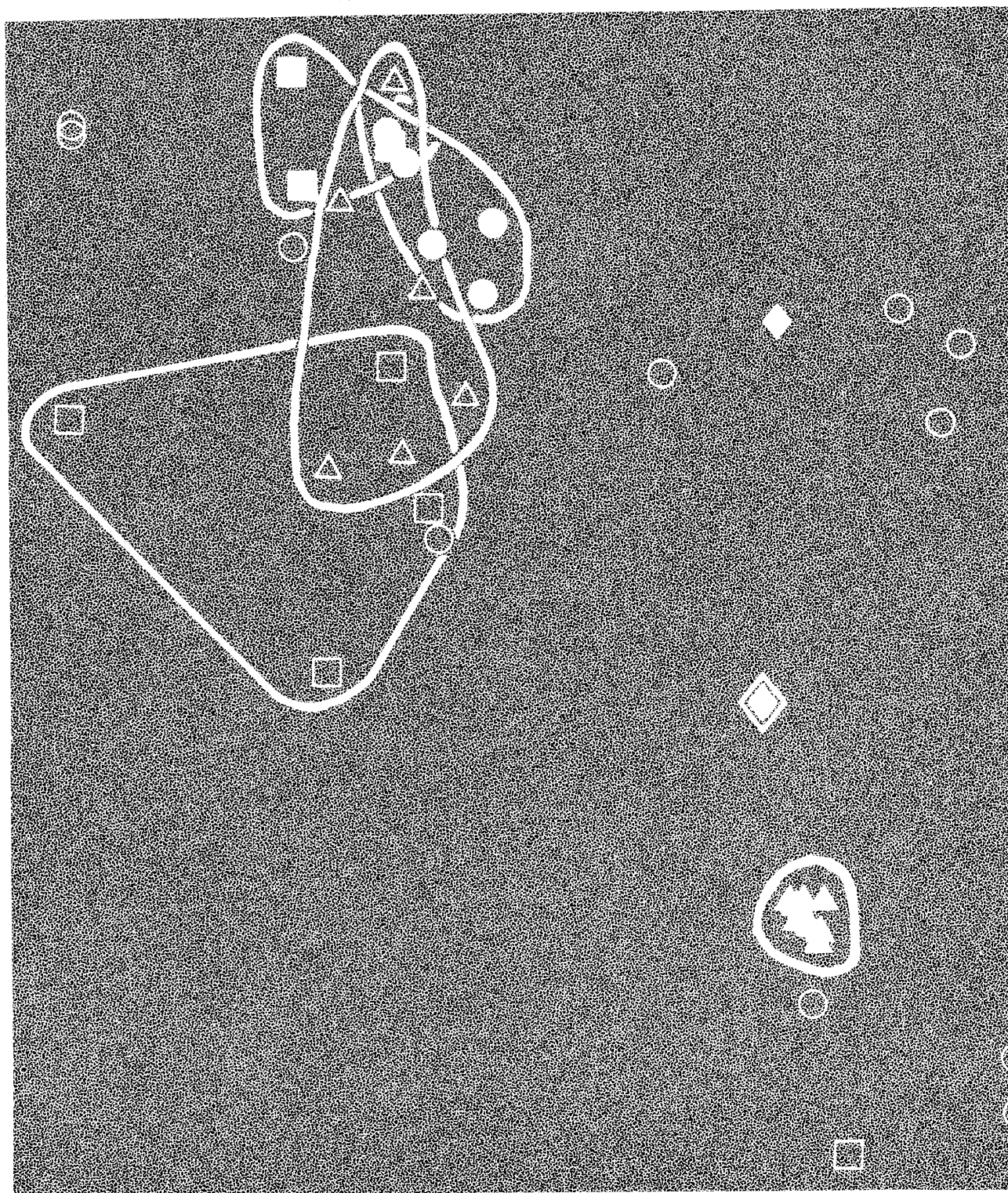Ontario

Ministry of
Transportation and
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Research and
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Branch

Differentiating Various Sources of Chlorides in Domestic Well Waters

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Technical Report Documentation Page

Differentiating Various Sources of Chlorides in Domestic Well Waters

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Abstract:	Road salt (chloride) contamination of domestic water supplies is frequently a problem adjacent to Ontario's highways. However, other chloride sources (such as chemical fertilizers, septic tank septage, agricultural manure leachate, landfill leachate, and bedrock formations) may also be a source of chloride in groundwater. The purpose of this study was to obtain a hydrochemical signature for the major ions and iodide to determine if various chloride sources could be differentiated. Concentrations of iodide showed a considerable range of values from 2 µg/L in a 10% solution of potash fertilizer, to values of 9000 µg/L in the groundwater of the Cambrian Eau Claire Formation and a maximum concentration of 54 000 µg/L in a 10% solution of triple superphosphate fertilizer. In contrast, road salt from four different sources including Windsor, Goderich, Cleveland and Esterhazy, showed a relatively constant 10 to 12 µg/L in 5% solutions. However, bedrock groundwaters for the Rochester, Salina, and Guelph Formations of southwestern Ontario were depleted in iodide relative to seawater. Landfill leachates, agricultural manure leachates, septic tank septage and most chemical fertilizers were enriched in iodide relative to seawater. It is concluded that iodide may be a key chemical parameter to assist in establishing the origin of chlorides in groundwater. Iodide should be a routine chemical analysis parameter in road salt groundwater contamination investigations.
Key words:	pollution, salt, chlorides, contamination, groundwater, water
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Differentiating Various Sources of Chlorides in Domestic Well Waters

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1/ Introduction

1.1/ Background

Homeowners who suspect that their water supplies have become contaminated from the application or storage of road salt may take action against the Ministry of Transportation and Communications (MTC). This action can result in costly individual claims, depending on the nature of remedial action needed to re-establish potable water.

Once a claim is made by a homeowner, the Claims Section of MTC's Office of Legal Services contacts the Ministry of Environment (MOE), who then undertake a hydrogeological investigation of the contaminated site to establish the probable source of contamination, the direction of groundwater flow and possible liability. In many cases, the determination of liability is obvious. In more complex situations, where liability is difficult to establish, it may be necessary to drill boreholes to monitor the suspected contamination or locate the contaminated groundwater using surface geophysical methods. Both of these methods add to the cost of claim investigation. In addition, surface geophysics is only effective for shallow well investigation in unconsolidated materials and is unreliable in bedrock investigations because of the variable resistivity of the bedrock*.

Liability can be difficult to establish in some cases, because chloride contamination may be due to a number of different sources such as mixing of bedrock groundwaters, contamination from landfill sites, septic tank leachate, barnyard manure leachate and the application of agricultural fertilizers. With some claims, it may be impossible to establish direct liability.

At the present time, claim investigation suffers from major disadvantages, namely:

1/ There are no distinguishing criteria for relating chloride content in groundwater to road salt contamination.

2/ While resistivity methods used by the MOE can distinguish differences in chloride content in water and map chloride plumes, such methods are limited in application to groundwater in unconsolidated surficial sediments, and are ineffective in most bedrock groundwaters.

1.2/ Study Objectives

The objectives of this project were:

1/ To develop a practical and inexpensive methodology for differentiating chlorides of various sources in groundwaters using key chemical parameters.

2/ To incorporate this methodology into the claim investigation procedure to facilitate the determination of liability.

1.3/ Scope of the Project

The work program consisted of establishing chemical signatures for sources causing elevated chloride levels in groundwater, and evaluating the usefulness of iodide as a key chemical parameter which would be useful in differentiating these various sources. Major chloride sources were grouped as follows:
• road salt
• chemical fertilizer
• barnyard manure leachate
• sanitary landfill leachate
• septic tank septage
• bedrock formation waters

A total of 42 samples were taken from areas determined from discussion with personnel from MTC, MOE, and the Ministry of Agriculture and Food (OMAF). An attempt was made to sample areas where road salting has been a problem in the past.

Personal communication from Ed Rodriguez, MOE, 1985.

2/ Project Design

2.1/ Introduction

Major ion chemistry, consisting of Ca, Mg, Na, K, SO$_4$, Cl and bicarbonate alkalinity, can be a useful tool in the recognition of groundwater types and the understanding of chemical processes affecting groundwater chemistry [5, 3, 19]

The Durov diagram has been utilized in groundwater classification schemes for surficial deposits in south-central Ontario [4, 18] and in chalk aquifers in Britain [17]. Different groundwater types plot in fields on the Durov diagram, reflecting natural and contaminant hydrochemical processes. The evolutionary sequence for groundwater controlled by carbonate equilibria is shown in Figure 1. Where groundwater chemistry is controlled by carbonate equilibria, uncontaminated recharging groundwaters occupy the calcium, magnesium, bicarbonate field of the Durov diagram, reflecting the dissolution of calcite and dolomite. As groundwaters move through the aquifer, ion exchange becomes a dominant process as calcium in the water is exchanged for sodium on the exchange sites in the aquifer. This shifts the major ion

chemistry toward the sodium-bicarbonate field. With increased residence time, the continuous dissolution of salts, particularly sodium chloride, shifts the composition slowly toward the sodium chloride field of the diagram.

The ionic strength of the groundwater increases due to the slow dissolution of minerals in the aquifer, or by mixing with groundwaters containing higher total dissolved solids, or from the input of contaminants (e.g., road salt). Ion exchange is less selective toward the adsorption of bivalent ions [33]. As a result, sodium may become adsorbed with the subsequent release of calcium, to cause a shift toward the calcium-chloride field of the diagram. Modifications to the main evolutionary sequence are brought about by dilution and mixing.

In addition to major ion chemistry, key minor ions may be useful in hydrochemical studies. One such parameter is iodide. Iodine geochemistry is described in standard geochemistry references [30, 38, 11] and was recently reviewed by Lloyd et al [25]. Iodine rarely forms minerals because its large ionic radius inhibits substitution into the mineral lattice. It is thought to

Figure 1/ Groundwater Evolutionary Sequence Controlled by Carbonate Equilibria
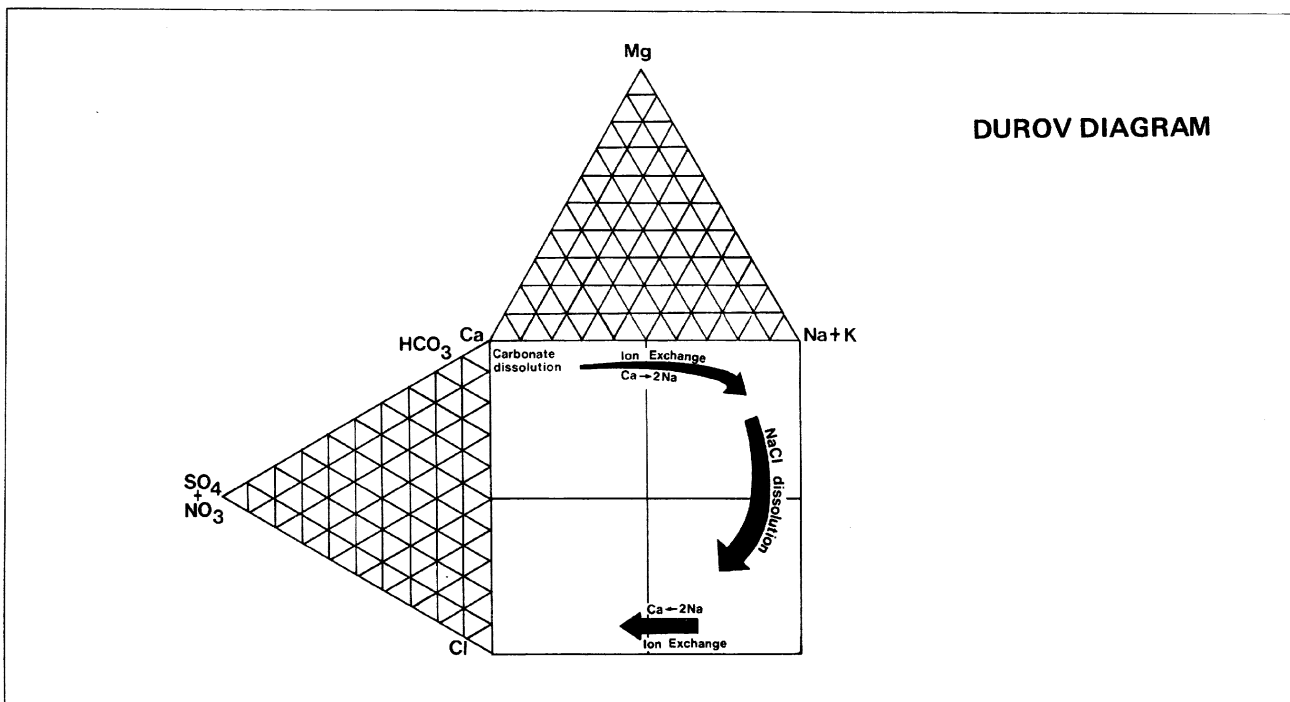
occur as fluid inclusions and as soluble salts along crystal boundaries. Iodine accumulation in rock varies from <1ppm in igneous and metamorphic rock to typically 1-20 ppm in sedimentary rock.

Marine argillaceous rocks typically contain the highest iodine concentrations due to adsorption on clay and bioaccumulation. Within the Eh-pH range of most groundwaters, iodide (I) is the stable form of iodine and its presence has been found to be a useful indicator of groundwater residence [25].

In south-central Ontario, iodide was not detected in precipitation, but recharging groundwater in surficial deposits generally contained <5 µg/L (microgram/-litre) iodide. Older groundwaters near discharge areas and bedrock groundwaters typically contained 15 and >25 µg/L iodide, respectively [4]. This is consistent with observations on Crimean groundwaters [28]. On the basis of a limited number of bedrock samples, high chloride groundwater from bedrock was differentiated from suspected road salt and septic tank contaminated groundwaters [4].

The Chilean Iodine Educational Bureau (CIEB) [11] found rock salt to be depleted in iodide relative to seawater. These observations are consistent with findings by Beck [4] who found that 1% solutions of road salt from two municipal road salt stockpiles averaged 4.2 µg/L iodide.

Whitehead [40] found that iodide was readily adsorbed by iron and aluminum hydroxides and organic matter in soils. It is, therefore, unlikely that road salt runoff, considering adsorption and dilution during infiltration, will contribute significant iodide to groundwater.

Major ion and iodide hydrochemistry appears to be, on the basis of previous work, a useful tool in the differentiation of certain sources of chloride. Its application to the investigation of road salt contamination claims may be most relevant where wells are affected by high chloride bedrock waters, and where geophysical methods of chloride plume mapping are ineffective.

However, before hydrochemical techniques can be applied, it is necessary to establish a hydrochemical data base for major ions and iodide for chloride sources. Firstly, it should be established whether or not groundwaters can be shown to occupy discrete regions on the Durov diagram according to their major ion chemistry. Secondly, if iodide is to be used as a hydrochemical fingerprint, it is necessary to establish the range of values of iodide concentration in chloride source groundwaters.

2.2/ Sampling

Chloride sources investigated in this study include road salt, chemical fertilizers, barnyard manure leachate, septic tank septage, sanitary landfill leachate, and bedrock groundwaters. Table 1 summarizes the sample types and the number of samples taken. Table 2 is a summary description of all samples. Sample locations are shown regionally in Figure 2 and locally in Appendix A (Figures A1 - A19).*

Road salt and chemical fertilizers were dry and granular. The remaining samples were liquid. Liquid samples were collected in acid-washed, 1 L soft white plastic containers or pomade jars for major ion analyses and 250 mL acid-washed, polyethylene bottles for iodide and chloride analyses. Liquid samples were not filtered in the field. Samples were stored on ice until they could be delivered to the laboratory. All parameters were measured in the laboratory.

Appendix B* provides a summary of laboratory analytical results; Appendix C provides a detailed discussion of the chloride sources investigated.

2.2.1/ Road Salt

Road salt samples were obtained directly from the four suppliers to the MTC and are listed below. The point of origin of the salt sample is given in brackets:
• Domtar, Toronto (Goderich, Ontario)
• Canadian Salt Co., Toronto (Windsor, Ontario)
• International Salt, Toronto (Cleveland, Ohio)
• Kleyson Transport, Winnipeg (Esterhazy, Sask.)

Approximately 500 g of sample was obtained. The Domtar sample was collected from a covered stockpile at Toronto Harbour. The remaining samples were mailed or picked up from the suppliers. Duplicate road salt samples were prepared for analysis in the laboratory. A 5% by weight solution was prepared with de-ionized water and analysed.

2.2.2/ Chemical Fertilizers

Chemical fertilizer samples were obtained from the CIL fertilizer plant at Courtright near Sarnia and from the Co-Op in Uxbridge. Chemical fertilizers were prepared for analysis in the laboratory as a 10% by weight solution with de-ionized water.

