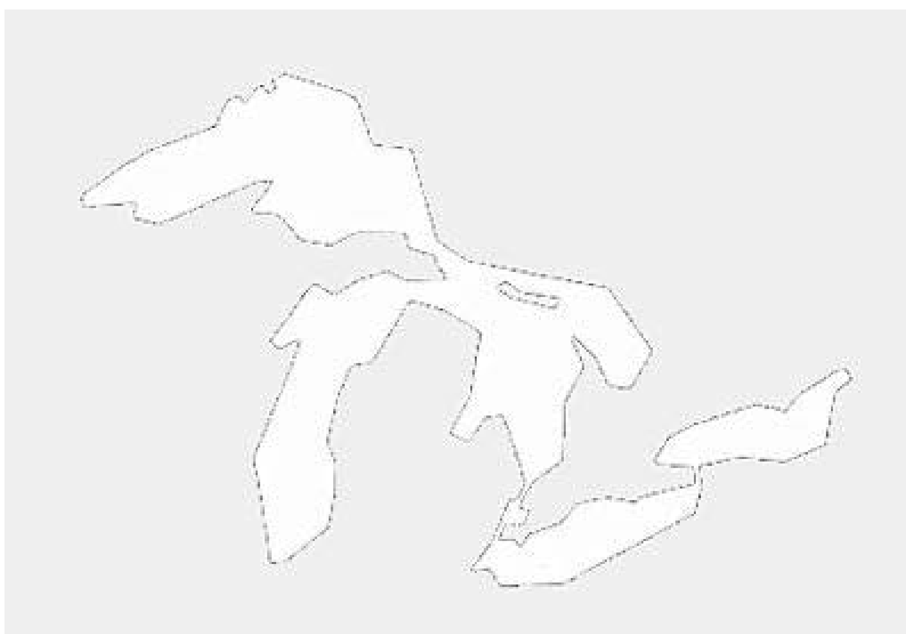
Environment Canada Environnement Canada

Ontario

Ministry of the Environment

Heavy Metals in Agricultural Lands Receiving Chemical Sewage Sludges

Research Report No. 9



Research Program for the Abatement of Municipal Pollution
under Provisions of the
Canada- Ontario Agreement on Great Lakes Water Quality

CANADA-ONTARIO AGREEMENT

RESEARCH REPORTS

These RESEARCH REPORTS describe the results of investigations funded under the Research Program for the Abatement of Municipal Pollution within the provisions of the Canada-Ontario Agreement on Great Lakes Water Quality. They provide a central source of information on the studies carried out in this program through in-house projects by both Environment Canada and the Ontario Ministry of the Environment, and contracts with municipalities, research institutions and industrial organizations.

The Scientific Liaison Officer for this project was Mr. S. Black, Ontario Ministry of the Environment.

Enquiries pertaining to the Canada-Ontario Agreement RESEARCH PROGRAM should be directed to -

Wastewater Technology Centre
Canada Centre for Inland Waters,
Environment Canada
P.O. Box 5050,
Burlington, Ontario, L7R 4A6.

Ontario Ministry of the Environment,
Pollution Control Branch,
135 St. Clair Avenue West,
Toronto, Ontario. M4V 1P5.

OKT3-1446. 04KT.KE 204-3-P092
Donald F. Runge Ltd., Pembroke, Ontario.

HEAVY METALS IN AGRICULTURAL LANDS RECEIVING CHEMICAL SEWAGE SLUDGES

by

J.C. Van Loon
Associate Professor
Departments of Geology, Chemistry and
The Institute of Environmental Sciences and Engineering
University of Toronto

RESEARCH PROGRAM FOR THE ABATEMENT OF MUNICIPAL POLLUTION WITHIN THE PROVISIONS OF THE CANADA-ONTARIO AGREEMENT ON GREAT LAKES WATER QUALITY

PROJECT NO. 72-5-3

MARCH, 1973

This document may be obtained from -

Training and Technology Transfer Division (Water)
Environmental Protection Service Environment
Canada Ottawa, Ontario
K1A 0H3

Ontario Ministry of the Environment
Pollution Control Branch 135 St. Clair
Avenue West Toronto, Ontario
M4V 1P5

REVIEW NOTICE

This report has been reviewed by the Technical Committee of the Canada-Ontario Agreement on Great Lakes Water Quality and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of either the Ontario Ministry of the Environment or Environment Canada, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

The disposal of sewage treatment plant sludges poses a serious problem. Potentially, these materials could be used as fertilizers on agricultural lands. This would be a double benefit acting as a disposal mechanism as well as a source of plant nutrients. On the other hand, a variety of reports have appeared urging caution in this regard for fear of contamination of the land by other matrix constituents. Among these are the potentially toxic heavy metals.

A series of reports, most of which have appeared in the past year, describe the metal content of domestic sewage plant sludges and sewage sludge fertilizers. A selection of references is given at the end of this report.

Researchers in several countries are presently developing projects designed to study the uptake by plants of heavy metals from sludged or otherwise metal contaminated soils. References on this subject also appear at the end of this report.

Despite a good deal of activity in this subject area, it is clear, from the references available to date, that very little data exist which reliably describe plant-metal interactions. Perhaps the most serious omission is that little attempt has been made in these papers to provide data on precision and accuracy of results.

The present study emphasizes the utilization of standard and control samples as tools for validating the data obtained. Because of the shortness of the investigation period no attempt was made to use statistical testing to provide a means for arriving at conclusions. It would seem too early to justify anything but a few generalizations.

Appendix I of this report lists additional references not cited in the text which may be of use to interested readers.

RESUME

L'utilisation des boues provenant des usines de traitement des eaux usees constitue un probleme serieux. A premiere vue, cette matiere pourrait servir a engraisser les terres arables. Ceci serait doublement avantageux, en ce sens qu'on pourrait A la fois se debarasser des boues et s'en servir comme source nutritive pour les vegetaux. D'autre part, it est paru une profusion de rapports insistant sur le danger possible d'une contamination du sol par des substances indesirables contenues dans ces boues. Parmi celles-ci on trouve les metaux lourds potentiellement toxiques.

Une serie de rapports, la plupart publies l'an dernier, decrivent le contenu en metal des boues des usines d'epuration des eaux domestiques et des engrais A base de boues d'eaux use-es. A la fin du rapport, on donne une bibliographie sommaire a ce sujet.

Des chercheurs de plusieurs pays mettent actuellement au point des projets visant a l'etude de l'absorption des metaux lourds par les plantes a parti de sols contamines par les metaux des boues ou d'autre origine. On trouvera aussi une bibliographie a ce sujet a la fin de ce rapport.

Malgre le travail considerable fait dans ce secteur, appert, d'apres la bibliographie actuellement publiee, quill n'existe que tres peu de donnees decrivant de facon fiable l'interaction entre les plantes et les metaux. L'ommission la plus grave qu'on puisse reprocher ces publications et le fait qu'on ne fournit pas assez des donne-es sur la precision et l'exactitude des resultats.

La presente etude insiste sur l'utilisation d'echantillons normalises et d'echantillons temoins comme moyen d'assurer la credibilitee des donne-es obtenues. A cause du peu de temps consacré a l'étude, on n'a pas tente de soumettre les donne-es a un traitement statistique afin d'en arriver A des conclusions quelconques. A l'heure actuelle, on ne peut que se permettre quelques generalisations.

