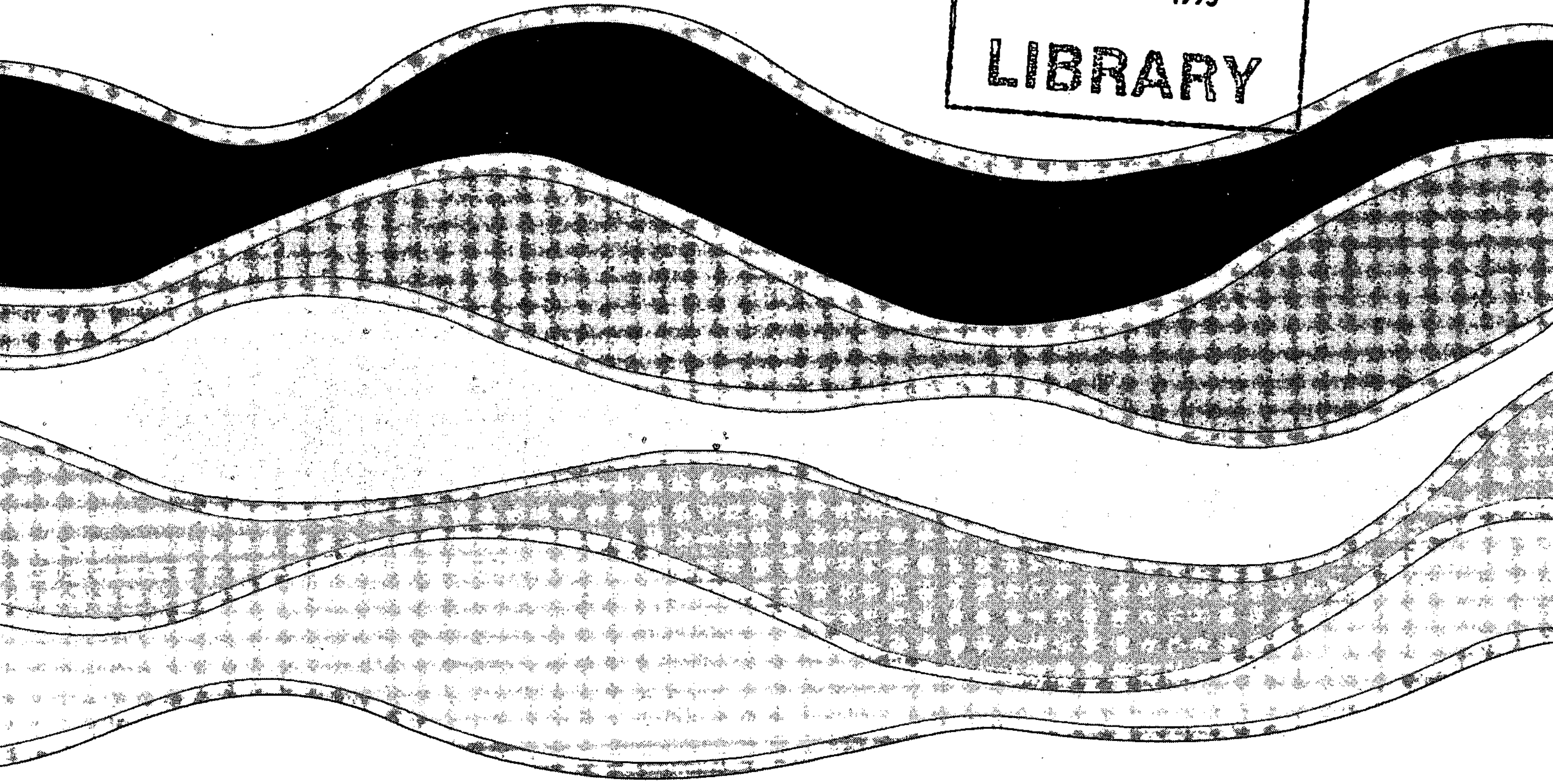
93-29

NATIONAL
WATER
RESEARCH
INSTITUTE

INSTITUT
NATIONAL
de RECHERCHE
sur les
EAUX



VOLATILE HALOCARBONS AS TRACERS OF PULP MILL EFFLUENT PLUMES

M.E. Comba, V.S. Palabrica and K.L.E. Kaiser

NWRI Contribution No. 93-29

VOLATILE HALOCARBONS AS TRACERS OF PULP MILL EFFLUENT PLUMES

M.E. Comba, V.S. Palabrica and K.L.E. Kaiser

Nearshore-Offshore Interactions, Lakes Research Branch, National Water Research Institute
P.O. Box 5050, Burlington, Ontario, L7R 4A6, CANADA

Submitted to: *Environmental Toxicology and Chemistry*
Date received:
Date accepted:

Running Head: Halocarbons as pulp mill effluent tracers

Corresponding Author: Dr. K.L.E. Kaiser
P.O. Box 5050
Burlington, Ont. L7R 4A6
Canada

Phone: 416-336-4756
Fax: 416-336-6430

MANAGEMENT PERSPECTIVE

Title: Volatile halocarbons as tracers of pulp mill effluent plumes

Authors: M.E. Comba (NOI/LRB)
V.S. Palabrica (NOI/LRB)
K.L.E. Kaiser (NOI/LRB)

Submitted to: *Environmental Toxicology and Chemistry*

Date: July, 1993

Perspective:

This work uses volatile halocarbons in a pulp mill effluent, including chloroform, bromodichloromethane, tri- and tetrachloroethylene, as tracers for the distribution and movements of effluent currents in a receiving water bay on the north shore of Lake Superior. The results indicate the simplicity and usefulness of the technique and the significantly improved resolution of effluent plume delineation over the customary use of conductance profiles.

In the specific case at hand, the distribution patterns of chloroform and a brominated analog, bromodichloromethane, also suggest the release of chloroform from sediments in the bay.

VOLATILE HALOCARBONS AS TRACERS OF PULP MILL EFFLUENT PLUMES

MICHAEL E. COMBA, VIRGINIA S. PALABRICA and KLAUS L.E. KAISER[1]

Nearshore-Offshore Interactions, Lakes Research Branch, National Water Research Institute
P.O. Box 5050, Burlington, Ontario, L7R 4A6, CANADA

(*Received* ....1993; *Accepted*....................)

Abstract - This work describes the use of volatile halocarbons in a pulp mill effluent, including chloroform, bromodichloromethane, tri- and tetrachloroethylene, as tracers for the distribution and movements of effluent currents in a receiving water bay (Jackfish Bay, Lake Superior) on the north shore of Lake Superior. The results indicate the simplicity and usefulness of the technique and the significantly improved resolution of effluent plume delineation over the customary use of conductance profiles.

In the specific case at hand, the distribution patterns of chloroform and a brominated analog, bromodichloromethane, also suggest the release of chloroform from sediments in the bay.

Keywords - Chloroform Bromodichloromethane Tracers Pulp mill,

INTRODUCTION

Bleaching methods for pulp and paper frequently use elemental chlorine which leads to the formation of a variety of chlorinated materials. The compounds formed are both low molecular weight chloro-methane/ethane products such as chloroform and their higher molecular weight polar precursors.

Chloroform has been shown to be a useful tracer of chlorinated effluents into oceans [1]. In

---

[1] To whom correspondence should be addressed.

addition, previous studies [2-6] have demonstrated the sensitivity and application of volatile halocarbon fingerprints to determine contaminant sources and differentiate water masses and plume dispersions in lakes, bays and rivers. In other work, a common association of chloroethylenes, carbon tetrachloride and chloroform with polychlorinated biphenyls (PCB), polynuclear aromatic hydrocarbons (PAH) and certain metals has been shown [7]. As volatile halocarbons serve as excellent tracers of industrial effluent plumes in lakes and rivers, it was expected that they would also be useful to track pulp mill effluents in receiving waters such as Jackfish Bay, Lake Superior.

