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International Council for the
Exploration of the Sea

C.M.1977/ E:25
Fisheries Improvement Committee

TRACE METAL DISCHARGES TO THE NORTH ATLANTIC FROM THE ST. LAWRENCE RIVER

by

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SUMMARY

The concentrations of iron, manganese, cobalt, nickel, copper, zinc and cadmium in the discharge of the St. Lawrence River have been determined and are shown to be considerably lower than those in the discharge of the Rhine. The fluxes of trace metals from these two rivers, and the metal concentrations within their marine receiving waters, are compared. Nearshore losses, through sedimentation in the estuary and Gulf of St. Lawrence, significantly reduce the fluxes of trace metals into the North Atlantic from the St. Lawrence River. Assessment of such nearshore losses is, therefore, important in quantifying metal fluxes into the ocean from rivers.

INTRODUCTION

Interest has recently been shown by several agencies in estimating the quantities and effects of fluvial discharges into the marine environment. Examples are the River Inputs to Ocean Systems (RIOS) program of SCOR (Working Group 46) and the Registry of Clean Rivers of UNEP. To complement both these programs and to satisfy national concerns, Canada has conducted a fairly comprehensive assessment of the quality of the St. Lawrence River. These studies have

partly been aimed at quantifying the discharge of certain chemical substances and determining their impact upon the marine environment.

This paper contains estimates, and discussion, of the fluxes of river-borne trace metals discharged at the mouth of the St. Lawrence River. The magnitude of trace metal transport by the St. Lawrence River is compared with that of the Rhine River of western Europe. We further show that it is important to consider the processes of nearshore sedimentation before equating fluvial metal fluxes directly with inputs to the deep marine environment. Nearshore sedimentation in estuarine and marginal sea environments of the Gulf of St. Lawrence significantly reduces the net fluvial fluxes of metals into the North Atlantic.

RESULTS AND DISCUSSION

River Discharge of Metals

We have determined the composition of the St. Lawrence River at its mouth by analyzing monthly samples collected at two stations on a transverse section across the River at Quebec City for the months April to September inclusive. During most of this period the River appears, from temperature, chlorinity and nutrient data, to be horizontally stratified. By weighting the analytical data by the corresponding monthly river discharge, we have estimated both the mean concentrations and the annual fluxes of suspended particulate matter (SPM), iron, manganese, cobalt, nickel, copper, zinc and cadmium in the outflow of the River. These data are shown in Table 1 together with similar data for the Rhine after Weichart (1973).

Our value for the discharge of suspended matter from the St. Lawrence River agrees fairly well with that of Holeman (1968) of $3.6 \cdot 10^9$ kg/yr. On any base of normalization, the Rhine has a higher trace metal flux than the

St. Lawrence. Indeed, in the cases of Zn, Ni, Cu, and Cd the actual discharges, without normalization, are higher. If the metal fluxes are normalized to flow, or to the area of the respective drainage basins, the fluxes of all the metals from the Rhine are greater than from the St. Lawrence River. Undoubtedly, the concentrations of population and industry, in relation to flow, are considerably larger in the case of the Rhine than in the case of the St. Lawrence. Further-

TABLE 1. Discharge of metals by the St. Lawrence and Rhine Rivers.

Metal	St. Lawrence River		Rhine River	
	Concentration µg/l	Flux kg/yr	Concentration* µg/l	Flux kg/yr
Fe	860	$3.8 \cdot 10^8$	1200	$8.0 \cdot 10^7$
Mn	23	$1.0 \cdot 10^7$	90	$6.0 \cdot 10^6$
Co	0.23	$1.4 \cdot 10^5$	-	-
Ni	1.7	$7.6 \cdot 10^5$	30	$2.0 \cdot 10^6$
Cu	3.2	$1.4 \cdot 10^6$	30	$2.0 \cdot 10^6$
Zn	5.0	$2.2 \cdot 10^6$	300	$2.0 \cdot 10^7$
Cd	0.27	$1.2 \cdot 10^5$	3	$2.0 \cdot 10^5$
Hg	-		1.5	$1.0 \cdot 10^5$
SPM	10,000	$4.4 \cdot 10^9$	6600 ⁺	$4.8 \cdot 10^{8+}$
Water	-	$4.4 \cdot 10^{14}$	-	$6.9 \cdot 10^{13\#}$

* Calculated by the division of Weichart's flux data by mean annual water discharge of Rhine.

