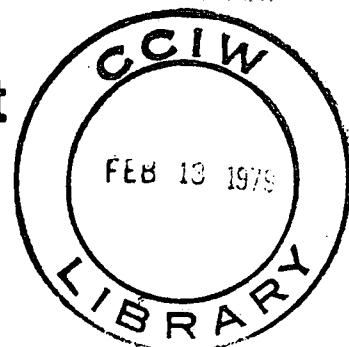**Environment Canada**

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VOLATILE CHLORO- AND CHLOROFLUOROCARBONS

IN LAKE ERIE - 1977 and 1978

Klaus L.E. Kaiser and Ilze Valdmanis

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UNPUBLISHED REPORT

RAPPORT NON PUBLIE

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Running head: CHLORO- AND CHLOROFLUOROCARBONS IN LAKE ERIE

<center>ABSTRACT</center>

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3   Water samples from the central and eastern basins of Lake Erie

4 were analyzed for volatile chloro- and chlorofluorocarbons for a one

5 week period each in 1977 and 1978. The following contaminants were

6 observed with mean concentrations and standard deviations in 1978

7 with the corresponding values for 1977 in parentheses: Dichlorodi-

8 fluoromethane (Freon 12) 76 ± 38 (73 ± 36) $ng \cdot \ell^{-1}$; trichlorofluoro-

9 methane 34 ± 26 (46 ± 40) $ng \cdot \ell^{-1}$; chloroform 15 ± 4 $ng \cdot \ell^{-1}$;

10 carbon tetrachloride 19 ± 11 (37 ± 20) $ng \cdot \ell^{-1}$; trichloroethylene

11 20 ± 13 (11 ± 9) $ng \cdot \ell^{-1}$.

12   Except for carbon tetrachloride and trichloroethylene, the

13 distribution patterns appear to show little correlation with each

14 other. Chloroform concentrations were relatively uniform, however

15 the carbon tetrachloride and trichloroethylene concentrations appear

16 to be point-source related with discharges along the south shore of

17 Lake Erie. Freon 12 concentrations were generally higher in the

18 eastern basin than in the central basin, while Freon 11 levels were

19 high and relatively uniform throughout the study area.

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INTRODUCTION

In recent years, the contamination of the biosphere with hazardous organic compounds has become of foremost concern. The identification and measurement of persistent contaminants is the subject of many research and monitoring activities. For some, the environmental pathways are known to a large extent; however, information is lacking on the transport of contaminants from air to water and vice versa. For example, theoretical calculations (Mackay and Leinonen, 1975; Dilling et al., 1975) show the rapid loss of poorly soluble, high boiling polychlorinated biphenyls (PCBs) from water surfaces. At the same time, however, analyses of dry and wet precipitations (Strachan et al., 1979; Murphy and Rzeszutko, 1977), indicate a considerable atmospheric fallout of such compounds onto land and water surfaces. As a result, it appears to be still in question whether large lakes act predominantly as sinks or as sources of such contaminants.

The findings of haloforms in raw and drinking waters (Symons et al., 1975) increased the interest in organic contaminants of aquatic systems, specifically with respect to the more volatile components. Actual haloform concentrations and potential haloform production from common, semi-naturally derived precursors are presently being investigated at varied locations in Canada (Lawrence, 1978). However, contaminants with little direct effect on aquatic life are seldom investigated in aquatic systems. The recent evidence

of chlorofluoromethane (CFM) induced modification of the stratospheric ozone layer (Wofsy et al., 1975) has brought much emphasis on CFM analysis and monitoring in air but without a corresponding interest in CFM distribution in aquatic systems.

This paper reports the distribution of Freon 12 and Freon 11 in the eastern and central parts of Lake Erie during one week in each of the summers of 1977 and 1978. In addition, information is presented on the occurrence and distribution of chloroform, carbon tetrachloride and trichloroethylene in such samples.

EXPERIMENTAL

Sampling and Processing

Water samples were taken from CSS LIMNOS with a Rosette Sampler with simultaneous temperature and depth recording EBT as a part of the Lake Erie Hypolimnion Oxygen Studies during the periods 1130 hours, August 8 to 0400 hours, August 12, 1977 and 1200 hours, June 19 to 0515 hours, June 23, 1978. Sampling depths at most stations included 1 m (surface) and bottom (1 m above bottom) and samples were also frequently obtained from one or more intermediate depths above or below the thermocline.

