

**Heavy Metals in Agricultural Lands
Receiving Chemical Sewage Sludges
Volume II**

Research Report No. 25

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

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RESEARCH REPORTS

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TD Heavy metals in agricultural lands
879 receiving chemical sewage sludges :
.H4 Volume II / Van Loon, J.C.
V36
1975 78868

**HEAVY METALS IN AGRICULTURAL LANDS
RECEIVING CHEMICAL SEWAGE SLUDGES**

VOLUME II

by

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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
October, 1975

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
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Information Canada
Ottawa, 1975

Cat. No.: En 43-11/25

TRI-GRAPHIC PRINTING LTD CONTRACT NO KE204-5-CA002

ABSTRACT

In the previous year of this contract (1) studies were initiated in the following areas:

- 1) Sludge heavy metal characterization of North Toronto, Newmarket and Point Edward sewage treatment plants.
- 2) Heavy metal contamination of farm soils and vegetation resulting from sludge applications (Newmarket area).
- 3) Surface water, heavy metal contamination resulting from sludge disposal,
- 4) Assessment of analytical data.

During the present year, work was continued in all these subject areas, Heavy metal contamination studies of soils, vegetation, groundwater and surface water were carried out at the Burlington Skyway plant disposal farm and the North Toronto plant disposal area. A study of garden vegetable contamination due to the use of sludge for home gardening was also initiated.

Again as in the previous year emphasis was placed on using standard reference materials to give validity to the analytical data.

RESUMÉ

Au cours de la première année du contrat, on a entrepris des études touchant les domaines suivants:

- 1) caractérisation des métaux lourds contenus dans les boues produites par les installations de traitement de North Toronto, Newmarket et Point Edward;
- 2) contamination par les métaux lourds des sols arables et de la végétation à la suite de l'épandage de boues (région de Newmarket);
- 3) contamination par les métaux lourds de l'eau de surface par suite de l'élimination des boues; et
- 4) évaluation des résultats des analyses.

Au cours de la présente année, les travaux se sont poursuivis dans tous les domaines mentionnés. Des études de la contamination des sols, de la végétation, de l'eau souterraine et de l'eau de surface par les métaux lourds ont été faites sur une ferme servant à l'évacuation des boues, près de Burlington, et sur le terrain d'épandage de l'installation de North Toronto. On a aussi entrepris une étude de la contamination des légumes par suite de l'utilisation de boues pour le jardinage.

Comme pour l'an passé, on a mis l'accent sur l'utilisation de matériaux témoins pour contrôler les résultats d'analyse.

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1. SLUDGE CHARACTERIZATION

1.1 Sludge Sampling

From earlier work it was concluded that monthly composite sampling was satisfactory for outlining the heavy metal content of the chemical sludges presently available. Ministry of the Environment and Canada Centre for Inland Waters personnel kindly agreed to provide sewage sludges as available. Monthly composite sampling of chemically treated, secondary digester sludge samples from North Toronto (April-July), Newmarket (April-September), Sarnia and Point Edward (April-February) were obtained. Also one monthly composite was obtained from each of the Bolton, Streetsville, Ashbridges Bay and Burlington plants. Sludges were collected and stored in clean glass or plastic bottles.

1.2 Methods of Analysis

1.2.1 Strong acid extractable metals

The method used for analysis was similar to that described in Part 1 of this contract (1), Van Loon and Lichwa (2) and Van Loon *et al* (3). A new method for mercury was adopted as follows:

Mercury Procedure. Mix sludge well in the bottle. Filter enough material to fill a 12.5 cm Whatman #541 filter paper (folded in a conical filter). Dry at 75°C.* Remove the dried material and place the contents into a mortar and grind and mix well.**

Weigh 0.1 to 1.0 g, depending on mercury content, into a BOD bottle supplied with the Coleman MAS 50 mercury analyzer. Add 0.1-0.5 g of KMnO_4 crystals, followed by 25 ml of 6N HNO_3 . Swirl to mix contents. Slowly and carefully add 5 ml of concentrated sulphuric acid. As the solution becomes warm swirl the bottles. Digest for 20 minutes, swirling the contents from time to time. Add more KMnO_4 crystals if the purple colour does not persist during this period. Solutions must be at room temperature and should be cooled if this is not the case. Add 25 ml of water. Add

* Drying temperatures of up to 100°C did not affect the mercury levels of the sludges tested. Most workers, however, recommend temperatures not exceeding 80°C for other sample types.

** It is not clear how fine a grind is necessary to allow proper homogenization. Present work suggests the powder should pass a 100 mesh screen.

sufficient hydroxylamine hydrochloride solution to remove the colour due to KMnO_4 and MnO_2 . Add 10 ml of 10% $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solution. Run on the Coleman MAS 50 or any properly converted atomic absorption unit containing a cold vapour absorption tube. Run appropriate reference standards, e.g. National Bureau of Standards Orchard Leaves, NBS #1571 Kodak TEG gelatin standards etc. This procedure is modified from that recommended by Hatch and Ott (4) for other sample types.

1.2.2 Acetic acid extractable metals

It is important to have some idea of the readily available metals as opposed to the strongly bound metals in sludges. This may have great significance to subsequent leaching or plant availability of metals. To date, the most generally acceptable method seems to be an acetic acid leach. Hence an acetic acid leach (pH 5) was carried out for representative sludge samples. The following procedure was used:

Weigh 0.5-1.0 g of a dried sample into a 150 ml beaker. Add 10 ml 0.5 N acetic acid. Digest on medium heat of a hot plate until almost dry. Add 2 ml of 0.5 N acetic acid and evaporate to dryness. Cool and add 1 ml of 0.5 N acetic acid to dissolve residue. Filter into a 25 ml flask using Whatman #44 paper and dilute with water. Run on atomic absorption spectrophotometer using aqueous standards with 1 ml of 0.5 N acetic acid in every 25 ml of standard.

Mercury analyses cannot be performed, as yet, in this solution matrix. Research is presently being carried out to look into this problem.

1.3 Results of Sludge Analyses

1.3.1 Strong acid extractable metals

The results of sludge analyses for strong acid extractable metals, on monthly composite samples, are shown in the following table.

* It is difficult to give explicit instructions on hydroxylamine hydrochloride. If solutions are too concentrated strong fizzing results upon addition to the nitric acid solution in the flask. This results in evolution of nitrogen oxide fumes which can cause interference in the subsequent determination. Present work suggests a concentration between 0.1 and 1% depending on the character of the solution in the flask. The proper concentration must be selected experimentally.

TABLE 1. Strong Acid Extractable Metals In Sludges, Monthly Composites.

<u>North Toronto (ferric chloride)</u>												
Date	W/L*	Fe	Al	Zn	Pb	Cu	Ag	Cr	Hg	Cd	Mn	Ni
	gm/ml	%					ppm					
April	0.07	7.0	1.8	0.21	0.09	0.10	22	350	30	15	300	27
May	0.07	6.5	1.1	0.28	0.10	0.11	25	400	25	15	380	37
June	0.07	6.6	1.9	0.27	0.11	0.13	25	350	29	17	380	30
July	0.07	6.6	1.9	0.24	0.10	0.13	23	430	32	16	380	30
1972-73 aver.	0.09	7.3	1.4	0.23	0.09	0.10	na	520	25	15	360	27

* dried solid weight to liquid ratio

na not available

<u>Newmarket (lime)</u>												
Date	W/L	Fe	Al	Cd	Pb	Zn	Mn	Cu	Ni	Ag	Cr	Hg
	g/ml	%		ppm								
April.	.08-.25	0.80	0.19	2	97	520	270	150	8	10	18	1
May	0.2	0.50	0.17	2	65	830	400	130	5	10	18	1
June	0.3	0.20	0.18	2	96	520	120	180	5	11	26	1
July	0.1	0.65	0.16	1	79	580	250	190	4	10	31	1
Aug.	0.09	0.54	0.14	2	58	330	190	120	7	10	24	1
Sept.	0.1	0.95	0.43	3	130	540	280	200	11	10	36	1
1972-73 aver.	0.13	0.32	0.13	2	95	570	220	160	7	10	15	1

TABLE 1. (CONT'D)