A l'annexe I du rapport, les lecteurs interesses trouveront une bibliographie de titres supplementaires non cites dans le corps du texts.

TABLE OF CONTENTS

		Page
ABSTRACT		i
TABLE OF CONTENTS		iv
	List of Figures	v
	List of Tables	v
1	SLUDGE CHARACTERIZATION OF NORTH TORONTO, NEWMARKET AND POINT EDWARD SEWAGE TREATMENT PLANTS	1
2	NEWMARKET SOILS AND VEGETATION	8
3	HEAVY METAL DISPERSION FROM SLUDGES THROUGH WATER TRANSPORT	16
4	PRECISION AND ACCURACY OF RESULTS	22
REFERENCES		25
APPENDIX I	ADDITIONAL REFERENCES	27
APPENDIX II	RECENT RESULTS OF VEGETATION STUDIES (March, 1973 - November, 1973)	31

LIST OF FIGURES

Figure		page
1	Newmarket Sludge Disposal Area 1971-72	9-10
2	North Toronto Sewage Treatment Plant	19

LIST OF TABLES

Table		page
1	North Toronto	4
2	Newmarket	6
3	Point Edward	7
4	Metal Contents of Newmarket Soils and Grass	13
5	Tomato Metals	15
6	Metals in Sludge Liquid	18
7	Run-off Metals in Filtrate	21
8	NBS Standards	22
9	Repeatability	23
10	EPA Water Standards	24

CHAPTER 1

SLUDGE CHARACTERIZATION OF NORTH TORONTO, NEWMARKET AND POINT EDWARD SEWAGE TREATMENT PLANTS

SLUDGE SAMPLING PROCEDURE

Sludge samples were kindly provided by the staff at the sewage treatment plants concerned. Sampling frequency was weekly starting at a date when suitable chemical sludge became available from the plants (approximately December 19). These samples provide the basis for the sludge characterization studies presented below. In addition, samplings were obtained on other days as required for other purposes. Sludge samples were dipped from tanks and placed in acid-washed plastic containers (North Toronto) and clean glass containers (Point Edward and Newmarket. Point Edward, North Toronto and Newmarket sewage treatment plants employ alum, ferric chloride and lime, respectively, for phosphorus removal. These are the three presently emphasized methods used in Ontario plants.

ANALYSIS PROCEDURE FOR SOLIDS

The method used was similar to that outlined by Van Loon and Lichwa (1) for the elements Cd, Cr, Pb, V, Ni, Zn, Cu, Mn, and Fe. Procedures for Ag and Al were developed and are outlined below. A method for analysing mercury similar to that of Hatch and Ott (2) was modified and tested prior to this contract (3) and was used for the analysis of sludge samples.

Procedure for V, Cd, Cr, Pb, Ni, Zn, Mn and Fe

Mix sludge well in the bottle. Filter enough material to fill a 12.5 cm Whatman #541 filter paper* (folded in a conical filter). Place in an oven and dry at 100^{0}C. Remove the filter and place the contents into a mortar,and grind and mix well. Store samples in acid-washed plastic bottles.

Weigh 0.5 g of sample into an acid washed 100 ml beaker and treat by acid extraction as recommended by Van Loon and Lichwa (1). Make appropriate dilutions and run for each element using the atomic absorption spectrometer.

Inclusion of Ag and Al into the Analytical Scheme

It was desirable to analyse Ag and Al routinely in sludge. Silver has been found to be extremely toxic to lower life forms, e.g. algae (4) and thus might interfere with important soil biochemical reactions. Aluminum, one of the proposed treatments (in the compound alum) for sludge, has been shown to inhibit the germination of seeds (5).

It was felt that the use of an aqua regia treatment, as recommended above, for the decomposition of sludge might result in the precipitation of silver as insoluble silver chloride, thus rendering it unavailable for analysis by atomic absorption spectrometry. A variety of tests on methods for sludge decomposition (dry ashing, nitric acid leach etc.) were instituted to try to avoid the addition of chloride in a concentrated form. Surprisingly, for most sludge samples, the aqua regia treatment gave best results.

____

* Metals are at least 1000 times more concentrated in the solids - comparatively very little being present in the liquid (see Table 6).

In several cases, however, particularly with the North Toronto sludge, very low recoveries of silver were obtained. It is therefore recommended that the aqua regia procedure for sludge decomposition be tested as to its suitability for silver extraction for each sludge type encountered. Should this procedure fail, a nitric acid extraction of a dry ashed sludge sample can be used on separate samples for silver analysis. This alternative procedure is not satisfactory for the extraction of some of the other elements (e.g. Cr, Ni and Pb in many sludges).

In the case of aluminum the acid extractable portion can be readily determined on the aqua regia main sample solution without any decompositional procedural modifications. A nitrous oxide acetylene flame must, however, be utilized in the atomic absorption step.

Results for the analyses of sludges at the various treatment plants are given in Tables (1, 2, 3). In all cases vanadium values were below the limit of detection (12 mg/L) and hence are not listed.

Table 1: North Toronto

		100°C Dried										
		Cd	Cr	Pb	Ni	Cu	Hg	Mn	Ag	Zn	Fe	Al
					(mg/L)						%	
Dec.20	$\bar{x}$	12	440	670	27	880	26	420	na	0.19	7.5	na
*	min	10	400	620	23	820	24	330	na	0.17	7.5	na
	max	16	460	710	30	920	37	480	na	0.20	7.5	na
Jan.5	$\bar{x}$	13	600	810	40	950	27	424	na	0.19	7.4	1.3
*	min	12	590	740	33	910	25	380	na	0.18	7.3	1.3
	max	13	625	840	48	1000	30	440	na	0.22	7.8	1.3
Jan.11	$\bar{x}$	12	620	770	24	960	27	420	na	0.20	7.9	1.3
‡	min	11	580	780	22	890	25	380	na	0.19	7.9	1.2
	max	13	650	810	27	1030	28	440	na	0.21	7.9	1.4
Jan.17	$\bar{x}$	12	604	760	23	930	26	275	na	0.23	7.9	1.2
‡	min	11	530	660	21	890	23	270	na	0.22	7.8	1.2
	max	15	640	830	30	1000	33	280	na	0.25	7.9	1.3
Jan.26	$\bar{x}$	12	530	820	27	860	24	275	na	0.22	7.6	1.2
+	min	12	480	800	26	845	22	270	na	0.22	7.5	1.2
	max	13	570	860	27	865	26	280	na	0.23	7.8	1.3
Feb.2	$\bar{x}$	16	510	910	26	1070	24	364	na	0.23	7.4	1.2
+	min	15	490	850	21	1030	19	350	na	0.22	6.8	1.2
	max	17	530	930	29	1120	29	370	na	0.25	8.0	1.3
Feb.8	$\bar{x}$	16	527	930	26	1160	21	370	na	0.23	7.0	1.4
+	min	13	482	840	21	1100	14	350	na	0.22	6.3	1.3
	max	18	572	1020	30	1230	24	410	na	0.24	8.1	1.4
Feb.15+	$\bar{x}$	17	480	1200	28	1170	16	330	12	0.24	6.0	1.3
Feb.22	$\bar{x}$	16	480	970	21	1130	25	360	10	0.24	8.2	1.3
+	min	15	470	930	16	1110	23	340	9	0.22	7.7	1.2
	max	17	520	1000	22	1160	27	380	13	0.24	8.4	1.3
Mar.2	$\bar{x}$	21	700	1080	51	1240	24	370	55	0.25	4.1	1.6
+	min	15	540	840	25	1100	18	330	47	0.20	1.4	0.8
	max	29	870	1380	72	1470	25	440	76	0.30	6.9	2.4

