, and the filtrate analysed for metal content by atomic absorption. The soil samples were also digested with aqua regia for metal content (Van Loon and Lichwa, 1973). All metal extractions were done in duplicate.

6.5.2 Results and Discussion

6.5.2.1 Thin Section Examination

Under the petrographic microscope the Ca-sludge in thin section of the surface soil was a grainy white precipitate with crystals, presumably, of $CaCO_3$; the Al-sludge appeared to have narrow slivers or fibres of crystalline compounds. The Fe-sludge appeared to be an amorphous precipitate with a few scattered crystals. Electron microprobe analysis showed P to be concentrated mainly with Fe, and to a lesser extent with Al. The movement downward of the Ca-sludge was evident but not the Al- and Fe-sludges. Iron-phosphorus accumulations in the Fe-sludge appeared to be decomposing.

6.5.2.2 Chemical Analysis - 1974 Samples

The distribution of ammonium oxalate and sodium dithionite extractable Al and Fe from about 7.5 cm downwards for soil treated with or without sludge was similar, therefore only changes to the 12.5 cm depth are shown in Table 6.4. At the 200 kg N/ha rate, the changes were confined only to the 0 to 2.5 cm depth (shown only for the Fe-sludge in Table 6.4). Ammonium oxalate extractable Fe was increased to the 5 cm depth by the Fe-sludge and to the 2.5 cm depth by the Al-sludge. Sodium dithionite extractable Fe was reduced by the Ca- and Al-sludges to approximately 5 cm deep, and was increased by the Fe-sludge to the 2.5 cm depth. The Al-sludge increased sodium dithionite and ammonium oxalate soluble Al to the 5 cm depth.

6.5.2.3 Chemical Analysis - 1979 Samples

Sludge application increased the organic C in the top 10 cm of soil (Fig. 6.1), with the Al-sludge having the greatest effect. Carbonate was increased, at least to the 20 cm depth (Table 6.5) by the Ca-sludge, to the 10 cm depth by the Al-sludge, and to the 5 cm depth by the Fe-sludge. Most of the carbonate is expected to be $CaCO_3$ in view of the preponderance of Ca over Mg added by sludge (Table 6.6). The carbonate in the 5 to 20 cm depth appeared to be decreased by the Fe-sludge. This is probably caused with the acidifying effect of the Fe-sludge (Table 6.7). The Al-sludge decreased soil pH only to the 5 cm depth, and the Ca-sludge increased soil pH at least to the 20 cm depth. It is concluded that acid generated by the mineralization of organic matter and by nitrification dissolved the carbonate in the soil below the sludge layer and decreased pH. The Fe-sludge had a higher N/base cation (K + Ca + Mg) ratio than the other sludges.

Oxalate extractable Fe (commonly used as a measure of amorphous iron oxide) was increased by sludge application with the bulk remaining in the top 5 cm of soil (Fig. 6.1). There was some movement of oxalate extractable Fe to the 15 cm depth with the Ca- and Fe-sludge treatments. The Ca-sludge applied in 1977 was chemically treated with Ca plus Fe, and thus resulted in the large increase in the amount of Fe added and extracted. The Fe-sludge added the most Fe (Table 6.6) but did not result in a proportionally greater amount of oxalate-extractable Fe than the Ca-sludge because much of it appeared to be associated with organic matter extracted by sodium pyrophosphate (Table 6.8). Sludge did not increase crystalline iron oxide content (as measured by dithionite soluble Fe (Fig. 6.1); its content in the top 5 cm of soil appeared to be reduced by sludge application probably because of dilution caused by the addition of organic matter and inorganic constitutents such as carbonates and amorphous iron oxide through sludge application.

Oxalate-extractable Al (commonly used as a measure of amorphous aluminum oxide) was increased by sludge application, with the Al-sludge having the greatest effect (Table 6.9). Sludge application appeared not to add any crystalline aluminum oxide, as determined by dithionite-soluble Al (Table 6.9), but rather to decrease the content in the top 5 cm through dilution effects as was noted for crystalline iron oxide. A considerable amount of Al in sludge was associated with organic matter extracted by pyrophosphate (Table 6.9).

Cadmium in the untreated soil was associated mainly with soil organic matter or organo-mineral complexes extracted with sodium pyrophosphate (Fig. 6.2). Other fractions may be present but were below the detection limit (0.02 μg/g soil). In Fig. 6.2 and 6.3 extractable metals below the detection limit, or constituting < 2% of aqua regia soluble metal are not represented. In soil treated with sludge, Cd was mainly soluble in pyrophosphate and in 1M HNO_3. The dilute acid soluble fraction is believed to be comprised of Cd coprecipitated with carbonates and sulfides (as indicated by effervescence and the distinctive odor of H_2S). The major portion of Cd added in the Ca-sludge is probably associated with the carbonate fraction. Little Cd appeared to be associated with Fe and Al dissolved by ammonium oxalate or by sodium dithionite. Cadmium added in sludge appeared to have moved to at least the 20 cm depth as shown by its recovery by aqua regia extraction (Fig. 6.2).

Copper in the untreated soil was associated mainly with oxalate-extractable Fe, i.e. with amorphous iron oxide, with smaller amounts associated with organic matter and coprecipitated probably as carbonates (Fig. 6.2). Sludge increased the fractions associated with organic matter and with amorphous iron oxide. There appears to be little difference in this respect between the sludges used. Copper added in sludge appeared to have moved at least to the 20 cm depth.

Zinc in the untreated soil was associated with (a) carbonates, (b) amorphous and crystalline iron and aluminum oxides, and (c) organic matter. Sludge application increased the fraction associated with organic matter most, followed by the fraction associated with amorphous iron and aluminum oxide. Zinc soluble in dithionite and in 1M HNO_3 increased slightly with sludge application, but appeared in Fig. 6.2 as smaller percentages than those of the untreated soil. This is not surprising as sludge added no measurable amount of crystalline iron and aluminum oxide. Sludge also increased the amount of exchangeable Zn; this is not represented in Fig. 7.2 because it constituted $< 2\%$ of the aqua regia soluble Zn. The Al-sludge applied at the 1600 kg N/ha rate increased exchangeable Zn from < 0.5 μg/g to 6.3 μg/g, and the Fe-sludge at 1600 kg N/ha rate to 2.5 μg/g. Zinc added in sludge appeared to have moved at least to the 20 cm depth.

Nickel in the untreated soil was mainly extractable by oxalate and by 1M HNO_3 about 20% by each (Fig. 6.3). Less than 10% of the aqua regia soluble Ni was pyrophosphate-soluble. About 45 to 60% of the aqua-regia soluble Ni was not extracted in the sequential extraction. Nickel added in sludge was mainly oxalate-extractable, i.e. was associated with amorphous iron and aluminum oxide. A smaller fraction was associated with organic matter. The Ca-sludge added the most Ni, and in this treatment Ni moved at least to the 20 cm depth. Much smaller amounts of Ni were added in the other sludges, and Ni moved no further than the 10 cm depth.

Only the soil treatments receiving 1600 kg N/ha from the Fe-sludge and 400 kg N/ha from NH_4NO_3 were fractionated for Cr and Pb analyses because the plant availability of these metals are low. These metals are considered by CAST (1976) to be less of a potentially serious hazard to the soil-plant-animal system than Cd, Cu and Zn.

Chromium in the untreated soil was bound to organic matter and amorphous and crystalline iron and aluminum oxides, and was also associated with the acid soluble fraction probably as carbonates (Fig. 6.3). Most of the Cr added in sludge appears to be associated with organic matter or organo-mineral complexes, with a smaller amount bound to amorphous iron and aluminum oxide. Sludge Cr appeared to have moved at least to the 15 cm depth.

Lead in the untreated soil was 1M HNO_3-soluble to a large extent (Fig. 6.3). This suggests that Pb may be coprecipitated as carbonates and even phosphates. A smaller amount of "native" Pb was bound to organic matter and amorphous iron and aluminum oxides. Lead added in sludge was mainly associated with organic matter in the soil, and coprecipitated as carbonates, sulfides or phosphate. A smaller amount appeared to be associated with the amorphous iron and aluminum oxide. Lead appears to have moved at least to the 20 cm depth.

6.6 Characterization of some chemical properties of field soils amended with sewage sludge

In this study, the effect of several applications of sewage sludge on the cation exchange capacity and organic matter content of soils in the corn experiments are determined.

6.6.1 Materials and Methods

Soil from the corn experiments at Elora and Cambridge were sampled from the 0 to 15 cm depth in Oct. 1976 and 1979, and analysed for organic matter as in Section 6.5.1 and for CEC (Bascomb, 1964).

6.6.2 Results and Discussion

The cation exchange capacities of the surface soil are presented in Table 6.10 and 6.12. Sludge treatments, in particular the Al- and Fe-sludges, increased soil CEC considerably. Data for some 1976 samples are presented in parentheses.

The organic C contents of the surface soil are presented in Table 6.11 and 6.13. The Al- and Fe-sludges increased soil organic C content to a greater extent than the Ca-sludge. From this it appears that the increase in soil CEC resulting from sludge application was due mainly to the organic matter added in sludge (organic matter = organic C x 1.72). The Ca-sludge added much dry matter, but the bulk of it was mainly inorganic compounds such as lime and iron salts or compounds. The organic C contents for some treatments in 1976 are presented in parentheses.

6.7 Summary and Conclusions

Iron added in Fe-sludges and Al added in Al-sludges are present in the soil mainly as amorphous compounds of Fe and Al respectively, and as Fe- and Al-organic matter complexes. There is some movement of these sludge constituents into the soil. Heavy metals added in sewage sludge also moved in the soil. In the bromegrass experiment in which the sludge was surface applied and not incorporated into the soil, metals were found as far as the 10 to 20 cm depth after seven years of repeated sludge application. The metals appear to be associated mainly with soil organic matter and amorphous hydrous iron and aluminum oxides and dilute acid-soluble components possibly including carbonates and sulfides. The bulk of the organic matter and iron and aluminum, however, was in approximately the top 5 cm. The heavy metals added in sludge were therefore solublilized and translocated downwards upon decomposition of sludge components, to be retained by soil organic matter and other components further down the soil.

Table 6.1: Preliminary identification of X-ray diffraction data on twelve sludges.

Sludge	Treatment	Quartz	Feldspar	Calcite	Silicate clays	Iron phosphate hydrate	Aluminum phosphate hydrate	Aluminum sulphate hydrate	Aluminum silicate hydrate
				Field Expt. 1973					
North Toronto	$FeCl_3$	x	<	<		<		x	
Newmarket	$Ca(OH)_2$	x	x	x		x			
Point Edward	$Al_2(SO_4)_3$	x		<			<		
				Greenhouse study					
Guelph	$Al_2(SO_4)_3$	x		x	x		<		
Fergus	$FeCl_3$	x			x		x		x
Toronto Humber	none	x	<		<		<	<	
Aurora	$Al_2(SO_4)_3$	x		x	x				
Point Edward	$FeCl_3$	x		x		<		x	
Sarnia	$FeCl_3$	x	<	x	x	<	<	<	
North Toronto	$FeCl_3$	x				<		x	
Newmarket	$Ca(OH)_2$	x		x		x	<		
Midland	$Ca(OH)_2$	x	<	x	<	<			

x - mineral dominant
< - mineral present

Table 6.2: Effect on soil Fe and Al of sludge application after four crops of ryegrass in the greenhouse experiment.

Sludge	Iron			Aluminum		
	Added	Extracted by pyrophosphate	Extracted by oxalate	Added	Extracted by pyrophosphate	Extracted by oxalate
			mg/g soil			
Aurora[1]	0.60	0.7	6.8	7.20	2.7	8.8
Midland[2]	2.37	1.1	6.5	3.26	1.2	2.9
Pt. Edward[3]	13.2	5.0	29.2	0.46	0.7	2.6
Sarnia[3]	9.43	3.3	20.2	0.51	0.6	2.0
Guelph[1/3]	2.09	1.5	6.8	1.51	1.8	3.3
Fergus[3]	2.60	1.5	6.8	0.20	1.0	2.3
N. Toronto[3]	5.53	2.6	14.5	0.84	1.2	2.5
Newmarket[2]	4.01	0.8	6.1	0.75	0.4	2.0
Toronto Humber[4]	1.89	1.7	6.7	0.69	1.2	2.4
Control	-	1.2	6.1	-	1.1	2.6

[1] Alum treatment
[2] Lime treatment
[3] Iron treatment
[4] No chemical treatment

Table 6.3: Total amount of Fe and Al added in sludge applied at 1600 kg N/ha rate from 1973 to 1975 at Elora and Cambridge.

Sludge added	Elora		Cambridge	
	Fe	Al	Fe	Al
		kg/ha		
Ca-sludge	2100	1020	1780	880
Al-sludge	536	4050	608	2056
Fe-sludge	6590	1100	6550	1300

Table 6.4: Effect of sludge treatment on soil iron and aluminum extracted by ammonium oxalate and by sodium dithionite; bromegrass experiment, Sept. 1974.