<u>Sarnia (ferric chloride)</u>												
Date	W/L	Fe	Al	Zn	Pb	Mn	Cd	Cu	Ni	Ag	Cr	Hg
	g/ml	%					ppm					
April	0.04	6.3	0.68	0.70	0.22	0.18	62	520	33	3	58	5
May	0.12	7.1	0.44	0.90	0.2b	0.24	76	5J0	33	3	280	5
June	0.18	6.6	0.86	0.78	0.25	0.23	69	570	33	3	84	4
July	0.18	8.4	0.65	0.76	0.25	0.26	63	650	26	4	145	5
August	0.17	7.2	1.1	0.78	0.23	0.18	63	660	31	3	160	5
Sept.	0.15	6.6	0.80	0.79	0.20	0.16	56	520	69	2	160	5
Oct.	0.19	8.8	2.1	1.3	0.35	0.35	70	840	30	17	135	6
Nov.	0.07	9.1	2.0	1.3	0.42	0.33	90	870	37	13	165	7
Jan/Feb	0.15	7.5	2.0	1.2	0.11	0.24	65	5d0	34	20	150	6

<u>Point Edward (alum)</u>												
Date	W/L	Fe	Al	Cd	Pb	Zn	Mn	Cu	Ni	Ag	Cr	Hg
	g/ml	%		ppm								
April	0.06	0.66	3.9	5	340	580	76	400	18	2	66	2
June	0.06	2.6	4.6	24	1000	3100	710	480	20	6	82	2
July	0.09	0.60	6.3	5	280	560	60	480	17	4	110	2
August	0.06	2.0	5.6	5	270	860	200	560	21	4	190	2
Sept.	0.06	2.4	4.8	4	270	810	220	610	22	3	160	1
Oct.	0.07	5.3	1.2	7	450	980	400	720	24	8	150	1
Nov.	0.07	7.1	1.9	7	700	830	450	710	22	7	95	1
Dec.		10.8	1.4	6	850	790	560	780	23	11	100	2
Jan/Feb	0.08	12.2	0.9	7	1060	800	520	840	30	21	100	3
1972-73 Aver.	0.06	0.64	4.0	6	250	920	60	530	22	4	65	3

<u>Other Plants</u>											
Plant	Date	W/L	Fe	Al	Cd	Pb	Zn	Mn	Cu	Ni	
		g/ml	%		ppm						
Bolton	June	0.06	1.5	0.80	5	325	480	430	280	30	
Streetsville	June	0.02	1.2	0.45	8	500	1500	330	1000	140	
Ashbridges	Oct.	na	1.5	1.2	57	2000	6700	230	1300	170	
Burlington	April	0.02	1.2	-	10	270	1100	310	450	16	

TABLE 1. (CONT'D)

Plant	Date	Other Plants		
		Ag	Cr	Hg
Bolton	June	1	45	2
Streetsville	June	6	300	2
Ashbridges	Oct.	41	760	12
Burlington	April	2	400	1

Feeds used for chemical analysis may carry trace metals (e.g. pickle liquors). Although it is not possible to conclude what portion of the heavy metals in sludges comes from this source, feeds were analysed for interest only. The following results are for one sampling of the feeds used at North Toronto, Point Edward and Newmarket.

TABLE 2. Analysis Of Chemical Feeds.

	Chemical Feeds ($\mu\text{g/ml}$)									
	Zn	Fe	Pb	Ni	Mn	Cu	Cr	Cd	Ag	Hg
Lime	8	400	8	77	1500	1	50	1	1	1
Alum	8	700	3	1	200	1	200	1	1	1
Ferric chloride	670	-	3	1	150	1	1	1	1	1

From these results and data obtained last year it is clear that the concentration of most metals in the North Toronto sludge, based on a dry weight basis, seldom varies by more than a factor of two. However, the Sarnia, Newmarket and Point Edward results show larger variations.

1.3.2 Acetic acid extractable metals

Sludges were picked at random from samples spanning the past two years. These were analyzed by the acetic acid method. Results are given in Table 3 showing a comparison of acetic acid (A) leachable and strong acid (S) leachable metals.

TABLE 3. Acetic Acid Extractable Metals In Sludges Compared With Strong Acid Extractable Metals.

<u>North Toronto Plant</u>															
Fe		Cd		Pb		Zn		Mn		Cu		Ni		Cr	
%		ppm													
S	A	S	A	S	A	S	A	S	A	S	A	S	A	S	A
6.4	0.04	10	4	1000	3	2200	560	390	72	1100	55	23	7	480	8
6.3	0.03	15	4	900	4	2400	660	340	52	1200	78	21	6	430	6
6.2	0.04	17	7	1000	6	2300	1000	360	110	1400	450	37	5	380	6
6.5	0.02	16	13	1100	2	2800	600	400	210	1100	220	33	7	360	3
6.6	0.04	15	2	1150	3	2400	440	340	66	1200	16	28	8	330	5

<u>Newmarket Plant</u>															
Fe		Cd		Pb		Zn		Mn		Cu		Ni		Cr	
%		ppm													
S	A	S	A	S	A	S	A	S	A	S	A	S	A	S	A
8500	15	2	0.5	97	20	640	57	190	75	134	3	11	6	lb	2
6000	10	2	0.5	68	13	750	74	220	50	130	3	8	5	19	2
6500	22	1	0.5	79	20	830	106	220	85	150	5	13	4	59	3
7200	25	2	0.5	58	5	580	44	190	90	145	3	10	7	36	2
9500	18	2	1.0	130	17	530	54	250	85	140	4	11	5	26	1

<u>Sarnia Plant</u>															
Fe		Cd		Zn		Mn		Cu		Ni		Pb		Cr	
%		ppm													
S	A	S	A	S	A	S	A	S	A	S	A	S	A	S	A
6.3	0.05	62	7	7000	306	1800	450	520	4	33	10	2200	nd	58	nd
8.4	0.08	63	14	7600	520	2600	880	650	8	34	10	2800	nd	145	nd
7.2	0.05	63	11	7800	520	1800	440	660	10	33	10	2500	nd	160	nd
6.6	0.01	56	8	7900	300	1600	510	520	6	69	10	2500	nd	160	nd

TABLE 3. (CONT'D)

<u>Point Edward Plant</u>															
Fe		Cd		Zn		Mn		Ni		Cu		Pb		Cr	
%		ppm													
S	A	S	A	S	A	S	A	S	A	S	A	S	A	S	A
0.66	0.02	5	4	580	260	76	42	18	7	400	8	340	nd	66	nd
2.60	0.07	24	11	3100	520	710	285	20	7	480	10	1000	nd	82	nd
0.60	0.03	5	4	560	240	60	-	17	11	480	16	280	nd	110	nd
2.40	0.05	4	4	810	260	220	140	22	12	610	12	270	nd	160	nd

Little can yet be said of a deciding nature regarding the acid extractable metal results. However, in general, Mn, Cd, Ni and Zn have better acetic acid extractability (10 to 90%) compared to Cr, Fe and Pb (0.1 to 10%). Perhaps coincidentally, these data are related to the respective solubilities of the metal hydroxides.

2. SOIL AND VEGETATION

Much sludge in the U.S.A., Canada and Great Britain is used as domestic and agricultural fertilizers. For example, Webber and Gaynor of Agriculture Canada, stated (5): "At the present time sewage sludges are applied to agricultural land in many parts of Canada, particularly to land used for market gardening, cereal and forage production."

The home gardener also has ready access to sludge through commercially available processed sludge fertilizer and often, free, from sludge dumps associated with local treatment plants. Particularly in the case of the latter source, while signs welcome the gardener to make use of the sludge, no instructions are given for its proper application.

Much difference of opinion exists regarding plant uptake of metals from sludged land. For example, Hinesly and Sosowitz (6) studied the uptake of several heavy metals, including mercury, by corn plants grown on fields which had received sludge for four years. On the basis of this study, the authors conclude "Trace elements added as constituents of sludge have not presented a toxicity problem detectable either by tissue analysis or pathological symptom."

La Riche (7) on the other hand, in a study of soils and crops from a market gardening area receiving sewage sludge annually, reported higher levels of zinc and nickel in beet and leek plants compared to levels in these vegetables grown on control plots. In a recent study, in which the pH of soils was considered, Linnman *et al* (8) reported plant uptake of cadmium by wheat grown on sludged land.

There is an abundance of evidence, much from Europe, outlining crop damage due to the application of sewage sludge to agricultural land. Patterson (9) for example, reported instances of poor growth of crops due to the presence of high levels of zinc and nickel.

At both the Berlin (sandy, acid soil) and the Paris (limey, loam soil) sludge disposal farms, Rohde (10) recorded that in early years of sludging high crop yields were obtained. However, recently, after "many" years of sludging, the land at both sites has shown signs of exhaustion. Rohde attributes this exhaustion to high concentrations of copper and zinc in soils resulting from extensive sludging.

