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A PRELIMINARY STUDY OF INORGANIC SUBSTANCES AND WATER QUALITY IN THE WELLAND-ST CATHARINES AREA

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MANAGEMENT PERSPECTIVE

Present concern for managing toxic chemicals and their effect on water quality in Lake Ontario has focussed on the loadings of contaminants from the Niagara River. Consonant with this position is the recognition that an assessment of contaminant sources within the Lake Ontario Basin should be carried out in addition to those located on the Niagara River.

The Welland River via the Niagara River, the Welland Canal and Twelve Mile Creek all drain to Lake Ontario. Cities and towns on these water courses have been a location for industrial activity since the mid-1850's because of the construction of the Welland Canal. Commercial activity in this century has been primarily in two areas: pulp and paper (Fraser, Domtar, Kimberly-Clark, Beaver Wood Fibre and Ontario Paper), and metals (Atlas Steels, Stelco, Union Carbide, General Motors, John Deere, Hayes Dana).

Our interest in inorganic substances (anions and metals) in this region stems from two reasons: 1) industrial and urban activity in the region can influence water quality in Lake Ontario in two ways i) from inputs to the Niagara River via the Welland River and the Power Canal and ii) from inputs via Twelve Mile Creek which has the largest tributary flow after the Niagara River, and the Welland Canal; 2) cities and towns (and since mid-1982, Niagara-on-the-Lake as well) obtain their drinking water from the old and new portions of the Welland Canal. This exploratory study shows that concentrations of some inorganics and bacterial populations were high at several stations on the one occasion the area was sampled in January, 1984. A detailed study of inorganics in water and suspended and bottom sediments is warranted on the basis of these preliminary results.

ABSTRACT

Water was sampled once in January, 1984, from ten sites in the Welland-St. Catharines area and were analyzed for chloride, nitrate, fluoride, sulphate, bacterial counts and dissolved copper, zinc, lead and cadmium. Comparison with the IJC water quality objectives for the protection of aquatic life shows that zinc concentrations were higher than the objective in nine samples and in the case of copper three water samples had concentrations above the objective. Samples taken on the Old Welland Canal Spillway generally showed the highest concentrations of inorganics and bacteria. Comparison with drinking water guidelines showed that metal concentrations were well within the allowable limits. High nitrate concentrations in five samples suggests that nutrient enrichment of surface waters is possible and this is an aspect of this study requiring futher investigation. The Spillway samples show poor water quality on the basis of their fecal coliform populations. Twelve Mile Creek and the Welland Canal are estimated to contribute a small amount of zinc and copper to Lake Ontario, but these amounts are minor compared to the loadings of these metals from the Niagara River.

INTRODUCTION

The study area considered in this report includes a portion of the Welland River, the Welland Canal, and Twelve Mile Creek. The Welland River discharges to the Niagara River through the Queenston-Chippawa Channel. The Welland Canal can be regarded as the lifeline of trade and commerce into the inland heart of North America (Jackson and Addis, 1982) and hence serves as the connecting shipping channel between Lake Erie and Lake Ontario. As part of the St. Lawrence Seaway system, the Canal is administered by the Federal Department of Transport. Water from the Welland Canal above Thorold is diverted to the DeCew Falls Electrical Generation Station to augment the flow of Twelve Mile Creek which ultimately drains to Lake Ontario at Port Dalhousie.

The area is the location of a wide range of commercial and industrial activity which includes the production of steel and farm equipment, engines, newsprint and fine paper, and the manufacture of food and textiles. The area is the home of many well-known companies (Jackson and Addis, 1982). Concern for contaminants in Lake Ontario has focussed on the loadings from the Niagara River. Industrial and municipal effluents arising from sources in the Welland River watershed contribute to loadings in the Niagara River (Kaiser and Comba, 1983; Comba and Kaiser, 1984). A further effect on Lake Ontario water quality can arise from municipal and industrial activities in the Welland Canal-Twelve Mile Creek Basin. A sediment plume flowing in an easterly direction to the mouth of the Niagara River has been observed in aerial photographs of the area and at times the suspended sediment load is visibly more concentrated compared with that from the Niagara River (Lane, 1970; Charlton, 1983).