+ From Holeman (1968).

Todd (1970).

more, the concentrations of suspended matter and trace metals in the discharge of the St. Lawrence River will undoubtedly be reduced by sedimentation within the Great Lakes.

Although the volume of the North Sea is about twice that of the Gulf of St. Lawrence, the multiplicity of major rivers such as the Elbe, Seine, Thames and Rhine, all of which drain highly industrialized regions of Europe, make it likely that the North Sea is more affected by anthropogenic inputs than is the St. Lawrence. This, of course, assumes that flushing of the two marginal seas is controlled by fresh water runoff and mixing. Any undue flushing by sea water from adjacent basins will have the effect of reducing the impact of local fresh water inputs, thereby producing trace metal concentrations nearer to those of uncontaminated sea water.

Table 2 shows the concentration of seven metals (iron, manganese, cobalt, nickel, copper, zinc, and cadmium) in the surface waters of the Gulf of St. Lawrence and the surface waters of the North Sea and English Channel.

TABLE 2. Concentrations of trace metals in the waters of the Gulf of St. Lawrence, North Sea, and English Channel. ($\mu\text{g}/\text{l}$)

Area	Fe	Mn	Co	Ni	Cu	Zn	Cd
Gulf of St. Lawrence	1.6	0.8	<u>0.032</u>	<u>0.39</u>	<u>0.61</u>	<u>1.8</u>	<u>0.07</u>
North Sea	1 ¹	0.37 ¹	<u>0.037</u> ²	0.4 ¹	0.9 ¹	3.9 ¹	0.41 ¹
	5 ³	0.7 ⁴		0.7 ⁴	0.6 ⁴	2.6 ⁴	0.1 ⁴
English Channel			<u>0.040</u> ²	0.5 ¹	2 ⁵		0.06 ¹
	0.5 ¹	0.36 ¹			0.9 ¹	4.2 ¹	0.80 ⁵
						5.0 ⁵	
Central Atlantic Water ⁶	1.8	<0.04	<u>0.023</u>	<u>0.23</u>	<u>0.39</u>	<u>1.07</u>	<u>0.04</u>

1. Preston *et al.* (1972)
 2. Robertson (1970)
 3. Eisma (1975)
 4. Jones *et al.* (1973)
 5. Abdullah and Royle (1974)
 6. Bewers *et al.* (1976)
- Underlined values are derived from the analyses of unfiltered samples and pertain to 'total' metal. Other values pertain to the 'dissolved' component of the metals and are derived from the analysis of filtered samples or result from the application of methods sensitive to dissolved metal only.

A comparison of the metal concentrations in these areas reveals that, generally, the levels are lower in the Gulf of St. Lawrence than in the two European marginal seas. It also reveals the dependence upon the actual data sets used in the comparison because this generality is unsupported in the cases of iron and manganese by the data of Preston *et al.* (1972). Obviously either regional variability, or problems of analytical accuracy, make such comparisons of limited value. Nevertheless, the similarity of the metal levels with those in Central Atlantic Water (Bewers *et al.*, 1976) shows that severe modifications of marginal sea trace metal compositions do not occur, except in the case of manganese. We might thus question why this situation arises. Is it merely the result of dilution of fresh water by sea water in nearshore mixing processes or are there other mechanisms which tend to reduce the metal levels in coastal waters? The solution of this question is important, not only to judgments of the susceptibility of coastal waters (usually those within national jurisdictions) to pollution, but also to assessing the cumulative effects of natural and anthropogenic fluxes of materials, such as heavy metals, entering the deep ocean through fluvial discharge.

Nearshore Metal Sedimentation

We have determined the composition of fresh and saline waters entering and leaving various segments of the nearshore zone within the Gulf of St. Lawrence and constructed a budget for the fluxes of dissolved and particulate trace metals and suspended matter in the region. This budget, based on conservation of water and salt within each segment of the system, reveals that nearshore sedimentation plays a major role in reducing the net

influx of metals to the deep ocean from rivers. Table 3 shows the proportions of fluvial iron, manganese, cobalt, nickel, copper, zinc, cadmium, and suspended particulate matter which are removed within the Gulf of St. Lawrence as determined by such a budget. The most pronounced nearshore losses occur for those metals that have important particulate components in the discharge from the St. Lawrence River, such as iron and manganese. Nearshore sedimentation reduces the flux of seagoing particulate matter by a factor of ten and has a correspondingly major effect on the precipitation of particulate iron and manganese.