Jackfish Bay currently receives, on average, 94,000 m^3/day of bleached kraft mill effluent which constitutes 65-90% of the flow of Blackbird Creek and originates near Terrace Bay, Ontario, some 14 km from the creek's discharge into Moberly Bay. Mill operation began in 1949 as an unbleached kraft process which discharged untreated effluent. Cold bleaching was introduced in 1959 which was converted into a fully hot bleached two-line kraft mill, in 1972. The bleaching process utilized chlorine gas which was produced on site until it was discontinued in 1978 [8]. At that time, several technical improvements were installed including primary effluent treatment by passage through two clarifying reactors.

Beginning with September 1989, the effluent stream receives secondary aeration and lagoon impoundment, which comprises three cells utilizing aerobic microorganisms to degrade organic matter, and which provides a 8-12 day retention time of the mill effluent. Daily solid discharges prior to 1989 which were reported at >5800 kg TSS, subsequently declined to 4000 kg after secondary treatment. The installation of secondary treatment eliminated most of the then documented acute toxic effects of the effluent, however there is insufficient information to conclude whether the treatment also removes any causative agents responsible for sublethal biological effects.

One major concern [9-11] has been the observation of no significant improvement in the mixed-function oxidase activity (MFO) in fish with improving physical conditions in Jackfish Bay. Hepatic ethoxyresofurin-o-deethylase (EROD) activities in longnose sucker, white sucker and whitefish were still induced one year after startup of secondary treatment and two weeks after mill shutdown. EROD activities were reduced after short-term shutdowns indicating that the causative agents may be more rapidly removed from fish tissues than previously expected. Spatial and species variations in EROD activity were observed which also could not be readily explained.

In Terrace Bay, chloroform originates from two treatment steps, the chlorination of the town's intake water which also supplies the mill and the chlorine based bleaching process. Chloroform concentrations measured in 1989 raw and treated lake water at the Terrace Bay pumphouse were 2.4 and 21 μg/L, respectively (P. Jordan, Ministry of the Environment, Thunder Bay, personal communication, 1993). These levels are several orders of magnitude higher than what can easily be determined with the headspace method [12]. Moreover, they have been shown to be perceived by fish [13], and longer term exposure to certain volatile chlorocarbons has shown to be toxic to some fish species at low μg/L levels [14, 15].

EXPERIMENTAL

Water samples for volatile headspace analysis were taken from a Boston Whaler in August and October of 1991. During August, the survey encountered an elevated conductivity plume wedged between the 6 to 8 m depth of the basin. Samples were collected at this depth for stations which had elevated conductivity readings. This wedge was not observed in the October survey. Samples were collected between the evening of August 20 to the mid-afternoon of August 22 within a span of 45 hours. In the fall, samples were collected from October 21 to 23, 1991. The sites sampled during the two surveys and the bay's bathymetry are described in Fig. 1 and 2.

Conductivity profiles to a depth of 15 m were taken with a YSI Model SS-SCT conductivity meter and measured in increments of 5 μS. Surface water (1 m), hypolimnion water (bottom less 1 m) and water samples selected on elevated conductivity readings were acquired using a 1 L Van Dorn water sampler. Temperature, depth and conductivity measurements were recorded for each sample. Detailed sampling and analytical data are given elsewhere [16].

The volatile portion of each sample was processed within 8 hours of collection and isolated using the headspace procedure [12]. The concentrations of the volatile halocarbons of interest were determined with cryogenic capillary column gas chromatography using electron capture detection. The procedure cited above has detection capabilities below 1 ng/L (ppt) for the compounds reported.

RESULTS

Volatile Halocarbon Concentrations in Jackfish Bay

The volatile halocarbon compounds observed in Jackfish Bay, listed in order of frequency of occurrence and concentration were: **chloroform** (CFM), **trichlorofluoromethane** (TCFM), **tetrachloroethylene** (TECE), **carbon tetrachloride** (CTC), **trichloroethylene** (TCE), **1,1,1-trichloroethane** (TCA), **bromodichloromethane** (BDCM) and **dibromochloromethane** (DBCM). Mean halocarbon concentrations are given in **Table 1**.

Chloroform levels near the mouth of **Blackbird Creek** in 1987 and 1988 were reported to be 175 and 100 μg/L [8]. In 1991, the concentrations of chloroform at the mouth of Blackbird Creek were 990 and 1600 ng/L, respectively. Levels higher than the source value of chloroform were found at some offshore stations, the largest being 2700 ng/L near the thermocline of station 42 in August. Based on the mean concentration levels (**Table 1**), chloroform was the predominant volatile halocarbon contaminant observed in Jackfish Bay.

Significant levels of **trichlorofluoromethane** were observed (up to 56 μg/L on one occasion). The highest concentrations were found in the hypolimnion of the bay waters during both surveys. Elevated levels of trichlorofluoromethane were observed in August in surface waters of the outer bay. Previous studies have shown that the area off Cape Victoria can be composed of up to 50% effluent [8], however, the water mass associated with trichlorofluoromethane was determined to consist of Lake Superior water by its non-similarity with contaminated bay water, as differentiated by means of the chloroform levels, as discussed later on.

Carbon tetrachloride was observed at concentrations considerably higher than typical ambient river and lake levels (normally 1-10 ng/L). In August 1991 concentrations of 2800 ng/L and 3000 ng/L were measured at stations 24B and 42T. The mean concentrations of carbon tetrachloride in bay waters were significantly influenced by the few higher values, as evident from differences in mean concentrations (**Table 1**). CTC was also found in samples at the mouth of Blackbird Creek but at levels much lower than those in bay waters.

Tetrachloroethylene, **trichloroethane** and **trichloroethylene** concentrations were also significantly higher than the levels in either Blackbird Creek or in the outer parts of Jackfish Bay. The highest concentrations were observed at the same sites as those that had elevated carbon tetrachloride levels. Maximum concentrations of trichloroethane were observed at 2100 ng/L for station 42T and 1600 ng/L at station 24B in August, while lower values of 88 ng/L, station 35B and 66 ng/L, station 21B, were observed during October.

Spatial Distribution of Chloroform

August

In **August**, The distribution of the pulp effluent plume as depicted through profiles of chloroform concentrations in **Fig. 3** was a function of the bay water's thermal structure. The lake hypolimnion temperature averaged 9°C while the effluent plume and bay epilimnion was 19°C. Based on conductivity measurements the plume from Blackbird Creek was wedged between the epilimnion and hypolimnion in a 1 to 2 m band approximately 8 m below the water surface. The position of the plume appeared to coincide with the thermocline, which has previously been reported [8] to be located at a depth of approximately 6-8 m.

Colder hypolimnion lake water, (characterized by low chloroform levels) was observed in the deeper central channel areas of Jackfish and Moberly Bays, even within metres of the mouth of Blackbird Creek. The **colder lake waters** penetrating the **bay hypolimnion** waters segregate the plume water along both shorelines which are characterized by remnants of higher chloroform levels. The profiles of chloroform distribution throughout the water column can be interpreted as being circulated in a counter-clockwise direction, with profiles to the north and east of St. Patrick Island exhibiting signs of **upwelling and mixing in the shallower areas** at the confluence of circulating bay surface and incoming lake waters.

October

In **October**, weather conditions were crisp, with a 5-6 cm snowfall. The preceding weeks also had experienced regular precipitation events. The **winds** were strong out of the northeast causing 1 m waves which were disrupted by large incoming lake swells in the middle of the bay. The conductivity of the stream outfall was 60% lower than in August, however **chloroform** concentrations were almost twice the levels found in August. The **effluent temperature** at the mouth of Blackbird Creek was 2.5 °C which would result in lower chloroform losses due to volatilization. The bays' epilimnion and hypolimnion ranged between 7-8 °C. Because the effluent temperature was colder, its plume rapidly mixed to 4 °C and sank into the deeper water layers of Moberly Bay and migrated towards the open lake in the central channel of Jackfish Bay.

Distribution of Trichlorofluoromethane

Distribution plots (**Fig. 4**) of **trichlorofluoromethane** are in direct contrast to those observed for chloroform. Based on volatile chlorocarbon distributions in conjunction with conductivity measurements a clear resolution between lake and plume water masses can be made.