Depth	Rate and source of nitrogen (kg N/ha)									
	None		Ca-sludge (1600)		Al-sludge (1600)		Fe-sludge (1600)		Fe-sludge (200)	
cm	%Fe	%Al	%Fe	%Al	%Fe	%Al	%Fe	%Al	%Fe	%Al
				Oxalate-extractable						
0-15	0.29	0.21	--	--	--	--	--	--	--	--
0-2.5	--	--	0.37	0.12	0.49	1.93	2.20	0.47	0.48	0.23
2.5-5.0	--	--	0.35	0.13	0.33	0.32	0.81	0.27	0.33	0.18
5.0-7.5	--	--	0.36	0.21	0.31	0.21	0.44	0.21	0.34	0.22
7.5-12.5	--	--	0.32	0.21	0.31	0.21	0.36	0.22	0.33	0.23
				Dithionite-extractable						
0-15	1.29	0.15	--	--	--	--	--	--	--	--
0-2.5	--	--	0.92	0.07	0.96	1.58	2.44	0.40	1.35	0.18
2.5-5.0	--	--	0.90	0.07	1.11	0.27	1.54	0.24	1.29	0.18
5.0-7.5	--	--	1.15	0.12	1.23	0.18	1.39	0.18	1.27	0.17
7.5-12.5	--	--	1.23	0.14	1.20	0.18	1.42	0.19	1.29	0.17

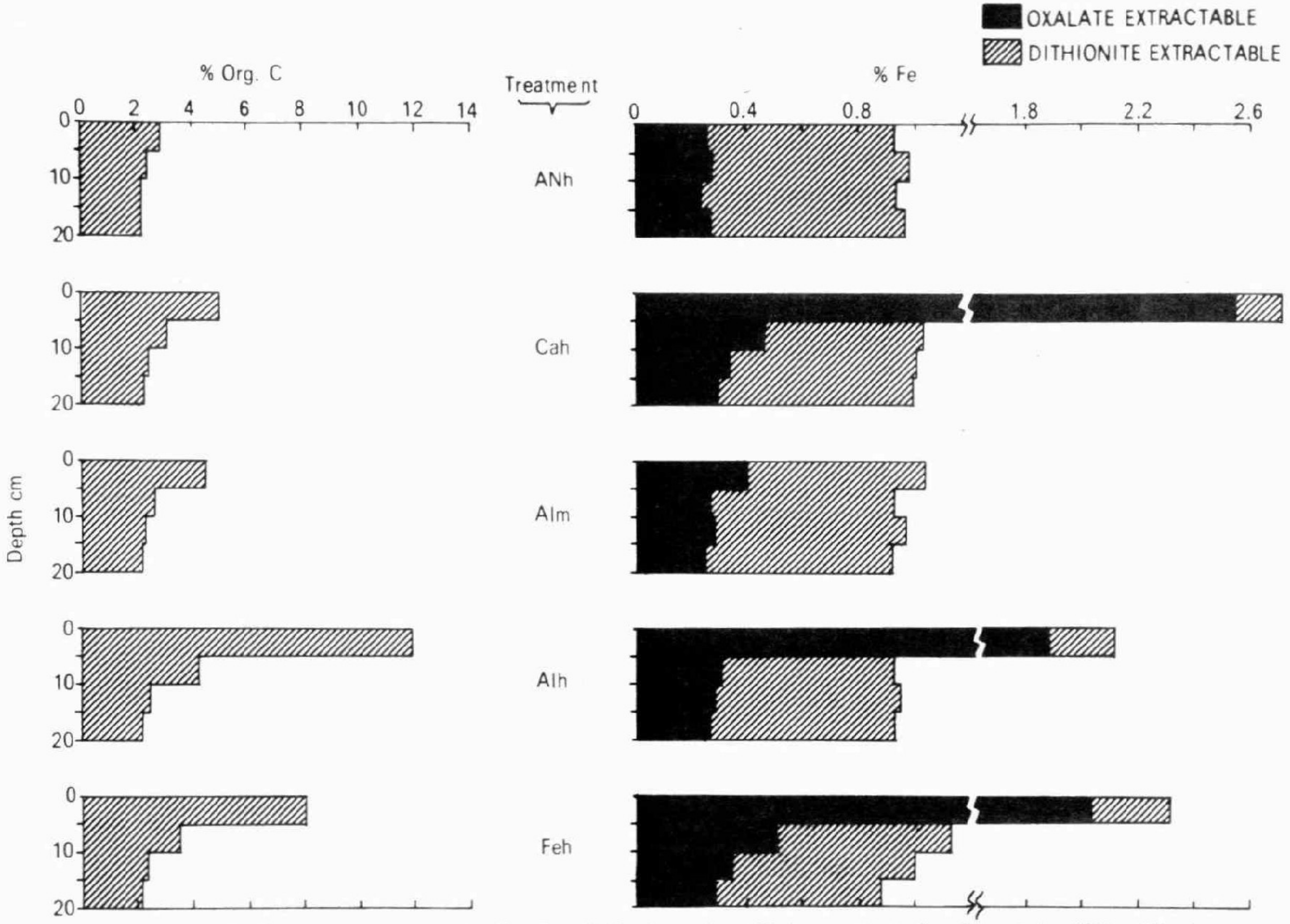


Figure 6.1 Organic C, ammonium oxalate; and sodium dithionite- extractable iron content of soil receiving 400kg N/ha from (i) NH_4NO_3 (ANh) and (ii) Al - sludge (Alm); and 1600kg N/ha from (iii) Ca sludge (Cah) (iv) Al - sludge (Alh) and (v) Fe - sludge (Feh). Bromegrass experiment, Oct. 1979.

Table 6.5: Carbonate-carbon distribution in surface soil of bromegrass expt., Oct. 1979.

Depth	Soil Treatment (kg N/ha)			
	NH_4NO_3 (400)	Ca-sludge (1600)	Al-sludge (1600)	Fe-sludge (1600)
cm	% CO_3-C			
0-5	0.16	2.13	0.92	0.34
5-10	0.16	2.03	0.27	0.10
10-15	0.20	0.80	0.18	0.13
15-20	0.20	0.38	0.32	0.15

Table 6.6: Total dry matter and metals added in the bromegrass experiment by annual application of sludge supplying 1600 kg N/ha from 1973 to 1979.

Constituent	Ca-sludge	Al-sludge	Fe-sludge
	t/ha		
Dry matter	471	273	242
Ca	80.2	15.5	9.1
Mg	2.99	1.76	1.41
Al	3.0	9.5	3.0
Fe	12.5	6.9	14.6
Zn	0.75	2.68	0.62
	kg/ha		
Cd	2.5	17.5	5.3
Cr	328	1008	146
Cu	168	432	344
Ni	624	40	7
Pb	128	288	408

Table 6.7: Effect of sewage sludge application on soil pH at various depths below the soil surface, Oct. 1979, bromegrass experiment.

Depth	Rate and source of nitrogen (kg N/ha)						
	NH_4NO_3	Ca-sludge		Al-sludge		Fe-sludge	
	(400)	(400)	(1600)	(400)	(1600)	(400)	(1600)
cm			pH				
0-5	6.3d*	7.3ab	7.6a	7.0bc	6.6cd	6.7cd	5.8e
5-10	7.2c	7.7b	7.9a	7.3c	7.3c	7.2c	6.6d
10-15	7.4c	7.8b	8.0a	7.3c	7.4c	7.3c	7.1d
15-20	7.3c	7.6b	7.8a	7.3c	7.3c	7.2c	7.1d

Avg. C.V. = 1.9%

* Treatment means in any one row not followed by a common letter are significantly different at 0.05 probability level by Duncan's Multiple Range test.

Table 6.8: Sodium pyrophosphate extractable Fe in surface soil of bromegrass expt., Oct. 1979.

Depth	Source and rate of N (kg N/ha)			
	NH_4NO_3 (400)	Ca-sludge (1600)	Al-sludge (1600)	Fe-sludge (1600)
cm	% Fe			
0-5	0.080	0.418	0.695	1.108
5-10	0.069	0.036	0.120	0.335
10-15	0.062	0.054	0.056	0.108
15-20	0.064	0.060	0.056	0.073

Table 6.9: Sodium pyrophosphate, ammonium oxalate, and sodium dithionite extractable aluminum in surface soil of bromegrass expt. Oct. 1979.

Depth	Source and rate of N (kg/ha)			
	NH_4NO_3 (400)	Ca-sludge (1600)	Al-sludge (1600)	Fe-sludge (1600)
cm	% Al (pyrophosphate extractable)			
0-5	0.066	0.230	0.930	0.210
5-10	0.058	0.045	0.475	0.105
10-15	0.057	0.041	0.094	0.070
15-20	0.058	0.044	0.073	0.058
	% Al (oxalate extractable)			
0-5	0.184	0.285	1.175	0.318
5-10	0.193	0.163	0.443	0.218
10-15	0.181	0.191	0.219	0.218
15-20	0.200	0.205	0.224	0.198
	% Al (dithionite extractable)			
0-5	0.095	0.022	0.035	0.032
5-10	0.100	0.080	0.095	0.900
10-15	0.100	0.100	0.095	0.100
15-20	0.100	0.105	0.085	0.900

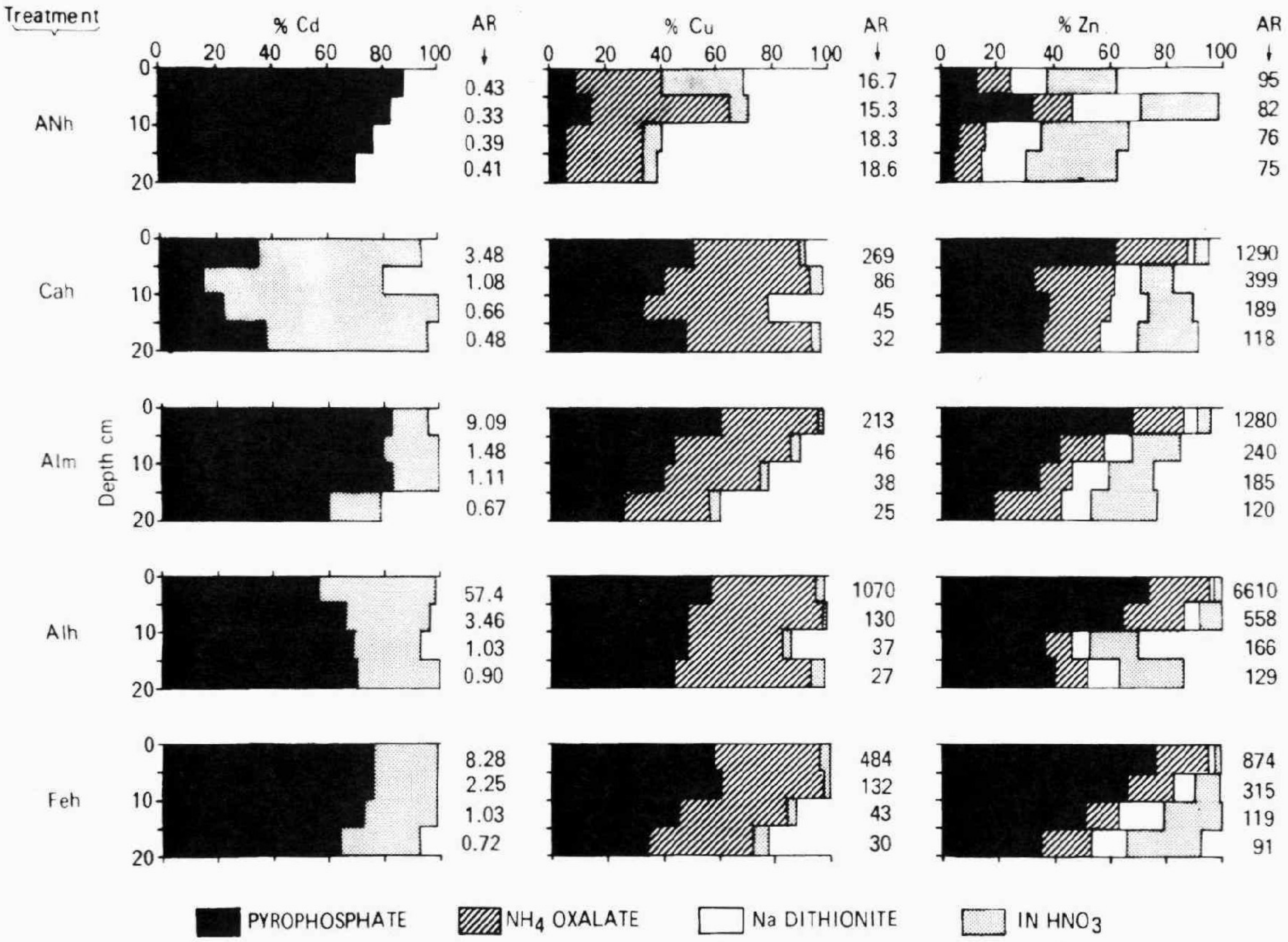


Figure 6.2 Soil cadmium, copper and zinc distribution expressed as percent of aqua regia (AR) soluble metal. The AR metal concentration to the right of each bar is in µg/g soil. Treatments are identified as in Fig. 6.1

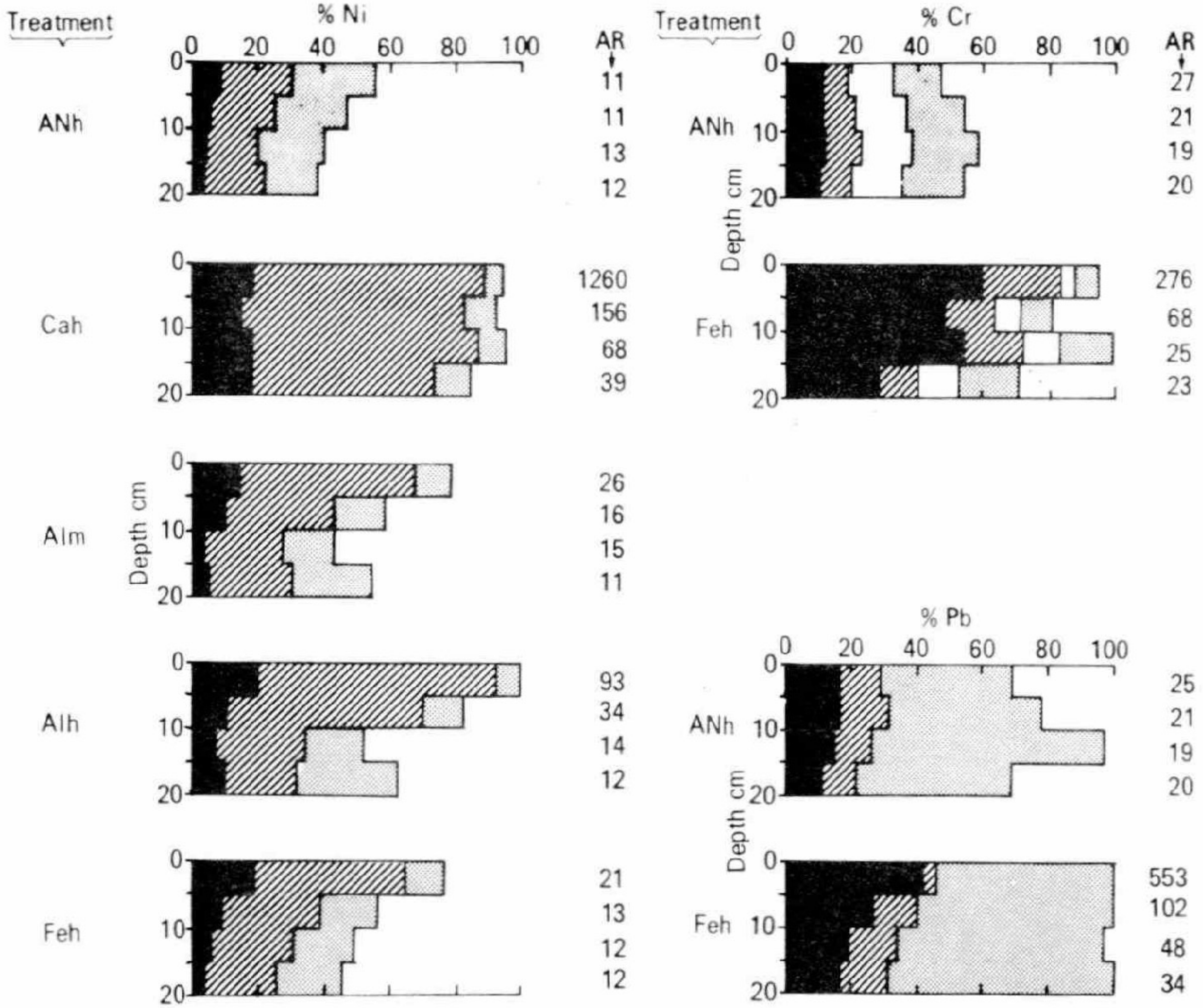


Figure 6.3 Soil nickel, chromium and lead distribution expressed as percent of aqua regia (AR) soluble metal. The AR metal concentration to the right of each bar is in µg/g soil. Treatmente are identified as in Fig. 6.1

Table 6.10: Cation exchange capacity of surface soil (0-15 cm), Elora corn experiment, Oct. 1979.

