## Environment Canada Water Science and Technology Directorate

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Tracking Bleached Kraft Mill Effluent with Volatile Halocarbons: The Jackfish Bay Example By: M. Comba, V. Palabrica, K. Kaiser NWRI Contribution # 93-28

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### Tracking Bleached Kraft Mill Effluent with Volatile Halocarbons: The Jackfish Bay Example.

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## TRACKING BLEACHED KRAFT MILL EFFLUENT WITH VOLATILE HALOCARBONS:

#### THE JACKFISH BAY EXAMPLE.

#### 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) 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.

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#### INTRODUCTION

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Bleaching methods for pulp and paper frequently use elemental chlorine which leads to the formation of chlorinated materials. The volatile compounds formed are mostly low molecular weight chloro-methane/ethane products such as chloroform, and their higher molecular weight precursors. These compound types are designated as "priority substances" by the Ministry of Ontario's MISA program and Environment Canada's CEPA regulations. Both programs call for the remediation and reduction in emissions of these compounds. The study site at Jackfish Bay on the north shore of Lake Superior was selected because of its unique characteristic of receiving large amounts of pulp mill effluent without being influenced by other activities. The objective of this work was to examine chloroform and other halocarbon emissions into the bay as they originate from the Bleached Kraft Mill (BKM) effluent. The work was supported in-part through CEPA funding and facilitated ongoing research activities of the Departments, Fisheries and Oceans and Environment Canada, both of whom participate in a Remedial Action Plan (RAP) at this site.

Chloroform has been shown to be a useful tracer of pulp effluent into oceans (Fogelqvist, 1982). In addition, previous studies by the authors (Kaiser and Valdmanis, 1979; Comba and Kaiser, 1984; Kaiser and Comba, 1986 a,b and Comba et al., 1989), have demonstrated the sensitivity and application of volatile halocarbon fingerprints to determine contaminant sources and differentiate water masses and plume dispersions into lakes. It is thought that such techniques may also be useful in addressing certain aspects of the proposed Environmental Effects Monitoring (EEM) strategy as they apply to pulp and paper discharges.

As outlined in the Stage I report (RAP, 1991), Jackfish Bay currently receives on average, 94,000 m<sup>3</sup>/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 was discontinued in 1978. According to the RAP report, chlorine was produced with a mercury electrolysis process (RAP, 1991), however a company representative has indicated this to be incorrect and stated a Matheson chlorine dioxide generator was used.

In 1978, 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.

There are no known significant point sources of contaminants to Jackfish Bay other than those from Blackbird Creek, ignoring atmospheric inputs and the railway track along the bay's shoreline. The area was a significant harbour for shipping traffic in earlier years with a 1911 shipwreck located in Tunnel Bay. There is no evidence indicating that any of the former activities or the two abandoned gold mines within the local drainage basin have contributed to the present environmental damage in the bay. A major Bunker Oil spill in the mid 1970's and numerous smaller spills, primarily from acid and alkali overflows have occurred from the mill and are detailed in the Stage 1 RAP report (RAP, 1991). The original containment lagoons, Lake A and Moberly Lake (Lake C) in the Blackbird Creek drainage basin contain deposits of debris from pulping activities, with Lake A being bypassed in the early 1980's.

Jackfish Bay is a designated Area of Concern (AOC) with a Stage 2 RAP inplace. Proposed monitoring strategies are being designed to examine which factors are responsible for impaired use, and to establish what requirements are necessary for the selection of alternate remedial measures needed to restore beneficial uses.

One other major concern has been the observation of no significant improvement in the mixed-function oxidase activity (MFO) in fish with improving physical conditions in Jackfish Bay (Munkittrick et al., 1991, 1992, and McMaster et al., 1991). 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. Since volatile halocarbon concentrations have been shown to be significantly correlated with higher concentrations of metals, organochlorine and polyaromatic hydrocarbons in sediments and water (Comba and Kaiser, 1985), and serve as excellent tracers of effluent plumes in lake waters, (Kaiser and Comba, 1986a; Kaiser and Valdmanis, 1979) it was expected that they would also track pulp mill effluents in Jackfish Bay.

#### EXPERIMENTAL

Water samples for volatile headspace analysis were taken from a Boston Whaler in August and October of 1991. Positions were fixed by visual triangulation and water depth. This method was accurate to within a few metres for inner bay stations and slightly greater for outer bay stations. During August, the survey encountered an elevated conductivity plume wedged between the 6 to 8 metre 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. Samples were collected from October 21-23, 1991, in a similar time frame. The sites sampled during the two surveys and the bay's bathymetry are described in Figure 1.

Conductivity profiles to a depth of 15 metres were taken with a YSI Model SS-SCT conductivity metre and measured in increments of 5  $\mu$ S. Surface water (1 metre), hypolimnion water (bottom less 1 metre) 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.

The volatile portion of each sample was processed within 8 hours of collection and isolated using the headspace procedure developed by Comba and Kaiser (1983). 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.

#### BACKGROUND

#### **Occurrences of Volatile Halocarbons**

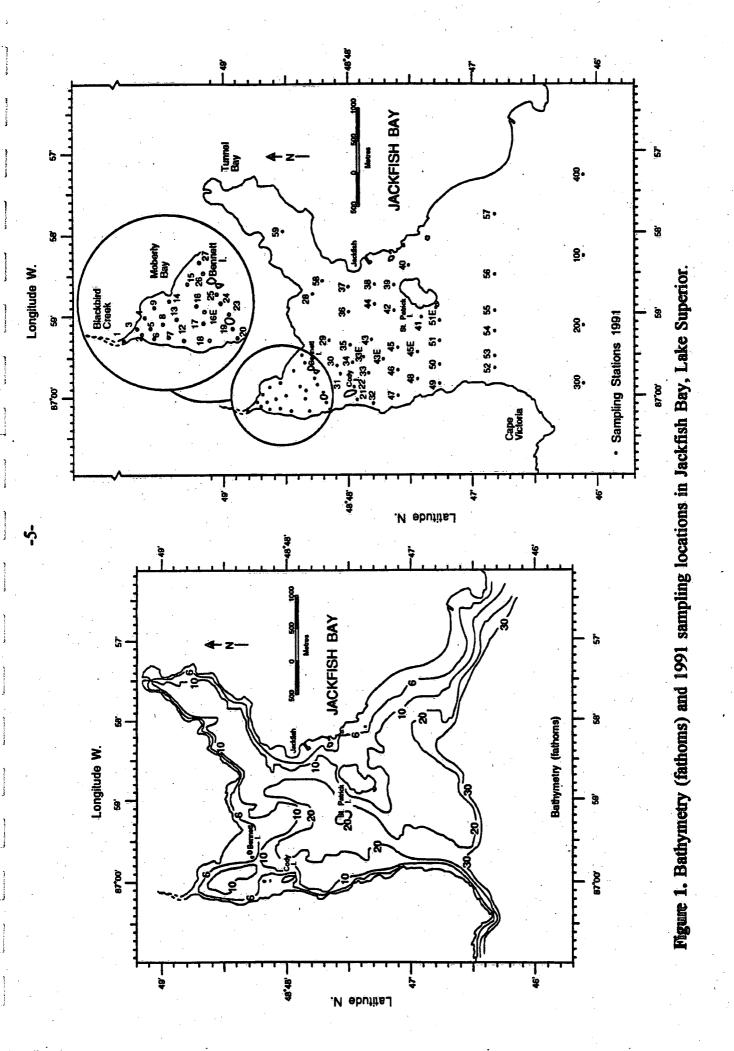
Chloroform originates primarily from the chlorination of raw water for potable water supplies, sewage chlorination or directly from industrial sources. In Terrace Bay, chloroform originates from two treatment steps, the chlorination of the town's intake water which also supplies the mill and the chlorine based bleaching process. Respective chloroform concentrations measured in 1989 raw and treated lake water at the Terrace Bay pumphouse were 2.4 and 21  $\mu$ g/L (MOE, 1993). Exact inputs of chloroform from each of the two chloroform treatment steps could not be determined since sampling at each source was not done. Atmospheric levels of chloroform downwind of the mill in July, 1985 were reported between 5.2 to 237  $\mu$ g/m<sup>3</sup> (RAP, 1991). Washout of atmospheric components as well as deposition of previous atmospheric fallout within the 62 km<sup>2</sup> drainage basin could additional amounts after major precipitation events. Release of chloroform into