A number of reports have suggested the importance of soil pH in controlling the uptake of heavy metals. In this regard, neutral or alkaline pH conditions seem to inhibit heavy metal assimilation. For this reason the pH of soils used in the following study was monitored and ascertained to be in the neutral or slightly alkaline range.

2.1 Soil Sampling Locations

Plant and soil studies were done at three main locations -

- (1) Burlington Skyway - Sludge Disposal Farm
- (2) North Toronto Plant - Sludge Dump Area
- (3) Home Gardens - mainly Jon C. Van Loon, 38 Paultiel, Toronto, Ont

2.1.1 Location 1 (See Figure 1)

Site Description. (See Map). The farm is approximately 200 acres on the North Service Road just east of Walker's Line and the Q.E.W. Soil is red to brown clay, friable to heavy. Existing vegetation is mainly weeds and grass.

Three elevated (2-6 feet) sludge lagoons (Nos. 1,2,3) can be seen on the southwest corner of the farm. Lagoon 1 was prohibited for use by the Health Department. Other lagoons were to be used only on the basis that sludge be removed for each load dumped. There appears to have been serious overflow from these lagoons into the surrounding area. Mainly this problem exists to the south of the sample point S7. Solid sludge and liquid covers large areas of ground in this region. It also appears that sludge has been dumped in areas S5, S6 and S8. Areas S5 and S6 are elevated and at least 40 yards from the street. Area S8 is sloping toward the stream and any liquid deposited here would drain directly to the stream. (Drainage ruts can be seen to flow directly from S8 to the stream). The soil and grass at S8 were observed to contain a surface covering of dry sludge. The stream is very full of cladophora algae.

The area sampled covered only the south segment of the farm where sludging had not recently been carried out. At the time of sampling sludging was progressing at the north end of the farm.

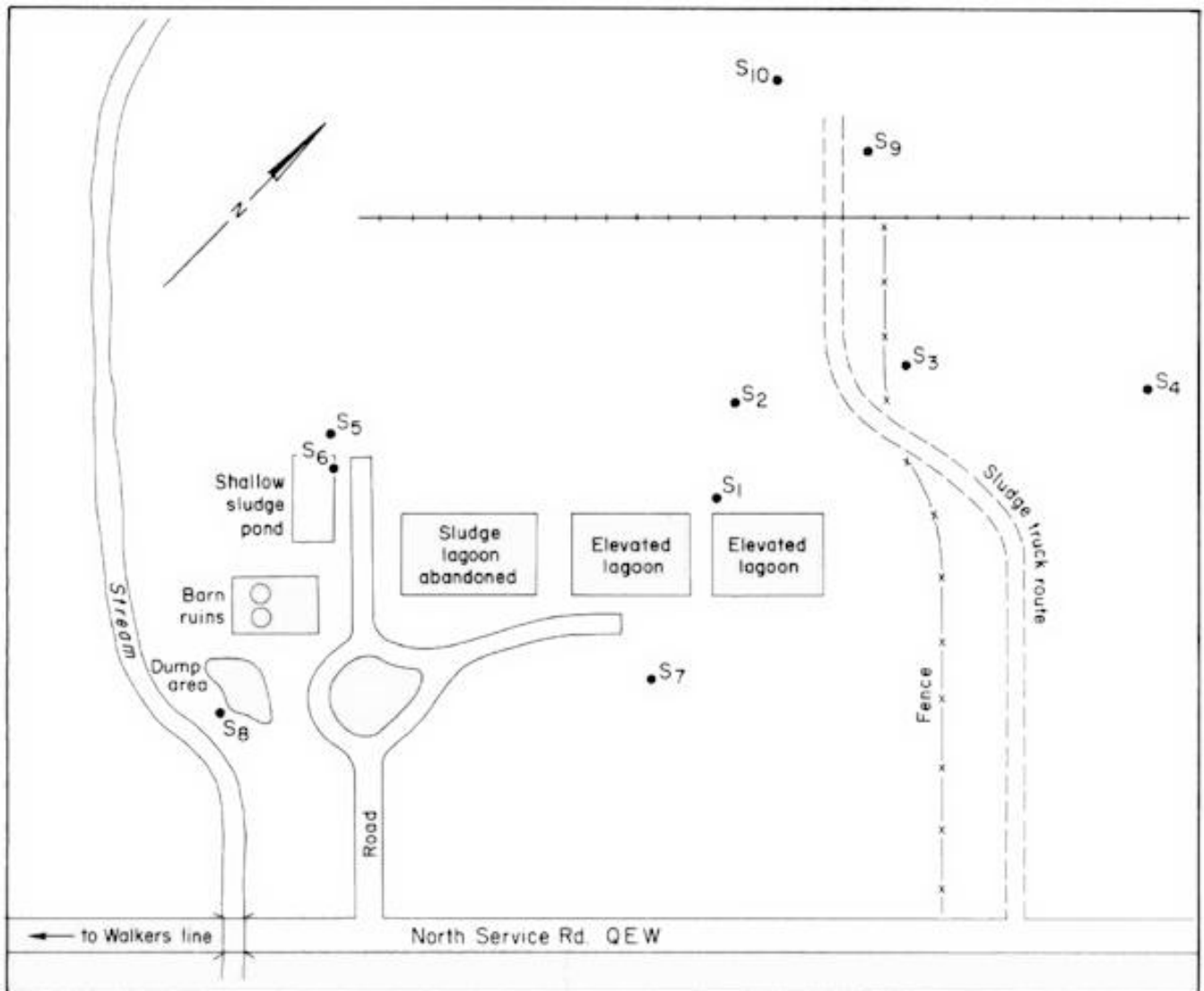


FIG. 1. Burlington Farm Disposal Site (200 acres).

- S1 - Sludge lies on the red loam soil surface. No ploughing of recent sludge into the soil has been done. Several wet drainage areas exist around lagoon 3. These probably result from either overflow or seepage from the lagoon. pH of soils was found to range from 6.2 - 8.6.
- S2 - Ploughed section of field. No cultivation, so chunks of sludge were visible. Soil was a red clay. Soil pH's were same as above.
- S3 - Unsludged section of field. There was a metal fence nearby but care was taken to avoid this problem in sampling. Soil was a red clay.
- S4 - Unsludged field. Soil was a brown clay.
- S5 - Sludged area north of old barn on western edge of field with samples S1 and S2. It appeared that sludge in large volume had been discharged at this point. Soil was a grey clay.
- S6 - Grey clay soil samples on dried pond bottom plus surface floating cake were taken and combined. Water pH was 8.6, soil pH was 6.5.
- S7 - This area appears to be contaminated by drainage from lagoons and/or overflow. Large amounts of sludge solids and liquid were noted on the grey clay soil.
- S8 - A red clay soil sample was taken 10 feet from stream on bank sloping into stream.
- S9, S10 - Recently sludged fields with grey clay.

The stream on the west border of the farm carries a heavy reddish brown silt flow. Minnows were present. Large growths of cladophora algae were noted. Two water samples were taken.

2.1.2 Location 2 (See Figure 2)

Soils range from loose sand to hard clay over short distances suggesting extensive land filling operations. Samples of soil and vegetation were taken from heavily sludged areas (S1-S7). Soil pH readings were 7.2 - 8.2 throughout the sampling period.

The river bank is eroded during periods of peak runoff and sludge piled on the bank edges directly enters the river e.g. S6-S9.

Vegetation around the site varies but consists in large part of wild barley (*Hordeum jubatum*) and quack grass (*Triticum repens* L), as well as sow thistles (*Sonchus arvensis* L) and lesser burdock (*Arctium minus* Beruh). Tomato plants (*Lycopersicon esculintum*) are commonly encountered.

2.1.3 Location 3 (Home Gardens)

Sludge may be readily obtained at the North Toronto plant for home gardening purposes. Samples of sludge were obtained and used in author's garden, freely, in a manner that the typically uninformed home gardener might employ. Tomatoes, beans, lettuce and carrots were grown in sludged and control plots. The soil was a sandy loam and the soil sludge pH was 7.2 - 7.8 throughout the study.

Samples of vegetation grown by other gardeners using sludge or commercially available sludge based fertilizer were also obtained and analyzed.

2.2 Sampling, Sample Preparation and Analysis Methods

These were, in the main, similar to methods reported by Van Loon (1). The drying temperature for vegetation was, however, reduced to 75°C to prevent loss of mercury.

