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A PRELIMINARY STUDY OF INORGANIC CONTAMINANTS AND WATER QUALITY IN THE WELLAND RIVER WATERSHED

K.R. Lum, M.E. Comba, P.R. Youakim and
E.A. Kokotich

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Inorganics Section
Environmental Contaminants Division
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, Canada L7R 4A6

Environment Canada

Executive Summary

Present concern for the environmental impact on and degradation of water quality in Lake Ontario has focussed on the loadings of contaminants from the Niagara River. The Welland River watershed has been a favoured 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). Water quality in the Welland River Watershed is of concern because of two reasons:- 1) cities and towns (and since mid-1982 Niagara-on -the-Lake) from Welland to St. Catherines obtain their drinking water from sources in the watershed (including the Old and New portions of the Canal) and 2) industrial and urban activity in the watershed influences water quality in Lake Ontario in two ways:- 1) from inputs to the Niagara River via the Welland River and the Power Channel and 2) from inputs via Twelve Mile Creek which has the largest tributary loading after the Niagara River, and the Welland Canal. This exploratory study shows that the efficiency of removal of some inorganic contaminants and bacterial populations is inadequate for the high loadings of these constituents in the watershed. A more detailed study of other inorganic contaminants in water as well as sediments is warranted on the basis of the results of this study.

Abstract

Surface water was sampled once from ten locations in the Welland River watershed and were analysed for dissolved Cu, Zn, Pb, Cd, Chloride, Nitrate, Fluoride, Sulphate and bacterial counts. The IJC Water Quality Objectives for the protection of aquatic life were exceeded at nine of the sites for zinc. The IJC objective for the protection of aquatic life was exceeded at three of the sites for Cu. The stations on the Old Welland Canal Spillway were found to be the most contaminated. Concentrations of the four metals were well within the maximum allowable concentrations for drinking water for all samples. Concentrations exceeding the maximum allowable drinking water guidelines for nitrate were measured at five stations. Effluents in the Spillway and those which have already received treatment show poor water quality on the basis of their fecal coliform populations. Total loadings of contaminants, in particular Zn and Cu, from the Welland Canal and the Spillway to Lake Ontario would be expected to be significant.

Introduction

The Welland River Watershed is the location of a wide range of commercial and industrial activity which include 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).Recent concern for increasing levels of 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). Further impact on Lake Ontario water quality can arise from inputs from activities in this area through the Welland Canal and Twelve Mile Creek. A sediment plume flowing in an easterly direction to the mouth of the Niagara River is often seen in aerial photographs of the area. At times the suspended sediment load is visibly more concentrated compared with that from the Niagara River (Charlton, 1983). Apart from a study of the biological impact of discharges from Cyanamid of Canada Limited on a section of the Lower Welland River (Dickman et al, 1980), there has been little work on the identification of trace inorganic contaminants and their levels in the watershed. Dickman et al observed high pulses ("shock loading") of nitrogenous and carbonaceous compounds from the Cyanamid plant. Their conclusions were, in part, based on conductivity measurements above and below this plant. This study was intended as a preliminary evaluation of the degree and extent of inorganic contamination of receiving waters in the Welland River Watershed and to serve as a guide to planning a more detailed study of loadings of contaminants from this area to Lake Ontario. Such a study has been recommended by the Niagara River Toxics Committee (See Section 7.4.4.4).

Sampling and Sample Processing.

Single water samples were collected in appropriate containers once only on January 10, 1984 at selected locations (Figure 1 and Table 1) on the organic contaminant sampling grid used by Comba and Kaiser (1985). All samples were stored at 4^oC. Samples for inorganic analysis were filtered the next day through acid-washed 0.4um polycarbonate membranes.

About 900ml of filtrate were batch extracted with 10ml of Chelex-100 (Na^+) for one hour with periodic agitation. The resin was collected in a glass column, washed with 20ml of double-distilled water and eluted with 15ml of 2M HNO_3 followed by 10ml of double-distilled water. A total of 25ml of eluate were collected in a volumetric flask.

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

Analytical Methods.

The Chelex eluates were analyzed for Cu, Zn, Pb and Cd by direct aspiration flame AAS using a 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 ug 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 ug l^{-1} fof Pb in the samples. The cadmium analyses were checked by Graphite Furnace determination of the filtrates (detection limit was 0.005 ug l^{-1}).

Fecal coliform and Escherichia 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 diluted (up to 100X) aliquots of the samples except for the Port Robinson tapwater.

Results .

IJC Water Quality Objectives for the protection of aquatic life were exceeded at the ten locations most frequently for zinc (Table 3). The objective for copper is exceeded at three sites, two of which are associated with pulp and paper manufacture. On the basis of these criteria the sites on the old Welland Canal Spillway in Thorold and St. Catherines are the most contaminated. Interestingly, the results show that the nonessential elements, Cd and Pb, are within the objectives at most of the sampling sites. As would be expected Port Robinson tapwater is within the IJC objectives and the Canadian Drinking Water Quality Guidelines for all four elements. It should be noted that our data are for the most readily-available fraction of the total elemental 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 very important.