bay waters by desorption from suspended and/or bottom sediments may be another possible route of introduction.

The chlorobromomethanes are by-products of potable water chlorination and are formed by reaction of the bromide ion in the raw water supply. This reaction and the levels and ratios of brominated organic products resulting from it depends on the concentration of bromide ion in the raw water (AWWA, 1993; Oliver and Lawrence, 1979). In large homogenous systems such as Lake Ontario or Lake Superior, potable water chlorination procedures produce relatively constant ratios of chloroform to chlorobromomethane compounds (Comba and Kaiser, 1984).

Trichlorofluoromethane is a common refrigeration fluid and also finds application as a blowing agent in the production of polyurethane and ethylene foams. Its occurrence in surface waters together with carbon tetrachloride has normally been associated with chemical manufacturing activities. The occurrence of both materials at relatively elevated concentrations in Jackfish Bay was not expected in view of the type of industrial processes here. In our previous observations, carbon tetrachloride has been exclusively related to activities involving primary production and synthesis of organochlorine chemicals and only as a minor component of the products of chlorinated water.

Chlorinated ethanes and ethylenes are commonly used in mixtures and solvents for degreasing operations. Minor amounts are also associated with chlorination of water but are frequently present already in the raw water supply rather than major products of chlorination. Tetrachloroethylene is a common dry cleaning fluid and often a principal groundwater contaminant due to poor disposal practices.



#### RESULTS

#### Volatile Halocarbons in Jackfish Bay

The volatile halocarbon compounds observed in Jackfish Bay, listed in order of frequency of occurrence and concentration were: chloroform  $(CHCl_3)$ , trichlorofluoromethane  $(CFCl_3)$ , tetrachloroethylene  $(C_2Cl_4)$ , carbon tetrachloride  $(CCl_4)$ , trichloroethylene  $(C_2HCl_3)$ , 1,1,1-trichloroethane  $(C_2H_3Cl_3)$ , bromodichloromethane  $(CHBrCl_2)$  and dibromochloromethane  $(CHBr_2Cl)$ . Individual halocarbon concentrations are given in Table 1 for the August survey, and Table 2 for the October survey.

Chloroform levels near the mouth of Blackbird Creek in 1987 and 1988 were reported to be 175 and 100  $\mu$ g/L (RAP, 1991). In August and October, 1991, the respective concentrations of chloroform at the mouth of Blackbird Creek were 990 and 1600 ng/L. 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. The mean chloroform concentration (Table 3) in the bay's epilimnion was 89 ng/L in August and 190 ng/L in October. Higher mean values were measured in the thermocline and hypolimnion during both surveys, but the August weighted mean values were significantly reduced when calculated without the elevated values for stations, 42T and 24B. Based on the weighted mean concentration levels (Table 3), chloroform was the predominant volatile halocarbon contaminant observed in Jackfish Bay.

Significant levels of trichlorofluoromethane were observed (up to 56  $\mu$ g/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 (RAP, 1991), 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. Above average but lower concentrations were found at stations 17S, 20S and 35B in August and 16S, 45S, 46S, 21B and 33B in October. The mean concentrations of carbon tetrachloride in bay waters were significantly influenced by the few higher values, as evident from differences in weighted mean concentrations (Table 3). Carbon tetrachloride was also found in samples at the mouth of Blackbird Creek but at levels much lower than those in bay waters.

COMPOUND	August Surface	August Thermo- cline	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

Table 3. Mean\* concentrations (ng/L) of volatile halocarbons in Jackfish Bay, 1992.

\* Mean and weighted mean concentrations in brackets after removal of outliers (Stations 42T, 24B in August, and 33B in October).

Tetrachloroethylene, trichloroethane and trichloroethylene concentrations were also significantly higher than ambient river or lake levels and occurred with greater frequency than carbon tetrachloride. 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. Respective concentrations of trichloroethylene and tetrachloroethylene were 4100 and 5200 ng/L, station 24B and 2300 and 3600 ng/L, for station 42T in August. There were no exceptionally high values of tetrachloroethylene in the October survey although elevated levels of 400 ng/L trichloroethane at station 46S and 66 ng/L at station 21B were observed. The highest concentration of trichloroethylene occurred at station 21B and was 120 ng/L.

#### Distribution of the Blackbird Creek Chloroform Plume August

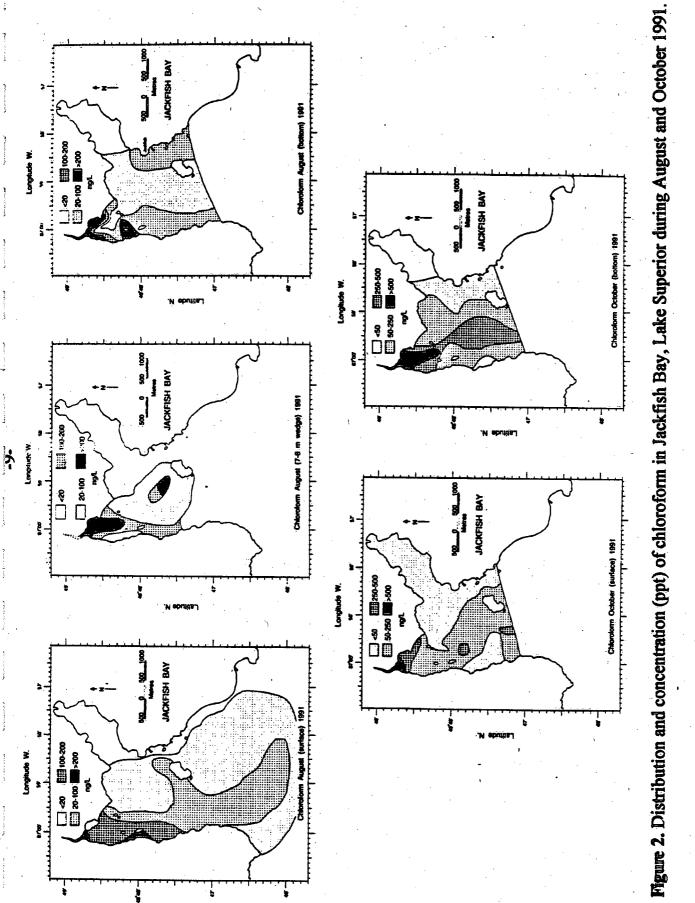
Water currents within the bay's confines are reported (RAP, 1991) to predominate in a counter-clockwise direction, entering from Lake Superior on the eastern side of Jackfish Bay and exiting on the western shoreline, in keeping with the Coriolis force. A model predicts the Blackbird Creek effluent stream would flow south through Moberly Bay following the western edge of Jackfish Bay. It was also stated that the prevailing westerly winds were thought to impact local surface currents in the bay (RAP, 1991).

