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Chemical Oceanographic Conditions in Blacks Harbour, N. B., 1989-91

BLACK'S

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November 1991

Canadian Manuscript Report of Fisheries and Aquatic Sciences No. 2132

Fisheries and Oceans Pêches et Océans

Canada

Canadian Manuscript Report of Fisheries and Aquatic Sciences

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CHEMICAL OCEANOGRAPHIC CONDITIONS IN BLACKS HARBOUR, N. B., 1989-91

by

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Cat. No. Fs 97-4/2132 ISSN 0706-6473

Correct citation for this publication:

Wildish, D. J., and V. Zitko. 1991. Chemical oceanographic conditions in Blacks Harbour, N. B., 1989-91. Can. Manuscr. Rep. Fish. Aquat. Sci. 2132: iii + 11 p.

ABSTRACT

Wildish, D. J., and V. Zitko. 1991. Chemical oceanographic conditions in Blacks Harbour, N. B., 1989-91. Can. Manuscr. Rep. Fish. Aquat. Sci. 2132: iii + 11 p.

Chemical oceanographic observations along a sampling transect from Blacks Harbour to Bliss Harbour show that a fish meal plant releasing effluent within Blacks Harbour is responsible for severe dissolved oxygen depletion within it. In low water conditions, over half of the surface water in Blacks Harbour may be completely anoxic, although the effect is less marked in bottom water. Chemical measurements show that actual mixing and advective processes have sufficiently diluted the effluent so that no further dissolved oxygen depletion occurs at a point just outside Blacks Harbour.

RÉSUMÉ

Wildish, D. J., and V. Zitko. 1991. Chemical oceanographic conditions in Blacks Harbour, N. B., 1989-91. Can. Manuscr. Rep. Fish. Aquat. Sci. 2132: iii + 11 p.

Des observations en océanographie chimique effectuées le long d'une transecte d'échantillonnage, de Blacks Harbour à Bliss Harbour, démontrent qu'une usine de farine de poisson déversant son effluent à la hauteur de Blacks Harbour, est responsable d'un grave épuisement de l'oxygène dissous qui s'y retrouve. À marée basse, plus de la moitié de l'eau de surface de Blacks Harbour pourrait être complètement anoxique, bien que l'effet soit moins prononcé dans l'eau de fond. Des mesures chimiques ont révélé que les procédés actuels de mélange et d'advection ont suffisamment dilué l'effluent pour que l'épuisement de l'oxygène dissous ne se produise plus à un point situé juste à l'extérieur de Blacks Harbour.

INTRODUCTION

Beginning in August 1989, concerns were expressed by salmon growers operating in Bliss Harbour regarding particulate fish wastes reaching their cage sites. During the August/September period, a fish meal rendering plant, operating seasonally within Blacks Harbour, received shipments of menhadden and was operating round the clock to produce fish meal. The wastes from their production, including bloodwater (blood, scales and wastes washed off the floor) and stickwater (wastes after cooking from the separators), were released untreated into Blacks Harbour. In 1989 (Wildish et. al. 1990) and again in 1990-91, we undertook to determine the receiving water effects of the organic wastes released by the fish meal plant. Organic wastes released into seawater undergo degradation chiefly by aerobic microorganisms (mostly bacteria). This results in an oxygen demand which, if it is of significant magnitude in relation to the available seawater oxygen balance, will result in oxygen depletion. It is this effect on dissolved oxygen concentrations which we have used to assess the environmental effects of the fish meal plant effluent in Blacks Harbour.

Other sources of organic pollution which might reach Blacks Harbour include municipal sewage wastes and wastes from the salmon growing industry. Organic pollution by pulp mill wastes occurs in the upper part of L'Etang, but at a sufficient distance for it to be unlikely to affect Blacks Harbour. Because of the multiplicity of possible organic pollution sources, we have also sought an independent chemical method to determine the cause of depleted dissolved oxygen concentrations.

METHODS

Field sampling was either from the J. L. HART or PANDALUS III. Vessel positioning was approximate from observations of shore position and/or ships radar and hence accurate to ~250 m. Surface samples were taken by bucket, and bottom samples (1 m above the sediment) in Niskin bottles. In one case, Secchi disc depth readings were also determined.