Nitrogen Rate	Nitrogen Source Ammonium Nitrate	Calcium Sludge	Aluminum Sludge	Iron Sludge	Sludge Mean
kg/ha			meq/100g		
100	26.7e*(25.1)†				
200		27.0de	30.6cc	29.0cd	28.8
800		31.2bc	30.5c	30.4c	30.7
1600		29.7c(28.2)	33.3ab(28.6)	33.7a(28.7)	32.2
Mean		29.3	31.4	31.0	20.6

C.V. = 4.0%

Table 6.11: Organic C content of surface soil (0-15 cm), Elora corn experiment, Oct. 1979.

Nitrogen Rate	Nitrogen Source Ammonium Nitrate	Calcium Sludge	Aluminum Sludge	Iron Sludge	Sludge Mean
kg N/ha			%C		
100	2.02e*(2.09)				
200		2.21de	2.44c	2.16e	2.27
800		2.40cd	2.56bc	2.68b	2.55
1600		2.54bc(2.57)	3.04a(2.80)	3.23a(3.15)	2.94
Mean		2.39	2.68	2.69	

C.V. = 5.0%

* In Table 6.10 and 6.11, treatment means not followed by a common letter are significantly different at 0.05 probability level by Duncan's Multiple Range test. Sludge sources and rates and source x rate interactions are significant at 0.01 probability by "F" test.

† Selected data for 1976 are presented within parenthesis.

Table 6.12: Cation exchange capacity of surface soil (0-15 cm), Cambridge corn experiment, Oct. 1979.

Nitrogen Rate	Nitrogen Source Ammonium Nitrate	Calcium Sludge	Aluminum Sludge	Iron Sludge	Sludge Mean
kg/ha			meq/100g		
100	16.5c*(13.2)				
200		17.6c	18.5bc	17.3c	17.8
800		18.9bc	19.1bc	18.6bc	18.9
1600		18.9bc(14.1)	20.9ab(13.7)	22.4a(14.0)	20.7
Mean		18.5	19.5	19.4	19.1

C.V. = 8.1%

Table 6.13: Organic C content of surface soil (0-15 cm), Cambridge corn experiment, Oct. 1979.

Nitrogen Rate	Nitrogen Source Ammonium Nitrate	Calcium Sludge	Aluminum Sludge	Iron Sludge	Sludge Mean
kg N/ha			%C		
100	2.20c*(1.52)†				
200		2.04c	2.19c	2.12c	2.12
800		2.13c	2.87b	2.55bc	2.52
1600		2.52bc(1.61)	3.03ab(1.59)	3.37a(2.03)	2.97
Mean		2.23	2.70	2.68	2.54

C.V. = 13.9%

Sludge sources and rates are significantly different at 0.01 and 0.05 probability levels, respectively.

* In Tables 6.12 and 6.13, treatment means not followed by a common letter are significantly different at 0.05 probability level by Duncan's Multiple Range test.

† Selected data for 1976 are presented within parentheses.

7. GREENHOUSE EXPERIMENT 1: EFFECTS OF SLUDGE ON CROP GROWTH AND METAL UPTAKE

7.1 Objectives

This experiment, started in 1974 with annual ryegrass (Lolium multiflorum L.) as the crop, is complementary to the field studies discussed in Section 3. Cycles of sludge application and cropping could be speeded up and more sludges studied under greenhouse conditions. The sludges were chosen for their high metal content. The objectives were to determine (i) the effects of various sewage sludges on crop growth, and (ii) the effects of metals in sewage sludge on metal uptake by plants.

7.2 Materials and Methods

The experiment was conducted on a Grimsby sandy loam (Typic Hapludalf) and started with nine fluid anaerobically digested Ontario sludges. The soil had an initial pH of 4.6. Treatments consisted of three rates of sludge supplying 200, 800 and 1600 kg N/ha. One set of treatment received 1600 kg N/ha from sludge in the first crop only and none thereafter. After drying, the soil and sludge were mixed and repotted. The control or check treatment received 200 kg N/ha as ammonium nitrate, 50 kg P/ha as 46% superphosphate and 20 kg Mg/ha as magnesium sulfate. For crops 1 to 5, the soil pH was adjusted with $CaCO_3$ to approximately 5 and 7. These were two replications per treatment and the pots were laid out in a randomized block design.

The pots were lined with plastic bags, so there was no drainage. Annual ryegrass was seeded and each crop was harvested 35 to 40 days after seedling emergence. Soluble salts were found to be a problem in the second crop. Therefore after the third sludge application and all subsequent odd-numbered applications, the soil was leached with deionized water to reduce soluble salt concentration before repotting and re-seeding.

After the fifth crop, the experiment was modified to study the effects of continuing and of discontinuing sludge application on metal uptake by ryegrass. The effect of soil pH was eliminated by liming all pots, to pH 6.5. Three of the sludges were eliminated from the experiment because they were not as high in metals as some of the other sludges. One sludge (from North Toronto) was retained because it was close to being average in metal content. The six remaining sludges were reapplied before each crop to only half of the pots in each treatment. No further sludge application was made to the other half of the pots, and ammonium nitrate was applied as required as a source of N. Nine crops (crops 6 to 14) were grown under this modified experimental set-up.

For crops 1 to 5, 7 kg of soil were used in a pot 30 cm in diameter at the top, and the final ryegrass stand was 15 plants per pot. Because the soil in each pot was sampled for chemical analysis after each crop, the 30-cm pot was eventually too large for the amount of soil left. Therefore for the sixth and subsequent crops, 4 kg of soil were used in plastic pots 20 cm in diameter. The final stand was 12 plants/pot.

Harvested plant material was washed and dried at 75°C. They and the sludges were ashed and analysed chemically as described in Section 3.2. Some metals are known to accumulate at greater concentrations in plant roots than in plant tops. In 1979, ryegrass roots from the fourteenth crop were separated from the soil, washed, dried and analysed for metal content. After washing, the roots appeared whitish. Furthermore, the ash was greyish, not the reddish colour characteristic of badly contaminated samples. Contamination is therefore, believed not to constitute a serious problem.

The following analyses were performed on soils from selected treatments: cation exchange capacity (Bascomb, 1964), organic matter (Tinsley III method described by Kalembasa and Jenkinson, 1973), DTPA-extractable Cd, Cu, Ni and Zn (Lindsay and Norvell, 1978) and aqua regia extractable metals. The procedure developed by Stover et al (1976) was adapted for the fractionation of metals in sludge and soil. In this procedure, the sludge or soil sample is sequentially extracted with 1M KNO_3, 0.5M KF, 0.1M $Na_4P_2O_7$, 0.1M EDTA and 1M HNO_3. The fractions of metal so extracted are, respectively, soluble plus exchangeable, adsorbed, organic, carbonate and sulphide fractions. The soils were also analysed for pH, sodium bicarbonate extractable P and ammonium acetate extractable K and Mg by the Ontario of Agriculture and Food's Soil Testing Laboratory.

7.3 Results and Discussion

7.3.1 Metals and nutrients added in sludge

The total amounts of metal and various other constituents added to the soil in 14 sludge applications at the 200 kg N/ha rate are presented in Table 7.1. A summary of sludges with NH_4^+-N/metal ratio below the minimum set by the Ontario sludge guidelines and the average metal addition per application at the 1600 kg N/ha rate is presented in Table 7.2. It can be seen from Tables 7.1 and 7.2 that the North Toronto sludge is not particularly high in any one metal.

Losses of metals during leaching of soil were generally small: about 0.1% of the metal added in currently applied sludge for immobile metals such as Cr and Pb; and between 1 to 2% of the more mobile metals such as Cd, Cu, Ni and Zn. On occasions, however, up to about 10% of the currently added Cu, Ni and Zn have been lost in leachates.

Losses of N in leachates ranged up to about 60% of the freshly applied N, and occasionally crop yields, especially at the 200 kg N/ha from sludge, may have been reduced because of this loss of N.

7.3.2 Metal extractability in sludge

Metals in sludges sequentially extracted by Stover et al's (1976) procedure are presented in Table 7.3. The aqua regia extractable metal content may be taken as an estimate of the total metal content. Results for sludges low in particular metals are not presented. Total recovery of Cd by the procedure was quite good. The organic, carbonate and sulphide fractions constituted most of the sludge Cd. With the Sarnia sludge, however, only 1% of the Cd was in the organic fraction.

Up to about 50% of the Cr in the sludges used was unextractable, and the organic, carbonate and sulphide fractions again constituted the bulk of the extractable fraction.

From zero to 77% of Cu in sludge was unextractable. Copper in the Fergus sludge was differently distributed than the other sludges with a relatively low % extractability across all fractions. However, because of the high total amount, even the concentration of the soluble plus exchangeable fraction was 435 µg

Cu/g of dry sludge. For the other sludges the main fractions appeared to be the inorganic (carbonate and sulphide) fractions with the organic fraction next in importance.

Extractability of Ni was nearly 100%, and was relatively more evenly distributed through the various fraction than the other metals studied. The two main fractions were the carbonate and sulphide fractions. The soluble plus exchangeable fraction was surprisingly high, in some cases higher than the organic fraction.

Extractability of Pb was almost complete with nearly all of the sludge Pb associated with the organic, carbonate and sulphide fractions.

Up to 87% of sludge Zn was unextractable. Of the extractable fractions, the organic was predominant, followed by the carbonate and sulphide fractions.

Such a fractionation must to a certain extent be arbitrary. The interpretation of the chemical fractionation follows that of Stover et al (1976). According to this interpretation, the carbonate fraction is selectively dissolved by EDTA. However, there is evidence showing that 0.1M EDTA also dissolves amorphous iron oxides (Borgaard, 1976). If such oxides are present in sludge then metals associated with them (by occlusion or coprecipitation) would be extracted by EDTA in addition to metals associated with carbonates.

Although there are some similarities, metal distribution in sludges can be quite different. For example, almost all of Cd in the Sarnia sludge was associated with the carbonate (plus iron oxide) and sulphide fractions, while 36% of the Cd in the Guelph sludge was associated with the organic fraction, and 58% associated with the carbonate (plus iron oxide) and sulphide fractions. Such differenes in extractability may explain the relative availability of Cd in these sludges (see section 7.3.6).

7.3.3 Effect on some soil physico-chemical properties

The effect of sludge on soil pH, CEC and organic matter content are presented in Table 7.4. Two of the sludges (N. Toronto and Fergus) decreased soil pH when applied at the high application rate. This was in spite of regular liming to maintain a pH of at least 6.5. The Midland sludge which was chemically treated with lime increased soil pH. No liming was necessary with this sludge. The effects of the other sludges were masked by liming.

All the sludges increased soil CEC and organic matter content. Cation exchange capacity was increased up to fourfold and organic matter about nine-fold by repeated sludge application. With the exception of the Fergus, and possibly the Sarnia sludge, there was no decrease in soil organic matter when only one sludge application was made initially and the soil was cropped to 14 crops of ryegrass. Characterization of the greenhouse soil is discussed in Section 6.3.

7.3.4 Crop Yield

Dry matter yields of ryegrass were significantly affected by sludge source and rate, and by source x rate interctions (Table 7.5). Yields have been reported in tonnes/ha rather than g/pot because different pot sizes had been used. In making the conversion, it is assumed that 1 ha of soil 15 cm deep weighs 2,200 tonnes. Yields of the 800 and 1600 kg N/ha rates tended not to be different, therefore only data for the 200 and 1600 kg Nha rates are presented. Crops were grown throughout the year and this resulted in seasonal variations in yields. Yields were low in spite of artificial lighting when crops were grown during November and December. Yields for the 12th crop were particularly low for some treatments. This is believed to be due to soil structural deterioration and compaction from excessive mechanical mixing of soil after sludge application. The treatment most severely affected was the ammonium nitrate (check) treatment. With sludge treatments, organic matter added by sludge may have stabilized soil structure.

Yields are not presented for treatments where sludge application was discontinued except where the Fergus sludge was applied at 1600 kg N/ha for the first five crops only. For this treatment, yield improved when sludge application ceased, indicating that the toxicity or growth limiting factor dissipated rapidly. Where the Fergus sludge was reapplied at the high rate before each crop, the degree of toxicity appeared to increase. Leaching of the soil appeared to reduce the toxicity somewhat. The toxicity is believed to be due mainly to excessive Cu in the Fergus sludge. This will be discussed in greater detail in Section 7.3.8.

7.3.5 Boron

The effect of sludge on B concentration in the ryegrass is presented in Table 7.6. The effect of source and rate and their interaction is highly significant. The Midland sludge resulted in the highest B concentration because it supplied the most B. The soils were leached before growing every odd-numbered crop beginning with the third crop. Leaching before seeding the 7th crop of ryegrass removed from 15 to 100% of the B added in the 7th sludge application. Therefore the B concentration in Table 7.6 was lower in the seventh crop than in the sixth. When sludge application was discontinued B concentration decreased slightly (not shown).

7.3.6 Cadmium

The effect of sewage sludge application on DTPA extractable Cd content of soils at the 1st, 5th and 14th crops is presented in Table 7.7. Application of a low Cd sludge such as the Aurora sludge had no measurable effect on DTPA extractable Cd. The Midland sludge added almost as much Cd as the North Toronto sludge but resulted in appreciably lower soil Cd concentration, presumably because of the higher soil pH induced by the Midland sludge. One initial sludge application followed by repeated cropping resulted in decreasing extractable soil Cd for the Sarnia, Guelph and Fergus sludges. Discontinuing the 1600 kg N/ha rate of sludge after five applications, however, resulted in no measurable reduction in soil Cd concentration after the 14th crop, except possibly for the Fergus sludge.