2.2.3/ Barnyard Manure Leachate

Manure leachate samples were collected in wide-mouthed pomade jars, and 250 mL polyethylene bottles. Sample MTC 85009 was collected from a beef cattle manure pile which had been exposed to weathering for about three months prior to sampling. Concentrated leachate was sampled near the base of the manure pile. Sample MTC 85032 was liquid chicken manure and was collected by lowering a pail into the manure pit and transferring the manure into the sample container. Sample MTC 85034 was taken from a small pile of horse manure. A light yellowish coloured leachate with very little solids was obtained from the base of the pile. Sample MTC 85035 was taken at a pig farm. The sample was obtained by lowering a pail into the manure pit and transferring the sample to a sample container. Sample MTC 85036 was fresh dairy cow manure obtained from the floor of a manure spreader. The sample consisted of mostly liquid but did contain some solids and straw bedding. Sample MTC 85036 was taken from slotted floor holding tanks on a dairy farm. A sample consisting mostly of liquid was obtained by lowering a pail into the effluent and transferring the sample into the proper container.

2.2.4/ Septic Tank Septage

Septic tank septage was obtained from three locations. Samples were collected in 1 L pomade jars or 1 L soft plastic containers and 250 mL polyethylene bottles. Sample MTC 85033 was mostly sludge and was sampled from the drain valve of a septic tank cleaning service truck, approximately 12 hours after the septic tank had been pumped out. Samples MTC 85038 and MTC 85039 were samples taken by the septic tank cleaning service operator at the time of

pumping out. Samples were later transferred to appropriate sample containers.

2.2.5/ Sanitary Landfill Leachate

Leachate samples were collected from four sanitary landfill sites. Samples were collected in 1 L soft plastic containers and 250 mL polyethylene bottles. Duplicate samples were taken at three of the sites by the Ministry of Environment, West Central Region. Duplicate samples were collected in 1 L glass jars for major ion analysis and 250 mL plastic bottles for metal analysis.

Samples MTC 85002 and MTC 85004 were sampled by suction lift from manholes at the Mountain Road and Glenridge Quarry landfill sites, respectively. Sample MTC 85006 was obtained directly from a surface leachate pond at the Grimsby landfill site by dipping a pail into the leachate and transferring to the appropriate containers. Samples MTC 85030 and MTC 85031 are duplicate samples taken at the Brock West landfill in Pickering. Leachate collects at a depth of about 15 m. The samples were obtained by lowering a pail into the leachate and transferring to the appropriate containers.

2.2.6/ Bedrock Groundwaters

Bedrock formation waters were taken from a number of sources. Samples MTC 85001, 85003, 85005, and 85007 were taken from domestic wells or monitoring piezometers in bedrock at, or adjacent to, landfill sites in the Niagara region. Samples MTC 85013 to 85017 were taken from oil producing formations in Lambton and Essex counties in south-western Ontario. Sample MTC 85008 was taken from a campground water supply at Morrisburg. Samples

Table 1/ Summary of Sample Types

Sample Type	Number of Samples
Road Salt	8
Table Salt	1
Chemical Fertilizer	6
Barnyard Manure Leachate	6
Septic Tank Effluent	3
Landfill Leachate	5
Bedrock Formation Waters	13
Total	42

Source: Hunter and Associates (1985)
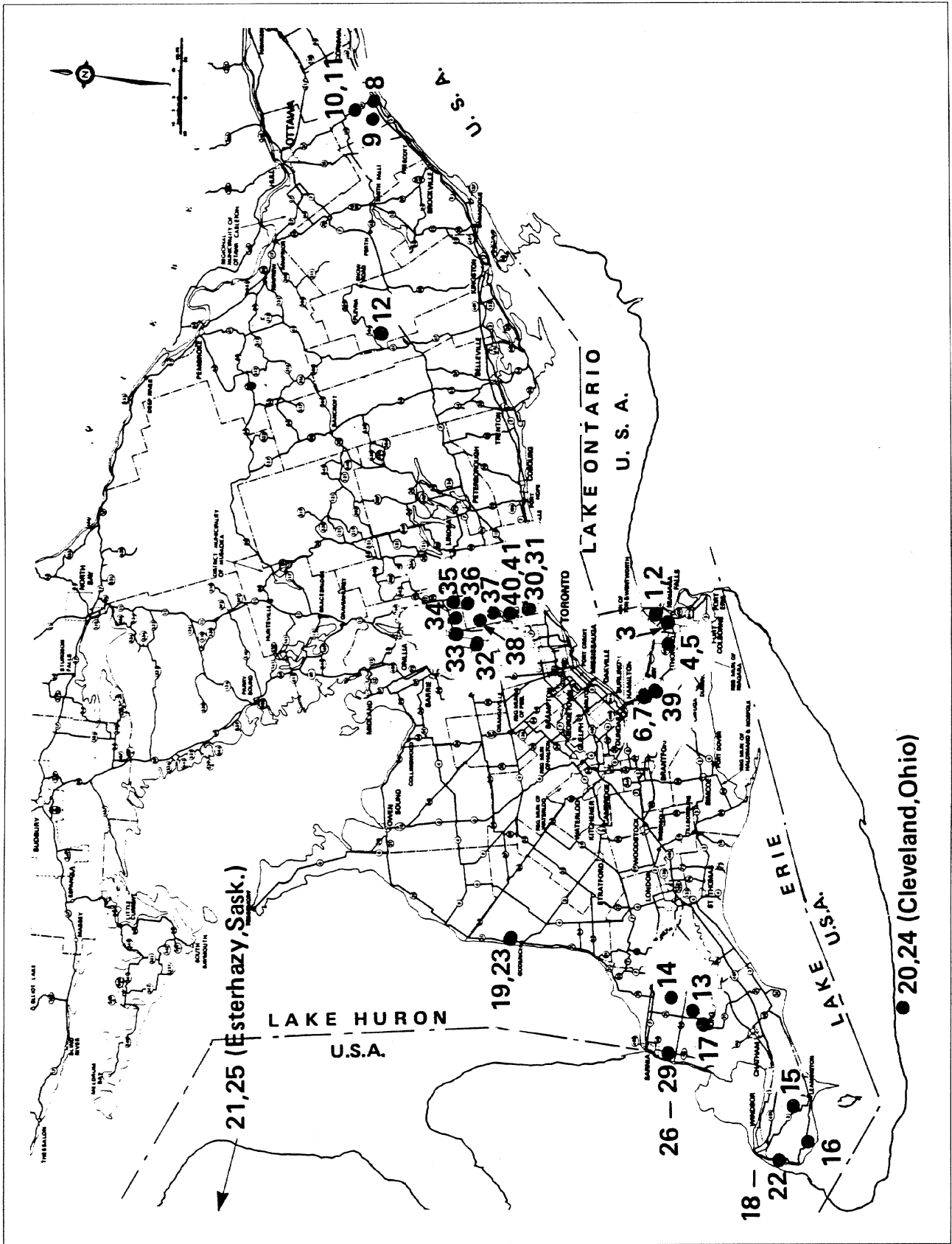
Figure 2/ Sample Locations

Table 2/ Summary of Sample Locations and Descriptions (See Figure 2)

MTC Sample Number	Location	Type	Source
85001	Mountain Road Landfill Site, Niagara Falls	Bedrock Groundwater	Gatehouse Well
85002	Mountain Road Landfill Site, Niagara Falls	Landfill Leachate	Leachate Collection Manhole
85003	Walker Brothers Landfill Borehole #17	Bedrock Groundwater	Rochester Shale
85004	Glenridge Quarry Landfill	Landfill Leachate	Leachate Collection Manhole
85005	Glenridge Quarry Landfill	Bedrock Groundwater	Deep Shale
85006	Grimsby Landfill Site	Landfill Leachate	Leachate Pond
85007	South of Grimsby Landfill Site	Bedrock Groundwater	Domestic Well, Kitchen Tap
85008	Riverside Cedar Park Morrisburg	Bedrock Groundwater	Drinking Water Tap
85009	Glen Becker	Beef Cattle Manure Leachate	Weathered Manure Pile
85010	Williamsburg Twp.	Bedrock Groundwater	Domestic Well, Outside Tap
85011	Duplicate of 85010		
85012	Cloyne	Bedrock Groundwater	Domestic Well, Bathroom Tap
85013	Dawn Twp. Lambton County	Guelph Formation Water	Separation Tank Tap
85014	Brooke Twp., Lambton County	Dundee Formation Water	Separation Tank Tap
85015	Gosfield North Twp., Essex County	Eau Claire Formation Water	Wellhead Tap
85016	Colchester Twp., Essex County	Trenton Formation Water	SeparationTank Tap
85017	Dawn Twp., Lampton County	Salina Formation Water	Separation Tank Tap
85018	Canadian Salt Co. Toronto	Salina Formation, F Unit, Rock Salt	Ojibway Mine, Windsor, Ontario

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Table 2/ (Continued) Summary of Sample Locations and Descriptions (See Figure 2)

MTC Sample Number	Location	Type	Source
85019	Domtar Inc. Toronto	Salina Formation A Unit, Rock Salt	Goderich Mine, Goderich, Ontario
85020	Iroquois Salt Products Ltd., Toronto	Silurian Salina Fm. Rock Salt	Sterline Cleveland Halite, Cleveland Mine Cleveland, Ohio
85021	Kleyson Transport Winnipeg	Prairie Formation Elk Point Group Rock Salt	By-product of Potash Mining Operation Esterhazy, Saskatchewan
85022	Duplicate of 85018		
85023	Duplicate of 85019		
85024	Duplicate of 85020		
85025	Duplicate of 85021		
85026	CIL, Courtright, Ontario	Chemical Fertilizer	Mono-Ammonium Phosphate
85027	CIL, Courtright, Ontario	Chemical Fertilizer	Di-Ammonium Phosphate
85028	CIL, Courtright, Ontario	Chemical Fertilizer	Urea (Prilled)
85029	CIL, Courtright, Ontario	Chemical Fertilizer	Ammonium Nitrate (Prilled)
85030	Brock West Landfill Site, Pickering	Landfill Leachate	Leachate Collection System
85031	Duplicate of 85030		
85032	Chicken Farm, East Lot 30, Conc. VII Gwillimbury Twp.,	Chicken Manure Leachate	Liquid Manure Pit
85033	Sutton Septic Service Sutton	Septic Tank Septage	Discharge Valve on Truck Tank
85034	Stormking Ranch Lot 19, Conc. VI Georgina Twp.	Horse Manure	Weathered Manure Pit
85035	Lot 25, Conc. II Georgina Twp.	Pig Manure Leachate	Liquid Manure Pit
85036	Lot 2, N 1/2, Conc. IV, Brock Twp.	Dairy Cow Manure Leachate	Fresh Manure on Spreader

Table 2/ (Continued) Summary of Sample Locations and Descriptions (See Figure 2)

MTC Sample Number	Location	Type	Source
85037	Lot 12, Conc. 6, Uxbridge Twp.	Dairy Cow Manure Leachate	Liquid Holding Tanks Below Barn
85038	Durham Region Road 1 N. of Leaksdale, N. of Zephyr Cutoff	Septic Tank Sludge	Pumped from Septic Tank
85039	340 Main Street Grimsby	Septic Tank Sludge	Pumped from Septic Tank
85040	Uxbridge Co-Op	Chemical Fertilizer	Triple Superphosphate (0-46-0)
85041	Uxbridge Co-Op	Fertilizer	Potash Fertilizer
85042	Canadian Salt Co.	Salt	Iodized Table Salt Sifto Salt, Windsor

Source: Hunter and Associates (1985)

MTC 85010 and 85011 are duplicate samples taken from a domestic well supply just north of Morrisburg. Sample MTC 85042 was taken from a deep domestic well just north of Kaladar on Highway 41 near Cloyne.

Well logs could only be found for two of the five bedrock wells (MTC 85007 and MTC 85010). Well depths were confirmed by the owner for MTC 85012 and by the St. Lawrence Parks Commission for MTC 85008. The depth of MTC 85001 could not be confirmed.

Depth of one of the two monitoring piezometers could not be confirmed but its location in bedrock was confirmed by the MOE (West Central Region) who regularly sample the site.

With the exception of sample MTC 85015, samples MTC 85013 to 85017 from oil producing formations were taken from brine tanks after the oil had been separated by heat treatment. Sample MTC 85015 was taken directly from the well head and consisted of a mixture of oil and brine. Depths for these samples are taken as the depth to the producing horizon.

Table 3 gives a brief description of the stratigraphy at each sampling site. Figure 3 shows the stratigraphy for southwestern Ontario and the approximate location of samples within the stratigraphic column.

2.3/ Sample Analysis

2.3.1/ Analytical Techniques

One litre samples were delivered to the MTC laboratory at Downsview in an ice cooler, where they were refrigerated until analysed. Duplicate samples taken by MOE (MTC 85001 to 85007 were not stored on ice and were not refrigerated prior to analysis). Samples of 250 mL size were transported on ice to Beak Analytical Service where they were refrigerated until analysed. A summary of the analy-tical techniques used by the various laboratories is given in Table 4.

Analytical techniques followed by the MTC laboratory are described by Welcher [39]*. The Beak laboratory follow the techniques described by the American Public Health Association [2]** for chloride and a modified version of the catalytic reduction method for iodide.

The MOE Drinking Water Lab and the Sewage Lab in Rexdale, follow techniques described by the MOE Handbook of Analytical Methods (1983)***.

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* *Personal communication, Rudy Sterk, Head, Chemicals Section, MTC.*
** *Personal communication, Richard Szawiola, Chief Chemist, Beak Analytical Services.*
* ***Personal communication, Stuart Barnes, Leader Domestic Waters Unit, and Peter Campbell, Supervisor, Industrial Waste Unit.*

Table 3/ Summary Lithology for Bedrock Groundwaters

MTC Sample No.	Type	Depth (m)	Lithological Unit		Lithological Description
85001	Gatehouse Well		Lockport Fm.	Silurian	dolostone, argillaceous dolostone, shale (1)
85003	Monitor Piezometer	28.8	Clinton Gp. Rochester Fm.	Silurian	dark grey shale, inter-bedded limestone (1)
85005	Monitor Piezometer		Clinton Gp.	Silurian	dark grey shale, inter-bedded limestone (1)
85007	Domestic Well	12.5	Lockport Fm.	Silurian	fine to medium crystalline, blue-grey dolostone and limestone (2)
85008	Trailer Park Well	51	Oxford Fm.	Lower Ordovician	sublithographic to fine crystalline limestone about 175 m thick at Winchester stromatolites and calcite filled vugs are common (3)
85010, 85011	Domestic Well	16.7	Bobcaygeon Fm.	Middle Ordovician	interbedded calcarenite and sublithographic to fine crystalline limestone up to 85 m thick (4)
85012	Domestic Well	135	Grenville Series Sediments	Pre-cambrian	crystalline limestone, dolomite, white quartzite with some beds of grey-wacke and quartzite (5)
85013	Oil Well	570	Guelph Fm.	Middle Silurian	cream to white coarsely crystalline biostromal dolostone 100 m thick (6)
85014	Oil Well	143	Dundee Fm.	Devonian	coarse crinoidal and finely crystalline limestone approximately 30 - 35 m thick (6)
85015	Oil Well	1020	Eau Claire Fm.	Cambrian	alternating orthoquartzitic sand and dolostone approx. 60 m thick (6)
85016	Oil Well	663	Trenton Gp.	Middle Ordovician	interbedded finely crystalline shaley limestone and coarse bioclastic limestone (6)
85017	Oil Well	573	Salina Fm.	Upper Silurian	dolostone and limestone with interbedded evaporite sequences of salt and anhydrite (6)