* From sludge filters
‡ From sludge filter tanks
\+ From digesters
na = not available

Typical sludge solid weight/liquid volume ratios (gm/ml)

January 11	0.081
January 17	0.080
January 26	0.079
February 8	0.073
February 15	0.075
February 22	0.096
March 2	0.12

Table 2: Newmarket

		100°C Dried										
		Cd	Cr	Pb	Ni	Cu	Hg	Mn	Ag	Zn	Fe	Al
Dec.19	$\bar{x}$	2	2	90	7	210	1	180	10	512	0.33	0.09
	min	1	1	80	6	188	1	155	10	500	0.31	0.08
	max	2	2	105	8	250	1	190	10	530	0.36	0.10
Jan.19	$\bar{x}$	1	16	85	5	136	1	195	8	520	0.28	0.10
*Jan.26		1	18	90	5	140	1	220	9	500	0.38	0.20
*Feb.2		2	14	70	7	130	1	210	10	530	0.32	0.11
*Feb.16		2	15	90	6	156	1	200	9	750	0.35	0.11
*Feb.19		2	14	80	9	145	1	180	10	600	0.29	0.13
Feb.23	$\bar{x}$	1	17	89	8	180	1	220	9	690	0.35	0.11
	min	1	14	83	7	170	1	200	3	600	0.30	0.10
	max	2	21	96	9	200	1	230	12	800	0.39	0.11
Mar.2	$\bar{x}$	2	19	90	9	200	1	270	15	760	0.41	0.14

Typical sludge solid weight/liquid volume ratios (gm/ml)

January 19	0.22
January 26	0.077
February 16	0.25
March 2	0.094

* single samples

Table 3: Point Edward

		100°C Dried										
		Cd	Cr	Pb	Ni	Cu	Hg	Mn	Ag	Zn	Fe	Al
						(mg/L)					%	
* Dec.7	$\bar{x}$	6	68	285	26	565	3	68	4	900	0.63	3.1
Dec.19	$\bar{x}$	6	70	290	29	575	4	68	4	925	0.65	3.4
Jan.19	$\bar{x}$	5	75	270	25	540	2	55	4	925	0.68	3.8
Jan.25	$\bar{x}$	6	87	280	25	550	2	55	4	975	0.63	4.4
Feb.2	$\bar{x}$	6	60	220	24	480	2	70	5	712	0.69	4.5
Feb.9	$\bar{x}$	5	60	283	18	530	2	44	3	812	0.22	na
Feb.15	$\bar{x}$	6	61	220	21	530	2	47	4	800	0.65	4.2
Feb.21	$\bar{x}$	6	67	220	20	535	4	83	5	875	0.53	3.8
Feb.23	$\bar{x}$	5	65	235	19	520	3	78	5	920	0.68	4.0
Mar.1	$\bar{x}$	5	57	200	20	540	4	83	4	710	0.64	4.4

Typical sludge solid weight/liquid volume ratios (gm/ml)

January 19	0.081
January 25	0.058
February 15	0.061
March 1	0.057

* $\bar{x}$ computed from 2 samples in each case

na = not available

CHAPTER 2

NEWMARKET SOILS AND VEGETATION

DESCRIPTION

A. Soils and Vegetation came from 2 Farms

1. Owned by Christian Bros. of Scarborough - Maryvale farm, foreman Albert Kenuel. Bounded by Davis Drive on north, Don Mills Road on east and Sharon Road on west. Soil is clay loam.

2. Owned by Jack Pegg and rented by M. Langford. Located north of Mount Albert Side Road just east of Don Mills Road. Soil is sandy loam.

B. Sample Sites (Refer to Figures 1a and 1b)

Farm 1

Soil samples were taken from fields 3 and 2 and wet sludge taken during application on Field 3.

Field 2 - two applications of sludge, once each in 1971 and 1972. Samples were taken after sludging in 1972.

Field 3 - Samples were taken before the 1972 application of sludge and thus represent conditions of no sludge.

Farm 2

Field 11 - Samples were taken after one application of sludge.

Sludge Lagoons - Samples were taken from the south lagoon which had been scraped free of its contents and also from the north lagoon which contained sludge.