Twelve stations were routinely sampled (transect A in Wildish et al. (1990 b)) as shown in Table 1 and Fig. 1.

Table 1 Transect A sampling location co-ordinates recorded on 16 July 1991; start 1358, finish 1515 h.

Station #	Latitude ° ' "	Longitude ° ' "	Depth m
1	45 03 21	66 47 80	3.4
2	45 03 16	66 47 88	6.7
3	45 03 10	66 48 02	8.9
4	45 03 08	66 48 11	9.6
5	45 02 94	66 48 34	7.6
6	45 02 81	66 48 61	12.6
7	45 02 61	66 49 04	29.0
8	45 02 42	66 49 48	25.6
9	45 02 24	66 49 70	27.4
10	45 02 05	66 50 12	24.0
11	45 01 98	66 50 59	16.6
12	45 02 20	66 50 38	18.0

A mercury thermometer was used to measure surface water and the reversing thermometer read for the bottom sample. Salinity was determined on subsamples collected in bottles and determined by measuring conductance on an Autosal salinometer.

Dissolved oxygen concentration in seawater was determined by the azide modification of the Winkler method in 300-mL bottles taken in the field and fixed by addition of 1-mL aliquots of manganous sulphate and alkaline iodide solutions (see Wildish et al. 1990a). The samples were titrated within 48 h and the results expressed as a percentage of the expected value at the same temperature and salinity.

Additional samples were taken directly from the plant (stickwater) and from near the submarine effluent pipe (bloodwater), as well as at the regular transect stations.