In the context of sources of contamination to Lake Ontario, it is desirable to have an estimate of the amounts of contaminants introduced via the Welland Canal and Twelve Mile Creek, particularly as the latter has the largest mean flow of the major tributaries to Lake Ontario (International Joint Commission, 1976b). Indeed, the definition of and subsequent management plan for the toxic chemical problems of Lake Ontario will require an assessment of contaminant sources within the Lake Ontario Basin in addition to those located on the Niagara River.

In this preliminary evaluation of the concentration levels of inorganic substances in the study area, we have chosen to measure dissolved constituents for three reasons: 1) dissolved species generally have the highest degree of bioavailability, 2) they reflect the biogeochemical equilibria at the time of sampling, i.e. the measurement is the snapshot that reflects the net result of sorption/uptake and desorption processes, and 3) loading estimates are obtained which are better related to potential biological effects.

SAMPLING AND SAMPLE PROCESSING

Water samples were collected in acid-washed plastic bottles for metals and in sterile, amber glass bottles for bacteriological examination on January 10, 1984 at ten locations (Figure 1 and Table 1). The samples were stored at 4°C and those for inorganic analysis were filtered the next day through acid-washed 0.4 μm polycarbonate membranes.

About 900 ml of filtrate were batch extracted with 10 ml of Chelex-100 (Na^+) for one hour with periodic agitation. The resin was collected in a glass column, washed with 20 ml of double-distilled water and eluted with 15 ml of 2M nitric acid followed by 10 ml of double-distilled water. A total of 25 ml of eluate were collected in a volumetric flask.

About 100 ml of filtrate were stored at 4°C until required for analysis by direct flame AAS.

ANALYTICAL METHODS

The Chelex eluates were analyzed for copper, zinc, lead and cadmium by direct aspiration flame AAS using a Hitachi 180-80 Polarized Zeeman Effect Spectrometer. The detection limits for these four elements in the water samples were 0.11, 0.06, 0.30 and 0.03 μg l^{-1}, respectively. The Zn results were confirmed by analyzing the filtrates by Flame AAS for samples which showed high levels of this element. Lead was also determined by graphite furnace atomization of the Chelex eluates because the sensitivity of the flame technique was generally inadequate for the concentrations present. GFAAS yielded a detection limit of 0.02 $\mu g\ l^{-1}$ for Pb in these samples. The cadmium analyses were checked by graphite furnace determination of the filtrates (detection limit was 0.005 $\mu g\ l^{-1}$).

Analytical accuracy was checked by running the NBS Standard Reference Material SRM 1643a, Trace elements in water, either by direct aspiration of the neat reference water for copper and zinc in Chelex eluates and zinc in filtrates or diluted for graphite furnace determinations of cadmium and lead. Triplicate blanks for the Chelex batch procedure gave the following ranges of concentrations which were determined by GFAAS; - copper, 0.02-0.12 µg/l; zinc, 0.04-0.05µg/l; lead, 0.015-0.020 µg/l and cadmium, 0.003-0.005 µg/l.

Fecal coliform and *Escherichi* coli (*E*. coli) were enumerated using standard laboratory procedures as outlined in the Methods for Microbiological Analysis (Environment Canada, 1978) and the procedure of Dufour *et al*. (1981).

Anions were determined on a Dionex 2010i Ion Chromatograph. Because of the wide range of concentrations found in the samples, the analyses were done on neat as well as serially diluted (up to 100X) aliquots of the samples except for the Port Robinson tap water.

RESULTS

The ten sites sampled on January 10, 1984 were chosen to obtain a preliminary picture of the distribution of selected inorganic substances in waters of the Welland-St. Catharines area. This exploratory sampling was viewed as necessary in order to identify those substances and sites which would then be subjected to further detailed sampling to establish temporal and spatial variability. Thus, our comments on the analytical results and the subsequent loading estimates are necessarily of a preliminary nature and hence it would be unwise to view them as either definitive of conditions at a sampling site or worse as the ultimate assessment of inorganic contamination in the study area. Where comparisons are made and estimates given, they are done for the purpose of providing information.