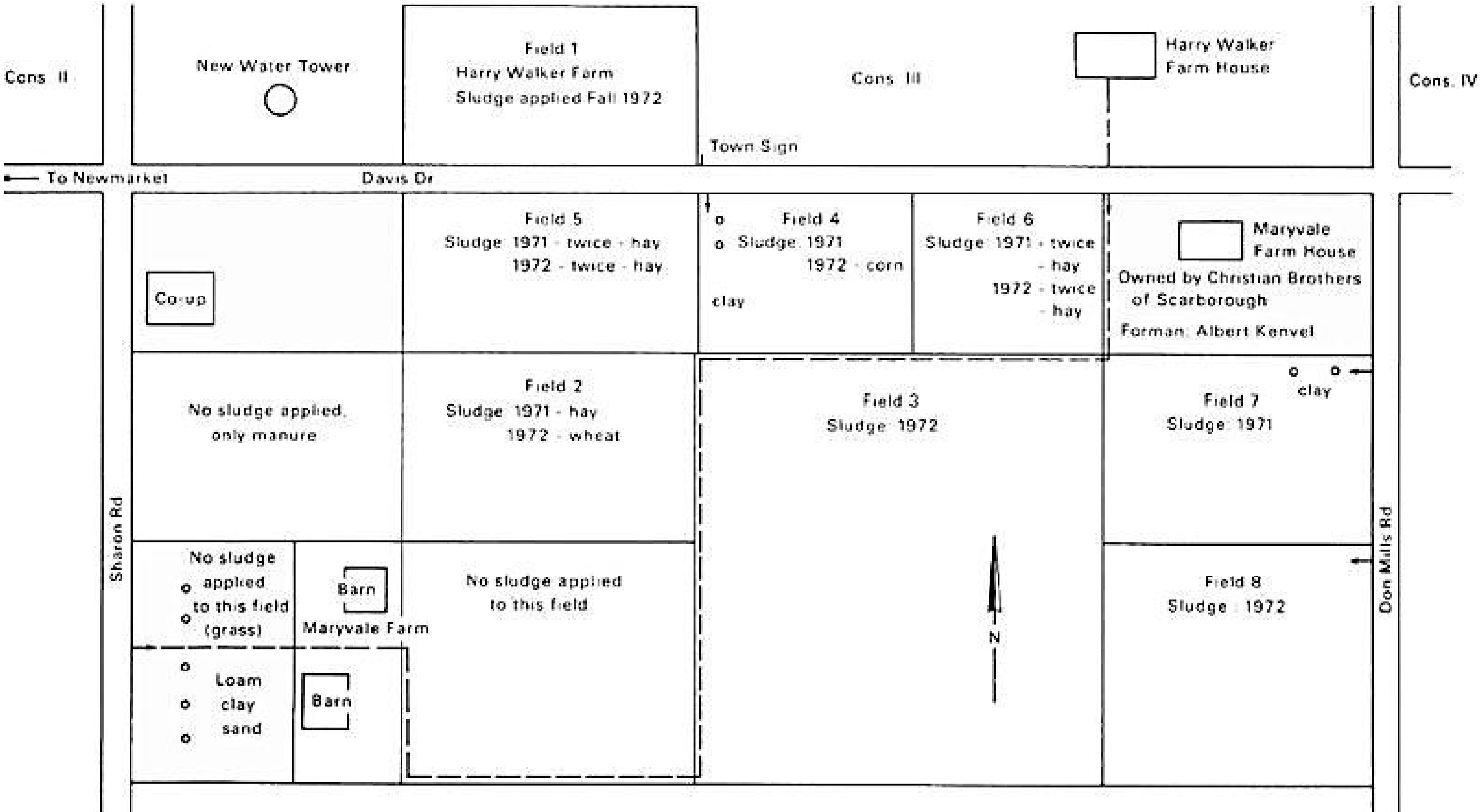
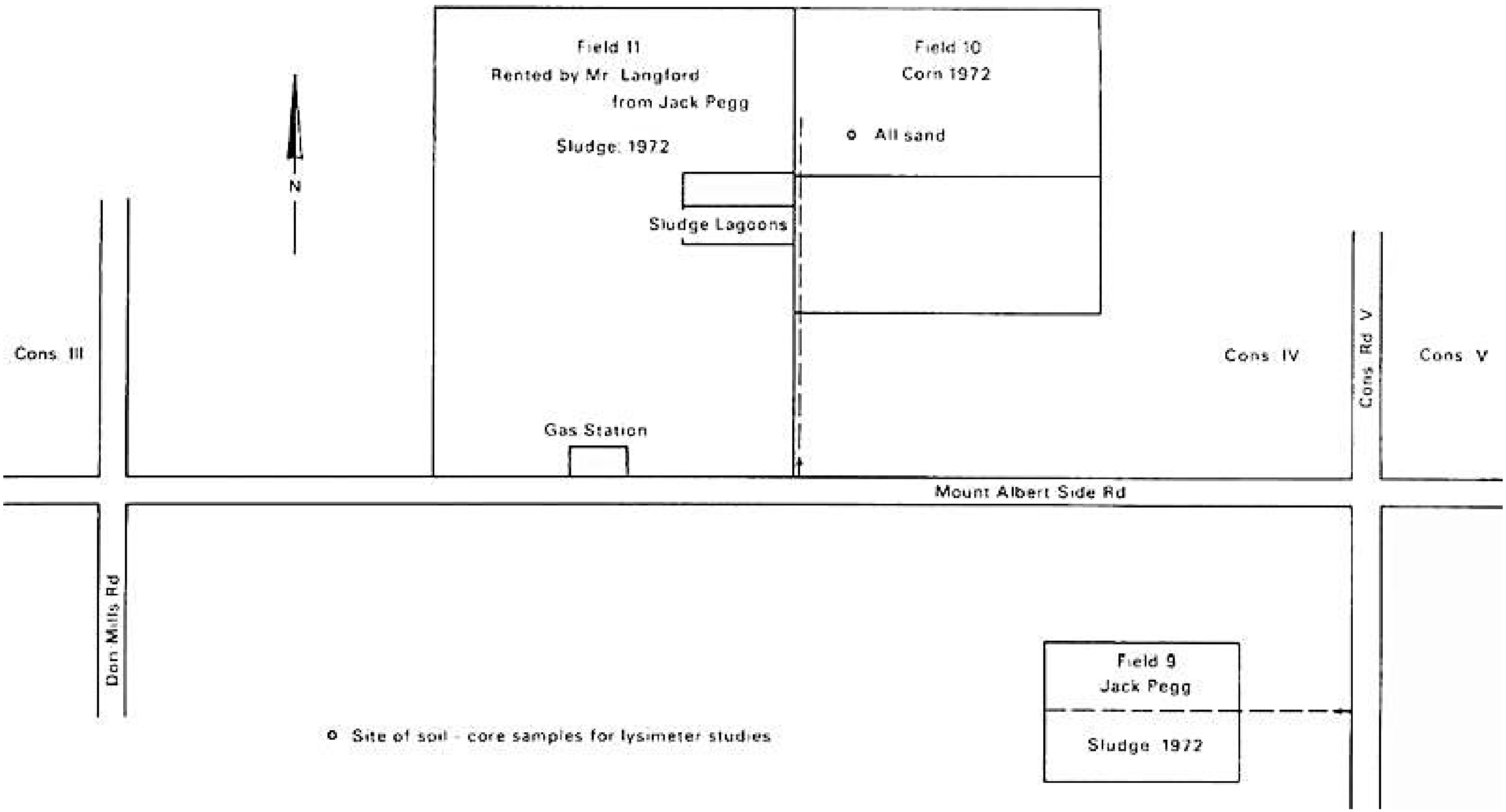


FIGURE 1a
Newmarket Sludge Disposal Area 1971 – 72



Field 11
Rented by Mr. Langford
from Jack Pegg
Sludge: 1972
Field 10
Corn 1972
All sand
N
Sludge Lagoons
Cons. III
Cons. IV
Cons. Rd. V
Cons. V
Gas Station
Mount Albert Side Rd
Don Mills Rd
Field 9
Jack Pegg
Sludge 1972
Site of soil - core samples for lysimeter studies

C. Sampling Strategy

Fields were traversed in a diagonal fashion and samples taken every 20 feet. Fields had been ploughed so the grab samples are representative of soil down to the depth of the furrow. These samples were combined to give five lots per field.

Vegetation - largely grass was also collected in the same manner.

Sample Preparation

Soils

Soils were sieved carefully to prevent contamination, to yield a -80 mesh particle size. These were homogenized by careful mixing on large sheets of paper and stored for use in separate plastic vials.

Vegetation

Soil was cleaned from vegetation by hand picking and finally by distilled water washing. In the case of the latter any surface contamination by sludge is removed.

PROCEDURES FOR SOIL AND VEGETATION DECOMPOSITION

Vegetation Ashing

Grass and tomato samples were ashed at 450^{0}C to a grey powder prior to decomposition. Sludge samples could also be treated in this manner but enhancement in metal recovery thus achieved was not sufficient to warrant the extra time involved.

To test possible loss of metals at this ashing temperature samples were placed in the HGA 70 Perkin Elmer Graphite furnace and run on the atomic absorption. No appreciable loss of metals other than mercury was noted at a temperature of 490°C.

Dissolution of Soils and Vegetation Ash

Samples were weighed (1.0 g of 100°C dried vegetation and 0.5 g of soil) into 100 ml beakers. Vegetation samples were ashed at 450°C. Both types of samples were decomposed with aqua regia as indicated for sludges.

Results for soil and vegetation samples are given in Table (4).

Each of the five lots was analysed for metals 3 separate times (A, B and C in the table below). The mean for each analysis is given. Grass samples (the only vegetation available from each field) were analysed and values recorded for each field. No grass metal values are reported for Cd, Ni, Cr and V because they are below the useful detection limit of 0.5, 1, 5 and 12 mg/L respectively. Mercury could not be determined because of losses on ashing. Enough samples did not exist when the mercury method became available to do separate analyses for mercury. This will be done in the future.