In **August**, water masses denoted as lake water by their levels of **TCFM** were evident along the eastern shoreline of Jackfish Bay and as far inshore as the hypolimnion waters of Moberly Bay. The highest concentrations were found at the northern edges of the deeper channel just outside Moberly Bay and to a lesser extent in the mixing zone to the east of St. Patrick Island, and graphically depict the confluence of counter-clockwise bay currents and incoming lake water.

In **October**, **TCFM** levels in Jackfish Bay were lower, in agreement with the conclusion that greater amounts of effluent are being retained within the bay. The mixing zone east of St. Patrick Island was less prominent although remnants of TCFM contaminated lake waters can be observed in the nearshore zones of Moberly Bay and the deeper central channels of Jackfish Bay. These observations correspond to the location of the stream plume by chloroform profiles, shown to occupy the deeper sections of the bay's hypolimnion and displace the (warmer) lake waters in the fall.

Plume Mixing in Jackfish Bay

The extent to which the Blackbird Creek stream flow mixes (as measured by % source value) with lake water in Jackfish Bay can also be estimated from the **chloroform to bromodichloromethane ratios (CFM/BDCM)**. This technique has been demonstrated successfully in the differentiation of separate water masses and chloroform source types (i.e. municipal and industrial) in waters of the Great Lakes basin [2-3, 17-18]. The CFM/BDCM ratio is dependant upon the formation of chloroform and bromodichloromethane, which is a function of the bromide ion concentration in the raw water supply from Lake Superior during water chlorination [19]. This ratio is significantly altered by subsequent additions of pure chloroform from the pulp bleaching process.

The **CFM/BDCM ratio** provides a better measurement of the source stream content than chloroform concentrations as this ratio minimizes any effect of fluctuations in concentrations as caused by changes in flow (i.e. runoff), intermittent discharge of contaminants and volatilization. In Jackfish Bay, Blackbird Creek constitutes the single most important point source of chloroform with a CFM/BDCM ratio distinct from that of lake water. The Blackbird Creek **CFM/BDCM ratio** value should remain constant over the short term, due to the mixing and retention capacity of the treatment lagoons. Hence, the use of ratio isopleths can provide better estimates of source stream content, based on the linear mixing relationship (**Fig. 5**) of the two water masses as quantitated by their individual CFM/BDCM ratios.

The August and October 1991 profiles (**Fig. 6**) of **% source value** were based on an August CFM/BDCM source ratio of 168:1, at station 1S (chloroform, 770 ng/L; bromodichloromethane, 4.6 ng/L) and an averaged October source ratio of 400. A lake CFM/BDCM ratio of 5:1, calculated from August outer bay and lake stations was used for both surveys, as no outer lake measurements were acquired during October. Ratios for some of the October samples were calculated for low level samples using the BDCM detection limit of 0.5 ng/L. This ratio is comparable to the 10:1 ratio measured in raw intake water in 1989 (P. Jordan, personal communication, 1993). Due to the large difference between the source and lake ratios, the lower precision of the open lake ratio values cause no significant shifts. This is apparent from the confidence intervals ranging between 0 to 10 CFM/-BDCM for lake ratios as shown in **Fig. 5** in units of percent resolution.

Profiles in October displayed higher % source values in Jackfish Bay waters compared to August. As mentioned earlier this is likely the result of a thermal gradient that restricts mixing and dilution between bay and lake waters. The effluent plume, which is then colder than the receiving water, followed the path of the deeper central channels, with most of the effluent located in the hypolimnion. Distribution profiles clearly indicate counter-clockwise circulation with overlapping waters and mixing in the western regions of the bay.

Good overall agreement of the plume in the receiving water was obtained with both chloroform and percent source value profiles. However, a number of subtle differences between the two profiles were observed that suggested contaminant concentrations and quantities of effluent are not necessarily contiguous. The argument here is that measurements defining the position and content of the source stream in nearshore receiving waters do not necessarily pinpoint those areas containing high levels of volatile halocarbon contamination, or vice-versa.

DISCUSSION

Nearshore-Offshore Interactions of Volatile Halocarbons

Principal component analysis provided three uncorrelated principal components (PC) of the variables. In PC Factor 1, the variables consisted of a group of **volatile halocarbons and chloroform**. The variability within PC Factor 2 was related to **temperature, depth and trichlorofluoromethane** while PC Factor 3 was weighted by the variables **chloroform and conductivity**. The correlation matrix of the variables examined is given in **Table 2**.

It was originally assumed that conductance and volatiles in Jackfish Bay would be highly correlated as the pulp effluent constitutes the principal flow of Blackbird Creek and is the only known major point source for these parameters. Although **conductance** profiles (**Fig. 7**) are in general agreement with the **chloroform** distribution, the linear correlation between conductance and chloroform was weak r= 0.33, although highly significant (P= 0.0000, for F= 26.6 and n= 204). Weaker correlations would be expected if any of the factors previously mentioned in the plume mixing predictions were true, namely that chloroform inputs fluctuate and therefore plume content as described by the conductivity does not necessarily coincide with the contaminant levels.

The correlation of **bromodichloromethane** and **chloroform** in Jackfish Bay was significant, with r = 0.51, (F = 76.6) but was also weaker than expected. The weaker correlation stems from the mixing between lake and plume waters which contain markedly different ratios of chloroform to bromodichloromethane.

Chloroethane/ethylenes and bromochloromethanes were highly correlated with each other. These volatile halocarbon compounds are normally found to be associated with chlorination of potable water and degreasing operations. There is sufficient evidence of oil and grease contamination in sediments of Jackfish Bay [8], the greatest concentrations found in the deeper embayments and on the downstream side of barriers, such as islands. These are the same areas for which high levels of chloroethane and chloroethylene volatile halocarbons were observed.

Carbon tetrachloride was also highly correlated with the chloroethane/ chloroethylene/bromomethane compounds. In our experience, high levels of CTC (i.e. >50 ng/L) are more often related to chemical production activities and are not typical for bleaching operations. A volatile chloroethylenes/CTC fingerprint was used to identify solvent/tars ("blob") at the bottom of the St. Clair River [4-5, 20-21], with a general composition similar to that of taffy tars which were formed during chlorine production with graphite electrode systems [22]. Taffy tars are thought to be the source of many of the highly chlorinated environmental contaminants, such as chlorinated styrenes, which are not commercially manufactured. The production of chlorine at the mill between 1972-1979 [8] may have been a source for the CTC. Co-produced volatile halocarbons could partition into any tars and other substrates and become sedimented out in the containment areas or sediments in Jackfish Bay.

The strong correlation of **carbon tetrachloride** and the **chloroethane** and **chloroethylenes**, normally associated with oils and grease, suggests that these compounds are being released slowly over time from materials settling or settled on the bottom of the bay. Findings made elsewhere [23] showed that materials released from pulp mill operations generated chloroform over a protracted period of time. The fact that carbon tetrachloride should not be present in substantial amounts under current mill practices would imply that some of these observed levels are from historic materials. Secondary contaminant releases from contaminated sediments would also explain the weaker correlations between chloroform, conductance and the other volatiles. A forward selection regression model with chloroform as the dependent variable, testing for linear relationships amongst the other volatile halocarbons (TCFM excluded) supported the conclusion that secondary sources contributed to the concentrations of volatile contaminants. Using the criteria, significance of $F \leq 0.05$ for acceptance and $F \geq 0.10$ for rejection, only bromodichloromethane was accepted by the model.

Trichlorofluoromethane was not significantly correlated with any of the other volatile compounds. The statistical separation of trichlorofluoromethane from the other volatile contaminants is interesting and supports the conclusion that this compound originates from other sources, as has been observed in other areas [2]. The route of its introduction to Jackfish Bay appears to be from inflowing lake water which are thought to be contaminated through atmospheric deposits. The latter may originate from mill stack emissions, which were observed to descend and closely contact the lake surface during both surveys. However we have no data to assess whether these stack emissions are indeed the source of trichlorofluoromethane.

CONCLUSIONS AND SUMMARY

1. The **volatile halocarbon** contaminant distribution patterns in Jackfish Bay appear to be primarily governed by the thermal regime of the receiving water in the bay and secondarily by wind driven currents.