The Ontario sludge guideline's maximum Cd addition of 1.6 kg/ha was exceeded by the Guelph and Sarnia sludges in one 1600 kg N/ha application and by the low Cd Aurora sludge in seven applications.

Cadmium concentrations in the 14th crop of ryegrass are presented in Table 7.8. The Guelph sludge added only slightly more Cd than the Sarnia sludge but resulted in considerably higher Cd concentrations in ryegrass. The Aurora and Midland sludges reduced ryegrass Cd concentration compared to ammonium nitrate. It has been suggested (CAST 1980) that sludges with high iron content have low Cd availability probably because Cd is coprecipitated with iron. This may explain the low available Cd in the Sarnia sludge which had

8.4% Fe in the dry sludge compared to 3.2% for the Guelph sludge. The Sarnia sludge also had a higher Zn content (1.33% compared to 0.99% for the Guelph sludge), and it is possible that high concentrations of Zn may compete with Cd for plant uptake. In Section 7.3.1 it was shown that the Sarnia sludge differed from the Guelph sludge in having much lower content of Cd in the organic fraction, and a higher amount of Cd in the sulphide fraction. As a result, Cd in the Sarnia sludge may be less available.

There was considerable variation in Cd concentration from crop to crop. However, it appears that continued high application of the Guelph sludge resulted in a slightly increasing Cd concentration in ryegrass (Table 7.9). When sludge application was terminated after the fifth crop, there appears to be no decrease in Cd concentration in ryegrass. This is in accord with the apparent lack of decrease in DTPA extractable Cd when sludge application was discontinued after five applications. It appears that once Cd is added to the soil in sufficient amounts to increase its availability, it will remain plant available for several years.

A stepwise multiple regression analysis was done to identify the potential variables affecting Cd concentration in plants (the dependent variable). The potential independent variables were soil pH, CEC, dry matter yield, the amounts of metals added in that particular sludge application, in all previous applications, and the total up to and including that particular application, % N in plants and DTPA extractable metals in soil. All first order interactions and the square root of each variable (to allow for non-linear correlations) were also included as potential independent variables. The equation developed using variables which contributed significantly to the equation at 0.01 probability showed that total Cd and Zn (CdT and ZnT), Cd and Zn added in the particular application (CdC and ZnC), and extractable soil Zn (SZn) explained 83% of the variation in plant Cd:

$$\begin{aligned}\text{Plant Cd} = {} & 0.377 + 1.31\ \text{CdT}^{1/2} - 0.141\ \text{ZnT}^{1/2} + 0.179\ \text{SZn}^{1/2} \\ & - 0.924\ \text{CdC}^{1/2} + 0.081\ \text{ZnC}^{1/2} \\ & (R^2 = 0.83)\end{aligned}$$

The variables $\text{CdT}^{1/2}$ and $\text{ZnT}^{1/2}$ explained 77% of the variation in plant Cd. Because the Sarnia sludge was high in both Zn and Fe, the effects of the two metals could not be separated.

Since total Cd addition (CdT) was highly correlated with DTPA extractable soil Cd ($r^2 = 0.915$), plant Cd concentration can also be predicted by substituting extractable soil Cd (SCd) for Cd added in sludge. In the equation developed using SCd, soil pH and extractable soil Zn (SZn) and Cu (SCn) also entered the equation:

$$\text{Plant Cd} = 0.543 + 0.159 \text{ SCd} \times \text{pH} - 0.0017 \text{ SCd} \times \text{SZn} - 0.0197 \text{ SCu}$$

$$(R^2 = 0.793)$$

Cadmium tends to accumulate in the roots (not shown). The ratios of Cd concentrations in soil, roots and shoots after 14 applications of sludge are summarized in Table 7.10. Root/shoot Cd concentration ratios ranged from about 4 to 8. The low soil/root ratios suggest that Cd is quite mobile in the soil.

7.3.7 Chromium

Chromium concentration in ryegrass was slightly but significantly affected by sludge source and rate (Table 7.11). When sludge application ceased, Cr concentration decreased slightly but repeated sludge application did not increase Cr concentration from one crop to the next. Chromium concentration in the roots ranged from 1 to 27 μg/g and better reflects the differences between sludge sources in the amount of Cr added. The data summarized in Table 7.10 for Cr concentration ratios in soils, roots and shoots show that Cr has a low mobility in the soil-plant system.

7.3.8 Copper

The effect of sludge source and rate on Cu concentration in ryegrass is presented in Table 7.12. The Fergus sludge added an average of 524 kg Cu/ha when applied at the 1600 kg N/ha rate. This resulted in very high Cu concentration in the ryegrass shoot. The poor growth obtained with the Fergus sludge is believed to be due mainly to Cu toxicity. When sludge application was discontinued, the toxicity was alleviated as evident from the nearly normal growth in the seventh and subsequent crops (Table 7.5). The Guelph and Sarnia sludges also resulted in quite high Cu concentration in ryegrass (Table 7.12). The Sarnia sludge added less than half as much Cu as the Guelph sludge (Table 7.1). The total Cu added in sludge explained only 48% of the variation in Cu concentration in ryegrass, not a very high correlation.

Copper concentration in 14 crops of ryegrass resulting from application of the Sarnia and North Toronto sludges is presented in Table 7.13. There is some variation from crop to crop, and there appears to be a slight overall increase in Cu concentration with repeated sludge application at the 1600 kg N/ha rate. When sludge application was discontinued after five crops, the resulting Cu concentration was lower than that in ryegrass continuing to receive sludge applications. However, there was no apparent decrease in Cu concentration when compared to those in the first five crops.

Copper concentration in the roots was high, ranging from 52 to 1108 μg/g. The highest Cu concentration of 1108 μg/g was in the roots of ryegrass receiving 800 kg N/ha from the Fergus sludge. There was no measurable amount of growth with the 1600 kg N/ha rate of the Fergus sludge. The Guelph and Sarnia sludges also resulted in high Cu concentration in the roots, ranging from 107 to 366 μg/g when the sludges were applied before cropping. This is still much lower than with the Fergus sludge. The much higher root Cu concentration supports the conclusion that Cu toxicity is the main cause of poor growth with the Fergus sludge. Root concentrations of Cu are probably a much better indicator of Cu toxicity than shoot concentrations. The ratios of Cu concentrations in the soil, root and shoot are summarized in Table 7.10. From the low soil/root Cu ratios it appears that Cu is readily absorbed by the roots. The absorbed Cu, however, tends to remain in the roots as indicated by the high root/shoot Cu ratios.

7.3.9 Lead

There was little effect of sludge treatment on Pb concentration in ryegrass (Table 7.14). The source of sludge had a small but highly significant effect. Increasing the application rate increased Pb concentration slightly but significantly. Discontinuing sludge application did not decrease Pb concentration.

Lead concentration in the roots ranged from 5 to 55 μg/g. The effects of sludge on soil/root, soil/shoot, and root/shoot Pb concentration ratios are summarised in Table 7.10. Lead appears to have a low mobility from soil to root and from root to shoot.

7.3.10 Manganese

Manganese concentration in ryegrass varied somewhat from crop to crop. This variation is probably due to variations in soil pH. The data for the 13th crop presented in Table 7.15 show some typical sludge source and rate effects. The Fergus and North Toronto sludges frequently caused appreciable increases in Mn concentration. This may be due to the lower soil pH associated with these sludge treatments. Considerable Mn, up to 70% of the Mn added in the sludge, was lost in the leachates of the treatments receiving the Fergus sludge. Of the six sludges used throughout the experiment, the Fergus sludge added the lowest amount of Mn. Application of the Midland sludge decreased the Mn concentration in ryegrass, probably due to increased soil pH.

7.3.11 Molybdenum

The Midland and Guelph sludges had relatively high Mo concentrations. Two applications of these sludges at the 1600 kg N/ha rate resulted in higher Mo addition than the maximum (4 kg/ha) set by the Ontario sludge guidelines. Continued sludge application resulted in increasing Mo concentration in ryegrass (Fig. 7.1). There was some variation in Mo concentration from crop to crop; the Mo concentration for the ammonium nitrate treatment ranged from 0.15 to 3.27 μg/g. With the Guelph sludge the Mo concentration appeared to increase from crop to crop and this effect appeared to be greater where sludge was not re-applied. Discontinuing the Midland sludge application did not appear to increase or decrease Mo concentration.

7.3.12 Nickel

The effect of continuing or discontinuing sludge application on DTPA extractable soil Ni is summarized in Table 7.7. Only the high Ni content Midland sludge increased extractable soil Ni content to any appreciable extent. One application of this sludge at the low rate (200 kg N/ha) added 38 kg Ni/ha, more than the maximum set by the Ontario sludge guidelines. When sludge application was discontinued, the DTPA extractable soil Ni concentration decreased, suggesting a conversion to less extractable forms. Nickel added in sludge was much more soluble than the other metals (10-30% soluble plus exchangeable).

Application of the Midland sludge resulted in very high Ni concentration in ryegrass (Table 7.16). The other five sludges resulted in much smaller increases in Ni concentration. The effect of the Midland and North Toronto sludges on Ni concentration in 14 crops of ryegrass is presented in Table 7.17. Repeated application at the 1600 kg N/ha rate appeared to result in a slight increase in Ni concentration from crop to crop for the Midland sludge but not the low Ni North Toronto sludge. When the Midland sludge was not reapplied after the fifth crop, the Ni concentration appeared to decrease in the eighth and subsequent crops of ryegrass. The Ni concentrations were still quite high even then. The Ni concentration also appeared to decrease the Midland when sludge application at the 200 kg N/ha rate ceased (not shown).

Sludge application resulted in Ni concentrations in the roots four to five times those of the shoots. Data comparing soil/root, soil/shoot and root/shoot Ni concentration ratios are summarized in Table 7.10. Nickel appears to be more readily absorbed by roots and translocated to the shoots than Pb or Cr.

7.3.13 Zinc

The effect of sludge application on DTPA extractable soil Zn is summarized in Table 7.7. There is a strong effect of sludge source and rate. The amount of DTPA extractable Zn (SZn) was closely correlated with the total amount of Zn added in sludge (ZnT) as shown by the following equation:

$$\text{SZn} = 7.31 + 0.046\ \text{ZnT} \qquad (r^2 = 0.93)$$

When sludge application was discontinued, the amount of extractable Zn decreased, Zn apparently converting to less extractable forms in the soil with time (Table 7.7).

The effect of sludge treatment on Zn concentration in ryegrass is presented in Table 7.18. Sludge source and rate had highly significant effects, with the high Zn content Sarnia sludge resulting in very high Zn concentrations. The effects of the Sarnia and North Toronto sludges on Zn concentration in 14 crops of ryegrass are presened in Table 7.19. Continued sludge application resulted in increasing Zn concentration, particularly with the Sarnia sludge. Discontinuing sludge application did not appear to decrease Zn concentration.

Eighty-five perent of the variation in Zn concentration in ryegrass was explained by DTPA extractable soil Zn (SZn). The inclusion of pH in a multiple regression equation improved the R^2 to 0.89:

$$\text{Plant Zn} = 40.7 + 30.9\ \text{SZn} - 0.33\ \text{pH} \times \text{SZn}$$

An increase in soil pH reduced Zn concentration in plants, and the pH effect was more pronounced at high Zn levels in soil.

In general, Zn concentration in ryegrass roots was slightly lower than the concentration in the shoots, apparently Zn was readily translocated from root to shoot. Data comparing soil/root, soil/shoot and root/shoot Zn concentration ratios are summarized in Table 7.10.

7.3.14 Cobalt, Mercury and Selenium

There was no apparent effect of sludge rate or source on Co, Mg or Se concentrations in ryegrass shoot.

7.4 Conclusions

Ryegrass yields were adversely affected by application of the Fergus sludge which was high in Zn, Cr and particularly in Cu. The poor yield is believed to be due mainly to Cu toxicity. Interactive effects with Zn are possible but appear secondary since Zn was very high in the Sarnia sludge but did not adversely affect yield. Copper concentration was very high in the roots of ryegrass receiving the Fergus sludge. When application of the Fergus sludge was discontinued, the yields became nearly the same as in the ammonium nitrate treatment.

Sludge source and rate had highly significant effects on B, Cd, Cu, Mn, Ni and Zn concentrations. With the exception of Mn, sludges high in these micronutrients and heavy metals resulted in high concentrations in the plants. With Mn, the effects appear to be related to the pH induced in the soil by sludge application. Sludges that decrease soil pH tend to increase Mn in ryegrass. There was no effect of sludge on Co, Hg and Se concentrations. There were slight but significant effects of sludge source and rate on Cr and Pb concentrations in ryegrass. Molybdenum was analysed only in treatments receiving the Guelph and Midland sludges, both relatively high in Mo. With these sludges, Mo concentration in ryegrass was increased.

When sludge application was discontinued after the fifth crop, B and Ni concentrations decreased in the subsequent crops. No apparent decrease in Cd, Cu and Zn concentrations occurred, however, when sludge was not reapplied.

Table 7.1: Total amounts of nutrients and metals added in 14 sludge applications at the 200 kg N/ha rate.*

	Aurora	Midland	Sarnia	Guelph	Fergus	N.Toronto
			kg/ha			
Solids (dry weight)	84100	225000	119400	72600	59500	61200
Total N	2800	2800	2800	2800	2800	2800
Soluble & Exch. NH_4-N	596	575	913	1060	1180	1100
P	2040	7450	2910	3300	2210	2770
K	359	367	574	218	172	224
Ca	4260	31300†	4780	4780	2730	2330
Mg	457	1840	1270	596	625	348
Na	974	626	310	360	512	220
Al	6820†	3040	739	1920†	181	790
Fe	2300	8350†	10,000†	2360†	3930†	4500†
Cd	0.39	1.51	10.6	12.1	0.77	1.64
Cr	919	326	18	210	479	40
Cu	48	107	78	200	917	92
Mn	22	81	618	20	13	34
Ni	13.1	533	3.6	6.4	9.7	1.8
Pb	33.0	127	498	113	18.3	112
Zn	91	555	1590	716	1040	164
B	4.38	8.74	2.99	2.86	2.28	1.35
Hg	0.70	1.88	0.87	0.63	0.22	1.25
Mo	1.37	3.87	2.60	4.44	0.75	2.26
Se	0.885	0.585	<0.008	1.19	0.031	0.016

* It was assumed that 1 ha of soil 15 cm deep weighs 2.2×10^6 kg.

† Compound added to sewage for phosphorus removal from effluents.