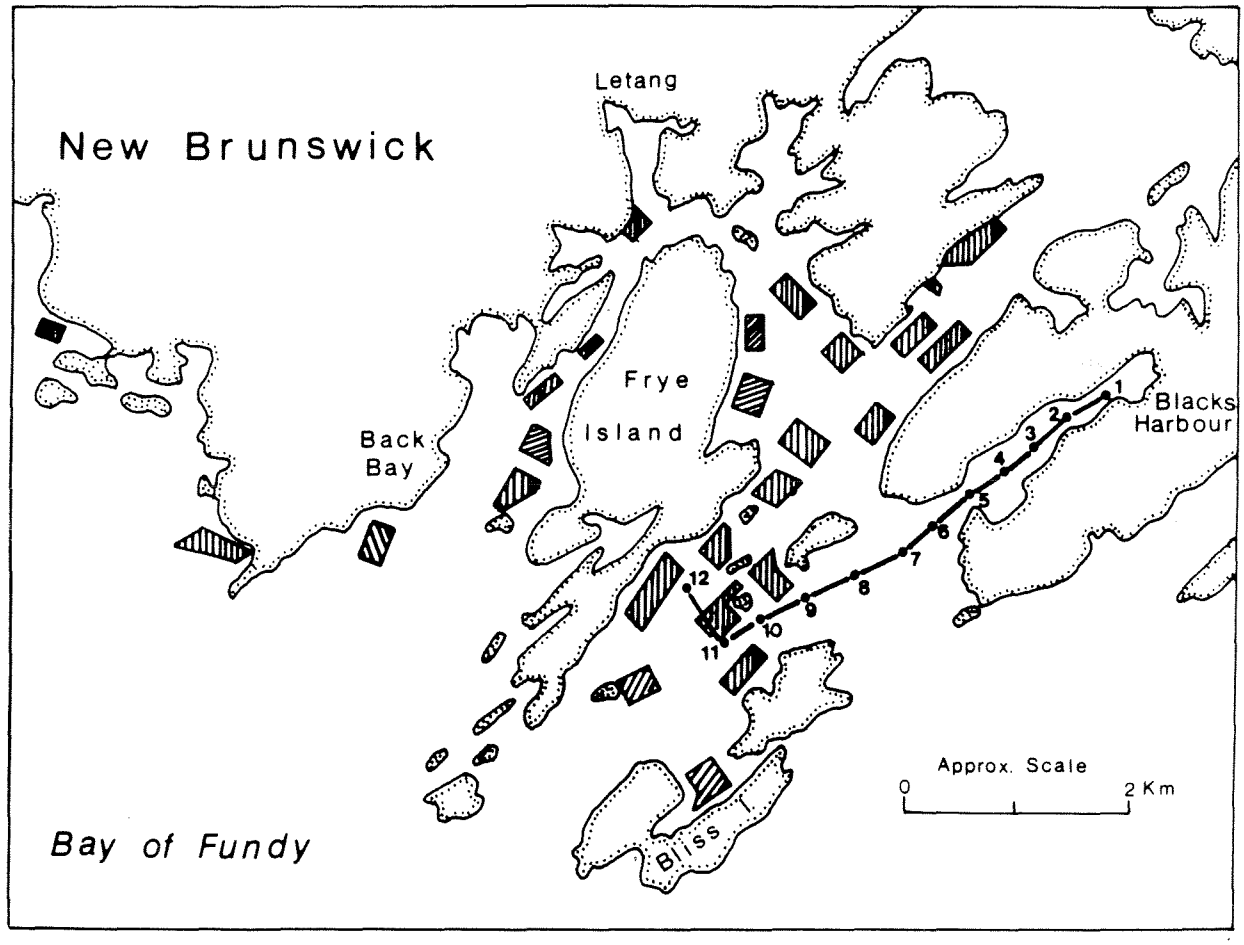

Fig. 1. Chart showing the transect sampling stations and salmon farms (hatched) in the L'Etang.

UV spectra were measured by an HP 8452A Diode Array Spectrophotometer from 200-350 nm against distilled water in 1990 and against air in 1991. The change was made because of poor spectral quality of distilled water at that time.

Files of spectra were transferred to Quattro (Borland) spreadsheets for further processing. Principal component analysis was performed by a procedure written in MATLAB (The Math Works, Inc., South Natick, MA 01760) on centered (mean = 0) and scaled (std = 1) data.

Thin layer chromatography was carried out on K5F 5 x 20 cm Whatman silica plates. The solvent was ethanol-water 7:3 for amino acids, and petroleum ether-ether-acetic acid 80:20:1 for lipids. Amino acids were visualized by a commercial ninhydrin spray, lipids by charring with 50% sulphuric acid.

A Sorvall bench-top centrifuge model GLC-2, with 50 mL stainless steel tubes was used at maximum speed (about 3800 rpm).

A Perkin-Elmer infrared spectrophotometer model 700 was used to record IR spectra in potassium bromide disks.

Stickwater (41.3 g) was centrifuged, yielding a sediment (1.9 g wet, 0.37 g air-dry weight), a small amount (about 0.02 g) of "scum," and a colloidal solution as the supernatant. The scum was extracted with methylene chloride, filtered, and examined by TLC. The supernatant (20 mL) was poured into 60 mL absolute ethyl

alcohol. This resulted in a precipitate (0.85 g air-dry weight), characterized by IR as a protein, and a supernatant (1.43 g) containing amino acids, other ninhydrin-positive substances, and salts.

Effluent (bloodwater, 180 mL) was centrifuged, yielding a small amount of "scum" and traces of sediment. The supernatant was poured into absolute ethanol (340 mL), yielding a precipitate (0.59 g). According to its IR spectrum, the precipitate was mostly sulphate and presumably sodium chloride. The supernatant was extracted with methylene chloride, yielding a lipid fraction (26 mg). Protein was isolated as an interphase on extraction of the effluent with carbon tetrachloride.

Another portion of the effluent (500 mL) was placed in a 500-mL graduated cylinder. Nitrogen was bubbled though an airstone and foam was collected. Foam was left to evaporate in a stream of air and the residue was extracted with methylene chloride.

A calibration curve for the effluent was prepared by diluting the effluent with filtered seawater.

RESULTS

Transect A sampling stations (Fig. 1) included locations in Blacks Harbour and in Bliss Harbour, where a number of salmonid farms are located. Sampling dates for this transect were: a) 6 September 1989, b) 7 September 1990, c) 12 March 1991, and d) 16 July 1991, where the letters in Fig. 2-4 indicate the sampling date.

Secchi disc depths were determined on 16 July 1991 near the time of high water (predicted at 1330 ADT), with sampling beginning at 1338 and ending at 1515 ADT. The results (Fig. 2) show that Secchi depths are affected, at least to station 6, due presumably to seawater discolouration and fine particulates which hinder sunlight penetration.