On August 21, winds were light at approximately 15 km/h out of the southwest producing a small chop. On August 22, the winds switched to the northwest and were brisk at about 20-30 km/h causing 1-2 metre seas. The distribution of the pulp effluent plume as depicted through profiles of chloroform concentrations in Figure 2 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 metre band approximately 8 metres below the water surface. The position of the plume appeared to coincide with the thermocline, which has previously been shown (RAP, 1991) to be located at a depth of approximately 6-8 metres. Based on the overall distribution patterns, the chloroform in the wedge appeared to mix vertically and horizontally within the bay, contaminating the surface waters on the westerly shoreline of the outer bay. The effluent distribution conformed to modelled results, (i.e.) the source materials were found predominately in the western portions of Jackfish Bay and also in the hypolimnion of Moberly Bay.

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 metre 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.



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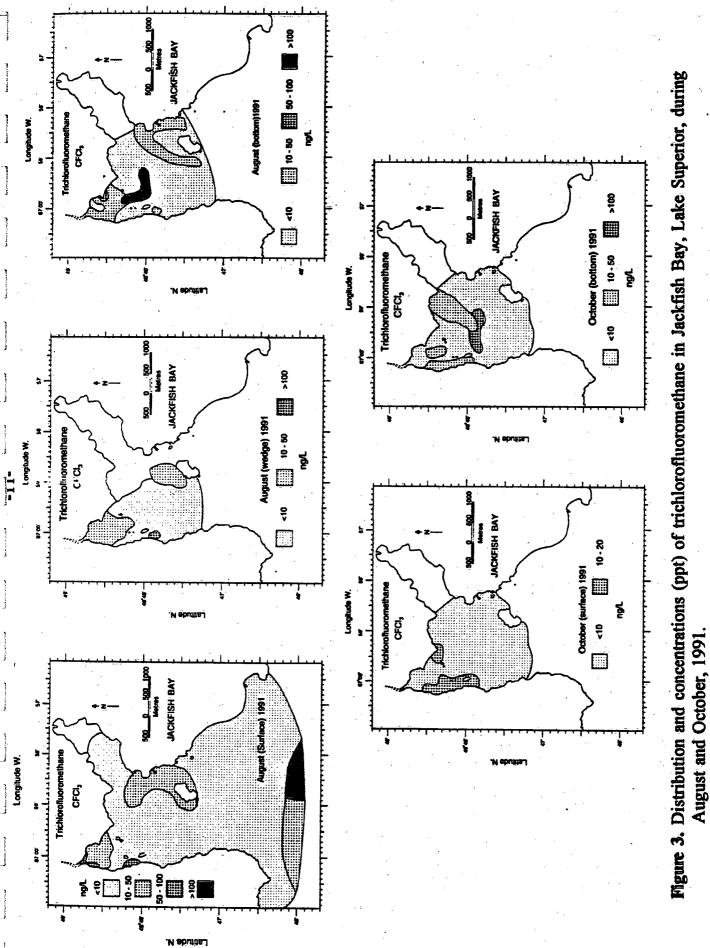
Because the effluent temperature was colder, its plume rapidly mixed to 4 °C and sank into the deeper water layers of Moberly Bay and migrated towards the open lake in the central channel of Jackfish Bay. As observed in August, the plume remained reasonably intact and slowly mixed vertically and horizontally with surrounding waters. The temperature difference between plume and bay waters resulted in a density gradient of 6 to 1, a reversal of the thermal bar structure formed during spring conditions, where the rates of warming are slower for lake than nearshore waters. A density gradient of this magnitude would be expected to restrict mixing and dilution of plume waters with lake waters and physically impede movement of the outflowing plume, which would require displacement of surrounding water masses to progress further into the lake. This process would account for the higher October mean levels of chloroform in bay waters, due mainly to limited dilution and to a lesser extent to smaller losses through volatilization.

#### Distribution of Trichlorofluoromethane

Distribution plots (Figure 3) 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 trichlorofluoromethane 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, trichlorofluoromethane 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



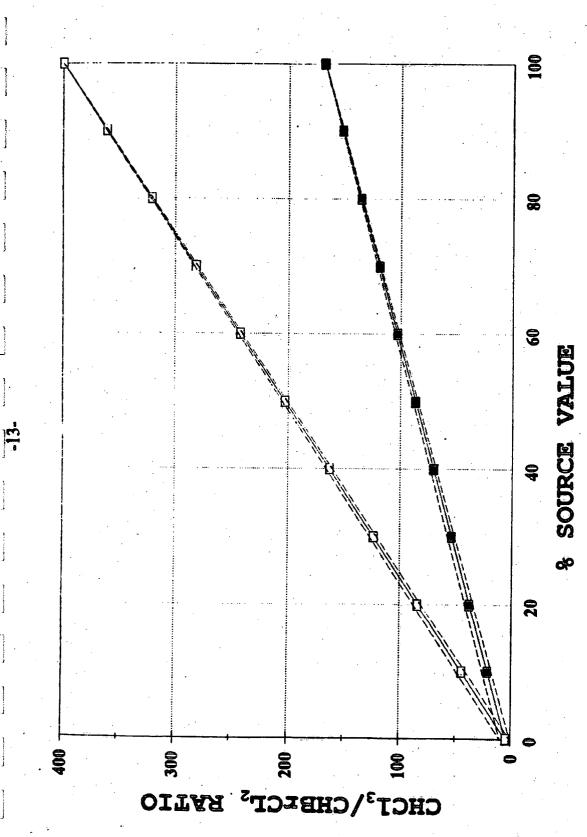
although remnants of trichlorofluoromethane contaminated lake waters can be observed in the nearshore zones of Moberly Bay and the deeper central channels of Jackfish Bay. These observations correspond to the location of the stream plume by chloroform profiles, shown to occupy the deeper sections of the bay's hypolimnion and displace the (warmer) lake waters in the fall.

#### Plume Mixing Predictions

The extent to which the Blackbird Creek stream flow mixes (as measured by % source value) with lake waters 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 (Kaiser and Valdmanis, 1979; Oliver and Lawrence, 1979, Kaiser and Comba, 1984, Comba and Kaiser, 1984). The CFM/BDCM ratio is dependent 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 (AWWA, 1993). This ratio is significantly altered by subsequent additions of pure chloroform from the pulp bleaching process.

The CFM/BDCM ratio provides a consistent gauge of source stream content compared to singular measurements, since ratios minimize the effects 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 accurate estimates of source stream content, based on the linear mixing relationship (Figure 4) of the two water masses as quantitated by their individual CFM/BDCM ratios.