Table 7.2: Sludges with NH_4^+-N/metal ratios below the minimum set by the Ontario sludge guidelines and average metal addition per application at the 1600 kg N/ha rate.

Sludge	NH_4^+-N/metal ratio	Avg. metal addition per application* (kg/ha)	Ontario sludge guidelines i) Min. NH_4^+-N/metal ii) Max. addition (kg/ha)
		Cadmium	
Midland	380	0.86	(i) 500
Sarnia	86	6.07	(ii) 1.6
Guelph	87	6.92	
		Chromium	
Aurora	0.9	391	(i) 6
Midland	1.8	186	(ii) 210
Guelph	5.0	120	
Fergus	2.5	274	
		Copper	
Midland	5.4	61	(i) 10
Guelph	5.3	114	(ii) 150
Fergus	1.3	524	
		Lead	
Midland	4.5	72	(i) 15
Sarnia	1.8	285	(ii) 90
Guelph	9.4	65	
N. Toronto	9.9	64	
		Nickel	
Midland	1.1	305	(i) 40 (ii) 32
		Zinc	
Midland	1.0	317	(i) 4
Sarnia	0.6	906	(ii) 330
Guelph	1.5	409	
Fergus	1.1	597	
		Molybdenum	
Midland	149	2.2	(i) 180 (ii) 4

* Based on average of 14 applications in Table 7.1.

Table 7.3: Heavy metal extractability patterns for selected sludges*.

Sludge Source	Aqua regia extractable	Sequential extractants					
		KNO_3	KF	$Na_4P_2O_7$	EDTA	HNO_3	Residual≠
	µg/g dry sludge	------% of aqua regia extractable----------					
				Cd			
Midland	7.0	4	1	24	34	25	12
N. Toronto	22.5	1	3	55	25	16	0
Sarnia	65.0	<1	<1	1	45	53	<1
Guelph	104	<1	1	36	39	19	5
				Cr			
N. Toronto	650	2	2	43	22	22	9
Fergus	9,470	<1	1	15	12	26	46
Aurora	8,250	<1	1	9	9	30	51
				Cu			
N. Toronto	1,250	5	7	18	23	47	0
Sarnia	463	1	2	4	12	81	0
Guelph	2,050	3	11	21	30	35	0
Fergus	16,500	3	2	8	5	5	77
				Ni			
Guelph	70	30	12	5	25	28	0
Aurora	35	15	10	12	33	30	0
Midland	2,350	10	6	20	38	25	1
				Pb			
N. Toronto	1,410	<1	2	8	64	26	0
Sarnia	3,630	<1	<1	24	52	23	1
				Zn			
N. Toronto	1,640	2	3	45	12	19	19
Fergus	15,000	1	1	5	3	3	87
Sarnia	8,000	1	1	10	6	5	77
Guelph	10,500	1	1	8	4	4	82

* Composite sample of sludges for crops 9 to 14 inclusive.

≠ Fraction denoted as residual was the portion of metal insoluble in 1M HNO_3 but soluble in aqua regia.

Table 7.4: Effect of sludge application on soil pH, CEC and organic matter content.

N Rate x no. of applications	Crop No.	N Source						
		NH_4NO_3	Aurora sludge	Midland sludge	N.Toronto sludge	Sarnia sludge	Guelph sludge	Fergus sludge
		pH						
200 x 14	14	6.6	7.4	7.8	7.1	7.2	7.2	7.3
1600 x 14	14	-	7.0	8.0	5.9	6.5	6.9	6.1
		CEC (meq/100g)						
200 x 14	14	8.8	10.0	12.3	14.9	11.4	13.2	16.6
1600 x 14	14	-	15.5	37.3	21.5	23.5	20.0	20.0
1600 x 1	1	-	9.3	9.8	8.7	11.5	9.6	6.4
1600 x 1	14	-	9.4	11.4	9.2	10.5	9.8	9.1
		Organic Matter (mg/g)						
200 x 14	14	10.5	16.2	16.7	16.9	24.2	18.1	18.6
1600 x 14	14	-	31.1	71.2	32.2	91.2	40.4	43.3
1600 x 1	1	-	12.9	13.1	13.2	22.4	14.6	23.4
1600 x 1	14	-	12.7	13.8	12.7	19.1	16.2	13.6

Table 7.5: Effect of rate and source of N on dry matter yields of 14 crops of ryegrass.

	N Rate x Number of Applications and N Source													
	200 x 14†							1600 x 14‡						1600 x 5§
Crop	NH_4NO_3	Aurora sludge	Midland sludge	Toronto sludge	Sarnia sludge	Guelph sludge	Fergus sludge	Aurora sludge	Midland sludge	Toronto sludge	Sarnia sludge	Guelph sludge	Fergus sludge	Fergus sludge
	tonnes/ha													
1	1.10	1.39	1.09	1.37	1.15	1.36	1.29	1.43	1.73	1.49	1.82	1.00	0.62	0.62
2	1.05	1.03	0.96	1.09	1.10	1.09	1.06	0.63	0.91	0.81	0.64	0.41	0.37	0.37
3¶	1.13	0.59	0.34	0.41	0.35	0.61	0.74	1.05	0.91	1.17	0.78	0.92	0.33	0.33
4	1.37	1.48	0.89	0.76	0.83	0.83	0.96	1.46	1.26	0.88	1.24	1.12	0.21	0.21
5¶#	0.79	0.62	0.65	0.62	0.55	0.61	0.61	0.71	0.62	0.69	0.65	0.68	0.30	0.30
6	1.40	1.33	0.87	1.35	1.47	1.12	1.55	0.72	1.33	0.98	0.89	1.03	0.08	0.81
7¶	1.75	1.08	0.75	0.97	0.94	0.92	0.81	2.02	2.18	1.89	2.28	1.59	1.43	1.10
8#	0.80	0.73	0.72	0.78	0.72	0.78	0.91	0.68	0.75	0.86	0.75	0.86	0.10	0.65
9¶	1.69	1.34	0.88	1.01	0.84	0.82	0.85	1.60	1.70	1.27	1.52	1.60	0.81	1.21
10	1.24	1.36	1.04	1.23	1.42	1.08	1.04	1.60	1.81	1.87	1.86	1.52	0.24	0.72
11¶	1.18	1.40	1.42	1.53	1.67	1.93	1.41	1.96	2.05	2.08	2.00	1.95	0.81	1.11
12††	0.21	0.75	1.01	1.83	1.80	1.63	1.47	1.18	1.15	1.14	0.63	1.02	0.00	2.22
13¶	1.53	1.40	1.67	1.24	1.61	1.44	1.36	2.20	2.50	1.92	2.03	2.13	0.27	1.56
14#	0.64	1.25	1.09	1.08	0.80	0.86	1.00	0.61	1.40	0.64	1.27	0.73	0.00	0.95

† 200 kg N/ha applied from sludge or NH_4NO_3 before each of 14 crops.

‡ 1600 kg N/ha applied from sludge before each of 14 crops.

§ 1600 kg N/ha applied from sludge before each of the first 5 crops and 200 kg N/ha from NH_4NO_3 before each of the last 4 crops.

¶ Crop leached after sludge application but before seeding.

\# Crop grown in NOV-DEC period.

†† Soils were mixed mechanically to the extent that structure was affected resulting in compaction of some treatments.

Table 7.6: Boron concentration in the 6th and 7th crops of ryegrass after addition of sewage sludge.

	6th crop					7th crop				
	N rate kg/ha									
Sludge	200	800	1600	1600*	Mean	200	800	1600	1600*	Mean
					B µg/g					
None					14					10
Aurora	19	23	29	27	24	16	16	20	20	18
Midland	30	56	108	58	63	19	38	41	38	34
Sarnia	20	30	39	28	29	12	15	19	19	16
Guelph	19	27	28	17	23	9	15	19	13	14
Fergus	14	20	37	20	23	11	12	15	13	13
N.Toronto	18	19	26	19	20	10	13	12	11	11
Mean	20	29	44	28	30	13	18	21	19	18

* Sludge not added before crops 2, 3, 4 and 5. In other treatments sludge was added before each crop.

Significance of "F" test at 0.05 and 0.01 probability
Sludge source - .01
Sludge rate - .01
Sludge x rate - .01

Table 7.7: Effect of sludge application on DTPA extractable soil Cd, Ni and Zn.

N rate x no. of applications	Crop* No.	N Source						
		NH_4NO_3	Aurora sludge	Midland sludge	Sarnia sludge	Guelph sludge	N.Toronto sludge	Fergus sludge
				Cd µg/g				
200 x 1	1	0.06	0.09	0.11	0.16	0.18	0.12	0.14
200 x 14	14	0.21	0.10	0.14	1.59	1.66	0.30	0.24
1600 x 1	1	-	0.12	0.13	2.01	1.56	0.19	0.70
1600 x 1	5	-	0.15	0.14	1.45	1.61	0.27	0.57
1600 x 1	14	-	0.16	0.19	1.42	1.03	0.19	0.37
1600 x 5	5	-	0.16	0.23	2.80	5.38	0.40	0.62
1600 x 5	14	-	0.14	0.27	2.86	5.49	0.45	0.45
1600 x 14	14	-	0.20	0.64	5.58	8.04	1.18	0.72
				Ni µg/g				
200 x 1	1	0.1	0.1	1.7	0.1	0.1	0.1	0.1
200 x 14	14	0.1	0.1	6.3	0.2	0.1	0.1	0.1
1600 x 1	1	0.1	0.1	13.9	0.3	0.2	0.2	0.3
1600 x 1	5	-	0.1	9.3	0.1	0.2	0.1	0.2
1600 x 1	14	-	0.1	6.1	0.1	0.1	0.1	0.1
1600 x 5	5	-	0.4	38.7	0.3	0.3	0.3	1.9
1600 x 5	14	-	0.2	17.5	0.2	0.2	0.2	0.2
1600 x 14	14	-	0.3	61.9	1.3	0.7	0.6	2.8
				Zn µg/g				
200 x 1	1	0.7	0.5	0.7	4.6	1.4	0.8	2.3
200 x 14	14	1.0	1.2	28.6	107	29.9	6.5	47
1600 x 1	1	-	0.8	4.6	138	17.8	5.1	50
1600 x 1	5	-	2.5	5.6	68	15.2	4.1	23.7
1600 x 1	14	-	1.5	5.1	52	5.9	2.1	10.9
1600 x 5	5	-	11.0	33.8	218	47.2	20.7	151
1600 x 5	14	-	6.8	35.8	188	43.7	14.3	72
1600 x 14	14	-	17.3	224	538	206	56	219

* Refers to crop after which the soils were sampled, dried and stored before extraction.

Table 7.8: Cadmium concentration in the shoots of the 14th crop of ryegrass.

	Sludge not added since 5th crop					Sludge added before each crop					Mean
	N rate kg/ha										
Sludge	200	800	1600	1600*	Mean	200	800	1600	1600*	Mean	
	µg Cd/g										
None											0.98
Aurora	0.40	0.40	0.30	0.68	0.44	0.15	0.25	0.28	0.38	0.26	0.35
Midland	0.25	0.38	0.25	0.28	0.29	0.18	0.15	0.20	0.35	0.22	0.25
Sarnia	0.78	1.40	0.90	0.73	0.95	1.35	1.42	1.17	1.45	1.35	1.15
Guelph	1.58	2.92	5.55	1.80	2.96	2.35	1.83	2.20	1.97	2.09	2.52
Fergus†	0.38	0.55	0.63	0.90	0.62	0.35	0.43	-	-	-	-
N.Toronto	0.55	2.00	0.48	0.42	0.86	0.40	0.65	0.70	0.73	0.62	0.74
Mean§	0.71	1.42	1.50	0.78	1.10	0.89	0.86	0.91	0.98	0.91	1.00

* Sludge was added before the first crop but not before crops 2, 3, 4 and 5.

† The Fergus sludge treatments were omitted from statistical analysis because of missing values due to poor plant growth.

§ Fergus sludge treatments were omitted from computation of rate means.

Significance of "F" test at 0.05 and 0.01 probability:

Sludge source	- .01	Source x addition	- .01
Sludge rate	- .01	Addition x rate	- .01
Source x rate	- .01	Source x rate x addition	- .01

Table 7.9: Cadmium concentration in crops 1 to 14 of ryegrass receiving sewage sludges from Guelph and North Toronto before each crop.†

Crop	Control (NH_4NO_3)	Guelph			North Toronto		
		kg N/ha					
	200	200	1600	1600§	200	1600	1600§
		µg Cd/g					
First	0.55	1.03	2.60	2.60	0.70	0.85	0.85
Second	0.35	1.10	5.61	5.61	0.45	0.40	0.40
Third*	0.40	0.65	2.45	2.45	1.45	0.70	0.70
Fourth	0.31	0.86	3.14	3.14	0.38	0.44	0.44
Fifth*	0.60	0.95	3.70	3.70	0.50	0.65	0.65
Sixth	1.31	2.05	5.20	3.75	1.00	0.50	0.55
Seventh*	1.40	2.08	6.18	6.88	0.89	0.75	1.00
Eighth	1.05	2.40	8.05	8.00	0.85	0.90	0.95
Ninth*	1.83	1.77	3.58	5.19	0.42	0.43	0.54
Tenth	2.25	2.33	4.51	6.60	0.67	0.85	0.85
Eleventh*	2.00	2.20	7.02	4.89	0.68	1.00	0.81
Twelfth	1.05	2.55	8.30	7.50	0.48	0.38	0.48
Thirteenth*	1.01	1.72	3.65	4.84	0.49	1.02	0.66
Fourteenth	0.98	2.35	2.20	5.55	0.40	0.70	0.48

† The sludge from Guelph supplied the greatest amount of cadmium in the experiment, while the cadmium content of the North Toronto sludge is near the average of the sludges used.

§ No sludge application after the fifth crop.

* Plots were leached after sludge application but before seeding.

Table 7.10: Ratios of metal concenrations in soils, roots and shoots after 14 applications of sludge supplying 1600 kg N/ha per crop.

Metal	No sludge			N. Toronto sludge*			Situations with Highest Conc.			
	Soil/Root	Soil/Shoot	Root/Shoot	Soil/Root	Soil/Shoot	Root/Shoot	Sludge	Soil/Root	Soil/Shoot	Root/Shoot
				Concentration Ratio						
Cd	0.20	0.72	3.7	0.43	2.7	6.4	Guelph	1.1	9.2	8.3
Cr	7.0	14.0	2.0	7.8	32.0	4.1	Aurora	15.0	184	12.3
Cu	0.29	1.7	5.9	0.79	5.4	6.8	Guelph†	0.83	7.8	9.4
Pb	0.53	14.0	26.0	6.6	199	30.0	Sarnia	36.0	1320	37.0
Ni	9.5	18.0	1.9	1.5	7.0	4.5	Midland	5.5	30.0	5.4
Zn	1.4	5.0	3.5	3.4	2.7	0.79	Sarnia	22.0	8.4	0.37

* The N. Toronto sludge is considered average in content of metals listed and is therefore chosen for comparison with the worst case situation. It has higher than the minimum allowable NH_4^+-N/metal ratio according to the Ontario sludge guidelines with the exception of the NH_4^+-N/Pb ratio.