The values in the brackets are for vegetation (100°C dried) and those without brackets are soils.

Table 4: Metal Contents of Newmarket Soils and Grass.

I Nickel (mg/L)

Samples		A	B	C
Field 3		11	12	17
2		14	13	14
11		8	8	8
Lagoon		11	10	12
Sludge truck	a	14	11	8
	b	15	15	11

II Cadmium (mg/L)

Samples		A	B	C
Field 3		0.7	na	0.8
2		0.9	na	0.8
11		0.7	na	0.8
Lagoon		2.5	2.8	2.7
Sludge truck	a	1.3	1.1	l.2
	b	1.6	1.6	2.5

III Manganese (mg/L)

Samples		A		B		C	
Field 3		416	(57)	406	(55)	450	(63)
2		450	(83)	430	(76)	490	(71)
11		221	(50)	260	(44)	216	(43)
Lagoon		200	(48)	195	(38)	218	(28)
Sludge truck	a		228		303		320
	b		260		260		313

IV Lead (mg/L)

Samples		A	B	C
Field 3		10 (3)	10 (3)	10 (3)
2		16 (6)	13 (7)	13 (6)
11		15 (6)	12 (5)	12 (5)
Lagoon		72 (4)	77 (4)	98 (4)
Sludge truck	a	52	35	38
	b	61	na	58

V Copper (mg/L)

Samples		A	B	C
Field 3		9 (7)	12 (8)	12 (6)
2		14 (11)	18 (14)	18 (11)
11		16 (11)	18 (12)	16 (11)
Lagoon		242 (15)	380 (16)	335 (17)
Sludge truck	a	136	138	125
	b	88	77	80

Table 4: (cont'd)

Metal Contents of Newmarket Soils and Grass

VI Chromium (mg/L)

Samples		A	B	C
Field 3		13	11	16
2		14	13	17
11		10	8	11
Lagoon		11	14	16
Sludge truck	a	15	17	16
	b	14	22	21

VII Zinc(mg/L)

Samples		A	B	C
Field 3		21 (27)	28 (26)	32 (24)
2		44 (68)	53 (67)	53 (57)
11		71 (43)	84 (47)	89 (46)
Lagoon		2170 (140)	1900	1950 (144)
Sludge truck	a	378	351	356
	b	543	553	541

VIII Iron %

Samples		A	B	C
Field 3		2.4 (0.05)	1.7 (0.04)	2.4 (0.07)
2		2.4 (0.13)	1.8 (0.08)	2.4 (0.13)
11		1.4 (0.02)	1.3 (0.02)	1.4 (0.02)
Lagoon		0.5 (0.02)	0.5 (0.01)	0.7 (0.01)
Sludge truck	a	0.8	0.5	0.8
	b	1.0	0.5	0.9

na = not available

Tomato fruit samples were collected from the sewage lagoon. These were analysed for metals. These values were compared with those obtained on tomatoes which were harvested from an area thought to be low in metals. See Table 5.

Table (5): Tomato Metals.

mg/L 100°C Dried	No Sludge	Sludge
Zinc	16	30
Copper	8	12
Iron	55	55
Lead	0.8	1.2
Manganese	8	14

No conclusions should be made from the above data. Much more work is essential before trends can be obtained in this regard.

CHAPTER 3

HEAVY METAL DISPERSION FROM SLUDGES THROUGH WATER TRANSPORT

Because of the high levels of heavy metals in sludges it is important to study the transport of these substances from the point of disposal to aquatic environments. This occurs as the result of leaching by precipitation and run-off, or through direct interaction of sludge with standing water or ground water. There are two modes of heavy metal transport in waters, with particulate matter and as soluble species.

Initial experimentation showed that the dividing line between "particulate" metal and "soluble" metal was hard to define. A good deal of effort during the early phases of this work must be spent in defining the size range.of materials transported in order that some hypothesis of dispersion can be obtained.

Water samples were collected from the area of the sludge disposal site near the North Toronto sewage treatment plant during episodes of precipitation especially during heavy spring run-off periods. These samples were filtered through membranes of varying pore sizes and the resultant licuids analysed for total heavy metals. The filters pore sizes chosen were 60µ (Whatman #44 paper), 5µ, 1.2µ, 0.81µ and 0.45µ. It was difficult, and in most cases impossible, to force these waters through membranes of smaller pore size. Most work was done with the 5µ and 0.45µ filters.

The filter apparatus used was obtained from Millipore Co. Ltd. (Montreal, Quebec). It consisted of a plastic filter holder (no metal parts) and disposable all plastic syringes. This equipment was acid washed and distilled water rinsed prior to use. Filter membranes were also treated the same.

The liquids obtained by the above filtration were treated with acids and evaporated to dryness to obtain a total decomposition of metal containing complexes and particles. The metals were dissolved in dilute acid, the solutions buffered and the metals extracted using ammonium pyrolidine dithiocarbonate (APDC) and methyl isobutyl ketone (MIBK) by a method similar to Brooks *et al* (6).

Filter membranes containing trapped particulate were placed in acid washed 100 ml beakers and ashed at 450°C. The residue was acid extracted as for sludge. The solutions were evaporated to dryness and the metal dissolved in dilute acid. A buffer was added and the metals extracted using APDC and MIBK as indicated above. Blank membranes were also ashed and analysed. The values thus obtained were subtracted from the sample values.

Results for both the liquid and particulate analyses were expressed on the basis of metal content per volume of liquid filtered. Units used are micrograms per litre (ppb) in these cases.

Samples studied include sludge liquids from the North Toronto Point Edward and Newmarket plants and run-off from the North Toronto plant sludge disposal area.

Results for Sludge liquids are given in Table (6).

Table 6: Metals in Sludge Liquid (ppb).

(A) Membrane Trapped Particulate

Location	Filter (μ)	Zn	Fe	Pb	Ni	Cu	Cd
Point Edward	5.0	0.3	20	4	2	9	0.7
	0.45	0.5	120	2	1	9	0.6
Newmarket	5.0	5	65	1	0.1	0.1	0.1
	11.2	9	250	4	3	2	0.6
	0.8	nd	20	2	nd	nd	0.1
	0.45	1	70	2	1	2	0.2
North Toronto	5.0	4	100	2	0.4	9	0.2
	0.45	5	120	2	0.2	3	0.1
*Don River	0.45	1	20	nd	nd	nd	nd

* Sample above North Toronto effluent flow

(B) Metals in Filtrate

Location	Filter (μ)	Zn	Fe	Pb	Ni	Cu	Cd
Point Edward	60	20	500	nd	27	10	1
	5	20	425	nd	22	10	1
	0.45	9	200	nd	25	3	1
Newmarket	60	70	56	nd	65	25	1
	5	70	43	nd	62	25	1
	0.45	110	116	nd	65	25	1
North Toronto	60	235	57	nd	125	530	1
	5	195	50	nd	115	550	1
	0.45	75	33	nd	110	540	1
*Don River	0.45	53	44	7	15	12	0.5

nd = not detected

Run-off Samples at North Toronto

Samples of water run-off during periods of precipitation and spring run-off were taken from in and around the sludge disposal area at the North Toronto sewage treatment plant. The following is a description of the sample sites. Please see Figure 2 also.