The August and October 1991 profiles (Figure 5) 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, to offset concentration effects caused by temperature differences and plume sinking, from stations 4B, 5B, 1S, 2S, 3S; chloroform 1200 ng/L; bromodichloromethane 3.0 ng/L). A CFM/BDCM lake 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 bromodichloromethane detection limit of 0.5 ng/L. This ratio is comparable to the 10:1 ratio measured in raw intake water in 1989 (MOE, 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 Figure 4 in units of percent resolution.



Maune 4. Graph of CHCl<sub>3</sub>/CHBrCl<sub>2</sub> 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).

The Blackbird Creek discharge during August appears to track through the central channels of Moberly and Jackfish Bay in the vicinity of the thermocline, above the level of stratification. The epilimnion and hypolimnion profiles display similar localities of the source stream, with high stream content values for the westerly nearshore zones of Moberly Bay. Their easterly direction towards the outer limits of Jackfish Bay however are inconsistent with chloroform concentration profiles and would seem to reflect directional effects from wind and water currents on older water masses.

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 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. Concentrations of chloroform in the hypolimnion water mass of the central channel and in the outer surface plume in August are different from profiled % source values. In contrast, in October, % source value profiles are consistent with the chloroform distribution pattern, but inconsistent with respect to concentration and % source stream. These differences likely reflect a number of physical factors that influence contaminant loadings and distribution, namely, fluctuations due to changes in stream flow, dilution by major precipitation events, rates of input, volatilization, secondary sources, adsorption and desorption, and other effects such as the bay's thermal structure, water and wind currents.

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.

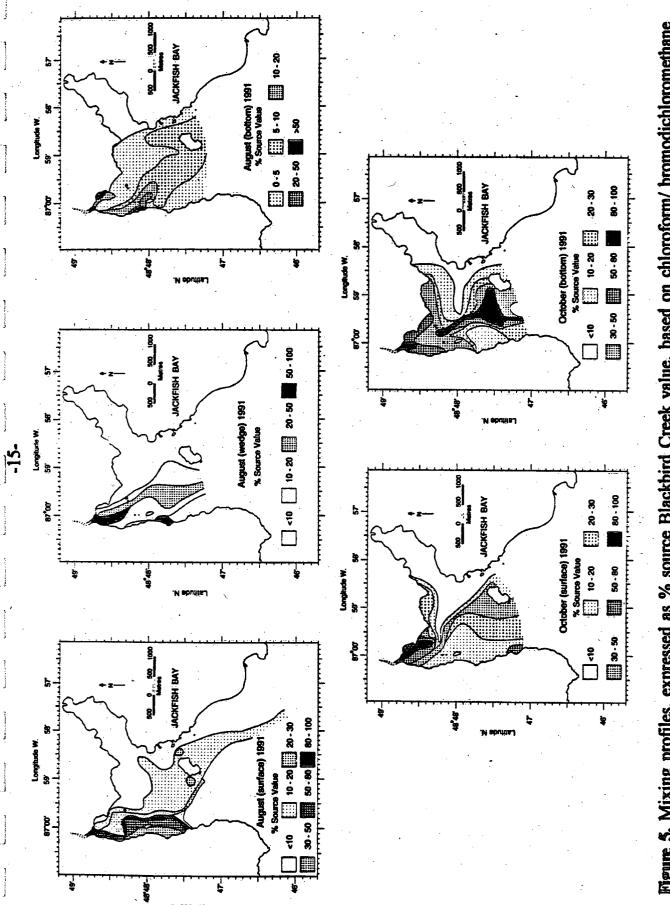


Figure 5. Mixing profiles, expressed as % source Blackbird Creek value, based on chloroform/ bromodichloromethane ratios in Jackfish Bay, Lake Superior, during August and October 1991.

#### DISCUSSION

#### Nearshore-Offshore Interactions of Volatile Halocarbons

Factorial analysis using the SPSS<sup>•</sup> (SPSS Inc.) Varimax method provided uncorrelated (orthogonal) principal component (PC) extraction of the measured variables with a rotated factor matrix. Three factors were extracted from the Jackfish Bay data set. Within the first PC Factor 1, the weighted 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 4.

In conjunction with temporal and spatial trends of volatile contaminants, the statistical relationships strengthened the conclusions on contaminant relationships, their distribution and sources. 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 (Figure 6) are in general agreement with the chloroform distribution, the linear correlation between conductance and chloroform was weak r= 0.33, although highly significant (significance of F, p=0.0000, for F= 26.6 and n=204). Weaker correlations would result if any of the factors previously mentioned in the plume mixing predictions were true, namely that chloroform inputs fluctuate and therefore plume 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 and 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 (Rap, 1991), 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.

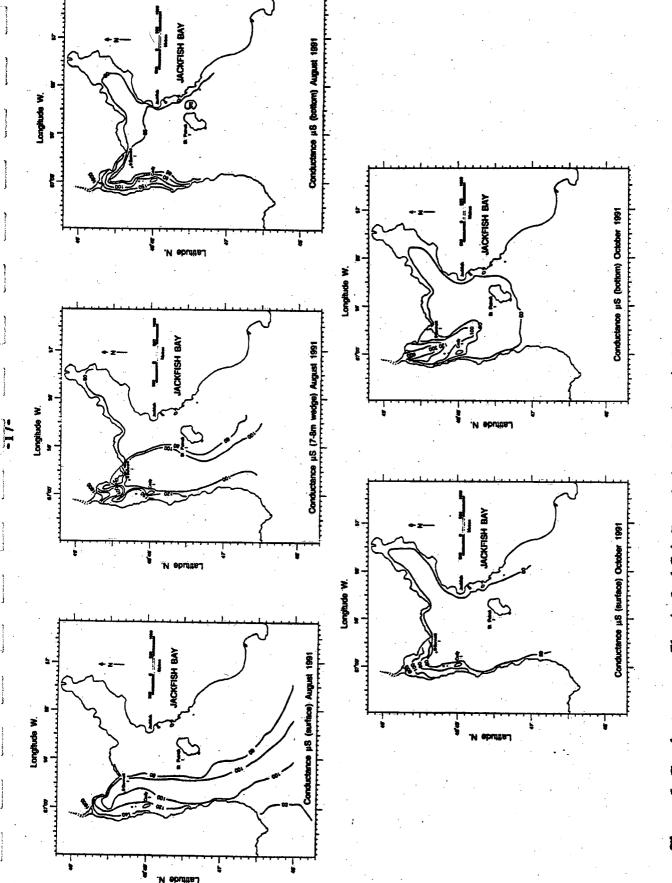


Figure 6. Conductance profiles in Jackfish Bay, Lake Superior, during August and October 1991.

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-	CFCl	CHCI,	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	CCl4	C,HCl,	CHBrCL	CHBr <sub>2</sub> Cl	C2C14	Cond
CFCl,	1.00	0.015	0.012	0.023	0.021	0.009	0.012	0.019	-0.02
CHCl,		1.00	0.50	0.50	0.47	0.51	ິ 0.50	0.49	0.33
C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>			1.00	0.98	0.91	0.99	0.99	0.94	-0.02
CCl,	,			1.00	0.97	0.96	0.98	0.99	-0.02
C <sub>2</sub> HCl <sub>3</sub>	1				1.00	0.87	0.91	0.99	-0.02
CHBrCl,				_		1.00	0.99	0.91	0.00
CHBr <sub>2</sub> Cl							1.00	0.94	-0.015
C <sub>2</sub> Cl <sub>4</sub>								1.00	-0.03
Cond									1.00

Table 4. Volatile Halocarbon and Conductance Linear Correlation (r) Matrix (n=204).