TABLE 3. Effect of nearshore losses upon influxes of trace metals to the North Atlantic from the St. Lawrence River.

Metal	St. Lawrence River Flux kg/yr	Proportion Lost in Nearshore Sedimentation %	Net Flux to the Ocean kg/yr
Fe	$3.8 \cdot 10^8$	89	$4.2 \cdot 10^7$
Mn	$1.0 \cdot 10^7$	47	$5.3 \cdot 10^6$
Co	$1.4 \cdot 10^5$	25	$1.1 \cdot 10^5$
Ni	$7.6 \cdot 10^5$	12	$6.7 \cdot 10^5$
Cu	$1.4 \cdot 10^6$	11	$1.3 \cdot 10^6$
Zn	$2.2 \cdot 10^6$	0.1	$2.2 \cdot 10^6$
Cd	$1.2 \cdot 10^5$	15	$1.0 \cdot 10^5$
SPM	$4.4 \cdot 10^9$	93	$3.1 \cdot 10^8$

A number of assumptions have, of course, been made in constructing the metal budgets. Not least of these is an assumption that the direct

input of metals to the nearshore zone from the atmosphere, in wet and dry precipitation, can be ignored. This assumption is forced on us by a paucity of data on the composition of atmospheric precipitation in this region. In practice, it seems unlikely that this process of injection of metals to marginal seas, such as the Gulf of St. Lawrence, is insignificant and we are taking steps to analyze regional precipitation and to quantify this input. Nevertheless, the crude budgetary approach we have adopted yields rates of nearshore metal removal which correspond closely with the composition and rate of formation of sediments within the Gulf of St. Lawrence. We, therefore, have some confidence that the method can be used to assess the magnitude of nearshore losses of metal which ameliorate oceanic metal inputs by rivers. It also serves to show that, in combination with dilution by oceanic sea water, the process results in metal concentrations in higher salinity nearshore waters which are not greatly dissimilar from those in open ocean water. This in turn compounds the experimental problems in determining the extent of metal pollution of coastal waters not immediately affected by local direct discharges or plumes.

If the discharges from all world rivers are affected to a similar degree as those from the St. Lawrence River the net fluxes of these trace metals become comparable with the rates of incorporation into oceanic sediments (Bewers and Yeats, 1977). Only in the cases of nickel and cobalt are there inadequate fluvial discharges to account for the rates of oceanic sedimentation thus suggesting that for a majority of these metals direct atmospheric inputs to the ocean are of minor importance. In the cases of cobalt and nickel similar quantities of metal to those introduced by rivers would need to be supplied from other sources such as atmospheric transport and deposition.

REFERENCES

- ABDULLAH, M.I. and ROYLE, L.G., 1974. A study of the dissolved and particulate trace elements in the Bristol Channel. *J. Mar. Biol. Assoc. U.K.* 54, 581-597.
- BEWERS, J.M., SUNDBY, B. and YEATS, P.A., 1976. The distribution of trace metals in the western North Atlantic off Nova Scotia. *Geochim. Cosmochim. Acta* 40, 687-696.
- BEWERS, J.M. and YEATS, P.A., 1977. Oceanic residence times of trace metals. *Nature*. In press.
- EISMA, O., 1975. Dissolved iron in the Rhine Estuary and the adjacent North Sea. *Neth. J. Sea. Res.* 9, 222-230.
- HOLEMAN, J.N., 1968. The sediment yield of major rivers of the world. *Water Resources Res.* 4, 737-747.
- JONES, P.G.W., HENRY, J.L. and FOLKARD, A.R., 1973. The distribution of selected trace metals in the water of the North Sea 1971-73. International Council for the Exploration of the Sea Document C.M. 1973/C:5.
- PRESTON, A., JEFFERIES, D.F., DUTTON, J.W.R., HARVEY, B.R. and STEELE, A.K., 1972. British Isles Coastal Waters: The concentrations of selected heavy metals in sea water suspended matter and biological indicators; A pilot survey. *Environmental Pollution* 3, 69-82.
- ROBERTSON, D.E., 1970. The distribution of cobalt in oceanic waters. *Geochim. Cosmochim. Acta* 34, 553-567.
- TODD, D.K., Ed., 1970. *The Water Encyclopedia*. Water Information Center, New York.
- WEICHART, G., 1973. Pollution of the North Sea. *Ambio* 2, 99-106.