Examination of the specific conductance values (Table 1) suggests that the degree of inorganic contamination is not necessarily a reflection of elevated ionic concentrations. For example, the pond isolating the slag and other waste 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 suggestive of iron oxides), removal of Cu, Pb and Cd from the dissolved phase is an efficient process. The high pH is very likely caused by the caustic sludge (75% NaOH) disposed in the site combined with slag containing lime which was used to build the walls of the site (Report of the Niagara River Toxics Committee, 1984).

The impact of steel manufacture on effluent quality is evident in the high dissolved Zn concentrations found in the McMaster Avenue storm sewer as it discharges into the Welland River. Contamination of the watershed by this element is widespread possibly because of the importance of galvanized steel to the production of farm machinery and engines in the study area. The high levels of Zn being discharged at the two STP effluents sampled in this study suggest that this element is inefficiently removed by treatment processes at the high input levels produced by industry.

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^{-1} (International Joint Commission, 1976b). The high concentration of fluoride in the Atlas Steel holding pond is most likely the result of the leaching of the sediment substrate by the alkaline water. 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 (Table 4) 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^{-1}. The two STP effluents are the sources of the largest loadings of this substance to Lake Ontario. 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 although there is still flow under the ice, one might have expected this to be lower than the ice free period and hence a level of chloride somewhat higher than the mean value for Lake Erie.

In the case of nitrate, five of the sites showed concentrations exceeding the Canadian drinking water guidelines for this substance on the basis of human health considerations. From a nutrient enrichment perspective, the high levels of nitrate can be compared with concentrations in the Great Lakes which are always less than 1 mg l^{-1} (Matheson,1973). The possible effect of the high loadings of nitrate from the Welland River watershed on the composition of phytoplankton in Lake Ontario is a subject that is beyond the scope of this investigation.

Sulphate concentrations at the sampling locations are within the maximum acceptable concentrations for drinking water at all sites. Sulphate levels in Lake Erie and Lake Ontario in 1968 averaged about 28 mg l^{-1} (Weiler and Chawla, 1969). The relatively high levels in the watershed, although in three cases exceeding the drinking water objectives (150 mg l^{-1}), would not be expected to be pose a threat to health or water quality.

Discussion.

It was beyond the scope of this preliminary study to assess the degree to which the samples collected are representative of effluents and discharges in the watershed on an annual basis. However, dissolved zinc values for the old Welland Canal Spillway (stations 31,32 and 36a) are within the range of levels reported by the Ontario Ministry of the Environment (1980) with an annual geometric mean of 60ug l^{-1}. Given an average flow of around 170,000 m^3 day^{-1} in the Spillway, combined with the effluents from McKinnon Industries (77,000m^3 day^{-1}), Beaver Wood Fibre (13,000m^3 day^{-1}) and the STP plants at Ports Weller and Dalhousie (272,000m^3 day^{-1}), a conservative loading of 12 tonnes of dissolved zinc enters Lake Ontario annually. Loadings of dissolved copper would be of the same order of magnitude. It should be noted that these calculated loadings do not take into account the dissolved metal loadings to the Niagara River via the Welland River eg from the McMaster Avenue Sewer. Nevertheless, nutrient and contaminant loadings via the Welland Canal and Twelve Mile Creek would be expected to be significant. Recently, Comba and Kaiser (1984) have shown that these two inputs constitute a more significant source of methylene chloride to Lake Ontario than the Niagara River. Twelve Mile Creek has the largest mean flow (180 m^3 sec^{-1}) of the major tributaries to Lake Ontario (International Joint Commission,1976b). In the case of zinc, the annual loadings to Lake Ontario via the Niagara River are ca. 136 tonnes (Report of the Niagara River Toxics Committee, 1984). To put this into perspective, the sources in the Welland River watershed considered in this report, constitute ca 0.1 % of the mean annual flow of the Niagara River, but contribute 9 % of the zinc loadings. This percentage could be larger because 1) our data refer to dissolved zinc and 2) the cessation in 1983 of steel-making operations at Bethlehem Steel Corp. which represents ca. 32 % of the loadings of total zinc to the Niagara River (Report of the Niagara River Toxics Committee, 1984). Effluents in the Spillway and those which have already received treatment (Port Dalhousie STP) exhibit poor water quality, high fecal coliform populations (Table 1) and often exceed IJC water quality objectives for the protection of aquatic life. Further work is required to extend the data base to other metals (eg. chromium, nickel and silver) and to delineate the degree and location of contamination in the sediments of receiving waters as an adjunct to evaluating pollution abatement measures. Also caution should be exercised in making too much of conductivity measurements as indicators of the degree of inorganic contamination.

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Table 1. Locations of sampling stations in the Welland River Watershed.

STATION	LOCATION
33	Below Kimberley-Clark (Spillway)
32	Below Fraser (Spillway)
29	Beaver Wood Fibre
27	McMaster Storm Sewer - Welland River
27a	Atlas Steel - Slag Heap Ditch
36a	St. Catherines (Spillway)
13a	Port Robinson Tap Water
31b	General Motors - McKinnon Industries
1a	Mouth of the Welland Canal - STP Discharge
2a	Port Dalhousie STP - final effluent

Table 2. pH, specific conductance and coliform counts of surface water samples from the Welland River Watershed.