· Carbon tetrachloride was also highly correlated with the chloroethane chloroethylene\bromomethane compounds. In our experience high levels of carbon tetrachloride (i.e. >50 ng/L) are more often related to chemical production activities and are not typical for bleaching operations. A volatile chloroethylenes/carbon tetrachloride fingerprint was used to identify solvent/tars ("blob") at the bottom of the St. Clair River (Carey and Hart, 1986, Halfon, 1986 and Kaiser and Comba, 1986 a,b), with a general composition similar to that of taffy tars which were formed during chlorine production with graphite electrode systems (Kaminsky and Hites, 1984). 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 (RAP, 1991) may have been a source for the carbon tetrachloride. Coproduced volatile halocarbons would have partitioned into the tars/emulsion substrates formed and become sedimented out in the containment lakes. 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 or lagoons. In laboratory experiments, chloroform generation from pulp mill wastes was found to continue over a protracted time period (Rogers and Mahood, 1982). 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 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 (trichlorofluoromethane 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 (Kaiser and Valdmanis, 1979). The route of its introduction to Jackfish Bay appears to be from inflowing lake waters which are thought to be contaminated through atmospheric deposits. The higher levels of trichlorofluoromethane in the lake water 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  $CHCl_3$  and  $CHBrCl_2$  concentrations and their ratios suggest that sediments may be secondary sources of these compounds.

3. 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.

4. 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. The precision and degree of resolution of this technique could be improved with a greater number of measurements over longer time periods to better estimate the average source stream and outer lake CFM/BDCM ratios.

5. Conductance measurements were weakly correlated with chloroform values and uncorrelated with the other volatile halocarbons. In conjunction 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.

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

#### REFERENCES

- AWWA, 1993. Brominated DBPS. J. Am. Water Works Assoc. (1): 1-103.
- Carey, J.H. and Hart, J.H. 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.
- Comba, M.E. and Kaiser, K.L.E. 1983. Determination of volatile contaminants in water at the ng/L level. Inter J. Environ. Anal. Chem., 16: 17-31.
- Comba, M.E. and Kaiser, K.L.E. 1984. Tracking river plumes with volatile halocarbon contaminants. The Niagara River - Lake Ontario example. J. Great Lakes Res., 10: 375-382.
- Comba, M.E. and Kaiser, K.L.E. 1985. Volatile halocarbons in the Detroit River and their relationship with contaminant sources. J. Great Lakes Res., 10: 404-418.
- Comba, M.E., Palabrica, V.S., Wasslen, J., Bengert, G.A. and Kaiser, K.L.E. 1989. St. Lawrence River trace organic contaminants study (Part II), 1985. National Water Research Institute, Contribution No. 89-51, 95 p.
- Fogelqvist, B., Josefsson, B. and Roos, C. 1982. Halocarbons as tracer substances in studies of the distribution patterns of chlorinated waters in coastal areas. *Environ. Sci. Technol.*, 16: 479-482.
- Halion, 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.
- Kaiser, K.L.E. and Comba, M.E. 1984. Volatile contaminants in the Welland River watershed. J. Great Lakes Res., 9: 274-280.
- Kaiser, K.L.E. and Comba, M.E. 1986, a. Tracking river plumes with volatile halocarbon contaminants: The St. Clair River - Lake St. Clair example. *Environ. Toxicol. Chem.*, 5: 965-976.
- Kaiser, K.L.E. and Comba, M.E. 1986, b. Volatile halocarbon survey of the St. Clair River. Water Poll. Res. J. Canada, 21: 323-331.
- Kaiser, K.L.E. and Valdmanis. I. 1979. Volatile Chloro- and fluorocarbons Lake Erie-1977 and 1978. J. Great Lakes Res., 5: 160-169.
- Kaminsky, R. and Hites, H.A. 1984. Octachlorostyrene in Lake Ontario: Sources and fates. Environ. Sci. Technol., 18: 275-279.
- McMaster, M.E., Van Der Kraak, G.J., Portt, C.B., Munkittrick, K.R., Sibley, P.K., Smith, I.R. and Dixon, D.G. 1991. Changes in hepatic mixed-function oxygenase (MFO) activity, plasma steroid levels and age at maturity of a white sucker (*Catostomus commersom*) population exposed to bleached kraft pulp mill effluent. *Aquatic. Toxicology*, 21: 199-218.

- MOE. Ministry Environment of Ontario. 1993. Personal communication by P. Jordan, MOE, Thunder Bay, Ontario.
- Munkittrick, K.R., Portt, C.B., Van Der Kraak, G.J., Smith, I.R. and Rokosh, D.A. 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.
- Munkittrick, K.R., McMaster, M.E., Portt, C.B., Van Der Kraak, G.J., and Dixon, D.G. 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.
- Oliver, B.G. and Lawrence, J. 1979. Halocarbons in drinking water. A study of precursors and precursor removal. J. Am. Water Works Assoc., 71: 161-163.
- RAP, Jackfish Bay Remedial Action Plan, 1991. Stage 1: Environmental conditions and problem definition. North Shore of Lake Superior Remedial Action Plan, Canada and Ontario: 1-157.

Rogers, I. H. and Mahood, H. W. 1982. Environmental monitoring of the Fraser River at Prince George. Chemical analysis of fish, sediment, municipal sewage and bleached kraft wastewater samples. Canadian technical report of Fisheries and Aquatic Sciences, 1135: 1-15.

Table 1.

Concentration (ppt) ng/L of volatile halocarbons, depth, conductivity and temperature of water from Jackfish Bay, Lake Superior, August 1991.

Street, Activity of the

			•							-
Istation Number	1 <u>S</u>	2S	35	100	200	300	400	4 S	55	6S
Sample Depth (metres)	-		-	-	-	-	-	اسب	-	-
Sample Date	21-6-91	21-6-91	21-6-91	20-6-92	20-6-92	20-6-92	22-6-92	21-6-91	21-6-91	21-6-91
Conductivity (u mhos)	1600	1600	1550	8	8	8	8	140	150	165
Temperature (°C)	61	20	61	17	17	16	16	22	18	19
Trichtorofluoromethane	41	24	81	150	34	47	2.0	23	35	8
Chloroform	770	940	(0)9	22	17	4,0	7.5	110	160	82
1.1.1-Trichloroethane	1.0	1.5	31	1.3	0.78	0.52	2.2	5.1	1.3	2.7
Carbon Tetrachloride	0.54	2.7	3.2	0.42	0.44	0.41	0.63	16.0	0.87	1.3
Trichloroethytene	Ξ	18	6.0	1.1	0.59	BDL	BDL	1.5	1.8	2.1
Bromodichloromethane	4.6	91	1.7	1.8	1.8	BDL	BDL	0.72	6,1	1.8
Dibromochlor omethane	1.3	17	BDL	BDL	BDL	BDL	BDL	BDL	1.5	0.55
Tetrachioroethylene	1:7	1.4	5.2	1.5	0.1	1.1	1.0	12	1.6	3.9
Station Number	- 7S	1 <u>85</u>	<u>56</u>	12 <sup>.</sup> S	13.5	14 S	15.S	16.S	17.S	18:5
Sample Depth (metres)	-					-	<u></u>			
Sample Date	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91
Conductivity (u mhos)	130	115	135	110	120	120	110	110	125	115
Temperature (°C)	19	2	61	61	61	19	19	18	19	17
					4					
Trichlorofluoromethane	8	33	48	Ξ	61	15	15	10	2.3	3.4
Chloroform	72	110	6.7	36	68	6.2	100	86	<b>490</b>	13
1, 1, 1-Trichbroethane	2.4	3.3	5.2	2.2	3.8	7.1	7.2	6.6	25	4.1
Carbon Tetrachloride	0.72	1.5	2.3	()8()	0.87	1.9	2.8	2.2	29	0.40
									t	100