Source: Hunter and Associates (1985)9

From: 1. *Telford (1975 b) [35]*
2. *Telford (1975 a) [36]*
3. *Williams et al (1985 b) [42]*
4. *Williams et al (1985 a) [41]*
5. *Meen and Harding (1942) [26]*
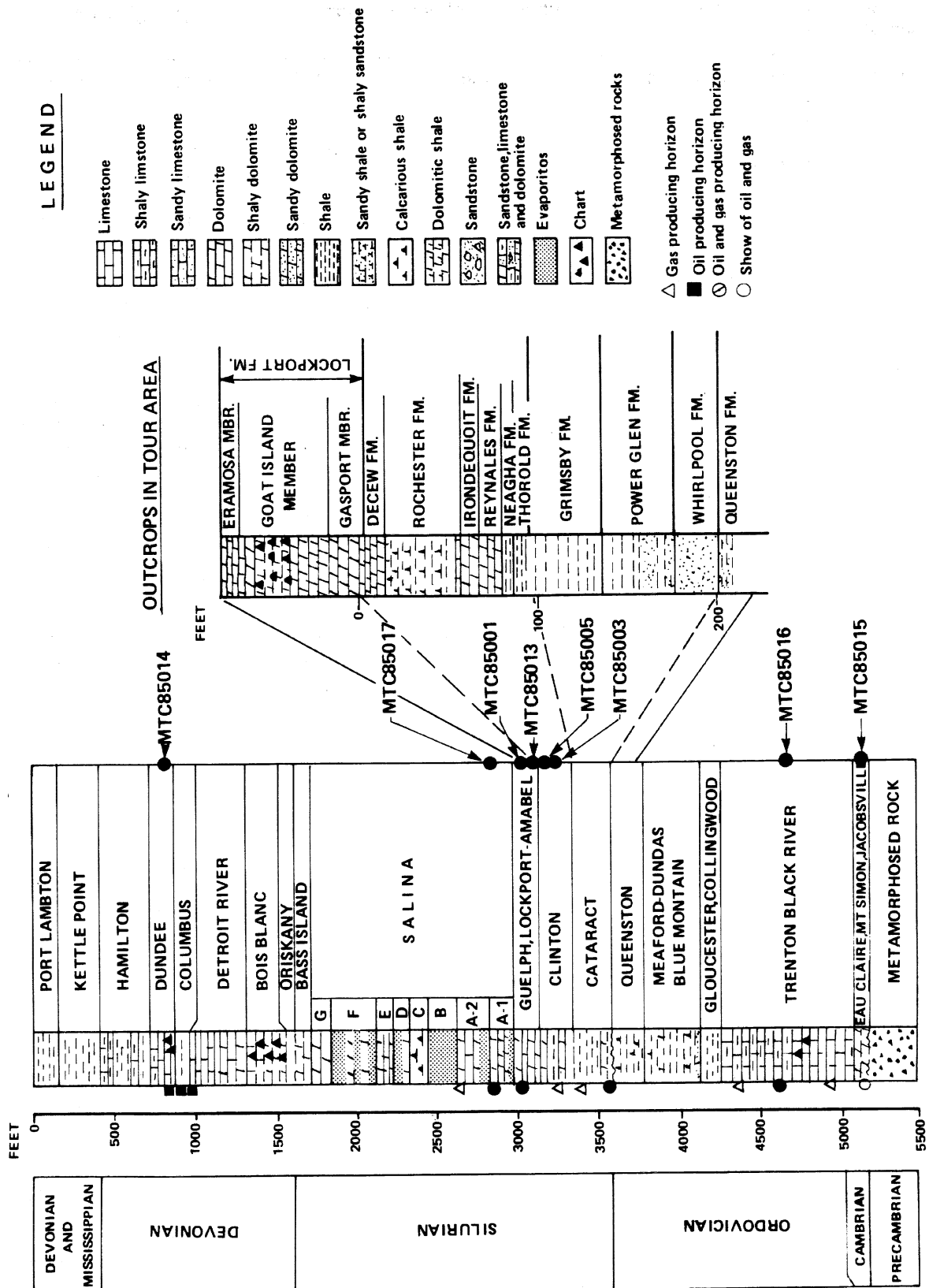6. *Poole et al (1970) [29]*

Figure 3/ Summary of Stratigraphy for Southwestern Ontario

The iodide analytical technique was a modification of the catalytic reduction method described by American Public Health Association [2], and is the method routinely used in the analysis of groundwater at the University of Toronto.

Samples of barnyard manure, septic tank septage, and one landfill leachate caused problems with instrumentation at the MTC laboratory because of the large amount of solids in the sample. These samples were transferred to the MOE laboratory on Resources Road for analysis. Nitrogen analyses were also conducted at this time, but the long storage time between sampling and analysis rendered these values unreliable.

2.3.2/ Duplicate Analyses

Duplicate field samples were taken of a domestic well water (MTC 85010 and 85011), a landfill leachate (MTC 85030 and 85031) and road salt samples (MTC 85018 and 85022, MTC 85019 and 85023, MTC 85020 and 85024 and, MTC 85021 and 85025). The landfill leachate samples contained variable amounts of suspended solids and the duplicate samples may not be truly homogeneous. Road salt samples contained dark coloured impurities in some grains which, again, may give rise to non-homogeneous duplicates. The results of the duplicate analyses are given in Table 5 as a positive or negative percentage difference of the first value.

Table 4/ Summary of Analytical Methods

Parameter	Laboratory			
	1 MTC Downsview Lab	2 MOE Drinking Water Lab Rexdale	3 MOE Sewage Lab Rexdale	4 Beak Analytical Services
pH Specific conductivity Total hardness	Potentiometric Conductivity meter Titrimetric	Potentiometric Conductivity meter Calculation		
Ca	Titrimetric	Atomic Absorption Spectrophotometry	Atomic Absorption Spectrophotometry	
Mg	Calculation	Atomic Absorption Spectrophotometry	Atomic Absorption Spectrophotometry	
Na	Atomic Absorption Spectrophotometry	Atomic Absorption Spectrophotometry	Atomic Absorption Spectrophotometry	
K	Atomic Absorption Spectrophotometry	Atomic Absorption Spectrophotometry	Atomic Absorption Spectrophotometry	
Alkalinity SO_4 Cl NO_3	Titrimetric Gravimetric Potentiometric Colorimetric	Titrimetric Colorimetric Titrimetric Colorimetric	Titrimetric Colorimetric Titrimetric Colorimetric	Titrimetric
NH_3			Colorimetric	
Total Kjeldahl-N			Colorimetric	
Fe I	Colorimetric Colorimetric			Colorimetric

Sources: 1) F.J.Welcher, Standard Methods of Chemical Analysis, 6th Edition, MTC Laboratory, Downsview ,1966.

2) & 3) Handbook of Analytical Methods for Samples, Vol. I and II, MOE Laboratory, Rexdale, Lab Services and Applied Research Branch, Dec. 1983.

4) Standard Methods for the Examination of Water and Wastewater, 15th Edition, Beak Analytical Services, American Public Health Association ,1981.

Table 5/ Duplicate Samples

	MTC Laboratory						MOE Laboratory		
	MTC 85010	MTC 85011	Diff. (%)	MTC 85030	MTC 85031	Diff. (%)	MTC 85030	MTC 85031	Diff. (%)
pH	8.5	8.4	+1.2	7.1	7.1	0			+0.5
Spec. Cond. (µmho/cm)	660	660	0	8400	9400	-11.9	10150	10100	+0.5
Total Hardness (ppm CaCO$_3$)	335	350	-4.5						
Ca (ppm/mg/L)	69	73	-5.8				755	751	+7.7
Mg (ppm/mg/L)	39	40	-2.6				258	258	0
Na (ppm/mg/L)	45	45	0	940	940	0	855	865	-1.1
K (ppm/mg/L)	16.6	16.6	0	581	572	+1.5	590	544	-7.8
Alkalinity (ppm/mg/L CaCO$_3$)	330	320	+3.0				4506	4548	-0.9
SO$_4$ (ppm/mg/L)	73	68	+6.8				46.5	40.0	+14.0
Cl (ppm/mg/L)	34	37	-8.8	1189	1207	-1.5	1229	1256	-2.1
NO$_3$ (ppm N/mg/L N)	<2	<2							
Fe (ppm)	<0.1	<0.1							

Duplicate Samples, Beak Laboratory									
	MTC 85010	MTC 85011	Diff. (%)	MTC 85018	MTC 85022	Diff. (%)	MTC 85019	MTC 85023	Diff. (%)
I	13	14	-7.7	10	10	0	12	10	+16.6
Cl	25	25	0	2560*	33400	-30.33	33900	33400	+ 1.5

Duplicate Samples, Beak Laboratory (Continued)									
	MTC 85020	MTC 85024	Diff. (%)	MTC 85021	MTC 85025	Diff. (%)	MTC 85030	MTC 85031	Diff. (%)
I	11	10	+9.1	10.5*	11	- 4.8	180	320	-78
Cl	25700	24500	+4.7	23900	29600	-28.8	1400	1440	-2.9

*Average of two samples.

Source: Hunter and Associates (1985)

3/ Presentation of Results

3.1/ Major Ion Analyses

Major ion analyses were completed by the MTC laboratory on samples MTC 85001 to 85008, MTC 85010 to 85017, and MTC 85037. Results were obtained within two weeks of sampling. Major ion analyses were completed by the MOE Drinking Water Laboratory on samples MTC 85001 to 85007 and results were obtained within a month of sampling. Samples MTC 85030 to 85037 were transferred from the MTC laboratory to the MOE sewage laboratory, and major ion analyses were completed within two months of sampling.

Analytical results are presented as reported by the individual laboratories in Appendix B.

Results from the MTC laboratory are reported in ppm; those from the MOE laboratory are reported in mg/L.

Cation-anion balances were conducted on all major ion analyses to determine charge-balance error and these are listed in Table 6. For the purposes of the ion balances, total alkalinity reported as equivalent calcium carbonate was converted to bicarbonate. Most balances were within 5% error. Samples MTC 85004 and MTC 85037 exceeded 10% error (-10.3% and -25.7%, respectively). The high error in sample MTC 85037 indicates a problem with the major ion analyses for this sample, and major ion results were subsequently eliminated. Cation-anion balances for samples MTC 85001 to 85007 analysed by the MOE laboratory show an error of less than ±10% except for sample MTC 85004 which had an error of +12.9%.

Analytical results from the MOE and MTC laboratories for samples MTC 85001 to 85007 were compared and plotted graphically in Figures 4 to 8 for Ca, Mg, Na, alkalinity, SO_4, chloride and conductivity. Overall, the cations appear to correlate fairly well. Calcium and magnesium concentrations plotted in Figures 4(a) and (b), respectively, show almost identical trends in variation in analytical results between the two laboratories. The results show that at lower concentrations, both Ca and Mg from the MTC laboratory concentrations are higher than the corresponding MOE laboratory results while, at concentrations greater than 1000 mg/L, MTC laboratory results are lower than the corresponding MOE laboratory results. Sodium, plotted in Figure 5, again shows the same trend as Ca and Mg, except at lower concentrations. There is less difference in sodium values between the two laboratories.

Alkalinity, plotted in Figure 6(a) shows a wide discrepancy in two of the seven samples. The MTC laboratory reported alkalinity of 225 ppm $CaCO_3$ for sample MTC 85002, while the MOE laboratory reported 1296 mg/L $CaCO_3$. In sample MTC 85005, the MTC laboratory reported an alkalinity of 2500 ppm $CaCO_3$ while the MOE laboratory reported only 76 mg/L $CaCO_3$. The cause of the discrepancy is not readily apparent since charge-balance errors are within 6%; however, it may be due to some combination of sample storage and preservation methods and analytical technique.

Conductivity, plotted in Figure 6(b), shows good agreement for all samples except MTC 85005. The MTC laboratory reported a conductivity for this sample of 11 000 μmho/cm compared to the MOE laboratory, which reported 128 000 μmho/cm. Considering the high chloride value reported (> 60 000 ppm) it seems reasonable that the value of specific conductivity reported by the MTC laboratory is too low.

Sulphate shows the widest variation in results between the two laboratories (Figure 7). At values greater than 1000 ppm SO_4, there is a consistency in both sets of values, but below 1000 ppm SO_4, there is a marked variation, with MTC laboratory results being consistently lower than MOE results. This may reflect the difference in analytical technique between the gravimetric method used by the MTC laboratory and the colorimetric method used by the MOE laboratory.

Chloride is plotted in Figure 8. Beak Analytical Services conducted chloride analyses on all samples and the MTC and MOE laboratories did chloride analyses on selected samples. Chloride results from all three labs follow the same general trends, but major discrepancies occur in sample MTC 85002 between the labs of MTC, MOE, and Beak. Sample MTC 85037 also displayed significant discrepancies.

Major ion analyses from the MTC and MOE laboratories were plotted on an expanded Durov diagram (Figure 9). With the exception of sample MTC 85002, both sets of analyses plot fairly close together, suggesting consistent results and fairly good correlation. Samples MTC 85002, 85004 and 85006 represent landfill leachate taken from sanitary landfills near Niagara Falls, St. Catharines and Grimsby, respectively. Except for the MTC laboratory analysis of MTC 85002, all the landfill leachates occupy the sodium (with Mg and Ca) bicarbonate field. The discrepancy in MTC 85002 between the chloride and alkalinity values from the various laboratories produces

Table 6/ Calculation of Charge-Balance Error

	MTC Laboratory		
Sample No.	Cations	Anions	Charge-Balance Error $(E = \dfrac{c - a}{c + a} \times 100)$
85001	31.4	34.1	-4.1
85002	51.2	58.6	-7.3
85003	947	981	-3.4
85004	83	102	-10.3
85005	1776	1884	-1.9
85006	129	134	-2.2
85007	40	36	+4.3
85008	14	13	+3.6
85010	9.0	9.1	-0.6
85011	9.3	8.8	+2.8
85012	6.8	7.4	-3.9
85013	6031	6013	+0.1
85014	296	254	+7.6
85015	3891	3519	+5.0
85016	3204	2945	+4.2
85017	6138	5938	+1.7
85018	3.2	5.4	-25.2
	MOE Laboratory		
85001	31	31.3	-0.4
85002	43	50	-7.3
85003	1085	1058	+1.2
85004	73	94	+12.9
85005	2021	2015	-2.0
85006	119	98	+9.7
85007	34	34	0

Source: Hunter and Associates (1985)

Figure 4(a)/ Comparison between MTC and MOE
Laboratory Analyses, Calcium
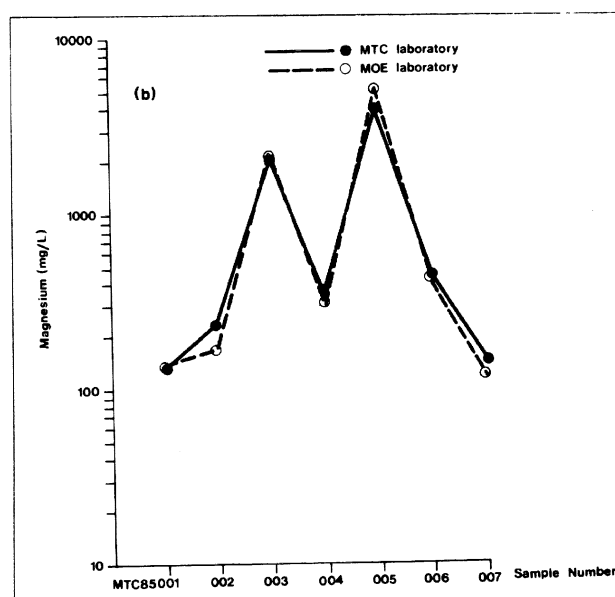
Figure 4(b)/ Comparison between MTC and MOE
Laboratory Analyses, Magnesium