Sample Sites

S (1) Drainage ditch receiving run-off from adjacent sludge piles taken 10 feet from piles.

S (2) Drainage ditch with grade higher than sludge piles receiving mainly water from the treatment plant road. Samples taken 20 feet from sludge piles.

S (3) Run-off water sample from a point within the sludge piles.

S (4) Drainage ditch receiving water from adjacent piled sludge. Sample taken 20 feet from piles.

S (5) Persistent puddle on road adjacent to sludge piles. Water commonly flows over the road into railway embankment on the other side.

S (6) Drainage ditch receiving run-off from adjacent piles of sludge. Samples taken 20 feet from piles. Water drains from here under the road into railroad drainage ditch near sample S (8).

S (7) Drainage from railroad ditch as it enters concrete abutment. From here drainage appears to be under the railroad tracks into the Don River.

S (8) Drainage from sludge pile ditches as it is received in the railroad ditch. Samples taken in the bottom of the railroad ditch.

Samples were filtered through 5µ and 0.45µ pore size membranes. Filtrates were analysed for metals and the results given in Table 7.

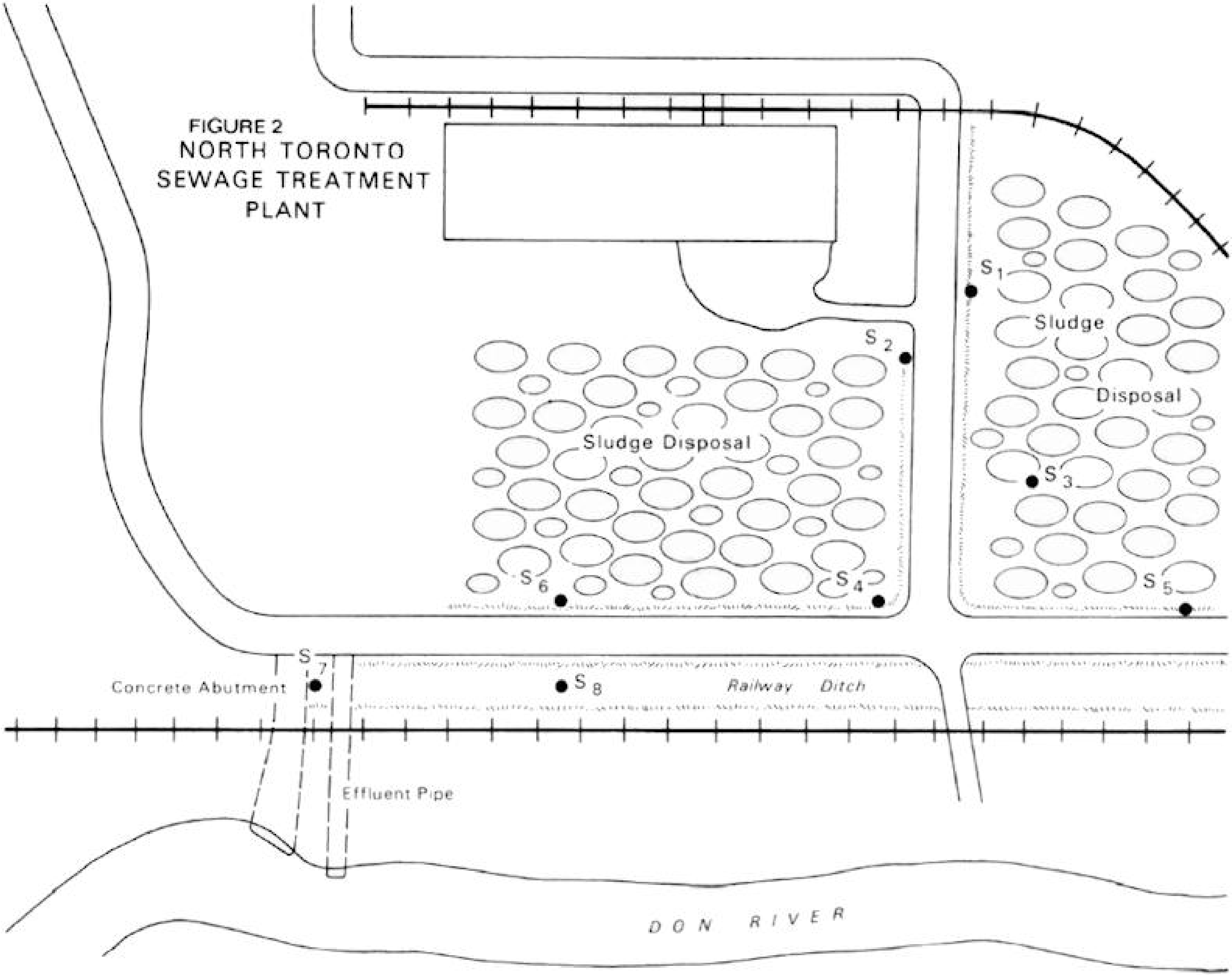


FIGURE 2
NORTH TORONTO
SEWAGE TREATMENT
PLANT
S1
Sludge
Disposal
S2
Sludge Disposal
S3
S4
S5
S6
S7
Concrete Abutment
S8
Railway Ditch
Effluent Pipe
DON RIVER

Table 7: Run-Off Metals in Filtrate (ppb).

Sample	Filter (µ)	Zn	Fe	Pb	Ni	Cu	Cd
S1	5.0	6	125	nd*	21	25	0.4
	0.45	nd	70	nd	20	25	0.2
52	5.0	21	250	nd	21	48	0.5
	0.45	7	95	nd	17	34	0.4
S3	5.0	19	na	8	33	20	0.5
	0.45	11	na	3	35	20	0.4
S4	5.0	7	15	nd	10	36	0.6
	0.45	8	19	nd	9	30	0.5
S5	5.0	4	na	nd	70	28	0.5
	0.45	nd	na	nd	70	19	0.4
S6	5.0	125	220	4	21	54	2
	0.45	175	210	3	21	53	2
S7	5.0	46	210	4	24	84	1
	0.45	65	200	nd	24	81	0.6
S8	5.0	49	185	2	25	81	1
	0.45	62	180	nd	25	76	1

* nd = not detected

Results for the analysis of particulate matter trapped by membranes were not completed and will appear in the next report.

Data, at this stage, suggest that the large proportion of all metals tested, except lead, pass through even an 0.45µ pore size. Because of difficulties in passing waters through lower pore sizes (even distilled water will not pass an 0.04µ filter) no conclusions regarding the form (i.e. soluble or particulate) of the metal can be made at this time. The fact that the metals will pass these fine pore sizes suggests a potential for long distance dispersion from the source.

CHAPTER 5

PRECISION AND ACCURACY OF RESULTS

A. SOLIDS

No standard sludge samples exist on which to test accuracy. However, the National Bureau of Standards (Washington D.C.) has available Standard Orchard Leaves S.R.M. #1571 and Bovine Liver S.R.M. #1577. These samples will give a good indication of the accuracy obtained on samples with an organic matrix. These samples were run during routine laboratory operations and the results given in Table (8).