2. The **CFM and BDCM** concentrations and their **ratios** suggest that sediments may be secondary sources of volatile halocarbons. The **CFM/BDCM ratios** allow the determination of source stream content in the receiving waters. The observed variations in volatile contaminant concentrations and % source values suggest that some discharges are intermittent, and therefore contaminants levels and source stream concentrations do not correlate very well.

3. **Conductance** measurements were weakly correlated with chloroform values and uncorrelated with the other volatile halocarbons. Together with paragraphs 2 and 3 above, we conclude that conductance measurements appear to be of limited use for determining areas of contamination. Volatile halocarbon profiles provided greater resolution, sensitivity and differentiated lake and effluent water masses, their movement and level of contamination.

4. The volatile chlorofluorocarbon **trichlorofluoromethane** appears to be associated more with lake water than the effluent entering Jackfish Bay. The source of this contamination is thought to be atmospheric deposition.

5. **Volatile halocarbon** measurements represent a cost-effective method that can be applied to address certain aspects of the EMM strategies and proposed new pulp and paper effluent regulations.

REFERENCES

1. **Fogelqvist, B., B. Josefsson and C. Roos.** 1982. Halocarbons as tracer substances in studies of the distribution patterns of chlorinated waters in coastal areas. *Environ. Sci. Technol.* **16:** 479-482.
2. **Kaiser, K.L.E. and I. Valdmanis.** 1979. Volatile Chloro- and chlorofluorocarbons in Lake Erie - 1977 and 1978. *J. Great Lakes Res.* **5:** 160-169.
3. **Comba, M.E. and K.L.E. Kaiser.** 1984. Tracking river plumes with volatile halocarbon contaminants. The Niagara River - Lake Ontario example. *J.Great Lakes Res.* **10:** 375-382.
4. **Kaiser, K.L.E. and M.E. Comba.** 1986a. Tracking river plumes with volatile halocarbon contaminants: The St. Clair River - Lake St. Clair example. *Environ. Toxicol. Chem.* **5:** 965-976.
5. **Kaiser, K.L.E. and M.E. Comba.** 1986b. Volatile halocarbon survey of the St. Clair River. *Water Poll. Res. J. Canada* **21:** 323-331.
6. **Comba, M.E., V.S. Palabrica, J. Wasslen, G.A. Bengert and K.L.E. Kaiser.** 1989. St. Lawrence River trace organic contaminants study (Part II), 1985. *National Water Research Institute, Contribution*, No. 89-51, 95 p.
7. **Comba, M.E. and K.L.E. Kaiser.** 1985. Volatile halocarbons in the Detroit River and their relationship with contaminant sources. *J. Great Lakes Res.* **10:** 404-418.
8. **RAP.** 1991. Jackfish Bay Remedial Action Plan. Stage 1: Environmental conditions and problem definition. North Shore of Lake Superior Remedial Action Plan, Canada and Ontario, 157 pp.
9. **Munkittrick, K.R., M.E. McMaster, C.B. Portt, G.J. Van Der Kraak and D.G. Dixon.** 1992. Changes in maturity, plasma sex steroid levels, hepatic mixed-function oxygenase activity, and the presence of external lesions in lake whitefish (*Coregonus clupeaformis*) exposed to bleached kraft mill effluent. *Can. J. Fish. Aquat. Sci.* **49:** 1-10.
10. **Munkittrick, K.R., C.B. Portt, G.J. Van Der Kraak, I.R. Smith and D.A. Rokosh.** 1991. Impact of bleached kraft mill effluent on population characteristics, liver MFO activity, and serum steroid levels of a Lake Superior white sucker (*Catostomus commersoni*) population. *Can. J. Fish. Aquat. Sci.* **48:** 1371-1380.
11. **McMaster, M.E., G.J. Van Der Kraak, C.B. Portt, K.R. Munkittrick, P.K. Sibley, I.R. Smith and D.G. Dixon.** 1991. Changes in hepatic mixed-function oxygenase (MFO) activity, plasma steroid levels and age at maturity of a white sucker (*Catostomus commersoni*) population exposed to bleached kraft pulp mill effluent. *Aquatic. Toxicology* **21:** 199-218.
12. **Comba, M.E. and K.L.E. Kaiser.** 1983. Determination of volatile contaminants in water at the ng/L level. *Inter J. Environ. Anal. Chem.* **16:** 17-31.
13. **Diamond, J.M., M.J. Parson and D. Gruber.** 1990. Rapid detection of sublethal toxicity using fish ventilatory behavior. *Environ. Toxicol. Chem.* **9:** 3-11.

14. **Loekle, D.M., A.J. Schecter and J.J. Christian.** 1983. Effects of chloroform, tetrachloroethylene, and trichloroethylene on survival, growth, and liver of *Poecilia sphenops*. *Bull. Environm. Contam. Toxicol.* 30: 199-205.

15. **Loekle, D.M.** 1987. The effects of chlorinated hydrocarbons on *Carassius auratus*. Ph.D. Thesis, State University of New York, Binghamton, NY.

16. **Comba, M.E., V.S. Palabrica and K.L.E. Kaiser.** 1993. Tracking bleached Kraft mill effluent with volatile halocarbons: The Jackfish Bay example. *National Water Research Institute, Contribution*, No. 93-19, 32 p.

17. **Oliver, B.G. and J. Lawrence.** 1979. Halocarbons in drinking water. A study of precursors and precursor removal. *J. Am. Water Works Assoc.* 71: 161-163.

18. **Kaiser, K.L.E. and M.E. Comba.** 1984. Volatile contaminants in the Welland River watershed. *J. Great Lakes Res.* 9: 274-280.

19. AWWA. 1993. Brominated DBPs. *J. Am. Water Works Assoc.* 85: 41-103.

20. **Carey, J.H. and J.H. Hart.** 1986. Gas chromatographic/Mass spectrometric (GC/MS) identification of the major components of non-aqueous material from the St. Clair River. *Water Poll. Res. J. Canada* 21: 309-322.

21. **Halfon, E.** 1986. Modelling the pathways of toxic contaminants in the St. Clair-Detroit River system using the TOXFATE model: The fate of perchloroethylene. *Water Poll. Res. J. Canada* 21: 411-421.

22. **Kaminsky, R. and R.A. Hites.** 1984. Octachlorostyrene in Lake Ontario: Sources and fates. *Environ. Sci. Technol.* 18: 275-279.

23. **Rogers, I.H. and H.W. Mahood.** 1982. Environmental monitoring of the Fraser River at Prince George. Chemical analysis of fish, sediment, municipal sewage and bleached kraft waste water samples. *Can. Tech. Rep. Fish. Aquat. Sci.* 1135: 1-15.

Table 1. Mean* concentrations (ng/L) of volatile halocarbons in Jackfish Bay.

COMPOUND	August Surface	August Thermocline	August Bottom	October Surface	October Bottom
Trichlorofluoromethane	16	16	89 (44)	7.1	1400 (12)
Chloroform	89	360 (240)	160 (98)	190	410
1,1,1-Trichloroethane	5.4	110 (6.6)	49 (8.4)	2.4	4.9
Carbon tetrachloride	6.6	140 (2.0)	80 (4.7)	1.5	3.6 (2.9)
Trichloroethylene	5.8	120 (4.0)	110 (1.7)	8.9	4.1
Bromodichloromethane	3.3	38 (1.5)	15 (3.5)	0.88	1.7
Dibromochloromethane	1.0	31 (0.54)	14 (2.1)	0.45	0.86
Tetrachloroethylene	8.6	190 (7.9)	150 (20)	2.1	3.1

* Weighted mean concentrations in parentheses after removal of outliers (Stations 42T, 24B in August, and 33B in October).

Table 2. Volatile halocarbon and conductance linear correlation (r) Matrix (n=204).