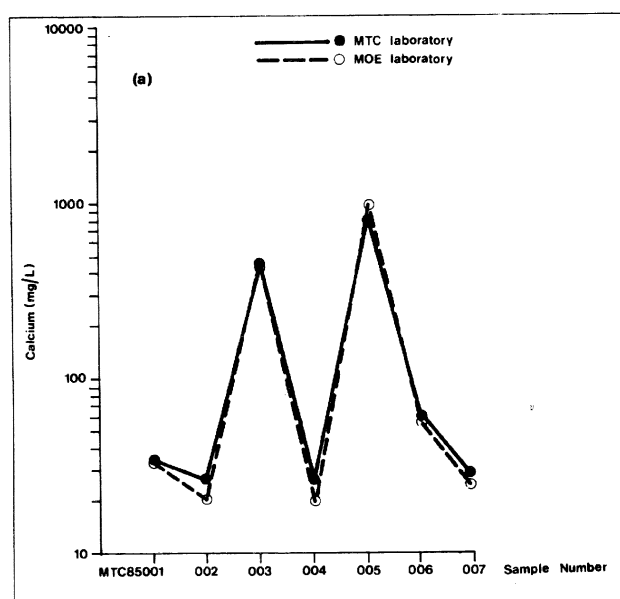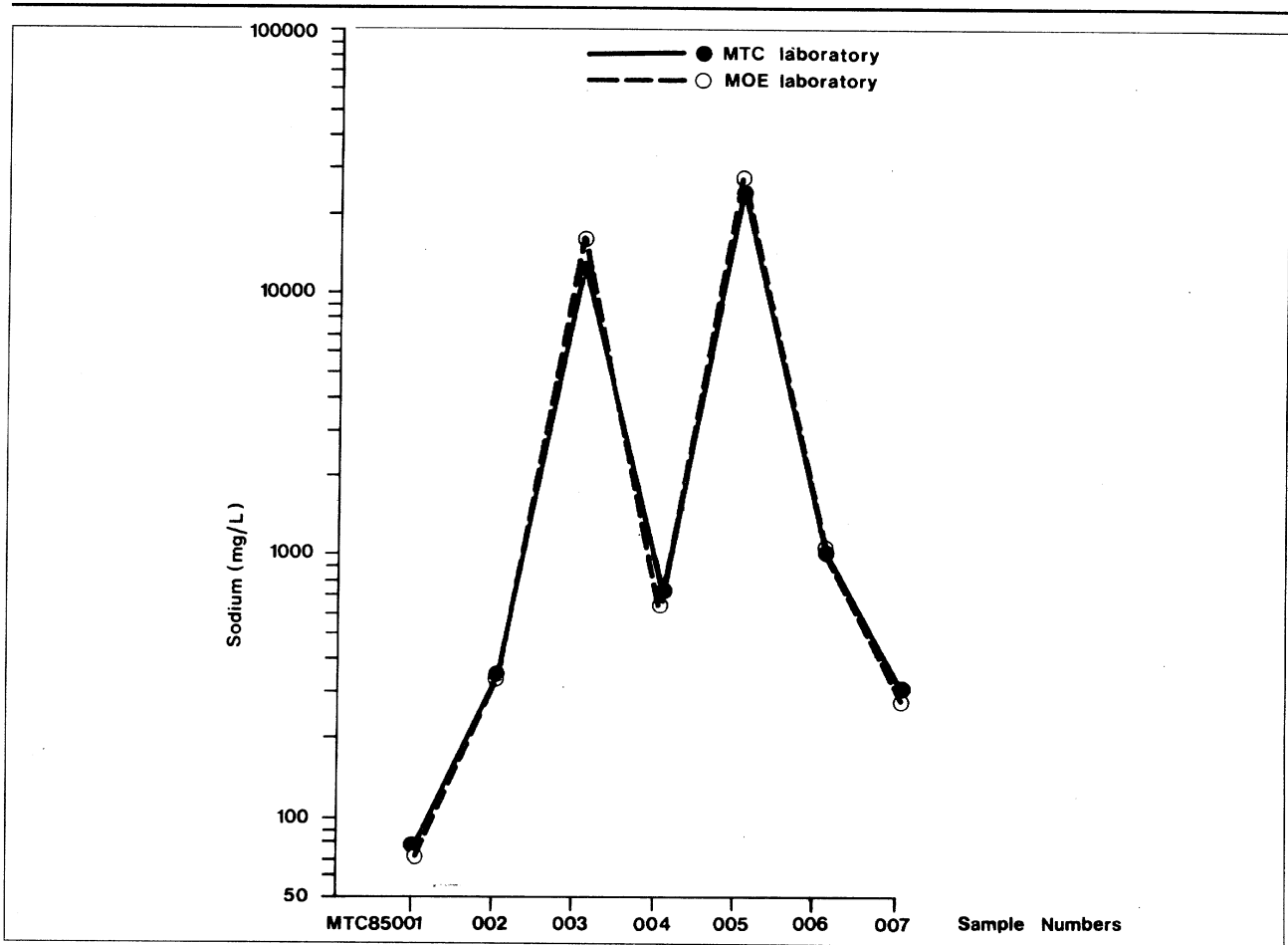Figure 5/ Comparison between MTC and MOE Laboratory Analyses, Sodium
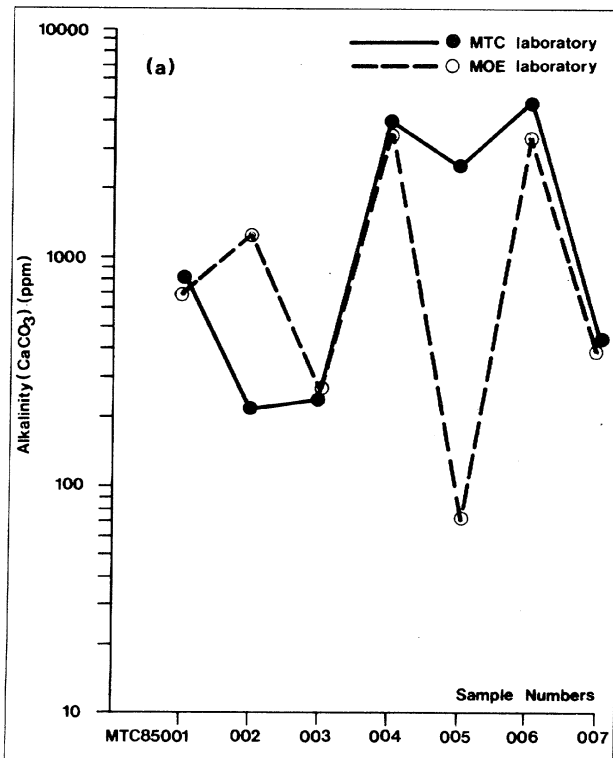
Figure 6(a)/ Comparison between MTC and MOE
Laboratory Analyses, Alkalinity
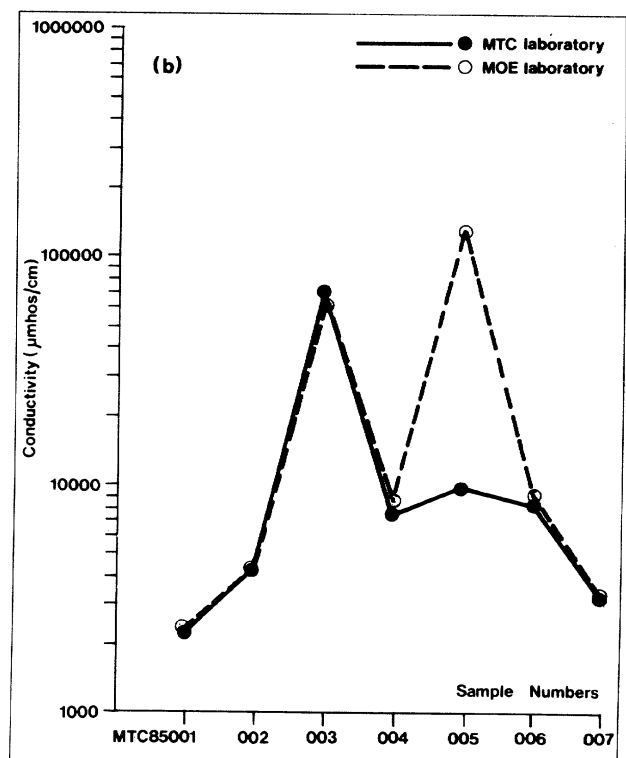
Figure 6(b)/ Comparison between MTC and MOE
Laboratory Analyses, Conductivity
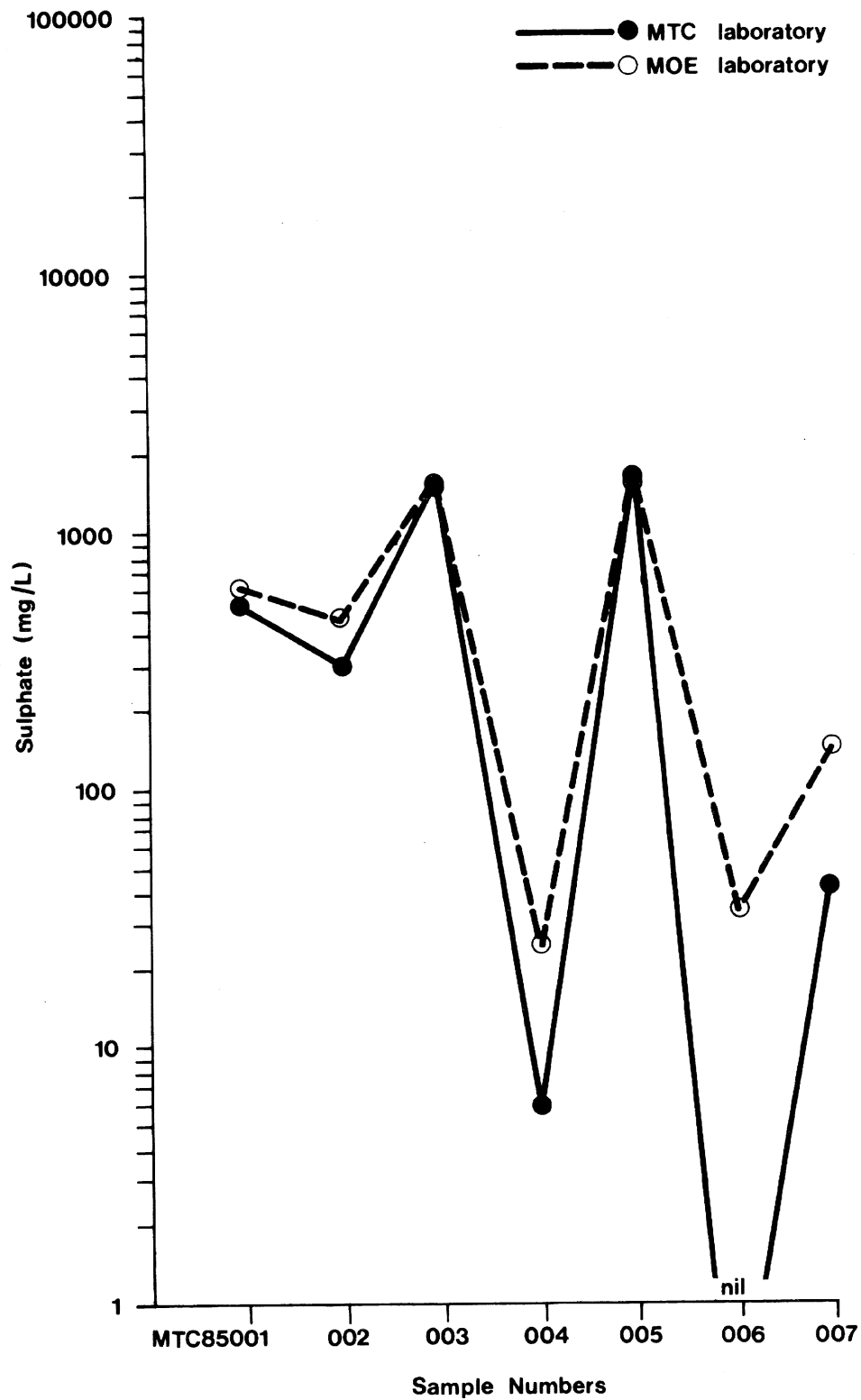
Figure 7/ Comparison between MTC and MOE Laboratory Analyses, Sulphate
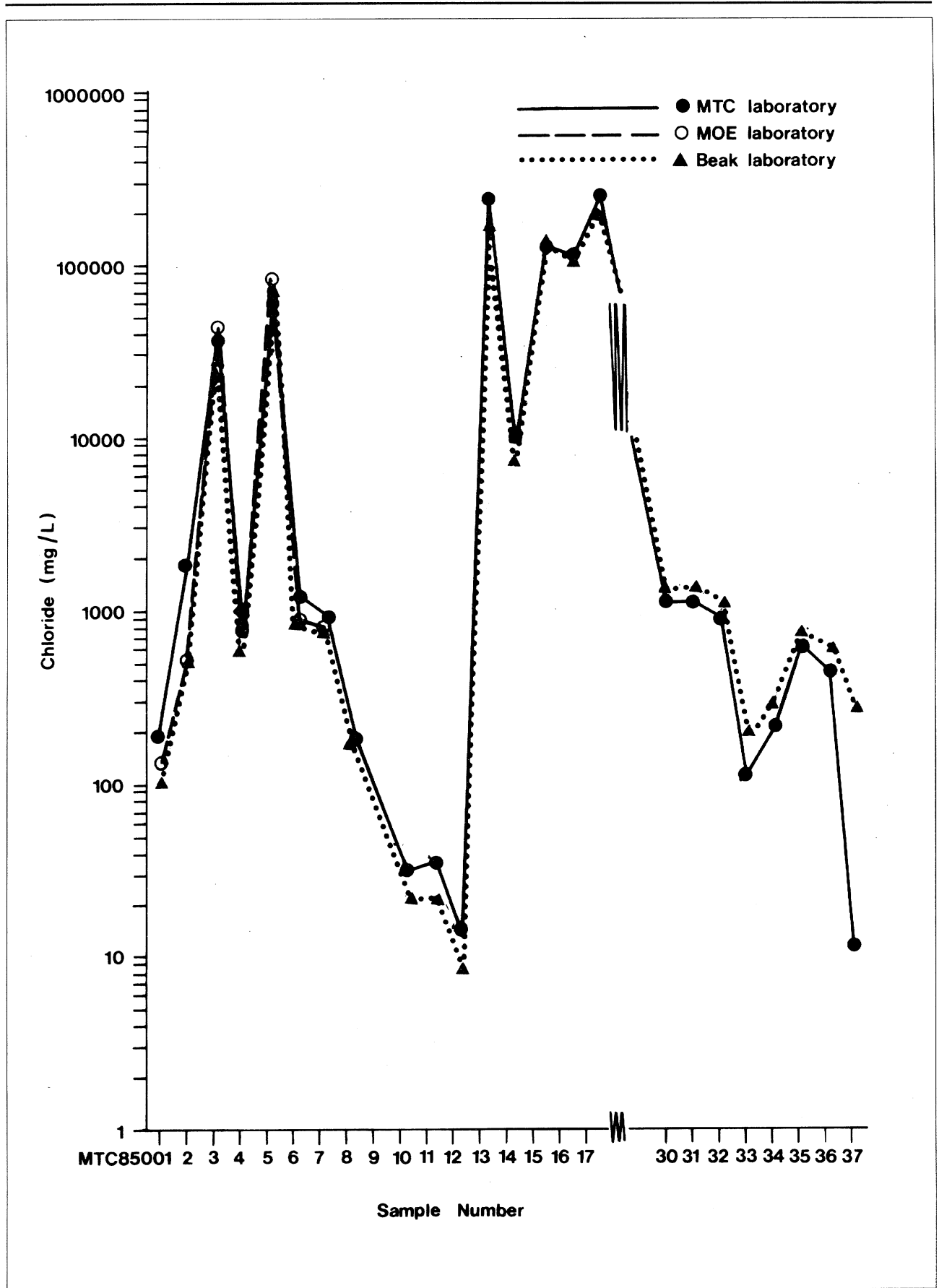
Figure 8/ Comparison between MTC, MOE and Beak Laboratory Analyses, Chloride

LEGEND

1 Niagara Landfill — bedrock
2 Niagara Landfill — leachate
3 Rochester Formation
4 Glenridge Quarry Landfill — leachate
5 Glenridge Quarry Landfill — bedrock
6 Grimsby Landfill — leachate
7 Grimsby Landfill — bedrock
8 Riverside Cedar Campsite Morrisburg
10,11 Bedrock — Williamsburg

12 Bedrock — Cloyne
13 Guelph Fm.
14 Dundee Fm.
15 Eau Claire Fm.
16 Trenton Fm.
17 Salina Fm.
MTC ○
MOE ● Bedrock Groundwater
MTC □
MOE ■ Landfill Leachate

Figure 9/ Durov Diagram of Major Ion Chemistry

the large scatter in the plot. In the cation portion of the Durov diagram, both samples of MTC 85002 plot fairly close together, but the high chloride of the MTC analysis produces a water in the predominantly sodium (with Mg and Ca) chloride field, whereas the high alkalinity of the MOE analysis produces a water in the predominantly sodium (with Mg and Ca) bicarbonate field.

The remaining 12 samples plotted in Figure 9 are bedrock waters. Seven of the 12 samples (MTC 85003, 85005, 85013 to 85017) are sodium chloride waters and occupy the lower right-hand region of the Durov diagram.