Dissolved oxygen sag curves along the transect are shown for surface (Fig. 3) and bottom (Fig. 4) seawater. The results suggest that dissolved oxygen depletion is greater in the surface water. Interpretation of the curves is

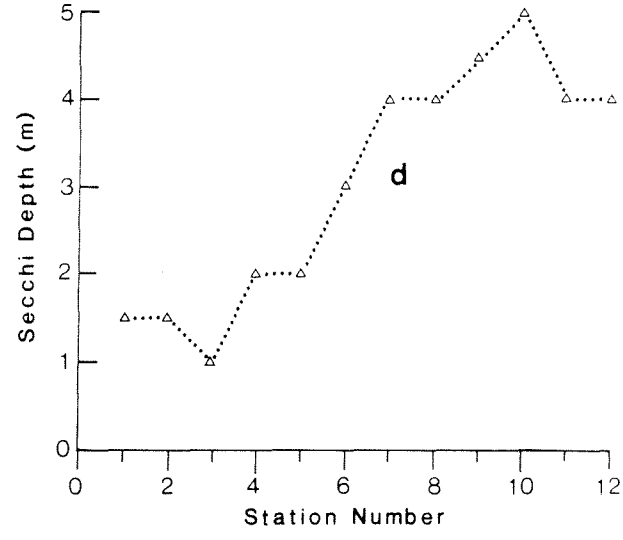

Fig. 2. Secchi disc depths observed at the 12 transect stations on 16 July 1991 (d) during the period 1338-1515 h.

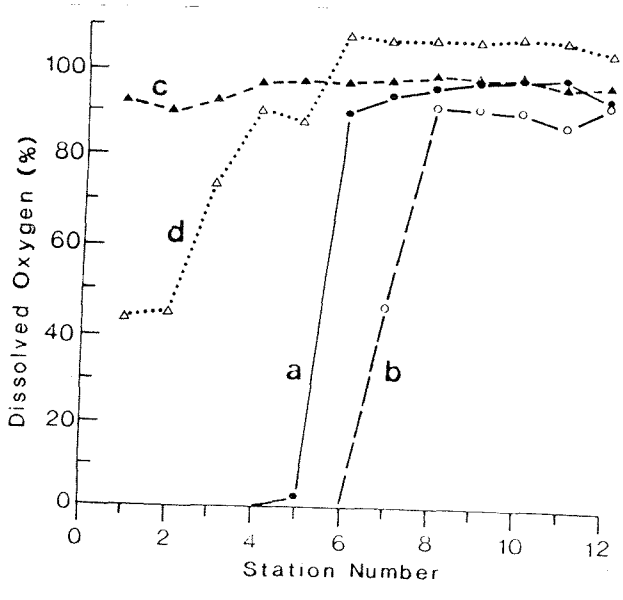

Fig. 3. Surface seawater dissolved oxygen concentrations at 12 stations along the Blacks-Bliss Harbour transect. Letters indicate sampling dates (see text).

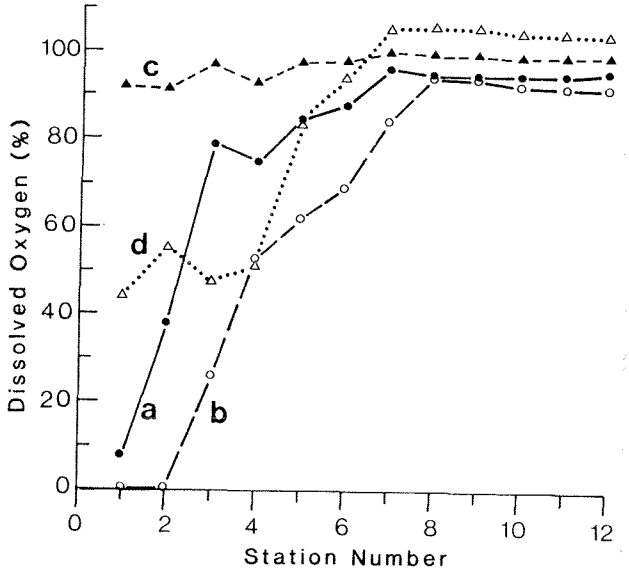

Fig. 4. Bottom seawater dissolved oxygen concentrations at 12 stations along the Blacks-Bliss Harbour transect. Letters indicate sampling dates (see text).

complicated by the fact that the sampling was done at different tidal times. Thus a and b were completed within 2 h of low water, whereas d was completed within 2 h after high water. Our results show that the oxygen balance within, and outside to just beyond station 7, in Blacks Harbour is affected by the organic wastes released into it. Salinity and temperature data at each station are given in Appendix 1.