	$CFCl_3$	$CHCl_3$	$C_2H_3Cl_3$	CCl_4	C_2HCl_3	$CHBrCl_2$	$CHBr_2Cl$	C_2Cl_4	Cond.
$CFCl_3$	1.00	0.015	0.012	0.023	0.021	0.009	0.012	0.019	-0.02
$CHCl_3$		1.00	0.50	0.50	0.47	0.51	0.50	0.49	0.33
$C_2H_3Cl_3$			1.00	0.98	0.91	0.99	0.99	0.94	-0.02
CCl_4				1.00	0.97	0.96	0.98	0.99	-0.02
C_2HCl_3					1.00	0.87	0.91	0.99	-0.02
$CHBrCl_2$						1.00	0.99	0.91	-0.00
$CHBr_2Cl$							1.00	0.94	-0.015
C_2Cl_4								1.00	-0.03
Cond.									1.00

List of Figures

Fig 1

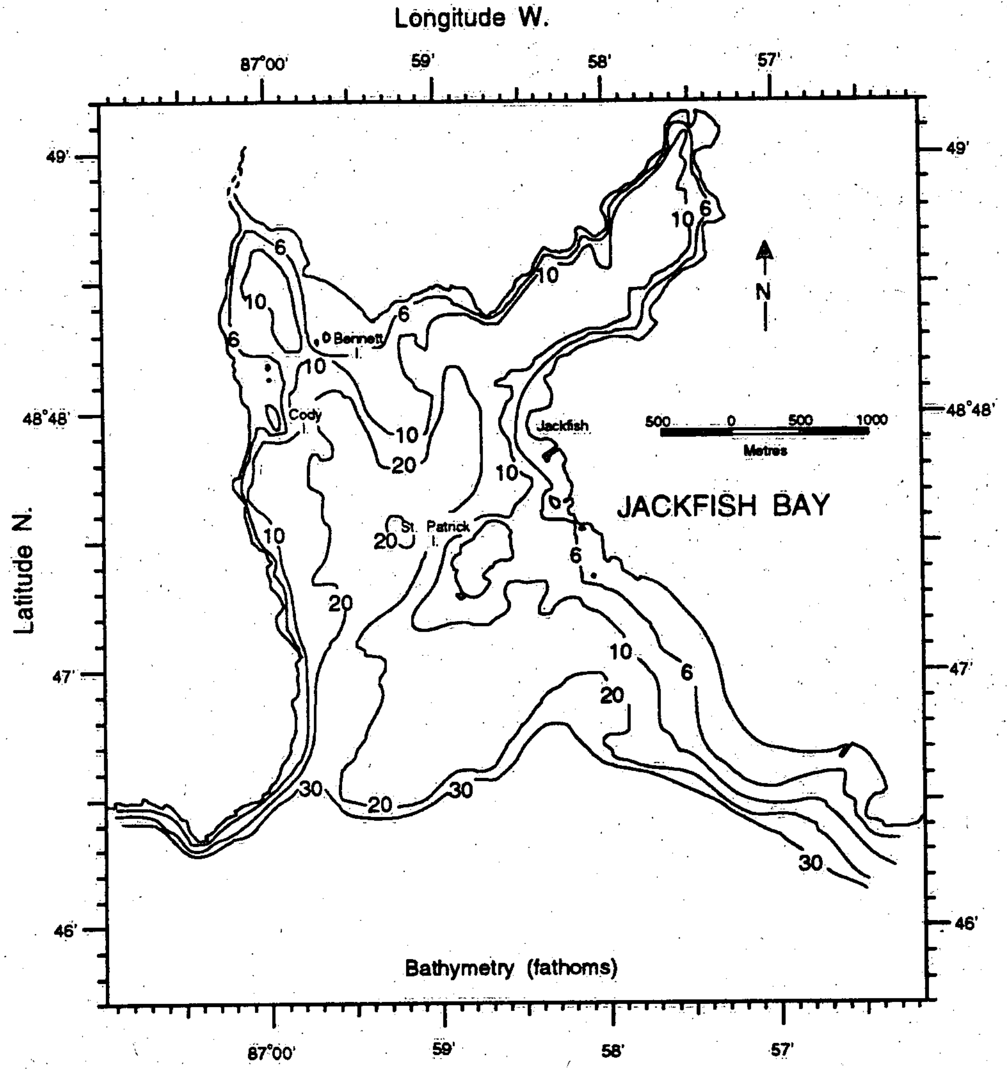


Fig. 1. Bathymetry (depth in fathoms) of Jackfish Bay, Lake Superior.

Fig 2

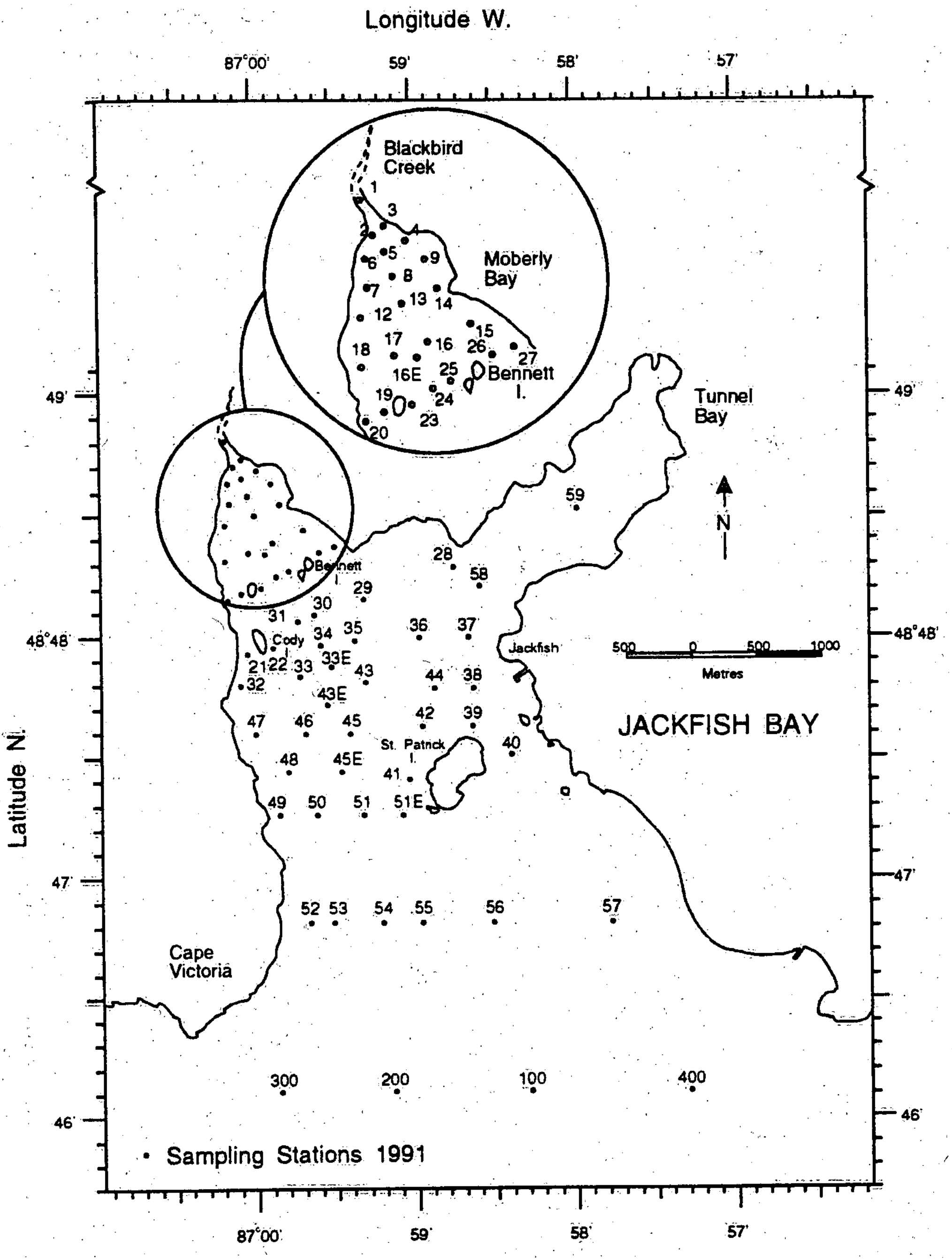


Fig. 2. Sampling locations in Jackfish Bay, Lake Superior.

