

Division Control No. ECD-114B

This manuscript is submitted as an NWRI Publication

COLLINGWOOD HARBOUR: A BRIEF SURVEY

K.R. Lum

NWRI Contribution No. 85-62

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

Executive Summary

Water, bottom sediment and oligochaetes were analysed for heavy metals as part of an environmental assessment of the contamination of Collingwood Harbour, Ontario by shipbuilding and industrial activity. Compared to Western Lake Ontario, Collingwood Harbour showed higher concentrations of dissolved, available Cd, Cr, Pb and Cu. Cadmium concentrations increase from the inner harbour to the outer harbour and this distribution appears to be related to release from the sediments. The concentration of this metal in the outer harbour exceeds the average value measured in a related study for the southeastern part of Hamilton Harbour. In general, the data show that Collingwood Harbour does exhibit contamination by Cd, Cu and Pb.

Sediment concentrations of Cd, Cr, Cu and Pb exceed those reported for Nottawasaga Bay. The speciation pattern obtained from sequential chemical extraction of the sediments is discussed in terms of the relationship to the metal chemistry of the overlying water and an explanation offered for the predictions arising from these results.

Tissue metal levels are in general unrelated to total metal concentration in the sediments. A better relationship is provided by the sequential chemical extraction data. This result supports the view that total metal determinations are practically useless as a measure of geochemical and biological availability and of limited value as indicators

Résumé administratif

Dans le cadre de l'étude environnementale sur la contamination du port de Collingwood (Ontario) par la construction navale et les activités industrielles, on a analysé l'eau, des sédiments de fond et des oligochètes afin d'en déterminer la teneur en métaux lourds. On a enregistré des concentrations plus élevées de Cd, Cr, Pb et Cu dissous et disponibles dans les eaux du port que dans la partie ouest du lac Ontario. Les concentrations de cadmium vont en augmentant de l'arrière-port à l'avant-port et on croit que ce phénomène est relié à la libération du métal par les sédiments. Dans l'avant-port, la concentration de cadmium est supérieure à la valeur moyenne obtenue à la suite d'une étude semblable sur la portion sud-est du port de Hamilton. D'une façon générale, les données démontrent que le port de Collingwood présente effectivement des signes de contamination par Cd, Cu et Pb.

Les concentrations de Cd, Cr, Cu et Pb dans les sédiments excèdent celles que l'on a enregistrées dans la baie de Nottawasaga. Le document renferme des discussions sur le modèle de différenciation des espèces, établi par extraction chimique successive des sédiments, par rapport à l'action chimique des métaux sur les eaux qui recouvrent les sédiments. Les prévisions faites sur la base de résultats sont également expliquées.

En général, il n'existe pas de relation entre les niveaux de métaux dans les tissus et la concentration totale de métaux dans les sédiments. Par contre, on remarque une corrélation plus significative en étudiant les données d'extraction chimique successive. Ceci démontre que pour mesurer la disponibilité géochimique et biologique des métaux, leurs concentrations totales ne présentent pas un grand intérêt et ont une utilité limitée comme indicateurs des répercussions sur l'environnement.

Preface

This report has been prepared at the request of the EPS-Ontario Region to provide information which may be useful in assessing the effectiveness of implementation measures proposed in the Remedial Plan of Action for Collingwood Harbour, Ontario.

Introduction

Contamination by metals is one type of problem leading to Collingwood Harbour being designated one of the 42 Areas of Concern in the Great Lakes Basin. The problems with contamination in this Harbour have been attributed to municipal point sources and in-place pollutants (IJC, 1985).

The data presented in this report are from samples collected in July, 1981.

Sampling and Analytical Procedures.

The samples were obtained from six locations (Fig. 1) in the inner Harbour by diver. Water was collected in acid-cleaned 1l polyethylene bottles at ca 1m off bottom taking care not to disturb the bottom mud. The sediment was obtained using a 12cm diameter core liner inserted to a depth of 4-6 cm and capping the core tube. Most of the sediment grab samples were sieved through a 400 μ m nylon mesh, and the sieved residue was stored in plastic jars to be hand-sorted at NWRI. The sediment and water samples were stored in a cooler and delivered the day of collection to the laboratory. After filtration through GF/C pads (nominal pore size 1.2 μ m), water samples were passed through Chelex-100 resin columns and the

Chelex eluates were analyzed for Cd, Cr, Cu and Pb by Graphite Furnace AAS as described by McIsaac et al (1982).