The concentration of organic matter in seawater samples from Blacks Harbour (see Fig. 1 for station locations) was estimated by ultraviolet spectra (Haberer 1985). The spectra were generally featureless, with the absorbance increasing more or less monotonously with decreasing wavelength (Fig. 5). A shoulder at 260 nm was visible in some of the samples containing high concentrations of organic matter. A "calibration curve" was obtained by diluting an effluent sample taken near the diffuser on 30 July 1991 (Fig. 6). The "strength" of the effluent is not constant, since two surface samples of effluent taken on 6 August 1991 contained organic matter at only 71 and 78 mL/L in terms of the 30 July 30 1991 effluent, which contained 100 mL/L. The

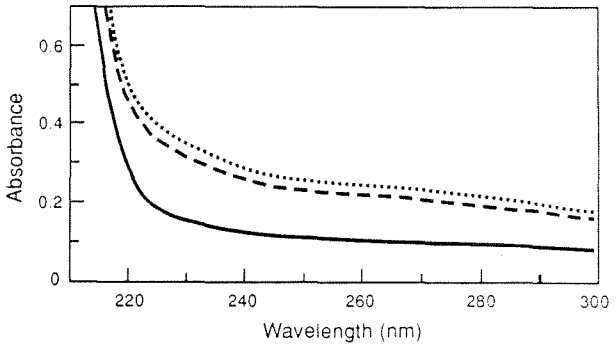

Fig. 5. UV spectra of water samples. Absorbances from station #2 and #4 (upper plots) are higher than for stations 6-9 (lower plot).

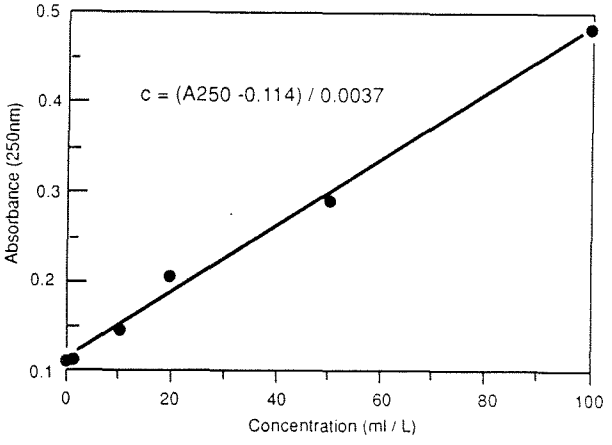

Fig. 6. Calibration curve obtained by diluting the effluent by filtered seawater.

concentration in a sample taken at the same time but at 1 m of the bottom, in 3 m water, was 17 mL/L.

The detection limit of organic matter in the effluent, based on absorbance at 250 nm, is about 2 mL/L (Fig. 5). In an earlier experiment, carried out by diluting a sample of stickwater obtained on 24 July 1991 at 1130 h, the detection limit was about 1 mL/L.

The detection limit can be improved by using more than one wavelength. The range of wavelengths, 220-290 nm, was selected from the spread of the absorbance values in the sample set (Fig. 7). The selection is based on the fact that little change in absorbance with sample location indicates that absorbance at that

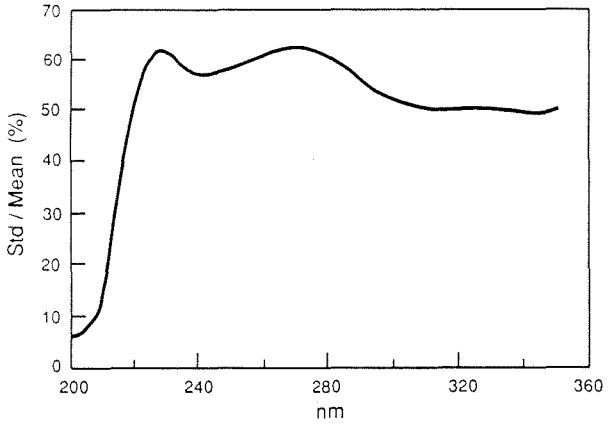

Fig. 7. Spread of the data expressed as standard deviation divided by mean, as a function of wavelength. An aid in selecting the range of wavelengths for Principal Component Analysis.

wavelength is not related to the concentration of organic matter.