Samples MTC 85013, 85015 to 85017 are brines from oil producing formations in southwestern Ontario. All have in excess of 100 000 mg/L chloride. They include formations of Cambrian, Ordovician and Silurian age. These waters are likely connate and probably represent waters originally trapped during initial burial of the sediments. Sample MTC 85014 also occurs within oil producing regions in south-western Ontario. It was sampled from the Dundee Formation of Devonian age. Its chloride content o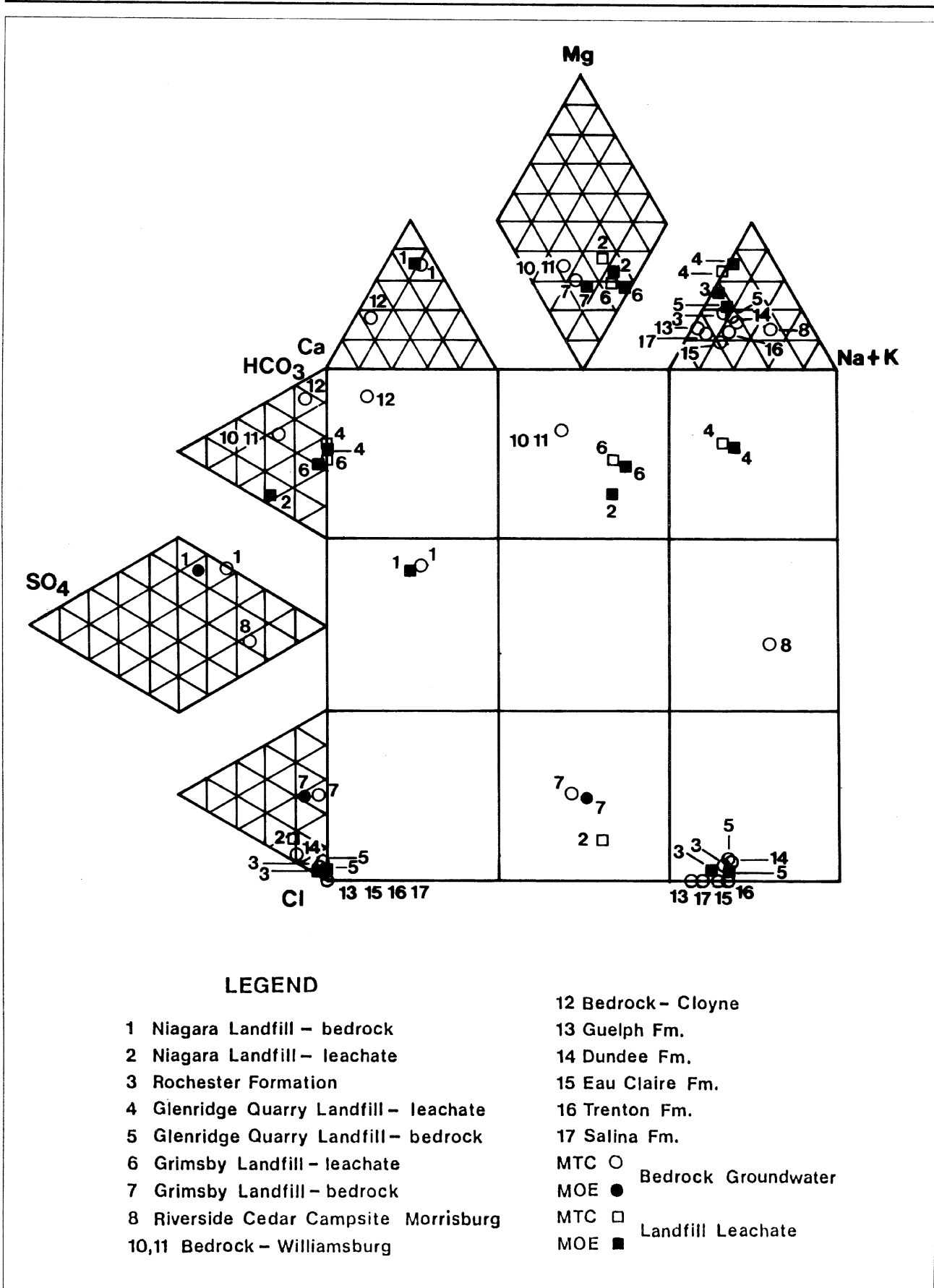f 6880 ppm is considerably less than the brines and much less than sea water. The low chloride along with the relatively shallow depth of sampling (143 m) suggests that this sample may be diluted by mixing with meteoric waters.

Sample MTC 85001 is a calcium-bicarbonate and sulphate water and plots in the central left portion of the diagram. Samples MTC 85003 and 85005 are groundwaters from the shale formation and have high salinity. They are sodium-chloride waters and plot in the lower right-hand corner of the diagram.

Sample MTC 85007 is from a domestic well which penetrates to a depth of 12.5 m in glaciolacustrine silt and is finished in fractured carbonate bedrock. It has a surprisingly high chloride content for a domestic well and plots in the calcium, sodium-chloride portion of the Durov diagram.

MTC 85008 occurs at a depth of 51 m in crystalline limestone in the Morrisburg area, and is overlain by approximately 20 m of gravel, sand, silt and clay. Assuming that most of the alkalinity in this sample is due to bicarbonate, then the low calcium and magnesium concentration relative to bicarbonate, and the high sodium relative to chloride, suggest that this groundwater has evolved to its present position by ion exchange and sodium chloride dissolution as depicted in Figure 1.

Sample MTC 85010 was taken from a depth of 16.7 m in crystalline limestone in the Morrisburg area. It plots in the calcium, magnesium-bicarbonate field of the diagram. Sample MTC 85012 is a calcium-bicarbonate groundwater taken from a depth of approximately 135 m in carbonate metasediment near Cloyne. This sample contained the lowest concentration of chloride of all the samples and, with the exception of

the samples from oil producing formations, was the deepest well sampled.

3.2/ Iodide and Chloride Analyses

Results of iodide and chloride analyses carried out by Beak Analytical Services are given in Appendix B. Iodide concentrations were reported in micrograms/-litre (μg/L) while chloride concentrations are reported in milligrams/litre (mg/L).

Data are plotted as Log I/Cl vs. Log Cl in Figure 10, which shows a fairly good clustering of sample types. For reference, seawater contains 60 μg/L iodine.

Road salt samples cluster very close together and show a depletion of iodide relative to sea water. The average iodide concentration for a 5% solution of road salt taken from 8 samples is 10.6 μg/L. Table salt to which iodide is added, contains 2.5 mg/L (2500 μg/L) in a 5% solution.

Landfill leachate and septic tank septage show relative enrichment in iodide and form a relatively tight grouping. The high iodide content of septic tank septage may reflect the use of iodized table salt in the human diet.

Chemical fertilizers show an extremely large variation both in iodide content and chloride concentration. MTC 85040, a sample of triple superphosphate, contained the highest concentration of iodide in fertilizer. It averaged 54 mg/L (54 000 μg/L) in two samples of a 10% fertilizer solution, while containing only 193 mg/L chloride. Sample MTC 85041, a potash fertilizer, on the other hand, contained only 2 μg/L iodide in a 10% solution but had a chloride concentration of 44 800 mg/L.

Animal manures occupy an area intermediate between the landfill leachates and septic tank septage and the chemical fertilizers. The use of iodine as a disinfectant in dairy farming was expected to produce high iodide in stable manure because of contamination of bedding and manure during washing of cows prior to milking. It was expected that sample MTC 85036 would have high iodide because iodine was known to be used as a disinfectant at the farm where the sample was taken. However, it was found that MTC 85036 had the second lowest concentration of iodide of the six different manure samples. The lowest value occurred in MTC 85037, also from a dairy operation, but one in which iodine was not used as a disinfectant for washing cows. The use of iodine in other livestock farming operations (pigs, horses, poultry, beef cattle), would be restricted to small-scale applications as an antiseptic* and, therefore, would not be expected to contribute significantly to iodide concentration in manure and bedding from cleaned stables. The surprisingly high iodide concentration in the beef cattle, poultry, horse manure and pig manure leachate most likely comes from a dietary source such as iodized salt rather than some external source, such as antiseptic.

Bedrock waters show a very interesting trend. Silurian bedrock water samples from the Rochester, Salina, and Guelph Formations (MTC 85003, 85017, and 85013, respectively) are all depleted in iodide relative to both sea water and road salts.

Bedrock waters from the Cambrian Eau Claire Formation (MTC 85015), the Ordovician Trenton Formation (MTC 85016), the Silurian Clinton Group, (Rochester Formation, MTC 85005), and the Devonian Dundee Formation (MTC 85014) show roughly the same order of magnitude or lower chloride concentration compared to the previous group of samples and yet they are considerably more enriched in iodide.

Bedrock waters MTC 85001 and MTC 85007 both occur within the Silurian Lockport Formation at Niagara Falls and Grimsby, respectively. The differences in iodide and chloride may reflect spatial variation in groundwater geochemistry, or mixing. Samples MTC

85008 and 85010 were taken from Lower and Middle Ordovician carbonate strata, respectively, in the Morrisburg area of southeastern Ontario. Both show high iodide relative to chloride.

Sample MTC 85012, from Cloyne, contains the lowest iodide concentration of all the bedrock waters.

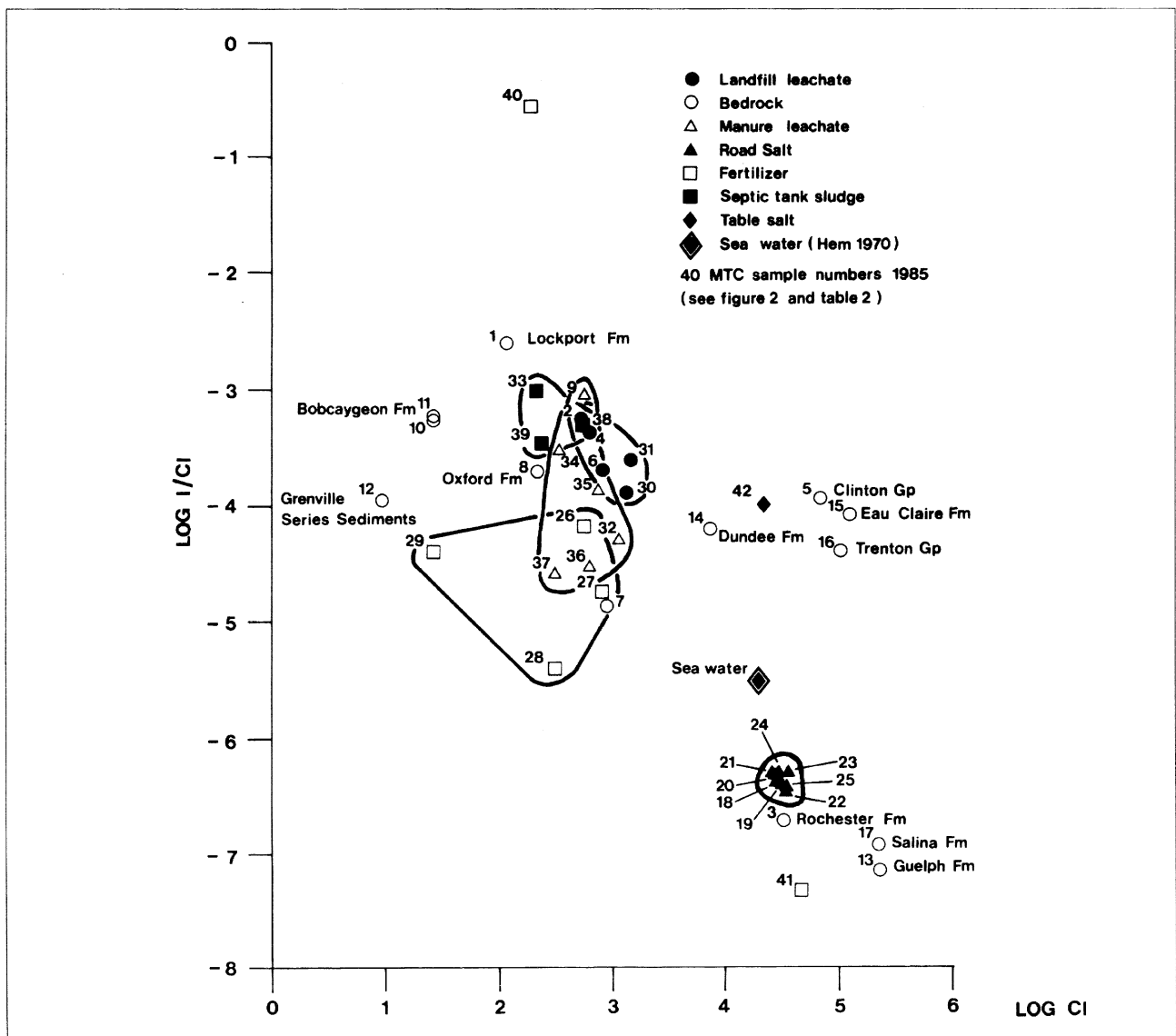*Personal communication, H. Bell, Ontario Ministry of Agriculture and Food, Uxbridge, 1985.*

Figure 10/ Plot of Log I/Cl vs. Log Cl

4/ Application to Road Salt Contamination Investigations

4.1/ Introduction

Rock salt obtained from the four companies which supply MTC with road salt shows fairly consistent low levels of iodide despite geographical variation in the source of the salt. Rock salt is depleted in iodide relative to seawater and to most of the bedrock groundwaters that were sampled during this study.

All of the near surface sources of chloride associated with human and farming activity are also sources of iodide, but there is some evidence that iodide is retarded during infiltration through the soil zone by adsorption onto iron and aluminum hydroxides. As well, leachate produced from landfills, septic tanks and manure piles are likely to influence the iodide concentration in groundwater only locally.

Iodide occurs in a variety of concentrations in bedrock groundwaters. Some Silurian bedrock waters from southwestern Ontario appear to be depleted in iodide relative to road salt, while other Silurian bedrock waters, as well as Cambrian, Ordovician, Devonian from Morrisburg and Cloyne in southeastern Ontario, appear to be considerably enriched in iodide relative to road salt. These variations may reflect spatial and/or temporal geochemical variations in the groundwaters, as well as influences such as mixing.

However, it appears that iodide is a useful parameter in certain road salt contamination investigations involving bedrock groundwaters where surface geophysical techniques may not be applicable. Each claim investigation involving bedrock groundwaters should establish the iodide concentration of the bedrock groundwater by sampling several wells known to be finished in bedrock. As well, a representative sample of road salt should be obtained from the MTC district yard and analysed for iodide.

Providing sufficient contrast exists between the bedrock groundwaters and the road salt, then it may be possible to determine the source of chloride from the iodide concentration.

Several hypothetical cases will be used to illustrate the application.

4.2/ Hypothetical Cases

4.2.1/ Introduction

A hypothetical case can be developed using the available data. Take, for example, sample MTC 85014, which is groundwater sampled from the Dundee Formation at a depth of 143 m. The chloride concentration of this groundwater is 6880 mg/L. Assume that groundwater recharging through the surficial sediments dilutes the chloride concentration of the Dundee Formation to 100 mg/L, and that a well drilled into the upper portion of the Dundee Formation intersects groundwater with this chloride concentration. At some time in the future, the chloride content rises to 1000 mg/L, causing the well owner to claim for road salt contamination damages.

4.2.2/ Hypothetical Case No. 1
(See Figures 11 and 12)

In this case, the Dundee Formation is overlain by thin sandy overburden. Recharging groundwater moves rapidly through the overburden, retaining its calcium bicarbonate character, before mixing with the bedrock groundwaters. Typically, this recharge water would contain low iodide and chloride. When the recharge water mixes with bedrock water, both chlorides and iodide increase in the mixed waters (D). If the recharge water is contaminated with road salt, chlorides would be increased but iodide would remain low in the recharge waters (E) (See Figure 12). Road salt contaminated recharge mixed with bedrock groundwater would have intermediate values of iodide for the 1000 mg/L chloride example.