Table 8: NBS Standards (mg/L).

Stn.	Cd	Cr	Pb	Ni	Zn	Cu	Fe	Hg	Mn
1571 NBS	0.1	2.3	45	1.3	25	12	300	0.16	91
Ours	0.2	2.5	43	1.3	32	9	260	0.12	81
1577 NBS	0.3	na	0.34	na	130	193	270	nd	10
Ours	0.3	34	3.5	1.1	131	170	252	0.016	9

To check on repeatability two control sludge samples were chosen and repeated with each set. This will give some indication of variation within the sample as well as operator repeatability. To try to obtain another measure of operator repeatability a single sample was dissolved and analysed five times using the same sample solution. This would eliminate variation from sample inhomogeneity. Results for these tests are given in Table (9).

Table 9: Repeatability.

	Cd	Cr	Pb	Ni	Cu	Hg	Mn	Ag	Zn	Fe	Al
					mg/L					%	
One Sample Solution Repeated 5 times											
$\bar{x}$	14	550	790	28	860	-	430	49	0.23	7.8	1.3
min	13	530	760	27	850	-	410	48	0.22	7.6	1.3
max	14	560	820	30	900	-	450	50	0.23	7.8	1.3
North Toronto Control											
$\bar{x}$	12	525	790	25	930	21	420	48	0.19	7.7	1.3
min	11	460	680	23	900	19	370	40	0.18	6.0	1.2
max	13	560	880	27	960	28	450	58	0.21	8.2	1.4
Newmarket Control									ppm		
$\bar{x}$	2	18	97	5	160	1	220	10	490	0.29	0.10
min	1	13	67	4	130	1	180	9	425	0.24	0.09
max	2	21	137	8	180	1	240	10	540	0.32	0.11

These data suggest a sample inhomogeneity problem. A test was made on several samples of sludges taken at the same time. Analyses of different bottles showed a spread similar to that shown by the control sample. Hence it is doubtful that a grab sludge sample is representative of the sludge in a digester tank. For this reason results for sludge samples (Tables (1) and (2) Chapter 1) were reported as mean values for the day with limits of maximum and minimum to indicate the spread in values.

B. LIQUIDS

The Environmental Protection Agency (Cincinnati, Ohio) provides water sample standards containing heavy metals. These were analysed during the routine laboratory operation and the results recorded in Table (10).

Table 10: EPA Water Standards .

		ppb					
		Zn	Fe	Pb	Ni	Cu	Cd
EPA 1	Ours	11	18	31	<1	9	1.5
	EPA	10	18	29	-	9	1.8
EPA 2	Ours	74	368	102	1	72	16
	EPA	79	402	92	-	67	16
EPA 3	Ours	370	720	na	<1	320	70
	EPA	367	769	350	-	314	73

na = not available

Because of the volumes of samples involved repeatability as assessed by control sample could not be obtained. EPA sample 1 was analysed 3 times and the repeatability was a follows (ppb) Zn ±1, Fe ±2, Cu ±0.5, Cd ± 0.2.

REFERENCES

1. J.C. Van Loon and J. Lichwa (1973). A Study of the Atomic Absorption Determination of Some Important Heavy Metals in Fertilizers and Domestic Sewage Plant Sludges. Envir. Lett. Vol. 4, pp. 1-8.

2. W.R. Hatch and W.L. Ott. Determination of Mercury by Flameless Atomic Absorption Spectrophotometry. Anal. Chem. Vol. 40, pp. 2085-2089.

3. J.C. Van Loon (In Press May 1973). A Potential Source of Mercury Contamination. Envir. Lett. Vol. 5, No. 1.

4. T.C. Hutchinson. (1972). Private Communication.

5. R.W. Pearson and F. Adams, eds. (1967). Soil Acidity and Liming. American Society of Agronomy, pp. 100-106.

6. R.R. Brooks, B.J. Presley and I.R. Kaplan (1967). Determination of Metal Cations in Water Using APDC and MIBK followed by Atomic Absorption Spectroscopy, Talanta, Vol. 14, pp. 809-815.

APPENDIX I

ADDITIONAL REFERENCES

ADDITIONAL REFERENCES

(A) <u>REFERENCES (METALS IN SLUDGES)</u>

M.L. Berrow and J. Webber (1972). Trace Elements in Sewage Sludges. J. Sci. Fed. Agric. Vol. 23, pp. 23-100.

J. Webber (1972). Effects of Toxic Metals in Sewage on Crops. Water Pollution Control, pp. 405-413.

R. Davies (1972). Where Have All the Metals Gone? Water and Pollution Control Vol. 109, pp. 19-21.

J.C. Van Loon (In Press May 1973). Agricultural Use of Sewage Treatment Plant Sludges, A Potential Source of Mercury Contamination. Environmental Letters Vols.

J.C. Van Loon and J. Lichwa (1973). A Study of the Atomic Absorption Determination of Some Important Heavy Metals in Fertilizers and Domestic Sewage Plant Sludges. Environmental Letters Vol. 4, pp. 1-8.

C.J. Rehling and E. Truog (1939). Activated Sludge - Milorganite, Constituents, Elements and Growth Producing Substances. Indust. and Eng. Chem. Vol. II, pp. 281-283.

M.S. Anderson (1956). Comparative Analyses of Sewage Sludges, Sewage Ind. Wastes Vol. 28, pp. 132-135.

H.A. Lunt (1953). The Case for Sludge as a Soil Improver. Water and Sewage Works Vol. 100, pp. 295-301.

T.D. Hinesly and B. Sosewitz (1969). Digested Sludge Disposal on Crop Land. Joun. Water Pol. Control Fed. Vol. 41, pp. 822-828.

K.G. Clark and V.L. Gaddy (1955). Composition and Nitrification Characteristics of Some Sewage and Industrial Sludges 1952, Farm Chemicals Vol. 118, pp. 41-45

R.A. Abbott (1971). Metals in Municipal Sewerage Systems. Ontario Water Resources Commission, 31 pp.

J.V. Lagerwerff (1967). Heavy Metal Contamination of Soils, Agriculture and the Quality of the Environment. Bradly N.C. Ed. Amer. Ass. Adv. Sci. Spec. Publ. Vol. 85, pp. 343-364.

S. Oden, B. Berggren and A. Engvall (1970). Metal Content in Sludge from Water Treatment Plants, Tidsskr-Grundforbattring Secilanr. Vol. 23, pp. 55-68.

N. Brink (1969). Transport of Nutrient Salts and Toxic Substances in the Soil-Plant-Animal Ecosystem.' (Mercury in Sewage fertilizer). Grundforbattring Vol. 22, pp. 33-41.

K.S. Shater, A.F. Eremina, A.I. Semeryak, V.V. Smirnov and A.V. Efremou (1970). Spectral Determination of Mercury in Sewerage, Industrial Laboratory USSR U. Vol. 36, Issue N12, p. 1876.

J.M. Walker, J.O. Legg, W.D. Bruge and R.D. Yeck, Agricultural Research Service and Soil Conservation Service,Bettsville Md. (USDA) Am. Soc. of Agron. (ASA) Abstract p. 188 64th Ann. Meeting 1972.