Mercury analysis in soil and vegetation: Weight 1.0 g into a BOD bottle. Add 0.3-0.5 g KMnO_4 and 50 ml of 1.3 HNO_3 . Swirl contents for 60 seconds. Very carefully add 5 ml of concentrated H_2SO_4 . The bottle and contents become quite warm to the touch. Allow the sample to digest for 30 minutes swirling from time to time. Add

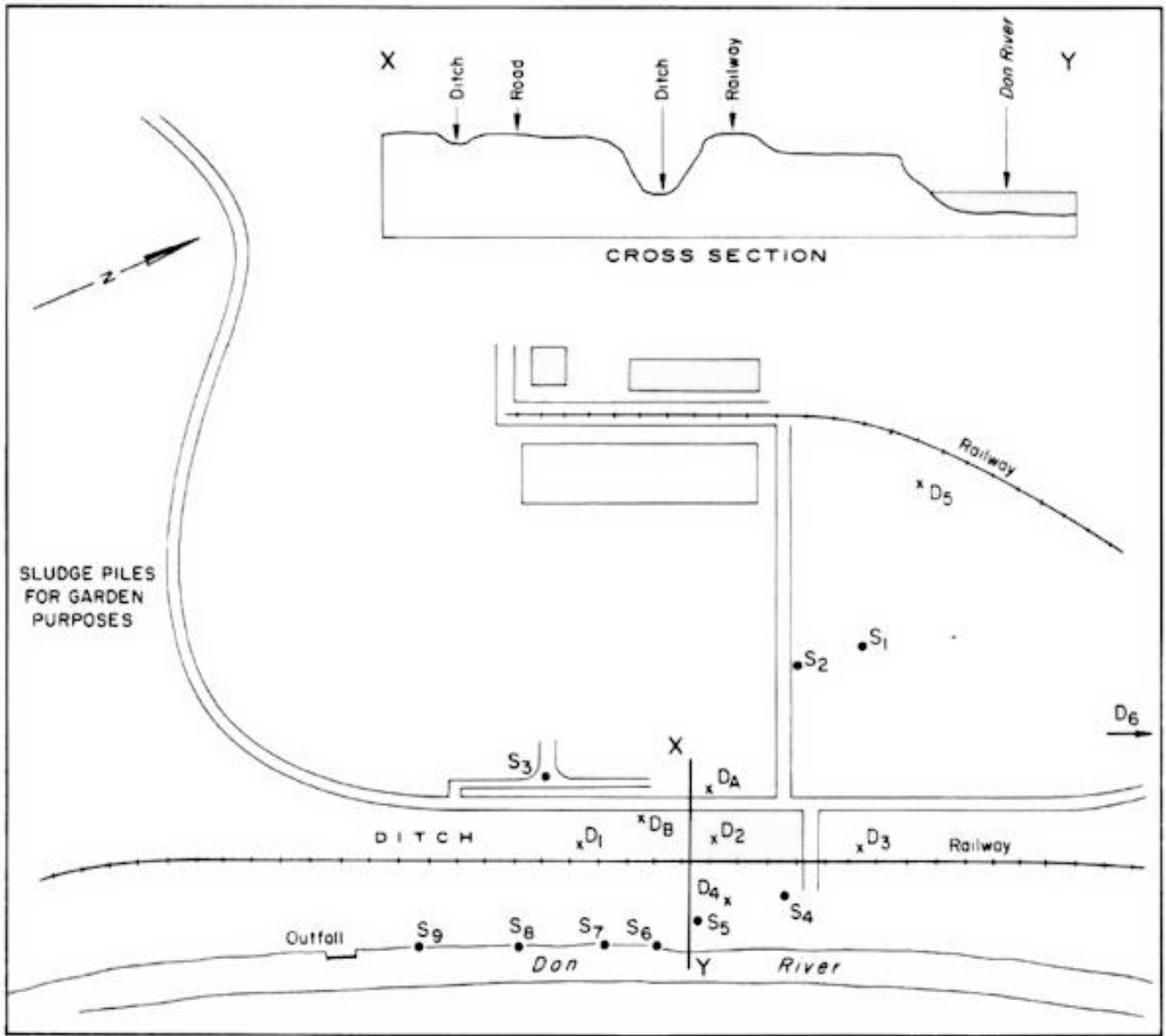


FIG. 2. North Toronto Disposal Site.

more KMnO_4 if this is necessary to maintain oxidizing conditions. The sample must then be cooled to room temperature (if this has not occurred naturally). Add 50 ml water followed by sufficient hydroxylamine hydrochloride crystals to destroy the excess KMnO_4 and MnO_2 . Add 10 ml of 10% stannous chloride solution and run on the mercury analyzer.

2.3 Results - North Toronto

Soil and vegetation analyses for North Toronto were as shown in the following table.

TABLE 4. Soil And Vegetation Analyses - North Toronto.

- A - soil, strong acid leach
- B - soil, acetic acid leach
- C - quack grass, spring shoots
- D - quack grass, mature plant leaves
- E - seed

Iron	A	B	C	D	E
	%	ppm			
S1	3.7	51	160	100	50
S2	1.7	27	125	95	190
S3	2.0	63	190	85	65
Control	2.0	-	220	-	-

Nickel	A	B	C	D	E
	ppm				
S1	10	11	1	<1	<1
S2	20	1	2	<1	<1
S3	10	6	3	<1	<1
Control	13	-	4	-	-

TABLE 4. (CONT'D)

Copper	A	B	C	D	E
	ppm				
S1	960	41	35	14	9
S2	94	5	14	12	16
S3	420	33	24	13	13
Control	30	-	2	-	-

Chromium	A	B	C	D	E
	ppm				
S1	513	6	5	<1	<1
S2	51	3	3	<1	<1
S3	145	5	3	<1	<1
Control	16	-	1	-	-

Mercury	A	B	C	D	E
	ppm				
S1	80	-	200	200	190
S2	5	-	150	140	50
S3	25	-	140	140	60
Control	0.1	-	50	50	50

Cadmium	A	B	C	D	E
	ppm				
S1	20	5	0.7	0.5	0.5
S2	2	<1	0.3	0.3	0.3
S3	7	2	0.3	0.4	0.3
Control	0.8	-	0.4	-	-

Lead	A	B	C	D	E
	ppm				
S1	800	1	8	3	5
S2	100	1	5	3	3
S3	300	4	6	3	3
Control	90	-	2	-	-

TABLE 4. (CONT'D)

Zinc	A	B	C	D	E
	ppm				
S1	194	288	70	45	60
S2	200	58	30	29	41
S3	1100	325	60	37	47
Control	190	-	45	-	-

Manganese	A	B	C	D	E
	ppm				
S1	390	120	34	22	13
S2	350	140	45	12	12
S3	240	120	40	33	20
Control	400	-	45	-	-

Wild barley was also analyzed. Results showed a very close similarity with above.

2.4 Erosional Hazard of Sludges at North Toronto

It is a common practice at this plant to land-fill sludge up to the edge of the Don River bank. Visual observation shows that during periods of peak runoff erosion of sludge occurs directly into the river.

The following table lists the metal content of material eroding into the river.

TABLE 5. Soil And Sludge Mixture On Don River Bank.

Sample	Hg	Cr	Cu	Ni	Mn	Cd	Pb	Fe	Al	Zn
	ppm							%		
S4	40	250	630	30	220	14	690	3.0	1.4	0.16
S5	15	180	570	55	220	9	620	5.3	0.6	0.14
S6	2	43	170	20	460	5	270	0.9	0.2	0.04
S7	50	480	720	45	240	21	800	2.0	0.5	0.21
S8	25	280	870	45	300	19	850	5.7	0.7	0.17
S9	40	290	940	45	300	24	880	3.7	0.9	0.21

Levels in the water close to the erosion were similar to S6 above.

2.5 Results - Burlington Farm

Samples of soils and vegetation *were* taken throughout the growing season. At least four specimens were taken at each sample point and analyzed separately. The data in the following table represent the mean of these determinations. Soil pH's were 7.5 - 8.5.

TABLE 6. Soil And VegetatiOn Analyses -BurlingtOn Farm.

- A - soils, strong acid extraction
- B - soils, acetic acid extraction
- C - quack grass (*Triticum repens* L)
- D - burdock (*Arctium minus Beruh*)
- E - tomato plants (*Lycopersicum esculintum*)
- F - unwashed grass

(Sample points S3 and S4 are not sludged and can be taken as controls.)