All the absorbances within the selected wavelength range could be combined into one component by principal component analysis (Malinowski and Howery 1980). This means that the organic matter as indicated by the spectra originated from a single source, and the differences in the absorbance values are due only to dilution.

The Blacks Harbour organic matter was detectable to somewhere between stations 7 and 8 during the 16 July 1991 survey (Fig. 8). Polluted samples are to the left, samples without detectable organic matter are to the right. The survey on 7 September 7 1990 resulted in a similar conclusion (Fig. 9, 10).

It was originally assumed that the effluent was "stickwater," and a sample (see above) was characterized. It contained 4.6% of suspended solids (0.9% on an air-dried basis), 2% protein, 3.5% of amino acids, other ninhydrin-positive substances and salts, and 0.05% lipids and other lipophilic substances. The last group contains very strong surface-active compounds. Seawater shaken with a small amount of the lipid fraction in carbon tetrachloride forms a very stable seawater-in-carbon-tetrachloride emulsion. Water samples from stations 1-7 behave similarly. This

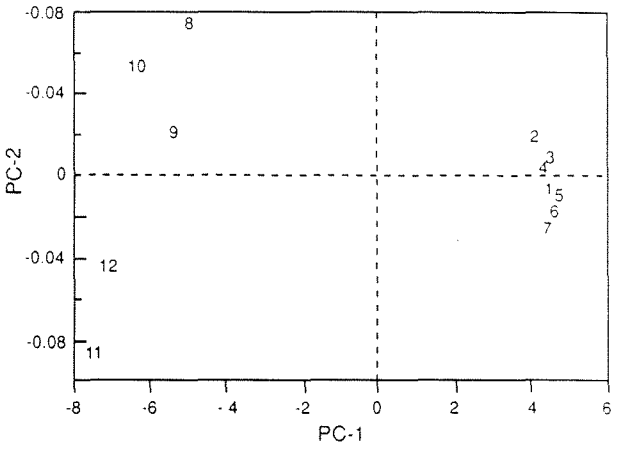

Fig. 8. Principal components 1 and 2 plot for the 16 July 1991 survey. Numbers indicate stations. Stations with high organic content are on the right hand side.

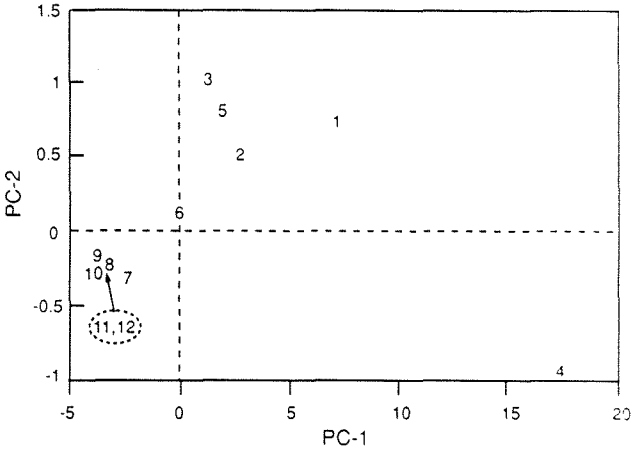

Fig. 9. Principal components 1 and 2 plot for the 7 September 1990 survey.

