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ESTIMATION OF HYDROCARBON CONCENTRATIONS IN THE
WATER COLUMN OF COME-BY-CHANCE BAY; 1971-1973

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ABSTRACT

Estimates of hydrocarbon concentrations in the water column of Come-by-Chance Bay, Newfoundland, were obtained by fluorescence spectroscopy during construction of the Newfoundland Refining Company refinery. Monthly average concentrations ranged from 0.6 to 5.5 $\mu\text{g/l}$. Temporal variations were apparent. On any given date however there were no consistent vertical or horizontal gradients in concentrations. These data can be used to help assess the environmental impact of the refinery after it begins operation in late 1973.

INTRODUCTION

In early 1971, the Newfoundland Refining Company Ltd. began construction of an oil refinery on the eastern shore of Come-by-Chance Bay, a coastal inlet near the northern end of Placentia Bay, Newfoundland (Fig. 1). Construction of the first phase was completed in October 1973 and the refinery began operation in late 1973.

There has been much concern expressed about how this refinery, and the associated transport by ship of crude oil into and refined petroleum products out of the area, might affect the general ecological health of Come-by-Chance and Placentia Bays. In order to determine if significant deleterious effects are produced by the refining activity, it is imperative that certain conditions in the environment be studied in a quantitative manner before operations begin. One parameter that warrants such study is the concentration of hydrocarbons in seawater. With the above purpose in mind, we have measured hydrocarbon concentrations in the water column at four stations in Come-by-Chance Bay (Fig. 1) at approximately monthly intervals between November 1971 and May 1973, during most of the construction period.

METHODS

On each sampling date, seawater samples were collected at four stations (Fig. 1) with 8-l polyvinylchloride Niskin bottles using the Fisheries Service patrol boats PORELLA and PISTOLET BAY. Sampling depths ranged between 0 and 10 m. Hydrocarbons were extracted from 2 l of seawater with carbon tetrachloride and the extracts were shipped to the Marine Ecology Laboratory for analysis. Extraction, concentration, and analytical procedures have been described in detail by Keizer and Gordon (1973). A medium Venezuelan crude oil (Tia Juana) was used as a standard.

After this study had commenced, methylene chloride was discovered to be a better solvent for extracting seawater than carbon tetrachloride (see Keizer and Gordon, 1973, for reasons). However, to maintain continuity, carbon tetrachloride was used for the duration of the study except on the next to last sampling date (17 April 1973) when duplicate samples were extracted with both solvents. The results of this comparison (Table 1) indicate that higher concentrations are observed when methylene chloride is used.

Analysis of hydrocarbons in seawater by fluorescence spectroscopy yields only approximate concentrations. Any compounds, regardless of origin, present in seawater which are extracted with carbon tetrachloride and fluoresce under the analytical conditions employed, will be detected. Since the

concentrations (and composition) of fluorescing compounds relative to total hydrocarbons (or petroleum hydrocarbons) in the seawater samples being analyzed is unknown and is undoubtedly quite variable with with place and time, it is impossible to calibrate the technique accurately. We used crude oil (about 35% aromatic by weight) as a standard since we were interested in estimating oil concentrations. All concentrations presented in this report are therefore in units of crude oil equivalents, even though it is possible that no oil is present.

Samples for particulate organic carbon and nitrogen analysis were collected on four dates. Between 1 and 2 liters of seawater were filtered through precombusted 47 mm, 0.8 μ silver filters (Selas Flotronics Inc., Spring House, Pa.) using vacuum. Filters, including numerous blanks, were stored frozen in plastic petri-dishes until analysis with a Perkin-Elmer Model 240 elemental analyzer.

RESULTS

The average hydrocarbon concentration observed on each sampling date is presented in Table 2. On any given date, there were no obvious vertical or horizontal concentration gradients. For each group of data, standard deviations were approximately equal to the means.

Concentrations between August and December 1972 were higher than at other times of the study. This is evident in Table 2 and the frequency distributions plotted in Fig. 2.

During this period, the average concentration was $4\mu\text{g}/\text{l}$ and the frequency distribution (Fig. 2B) was similar to that observed in Bedford Basin, a moderately polluted inlet at the head of Halifax Harbour, N.S. (Keizer and Gordon, 1973). During the remainder of the study, before and after this period, the average concentration was about $1\mu\text{g}/\text{l}$ and the frequency distribution was similar to that of oceanic surface waters (Keizer and Gordon, 1973).