Iron	A	B	C	D	E	F
	%	ppm				
S1	1.5	95	120	440	-	-
S2	1.6	65	150	-	-	-
S3	1.6	100	130	-	-	-
S4	1.4	100	100	-	140	-
S5	1.5	120	80	-	-	-
S6	1.4	-	120	-	-	-
S7	1.7	130	-	400	90	-
S8	2.0	60	-	-	-	-
S9	1.6	-	-	-	99	-
S10	1.8	-	-	-	-	0.15

TABLE 6. (CONT'D)

Cadmium	A	B	C	D	E	F
	ppm					
S1	9	4	0.2	3	-	-
S2	3	2	0.2	-	-	-
S3	0.6	<1	0.1	-	-	-
S4	0.6	<1	0.2	-	1	-
S5	1	0.5	0.3	-	-	-
S6	2	-	-	-	-	-
S7	18	5	0.4	1	2	-
S8	1	1	-	-	-	-
S9	7	-	-	-	5	-
S10	7	-	-	-	-	5

Lead	A	B	C	D	E	F
	ppm					
S1	150	<1	2	3	-	-
S2	50		2	-	-	-
S3	16	<1	1	-	-	-
S4	17	<1	1	-	-	-
S5	50	<1	1	-	-	-
S6	50	<1	-	-	-	-
S7	220	<1	4	8	4	-
S8	50	<1	-	-	-	-
S9	130	<1	-	-	4	-
S10	140	<1	-	-	-	80

Zinc	A	B	C	D	E	F
	ppm					
S1	900	430	100	350	-	-
S2	170	60	150	-	-	-
S3	63	7	35	-	-	-
S4	65	12	35	-	45	-
S5	300	110	90	-	-	-
S6	400	-	-	-	-	-
S7	1000	260	130	70	200	-
S8	200	48	-	-	-	-
S9	900	-	-	-	-	-
S10	1250	-	-	-	-	900

TABLE 6. (CONT'D)

Manganese	A	B	C	D	E	F
	ppm					
S1	600	280	400	880	-	-
S2	700	250	350	-	-	-
S3	700	300	100	-	-	-
S4	500	180	90	-	60	-
S5	610	250	65	-	-	-
S6	350	-	-	-	-	-
S7	500	240	130	125	300	-
S8	720	400	-	-	-	-
S9	750	-	-	-	-	-
S10	700	-	-	-	-	150

Copper	A	B	C	D	E	F
	ppm					
S1	250	30	24	25	-	-
S2	60	5	22	-	-	-
S3	15	3	18	-	-	-
S4	18	3	16	-	13	-
S5	80	7	19	-	-	-
S6	110	-	-	-	-	-
S7	400	25	30	18	16	-
S8	70	5	-	-	-	-
S9	200	-	-	-	18	-
S10	180	-	-	-	-	190

Nickel	A	B	C	D	E	F
	ppm					
S1	60	23	2	-	-	-
S2	17	4	2	-	-	-
S3	15	<1	1	-	-	-
S4	13	3	1	-	-	-
S5	35	2	1	-	-	-
S6	25	-	-	-	-	-
S7	45	2	2	2	7	-
S8	25	<1	-	-	-	-
S9	40	-	-	-	3	-
S10	40	-	-	-	-	23

TABLE 6. (CONT'D)

Chromium	A	B	C	D	E	F
	ppm					
S1	300	8	2	4	-	-
S2	70	3	2	-	-	-
S3	20	2	1	-	-	-
S4	40	<1	1	-	2	-
S5	120	1	1	-	-	-
S6	100	-	-	-	-	-
S7	300	4	1	3	1	-
S8	55	2	-	-	-	-
S9	200	-	-	-	-	-
S10	200	-	-	-	-	90

Mercury	A	B	C	D	E	F
	ppb					
S1	1600	-	120	220	-	-
S2	600	-	100	-	-	-
S3	100	-	20	-	-	-
S4	100	-	50	-	190	-
S5	800	-	60	-	-	-
S6	800	-	-	-	-	-
S7	210	-	100	100	100	-
S8	2100	-	-	-	-	-
S9	1200	-	-	-	90	-
S10	1000	-	-	-	-	1000

2.6 Results - Home Gardening

The sludge was applied liberally in a manner such as a home gardener might use. Soils thus produced often consisted of more than 1/3 sludge by weight. Control plots were grown close by. No other soil amendments were used in either case. Vegetables grown were beans, carrots, tomatoes and lettuce.

2.6.1 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.

TABLE 7. Soil And Vegetation Analyses - Home Gardens.

A	- Control	L.	- Lettuce leaves
B	- Sludge	C.T.	- Carrot tops
T.P.	- Tomato plant	C.R.	- Carrot roots
T.G.F.	- Tomato green fruit	B.	- Bean pod
T.R.F.	- Tomato red fruit	B.P.	- Bean plant

	(ppm)									
	Iron		Cadmium		Lead		Zinc		Manganese	
	A	B	A	B	A	B	A	B	A	B
T.P.	150	210	1	3	4	3	40	100	60	100
T.G.F.	55	45	0.3	0.6	1	1	30	30	10	10
T.R.F.	55	45	0.3	0.6	1	1	30	35	10	10
L.	95	110	1	2	5	10	40	40	25	35
C.T.	130	120	0.1	0.1	4	4	30	30	50	45
C.R.	30	25	0.1	0.4	2	2	15	15	10	15
B.	85	240	0.1	0.1	4	2	25	30	10	20
B.P.	330	450	0.1	0.1	2	2	20	30	330	330

	Copper		Nickel		Chromium		Aluminum		Mercury	
	A	B	A	B	A	B	A	B	A	B
T.P.	10	25	1	3	2	1	90	55	0.3	0.4
T.G.F.	3	10	0.5	0.5	0.2	0.6	10	30	0.3	6.0
T.R.F.	3	5	0.5	0.6	0.2	0.7	10	25	0.3	12.2
L.	10	7	2	3	1	1	60	65	0.3	0.3
C.T.	15	15	4	1	1	1	110	90	0.3	0.3
C.R.	5	5	2	2	0.8	0.5	10	10	0.3	0.3
B.	5	5	1	4	0.2	0.3	-	-	0.2	6.0*
B.P.	10	10	1	2	0.2	1	-	-	0.3	0.3

* only limited sample

2.7 Conclusions

(a) Plant Uptake of Metals.

Throughout these results there is little evidence of high heavy metal uptake by vegetation. An exception occurred in the case of mercury levels found in tomato fruit and possibly bean pods grown on sludged soil. In this instance, on a dry weight basis, the mercury levels were found to be 20 times or more than in the control samples. On a wet weight basis the mercury levels in tomatoes would be up to 1 ppm.

Zinc and copper, in most cases, were elevated in vegetation grown on sludged land. Here, however, the increases were generally less than twice the control plant levels.

Linnman *et al* (8) point out that the normally used methods for cadmium analysis may not be sensitive enough to show reliably cadmium variation in vegetation. In this regard work has been initiated to improve the lower limit of cadmium detection in these sample matrices. Early results tend to substantiate these comments (8). It will thus be important to continue methods development research related to cadmium.

All soils and sludges used above were alkaline in pH (a common situation in Southern Ontario). Uptake from acidic soils is more probable and this possibility should be explored.

(b) Surface Contamination of Vegetation by Sludge.

Perhaps the most serious potential problem comes from surface contamination of vegetation. Research showed that unless vegetation was scrupulously washed (i.e. rub surfaces with fingers and use a mild detergent) elevated metal *levels* for vegetation were recorded. It is well known that most people do not wash vegetation with detergent as indicated above. In the case of forage crops sludge is commonly applied after sprouting and hence can easily remain on the plant surfaces to be ingested by farm or wild animals.

(c) Plant Age vs. Metal Content.

In general, a decrease in metal content with increasing age of vegetation was noted. Gorsline *et al* (11) record a similar effect for corn in a study of zinc, iron and manganese levels.

3. METAL CONTENT OF GROUNDWATERS

Six wells were drilled by Henry Kronis of the Ministry of the Environment on the property of the Canadian National Railway and North Toronto Sewage Treatment Plant to sample possible groundwater contamination from sludge landfilling and piling (see points D in Figure 2). Wells are plastic pipe lined to the bottom except in the case of 5 and 6 which had a stainless steel well point at the beginning. The stainless steel well points were removed from these holes in December.

Hole Number 6 is some distance from the present sludge disposal area. It was hoped this well would provide control results. However, the analysis of soil borings taken during drilling shows metal levels similar to those from the disposal property wells.