Comparison with the IJC Water Quality Objectives for the protection of aquatic life indicates that zinc concentrations were higher than the objective in nine samples and for copper, three water samples had concentrations above the objective for this metal (Table 2). Comparison with these objectives indicates that the sites on the old Welland Canal Spillway in Thorold and St. Catharines generally have the highest concentrations of four metals. Interestingly, the results show that the non-essential elements, cadmium and lead, are within the objectives at most sites. As would be expected, Port

Robinson tap water is well within the IJC objectives and the Canadian drinking water quality guidelines for all four elements. Note that our data are for the most readily-available fraction of total metal content viz the dissolved fraction, and comparison with the various objectives/guidelines which refer to total concentrations is for information only. In the study area, the suspended load would be expected to be high and hence particulate metal forms could be quantitatively important.

Examination of the specific conductance values (Table 3) suggests that the degree of inorganic contamination is not necessarily a reflection of elevated ionic concentrations. For example, the pond isolating the slag deposits of Atlas Steel from the Welland River has the highest specific conductance, but because of the high pH and the abundance of iron (the sediment in the pond has an ochre colour indicative of iron oxides), removal of copper, cadmium and lead from the dissolved phase is an effective process. The high pH is very likely caused by the caustic sludge (75% sodium hydroxide) disposed on the site combined with slag containing lime, which was used to build the walls of the site (Report of the Nigara River Toxics Committee, 1984).

The effect of steel manufacture on the concentration of zinc is suggested by the relatively high level measured in the sample taken close to the outflow of the Atlas Steel-Mansfield sewer in the Welland River. Fairly high concentrations of this common element in the waters of the area is not surprising, possibly because of the importance of galvanized steel to the production of farm machinery and engines in the study area. The moderately high levels of zinc measured in the final effluent at the Port Dalhousie WPCP and in water taken close to the outflow of the Port Weller WPCP, can be viewed as evidence to support the above argument.

Fluoride levels in the ten samples are not elevated compared with background or natural levels which have been reported as ranging from 0.20 to 0.40 mg/l (International Joint Commission, 1976b). The high concentration of fluoride in the Atlas Steel holding pond most likely reflects the straightforward chemical leaching of the sediment substrate by the alkaline water in the pond. Although the pond is immediately adjacent to the Welland River, any effect on water quality in the river would be expected to be minimal as the pond is small and contact with the river is restricted by a concrete weir except during overflows (Report of the Niagara River Toxics Committee, 1984). The guidelines for Canadian drinking water quality are exceeded only at the site immediately downstream of the Beaver Wood Fibre plant.

The average concentration of chloride in Lake Erie and Lake Ontario in 1968 was reported to be about 24 mg/l. The samples taken at or close to the two WPCP sites described above have the highest concentrations of chloride in our data presumably because of road salting operations. The significantly lower chloride level in Port Robinson drinking water relative to Lake Erie, which is the source water, cannot be explained at this time. The Welland Canal was ice-bound during sampling and, flows under the ice would be expected to be lower than the ice-free period and hence the concentration of chloride might have been higher than the mean value for Lake Erie because of road salting in the area. Welland Canal flow on January 10, 1984 was just over 1 million cubic metres per day which was the average flow for the month (personal communication: T. Copeland, St. Lawrence Seaway Authority). The June average flow for 1984 was about 3.4 times the January flow.

In the case of nitrate, high concentrations were measured at sites close to pulp and paper manufacture and the Spillway sampling site at the confluence with Twelve Mile Creek was also high in nitrate. As for the other anions analyzed in this study, the drinking water guideline is provided for information. High concentrations of nitrate were also measured at the outflows of the two water pollution control plants. As these are located near the mouths of the Twelve Mile Creek and the Welland Canal, an estimated 287 kg/day of nitrate are discharged based on a mean daily flow of 69,000 cubic metres (Report on the 1984 discharges from municipal wastewater treatment facilities in the Great Lakes Basin: Ontario, October 1985). This estimated loading is ca 0.2% of the average daily loading from the Niagara River in 1982 and 1983 (Kuntz, 1985). From a nutrient enrichment perspective, the high levels of nirate can be compared with concentrations in the Great Lakes which are always less than 1 mg/l (Matheson, 1973). The possible effect of the high concentrations of nitrate in waters of the area on the composition of algae and phytoplankton is a subject that is beyond the scope of this investigation.