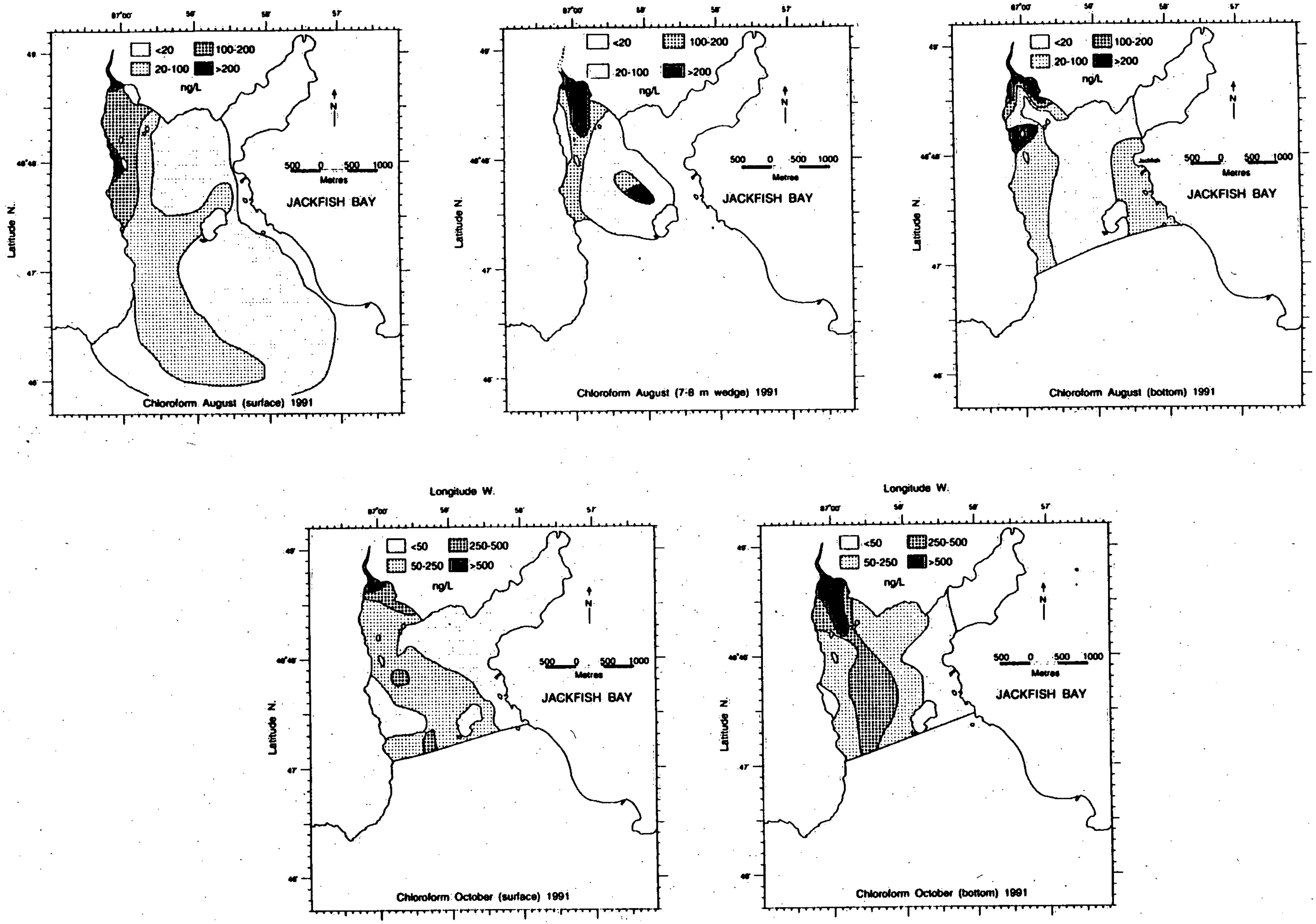


Fig. 3. Distribution and concentration (ng/L) of chloroform in Jackfish Bay, Lake Superior during August (surface; 7-8 m depth; bottom) and October (surface; bottom), 1991.

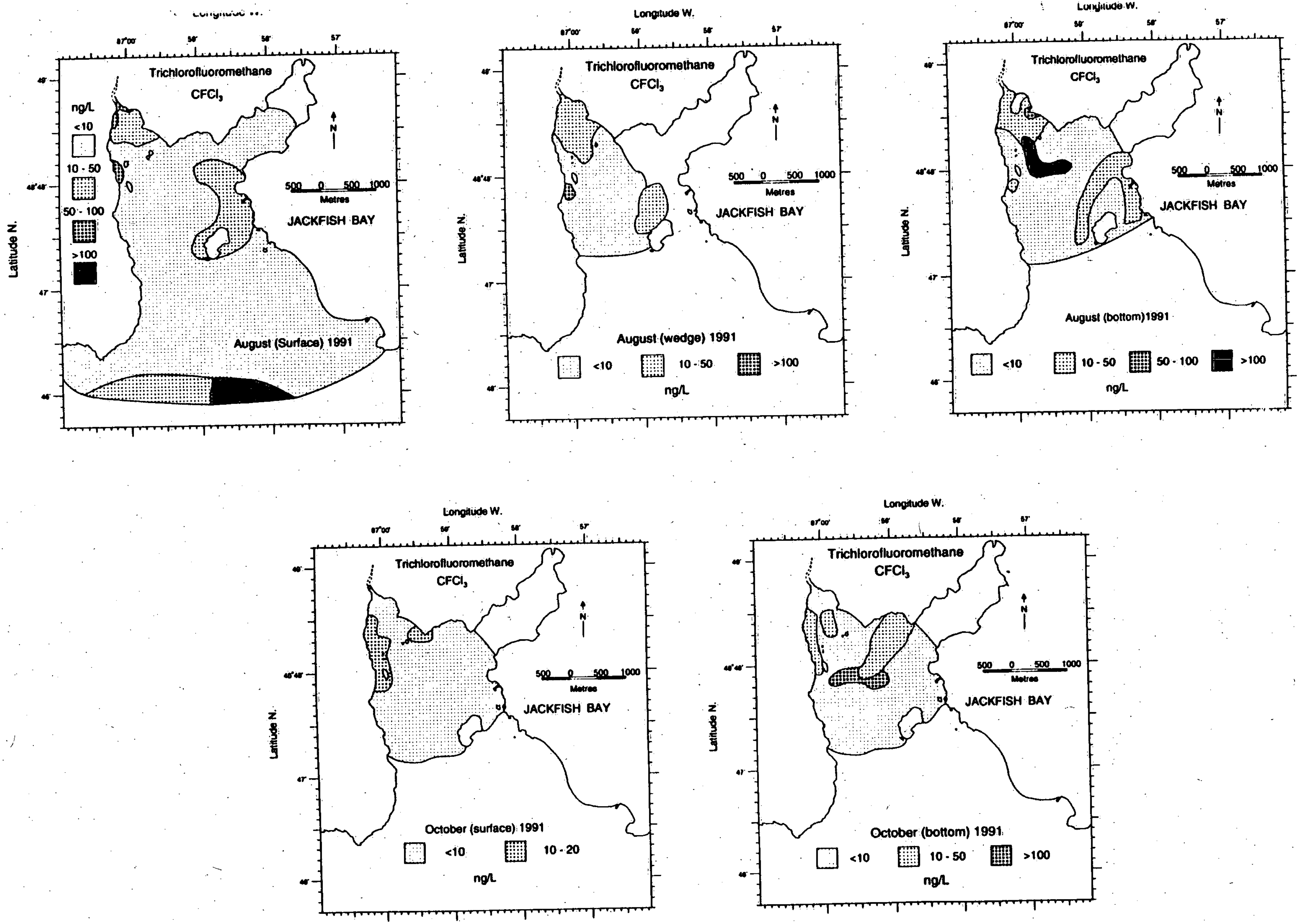


Fig. 4. Distribution and concentrations (ng/L) of trichlorofluoromethane in Jackfish Bay, Lake Superior, during August and October, 1991.