† The highest plant Cu concentration was with the Fergus sludge. There was no plant material at harvest because of acute toxicity. Therefore the next highest plant Cu involving the Guelph sludge is presented instead.

Table 7.11: Chromium concentration in the 14th crop of ryegrass resulting from termination of or continuation of sludge application.

	Sludge not added since 5th crop					Sludge added before each crop					Mean
	N rate kg/ha										
Sludge	200	800	1600	1600*	Mean	200	800	1600	1600*	Mean	
	µg Cr/g										
None											1.0
Aurora	1.1	1.4	1.2	1.6	1.3	1.2	1.1	1.4	1.8	1.4	1.3
Midland	1.3	1.4	2.0	1.7	1.6	2.1	1.3	1.5	1.5	1.6	1.6
Sarnia	1.1	1.5	1.6	1.3	1.4	2.0	2.4	1.8	1.8	2.0	1.7
Guelph	1.0	0.9	1.1	1.1	1.0	1.2	1.4	1.2	1.1	1.2	1.1
Fergus†	0.7	1.0	1.6	1.3	1.2	1.7	1.6	-	-	-	-
N.Toronto	1.1	1.5	1.4	1.0	1.2	1.3	1.5	1.7	1.5	1.5	1.4
Mean§	1.1	1.3	1.5	1.3	1.3	1.5	1.5	1.5	1.5	1.5	1.4

* Sludge was added before the first crop but not before crops 2, 3, 4 and 5.

† The Fergus sludge treatments were omitted from statistical analysis because of too many missing values.

§ Fergus sludge treatments were omitted from computation of rate means.

Significance "F" test at 0.05 and 0.01 probability: -

Sludge source	- .01	Source x rate	- .05
Sludge addition	- .01	Source x addition	- .01

Table 7.12: Copper concentration in the 13th crop of ryegrass.

	Sludge not added since 5th crop					Sludge added before each crop					Mean
	N rate kg/ha										
Sludge	200	800	1600	1600*	Mean	200	800	1600	1600*	Mean	
	µg Cu/g										
None											21
Aurora	14	18	15	16	16	11	19	19	17	16	16
Midland	14	17	19	17	17	12	23	29	28	23	20
Sarnia	19	24	28	31	25	14	27	34	28	25	25
Guelph	17	26	25	23	22	17	26	33	26	25	24
Fergus	18	28	30	21	24	22	39	49	48	39	32
N.Toronto	16	24	23	17	20	15	23	28	25	23	21
Mean	16	23	23	21	21	15	26	32	28	25	23

* Sludge was added before the first crop but not before crops 2, 3, 4 and 5.

Significance "F" test at 0.05 and 0.01 probability: -

Sludge source - .01
Source x rate - .05
Sludge addition - .01
Source x addition - .01
Sludge rate - .01
Rate x addition - .01

Table 7.13: Copper concentration in crops 1 to 14 of ryegrass receiving sewage sludges from Sarnia and North Toronto before each crop.

Crop	Control (NH_4NO_3)	Sarnia			North Toronto		
		kg N/ha					
	200	200	1600	1600§	200	1600	1600§
		µg Cu/g					
First	11	15	20	20	13	17	17
Second	17	25	31	34	26	27	27
Third*	10	6	11	11	8	13	13
Fourth	14	12	25	25	11	19	19
Fifth*	14	14	20	20	10	18	18
Sixth	22	14	33	28	21	24	21
Seventh*	13	10	34	31	12	19	14
Eighth	10	18	35	23	21	26	12
Ninth*	13	10	26	15	12	23	16
Tenth	9	9	27	11	12	23	9
Eleventh*	8	10	30	10	9	22	10
Twelfth	10	19	32	26	12	18	14
Thirteenth*	21	14	34	28	15	28	23
Fourteenth	15	19	27	24	18	27	18

* Plots were leached after sludge application but before seeding.

§ Sludge not applied after the fifth crop.

Table 7.14: Lead concentration in the 6th crop of ryegrass resulting from termination of or continuation of sludge application.

	Sludge not added since 5th crop					Sludge added before each crop					Mean
	N rate kg/ha										
Sludge	200	800	1600	1600*	Mean	200	800	1600	1600*	Mean	
	Pb µg/g										
None											0.6
Aurora	0.6	0.9	0.7	0.4	0.6	0.5	0.8	1.0	0.9	0.8	0.7
Midland	0.6	0.8	0.8	1.2	0.8	0.6	1.0	0.9	0.5	0.7	0.8
Sarnia	0.6	0.8	1.4	0.9	0.9	0.8	1.0	0.9	1.0	0.9	0.9
Guelph	0.8	0.8	1.0	0.7	0.8	0.8	0.8	1.0	0.9	0.9	0.8
Fergus	1.5	1.3	0.8	0.7	1.1	0.8	0.8	1.6	1.1	1.1	1.1
N.Toronto	0.6	0.8	1.1	0.6	0.8	0.9	0.6	0.7	0.9	0.8	0.8
Mean	0.8	0.9	1.0	0.7	0.8	0.7	0.8	1.0	0.9	0.9	0.8

* Sludge was added before the first crop but not before crops 2, 3, 4 and 5.
Significance "F" test at 0.05 and 0.01 probability: -
Sludge - .01
Sludge rate - .05

Table 7.15: Manganese concentration in the 13th crop of ryegrass.

	Sludge not added since 5th crop					Sludge added before each crop					Mean
	N rate kg/ha										
Sludge	200	800	1600	1600*	Mean	200	800	1600	1600*	Mean	
					Mn µg/g						
None											164
Aurora	71	78	44	154	87	54	26	54	106	60	73
Midland	55	84	80	209	107	60	83	48	34	56	81
Sarnia	81	92	123	215	128	92	230	199	172	173	150
Guelph	117	70	199	250	159	127	116	123	83	112	136
Fergus	73	101	103	148	106	104	131	455	474	291	198
N.Toronto	96	48	59	49	63	81	84	234	216	154	108
Mean	81	79	101	170	108	86	112	185	181	141	124

* Sludge was added before the first crop but not before crops 2, 3, 4 and 5.

Significance "F" test at 0.05 and 0.01 probability: -

Sludge source	- .01	Source x rate	- .01
Sludge rate	- .01	Source x addition	- .01
Sludge addition	- .01	Addition x rate	- .01
		Source x rate x addition	- .01

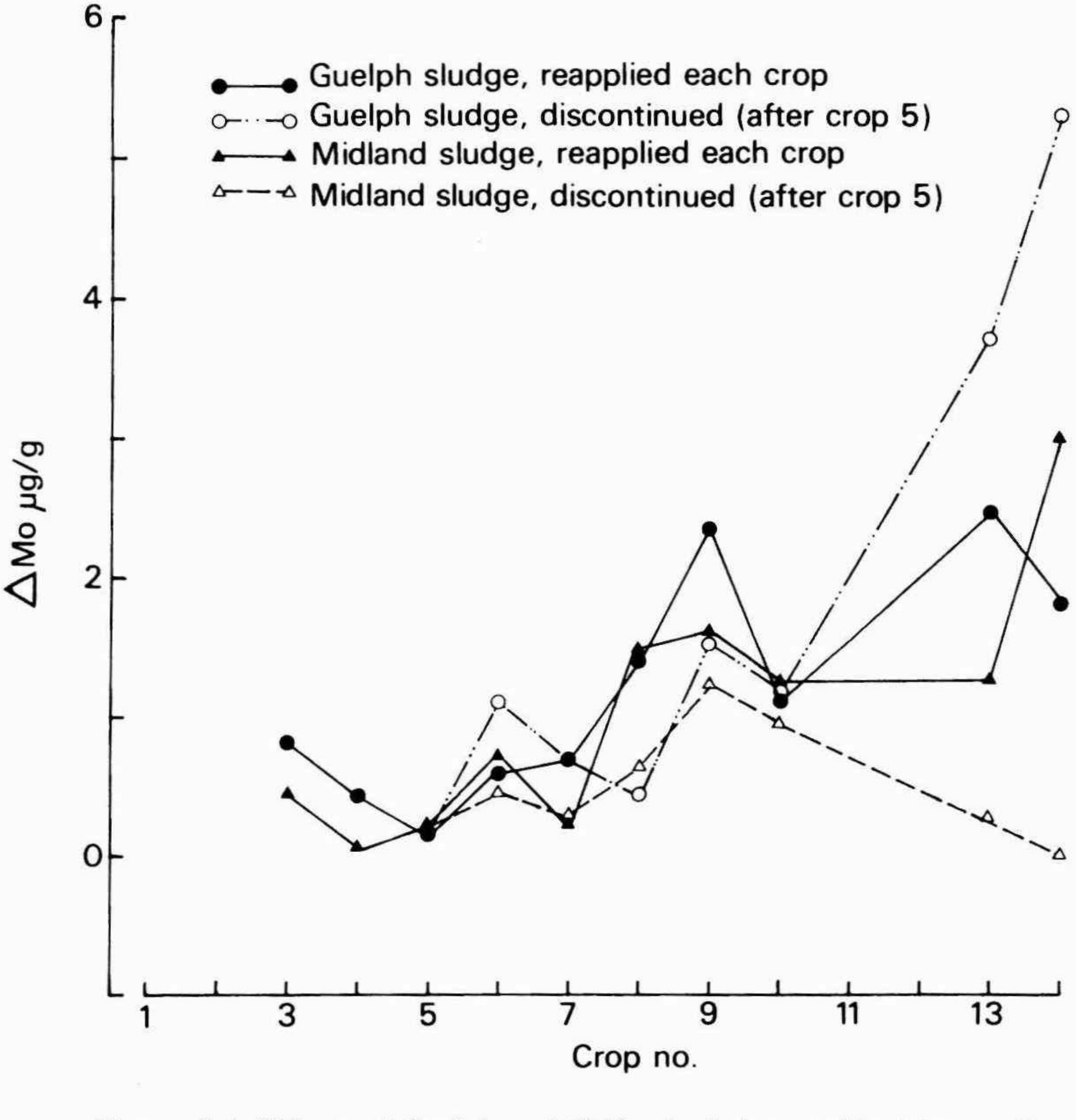


Figure 7.1 Effect of Guelph and Midland sludge application on Mo concentration in ryegrass (plotted as deviation from the NH_4NO_3 treatment).

Table 7.16: Nickel concentration in the 14th crop of ryegrass.

	Sludge not added since 5th crop					Sludge added before each crop					Mean
	N rate kg/ha										
Sludge	200	800	1600	1600*	Mean	200	800	1600	1600*	Mean	
					µg Ni/g						
None											0.7
Aurora	0.7	0.9	0.8	0.8	0.8	0.7	0.9	1.1	1.2	0.9	0.9
Midland	8.0	19.2	25.9	20.2	18.3	14.9	30.7	46.7	46.5	34.7	26.5
Sarnia	0.6	1.2	1.1	0.8	0.9	1.1	1.9	2.7	1.4	1.8	1.3
Guelph	0.6	0.9	0.8	0.5	0.7	0.7	1.0	2.3	1.6	1.4	1.0
Fergus†	0.5	0.8	1.8	0.8	1.0	0.9	3.1	-	-	-	-
N.Toronto	0.7	1.0	0.7	0.5	0.7	0.6	1.4	2.4	2.0	1.6	1.1
Mean§	2.1	4.6	5.9	4.6	4.3	3.6	7.1	11.0	10.5	8.1	6.2

* Sludge was added before the first crop but not before crops 2, 3, 4 and 5.

† The Fergus sludge treatments were omitted from statistical analysis because of too many missing values.

§ Fergus sludge treatments were omitted from computation of rate means.

Significance "F" test at 0.05 and 0.01 probability: -

Sludge source	- .01	Source x rate	- .01
Sludge rate	- .01	Source x addition	- .01
Sludge addition	- .01	Addition x rate	- .01
		Source x rate x addition	- .01

Table 7.17: Nickel concentration in crops 1 to 14 of ryegrass receiving sewage sludges from Midland and North Toronto before each crop.

Crop	Control (NH_4NO_3)	Midland				North Toronto	
		kg N/ha					
	200	200	800	1600	1600§	200	1600§
		µg Ni/g					
First	2.0	8.5	32.0	32.0	32.0	3.5	4.5
Second	1.8	14.6	36.3	40.8	40.8	1.0	1.9
Third*	0.5	14.5	22.5	34.5	34.5	1.0	2.0
Fourth	2.0	18.9	24.7	40.7	40.7	3.9	4.4
Fifth*	3.0	8.1	23.0	29.0	29.0	1.0	3.5
Sixth	1.2	12.0	35.0	36.0	33.5	0.8	2.4
Seventh*	1.3	11.5	32.5	40.0	39.5	0.5	1.2
Eighth	0.9	12.9	28.0	42.0	30.0	1.5	1.6
Ninth*	0.8	7.5	20.2	33.8	21.2	0.7	1.1
Tenth	1.3	10.8	29.8	43.9	18.7	1.0	1.3
Eleventh*	0.9	10.4	27.3	39.7	21.4	1.0	1.6
Twelfth	0.5	10.3	28.3	41.3	18.5	0.3	1.3
Thirteenth*	1.6	13.9	32.5	49.5	23.0	2.5	5.1
Fourteenth	0.7	14.9	30.8	46.8	25.9	0.6	2.4

* Indicates pots were leached after sludge application but before seeding.

The sludge from Midland supplied the greatest amount of nickel in the experiment, while the North Toronto sludge may be considered to be average among the sludges used in its nickel content.

§ No sludge application after the fifth crop.

Table 7.18: Zinc concentration in the shoots of the 14th crop of ryegrass.

	Sludge not added since 5th crop					Sludge added before each crop					Mean
	N rate kg/ha										
Sludge	200	800	1600	1600*	Mean	200	800	1600	1600*	Mean	
					µg Zn/g						
None											12
Aurora	19	35	42	20	29	24	43	53	45	41	35
Midland	29	44	59	35	42	52	80	121	107	90	66
Sarnia	58	143	173	90	116	134	328	492	404	339	228
Guelph	41	60	93	41	59	69	105	207	176	139	99
Fergus†	41	86	145	59	83	92	216	-	-	-	-
N.Toronto	29	72	45	30	44	35	78	117	88	79	61
Mean§	35	71	82	43	58	63	127	198	164	138	98

* Sludge was added before the first crop but not before crops 2, 3, 4 and 5.