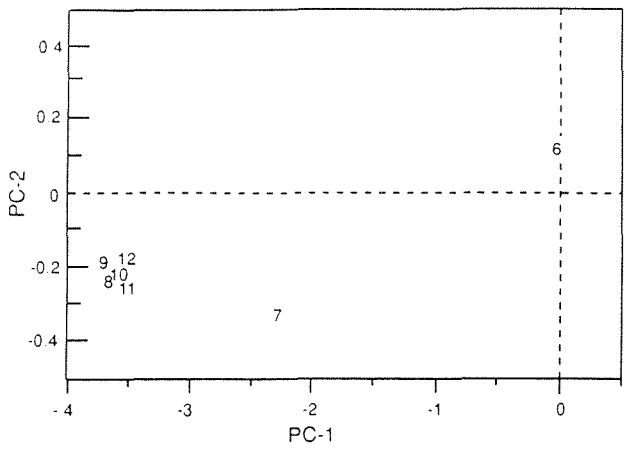

Fig. 10. Magnified left-hand side of Fig. 6.

test, or a modified version (carbon tetrachloride is too toxic for routine use), is an alternate method for detecting the effluent. The surface activity may also have some undesirable environmental effects.

A sample of the partially diluted bloodwater discharging from the effluent pipe was characterized in a similar fashion. It contained only traces of suspended solids, some protein, traces of amino acids and ninhydrin-positive substances, and 0.014% lipids and other lipophilic substances. A small amount of "scum" separated as the top layer during the centrifugation. The characterization of the composition of the effluent was more difficult than the characterization of stickwater since the effluent was in seawater. The surface activity of the effluent was also very strong. The activity seems to be caused by the more polar lipophilic substances rather than by triglycerides.

In an attempt to isolate lipophilic substances from the effluent on a larger scale, nitrogen was bubbled through 500 mL of effluent and the foam was collected. As can be seen from thin layer chromatography, the "scum" and the foam contain mostly the more polar lipophilic compounds and triglycerides are present in the lipid fraction (Fig. 11).

The "protein" which separates as a voluminous "interphase" during the extraction of the effluent with carbon tetrachloride absorbs at 1630, 1550, and 1150 cm^{-1} in the IR.

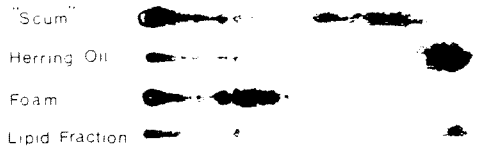

Fig. 11. Thin layer chromatography of effluent lipid fractions.

DISCUSSION

Low dissolved oxygen concentrations within Blacks Harbour are associated with high concentrations of organic matter. Chemical characterization of the organic matter (amino acids, proteins, lipids, surface activity) shows that it originates at a fish meal plant with an effluent discharging into Blacks Harbour, N.B. The effluent has a high oxygen demand and is produced in sufficient quantities at certain times of the year to deplete the local dissolved oxygen. The depletion effect can be noticed to a point just outside the mouth of Blacks Harbour. Chemical characterization of the diluted effluent by UV method can be used to an approximately similar point outside Blacks Harbour. Beyond this point the fish meal wastes become too diluted for chemical characterization and for aerobic microbial activity to have noticeable effects on the dissolved oxygen balance.

Other possible effects of the effluent on the nearby salmonid culture industry are disease transmission and the strong surface activity in the lipid fraction of both bloodwater and stickwater which may have undesirable environmental effects. These possibilities have not been assessed by the work reported here.

Chemical characteristics of stickwater suggest that it contains high levels of carbon, nitrogen and salts which are wasted by disposal at sea. Efforts should be encouraged to further utilize the waste product, e.g. as a plant fertilizing product.

ACKNOWLEDGEMENTS

We wish to thank Michelle Ringuette, Art Wilson and Peter Fenety for assistance with sampling and analysis, DFO Inspection, Blacks Harbour and Connors Brothers for assistance in obtaining the stickwater sample and Elaine Maillet and Brenda Best for preparing the manuscript for publication. Frank Cunningham drew and photographed the figures.

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APPENDIX I

6 September 1989

Station #	Depth m	Sample depth m	Temp (°C)	Salinity o/oo	Dissolved oxygen % sat.
1	3.5	0 2.5	13.1 13.5	32.2 32.4	0 8.9
2	4.8	0 3.8	13.2 12.9	32.2 32.3	0 38.8
3	6.9	0 5.9	13.0 12.5	32.2 32.3	14.4 79.0
4	7.7	0 6.7	14.0 12.5	32.2 32.3	0 75.0
5	12.0	0 11.0	13.7 12.5	32.2 32.3	2.6 84.7
6	19.0	0 18.0	12.4 12.2	32.3 32.3	90.4 87.6
7	23.0	0 22.0	12.5 12.6	32.3 32.3	94.8 96.7
8	23.0	0 22.0	12.9 12.2	32.3 32.3	96.6 94.9
9	22.0	0 21.0	13.2 12.0	32.3 32.3	98.5 94.9
10	16.0	0 15.0	13.2 12.1	32.3 32.3	98.9 95.1
11	14.0	0 13.0	12.7 12.1	32.3 32.3	98.9 95.3
12	10.0	0 9.0	13.0 12.5	32.3 32.3	94.0 95.9