Concentrations of particulate carbon and nitrogen, as well as CN ratios, are summarized in Table 3. As with the petroleum residue concentrations, there were no apparent differences between stations and depth, only time.

DISCUSSION

These results indicate that at the present time the water column of Come-by-Chance Bay contains very low concentrations of petroleum hydrocarbons. The reported concentrations represent the maximum amounts of crude oil that could be present. The concentrations are actually quite low, at the lower end of the range of concentrations observed by Levy (1971) in eastern Canadian marine waters.

The observed temporal variation in hydrocarbon concentrations could have been caused by a number of events.

1. Through June 1972, two or three ships per month delivered construction and processing equipment to the refinery site. In July and September 1972, about the

time when the concentrations increased, traffic increased to five ships per month. These higher concentrations therefore may represent various petroleum products commonly used in ships which became more apparent in the water because of the increased shipping activity.

2. The higher concentrations may represent asphalt residues or polynuclear aromatic hydrocarbons from exhaust fumes of construction equipment entering the water from the construction site.
3. Another possibility is that there are seasonal variations in naturally occurring organic compounds which fluoresce under the analytical conditions employed. At the present time this possibility is not considered to be very likely. As indicated by the particulate nitrogen and carbon data (Table 3), the annual cycle of organic production appears to peak during the spring, while hydrocarbon concentrations did not increase until August. Also, similarly higher concentrations during late summer and fall have not been observed in seasonal studies of the same nature in Bedford Basin and over the Scotian Shelf.

It will be interesting to see what happens to these concentrations after the refinery has begun operation. Unless pollution control practices in the refinery and on ships visiting the site are one hundred percent effective, the concentrations will undoubtedly increase. To illustrate the

kinds of concentrations that might be expected, an average concentration of about 70 $\mu\text{g}/\text{l}$ has been observed in surface water just off the Imperial refinery in Dartmouth, N.S. (Michalik and Gordon, 1971).

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Table 1 - Comparison of petroleum residue concentrations ($\mu\text{g}/\text{l}$) observed when seawater is extracted with carbon tetrachloride (CCl_4) and methylene chloride (CH_2Cl_2). Samples collected on 17 April, 1973. See Fig. 1 for station locations.

Station	Depth (m)	CCl_4	CH_2Cl_2
1	0	2.1	4.9
	2	2.3	0.9
	6	0.6	1.3
2	0	-	1.5
	2	0.9	1.2
	5	0.4	1.0
	10	0.1	1.6
3	0	0.9	1.7
	2	0.1	0.7
	5	0.5	1.5
	10	0.1	3.6
4	0	0.9	2.2
	2	1.4	1.5
	5	0.0	1.0
	10	0.3	1.0
Mean =		0.7	1.7

Table 2 - Estimated hydrocarbon concentrations observed in Come-by-Chance Bay during the study. All concentrations from a given date are averaged.

Date	Average Conc. ($\mu\text{g}/\text{l}$)	S.D.	n
24 Nov. 1971	1.2	1.6	12
3 Feb. 1972	1.5	1.4	12
1 March	0.8	1.1	8
5 April	0.6	0.6	6
1 May	1.6	1.1	8
29 May	0.6	0.7	8
26 June	1.3	0.9	9
3 August	2.9	1.8	16
25 August	5.4	2.9	14
29 Sept.	3.9	3.1	16
6 Nov.	2.5	2.5	15
6 Dec.	5.5	2.6	14
7 Feb. 1973	0.6	0.3	16
7 March	1.9	0.6	14
17 April	0.8	0.7	14
2 May	2.3	1.0	14

Table 3 - Particulate carbon and nitrogen concentrations;
all concentrations observed on a given date
averaged. Samples collected in 1972.

Date	$\mu\text{g C/l}$	$\mu\text{g N/l}$	C/N
24 Jan	94.6	11.3	8.4
1 May	180.8	19.0	9.5
25 Aug	172.7	16.9	10.2
6 Dec	85.6	8.3	10.2

FIGURE LEGENDS

- Fig. 1 - Chart of Come-by-Chance Bay. Inset indicates the general location of the Bay in Newfoundland. Depth in meters is indicated at each station.
- Fig. 2 - Frequency distribution of petroleum residue concentrations during three successive stages of the study: A, November 1971-June 1972; B, August-December 1972; C, February-May 1973.