† The Fergus sludge treatments were omitted from statistical analysis because of too many missing values.

§ Fergus sludge treatments were omitted from computation of rate means.

Significance "F" test at 0.05 and 0.01 probability: -

Sludge source - .01
Sludge rate - .01
Sludge addition - .01
Source x rate - .01
Source x addition - .01
Addition x rate - .01
Source x rate x addition - .01

Table 7.19: Zinc concentration in crops 1 to 14 of ryegrass receiving sewage sludges from Sarnia and North Toronto before each crop.

Crop	Control (NH_4NO_3)	Sarnia				North Toronto		
			kg N/ha					
	200	200	800	1600	1600§	200	1600	1600§
			µg Zn/g					
First	43	59	167	241	241	53	72	72
Second	38	105	218	211	211	37	81	81
Third*	31	92	146	245	245	41	102	102
Fourth	32	64	156	103	103	29	112	112
Fifth*	33	44	122	165	165	30	92	92
Sixth	51	104	292	490	303	61	130	86
Seventh*	36	99	209	426	343	47	86	72
Eighth	33	177	309	530	318	60	130	78
Ninth*	36	102	275	459	191	42	93	54
Tenth	32	117	420	591	163	39	119	49
Eleventh*	55	136	553	784	153	38	117	43
Twelfth	16	144	390	447	117	36	99	48
Thirteenth*	16	126	349	648	208	38	191	61
Fourteenth	12	134	328	492	173	35	117	45

* Indicates pots were leached after sludge application but before seeding.
The sludge from Sarnia supplied the greatest amount of zinc in the experiment, while the North Toronto sludge may be considered to be average among the sludges used in its zinc content.

§ No sludge application after the fifth crop.

8. GREENHOUSE EXPERIMENT 2: COMPARISON OF CHEMICAL EXTRACTANTS FOR PLANT AVAILABLE HEAVY METALS IN POLLUTED SOILS

8.1 Objectives

The objective of this study was to find an extractant or extractants that would provide a measure of plant available heavy metals in a variety of polluted soils.

8.2 Materials and Methods

Forty-six surface mineral soil materials were collected from cultivated fields, unattended grassed areas and woodlands in southern Ontario, and from two sites in the Sudbury district of northern Ontario. These soils had been polluted over a period of years and to varying degrees with heavy metals by sewage sludges and pesticides, by dumping of snow from city streets, or by emissions from metal smelters.

Fertilizers to supply NPK were added to the soils before growing a crop of Swiss chard (*Beta vulgaris* L. "Fordhook Giant"). Two kg of soil were used per pot. There were two replicates per soil. Ten seeds were placed in each pot, and three days after emergence, the seedlings were thinned to six per pot. The soils were watered to 0.3 bar tension with distilled water as required. Growth was excellent with no sign of nutrient deficiency or toxicity. The Swiss chard tops were harvested after 40 days, washed and dried.

One gram of finely ground plant material was ashed in a muffle furnace at 450°C; the ash was dissolved in 3 ml of aqua regia (3 parts of HCl and 1 part of HNO_3 by volume), and diluted to 10 ml with distilled water. Metal concentrations were determined by atomic absorption.

The following chemical soil extractants were tested:-

Water (H_2O) - 100 g of soil shaken with 200 ml of distilled water for 4h and filtered through a Sartorius membrane filter with 0.45 μm pore size. The extract was concentrated using APDC (ammonium 1-pyrrolidine dithiocarbonate) in MlBK (methyl isobutyl ketone) according to Parker (1972).

Ammonium acetate (CH_3COONH_4) - 1M at pH 7.0; 1:10 soil-to-extractant ratio with 30 min shaking. With this and the following extractants, a Whatman No 42 filter was used to filter the extracts.

Acetic acid (CH_3COOH) - 0.5M; procedure identical to ammonium acetate.

Acid ammonium oxalate - prepared by dissolving 12.6g oxalic acid [$(COOH)_2$] and 25 g of ammonium oalate [$(COONH_4)_2$] in distilled water and diluting to 1L; 1:10 soil-to-extractant ratio with 15h of shaking (Grigg, 1953).

DTPA - this extractant was 0.005M in DTPA (Diethylenetriaminepentaacetic acid), 0.1M in TEA (Triethanolamine) and 0.01M in $CaCl_2$, and buffered at pH 7.3: 1:2 soil-to-extractant ratio with 2h shaking (Lindsay and Norvall, 1978).

EDTA - this extractant was 0.01M in EDTA (Ethylenediamine tetraacetic acid) and 1M in $(NH_4)_2\ CO_3$ and bufferd at pH 8.6; 1:2 sol-to-extractant ratio with 30 min shaking (Trierweiler and Lindsay, 1969).

NTA- this extractant was 0.025M in NTA (nitrolotriacetic acid) and 0.025M in sodium citrate, at pH 6.0; 1:5 soil-to-extractant ratio with 1h shaking. This extractant was included in this study after some preliminary testing and development. This study represented to our knowledge, the first attempt to use NTA to extract "available" metals from soils.

HCl + $AlCl_3$ - This extractant was 0.6N in HCl and 0.05 N in $AlCl_3$; 1:5 soil-to-extractant ratio with a 5 min shaking (Mehlich and Bowling, 1975).

Aqua regia - (HNO_3 + HCl in a ratio of 1:3); 1:2 soil-to-extractant ratio with a 30-min digestion at 110-120°C on a hot plate; diluted to 25 ml with distilled water after filtration (van Loon and Lichwa, 1973).

Metal concentrations in the extracts were determined by atomic absorption. A forward stepwise multiple regression program was used to develop equations for each extractant describing the concentration of each metal in Swiss chard as a function of extractable soil metals, sol pH, % clay, % organic matter (OM) and cation exchange capacity (CEC). All first order interactions among these factors and the square of each factor (to allow for non-linear patterns) were also included as possible variables in the equation. The reader is referred to Haq et. al. (1980) for a fuller treatment of the materials presented in this section.

8.3 Results and Discussion

The metals included in this study are Cd, Cu, Ni, Pb and Zn. The results for Pb are not presented in this summary report because the predictability of its concentration in Swiss chard was low with the extractants tests. Low predictability of Pb concentration is attributed largely to the narrow range of lead concentrations in the plant material. The predictability of Cu concentration in Swish chard with the extractants tested was not satisfactory, so only limited results for Cu will be presented. This report will concentrate on the metals, Cd, Ni and Zn for whch several extractants are satisfactory. Equations for the three most promising extractants for each of these metals will be presented.

The range and mean values of some soil physical and chemical properties are presented in Table 8.1, as are Swiss chard yields and metal concentrations. Mean values of Cd, Cu, Ni and Zn in Ontario agricultural soils as estimated by Frank et al (1976) are also presented for comparison.

The amounts of Cd, Cu, Ni and Zn removed by the various extractants are shown in Table 8.2. Data from one soil was deleted from the Cd and Ni equations because the plant Cd and Ni concentrations were much higher than those for other soils, and would have unduly influenced the regression equations developed.

8.3.1 Cadmium

Correlations of Cd concentrations in Swiss chard with extractable soil Cd were all significant at 0.01 probability (Table 8.3). Water soluble Cd alone accounted for 56% of the variability in plant Cd. The chelating extractants NTA, DTPA and EDTA, each explained about 35% of the variability in Cd concentration in Swiss Chard. Thus extractable soil Cd although highly significantly correlated with plant concentration is not sufficiently highly correlated to be a good predictor of plant Cd when used alone.

Regression equations developed with DTPA, NTA and acetic acid produced promising predictions of plant Cd concentration (Table 8.4), and show that soil pH is an important factor affecting the plant availability of extractable soil Cd. In each case a negative coefficient indicates that an increase in pH decreases plant Cd, and the relation is curvilinear as suggested by the entry of the term

pH^2.

Ammonium acetate-extractable Cd alone explained 29% of the variability in plant Cd concentration. Adding pH and pH^2 to the equation increased the R^2 value to 65% (not shown). Addition of extractable Zn and Zn x OM as independent variables further increased R^2 to 0.77, indicating that Zn affects Cd concentration in plants. However when the extractable Cd/Zn ratio was included as a potential independent variable, it did not enter any equation. The ratio is apparently not a useful indicator of Cd availability.

Soil pH in combination with EDTA-extractable Cd or acetic acid-extractable Cd explained 61% and 64%, respectively, of the variability in plant Cd. The equation for acetic acid as the extractant is presented in Table 8.4. The equation developed using the EDTA extractant include the same variables as the NTA and DTPA equations up to the third step. This illustrates the close similarity of the three chelating extractants. The constants and coefficients are of the same sign (positive or negative) but differ in magnitude.

With water-soluble Cd, the first variable entering the equation was Cd x CEC with R^2 of 0.72 (not shown). The next variable was Cu^2 and improved R^2 to 0.77. The positive coefficient suggests that as water-soluble Cu increases plant availability of Cd increases.

8.3.2 Copper

Correlations of Cu in Swiss chard with extractable soil Cu were all low, but were significant at 0.01 probability (Table 8.3). Prediction equations developed using other soil variables as potential independent variables predicted plant Cu concentrations moderately well with R^2 of 0.61 to 0.82. The equation with water as the extractant included extractable Cu as an independent variable at the third step, after Zn x OM and Zn x CEC ($R^2 = 0.76$). None of the other equations even included extractable soil Cu as a variable. The equation with the highest R^2 (= 0.82) was with EDTA as the extractant and involved four soil variables:

$$\begin{aligned}\text{Cu in Swiss chard} = {} & 20.5 - 0.53\ \text{EDTA Zn} - 0.68\ \text{pH} \times \text{CEC} \\ & + 0.71\ \text{OM} \times \text{CEC} - 0.48\ \text{OM} - 0.022\ \text{CEC}^2 \\ & + 1.31\ \text{CEC}\end{aligned}$$

Thus none of the extractants provided a satisfactory contribution to the prediction of soil Cu availability.

8.3.3 Nickel

Acetic acid-extractable Ni accounted for 42% of the variability in plant Ni (Table 8.3). Other extractants gave even poorer r^2 values. Again the three chelating extractants were similar, explaining 17 to 19% of the variability in plant Ni.

Equations developed to predict plant Ni concentration using extractable soil Ni in combination with other soil variables were satisfactory with EDTA, DTPA and acetic acid, accounting for up to 91% of the variability in plant Ni concentration (Table 8.5). The interactions of Ni with organic matter, pH, CEC and clay appear to be important in determining Ni availability. The negative coefficients for the interactions of extractable Ni with pH, CEC and clay in Table 8.5 show that those factors decrease the availability of extractable soil Ni. The effect of organic matter is not so easily interpreted the coefficient being positive for the DTPA equation and negative for the acetic acid equation.

With NTA-extractable Ni, the R^2 value (=0.87) was lower than when DTPA or EDTA extractable Ni was used with soil pH, organic matter and clay to predict Ni concentration in Swiss chard.

Acetic acid may be the best extractant of those tested because with only pH (which is easily measured) and extractable Ni in the equation, an R^2 of 0.82 was obtained. None of the other extractants gave R^2 values approaching 0.82 when extractable Ni was used as an independent variable with soil pH or any other single variable.

8.3.4 Zinc

The r^2 values for linear correlations between Zn concentrations in Swiss chard and Zn extracted from soil by various extractants showed highly significant correlations except for acid ammonium oxalate (Table 8.3). Ammonium acetate-extractable Zn gave the highest correlation ($r^2 = 0.81$). This extractant provided a useful soil test for plant available Zn without the addition of any other variables. The three chelating extractants gave similar r^2 of 0.63 to 0.65.

The three best prediction equations were developed using DTPA, NTA and ammonium acetate as extractants (Table 8.6). For these extractants, soil pH appears to be an important factor, predicting Zn concentration in Swiss chard followed by clay content. For DTPA, a negative coefficient for the Cd x clay interaction suggests that plant available Zn was decreased in high clay soils and that this effect was more pronounced at high levels of extractable cd.

Similar to its effect on Cd availability, increasing pH decreased Zn availability.

The equation developed with ammonium acetate extractable Zn is the simplest, requiring only one other parameters, soil pH. Ammonium acetate is commonly used to extract soil K, Ca and Mg, and soil pH is routinely measured in soil testing laboratories. Therefore it is relatively easy to include Zn in a soil test program to predict plant Zn levels. A disadvantage is the small amount of Zn extracted by ammonium acetate which may require preconcentration or analysis by electrothermal atomization.

Although the equation developed using DTPA extractable Zn gave a similar R^2 value as ammonium acetate extractable Zn, it required the determination of clay content which is time-consuming. The advantage of DTPA, however, is that it is often used to extract other metals. In this study it is also suitable for Cd and Ni.

The equations developed using EDTA and HCl + $AlCl_3$ as extractants (not shown) to predict plant Zn concentration were similar to that using NTA. The variables, their order of entry and R^2 values were quite similar.

8.4 Conclusions

Acid ammonium oxalate dissolves amorphous iron oxides in soils and is often used to measure the free iron content of soils. It was a poor predictor of plant-available heavy metal contents of soils in this study. Iron oxide is an important sink for heavy metals in soils. Estimates of iron and aluminum oxides were made on the soils studied and were entered as potential independent variables in the equations using NTA as extractant. The iron and aluminum oxide content did not enter any of the equations predicting metal concentration in Swiss chard. This together with the poor results with acid ammonium oxalate as extractant suggest that metals with iron and aluminum oxides are not readily plant-available.

Of the nine extractants tested, DTPA is the most suitable for a number of metals being effective for Cd, Ni and Zn. None of the extractants is suitable for Cu and Pb in the soils studied. Acetic acid is also an efective extractant for Cd and Ni when soil pH is the only other independent variable.

Table 8.1: Range, mean and standard deviation of soil characteristics and metal concentrations in soils and Swiss chard.

	Soil								Plant				
	pH	OM %	Clay %	CEC meq/100g	Cd†	Cu†	Ni†	Zn†	Cd	Cu	Ni	Zn	DM g/pot
					------ µg/g ------------				----------- µg/g --------				
Minimum	5.2	1.4	2.7	5.4	0.50	10	3	20	0.01	7	0.01	29	8.6
Maximum	7.9	17.0	54.0	67.4	9.25	325	525	745	8.45	41	48.00	1550	21.3
Mean	7.0	4.8	19.0	29.3	1.76	66	59	206	1.55	19	4.60	220	14.3
Standard Deviation	0.9	3.7	12.5	13.8	1.80	74	124	171	2.00	8	8.16	340	2.8
Mean, Ontario Soils (Frank et al., 1976)					0.7	25	16	54					

† Metals extracted with aqua regia.