Benthic invertebrates were hand-picked and stored in distilled water and at 4 deg C to facilitate the voiding of their gut contents. This procedure was adopted to minimize the problems caused by the inclusion of unassimilated food or sediment particles in the determination of tissue metal contents. After 24h, the organisms were decanted onto a 100 um nylon screen, copiously washed with a gentle stream of distilled water and finally collected on pre-weighed Unipore polycarbonate membranes. The organisms and membrane were then oven-dried at 40-45 deg C for 24h and then weighed.

Sequential Chemical Extraction of metal forms in sediments.

Approximately 1.00 gram (wet weight) of sediment (kept at 4 deg C) was extracted using the procedure of Tessier et al (1979). Dry weights were determined by obtaining the % moisture content on a separate 1.00 g sub-sample. The extraction procedure fractionates metal ions into five groups with decreasing ease of dissolution :- A) exchangeable metal forms, B) Forms bound to surface oxides and carbonates, C) Forms bound to Fe - Mn oxides, D) Organically-bound forms and finally E) Residual metal forms.

Dissolution of benthic invertebrates.

The organisms on the polycarbonate membrane were gently heated in a teflon beaker with 10 ml of concentrated nitric acid. After the initial reaction had subsided the membrane was removed and washed with a fine spray of water. Then 1 ml of 30 % hydrogen peroxide, 1 ml of concentrated hydrochloric acid and 0.5 ml of hydrofluoric acid were added. The mixture was carefully reduced to ca 1 ml. A further addition of hydrogen peroxide and hydrochloric acid was made if necessary, and the final digest was made up to 25 ml using 1% nitric acid.

Analysis of sediment extracts and benthic invertebrate digests.

The concentrations of the selected metals were determined by D.C. Argon Plasma Atomic Emission Spectrometry (DCPAES) using a Spectraspan III B, equipped with a DBC-33, background compensator module. The analytical and calibration conditions are described in McIsaac et al (1982).

Results and Discussion.

Dissolved metals and their availability.

Bioavailability of a metal ion is difficult to define since in addition to chemical availability (i.e form and speciation), the type, physiological state and life stage of the organisms are essential interdependent factors. Despite such complexities, dissolved metal ions are the most readily available form at least to phytoplankton which form the base of the food chain (Jackson and Morgan, 1978). Chelating ion-exchange resins do not concentrate colloidal forms which are still present after filtration. In addition, non-labile complexes would be expected to dissociate slower than the kinetics of uptake on a resin column and would also not be concentrated. In short, therefore, levels of dissolved metals yielded by the chelating ion-exchange resin procedure are considered to be a realistic measure of bioavailable metal ions, although the molecular nature of these dissolved forms is not known (Lum and Leslie, 1983).

The results for dissolved Cd, Cr, Cu and Pb show considerable variation (Table 1). They are all higher than the concentrations measured using the same method on samples taken from the Western Basin of Lake Ontario where during May-August 1981, the average concentrations for Cd,

Cr, Cu and Pb were 0.046, 0.41, 1.19 and 0.38 ug/l respectively (K.R. Lum, unpublished data). Note that a comparison with more recent data, even though the latter may be more accurate in an absolute sense, is not warranted, as internal consistency with the same method used on samples from a variety of waters, allows one to compare data having the same precision.

The trend for cadmium shows that there is a progressive increase in concentration from the inner to the outer harbour, in other words, the area immediately adjacent to the shipyard had the lowest concentration. A comparison with the southeastern portion of Hamilton Harbour (data in McIsaac et al, 1982) indicates that station 6 exceeded the average value of 0.14 ug/l found in Hamilton Harbour in July-August 1981.

The area adjacent to the Collingwood shipyard is also not contaminated by chromium, the concentrations generally being less than half that measured in southeastern Hamilton Harbour and lower than the average for the western basin of Lake Ontario.

The copper distribution shows two spikes; a high value off the shipyard and again at station six at the entrance to the Harbour. The remaining stations have concentrations which are less than the average for western Lake Ontario. The high values even exceed the average value (1.96 s.d. = 0.43 ug/l) for southeastern Hamilton Harbour.

The lead results are somewhat similar to those for copper in that

there are clearly two spikes; one adjacent to the shipyard and the second near the entrance to the Harbour. In the middle, the concentrations are similar to those for Western Lake Ontario but all are less than the average value for southeastern Hamilton Harbour.