|	Cl(mg/L)	I (µg/L)
A) Original Dundee Formation groundwater	6880	400
B) Uncontaminated recharge groundwater in surficial sediments	6	3
C) Dilution of Dundee Formation groundwater (A) to 100 mg/L by recharge groundwater	100	9
D) Increase in chloride content of (C) to 1000 mg/L due to mixing with Dundee Fm. groundwater	1000	60
(E) Increase in chloride content of (C) to 1000 mg/L due to mixing with road salt runoff	1000	9
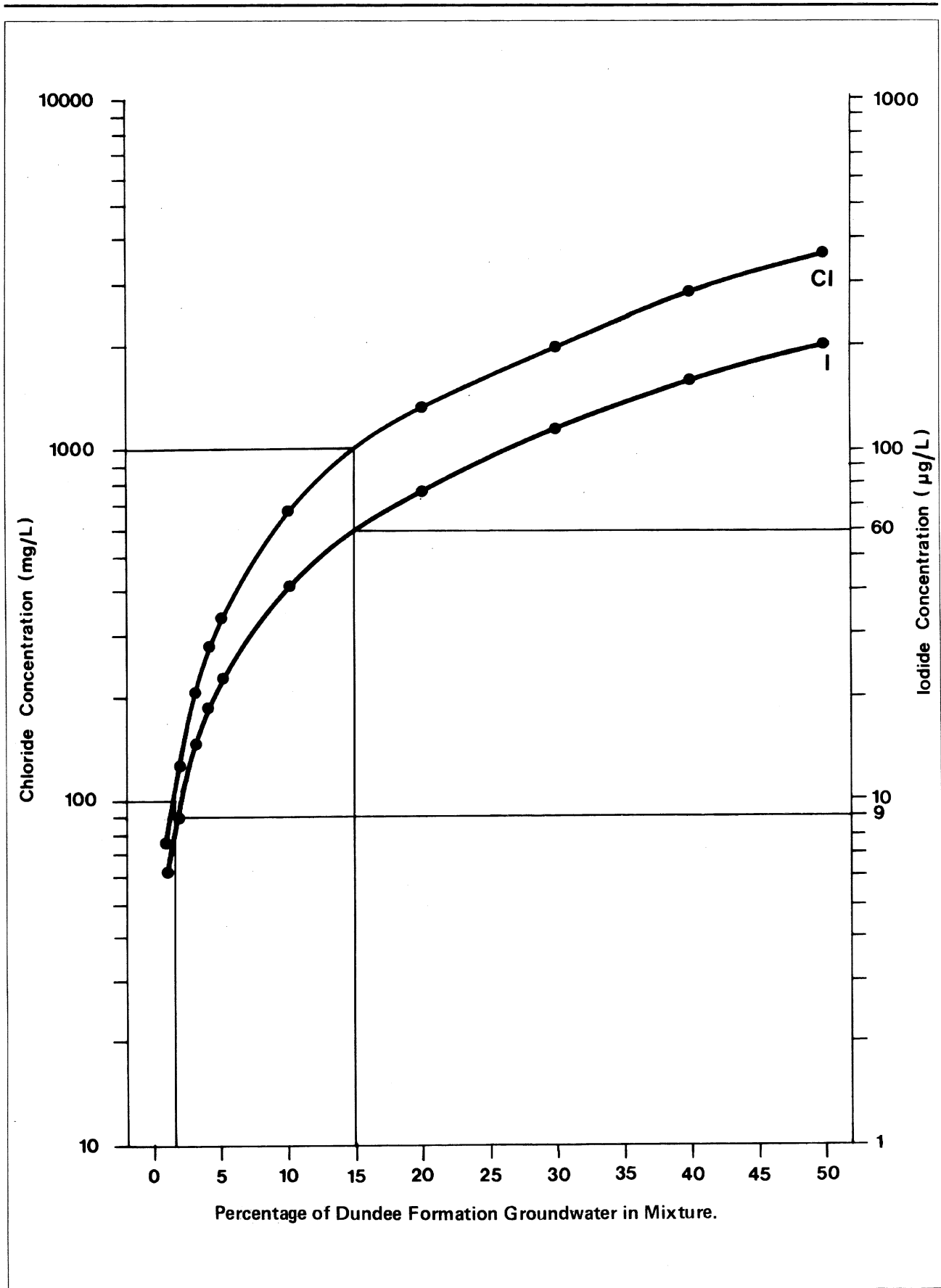
Figure 11/ Chloride and Iodide Dilution Curves for Dundee Formation Groundwater, Hypothetical Case 1
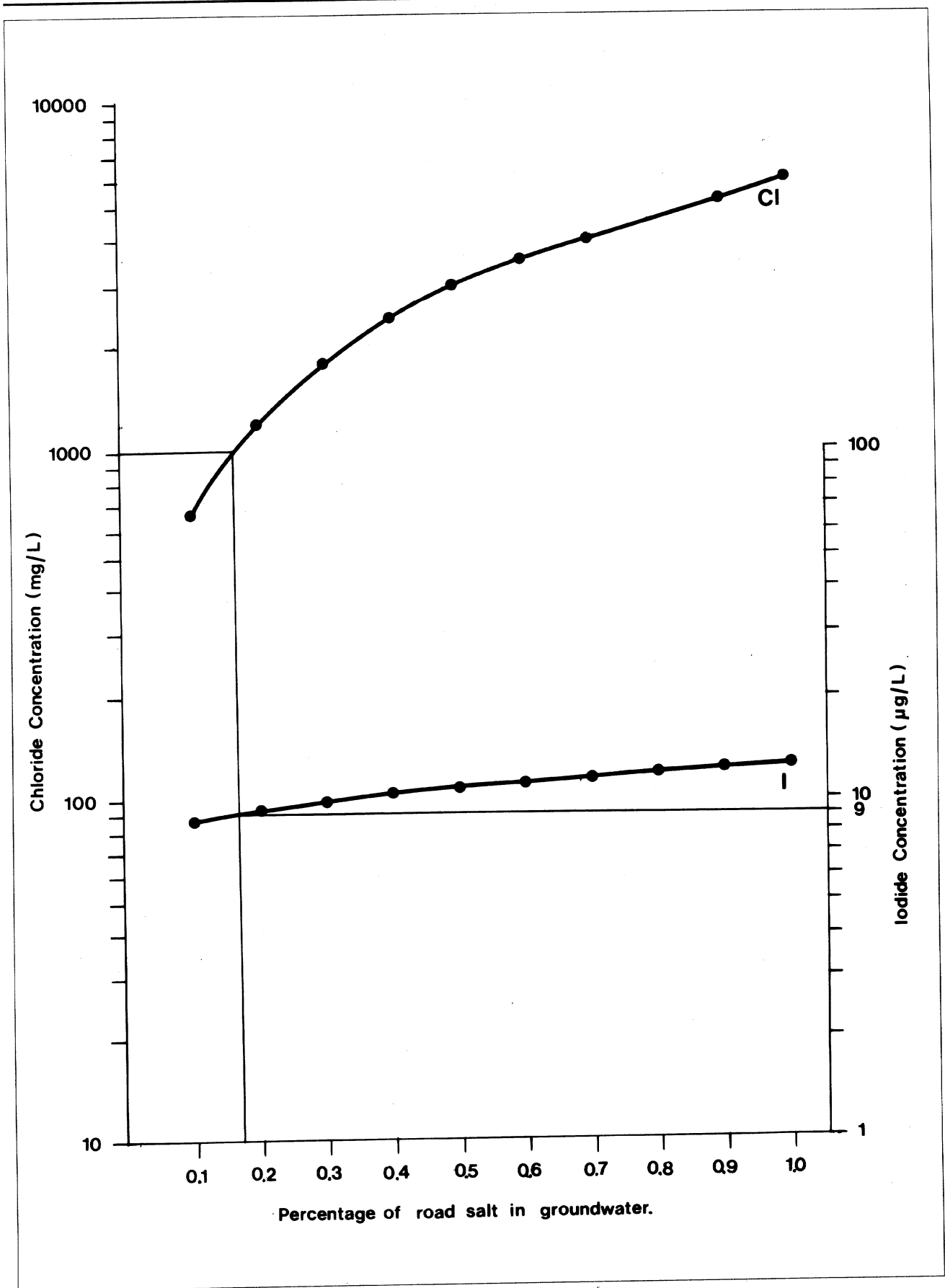
Figure 12/ Chloride and Iodide Dilution Curves for Road Salt, Hypothetical Case 1

4.2.3/ Hypothetical Case No. 2
(See Figures 13 and 14)

In this case, the Dundee Formation is overlain by a thick silty cover. Recharge groundwater moves slowly through the overburden and evolves to an uncontaminated, mature ion exchange groundwater of sodium bicarbonate composition and contains 13 mg/L chloride and 26µg/L iodide.

	Cl(mg/L)	I(µg/L)
A) Original Dundee Formation groundwater	6880	400
B) Mature ion exchange ground-water in surficial sediments	13	26
C) Dilution of Dundee Formation (A) to 100 mg/L by (B)	100	37
D) Increase in chloride content of (C) to 1000 mg/L due to mixing with Dundee Fm. groundwater	1000	80
E) Increase in chloride content of (C) to 1000 mg/L due to mixing with road salt runoff	1000	38

4.2.4/ Discussion

In the first case, the Dundee Formation groundwater is diluted to a potable water by mixing with an uncontaminated recharge water. Figure11 is a dilution curve for both chloride and iodide for the mixing of both waters. Using these curves, the proportion of each groundwater type can be determined for any chloride or iodide concentration and *vice versa*. Therefore, when the chloride concentration in the Dundee Formation groundwater is diluted to100 mg/L by mixing with the recharging groundwater, the approximate proportion of Dundee to recharge is 1.5%. The iodide concentration of this mixture can be read from the graph and is approximately 9 µg/L, which is shown in line (C) in Section 4.2.2.

If the sudden increase in chloride concentration to 1000 mg/L is due strictly to input from the Dundee Formation, then the proportion of Dundee Formation groundwater increases to 15%. This value is read directly off the dilution curve at the 1000 mg/L chloride concentration. The corresponding iodide concentration read from the curve is 60 µg/L and is reported on line (D).

Therefore, the increase in chloride to 1000 mg/L due strictly to the increased proportion of Dundee Formation groundwater increases the iodide concentration in the mixture to 60 µg/L. This corresponds to an I/Cl $= 6.0 \times 10^{-5}$. If, however, the increase to 1000 mg/L chloride is due strictly to road salt, then the final iodide value will be considerably less. Figure 12 is a dilution curve for chloride and iodide for mixing of road salt with groundwater containing 100 mg/L chloride and 9 µg/L iodide (line (C)). At 1000 mg/L chloride, the proportion of road salt to groundwater read from the curve is 0.16%. At this proportion, the value of iodide would be in the order of 9 µg/L, and the mixture would have an I/Cl $= 9.0 \times 10^{-6}$.

In this case, when the chloride increase is due to road salt contamination, the I/Cl is an order of magnitude lower compared to the situation where the chloride increase is due to an increase in the proportion of Dundee Formation groundwater.

In the second case, groundwater movement in the surficial material overlying the Dundee Formation is restricted by the finer grained nature of the aquifer materials compared to the first case. Recharge waters also contain considerably higher iodide than recharge waters in the first case (see line (B), Section 4.2.3.). Figure 13 is a dilution curve for the mixture of recharging groundwater and Dundee Formation groundwater. At a chloride concentration of 100 mg/L, the mixture contains less than 1.5% Dundee Formation water and the iodide concentration of the mixture is about 31 µg/L. Increasing the proportion of Dundee Formation groundwater in the mixture to roughly 15% will cause an increase in the chloride concentration to 1000 mg/L and a corresponding increase in iodide concentration to 80 µg/L. The ratio of I/Cl $= 8 \times 10^{-5}$ for this mixture. Figure 14 is a dilution curve for road salt mixed with groundwater with a chloride and iodide concentration of 100 mg/L and 37 µg/L, respectively (see line (C)). If the increase in chloride concentration to 1000 mg/L is attributed to road salt, then the proportion of road salt in the mixture is similar to the first case, about 0.16%. The iodide concentration can be read from the graph and is about 38 µg/L. The high value is due to the contribution from the groundwater. This produces a ratio of I/Cl $= 3.8 \times 10^{-5}$ which is about one-half the value if the chloride increase is due solely to Dundee Formation groundwater.
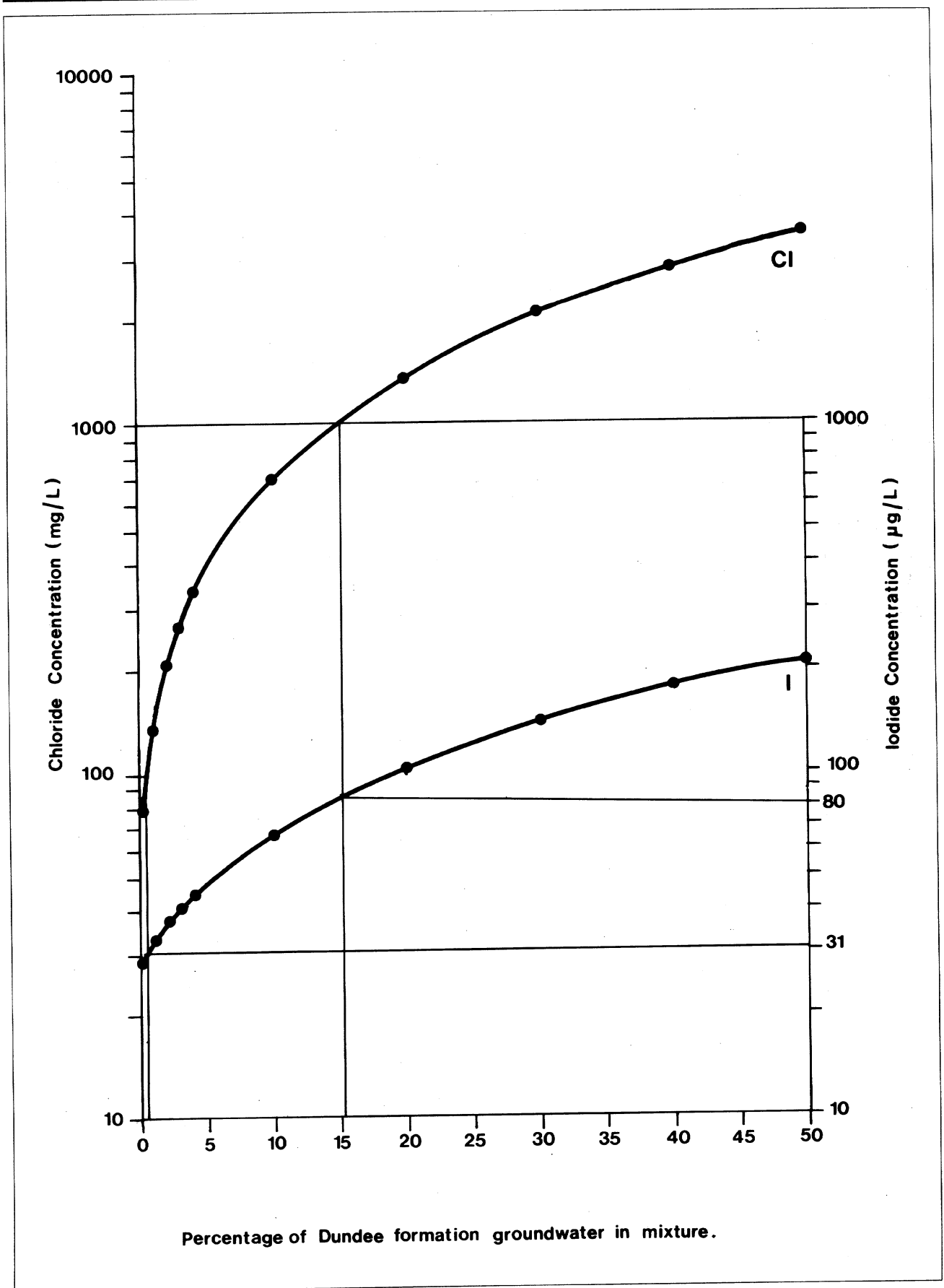
Figure 13/ Chloride and Iodide Dilution Curves for Dundee Formation Groundwater, Hypothetical Case 2
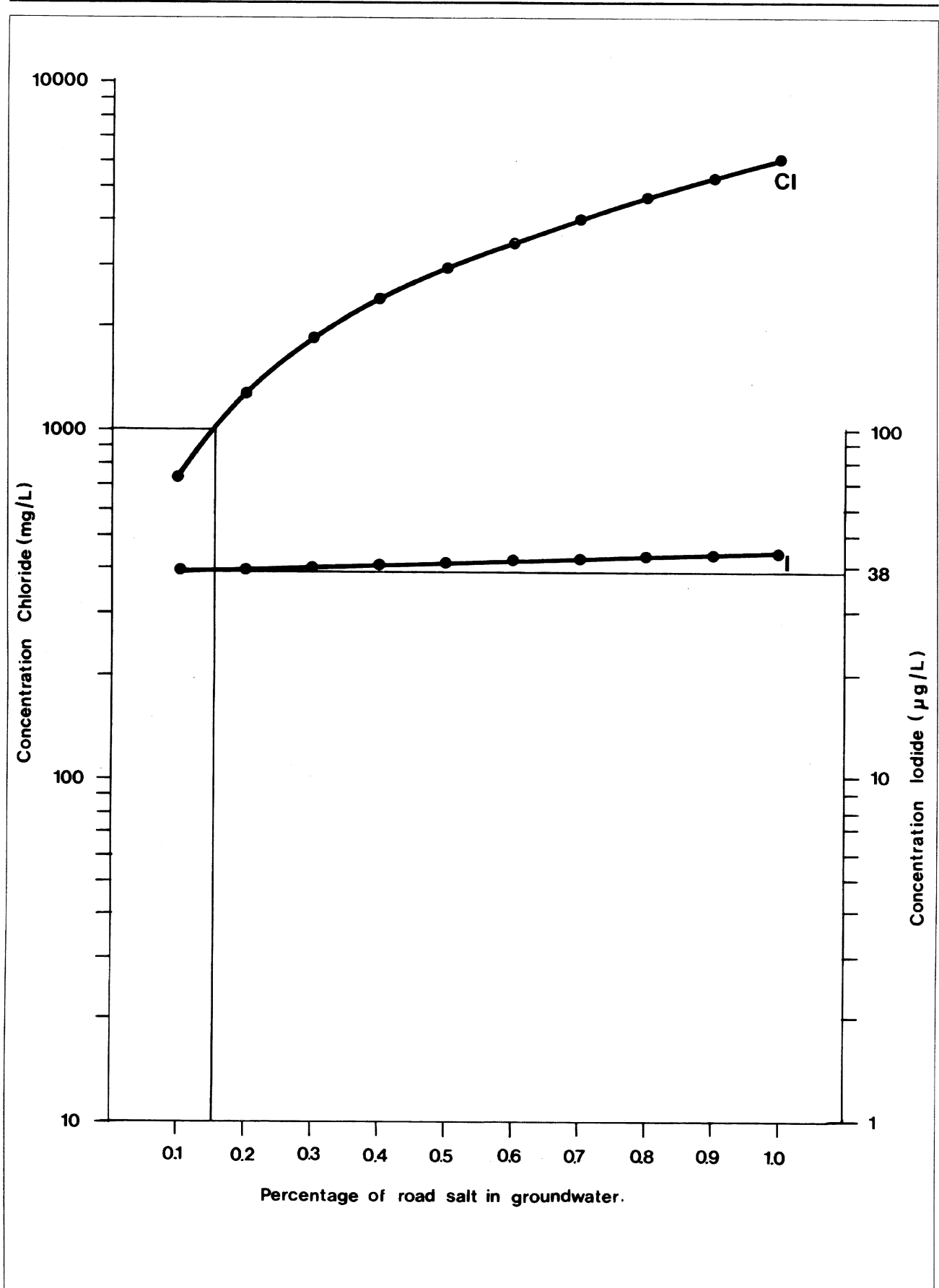
Figure 14/ Chloride and Iodide Dilution Curves for Road Salt, Hypothetical Case 2

5/ Conclusions and Recommendations

5.1/ Conclusions

1/ Iodide can be measured rapidly and inexpensively using a colorimetric technique that is described in standard analytical chemistry method literature. The method is capable of detecting levels to several micrograms per litre.