Table 8.2: Soil Cd, Cu, Ni and Zn removed by various extractants.

Extractant	Cd			Cu		
	Range	Mean	S.D.	Range	Mean	S.D.
	µg/g					
H_2O	0.00-0.04	0.01	0.01	0.0-0.4	0.1	0.08
CH_3COONH_4	0.19-2.3	0.26	0.39	0.2-12.4	1.7	2.7
CH_3COOH	0.2-5.7	0.76	1.23	0.5-68	8.1	14
$(COOH)_2 + (COONH_4)_2$	-----	---	---	3-136	34	33
DTPA	0.09-5.1	0.66	0.99	2.8-188	31	39
EDTA	0.08-6.3	0.77	1.26	2.7-135	24	28
NTA	0.05-5.3	0.65	1.09	2.3-139	23	30
$HCl + AlCl_3$	0.18-8.0	1.10	1.80	3-240	30	48

Extractant	Ni			Zn		
	Range	Mean	S.D.	Range	Mean	S.D.
	µg/g					
H_2O	0.0-0.48	0.1	0.1	0.00-3.38	0.1	0.5
CH_3COONH_4	-----	---	---	0.7-35.6	5.9	8.6
CH_3COOH	0.02-7.0	0.6	1.3	4-407	67	108
$(COOH)_2 + (COONH_4)_2$	4.5-150	25.1	38	6-191	69	49
DTPA	0.2-168	11.2	29	2-362	48	82
EDTA	0.2-80	5.6	15	3-386	57	92
NTA	0.5-140	11.0	27	2.4-292	43	68
$HCl + AlCl_3$	1-180	16.5	38	2-462	67	109

Table 8.3: Linear correlations of plant Cd with soil Cd, plant Cu with soil Cu, plant Ni with soil Ni, and plant Zn with soil Zn extracted by various soil extractants.

Extractant	Cd	Cu	Ni	Zn
	r^2			
H_2O	0.56	0.25	0.38	0.35
CH_3COONH_4	0.29	0.29	--	0.81
CH_3COOH	0.30	0.36	0.42	0.60
$(COOH)_2 + (COONH_4)_2$	--	0.31	0.08	0.01
DTPA	0.35	0.35	0.18	0.65
EDTA	0.34	0.34	0.17	0.63
NTA	0.34	0.35	0.19	0.64
$HCl + AlCl_3$	0.28	0.34	0.26	0.53
$HNO_3 + HCl$ (Aqua regia)	0.23	0.22	0.05	0.31

Required r^2 values for significance at 0.05 and 0.01 probabilities are 0.083 and 0.138 for Zn and Cu and 0.085 and 0.142 for Cd and Ni.

Table 8.4: Regression equations for the prediction of Cd concentrations in Swiss chard using extractable metals and other soil characteristics as independent variables.

Regression Step	R^2	Variable Added	Final Equation Coefficient	Final Equation F Ratio
		Extractant - DTPA		
1	0.35	Soil Cd	0.0921	13.1**
2	0.62	pH	-11.9	11.3**
3	0.72	pH^2	0.811	9.6**
4	0.77	S. Cd x OM	-0.0019	13.8**
5	0.80	S. Cd x pH	-0.0106	7.8**
		Constant	43.8	
		Extractant - NTA		
1	0.34	Soil Cd	1.04	44.7**
2	0.62	pH	-16.0	16.6**
3	0.72	pH^2	1.08	13.6**
		Constant	59.8	
		Extractant - CH_3COOH		
1	0.34	pH	-11.2	10.4**
2	0.64	Soil Cd	0.0756	25.5**
3	0.73	Soil Cd^2	-0.0004	11.5**
4	0.78	S. Cd x pH	-0.0071	12.6**
5	0.81	pH^2	0.738	8.1**
		Constant	42.0	

Table 8.5: Regression equations for the prediction of Ni concentration in Swiss chard using extractable metals and other soil characteristics as independent variables.

Regression Step	R^2	Variable Added	Final Equation	
			Coefficient	F Ratio
		Extractant - EDTA		
1	0.17	Soil Ni	10.5	96.5**
2	0.46	S. Ni x pH	-1.18	49.4**
3	0.85	S. Ni x CEC	-0.025	135.4**
4	0.90	S. Ni x clay	-0.023	15.9**
		Constant	1.50	
		Extractant - DTPA		
1	0.18	Soil Ni	3.76	82.6**
2	0.48	S. Ni x OM	0.0725	87.5**
3	0.81	S. Ni x pH	-0.411	39.6**
4	0.87	S. Ni x clay	-0.0090	17.9**
5	0.91	S. Ni^2	0.0034	16.2**
		Constant	1.74	
		Extractant - CH_3COOH		
1	0.43	Soil Ni	56.6	132**
2	0.82	S. Ni x pH	-7.09	101**
3	0.86	S. Ni x OM	-0.252	10.6**
4	0.88	S. Ni x clay	-0.005	8.1**
		Constant	2.37	

Table 8.6: Regression equations for the prediction of Zn concentration in Swiss chard using extractable metals and soil characteristics as independent variables.

Regression Step	R^2	Variable Added	Final Equation	
			Coefficient	F Ratio
		Extractant - DTPA		
1	0.65	Soil Zn	27.8	99.6**
2	0.80	S. Zn x pH	-3.53	71.7**
3	0.90	Cd x clay	-0.56	41.5**
		Constant	119	
		Extractant - NTA		
1	0.64	Soil Zn	7.72	177**
2	0.80	S. Zn x clay	-0.21	53.6**
3	0.87	pH	-1663	18.1**
4	0.91	pH^2	113.6	15.3**
		Constant	6091	
		Extractant - CH_3COOH_4		
1	0.85	Soil Zn^2	1.01	315**
2	0.89	pH	-1309	12.0**
3	0.91	pH^2	89.9	10.3**
		Constant	4830	

LITERATURE CITED

Bascomb, C.L. 1964. Rapid method for the determination of cation exchange capacity of calcareous and non-calcareous soils. J. Sci. Fd. Agric. 15:821-823.

Beauchamp, E.G. and J.R. Moyer. 1974. Nitrogen transformation and uptake. p 153-173 In Sludge Handling and Disposal Seminar. Conf. Proc. no. 2, 18-19 Sept. 1974. Environ. Canada - Ont. Ministry of the Environ., Toronto, Canada.

Beauchamp, E.G., G.E. Kidd and G. Thurtell. 1978. Ammonia volatilization from sewage sludge applied in the field. J. Environ. Qual. 7:141-146.

Beauchamp, E.G., Y.K. Soon and J.R. Moyer. 1979. Nitrate production from chemically treated sewage sludge in soil. J. Environ. Qual. 8:557-560.

Borgaard, O.K. 1976. Selective extraction of amorphous iron oxide by EDTA from a mixture of amorphous iron oxide, goethite and hematite. J. Soil Sci. 27:478-486.

Canada Department of Agriculture. 1974. The system of soil classification for Canada.

CAST. 1976. Application of sewage sludge to cropland: Appraisal of potential hazards of the heavy metals to plants and animals. Report No. 64, 63p. Council for Agricultural Science and Technology, Ames, Iowa.

CAST. 1980. Effects of sewage sludge on the cadmium and zinc content of crops. Report No. 83, 77p. Council for Agricultural Science and Technology, Ames, Iowa.

Chawla, V.K., J.P. Stephenson and D. Liu. 1974. Biochemical characteristics of digested sewage sludge. p63-94. In Sludge Handling and Disposal Seminar Conf. Proc. no. 2, 18-19 Sept. 1974. Environ. Canada - Ont. Ministry of the Environ., Toronto, Canada.

Coffin, D.E. 1963. A method for the determination of free iron in soils and clays. Can. J. Soil Sci. 43:7-17.

Frank, R., P. Ishida and P. Suda. 1976. Metals in agricultural soils of Ontario. Can. J. Soil Sci. 56:181-196.

Grigg, J.L. 1953. A rapid method for the determination of molybdenum in soil. Analyst 78:470-473.

Hamm, J.W. and J.W.B. Stewart. 1973. A simplified procedure for the determination of total mercury in soils. Comm. in Soil Sci. and Pl. Anal. 4:233-240.

Kalembasa, S.J. and D.S. Jenkinson. 1973. A comparative study of titrimetric and gravimetric methods for the determination of organic carbon in soil. J. Sci. Fd. Agric. 24:1085-1090.

Keeney, D.R., K.W. Lee and L.M. Walsh. 1975. Guidelines for the application of wastewater sludge to agricultural land in Wisconsin. Tech. Bull. 88. Dept. Nat. Resour., Madison, Wis.

Lindsay, W.L. and W.A. Norvall. 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. Soil Sci. Soc. Am. J. 42:421-428.

McKeague, J.A., J.E. Brydon and N.M. Miles. 1971. Differentiation of forms of extractable iron and aluminum in soils. Soil Sci. Soc. Am. Proc. 35:33-38.

Mehlich, A. and S.S. Bowling. 1975. Advances in soil test methods for copper by atomic absorption spectrophotometry. Comm. Soil Sci. Pl. Anal. 6:113-128.

Parker, C.R. 1973. Water analysis by atomic absorption spectroscopy. Varian Techtron, Springvale, Victoria, Australia.

Pratt, P.F., F.E. Broadbent and J.P. Martin. 1973. Using organic wastes as nitrogen fertilizers. Calif. Agric. 29(6):10-13.

Premi, P.R. and A.H. Cornfield. 1971. Incubation study of nitrogen mineralization in soil treated with dried sewage sludge. Environ. Pollut. 2:1-15.

Stover, R.C., L.E. Sommers, and D.J. Silviera. 1976. Evaluation of metals in wastewater sludge. J. Wat. Pollut. Cont. Fed. 48:2165-2175.

Thomas, R.L., R.W. Sheard, and J.R. Moyer. 1967. Comparison of conventional and automated procedures for nitrogen, phosphorus and potassium analysis of plant material using a single digest. Agron. J. 59:240-243.

Trierweiler, J.F. and W.L. Lindsay. 1969. EDTA-ammonium carbonate soil test for zinc. Soil Sci. Soc. Am. Proc. 33:49-53.

Van Loon, J.C. and J. Lichwa. 1973. A study of the atomic absorption determination of some important metal in fertilizers and domestic sewage plant sludges. Environ. Lett. 4:1-8.

Webber, L.R. and T.H. Lane. 1969. The nitrogen problem in the land disposal of liquid manure. p124-130. In Animal Waste Management. Cornell Univ. Agric. Waste Mange. Conf. 13-15 Jan. 1969. Syracuse, N.Y.

BIBLIOGRAPHY

A. Canada-Ontario Agreement Reports dealing with this program*:

1. "Land Application of Sewage Sludge", Research Report No. 1, 1973.
2. "Land Disposal of Sewage Sludge", Volume I, Research Report No. 16, 1975.
3. "Land Disposal of Sewage Sludge", Volume II, Research Report No. 24, 1975.
4. "Land Disposal of Sewage Sludge", Volume III, Research Report No. 35, 1976.
5. "Land Disposal of Sewage Sludge", Volume IV, Research Report No. 60, 1977.
6. "Land Disposal of Sewage Sludge", Volume V, Research Report No. 73, 1978.
7. "Land Disposal of Sewage Sludge", Volume VI, Research Report No. 90, 1979.
8. "Land Disposal of Sewage Sludge", Volume VII, Research Report No. 98, 1980.

B. Scientific publications arising from this program:

1. Bates, T.E., A.U. Haq, Y.K. Soon and J.R. Moyer, "Uptake of Metals from Sewage Sludge Amended Soils", in Proc. Int. Conf. heavy Metals in the Environment. Vol. II, October 27 to 31, 1975, Toronto, Canada, pp. 403-416, 1975.
2. Beauchamp, E.G., G.E. Kidd, and G. Thurtell, "Ammonia Volatilization from Sewage Sludge Applied in the Field", J. Environ. Qual. 7:141-146, 1978.
3. Soon, Y.K., T.E. Bates, E.G. Beauchamp and J.R. Moyer, "Land Application of Chemically Treated Sewge Sludge: I. Effects on Crop Yield and Nitrogen Availability", J. Environ. Qual. 7:264-269, 1978.

---

* Research Reports may be obtained from Training and Technology Transfer Division (Water), Environmental Protection Service, Environment Canada, Ottawa, Ontario K1A 1C8, or Ontario Ministry of the Environment, Pollution Control Branch, 135 St. Clair Avenue West, Toronto, Ontario M4V 1P5.

4. Soon, Y.K., T.E. Bates, and J.R. Moyer, "Land Application of Chemically Treated Sewage Sludge: II Effects on Plant and Soil Phosphorus, Potassium, Calcium and Magnesium and Soil pH", J. Environ. Qual. 7:269-273, 1978.

5. Beauchamp, E.G., Y.K. Soon, and J.R. Moyer, "Nitrate Production of Chemically Treated Sewage Sludges in Soil" J. Environ. Qual. 8:557-560, 1979.

6. Soon, Y.K., T.E. Bates, and J.R. Moyer, "Land Application of Chemically Treated Sewage Sludge: III Effects on Soil and Plant Heavy Metal Content", J. Environ. Qual. 9:497-504, 1980.

7. Haq, A.U., T.E. Bates, and Y.K. Soon, "Comparison of Extractants for Plant Available Zn, Cd, Ni and Cu in Ontario Soils", Soil Sci. Soc. Am. J. 44:772-777, 1980.

8. Webber, M.D., Y.K. Soon, and T.E. Bates, "Lysimeter and Field Studies on Land Application of Wastewater Sludges". Prog. Wat. Tech. 12:905-917.

9. Soon, Y.K., "Solubility and Sorption of Cadmium in Soils Amended with Sewage Sludge", J. Soil Sci., 32:85-95, 1981.

10. Lee, C.C., Y.K. Soon, and T.E. Bates, "Phosphate Adsorption by Soil Amended with Chemically Treated Sewage Sludges". Can. J. Soil Sci. 61:165-168, 1981.

11. Remmen, S.F., T.E. Bates, Y.K. Soon and A.U. Haq, "Extractability of Heavy Metals in Sludge and in Soil Amended with Sewage Sludge". J. Environ. Qual. (submitted).

12. Remmen, S.F., T.E. Bates, Y.K. Soon and A.U. Haq, "Growth and Metal Uptake of Ryegrass Grown on Soil Amended with Sewage Sludge". J. Environ. Qual. (submitted).