Interpretation of these data in terms of the degree of contamination of Collingwood Harbour by these metals cannot be made in the absence of information on the mixing regime at the time of sampling and the chemical nature of effluents to the Harbour. Clearly though, Collingwood does exhibit contamination by cadmium, copper and lead at least in July 1981.

Total metal concentrations in sediments of
Collingwood Harbour.

The average concentrations of Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in Collingwood Harbour are compared with data from other areas in the Great Lakes (Table 2). The data from Fitchko and Hutchinson (1975) are averages of the analysis of outlet sediments from 15 North Channel and Georgian Bay tributaries; the means do not include the outliers asterisked by these workers in their Table 8 and hence can be regarded as background concentrations representative of the Georgian Bay watershed. Also for comparison, the data from Station 15, 0-1cm sediment layer, from the depositional basin of Nottawasaga Bay, have been abstracted from Kemp et al (1978). The concentrations of Pb, Cu, Cr and Cd in Collingwood Harbour on average, exceed those reported for Nottawasaga Bay. The concentrations of

Zn, Ni, Mn, and Co are well above background which is not surprising for an industrial harbour.

Geochemical availability of metal forms in
Collingwood Harbour sediments.

Because of the variable and complex nature of sediments, the partitioning of a given element yielded by the sequential chemical extraction procedure may not necessarily reflect the scavenging of conceptually distinct solid phases. In spite of the inherent limitations on the selectivity of the method used in this study, and indeed of other available methods, the results can nevertheless be used for estimating the relative importance of various sediment phases in affecting metal ion mobility and availability (Rendell et al, 1980). Thus, the extraction procedure can be regarded as simulating actual environmental conditions to which sediments may be subjected eg after dredging and confined disposal.

The results of the sequential sediment extraction are summarized in table 3 and the geochemical behaviour of the heavy metals is discussed individually as follows:-

Cadmium

Exchangeable forms of cadmium were detected at all stations,

representing between 10 and 31 % of the total cadmium content. Interestingly, the concentration of exchangeable forms generally increases from station 1 through 6 as one moves from the inner harbour to the outer harbour. This trend is reasonably well-reflected in the dissolved metal determinations at the 1m from bottom level which is suggestive of cadmium release from the sediments. The lability of cadmium forms and the preference of this metal for the dissolved phase have been discussed in Lum and Leslie (1983). The carbonate- surface oxide bound fraction as well as the organic fraction are unimportant; iron and manganese oxides comprise the only other significant phase regulating the geochemical availability of this metal. Most of the cadmium is in residual form which is unavailable.

Cobalt

This element is dominated by the residual phase, although the other phases/fractions show measurable amounts of cobalt associated with them. Generally, the most important non-residual phase is the Fe-Mn oxide fraction.

Chromium

The first two fractions are insignificant and apart from the predominant residual forms, only the Fe-Mn oxide fraction is important in the geochemistry of this element in Collingwood Harbour. The relative

non-lability of chromium is in reasonable agreement with the small amount of variation observed in the water chemistry.

Copper

Generally, detectable amounts of copper were found in all fractions. Unlike the preceding metals, copper is significantly present in the organic fraction and as well the residual phase does not dominate the speciation pattern. The association between this pattern and the water chemistry is not clear perhaps because no one phase is of over-riding importance at all sites.

Nickel

The most important fraction is the Fe-Mn oxide phase. The first two fractions which may be regarded as the readily-available forms, are reasonably constant in concentration. In an oxic environment, this likely would result in equilibrium concentrations of dissolved nickel being established (in the absence of significant inputs of this element in readily available forms). This interpretation appears to be borne out by the constancy in the dissolved nickel concentration found in the offshore waters of Lake Erie (Lum and Leslie, 1983).

Lead

The particulate speciation of lead is dominated by the Fe-Mn oxide fraction and very little if any lead is found in readily available forms (the first two fractions). The variation observed in the dissolved lead distribution in this area is likely caused by contamination of the samples. This effect has been observed by other workers and is discussed in some detail in Lum and Leslie (1983). The speciation pattern would suggest that under oxic conditions, the dissolved lead concentrations should be relatively uniform throughout Collingwood Harbour.

Zinc

As for nickel and lead, zinc was found to be predominantly bound to Fe-Mn oxides. The organically-bound fraction is appreciable and a relatively constant proportion of the total. Interestingly, there is considerable variability in the readily-available fractions which should be reflected in the dissolved metal distribution. Regrettably, this element is more prone to contamination problems than even lead, and the determination was not attempted for these samples.