2/ Iodide occurs in variable concentrations in bedrock groundwaters. The consistency of concentrations within a single formation over a relatively small area has yet to be determined.

3/ Iodide occurs in solution in a number of near surface chloride sources associated with contamination from human activity. Iodide concentrations in some samples are relatively high, but the fate of iodide infiltrating through the unsaturated zone is not well known. Previous work suggests that iodide may be absorbed in the soil.

4/ Iodide concentrations in road salt are very low relative to the chloride content. Road salt is considerably depleted in iodide relative to sea water and most bedrock groundwaters.

5/ The depletion of iodide in road salt, compared to some bedrock groundwaters, may be useful in differentiating the source of chloride in domestic well waters. The application is best suited to situations where:

i) The iodide concentration of recharging groundwater is low due to rapid infiltration through glacial cover which is thin and/or relatively coarse grained.

ii) There is sufficient contrast in iodide concentration between road salt and bedrock groundwaters.

iii) Point sources of chloride (landfill, manure and septic tank leachate) are not likely to affect regional groundwater chemistry. The affect of fertilizer application on iodide concentrations in groundwater requires further study.

5.2/ Recommendations

During groundwater investigations of road salt contamination, groundwater should be routinely analysed for iodide to provide baseline data for iodide concentrations in groundwater from a variety of hydrogeologic conditions. In particular cases where contaminated wells are finished near or within bedrock known to contain high chloride waters, iodide may be a key chemical parameter to assist in establishing the origin of chloride.

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Appendix A/
Sample Locations

Appendix B/
Chemical Analyses

Editor's Note: — The collection of maps comprising Appendix A may be viewed at MTC Head Office in Downsview. Contact Mr J.E. Gruspier, Materials Research Office, Research and Development Branch.

Editor's Note: — Appendix B is a rather large volume of limited interest, thus it is not included in the present report. Those wishing to view the chemical analyses in detail may contact Mr J.E. Gruspier, Materials Research Office, Research and Development Branch.

Appendix C/
Discussion of
Major Sample Groups

C.1/ Road Salt Samples

Four companies supply road salt to MTC. South-western Ontario sources include the Canadian Salt Company mine at Windsor, and the Domtar Inc. mine at Goderich. Iroquois Salt Products Ltd. of Mississauga, imports and distributes rock salt mined at Cleveland, Ohio. Kleyson Transport of Winnipeg, distributes road salt to northwestern Ontario from a source at Esterhazy, Saskatchewan.

Salt deposits in southwestern Ontario have been described by Hewitt [16] and Sanford [32].

Salt is mined from the Salina Formation of Silurian Age. This formation subcrops east of London and dips southwesterly. Trending northeasterly through southwestern Ontario, are regional structural features, the Cincinnati Arch and the Algonquin Arch which separate the Michigan Basin to the northwest from the Appalachian Basin to the southeast.

Structural features and regional geology are shown in Figure C-1.

The Salina Formation has been subdivided into seven lithologic units A-G, and is illustrated in Figure C-2. It reaches a thickness of 460 m near Sarnia. At Windsor, the Canadian Rock Salt Company operates the Ojibway Mine and mines an 8 m thick lens of rock salt in the F unit at a depth of between 290 and 300 m below surface.

At Goderich, Domtar Inc. mines a 24 m thick bed of salt from the A unit of the Salina at depths of between 510 and 535 m.

Salt deposits in Ohio have been described by Landes [23]. They occur within the Appalachian Basin in salt and gypsum beds deposited contemporaneously with the Michigan Basin. These two separate basins may have been hydraulically connected across the Algonquin Arch in the vicinity of Chatham (Hewitt [16]. Salt deposits occur within the Salina Formation which lies south and eastward, away from the Cincinnati-Algonquin Arches. Maximum aggregate thicknesses of salt reach greater than 90 m in the central portion of Ohio. At Cleveland, the International Salt Company mines salt from the Salina Formation at a depth of about 540 m below surface.

At Esterhazy, the International Mining and Chemicals Company produce rock salt as a by-product of potash mining in the Prairie Formation of the Middle Devonian Elk Point Group, from a depth of about 2900 m.

C.2/ Chemical Fertilizers

A description of chemical fertilizer manufacture and use is given by The Fertilizer Institute [37]. Chemical fertilizers apply to materials containing the primary nutrients for plant growth -- nitrogen, phosphorus and potassium. Samples of fertilizer containing nitrogen and phosphorus were obtained from the C.I.L. fertilizer plant in Courtright and from the Co-Op in Uxbridge. These include urea, ammonium phosphate and ammonium nitrate, triple superphosphate, and potash.

Urea, $CO(NH_2)_2$ is formed by the reaction of ammonia with carbon dioxide at elevated temperature and pressure to produce a liquid that is evaporated to produce a solid.

Ammonium phosphate is produced when ammonia is combined with phosphoric acid. Diammonium phosphate (D.A.P.) is the more common form and contains higher nitrogen than monoammonium phosphate (M.A.P.).

Triple superphosphate (TSP) is produced by the reaction of phosphate rock with phosphoric acid. Problems with phosphate sources, particularly those in Florida, relate to the increasing impurity content of iron, aluminum, and magnesium in the rock.

Superphosphate fertilizer from Florida averaged 17 770 μg/kg iodine in two samples [11].

Phosphate fertilizers are produced from the processing of naturally occurring phosphate rock. Most of the world's phosphate is produced in the United States and North Africa. The Phosphoria Formation of Permian Age in northwestern United States is a major source of North American phosphates. Phosphatic rock consists mainly of dark carbonaceous, argillaceous rocks of marine origin. Phosphate occurs in the form of fluorapatite $Ca(PO_4)_3F$ which may make up approximately 80% of the rock [6]. However, fluorapatite is very insoluble and must be processed in order to produce a form of phosphate which can be used by plants.

Potash fertilizers occur naturally in evaporate sequences as KCl. Extensive deposits occur in Saskatchewan. These fertilizers may require extensive processing to remove impurities.

C.3/ Barnyard Manure Leachate

Livestock manure is applied to agricultural lands to supply the soil with nitrogen, phosphorus, potassium and micronutrients. As well, the addition of manure can improve porosity, soil structure and moisture retention capacity. Sweeten and Mathers [34] reviewed the effect of manure spreading on the physical properties of Great Plains soils using different types of manure and variable application rates. They found that application rates of 10 tons/acre provide sufficient nitrogen for most crops. At higher application rates of 50 to 100 tons/acre, significant beneficial changes occurred in the physical properties of the soil. Porosity, infiltration rate, water holding capacity, organic matter content, and soil aggregate particles increased while bulk density was reduced. Fibrous manure from horses, dairy and beef cattle increased bulk density more than non-fibrous poultry manure. Heavy application rates can produce high soil salinity, and concentrations of sodium and potassium in the soil cause dispersion of soil particles which decrease hydraulic conductivity.

Salt concentrations in manure are directly related to salt concentrations in the cattle rations, since most of the dietary sodium and chlorine is excreted.

Robertson [31] conducted a study on the effect of agricultural activity on groundwater quality in interbedded unconsolidated Pleistocene units of gravel, sand, silt and clays near Millsboro, Delaware. Chicken farming is the main agricultural activity in the area and highest nitrate values in groundwaters were associated with wells on or near chicken farms.

Linear regression analysis of chloride and nitrate values showed a strong correlation. The relationship is shown graphically in Figure C-3.

C.4/ Sanitary Landfill Leachate

Infiltration of precipitation through landfill covers and the subsequent leaching of buried refuse produce a leachate which may be potentially harmful to groundwater supplies. Table C-1, taken from Freeze and Cherry [13], lists representative values for inorganic constituents found in landfill sites. It can be seen from this table that chloride is a major inorganic constituent of sanitary landfills and because of its conservative nature, is commonly used to monitor landfill leachate plumes [43]. Figure C-4, taken from Jackson et al. [20], shows a chloride plume emanating from the Gloucester landfill and dispersing in the direction of groundwater flow.

Leachate chemistry is extremely variable in composition due to a number of variables including the age of the leachate, the degree of dilution with groundwater, the amount of infiltration through the cover, chemical processes such as sorption, and biological composition of the refuse.

At Long Island, leachate plumes associated with a landfill were studied by Kimmel and Braids [22], who suggested that the chemical composition of the leachate plume directly at source was most variable due to the "pulsating" nature of the leachate during infiltration. Recharge periods produce pockets of high density leachate which move as discrete slugs through groundwater flow lines towards the base of the aquifer. At Long Island, extensive plumes were developed in the direction of groundwater flow, but they were laterally restricted. No data were found pertaining to iodide concentrations in landfill leachate.

C.5/ Septic Tank Septage

Septic tank systems are the most common form of domestic sewage disposal in areas not serviced by municipal systems. In Ontario, sewage systems are regulated by Ontario Regulation 374/81, under The Environmental Protection Act [14]. A description of domestic and larger systems, including construction details as they apply in Ontario, is available from the Ontario Ministry of Environment.

Brandes [9] estimated the total amount of daily discharge to a septic system at about 126 L per person per day. This discharge consists of black water, which is drained from the toilet, and grey water, which is less polluted and drains from the bathtub and shower, bathroom sink, laundry and kitchen.

The solid material which remains in the septic tank is termed sludge. The supernatant liquid that drains through the tile field is effluent. Regular cleaning of septic systems is necessary to prevent sludge from overflowing the tank and clogging the tile system and soils. The mixture of sludge and supernatant that is pumped out of the tank is called septage.

Chemical analysis of the various components is given in Table C-2. Chloride concentrations are higher in the effluent than in the sludge for the samples from Hawkestone Farm and Orillia Hospital House. They range from 98 to 168 mg/L in the effluent and from 50 to 83 mg/L in the sludge.

The sludge sample from Whitby Experimental Station contained higher chloride in the sludge, which ranges from 139 to 156, compared to the effluent, which ranges from 94 to 96 mg/L. Values for septage lie somewhere between the values for sludge and effluent.

Black water effluent had a mean chloride concen-
tration of 98 mg/L compared to 48 mg/L for grey water.
Chloride from septic tank systems in the United States
ranged from 43 to 75 mg/L.

Brandes [7], from literature and effluent measure-
ments, reported a range of chloride in septic tank
effluent at between 30 and 80 mg/L Depending on
drainage conditions and water table elevations, poorly
sited and inefficient septic tanks can be a source of
chloride contamination to wells and to groundwater.
Chloride is relatively unreactive and moves with the
groundwater.

Dudley and Stephenson[12] found chloride
concentrations in groundwater at least 10 times higher
than background levels in the vicinity of all 11 septic
systems sites tested. Chloride showed a strong
correlation with high nitrate concentrations. At one
site where background chloride concentration was
about 1 mg/L, chloride values of 31.3 mg/L were
reported in groundwater sampled below a septic tank
tile absorption field.

Table C-1/ Representative Ranges for Various Inorganic Constituents in Leachate From Sanitary Landfills

Parameter	Representative Range (mg/L)
K^+	200-1000
Na^+	200-1200
Ca^{2+}	100-3000
Mg^+	100-1500
Cl^-	300-3000
SO_4^{2-}	10-1000
Alkalinity	500-10000
Fe (Total)	1-1000
Mn	0.01-100
Cu	<10
Ni	0.01-1
Zn	0.1-100
Pb	<5
Hg	<0.2
NO_3^-	0.1-10
NH_4^+	10-1000
P as PO_4	1-100
Organic Nitrogen	10-1000
Total Dissolved Organic Carbon	200-30000
COD (Chemical Oxygen Demand)	1000-90000
Total Dissolved Solids	5000-40000
pH	4-8

Source: *Freeze & Cherry 1979*

Table C-2/ Concentration of Contaminants in Septic Tank Systems (Average Data)[1]

Location of Septic Tank	Supernatant						Sludge					
	Hawkestone Farm		Orillia Hospital		Whitby Experimental Station		Hawkestone Farm		Orillia Hospital		Whitby Experimental Station	
Septic Tank Compartment	I	II	I	II	I	II	I	II	I	II	I	II
Total Phosphorus	24.0	19.2	17.0	15.0	10.0	2.4	610	18	170	160	200	135
Soluble Phosphorus	3.6	15.8	12.0	12.0	5.3	1.4	1.7	2.8	33.0	19.0	23.5	6.1
Total Solids	1100	630	1695	840	1700	665	23 350	620	33 550	28 495	35 400	27 070
Suspended solids	400	80	760	65	147	30	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.
BOD$_5$	260	74	300	160	110	34	6 000	380	13 500	15 000	12 000	4 900
TOC	N.T.[2]	N.T.	555	250	65	18	N.T.	100	N.T.	10 400	3 525	2 545
COD	N.T.	N.T.	1424	448	315	75	N.T.	N.T.	35 600	44 200	20 000	17 050
pH	7.7	7.7	7.3	7.2	7.2	7.4	N.T.	8.4	6.8	6.2	6.2	6.8
Ammonia (as N)	160	141	56	68	8.7	10.3	19	22	88	92	47	26
Total Kjedahl (as N)	210	153	85	75	18.7	14.7	2 200	170	630	650	900	298
Nitrite (as N)	0.01	0.01	0.03	0.02	0.04	0.39	0.01	0.01	0.02	0.05	0.01	0.02
Nitrate (as N)	0.44	<0.1	<0.1	0.1	0.17	0.23	0.98	<0.1	<0.1	<0.1	<0.1	<0.1
Chlorides (as Cl)	100	100	165	98	94	96	50	57	78	83	156	139
Sulphates (as SO$_4$)	50	41	41	40	76	80	28	19	21	17	33	51
Aluminum (as Al)	4.0	0.17	0.6	0.14	0.82	0.14	5.3	0.29	14	4	10	7.9
Iron (as Fe)	3.9	1.0	1.3	0.6	0.83	0.80	160	0.75	50	70	380	158
Calcium (as Ca)	60	50	61	55	106	111	66	22	56	82	132	153
Magnesium (as Mg)	7.0	5.0	24	33	15	15	10	6	41	36	34	8
Sodium (as Na)	71	60	93	76	45	46	55	53	89	82	64	61
Potassium (as K)	41	41	20	24	4	4	22	20	26	28	16	10
Hardness (as CaCO$_3$)	88	88	252	274	358	370	N.T.	N.T.	308	352	470	432
Alkalinity (as CaCo$_3$)	680	673	534	539	260	257	N.T.	N.T.	2 070	2 660	704	1 254
Electrical Conductivity (µmho/cm)	1700	1775	1240	1380	922	956	N.T.	N.T.	1 600	1 650	N.T.	1 750

1) Note: — All data except pH and electrical conductivity are given in mg/L.