Sulphate concentrations in the ten samples were less than the maximum acceptable concentrations for drinking water. Sulphate concentrations in Lake Erie and Lake Ontario in 1968 averaged about 28 mg/l (Weiler and Chawla, 1969). The relatively high levels in the samples, although in three cases higher than the drinking water objective (150 mg/l) would not be expected to pose a threat to health or water quality.

DISCUSSION

Measurements of chemicals in streams and in pipe discharges from industries are commonly used to obtain loadings to receiving waters. For the Report of the Niagara River Toxics Committee (1984), loadings were estimated from the analysis of one to eight composite or grab samples. As stated in the introduction to this report, an assessment of contaminant sources in addition to the Niagara River would be helpful in devising a management plan for toxic chemicals in Lake Ontario. Loading estimates were therefore made using the Spillway samples with this objective in mind. Clearly, the same provisos would have to be made for this exercise as for the Niagara River Report viz loadings can vary with the level of production at the time of sampling. Nevertheless, the Data Quality Subcommittee of the Niagara River Toxics Committee concluded that, despite the limited data from each point source, the results could be viewed as indicators to characterize a discharge and to estimate loadings. Our objective in estimating loadings of zinc and copper was to compare the relative contribution from sources in the Welland-St. Catharines area to the Niagara River.

Dissolved zinc concentrations for samples from the old Welland Canal Spillway (stations 32, 33 and 36b) are within the range reported by the Ontario Ministry of the Environment (1982) for the old Welland Canal at Glenridge Avenue, St. Catharines, viz 20-690 µg/l with an annual geometric mean of 60 µg/l. The total flows from the Ontario

Paper Co., Fraser, Inc., Kimberly Clark of Canada Ltd. and Domtar Fine Papers to the Spillway amount to 162,400 cubic metrs per day (Report on the 1984 Industrial Discharges into the Great Lakes Basin: Ontario, June, 1986). Using an average concentration in the Spillway of 130 µg/l, the daily loading of dissolved zinc is estimated to be 22 kg. Similarly, based on a 1984 flow of 120,900 cubic metres per day the loading downstream of the GM-McKinnon Industries plant is estimated to be 10.8 kg per day. Flow from Beaver Wood Fibre in 1984 was 14,700 cubic metres per day and an estimated zinc loading in this area would be 5 kg per day. The discharge for the Port Dalhousie WPCP has been used in the estimation fo nitrate loadings and for zinc the loading is estimated to be 2 kg per day. And from the Port Weller WPCP, the estimate is 3.5 kg of zinc per day. This estimate is conservative because the sample was not taken in the final effluent discharge but at a point at which contributions from the Welland Canal could not be excluded. As the flow of the Canal during this ice-bound period was just over 1 million cubic metres per day, the estimate at Port Weller could be low. Even if the dissolved zinc at these sites becomes bound to fine particles, the likelihood of sedimentation is small and hence most of the estimated zinc loading would enter Lake Ontario. The total daily loading of zinc from Twelve Mile Creek and the Welland Canal is therefore estimated to be about 43 kg which is about 1.5 to 1.9% of the loadings from the Niagara River for 1983 and 1982 (Kuntz, 1985). On an annual basis, the loadings from sources in our study area work out to be 14 tonnes of zinc. While extrapolation of a daily loading in this fashion is not strictly justified, comparison with Kuntz's annual loadings from the Niagara River shows the same picture viz our loadings are 1.4 to 1.8% of the figures for the Niagara River. To put this into perspective, the sources in our estimates constitute ca 0.1% of the zinc loadings, not including contributions to the Niagara via the Welland River. Once again, it should be noted that our data are for dissolved zinc and we are comparing them to total zinc loadings. Hence, although the actual percentages may be slightly higher, the essential point is that the Welland Canal and Twelve Mile Creek are a minor source of zinc to Lake Ontario in comparison to the Niagara River. In contrast, loadings of zinc to Lake Ontario from Hamilton Harbour might be expected to be significant relative to the Niagara River. On an annual basis, between 24 and 65 tonnes of dissolved and particulate zinc are discharged from Hamilton Harbour (OME, 1985) which represent between 3 and 8% of the annual loadings from the Niagara River for 1982.