Metal content of oligochaetes

Only oligochaetes were found in the sediments of Collingwood Harbour. No chironomids, amphipods, isopods or fingernail clams were present in the sediment samples. The dry weight of organisms was in the range 60-80 mg but at station 6, only 6 mg were obtained and this was considered at the time, too small a sample size for analysis. The results for stations 1 - 5 are presented in Table 4.

The detection limit for cadmium was 2 ug/g (given the solution detection limit and the weight of material) and was inadequate for yielding any information on cadmium in the oligochaetes. The values for cobalt at stations 3 and 5 are not particularly striking. The relative constancy in the chromium levels seem consistent with the unavailability of this element as shown by the speciation data. Clearly there is not a good relationship with total chromium content of the sediments. This lack of relationship between total metal content and tissue level is even more striking for copper where station 5 has the second lowest total copper but the highest tissue level. Examination of the speciation data does not provide an answer either. although the water chemistry shows a high value of copper at this station. The tissue levels of lead and zinc are quite constant and this appears to be consistent with the relatively invariant proportion of forms of these metals associated with Fe - Mn oxides. The results for nickel are similar to those for copper and cannot be explained at this time using such a limited data base. Nevertheless, this study provides evidence that total metal content is practically useless as a measure of geochemical and biological availability and hence of very limited value as an indicator

of environmental impact.

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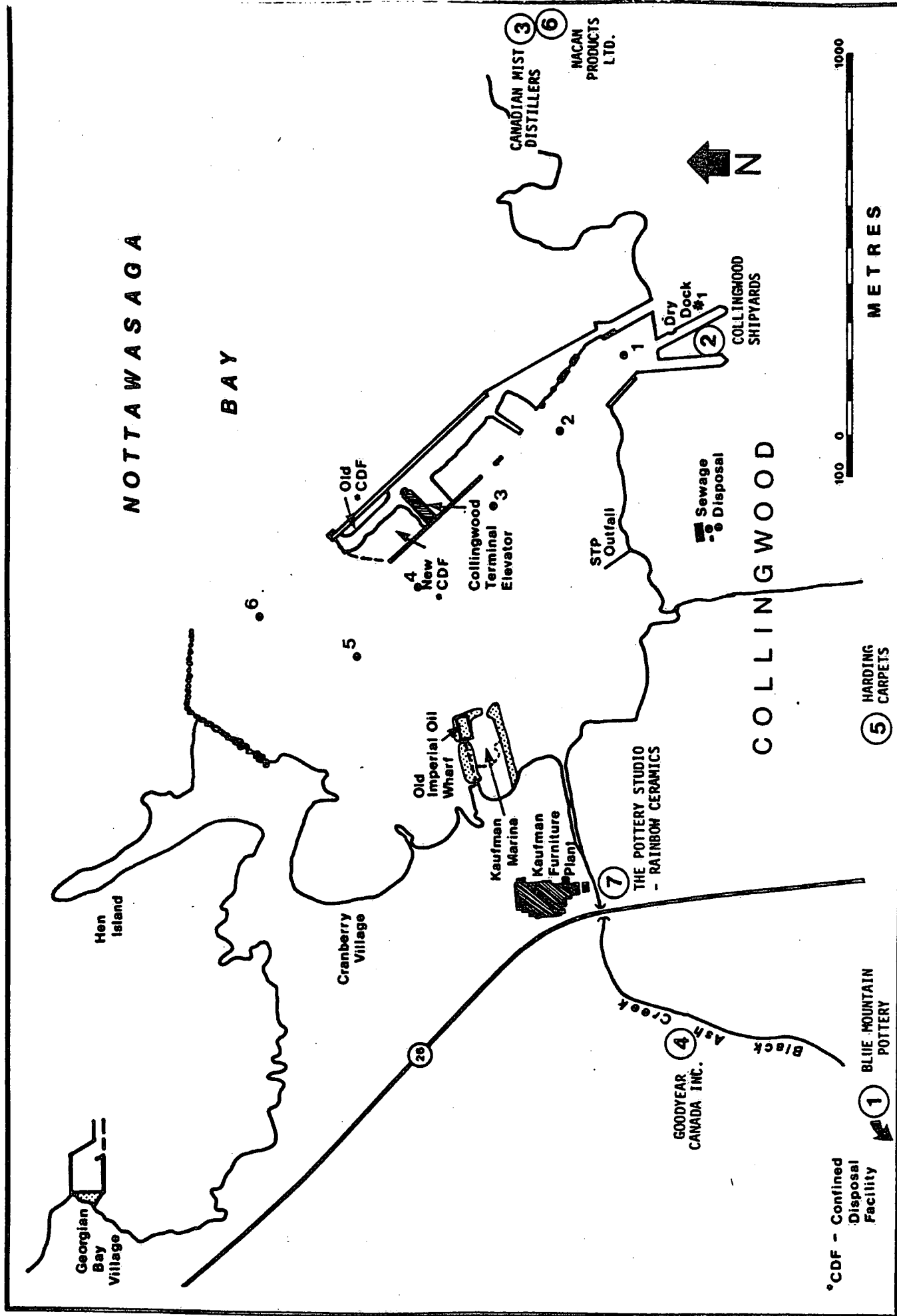