Unsuccessful attempts were made to place wells at points A and B, close to the main site for sludge piling. Water samples at frequent intervals were kindly provided by Henry Kronis of the Ministry of the Environment. Samples were pumped from the well with a "reversed" bicycle pump through polyethylene tubing into clean glass or plastic bottles. In the laboratory, usually before 24 hours had elapsed, the samples were filtered through various membrane porosities to give some data on the size fraction of metal in the wells. Metals except mercury were analyzed by the method reported by Van Loon *et al* (3). Mercury required a separate sample and was done only occasionally because of time and financial constraints.

3.1 Method for "Total" Mercury

Place 200 ml of filtered water into a 250 ml beaker. Add 0.1 g of KMnO_4 crystals and 5 ml concentrated HNO_3 . Place on a hot plate and evaporate to 100-150 ml on medium heat (do not boil). Transfer to a BOD bottle and treat with hydroxylamine hydrochloride and stannous chloride as indicated in the method for sludge and soils. Run on the MAS 50 mercury analyzer.

3.2 Results - Soil Borings

Analyses were made on soil borings retrieved from the holes during drilling. The following table gives the results.

TABLE 8. Analyses Of Drill Hole Soil Borings.

Hole	Depth (ft)	(ppm)								
		Hg	Cd	Pb	Zn	Mn	Cu	Ni	Ag	Cr
D1	0-3	0.8	0.6	27	58	100	20	6	1	22
	3-6	0.3	0.4	4	26	120	11	2	1	11
	6	0.3	0.6	3	18	120	8	2	1	8
D2	3-6	2.9	1.3	290	380	260	81	9	2	37
	6-9	2.9	0.5	260	275	170	60	6	3	16
	9-12	2.5	0.6	200	300	200	60	6	3	20
D3	0-3	0.6	1.1	49	112	192	32	7	2	18
	3-6	0.3	0.3	18	42	115	15	7	2	11
D4	0-3	0.1	0.7	40	44	140	27	6	0.8	7
	3-6	0.1	0.7	15	18	100	9	6	0.5	7
	6	0.1	0.5	12	14	95	10	6	0.7	8
D5	1	3.3	2	107	148	210	55	10	2	40
	3	2.0	1	82	104	134	35	7	2	25
	6	1.8	2	36	40	165	17	5	0.5	15
	9	0.8	1	13	41	170	12	10	1	23
	10	0.3	1	9	34	120	13	8	0.5	19
	12	0.3	0.5	9	20	140	10	6	1	17
D6	1	2.0	2	140	60	225	60	10	4	35
	3	1.0	2	20	40	270	30	8	2	20
	6	1.0	2	6	20	340	13	10	1	20
	9	0.5	2	4	13	120	6	5	1	15
	12	0.5	2	6	20	140	8	5	1	15

3.3 Metal Content of Well Waters

After the filtration described above 1 ml of HNO₃ is added and the samples evaporated to dryness. Add 2 ml HCl and 1 ml HNO₃ and evaporate to dryness. Dilute to 200 ml with water and analyze as described by Van Loon *et al* (3). Results for the six wells are given in the following table. Precipitation episodes which occurred near sampling time are given in Appendix.

TABLE 9. Metal Content Of Well Waters (ppb)

Well	Date	Filter (μ)	Zn	Fe	Pb	Ni	Cu	Cd
1	7/18/73	5	25	100	65	15	10	8
		0.45	30	25	30	10	8	8
	7/26/73	5	30	95	45	15	10	12
		0.45	35	25	50	15	8	12
	8/1/73	5	11	150	30	13	12	13
		0.45	10	30	15	12	10	13

TABLE 9. (CONT'D)

Well	Date	Filter	(μ)	Zn	Fe	Pb	Ni	Cu	Cd
1	8/16/73	5		40	2*	330	15	20	7
		0.45		40	2*	320	15	20	7
	9/5/73	60		3	1.3*	-	-	-	-
		5		7	750	25	10	10	5
	9/24/73	0.45		7	580	15	10	20	2
		5		20	240	5	10	8	3
	10/5/73	0.45		25	80	2	10	8	3
		60		10	3.7*	30	10	10	3
	10/16/73	5		10	780	8	10	10	2
			0.45		10	480	4	10	10
		60		5	4.6*	5	15	12	0.6
	10/23/73	2		2	700	3	10	7	0.2
			0.45		2	30	3	10	7
		60		5	3*	7	13	20	7
	10/31/73	5		5	3*	7	13	20	7
			0.45		5	3*	8	13	20
		60		280	2*	7	13	10	2
	11/8/73	5		210	400	1	10	10	2
			0.45		210	85	1	10	10
		0.45		15	35	1	12	6	0.1
	11/14/73	0.45		550	70	2	12	15	0.9
	11/20/73	0.45		60	50	1	12	15	0.3
	11/28/73	60		10	220	300	10	25	0.4
			5		10	40	10	11	24
		0.45		10	60	2	13	12	0.4
	12/13/73	60		20	700	20	8	20	0.1
			5		20	170	10	8	20
		0.45		12	20	3	9	20	0.1
	1/3/74	60			0.4)				
			5			0.2)	Hg only		
0.45				0.2)					
1/15/74	60		40	1.6*	25	13	25	0.1	
		5		35	88	10	12	6	0.1
1/31/74	60		5	300	110	15	30	0.3	
		5		5	140	60	15	30	0.3
2/14/74	0.45		Hg	3	30	25	15	30	0.3
		60	0.9						
2/28/74	0.45		0.9	13	17	2	5	23	0.1
		60		10	160	9	5	9	0.3
	5		10	10	1	5	5	0.1	
2/28/74	0.45		10	10	1	5	5	0.1	
		60							
	5								
2	10/31/74	0.45		4	50	6	16	50	2
			60		50	15*	25	12	25
	12/13/74	5		20	2	5	12	15	0.1
			0.45		20	1	2	12	15
	1/3/74	60				0.5)			
5					0.2)	Hg only			
0.45				0.2)					

TABLE 9. (CONT'D)

Well	Date	Filter	(μ)	Zn	Fe	Pb	Ni	Cu	Cd	
2 (cont)	1/15/74	60		60	4*	30	20	55	0.1	
		5		25	220	6	20	35	0.1	
		0.45		25	100	6	20	30	0.1	
	1/31/74	60		20	13*	30	20	50	0.1	
		5		20	0.1	10	20	50	0.1	
		0.45	Hg	20	120	5	20	50	0.1	
	2/14/74	60	1.4							
		0.45	1.1	20	37	3	6	30	0.1	
	2/28/74	60			40	10*	10	10	35	0.1
		5			8	0.1*	10	8	30	0.1
		0.45			4	20	1	8	30	0.1
	3	7/18/73	5		30	2*	450	24	25	4
0.45				25	2*	450	13	20	4	
7/26/73		5		20	2*	10	10	10	5	
		0.45		30	150	5	10	10	5	
8/1/73		5		20	150	25	10	30	1	
		0.45		20	120	3	10	15	1	
8/16/73		5		5	2*	13	5	10	1	
		0.45		5	2*	2	5	10	1	
9/24/73		60		10	3*	9	5	10	0.5	
		5		15	190	2	5	10	0.3	
		0.45		15	50	1	5	10	0.3	
10/5/73		60		10	7*	10	5	15	0.7	
		5		10	800	3	5	15	0.3	
		0.45		16	350	1	5	15	0.1	
10/16/73		60		1	2*	5	5	10	0.5	
		55		1	650	1	5	5	0.1	
		0.45		1	20	1	5	5	0.1	
10/23/73		60		1	1*	1	5	20	0.7	
		5		1	500	1	5	10	0.5	
		0.45		1	20	1	5	10	0.4	
10/31/73		60		2	3*	2	5	5	0.4	
		5		5	500	1	5	5	0.2	
		0.45		5	80	1	5	5	0.2	
11/8/73		0.45		9	10	1		8	0.1	
11/14/73		0.45		110	10	2	5	20	0.6	
11/20/73		0.45		45	10	1	5	10	2	
11/28/73		60		50	110	200	5	10	0.3	
		5		50	10	10	5	10	0.3	
		0.45		50	1	4	5	10	0.3	
12/13/73		60		20	120	15	5	20	0.2	
		5		20	20	25	5	20	0.3	
		0.45		20	20	10	5	20	0.3	
1/3/74		60				0.4)				
		5				0.2)	Hg only			
		0.45				0.2)				
1/15/74		60		25	50	10	15	25	0.1	
		5		30	20	5	15	25	0.1	
		0.45		5	15	4	15	25	0.1	