0.40 BDL BDL

<u>62 7:25</u>

2.8 BDL

BDL 4.2 0.62

BDL BDL

2.3 1.8 BDL

BDL BDL

**Bromodichloromethane** Dibromochloromethane

Trichloroethylene

<u>15</u> 5.4 01 1.6

1.6 BDL 1.3 2.2

> BDL 31

0.73 7.0

0.32

24

1.7

2

5.8

0.41

21

1.3

Tetrachloroethylene

Concentration (ppt) ng/L of volatile halocarbons, depth, conductivity and temperature of water from Jackfish Bay, Lake Superior, August 1991.

Table 1.

· ·					[							Ţ	Ċ		<b>C</b> 1176									
28 S	ايندي ايندي	21-6-91	8	14		0.81	1.7	2.4	0.42	BDL	BDL	BDL	0.35	38.5	1	22-6-91	S	91	19	38	3.6	1.7	BDL	3.1
27S	<del></del>	21-6-91	<u>8</u>	16		3.8	32	BDL	BDL	BDL	BDL	BDL	0.31	37 S	Ţ	22-6-91	Ş	<u>9</u>	16	10	3.1	1.5	1.7	BDL
26 S	<del>.</del>	21-6-91	<b>1</b> 00	15		3:0	BDL	BDL	BDL	BDL	BDL	BDL	0.46	36.5	:	10-2-00	ŝ	3 2	14	R	3.0	1.2	BDL	4.1
25.5	<del>, ,</del>	21-6-91	110	15		5.0	43	4.4	0.25	52	1.3	0.91	58	35.5	Ť	10.7.00		3 5	3.7	=	5.7	2.1	0.64	BDL
24 S	1	21-6-91	105	15		4.3	110	6.5	2.3	BDL	BDL	BDL	1.0	34 S	-	10.2.00	00	99 91	16:0	27	BDL	1.8	BDL	1.4
23.5	-	21-6-91	120	15		1.6	57	3.8	0.64	BDL	BDL	BDL	0.41	33.S		77.6.01		5 2	4.8	11	2.2	0.89	BDL	BDL
22 S	-	21-6-91	125	16		0.9	110	1.3	0.8	BDL	BDL	BDL	0.80	32 S	-	27 6 01	1/1-77	9	8.5	92	2.4	1.3	0.68	0.82
21 S		21-6-91	110	18		01	300	5.9	2.6	1.4	8.6	1.2	1.2	315	-	10 7 11	16-0-77	19 19	1.2	25	2.2	0.61	BDL	0.65
20-S	-	21-6-91	120	18		11	250	7.3	300	3.1	2.6	0.36	220	SUE	-	1 2 01	16-0-17	3 2	12	92	0.84	0.55	BDL	16
19:S		21-6-91	120	18		9.1	02	2.7	0.92	0.16	BDL	BDL	2.9	20.5	). ) )		16-0-17	8 ≍	67	13	0.57	0.33	BDL	11
Station Number	Sample Depth (metres)		Conductivity (u mhos)	Temperature (°C)		Trichtorofluoromethane	Chloroform	1 1 1 - Trichloroathone	Carbon Tetrachlaride	Trichtoroethylene	Bromodichloromethane	Dibromochloromethane	Tetrachior oethylene	Ctation Number		Sample Veprn (merres)	Survey	Conductivity (ju mhos)	Trichiorofillaromethone	Chloroform	1 1 1-Trichloroathone	Carbon Tatrachlorida	Trichloroethylene	Dromodichloromethane

------

BDL 0.38

BDL 0.50

BDL 0.72

BDL

1.7

BDL 0.41

**BDL** 0.28

BDL 0.63

BDL 0.42

BDL 0.37

0.54 0.52

> Dibromochloromethane Tetrachloroethylene

Concentration (ppt) ng/L of volatile halocarbons, depth, conductivity and temperature of water from Tackfish Ray Take Sumerior Anoust 1991.

·	water from		Jackfish Bay, Lake Superior, August 1991	ake Supe	rior, Aug	IST 1991.					·
Station Number	395	40 S	41 S	42 S	43.5	44.S	45.S	46 S	47 S	48S	
Sample Depth (metres)		-			, <b></b> 1					-	
Sur vey	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	
Conductivity (µ mhos)	8	8	5 S	8	8	8	8	8	102	8	
Temperature (°C)	91	- 14	15	15	16	91	15	15	15	15	
Trichlorofluoromethane	14	23	15	5.4	2.1	5.3	0.89	3.7	1.4	2.4	
Chloroform	63	13	36	7.8	24	49	01	100	31	13	
1, 1, 1-Trichloroethane	4.0	8.7	2.9	23	4.4	5.2	4.5	4.5	1.5	3.9	
Carbon Tetrachloride	2.2	1.5	1.9	0.73	3.4	2.1	1.2	2.6	0.42	0.65	
<b>Trichloroethylene</b>	BDL	12	BDL	BDL	5.9	4.7	BDL	BDL	BDL	BDL	
<b>Bromodichloromethane</b>	5.3	BDL	BDL	BDL	1.9	2.8	BDL	5.9	BDL	1.6	
Dibromochloromethane	0.64	BDL	BDL	0.09	1.7	0.66	BDL	2.5	BDL	BDL	
Tetrachloroethylene	0.39	0.48	3.4	0.37	14	4.7	0.58	0.50	0.19	5.9	
		•									
Station Number	49 S	50S	51S	52 S	S 83 S	54S	<u>555</u>	56S	- 57S	<b>58S</b>	S 65
Sample Depth (metres)	<u></u>	-	<u></u>		1	<u>-</u>	1	<del></del> -		•••••	<b>,</b> 1
Survey	22-6-91	22-6-91	22-6-91	22-6-91	22-6-91	22-6-91	22-6-91	22-6-91	22-6-91	22-6-91	22-6-91
Conductivity (y. mhos)	100	8	33	8	85	82	8	8	8	8	8
Temperature (°C)	15	15	15	15	15	15	15	2	15	15	15
Trichtorofluoromethane	3.4	0.72	1.1	2.1	4.1	1.6	3.4	2.3	0.93	BDL	0.78
Chlor of or m	29	2.6	12	30	7.8	27	6:6	11	5.3	0.34	4.0
1, 1, 1-Trichloroethane	8	1.7	2.0	1.5	2.7	9.1	1.4	1.4	1.7	2.7	1.0
Carbon Tetrachloride	0.78	0.32	0.70	1.0	2.0	0.66	0.64	1.4	0.5	1.3	0.28
Trichloroethylene	18	BDL	BDL	0.26	BDL	BDL	0.10	BDL	BDL	BDL	BDL
Bromodichloromethane	4.1	BDL	8.1	6.6	1.6	8.5	1.6	2.0	0.63	BDL	0.47
Dibromochlor omethane	BDL	BDL	1.0	0.69	BDL	0.1	BDL	BDL	BDL	BDL	BDL
										-  -	•

0.47 BDL 0.32

23

0.32

22

0.43

0.60

5.0

1.1

0.37 8.1

0.77

120

**Tetrachloroethylene** 

Table 1.