Immediately upon surfacing of the Rosette Sampler, 125 ml of the appropriate water samples were transferred into 125 ml volume cylindrical separatory funnels, equipped with 2 mm bore Teflon R

1 stopcocks and Teflon ^{R} sleeve-lined glass stoppers. Upon transfer

2 to the laboratory aboard the ship, each separatory funnel was drained

3 to a sample volume of 100 ml and was again sealed with the stopcock

4 and immediately evacuated with a rotary pump for approximately ten

5 seconds through the funnel stopcock. The funnel stopcock was

6 closed and the evacuated funnel, with a headspace of approx. 25 ml and

7 100 ml of the water sample, was inverted and placed vertically in a

8 water bath of 90°C, with the level of the water bath above the water

9 level of the sample but below the stopcock of the separatory funnel.

10   Each funnel was kept in the water bath for a minimum of 10

11 minutes during which the funnel was a few times vigorously shaken by

12 hand. It was then taken from the water bath and connected in the

13 inverted position to a 15 cm long rubber tube (6 mm ID, 16 mm OD) and

14 the tubing and glass stem of the funnel were evacuated. A 10 ml glass

15 ampoule, previously baked at 450°C and also attached to the rotary

16 pump with a Tygon ^{R} tube, was also evacuated and then placed in liquid

17 nitrogen. A straight, 2 mm bore, three-way glass stopcock connected

18 the separatory funnel via the rubber tube to the rotary pump and to the

19 ampoule via the Tygon ^{R} tubing and was used to transfer the headspace

20 volatiles to the glass ampoule. Care was taken to ensure that only the

21 headspace gases and water vapour from the sample were transferred to

22 the ampoule by slowly opening the funnel stopcock and closing it again

23 after approximately 10 seconds. The glass ampoule was then taken

24 from the liquid nitrogen bath and quickly sealed while under vacuum

25 with a propane torch. The sealed ampoules were kept in the dark at

26 room temperature until analysis.

1. <u>Analysis</u>

2.   Prior to the gas chromatographic (GC) analysis of the headspace

3. samples contained in the sealed ampoules, the gas samples were quantita-

4. tively transferred into graduated 15 ml centrigute tubes with ground

5. glass stoppers. For this, a centrifuge tube was filled with distilled

6. water, placed in a large beaker containing 2 ℓ distilled water and

7. inverted, taking care that no air was trapped inside. A small glass

8. filtering funnel was inserted into the centrifuge tube and the ampoule

9. placed beneath the cone of the filtering funnel. Upon breaking the tip

10. of the ampoule, its gaseous content escaped through the inverted filter

11. funnel into the centrifuge tube, displacing part of the water, normally

12. a 10 to 12 ml volume. Upon completion of the gas transfer, the centri-

13. fuge tube was stoppered under water and placed upside-down in a wire

14. rack. The remaining portion of the water in the centrifuge tube thus

15. sealed the gas sample from the air.

16.   For the GC injection, a centrifuge tube was turned right side

17. up and the glass stopper raised by approximately 5 mm to create a small

18. slit between the tube and stopper. Through this slit, the needle of a

19. 100 µℓ gas tight syringe (needle length, 7.5 cm; 0.4 mm OD) was inserted

20. until the needle tip was approximately 1 cm from the surface of the

21. water.   After sampling, the syringe was

22. withdrawn from the centrifuge tube, the tube again stoppered and

23. inverted for storage. The volume of the sample in the syringe was

24. adjusted to 100 µℓ, and then immediately injected into the gas

25. chromatograph. This method of sample withdrawal allows only one

1   quantitative injection, but further injections can be made for

2   qualitative confirmation and to give concentration estimates analogous

3   to the method by Mackay et al. (1975).

4   For the GC analysis, a Tracor 220 M gas chromatograph with

5   electron-capture detector and linear electrometer was used. Columns

6   used were (i) 1.8 mm x 3.2 mm (I.D.) glass with 3% Dexsil-300 on

7   80/100 mesh Gas Chrom Q, conditioned at 150°C; (ii) 1.8 m x 3.2 mm

8   (I.D.) glass with 100/120 mesh Porapak Q, precleaned by Soxhlet

9   extraction with acetone and hexane, conditioned at 220°C; (iii) 1.8 mm

10   x 3.2 mm (I.D.) stainless steel with 0.2% Carbowax 20 M on 80/100 mesh

11   Carbopack C, conditioned at 180°C.

12   Chromatograph parameters were: Inlet temperature: 225°C;

13   detector temperature: 310°C; carrier gas: nitrogen at 35 ml/min

14   (pressure 2.0 kg·cm^{-2}); oven temperature: ambient for Dexsil-300

15   column, 170°C for Parapak Q column, and 120°C for Carbowax 20M column.

