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**DISSOLVED AND PARTICULATE CADMIUM
IN THE ST. LAWRENCE RIVER**

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Management Perspective

This paper is to be published in the Proceedings of the Second International Conference on Environmental Contamination, Amsterdam, September 1986.

The results of our first year of measurements of cadmium in the St. Lawrence River are summarized. Compared with previous work by researchers at Bedford Institute of Oceanography, the NWRI work shows that levels of cadmium are considerably lower than the earlier measurements. This is almost entirely due to our much better sampling and analytical capability. The results show that the Montreal area is the only very obvious hot spot for cadmium and this will be checked for again in the 86-87 field season.

More reliable estimates of the flux of particulate-bound and dissolved cadmium can now be made. As well, our results are now the baseline against which trends in the contamination of the St. Lawrence River can be assessed.

Gestion

Ce document doit être publié dans les actes de la Deuxième conférence internationale sur la contamination de l'environnement prévue pour septembre 1986 à Amsterdam.

Nous présentons un sommaire des résultats obtenus pour notre première année de mesure du cadmium dans les eaux du fleuve Saint-Laurent. L'étude de l'Institut national de recherche sur les eaux démontre que les niveaux de cadmium sont bien inférieurs à ceux qu'établissait la recherche menée par les chercheurs de l'Institut océanographique de Bedford. Cet écart s'explique presque entièrement par notre capacité supérieure d'échantillonnage et d'analyse. Les résultats démontrent que la région de Montréal est le seul endroit où la présence importante de cadmium est très évidente et nous vérifierons à nouveau ces résultats lors de nos études sur le terrain en 1986-1987.

Nous sommes maintenant en mesure d'évaluer de façon plus fiable le flux de cadmium dissous ou particulaire. De plus, nos résultats servent maintenant de base pour évaluer les tendances observées dans la contamination du fleuve Saint-Laurent.

CADMIUM DISSOUS ET PARTICULAIRE DANS LE FLEUVE SAINT-LAURENT

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RÉSUMÉ

Des formes de cadmium dissous et particulaire ont été mesurées dans des échantillons recueillis dans le fleuve Saint-Laurent, du lac Ontario à la ville de Québec. La concentration moyenne de Cd dissous pour le fleuve est de 15 ng L⁻¹. Celle du cadmium particulaire est de 1,88 ug g⁻¹. Le coefficient de répartition va de 0,91 jusqu'à 2,01 x 10⁻⁷ litres/ng. Les calculs de débit démontrent que le décharge de cadmium dissous et particulaire dans le fleuve Saint-Laurent est bien inférieure aux estimations antérieures.

DISSOLVED AND PARTICULATE CADMIUM IN THE ST. LAWRENCE RIVER

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ABSTRACT

Dissolved and particulate cadmium forms have been measured in samples from the St. Lawrence River from Lake Ontario to Quebec City. The average concentration of dissolved Cd for the river is 15 ng L^{-1} . Particulate cadmium averages $1.88 \text{ } \mu\text{g g}^{-1}$. The distribution coefficient ranges from 0.91 to 2.01×10^{-7} litres/ng. Flux calculations show the discharge of dissolved and particulate cadmium by the St. Lawrence River to be much lower than previous estimates.

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INTRODUCTION

The St. Lawrence River drains one of the most heavily populated and industrialized regions of North America, viz, the Great Lakes Basin. Upstream sources combined with contaminant inputs in the Province of Quebec have led to public concern for the restoration of the St. Lawrence River in large measure because the river is the source of drinking water for nearly five million Canadians. In addition, there is likely to be environmental impact in the Estuary and the Gulf of St. Lawrence because of the discharge of contaminants from the river and their increased residence time in the estuary.

This paper will focus on the distribution of cadmium between the dissolved and particulate phases in the river from the outflow of Lake Ontario to Quebec City. The high degree of geochemical mobility of this element in suspended and bottom sediments is well-documented (e.g., ref. 1, 2). It is surprising how limited information there is on the partitioning of cadmium in the St. Lawrence River. Previous work has emphasized total cadmium in the estuary as part of an investigation of the anthropogenic input of this element to the ocean (ref. 3-5).

OUTLINE OF STUDY AND METHODS

Samples were collected in May and October, 1985, from stations between the outflow of Lake Ontario and Quebec City. Phase separation was accomplished by continuous-flow centrifugation of at least 600 litres of water (ref. 6). Centrifugate was collected in 125 ml acid-cleaned polyethylene bottles and preserved with 0.25 ml of nitric acid which had been purified by double sub-boiling distillation from quartz (Seastar Chemicals, Sidney, BC). The suspended solids were freeze-dried, weighed and stored in acid-cleaned plastic jars. Operationally-defined dissolved cadmium was determined by electrothermal atomization using a Hitachi 180-80 Zeeman Effect AAS (ref. 7). Suspended particulate material (0.50 gram) was subjected to a two part extraction using 1 N HCl for two hours followed by wet chemical digestion of the residue (ref. 8). The sediment extracts were analyzed by Zeeman Flame AAS (ref. 2).