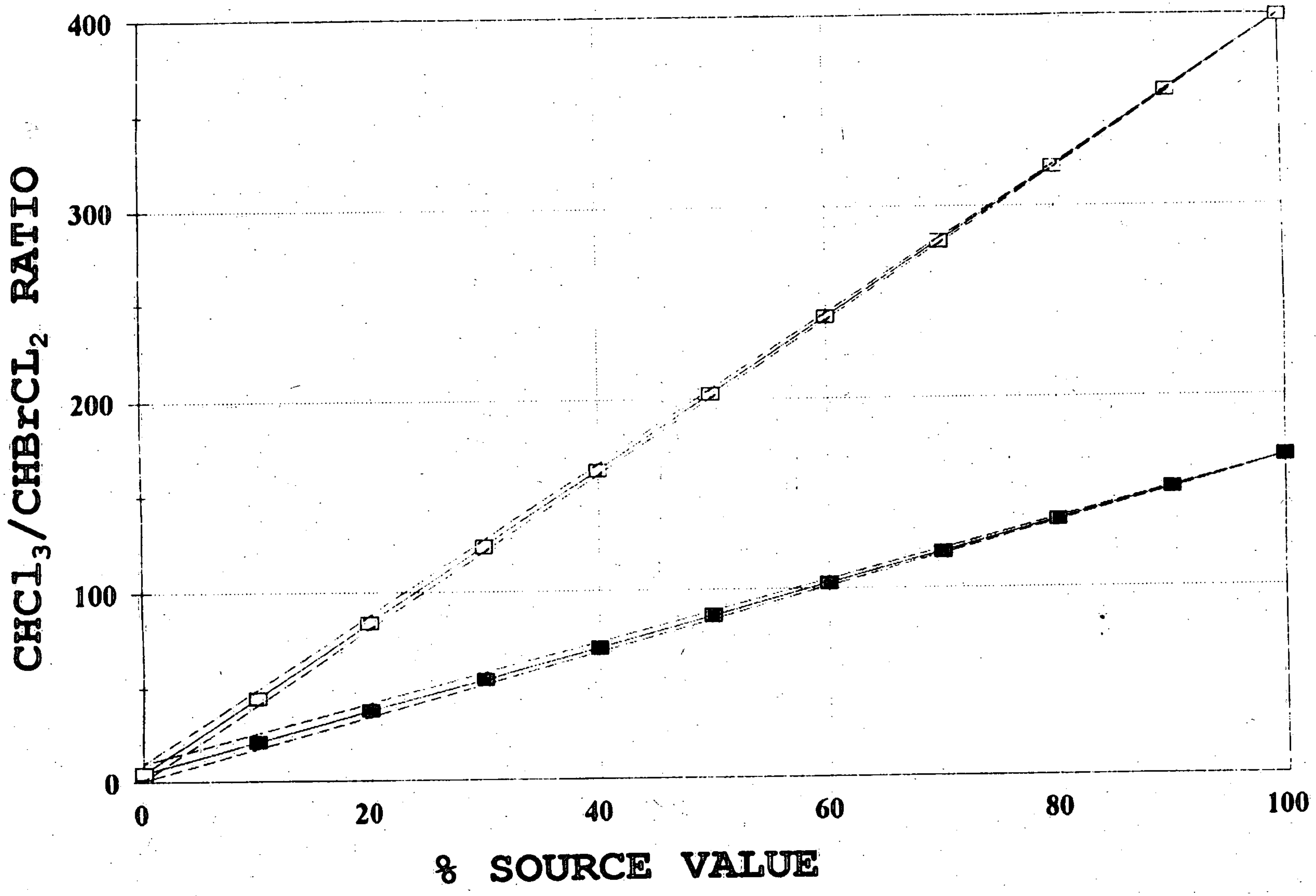


Fig. 5. Graph of CHCl$_3$/CHBrCl$_2$ ratios as linear functions of the mixing of Blackbird Creek effluent (100 % source value) with Lake Superior water (0 % source value) in Jackfish Bay, for August (■) and October (□), 1991 with 10% confidence intervals (dotted lines).

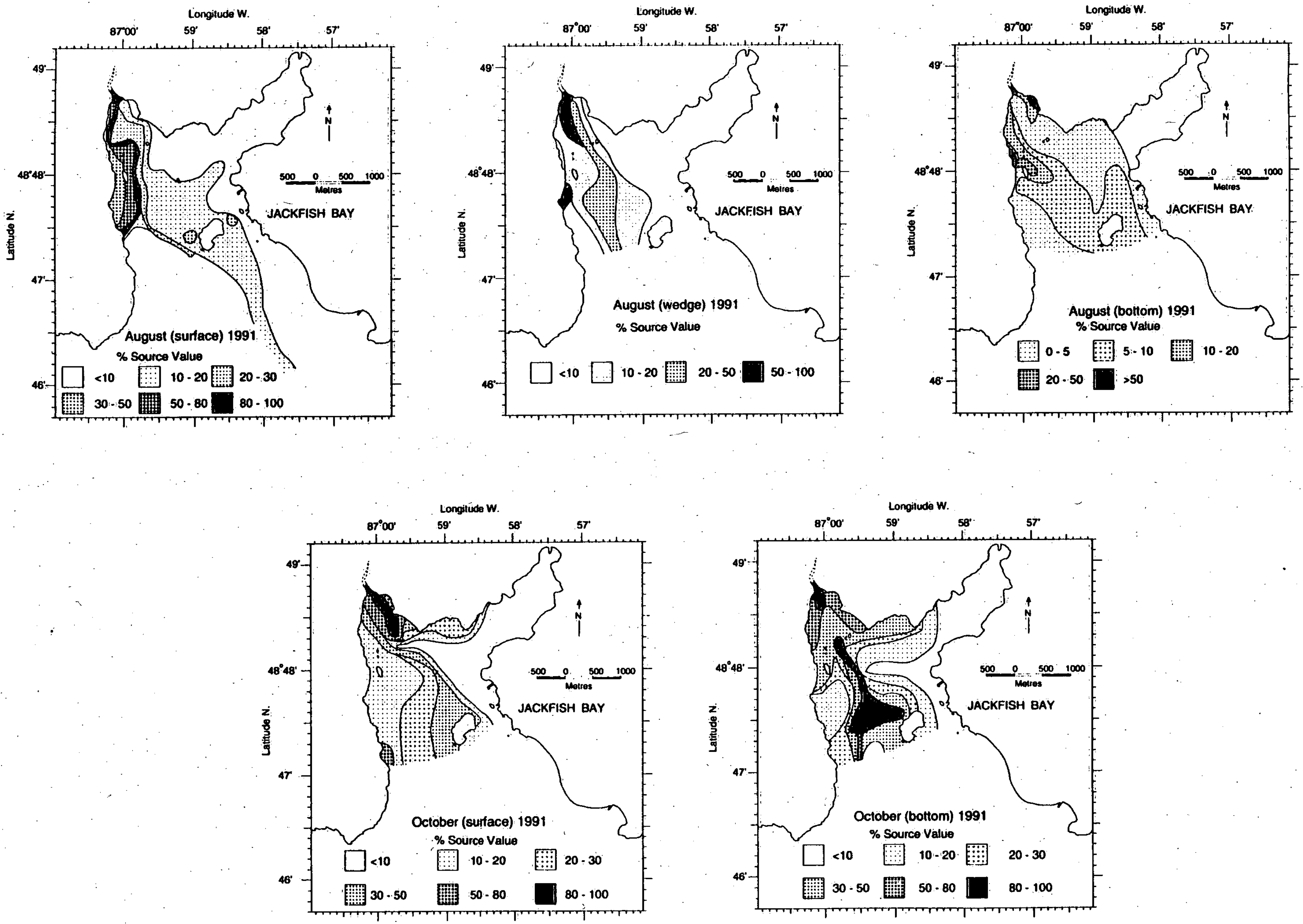
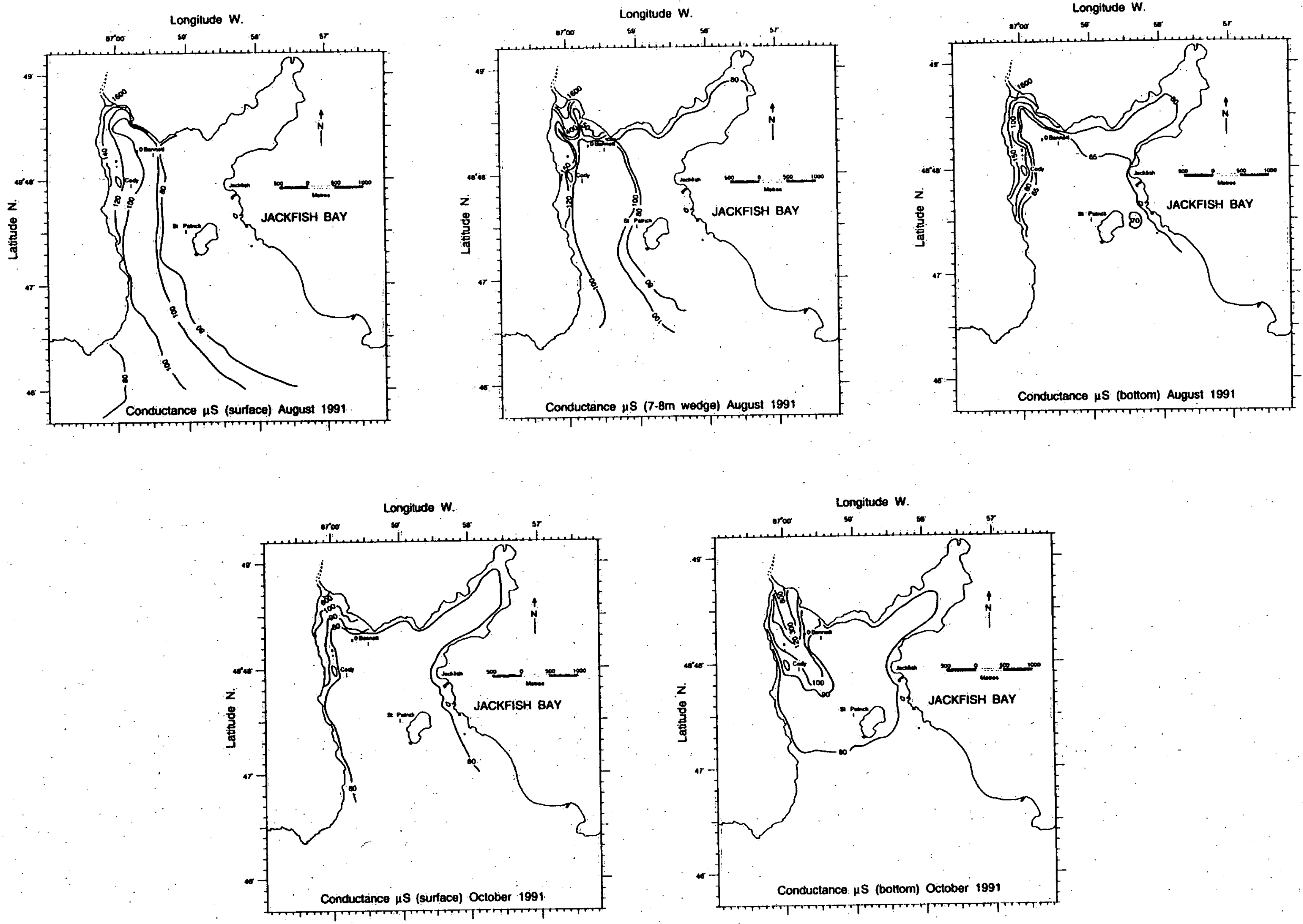