TABLE 9. (CONT'D)

Well	Date	Filter (μ)	Zn	Fe	Pb	Ni	Cu	Cd	
3 (cont)	1/31/74	60	90	250	10	20	40	0.1	
		5	40	50	5	20	40	0.1	
	2/14/74	0.45	Hg	-	-	-	-	-	
		60	1.4	-	-	-	-	-	
	2/28/71	0.45	1.3	10	20	2	10	30	0.1
		60		10	170	2	10	20	0.1
5			5	10	2	10	20	0.1	
		0.45	5	15	2	10	2G	0.1	
4	7/18/73	5	70	320	15	25	50	1	
		0.45	50	120	15	10	40	1	
	8/1/73	5	25	2*	1*	55	200	10	
		0.45	15	2*	10	8	15	1	
	10/5/73	60	20	350	5	13	20	1	
		0.45	20	180	3	13	20	3	
	10/16/73	5	10	25	5	10	15	0.5	
		0.45	5	10	<1	10	15	0.1	
	10/23/73	60	10	130	3	10	20	0.9	
		5	10	35	3	10	20	0.8	
	10/31/73	5	1	20	1	10	25	0.5	
		0.45	15	20	1	10	20	0.5	
	11/8/73	60	15	80	150	10	25	0.5	
		5	20	70	140	10	25	0.5	
		0.45	20	30	130	10	25	0.5	
	11/14/73	60	22	10	2	7	15	0.1	
		5	20	10	1	7	15	0.1	
		0.45	20	10	1	7	15	0.1	
	11/20/73	60	35	5	1	8	20	0.1	
		5	25	5	1	8	20	0.1	
		0.45	30	5	1	8	20	0.1	
	11/28/73	60	20	250	5	5	15	0.1	
		5	20	10	2	5	15	0.1	
		0.45	20	10	2	5	15	0.1	
	12/6/73	60	1	90	5	5	15	0.2	
		0.45	1	90	2	5	15	0.1	
	12/3/73	60	60	150	5	10	20	0.3	
		5	40	25	5	5	15	0.1	
	12/18/73	60	20	230	10	10	20	0.3	
		5	20	25	10	10	20	0.1	
		0.45	20	15	10	10	20	0.1	
	1/3/74	60				0.5)			
		5				0.2)	Hg only		
		0.45				0.2)			
	1/15/74	60	25	140	3	10	25	0.1	
		5	25	35	2	10	25	0.1	
0.45		15	25	2	10	25	0.1		
1/31/74	60	25	25	10	20	35	0.1		
	5	25	25	5	20	35	0.1		
	0.45	25	25	5	10	35	0.1		

TABLE 9. (CONT'D)

Well	Date	Filter	(μ)	Zn	Fe	Pb	Ni	Cu	Cd
4 (cont)	2/14/74	60	Hg 1.2	-	-	-	-	-	-
		0.45	1.2	10	20	20	5	10	0.1
	2/28/74	60		10	200	2	5	15	
		5		10	20	1	5	15	
		0.45		10	20	1	5	15	
5	10/31/73	60		45*	600	15	35	15	5
		5		40*	200	10	35	10	5
		0.45		40*	35	10	35	10	5
	11/8/73	60		55*	220	25	20	15	1
		5		55*	70	20	23	10	1
		0.45		55*	25	20	20	10	1
	11/14/73	60		80*	450	25	15	10	2
		5		30*	100	20	15	10	2
		0.45		75*	20	10	15	10	2
	11/20/73	60		5	680	15	10	10	1
		5		5	350	5	10	10	0.3
		0.45		5	70	5	10	10	0.2
	11/2b/73	60		12*	100	30	10	20	0.7
		5		12*	90	30	10	15	0.7
		0.45		11*	50	20	10	20	0.7
	12/6/73	60		3*	650	10	5	10	0.5
		5		3	340	10	5	15	0.5
		0.45		3*	40	5	5	10	0.5
	12/13/73	60		3*	660	15	5	20	0.2
		5		3*	170	5	5	20	0.1
		0.45		2*	25	5	5	20	<0.1
	1/3/74	60					0.7)		
		5					0.5)	Hg only	
		0.45					0.3)		
	1/15/74	60		1*	120	5	15	25	0.1
		5		1*	70	5	15	25	0.1
		0.45		1*	60	5	15	25	0.1
	1/31/74	60		60	70	25	10	25	0.1
		5		50	30	2	10	25	0.1
		0.45		30	20	2	10	25	0.1
2/14/74	60	Hg	-	-	-	-	-	-	
	0.45	1.2	10	20	5	4	10	0.1	
2/26/74	60		40	125	2	10	15	0.1	
	5		40	25	1	10	15	0.1	
	0.45		40	15	1	10	15	0.1	
6	10/31/73	60		20	200	5	3	8	0.3
		5		30	30	5	3	8	0.3
		0.45		30	20	2	3	8	0.3
	11/8/73	5		25	15	2	2	0.4	0.1
		0.45		25	15	2	2	0.3	0.1
	11/20/73	60		1*	100	5	7	5	0.4
		5		1*	20	5	7	5	0.3
0.45			1*	5	1	7	5	0.2	

TABLE 9. (CONT'D)

Well	Date	Filter (μ)	Zn	Fe	Pb	Ni	Cu	Cd
6 (cont)	11/28/73	60	3*	310	6	10	10	0.5
		5	2*	20	2	10	10	0.5
		0.45	2*	20	2	10	10	0.5
	12/6/73	60	5*	250	4	10	10	0.5
		5	5*	70	4	10	10	0.5
		0.45	5*	30	4	10	10	0.5
	12/13/73	60	5*	1*	5	10	10	0.2
		5	5*	80	5	10	10	0.2
		0.45	5	23	5	10	10	0.2
	1/3/74	60				0.5)		
		5				0.3)	Hg only	
		0.45				0.3)		
	1/15/74	60	3*	70	5	10	30	0.4
		5	3*	40	5	10	30	0.4
		0.45	3*	35	5	10	30	0.4
	1/31/74	60	5*	100	10	10	20	0.7
		5	5*	50	10	10	20	0.6
		0.45	5*	25	10	10	20	0.6
2/14/74	60	Hg 1.1	-	-	-	-	-	
	0.45		8*	14	90	4	30	<0.1
2/28/74	60	1.1	9*	160	5	4	20	0.1
	5		8*	40	14	4	14	<0.1
	0.45		8*	10	4	4	14	<0.1

* Values in ppm.

Analyses above represent "total" metal in each size fraction.

3.4 Conclusion

Little can yet be said in detail about these results. More holes at other properties are necessary. To obtain the proper perspective holes containing uncontaminated water must be established and analyzed.

In general, the North Toronto well results show large variations in iron and zinc values and little variation in copper and nickel values within the period of study. Iron appears to be most strongly affected by filtration and copper and nickel least. Zinc from time to time shows increasing values with decreasing porosity of the filter medium. This latter observation is not to be expected and may be due to contamination. Work is presently proceeding to uncover the reason for the problem with zinc.

4. METAL CONTENT OF SURFACE WATERS IN AREAS BEING SLUDGED

4.1 North Toronto

Samples of surface water (pH 6.7 - 7.5) running in ditches and from piles of sludge were filtered and analyzed for "total" metals (3). The following table summarizes results obtained on various filter porosity sizes, averaged over a year of sampling. Table 7 in last year's report (1) gave detailed results for a variety of sample locations. Material passing through 0.45 μ porosity filters is often defined as "soluble."

TABLE 10. Metal Content Of Surface Runoff At North Toronto - Yearly Average.

Sample	Filter (μ)	(ppb)						
		Hg	Zn	Pb	Fe	Ni	Cu	Cd
Railroad Ditch	60	1.6	100	32	1200	45	100	1.0
	5	1.0	68	5	900	45	98	0.6
	0.45	1.0	25	4	300	45	90	0.5
Sludge Fields	60	1.8	100	30	1800	49	110	1.0
	5	1.2	75	8	1000	47	96	0.6
	0.45	1.2	30	3	300	47	96	0.4

Light particulate in the surface water trapped on the 60 μ filter was analyzed for metal and the results expressed as μg per ml of liquid filtered. Averages for the year were Hg 0.1, Zn 2, Fe 200, Pb 2.5, Ni 0.1, Cu 1, Cd 0.05. These are in all cases at least ten times higher than values in the filtrate samples analyzed above.

4.2 Burlington Farm Disposal Area

Water samples were taken on three occasions characteristic of Spring, Summer and Fall weather patterns, for some of the sample points listed in Figure 2. No significant seasonal variations were noted and hence the results shown in the following table are an average for the sample.