Concentration (ppt) ng/L of volatile halocarbons, depth, conductivity and temperature of water from Jackfish Bay, Lake Superior, August 1991.

					- <u>10 m</u> -	14 SI	17 17	101	704	717
Station Number	5T	6T	1.	2	1.71					; `
	8	<u>د</u>	۲	~	0	2	7	2	~	٥
Sample Lepin (meires)		10 2 10	21.6.01	10.4.10	16-9-16	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91
Survey	16-0-17	16-0-17	16-0-17				120	150	130	120
Conductivity (u mhos)	200	460	200	790	£	074	3	3	3	
Temperature (°C)	50	19	81	17.	15	17	61	×	18	9 1
							ļ			
Tricklersfinerandhome	17	12	37	84	38	31	23	6.0	3.9	14
	151	50	120	38()	83	<u>560</u>	840	59	2.8	110
Chiorororm	31	14	26	48	5.4	4.8	8.4	2.0	5:2	5.9
	190			11	14	2.9	29	01	1.4	1.8
Carbon letrachloride		1	680	69	BDL	6.1	6.2	23	BDL	0.83
I richloroethylene			70.0	00	22	3 8	25	BDL	BDL	2.2
Bromodichloromethane	0.50	2,9	* '0	7.7	100	0.50		I Ga	RDI	RDI
Dibromochlor omethane	BDL	0.74	BDL	0.67	BUL	7C'N		173		2
Tetrachloroethylene	1.2	1.7	1.6	6.0	21	1.5	1:8	2.1	1:0	Ŗ
		× .								
CALITY Number	74.1	111	1 32 T	1 34 1	1 35 T	42 T*	43 T	44 T	45 T	48 T
			×	7	٢	~	2	9	7	7.5
Sample Veptin (Meires)	01 £ 01	22.6.01	22.4.91	16-9-22	22-6-91	22-6-91	22-6-91	22-6-91	22-6-91	22-6-91
Survey						S	105	100	110	8
Conductivity (µ mhos)	21	2	<u>ş</u> 2	12	15	5	15	15	15	15
lemperature / - u/		2								
	1	73	68	1 0.34	0.40	25	0.52	14	4.3	2.2
	720	2	140	n	92	2700	130	99	83	20
	ž	23	06	=	BDL	2100	16	3.3	3.6	3.2
	25	168	14	13	1.5	2800	3.2	2	1.4	0.67
				BDL	BDI	2300	6.1	0.92	0.63	BDL
I richlor oetnylene	, , ,			BDI	BDI.	740	35	1.4	0.68	2.3
Bromodichloromerhone				BDI	BDL	610	0.89	BDL	BDL	BDL
Ulbromochiol omethane	1)3.			01.0	02.0	NAN	63	28	0.45	3.0
Tetrachloroethylene	1.0	0.49	00.0	4000	~~~~	2225				

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Table 1.

Table 1.

Concentration (ppt) ng/L of volatile halocarbons, depth, conductivity and temperature of water from Jackfish Bay, Lake Superior, August 1991.

Million Contract

Station Number	4B	5 B	68	78	8 8 8 B	9B	12B	13 B	14 B	16 <sup>B</sup>
Sample Depth (Metres)	3	15	11	15	15	4	12	19	3.5	7
Survey	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91
Conductivity (µ mhos)	145	8	105	95	8	180		2	120	150
Temperature (°C)	14	11	12	10	10	19	12	6	19	15
<b>Trichlorofluoromethane</b>	2.4	27	17	40	4.3	13	28	24	63	13
Chloroform	32	6†	64	400	6.2	420	142	50	170	430
1, 1, 1-Trichloroethane	0.38	2.2	2.8	3.4	0.54	13	9.4	3.2	11	11
Carbon Tetrachioride	0.28	0.66	1.3	1.4	BDL	4.0	2.5	1.1	33	4.6
Trichloroethylene	0.52	0.67	1.0	4.3	BDL	4.2	1.4	BDL	13	3.5
Bromodichloromethane	BDL	5.4	1.5	ह	BDL	1.0	3.4	2.8	3.9	2.4
Dibromochloromethane	BDL	1.6	BDL	11	BDL	BDL	0.51	BDL	BDL	BDL
Tetrachlor oethylene	0.98	1.6	2.0	1.5	BDL	2.5	2.6	0.78	5.6	1.9
Station Number	17B	18 <sup>.</sup> B	19.B	20.B	21 B	22.B	24 B	28 B	29B	30 B
Sample Depth (Metres)	50	6	Q	Š	14	×	- 17	6	61	29
Survey	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91	21-6-91

Station Number	17B		19.8	20B	21 B	22 B	24 B	28 B	29B	30B	
Sampte Depth (Metres)	50			<u>i</u> n	14			6	19	50	
Survey	21-6-91			21-6-91	21-6-91			21-6-91	21-6-91	21-6-91	
Conductivity (µ mhos)	2	145		150	8			8	8	8	
Temperature (°C)	8	1	1	. 16	11			- 13	10	<b>.</b>	
<b>Trichlorofiuoromethane</b>	17	6.6	0.84	0.88	15	2.3	1800	0.96	3.2	3.7	
Chloroform	3.3	50	6()0	720	2.3	28	2500	14	15	35	
1, 1, 1-Trichloroethane	9.4	8.8	23	10	9.2	4.4	1600	1.0	1.3	4.4	
Carbon Tetrachloride	3.6	1.3	3.9	4.4	3.6	0.68	3000	0.48	0.63	1.8	
Trichtoroethylene	0.86	BDL	4.4	8.8	1.3	BDL	4100	BDL	BDL	2.8	
<b>Bromodichloromethane</b>	0.73	1.1	6.7	2.7	0.95	BDL	470	1.4	1.6	2.8	<b></b>
Dibromochlor omethane	BDL	BDL	1.0	0.59	BDL	BDL	470	0.80	0.63	0.86	_
I etrachloroethylene	1.4	0.57	1.4	570	1.3	11	5200	0.84	0.51	0.62	
											•

Concentration (ppt) ng/L of volatile halocarbons, depth, conductivity and temperature of water from Jackfish Bay, Lake Superior, August 1991.

Table 1.