Appendix I. (cont'd)

7 September 1990

Station #	Depth m	Sample depth m	Temp (°C)	Salinity ‰/oo	Dissolved oxygen % sat.
1	2.6	0 1.6	13.2 12.5	30.74 31.77	0.0 0.0
2	3.9	0 2.9	12.9 12.2	31.74 31.86	0.0 0.0
3	5.4	0 4.4	13.1 11.9	31.78 31.90	0.0 26.0
4	6.8	0 5.8	12.9 12.0	31.70 31.92	0.0 52.9
5	9.5	0 8.5	13.0 11.8	31.74 31.92	0.0 61.7
6	10.0	0 9	13.0 11.8	31.71 31.92	0.0 68.7
7	23.0	0 22	12.0 11.5	31.80 32.00	46.9 84.7
8	24.0	0 23	11.8 11.5	31.82 32.06	92.1 94.5
9	22.0	0 21	11.7 11.6	32.03 32.12	92.2 93.7
10	18.0	0 17	11.8 11.3	32.05 32.15	91.0 92.5
11	13.0	0 12	11.5 11.1	32.06 32.19	88.0 92.2
12	13.0	0 12	11.5 11.0	32.05 32.11	93.3 92.3

Appendix I. (cont'd).

12 March 1991

Station #	Depth m	Sample depth m	Temp (°C)	Salinity o/oo	Dissolved oxygen % sat.
1	5.	0 4.2	2.5 2.60	31.70 31.60	92.08 92.06
2	6.0	0 5.0	2.3 2.60	31.63 31.69	89.66 91.69
3	8.4	0 7.4	2.4 2.50	31.70 31.66	93.12 97.74
4	8.9	0 7.9	2.4 2.55	31.67 31.68	97.58 92.95
5	6.7	0 5.7	2.5 2.60	31.72 31.64	98.04 97.80
6	12.6	0 11.6	2.3 2.55	31.69 31.66	97.60 97.95
7	27	0 26	2.3 2.55	31.68 31.70	98.80 100.48
8	18	0 17	2.6 2.55	31.68 31.65	99.64 99.32
9	25	0 24	2.6 2.55	31.61 31.67	98.82 99.68
10	22	0 21	2.2 2.55	31.64 31.69	97.92 98.57
11	14	0 13	2.3 2.58	31.64 31.63	96.80 99.39
12	14	0 13	2.5 2.58	31.68 31.61	96.97 99.20

Appendix I. (cont'd)

16 July 1991

Station #	Depth m	Sample depth m	Temp (°C)	Salinity o/oo	Dissolved oxygen % sat.
1	2.4	0 1.4	13.4 10.50	31.64 31.60	44.1 44.6
2	5.7	0 4.7	12.9 10.25	31.62 31.66	45.57 55.60
3	7.9	0 6.9	12.6 10.25	31.66 31.66	73.78 47.76
4	8.6	0 7.6	12.6 10.13	31.70 31.66	91.61 52.01
5	6.6	0 5.6	13.3 10.16	31.67 31.66	88.15 84.28
6	11.6	0 10.6	12.4 9.90	31.73 31.67	109.43 93.97
7	28.0	0 27.0	10.8 9.80	31.74 31.70	107.43 106.20
8	24.6	0 23.6	11.6 9.70	31.72 31.77	107.35 106.84
9	26.4	0 25.4	11.4 9.69	31.76 31.78	107.78 106.41
10	23.0	0 22.0	11.2 9.75	31.77 31.78	108.92 103.65
11	15.6	0 14.6	11.2 9.69	31.77 31.78	108.07 104.66
12	17.0	0 16.0	11.4 9.75	31.73 31.82	105.07 104.30