16

17   Standards and Injection

18   For quantitative purposes, both a chlorofluorocarbon and a

19   chlorocarbon standard were applied. The chlorocarbon standard was

20   prepared by addition of each of 50 μℓ CH_2Cl_2, 2 μℓ $CHCl_3$, 1 μℓ CCl_4,

21   5 μℓ C_2HCl_3, and 3 μℓ C_2Cl_4 to 5 ml hexane, resulting in the primary

22   standard solutoin (A). Five μℓ of A were injected into an air-filled

23   1 ℓ separatory funnel where it quickly volatilized to become a 1 ℓ

24   reservoir of working standard (B). Standard B was freshly prepared

25   every week. Chlorofluorocarbon standards were prepared in a room

1   separate from the analytical laboratory in the following way. Four

2   μℓ of liquid Freon 11 (at 0°C) were injected into the airspace of a

3   125 ml separatory funnel. A volume of 1000 μℓ of gaseous Freon 12

4   was added to this separatory funnel to result in the primary (gaseous)

5   Freon Standard (C). After shaking the funnel C to ensure homogenisa-

6   tion, 30 μℓ of the gas were withdrawn and injected into an air-filled

7   1 ℓ separatory funnel to result in the working standard (D) which was

8   prepared twice a week.

9   For the preparation of the standard solution, appropriately

10   sized gas-tight syringes were used. For the injections into the

11   chromatograph, a 100 μℓ glass syringe with luer tip, fitted with Kel-F

12   hub and stainless steel needle, 75 mm, 0.6 mm O.D. was used throughout.

13   All such injections were done using an injection volume of 100 μℓ .

14   For the analysis of volumes of less than 100 μℓ of either the standards

15   or samples, the desired volume was withdrawn from the standard or

16   sample and made up to 100 μℓ volume with air. This technique was also

17   used   for the spiking of samples and the quick preparation of other

18   mixed gases.

19   Prior to the quantitation of samples or standards, several

20   injections of 100 μℓ each of air were made into the chromatograph to

21   ensure proper and stable functioning of the system. Gas leaks, aris-

22   ing in particular from a worn septum, tended to result in a baseline

23   drop prior to the elution of the oxygen, providing a simple means of

24   checking the performance and sensitivity of the instrument and detector.

25   The routine analytical detection limits were 5 ng.ℓ^{-1} Freon 12,

1 2 ng. ℓ^{-1} Freon 11, 4 ng. ℓ^{-1} chloroform, 2 ng. ℓ^{-1} carbon tetra-

2 chloride, and 2 ng. ℓ^{-1} trichloroethylene.

3

4

5 RESULTS AND DISCUSSION

6

7 Individual measurements for each contaminant from various depths

8 at each station were combined to result in arithmetic station means of

9 a contaminant for each station for each of the sampling periods in 1977

10 and 1978. The number of individual samples per station varied from

11 station to station and between years; however, most stations comprised

12 at least one sample each of surface (1 m below surface) and bottom (1 m

13 above bottom) water. The mean number of samples per station were 2.14

14 for 1978 and 2.27 for 1977. Due to incomplete sampling, loss of samples

15 during processing and analysis, only 96 out of 107 (in 1977) and 110

16 (in 1978) stations are represented by the data.

17 Combination of station means resulted in arithmetic cruise means

18 of the contaminants for each of the study periods in 1977 and 1978.

Table near

19 Table 1   gives a summary of such cruise means, the respective standard

20 deviations, relative standard deviations and concentration ranges

21 observed. A more detailed calculation of the cruise mean and standard

22 deviation for the 205, individual sample results for Freon 12 (1978)

23 gives 74 ± 44 ng·ℓ^{-1}, an insignificantly different mean and higher

24 standard deviation from those calculated for the 94 stations means for

25 Freon 12 (1978) of 76 ± 38 ng·ℓ^{-1}. These differences appear small enough

1   to justify the use of the ungrouped station means rather than that of

2   each sample for the calculation of the cruise means and standard

3   deviations. The distribution of the measured contaminants, however,

4   was found to vary considerably from station to station for each of

5   the cruises as well as in between the cruises. Attempts to correlate

6   chlorocarbon and Freon concentrations with either the depth or tempera-

7   ture of the individual water samples were unsuccessful. Possibly a much

8   larger number of stations and more samples per station might show such

9   correlations if they exist at all.

10

11   Freons

12   The chlorofluorocarbons - Freon 12 (CCl_2F_2, dichlorodifluoromethane)

13   and Freon 11 (CCl_3F, trichlorofluoromethane) - were observed in samples

14   from all stations, ranging in concentration from near the detection

15   limits to over 200 ng$\cdot \ell^{-1}$. Chlorofluorocarbons have been observed in

16   trace quantities in a few finished drinking water samples from the U.S.