					-	ſ		<u> </u>						<b></b>	1			- e	<del>,</del>		- 1	j						
40B	10	20.2	12-0-77	92	13		15	2	4.2	2.0	BDL	3.7	0.63	5.1		<b>51 B</b>	38	22-6-91	8	6	2.4	12	2.3	06'0	BDL	3.2	0.29	0.53
39 B	26	10 2.00	16-0-77	8	12		8.5	09	5.1	2.2	BDL	3.5	0.57	0.37		49B	32	22-6-91	99	10	4.2	61	11	0.94	BDL	14	1.6	1.3
38 B	40		16-0-77	8	10		9.3	64	4.0	1.7	BDL	5.8	0.78	0.61		48 B	32	22-6-91	3	6	2.1	2.5	1.8	0.79	BDL	BDL	BDL	0.34
37.B	74				11		17	<b>98</b>	- 6'L	2.8	BDL	5.2	0.88	0.95		47 B	22	22-6-91	65	10	1.5	5.5	2.2	1.3	BDL	0.86	BDL	0.75
36.B	10			8	12		4.9	7.4	2.2	1:1	BDL	BDL	BDL	0.50		46 B	<b>2</b>			6	4.9	20	1.1	3.3	BDL	1.2	0.69	0.48
35.B			22-6-91	<b>5</b>	10		230	<b>4</b> 9	ž	<u>1</u> 0	·	13	2	110		45 B	43			30	4.3	16	13	4.5	61	0.76	0.5	0.86
34 B	YK	Ş		93	6		0:59	39	4.9	23	BDL	1.4	BDL	0.42		AAR I	\$	-		3 0	15	6.0	43	81	0.57	0.43	¥	6.1
33.8			22-6-91	65	6		17	83	41	61	BDL	BDL	BDI	0.89		AAR	202	10.7.00	¥2	3 5	6.2	23	××	47	11	140	0.69	9.6
TOR I				92	0		32	15	13	12	BDL	22	RDI	040		A CA		10.7.6	720-77	30	11	13	12	47	57	01	13	18
1101		18	21-6-91	20	2 9		1100	Ē	36	1 8	RDI	BDI		16		11.6	a ;	8 V V	16-0-77	3 0	- 11	BDI	4 4				RDI RDI	0.50
	Station Number	Sample Depth (Metres)			Conductivity (J. Million) Temperature (OC)		Trichlandfinnamathana		Cruci Ol Of III	1, 1, 1-1110100 Contract	televised the acting the	11 ICI ROL UCITI FIRMS		UIDE OF INDERNOL OF INDERNOL				ueptn (meires)		Conductivity (JI mnos)	T-ichicarefinaremethone						Bromodichior omerinune	Tetrachloroethylene

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Table 2.

Concentration (ppt) mg/L of volatile halocarbons, depth, conductivity and temperature of water from Jackfish Bay, Lake Superior, October 1991.

Station Number	- 1 S	2.5	3 S -	4 S	5.S	6S	15	8S8	S6	12 S
Sample Depth (metres)	-		-	-	<b>.</b>	-	-			-
Survey	21-10-91	21-10-91	21-10-91	21-10-91	21-10-91	21-10-91	21-10-91	21-10-91	21-10-91	21-10-91
Conductivity (u mhos)	009	510	<u>500</u>	8	120	100	95	8	<u>95</u>	110
Temperature (°C)	2.5	2.5	2.5	4	4	4	4	3	3	6.5
Trichlorofluoromethane	0.21	6.6	0.29	0.44	0.46	1.5	47	0.65	0.47	1.8
Chloroform at the second second	1200	1600	1200	180	420	99	52	340	330	200
1, 1, 1-Trichloroethone	1.4	3.1	1.2	1.4	0.85	1.6	1.8	1.8	1.7	1.5
Carbon Tetrachloride	0.6	0.62	0.46	0.50	0.52	0.35	0.36	1.2	0.78	0.57
Irichlor oethylene	23	3	3.2	5.4	0.72	BDL	BDL	0.68	0.55	BDL
Bromodichloromethone	3.5	4.8	2.9	BDL	0.84	BDL	BDL	0.71	0.68	BDL
Dibromochloromethane	0.76	0.97	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Tetrachioroethytene	0.36	0.39	1.2	0.93	0.54	0.39	1.1	0.50	13	0:30
Station Number	13 S	14 S	15 S	16 S	17S	18 S	S 61	20S	21 S	22 S
Sample Depth (metres)	-	T	Ħ	1	<b>, 1</b>	=	=	- 	-	
Survey	21-10-91	21-10-91	21-10-91	21-10-91	21-10-91	21-10-91	21-10-91	21-10-91	21-10-91	21-10-91
Conductivity (u mhos)	100	100	8	100	8	75	8	8	8	75
Temperature (°C)	6.5	6.5	7	6.5	6.5	7	7	6.5	6.5	8
Trichlor of luor omethane	4.2	0.22	<b>7.9</b>	6.4	52	3.6	27	15	12	11
Chloroform	190	290	260	200	180	47	82	120	67	58
1, 1, 1-Trichloroethane	1.5	3.3	4.6	1.6	1.7	0.32	1.3	1.3	1.7	1.5
Carbon Tetrachloride	0.62	0.66	1.4	7.3	0.9	BDL	0.77	0.54	0.4	0.78
Trichloroethylene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Bromodichloromethane	0.58	0.77	1.2	BDL	0.91	BDL	0.66	BDL	BDL	BDL
Dibromochloromethane	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Tetrachloroethylene	0.44	0.48	9.2	5.2	1.2	BDL	0.43	0.34	0.16	BDL

Concentration (ppt) ng/L of volatile halocarbons, depth, conductivity and temperature of water from Jackfish Bay, Lake Superior, October 1991. Table 2.

	S W	45 S	46 S	47 S	48 S	49 S	<u>50S</u>	51S	58S	
				-	<b>,</b>		_	÷		
Somple Leptin (merres)	71.10.01	23-10-91	23-10-91		23-10-91		23-10-91	23-10-91	23-10-91	
			2		75	75	75	75	8	
Conductivity (primos)	2.2	5 S	<b>∞</b>	8.5	8.5		6	8.5	8.5	
The second s	38	60	1.4	2.1	2.6	22	2.2	2.1	2.0	
I FICTION OF MON OF THE HARME	11	120	62	36	13	200	88	260	11	
Unororen	-	1.1	2.5	27	2.8	5.8	3.0	<b>5.8</b>	2.4	
1. 1. 1-Irichor oeinone	1.0	2.7	C L	100	1.2	14	1.4	1.5	0.83	
Corbon Tetrachioride	0.1	CT 0 0	7.1	IUB	ICE	RDI	BDL	BDL	BDL	
Trichloroethylene	BUL	07		100		i Ca	020	20	RDL	
Bromodichloromethane	BDL	BDL	BDL	BUL	BUL	DUL	2.0			
Dihromochloromethane	BDL	BDL	BDL	BDL	BDL	BDL	BUL	BUL	BUL	
Tatrachlarnathulana	0.68	17	1.0	0.66	1.6	0.41	1.6	0.33	0.40	
										·

13 T 14 22-10-91 180 6.5	•
51 9 22-10-91 120	
8	
Aly Iure	
lation # ample L urvey conductiv empera	

Trichlorofivoromethane	0.32	4
Chloroform	17	350
1.1.1-Trichloroethane	1.8	1.8
Carbon Tetrachloride	0.29	BDL
Trichlor oethylene	BDL	BDL
BromodicNoromethane	BDL	0.92
Dibromochioromethane	BDL	BDL
Tetrachloroethylene	0.50	0.62



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