Fig. 6. Mixing profiles, expressed as % source Blackbird Creek value, based on chloroform/



Conductance µS (surface) August 1991

Conductance µS (7-8m wedge) August 1991

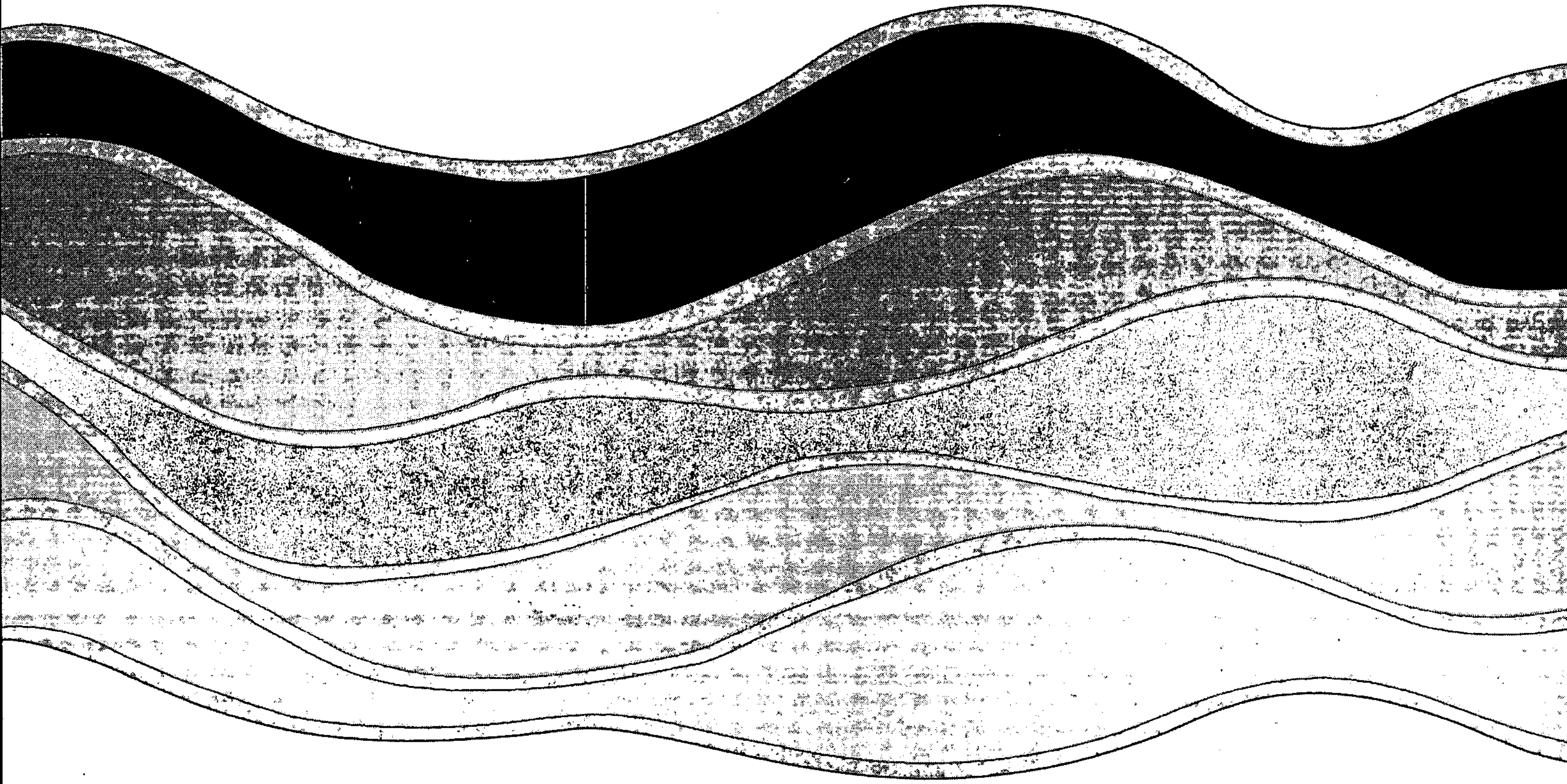
Conductance µS (bottom) August 1991

Conductance µS (surface) October 1991

Conductance µS (bottom) October 1991

Fig. 7. Conductance profiles in Jackfish Bay, Lake Superior, during August (surface; 7-8 m depth;

20344



NATIONAL WATER RESEARCH INSTITUTE
P.O. BOX 5050, BURLINGTON, ONTARIO L7R 4A6

Environment Canada Environnement Canada

Canada

INSTITUT NATIONAL DE RECHERCHE SUR LES EAUX
C.P. 5050, BURLINGTON (ONTARIO) L7R 4A6

Think Recycling!

Pensez à recycler !