TABLE 11. Metals In Water At Burlington Sludge Disposal Area.

Sample	Filter (μ)	ppb						
		Zn	Fe	Pb	Ni	Cu	Cd	Hg
S1	60	50	740	24	40	95	30	0.5
	5	20	450	15	35	65	15	0.3
	0.45	10	260	5	30	50	1	0.2
S6	60	20	1200	10	7	25	1	0.5
	5	10	1100	10	7	15	1	0.3
	0.45	10	800	5	7	15	0.4	0.3
S7	60	60	1200	25	45	45	2	0.6
	5	40	1100	10	40	45	2	0.4
	0.45	30	600	10	40	40	2	0.3
Stream A	60	5	65	5	10	15	1	0.2
	5	2	50	3	5	15	0.5	0.2
	0.45	2	35	2	5	15	<0.1	0.2
Stream B	60	1	2	<1	<1	5	<0.1	0.2
	5	1	2	<1	<1	4	0.1	0.2
	0.45	1	2	1	<1	4	0.1	0.2

The light particulate matter flowing in the ground water and trapped by the 60 μ filter was analyzed for metal. Results, expressed as μg metal in either a ml or liter of water, are given in the table below.

TABLE 12. Burlington Disposal Area Metal In Trapped Particulate.

Sample	Zn	Fe	Pb	Ni	Cu	Cd	Hg
	mg/ml						
S1	0.5	26	100	45	120	5	5
S6	2	26	300	40	550	10	10
S7	2	40	500	100	500	20	10
Stream A	0.05	2	23	10	10	5	2
Stream B	0.03	0.08	3	<1	1	<1	<1

4.3 Conclusion

Metal in surface water is largely in the particulate fraction. Very appreciable drops are noted for most metals as the water is filtered through fine porosity membranes.

5. ANALYTICAL CONTROL

Of paramount importance is the continual, critical evaluation of data obtained during routine analyses in a laboratory. This can only be done if suitable "standard" materials exist which are utilized on a regular basis for control purposes. In this regard several sludge samples have been prepared as standards by workers at the Canada Centre for Inland Waters. Initial analyses were done by 10 laboratories (including that of the author), all except one using atomic absorption spectroscopy. It is unwise to rely heavily on one technique for fear of systematic bias and hence the samples will now be further analyzed by groups with an expertise in X-ray fluorescence, emission spectrographic, neutron activation and electrochemical analysis.

The following table gives our results compared to the mean reported after the work by the first nine laboratories.

TABLE 13. Analysis Of CCIW Standard Sludges.

Sample	ppm							%	
	Zn	Cd	Cu	Ni	Pb	Mn	Cr	Fe	Al
Lime (1)	700	1	150	6	90	220	23	0.5	0.3
(2)	731	5	159	29	136	257	25	0.6	0.3
Ferric Chloride									
(1)	2000	14	1200	28	980	370	350	7.0	1.6
(2)	2543	19	1328	36	1149	397	369	8.1	1.8

(1) author's laboratory

(2) mean of study

In general these values, although lower, fall close to the means. However, in the case of Ni, Pb and Cd, particularly in the lime sludge, author's values were very much lower. It is the opinion of the author that the values recorded in his laboratory are closer to the correct values. This is due to long experience with the use of background correction techniques. Recent intensive work on nickel at CCIW (personal communication) suggests that the nickel value should be lower than reported in the mean above.

The group which has organized this standards program is to be commended. It is hoped that the list of materials will be expanded to include soils and perhaps even waters and vegetation.

A new organic sample became available from the National Bureau of Standards, Bovine Live NBS SRM #1577. A tomato leaves standard has also been prepared but no results have yet been circulated by NBS. Both these materials and the NBS Orchard Leaves (available for the past three years) were utilized in the author's laboratory. The following is a compilation of results on these substances obtained over the past year.

TABLE 14. NBS Analytical Control Standards.

		(ppm)									
		Fe		Cd		Pb		Zn		Mn	
		M	Sx	M	Sx	M	Sx	M	Sx	M	Sx
O.L.	(1)	220	20	0.3	0.1	38	5	22	3	72	5
	(2)	300		0.1		45		25		91	
B.L.	(1)	255	30	0.2	0.1	<0.5	-	150	10	10	1
	(2)	270		0.3		0.34		130		11	
T.L.	(1)	350	35	1.6	0.2	4.2	1	52	5	175	10
		Cu		Ni		Cr		Hg			
		M	Sx	M	Sx	M	Sx	M	Sx		
O.L.	(1)	10	2	1.2	0.3	2.3	0.3	0.13	0.02		
	(2)	12		1.3		2.3		0.16			
B.L.	(1)	150	5	1.0	0.3	1.6	0.3	-			
	(2)	193		na		na		-			
T.L.	(1)	10	3	0.8	0.3	0.5	0.2	-			

- (1) author's laboratory
- (2) NBS provisional values
- M - Mean value
- Sx - Standard deviation
- na - not available

No suitable standards yet exist for analyzing heavy metals in waters of the type in this study. However, the Environmental Protection Agency, Cincinnati, supplies distilled water metal "salted" standards which were used as reported in the earlier report (I) of this contract. The EPA also produced a mercury water standard newly available this year. The following are author's results over the year.

TABLE 15. EPA Mercury Water Standard.

(ppb)

STANDARD No.	Author		EPA
	M	Sx	
(1)	0.4	0.2	<0.4
(2)	2.4	0.5	2
(3)	7.0	0.5	8

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APPENDIX

DESCRIPTIVE WEATHER INFORMATION

APPENDIX

DESCRIPTIVE WEATHER INFORMATION (12) (rain in inches)

July

July 1973 was warmer and drier than average.

Rains occurred	July 4	0.16
	July 12	0.13
	July 13	0.15
Sample (1)	July 18	
	July 24	0.38
	July 25	0.13
	July 26	0.02
Sample (2)	July 26	

There were only small amounts of water available in the holes (they could be pumped dry). Hole 2 had no water.

August

August 1973 was the second warmest August on record and had lower than average rainfall.

Rains affecting sampling occurred

	July 27	0.62
	July 28	0.14
	July 31	1.2
Sample (3)	August 1	
	August 2	0.05
	August 4	0.05
	August 9	0.05
Sample (4)	August 16	

There was little water in the holes. Again no water was available from hole 2.

September

Less rain than normal fell during September 1973. Hot and dry weather continued for the first half of the month.

Rains affecting sampling occurred

	August 26	0.02
	September 3	0.25
Sample (5)	September 5	
	September 17	0.58
	September 21	0.23

September 22	0.69
September 23	0.44

Water supply improved but still hole 2 had no useful amounts of sample.

October

October 1973 was warm and wet.

Rains affecting sampling occurred

	October 1	0.23
	October 2	0.10
	October 4	0.11
	October 13	0.32
Sample (6)	October 16	
	October 16	0.01
	October 17	0.05
	October 16	0.07
	October 19	0.07
Sample (7)	October 23	
	October 27	0.05
	October 28	1.7
	October 29	1.3
	October 30	0.51
	October 31	0.71
Sample (8)	October 31	

Hole 2 began to give appreciable water after October 31.

Other holes (5) and (6) were sampled for the first time.

November

November 1973 was warm, wet and windy.

Rains affecting sampling occurred

	October 28	1.7
	October 29	1.3
	October 30	0.51
	October 31	0.71
	November 2	0.3
Sample (9)	November 8	
	November 14	0.58
Sample (10)	November 14	
	November 15	0.77
Sample (11)	November 20	
	November 21	0.19
	November 24	0.39

November 27	0.20
November 28	0.50

Sample (12) November 28

December December 1973 had more rain than normal but average temperatures. Temperature was above freezing on the average up to December 13, so water which fell on the ground did not become trapped on the surface as snow and ice.

Rains affecting sampling occurred

December 4	0.30
December 13	0.05

Sample (13) December 13

January January 1974 had both below normal temperatures and precipitation.

Precipitation affecting sampling was as follows

December 25	0.35
December 26	0.62
December 29	0.06

Precipitation then became snow and roughly 3 inches was on the ground by January 3. Temperatures average below freezing (maximum temperatures also) between December 30 and January 3.

Sample (14) January 3.
Accumulations of about 8 inches of snow were present up to January 15. No rain occurred during this interval. The only day with melting temperatures occurred on January 14 (temperature maximum 37°F, average 26°F).

Sample (15) January 15.