STATION	pH	Sp.Cond. uS cm-1	Fecal Coliform Counts/100ml	E.Coli Counts/100ml
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.
36a	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/100ml

IJC Guidelines:Fecal Coliform <200 counts/100ml

Table 3. Concentrations (ug l^{-1}) of dissolved Cu, Zn, Pb and Cd in surface waters of the Welland River Watershed.

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
36a	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 4. Concentrations (mg l^{-1}) of anions in surface waters from the Welland River Watershed.

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
36a	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

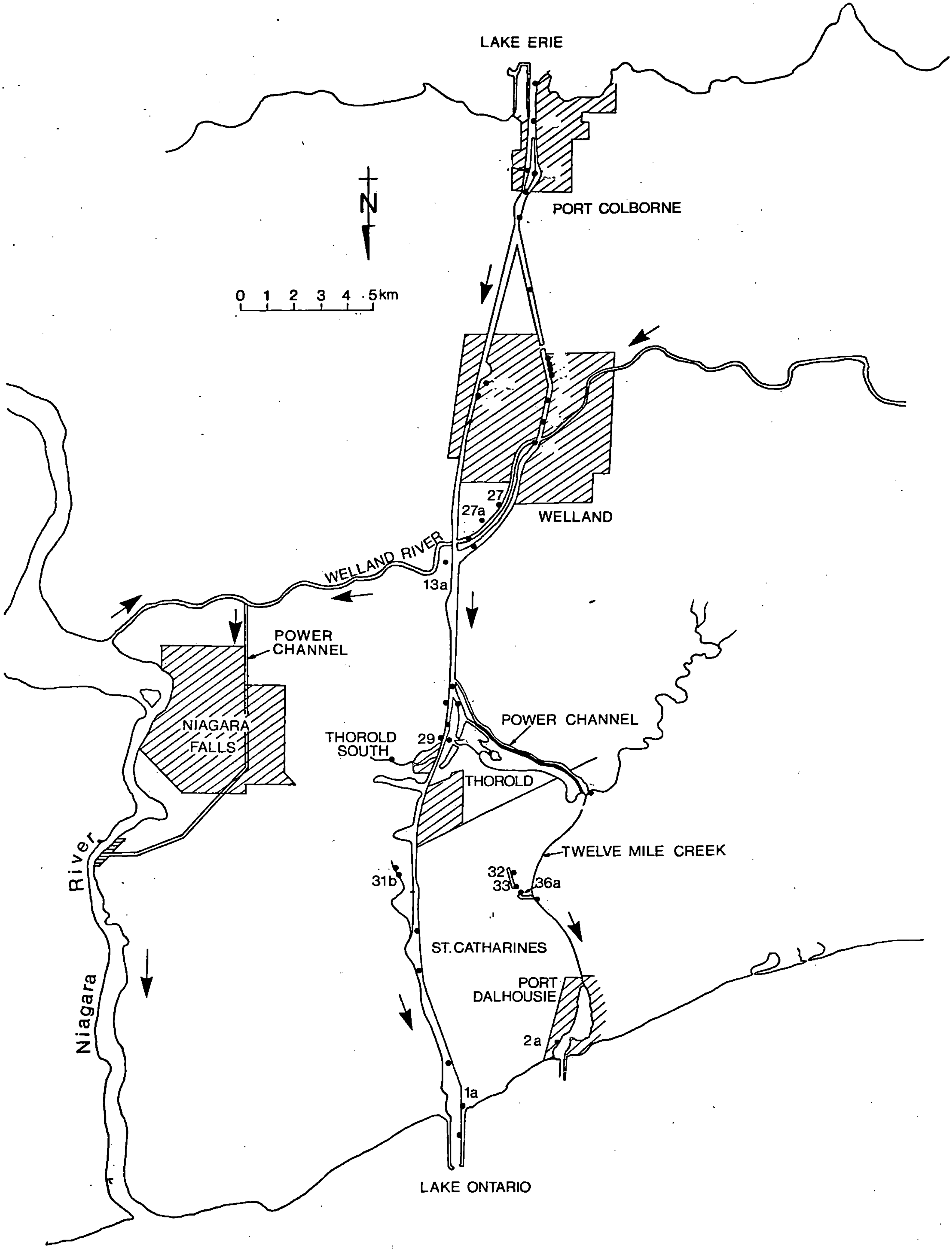
LAKE ERIE
PORT COLBORNE
N
0 1 2 3 4 5km
WELLAND
27
27a
WELLAND RIVER
13a
POWER CHANNEL
NIAGARA FALLS
POWER CHANNEL
THOROLD SOUTH
29
THOROLD
TWELVE MILE CREEK
32
33
36a
31b
ST. CATHARINES
PORT DALHOUSIE
2a
1a
Niagara River
LAKE ONTARIO

FIGURE 1.