CONCLUSIONS AND RECOMMENDATIONS

Water samples from the old Welland Canal Spillway and the outflow of the Port Dalhousie WPCP which has received treatment show high fecal coliform populations and concentrations of zinc which were higher than the IJC water quality objectives for the protection of aquatic life on the day of sampling. Estimates of the loadings of zinc from Twelve Mile Creek and the Welland Canal to Lake Ontario suggest that these streams are minor contributors of zinc to Lake Ontario compared with the Niagara River. Further intensive sampling over at least one year is required to determine whether these preliminary results are representative of conditions in the study area or were a single sporadic event. Such sampling would be necessary in order to obtain the most accurate loadings of chemicals of concern to Lake Ontario. The investigation should also include other elements classified as Group I (i.e., requiring immediate attention) e.g. chromium, nickel, silver, mercury, beryllium, selenium and antimony (Niagara River Toxics Report, 1984). As well, suspended and bottom sediments should be sampled to determine biogeochemical availability and transport pathways of the above elements.

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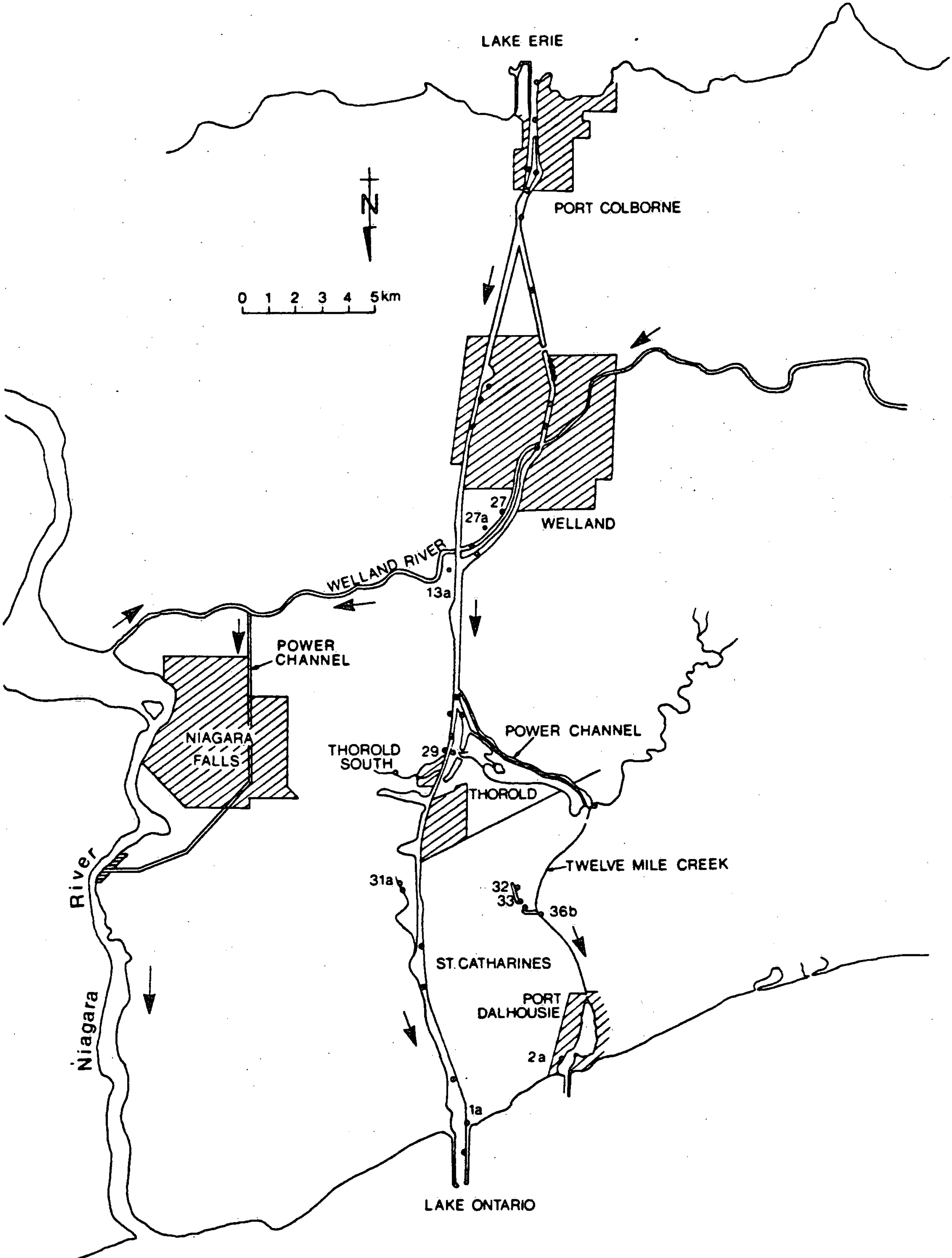