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RESULTS

The results (Table 1) show that for 24 samples distributed throughout the river, the average concentration of dissolved cadmium was 14 (s.d. = 8) ng/L in May. Markedly elevated levels were found at two stations in the Montreal area (200 and 111 ng/L) and the calculation of the mean value for the river does not include them. Two stations within a kilometre of each other at Ile D'Orleans (Quebec City) showed values of 9 and 11 ng/L. In October 1985, 32 samples were collected throughout the river and the average concentration and standard deviation was 20 and 19 ng/L, respectively. Again, if one deletes two stations at Montreal showing the highest concentrations, the average value and standard deviation are 16 and 12 ng/L (Table 1).

TABLE 1. DISSOLVED CADMIUM IN THE ST. LAWRENCE RIVER (ng L⁻¹)

<u>Sampling Period</u>	<u>[Cd]</u>	
May	14	8
October	16	12
October/Quebec City	15	7

During the October cruise, ten samples were collected at 1 m and 3 m off bottom at two-hourly intervals at an anchor station at Quebec City. The average concentration found was 15 (s.d. = 7) ng/L. On the basis of the data obtained in this study, the annual flux of dissolved cadmium based using a mean dissolved cadmium concentration of 15 ng/L and a mean discharge of 12,000 m³/sec at Quebec City is 5675 kg. This is an order of magnitude less than that reported by Yeats and Bewers (ref. 5).

The concentration of cadmium in suspended particulate material from the St. Lawrence River is relatively uniform and remarkably similar to the average concentration for the Niagara River. The value shown in Table 2 is the mean of 52 samples collected in May and October, 1985. The mean value for 9 samples taken at the anchor station at Quebec City

TABLE 2. CADMIUM IN SUSPENDED PARTICULATE MATERIAL FROM THE ST. LAWRENCE RIVER (ug g⁻¹)

<u>Sampling Period/Area</u>	<u>[Cd]</u>	
May/October	1.88	0.76
October/Quebec City	1.09	0.37
Niagara River	1.80	1.00

in October was 1.09 ug/g. The discharge of particulate-bound cadmium from the St. Lawrence River can be estimated using the average cadmium content of particulates at Quebec City and the annual suspended solids loadings. This gives an annual discharge of 5670 kg. Alternatively, the particulate cadmium flux may be calculated from the average concentration of suspended particulate material at the time of sampling, viz 9.67 mg/L (s.d. = 1.16) and their average cadmium content in ng/L. The particulate cadmium discharge in October 1985 is therefore 3980 kg. These estimates are about one-third to a half less than the figure of 9000 kg/yr calculated by Yeats and Bewers (ref. 5).

The speciation of cadmium is generally regarded as being dominated by dissolved forms except for situations where the concentration of

suspended particulate material is high (ref. 5,6,9-12). Dissolved forms in the St. Lawrence River account for ca 60% of the total cadmium transported by the river which is characterized by a particulate matter concentration which averages 10 mg/L. In contrast, the 200-300 mg/L suspended load of the Mississippi River presents much greater amounts of sorption sites and this is evident in the low proportion of dissolved forms in this system (ref. 9). Recent measurements on the tidal Elbe (ref. 12) show that ca 63% of the cadmium input to the estuary is as dissolved forms. The distribution coefficient, expressed in liters/ng range from 0.92 to 2.01×10^{-7} for all the samples from the St. Lawrence River (Table 3). It is tempting to speculate on the use of the relatively constant K_d for predicting the particulate elemental concentration, for example from measurements of the concentrations of suspended

TABLE 3. PARTITIONING OF CADMIUM IN THE ST. LAWRENCE RIVER

Area/Sampling Period	Z Dissolved		K_d	
May	60	22	2.01	1.74×10^{-7} litres/ng
October	69	17	1.86	2.11×10^{-7} litres/ng
October/Quebec City	56	15	0.92	0.53×10^{-7} litres/ng

particulate matter and dissolved elemental forms. Such predictive capability would be valuable in fluvial and estuarine environments where suspended particulate matter concentrations vary over a wide range. Using the equation for calculating K_d which incorporates the suspended matter concentration (ref. 13), predicted concentrations of particulate Cd were obtained for the 26 stations sampled during May 1985. The range of dissolved cadmium concentrations was 3 to 200 ng/L and the particulate matter concentrations ranged from 1.42 to 13.5 mg/L. The particulate cadmium concentrations obtained from the sum of the cadmium contents in sequential 1 N HCl and residual extracts of 0.500 g of sample ranged from 1.1 to 23.1 ng/L. Of the 26 stations, there was agreement (for this exercise assumed to be within 30% of each other) for only ten pairs of measured and predicted values.

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