2) Note: — N.T. indicates "not tested"
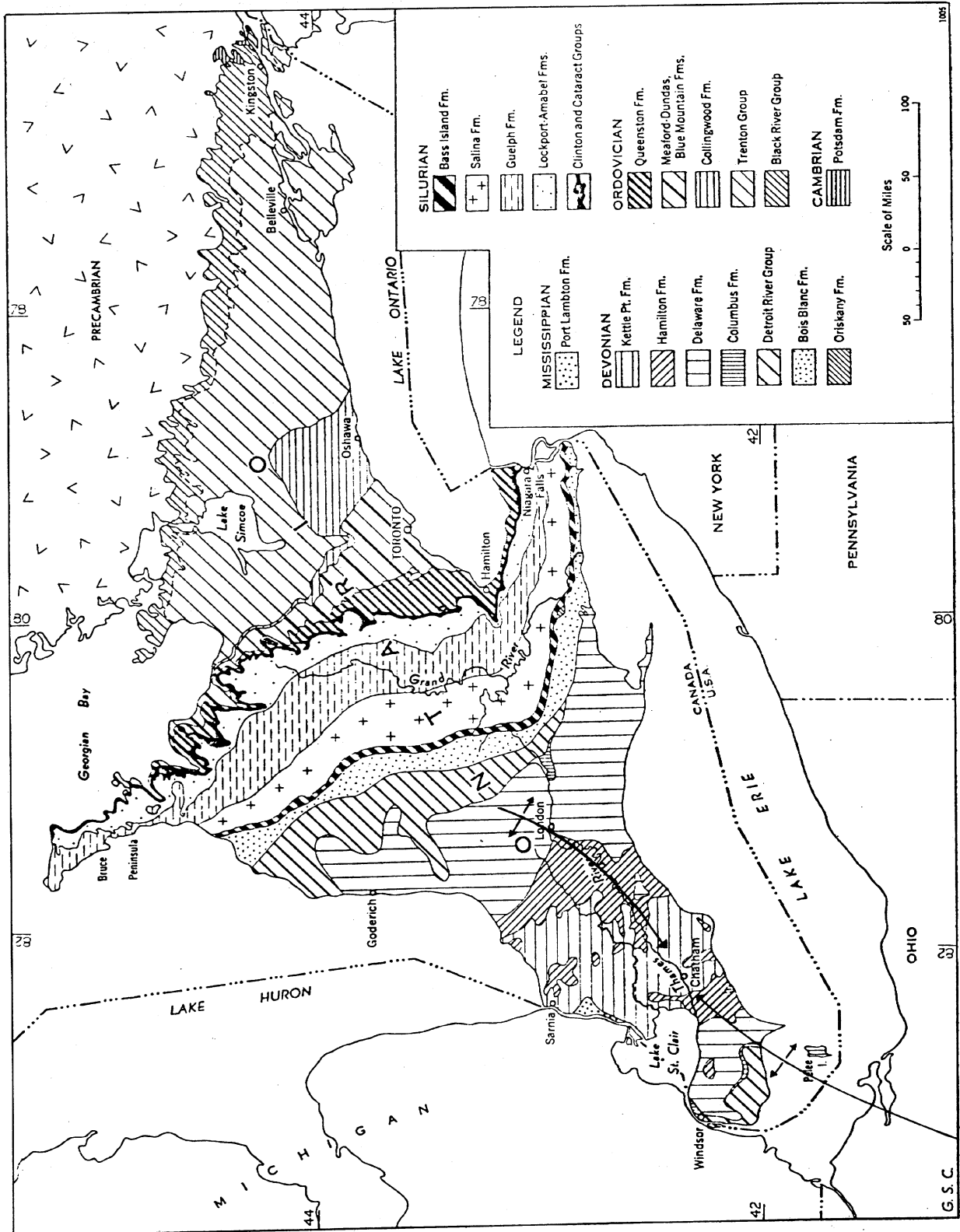
Source: Brandes, 1977 (a)

Figure C1/ Regional Geology of Southwestern Ontario

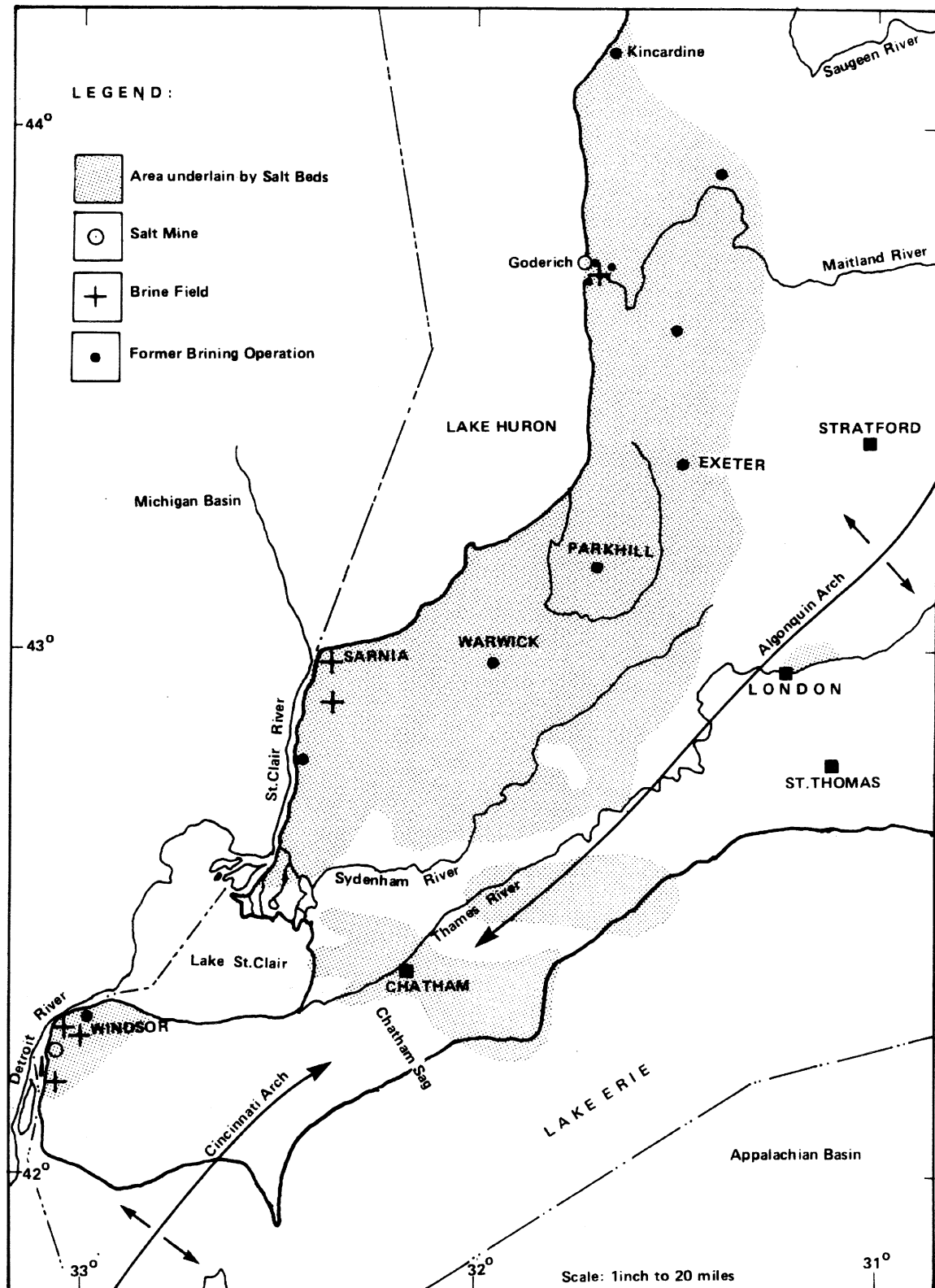*(Courtesy Geological Survey of Canada)*

LEGEND:

Area underlain by Salt Beds

Salt Mine

Brine Field

Former Brining Operation

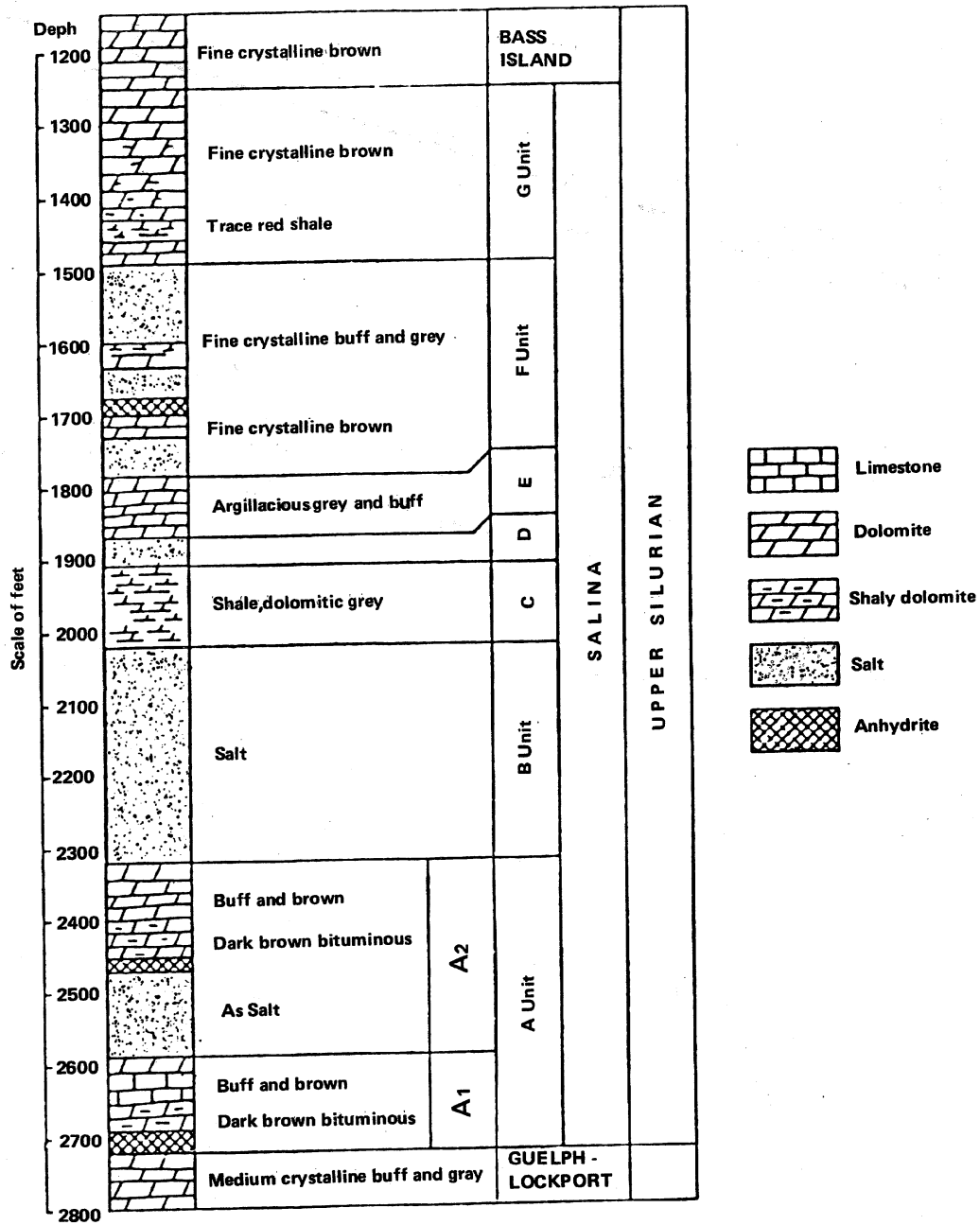Figure C2/ Distribution of Salt in Southwestern Ontario

Figure C3/ Subdivision of the Salina Formation
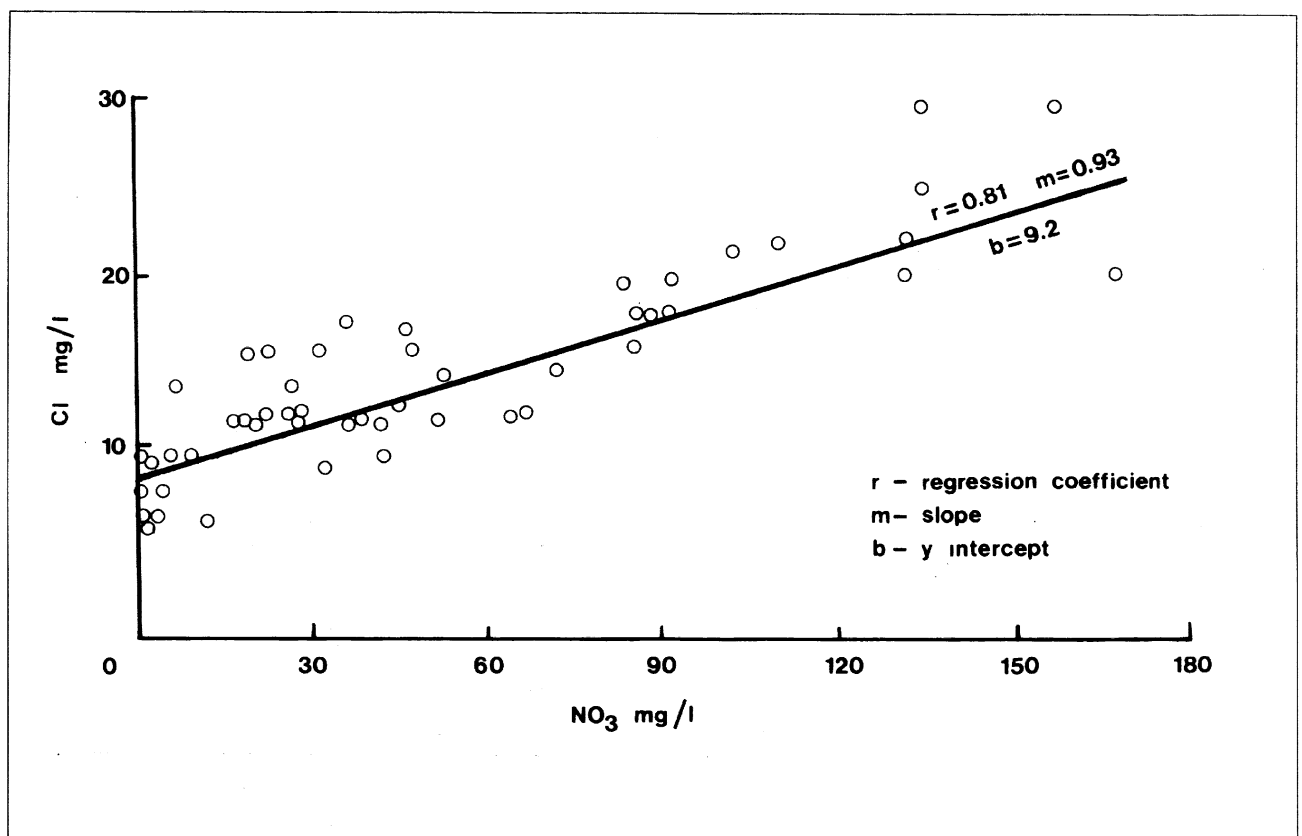
(Source: Hewitt, 1982)

Figure C4/ Relationship of Chloride to Nitrate
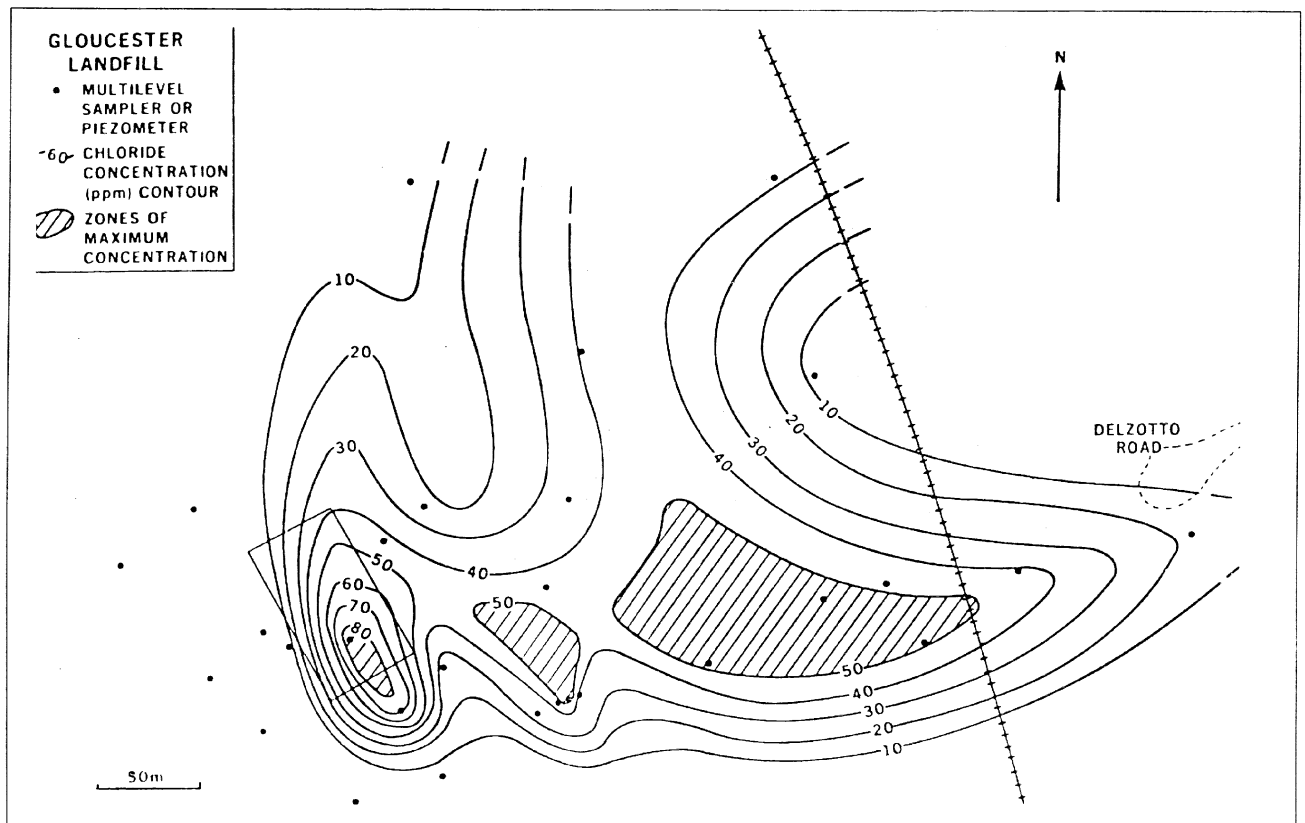
(Source: Robertson, 1977)

Figure C5/ Plan View of Chloride Plume

(Source: Jackson et al., 1985)