LAKE ERIE
PORT COLBORNE
N
0 1 2 3 4 5km
27
27a
WELLAND
WELLAND RIVER
13a
POWER CHANNEL
NIAGARA FALLS
POWER CHANNEL
THOROLD SOUTH
29
THOROLD
TWELVE MILE CREEK
31a
32
33
36b
River
Niagara
ST. CATHARINES
PORT DALHOUSIE
2a
1a
LAKE ONTARIO

FIGURE 1.

Table 1. Locations of sampling stations in the Welland-St. Catharines area.

Station	Location
33	Below Kimberley-Clark (Spillway)
32	Below Fraser (Spillway)
29	Below Beaver Wood Fibre
27	Atlas-Mansfield Storm Sewer - Welland River
27a	Atlas Steel - Slag Heap Ditch
36b	St. Catharines (Spillway)
13a	Port Robinson Tap Water
31b	General Motors - McKinnon Industries
1a	Mouth of the Welland Canal - WPCP Discharge
2a	Port Dalhousie WPCP - Final Effluent

Table 2. Concentrations ($\mu g\ l^{-1}$) of dissolved Cu, Zn, Pb and Cd in waters of the Welland-St. Catharines area.

Station	Cu	Zn	Pb	Cd
33	51	137	3.8	0.405
32	9.5	129	2.4	0.100
29	3.8	345	2.7	0.162
27	3.2	134	1.1	0.026
27a	<0.1	42	0.8	<0.005
36b	25	150	7.7	0.156
13a	4.5	6	0.21	0.026
31b	2.5	89	2.7	0.216
1a	1.3	95	1.0	<0.005
2a	1.4	62	0.50	0.055
IJC Water Quality Objective	5	30	5	0.2
Drinking Water Quality Guidelines	1000	5000	50	5

Table 3. pH, specific conductance and coliform counts of water samples from the Welland-St. Catharines area.

Station	pH	Sp. Cond. uS cm^{-1}	Fecal Coliform Counts/100 ml	E. coli Counts/100 ml
33	6.58	680	28,000	N/A
32	6.76	690	110,000	40,000
29	6.80	835	N.S.	N.S.
27	7.90	1630	<10	<10
27a	12.4	2850	N.S.	N.S.
36b	7.40	810	240,000	40,000
13a	8.14	375	N.S.	N.S.
31b	7.66	400	180	100
1a	7.29	1275	N.S.	N.S.
2a	6.97	1250	107,000	67,000

N.S. - Not Sampled.

N/A - Severe Bacterial Contamination (no accurate count).

MOE Guidelines: Fecal Coliform (geometric mean) <100 counts/100 ml.

IJC Guidelines: Fecal Coliform <200 counts/100 ml.

Table 4. Concentrations (mg l^{-1}) of anions in waters from the Welland-St. Catharines area.

Station	Fluoride	Chloride	Nitrate	Sulfate
33	0.62	40	50	196
32	0.72	42	53	125
29	2.4	36	76	315
27a	8.3	676	14	110
36b	0.65	76	47	162
13a	0.19	18	7.0	38
31b	0.31	24	18	60
1a	0.53	142	47	148
2a	0.54	160	36	117
Drinking Water Quality Guidelines	1.5	250	45	500