Fig. 1. Sampling Locations in Collingwood Harbour.

Table 1. Dissolved metal ions in Collingwood Harbour.

Concentrations in ug/l.

Station	Cd	Cr	Cu	Pb
1	0.06	0.10	8.50	1.24
2	0.09	0.08	0.54	0.19
3	0.07	0.33	0.70	0.18
4	0.10	0.34	0.81	0.43
5	0.12	0.24	0.54	2.32
6	0.22	0.27	3.52	0.86

Table 2. Average concentrations of metals in
Collingwood Harbour. Concentrations and standard deviation (sd)
in ug/g except where noted.

Element	Collingwood	Ref. 6	Ref. 5
Al	4.50% (0.17)	---	6.07%
Cd	3.4 (0.6)	0.7 (0.4)	2.8
Co	17.6 (2.5)	9.7 (3.9)	31.2
Cr	93 (66)	7.2 (4.5)	41
Cu	100 (34)	10.9 (5.4)	78
Fe	2.16% (0.45)	---	5.52%
Mn	1070 (180)	220 (140)	4500
Ni	89 (36)	12.7 (6.0)	115.6
Pb	167 (57)	18.5 (8.3)	141.5
Zn	168 (55)	35.7 (24)	222

Table 3. Speciation of metal ions in sediments from Collingwood Harbour. Concentrations in ug/g. Percentages of total metal content.

Station		Cd	Co	Cr	Cu	Ni	Pb	Zn
1	%A	10	nd	nd	2.5	2	nd	2
	%B	25	nd	1	0.5	1	nd	1
	%C	nd	22	13	28	43	66	67
	%D	nd	nd	5	32	6	12	10
	%E	65	78	81	37	48	22	20
	TM	2.8	15.5	114	142	96	218	202
2	%A	16	3	nd	1	1	nd	3
	%B	7	5	nd	2	2	3	7
	%C	nd	16	7	40	31	65	62
	%D	nd	nd	3	40	3	8	6
	%E	77	76	90	17	63	24	22
	TM	4.3	19.8	217	110	155	224	230
3	%A	22	4	nd	3	2	nd	6
	%B	8	5	2	1	2	3	11
	%C	nd	15	26	59	65	70	55
	%D	nd	3	6	27	6	6	8
	%E	70	73	66	10	25	21	20
	TM	3.6	17	68	121	82	181	178
4	%A	21	5	.5	2	1	nd	nd
	%B	nd	6	.5	1	2	2	nd
	%C	13	13	22	54	63	77	61
	%D	nd	9	4	27	8	4	11
	%E	66	67	73	16	26	17	28
	TM	3.7	20	62	97	85	146	157
5	%A	22	3.5	nd	1	2	nd	nd
	%B	nd	9.5	nd	1	2	2	1
	%C	16	17	21	46	60	75	64
	%D	nd	12	5	37	7	6	12
	%E	62	58	74	15	29	17	23
	TM	3.1	19.5	63	89	70	166	171
6	%A	31	5	nd	nd	2.5	nd	nd
	%B	nd	10	1	2	3.5	1	4
	%C	24	10	19	59	64	79	48
	%D	nd	11	4	24	5	3	10
	%E	45	64	76	15	25	17	38
	TM	2.9	14.0	34	43	46	67	68

Table 4. Tissue metal levels in oligochaete sp from
Collingwood Harbour. Concentrations in ug/g dry weight.

Station	Cd	Co	Cr	Cu	Ni	Pb	Zn
1	<2.0	<2.0	34	41	16	57	126
2	<2.0	<2.0	34	26	127	57	139
3	<2.0	10	24	197	1912	67	139
4	<2.0	<2.0	22	163	1410	68	136
5	<2.0	9	26	368	2388	55	152