J.V. Lagerwerff, G.T. Brersdorf, W.D. Kemper and D.L. Brower. Retention of Sr and Cs by Sewage Sludge, Agricultural Research Service (USDA) Bettsville Md. ASA Abstract P 182, 64th Ann. Meeting 1972.

(B) <u>REFERENCES (PLANTS)</u>

A.J. MacLean, R.L. Halstead and B.J. Finn (1969). Extractability of Added Lead in Soils and its Concentration in Plants, Can. J. Soil Sc., Vol. 49, pp. 327-334.

R.L. Halstead, B.J. Finn and A.J. MacLean. Extractability of Nickel added to Soils and its Concentration. Idem. pp. 335-342.

H.V. Warren, R.E. Delavantt and K.W. Fletcher (1971). Metal Pollution - A Growing Problem in Industrial and Urban Areas. The Canadian Mining and Metallurgy Bul. July. pp. 34-45.

T.D. Hinesly, R.L. Jones and E.L. Zegler (1972). Effects on Corn of Heated Anaerobically Digested Sludge. Compost Science July, August, pp. 26-29.

G.R. Findemegg, E. Haunold (1971). Uptake of Hg by Summer Wheat from Various Soils, Oesterr. Studienges Atonererg. Sgae. Issue Sgae L.A. 7/1971, p. 5.

M.J. Frissel, P. Poelstra and P. Reiniger (1971). TNO NIEUWS Vol. 26, Issue 7 pp. 387-9. Transport of Hg and its Compounds in Soil.

G.I. Mekhonin (1969). Influence of Aqueous Extracts from Plant Material on the Availability of Mercury in Soils. Pochvoedenie Vol. 1969, Issue 11, pp. 116-120.

J.V. Lagerwerff (1971). Uptake of Cd, Pb and Zn by Radish from Soil and Air. Soil Sci. Vol. III, Issue 2, pp. 129-133.

H. Kick, R. Nosbers and J. Warnusz (1971). The availability of Cr, Ni, Zn, Cd, Sn and Pb for Plants - Sludge, International Symposium on Soil Fertility Evaluation, Vol. 1, J.S. Kanwar Ed. Indian Society of Soil Science, Indian Agricultural Research Institute New Delhi, India, pp. 1039-1045.

M.J. Buchaner (1971). Effects of Zn and Cd Pollution on Vegetation and Soils. Thesis, 349 pp.

R.H. Dowdy and W.E. Larson (1972). USDA Agricultural Research Service University of Minnesota. Metal Uptake by Barley and Corn Seedlings Grown on Sewage Sludge Amended Soils. Abstract p. 179, ASA 64th Ann. Meeting 1972.

R.L. Chancy. USDA Agricultural Research Service, Beltsville Md. Heavy Metal Toxicity to Crops Grown in Sewage Sludge Amended Soil. Abstract p. 178 ASA 64th Ann. Meeting 1972.

R.A. Root and P.E. Kieppe. Dept. of Agronomy University of Illinois, Uptake of Cd and Its Toxicity on Hydropunically Grown Corn. Abstract p. 113, ASA 64th Ann. Meeting 1972, Oklahoma State Univ.

J.M. Baker and B.B. Tucker, Toxic Soil Levels of Zn and Cd. Abstract p. 103, ASA 64th Ann. Meeting 1972.

APPENDIX II

RECENT RESULTS OF VEGETATION STUDIES

Recent Results on Vegetation Studies

(March 1973 - November 1973)

This research was carried out during the 1973-74 contract period and will appear as part of the final report for that contract in March 1974.

Recently, mercury results have been obtained which should be made available to interested workers as quickly as possible. For this reason, the following section has been added to what is basically the final report of work done on a contract covering the period up to March 1973.

Growing Medium: Sludges from the North Toronto plant containing up to 40 mg/L mercury were applied to a sandy loam soil. Soils thus produced had mercury levels up to 15 mg/L. The soil pH at the beginning and end of the experiment was about 7.5.

Sample Preparation for Analysis: Samples were taken at all stages of growth. Most of the vegetation was meticulously washed with a laboratory detergent solution, each piece being individually rubbed by hand. Some was left unwashed to document possible problems due to surficial contamination.

Material was analyzed both fresh, as received and after drying at 75°C. No loss of mercury was detected at this drying temperature for the samples studied.

The analytical method involved flameless atomic absorption. Standard Reference Material 1571 (Orchard Leaves) was used as a control sample. Results ranged from 0.11 to 0.14 mg/L compared with the NBS provisional value of 0.155 ± 0.02 mg/L.

Vegetation Grown on Sludges Soil - Samples Washed Carefully: The following table lists the mercury content of vegetation grown on sludged soils compared to control plots. Samples were meticulously washed prior to analysis.

Table. Mercury Content of Vegetation.

		Material Dried at 75^{0}C	
Sample	Part	Sludged	Control
		mg/L	
Wild Barley	Leaf	0.18	0.12
	Seeds	0.12	0.09
Quack Grass	Leaf	0.16	0.14
	Seeds	0.13	0.10
Bean	Pods*	0.60	0.14
	Plant	0.24	0.28
	Roots	0.24	0.14
Tomato(Green)	Fruit	6.0	0.26
(Red)	Fruit	12.2	0.24
	Plant	0.36	0.32
	Roots	0.35	0.33
Carrot	Root	0.30	0.30
	Tops	0.31	0.28
Lettuce	Leaf	0.24	0.24

* All results in this table are the mean of at least 10 determinations except in the case of the bean pod where sample availability restricted determinations to two.

Statistically the variation is such that there is no significant difference between the mercury content of sludge or control plot vegetation except in the case of the tomato fruit and bean pods. In these cases the mercury content of sludge grown vegetation is up to 50 times that of the control.

In terms of a fresh tomato (not dried as in Table) the level of mercury in the fruit of samples grown on sludged plots is up to 1 mg/L. In Canada and the U.S.A. the permitted level of mercury in food stuffs is 0.5 mg/L.

Vegetation Grown on Sludged Soil - Samples Unwashed: Samples analyzed above were meticulously washed to exclude, as much as possible, mercury bearing sludge dust which might contaminate the surface of the plant.

From a practical point of view a house-wife seldom washes vegetables as carefully as outlined above. It is felt in some cases it is likely that little, if any, effective washing occurs. This would certainly be the case when vegetables are consumed while walking in the garden.

With these possibilities in mind unwashed vegetation was analyzed. Unwashed samples of all types on a fresh, undried, basis were found to have as much as 3 mg/L mercury on a wet weight basis.

Mercury Contamination of Forage Crops Due to Improper Sludging Practice: The Ontario Government requires the sludge be applied to plowed fields or that the sludges area be plowed to prevent surface contamination of vegetation. Despite this regulation, due to a lack of supervision, large areas of forage grasses are sludged but not subsequently plowed. As a result animals can ingest vegetation with up to 3 mg/L mercury.

Conclusion: Obviously a good deal more data is essential before final conclusions can be made regarding the plant uptake of mercury. The present data suggests an appreciable uptake in the case of tomato fruit and possibly bean pods. Levels were found to be up to 50 times higher in material grown on sludged plots compared to control samples. It must be again emphasized that this data was obtained on plants grown in alkaline rather than acidic soils.

Present data is inconclusive regarding plant uptake of heavy metals. However, as in the case with mercury, unwashed samples contained high levels of all metals being studied.