17   (Shackleford and Keith, 1976) and they were also reported as contaminants

18   in large areas of the Atlantic (Lovelock et al, 1973). Most commonly

19   used analytical techniques for the determination of volatile constituents

20   of water are unsuited for the detection and quantification of the

21   chlorofluoromethanes as the adsorption and desorption steps are

22   presumably less quantitative for these relatively non-polar compounds.

23   In addition, the Freons are not separated from the solvent front under

24   regular gas chromatographic conditions. The techniques used here are

25   adopted from the procedure by Kaiser and Oliver (1976), which does not

1   involve any adsorption steps. For Freon 12, the cruise means and

2   associated standard deviations (Table 1) were virtually identical for

3   both 1977 and 1978. Figure 1 shows the distribution of Freon 12 in

4   1978. In that year, levels were found to be relatively uniform

5   throughout the lake with most stations having mean values of 50 to

6   100 $ng \cdot \ell^{-1}$ levels, but approximately half of the stations in the

7   eastern basin showed means of less than 50 $ng \cdot \ell^{-1}$ and one zone of

8   stations between the Sandusky and Cleveland areas and extending in

9   a northerly direction showed station means generally above $100 \cdot \ell^{-1}$.

10   Overall, there has been little change from the results for Freon 12

11   in 1977.

12   Freon 11 concentrations were less than those of Freon 12 in

13   both 1977 and 1978. However, the relative standard deviations of

14   the cruise means of 87 and 76 per cent were significantly greater for

15   the Freon 11 levels than for the corresponding Freon 12 levels

16   (Table 1). This is primarily a result of the much less even distribu-

17   tion of Freon 11. As can be seen from the distribution of Freon 11 in

18   1978 (Figure 2), stations in the eastern basin of Lake Erie generally

19   had levels greater than 50 $ng \cdot \ell^{-1}$, while the central basin had levels

20   predominantly less than 50 $ng \cdot \ell^{-1}$. In 1977, a similar situation was

21   observed with Freon 11 levels predominantly in the range of 25 to

22   99 $ng \cdot \ell^{-1}$ in the eastern basin and mostly below 25 $ng \cdot \ell^{-1}$ in the

23   central basin of the lake.

24   Correlations of the Freon and chlorocarbon data for both sampling

25   periods are given in Table 2. In 1978, for example, the correlation

1   coefficient for the station means of Freon 12 with those of Freon 11

2   of 0.09 is very low and indicates a different distribution pattern of

3   the two contaminants which is also evident from a visual comparison

4   of Figure 1 and Figure 2. In contrast, with a correlation coefficient

5   of 0.31, the Freon 12 levels of 1977 correlate much better with the

6   Freon 11 levels of the same year.

7   A variety of chlorofluoromethanes and chlorofluoroethanes have

8   found large scale use as propellants, refrigerants and blowing agents.

9   In particular, Freon 12 and Freon 11 are common materials for such

10 purposes (Howard and Hanchett, 1975). The magnitude of the consumption

11 of these materials is apparent from the world, U.S. total, and U.S.

Table 3
ne●here   12 Great Lakes basin production rates, as given in Table 3. McCarthy

13 et al. (1977) estimated that approximately 90 per cent of the cumulative

14 world production up to the year 1975 has been released into the

15 atmosphere.

16   No direct toxic effects of either Freon 12 or Freon 11 to biota

17 at the environmental levels observed are known. However, in recent

18 years, concern has arisen with respect to the adverse effect of

19 chlorofluorocarbons on ozone in the stratosphere. Such concern appears

20 to be well founded and has resulted in an international effort to

21 restrict the production and release of chlorofluorocarbons. Seigneur

22 et al. (1977) noted the effects of organic solutes in water on the

23 water solubility of Freons. For common practical purposes, the solu-

24 bility of chlorofluorocarbons in water is negligible. With the

25 presence of many solutes, most of which lower the surface tension of

1   water dramatically, an increased exchange of Freons between the

2   atmosphere and water may be possible. It is assumed that the distribu-

3   tion of Freons in the Lake Erie water samples is primarily a function

4   of the Freon concentrations in the overlying air and diffusion into

5   and out of the water. This assumption appears to be supported by the

6   interpretation of Figures 1 and 2, respectively, which do not show any

7   recognizable plumes or concentration gradients originating from the

8   larger urban and industrialized areas of the shores of the lake. The

9   observed station means result in a higher ratio of Freon 12 to Freon 11

10   the central basin and a lower ratio in the eastern basin of Lake Erie.

11   With the assumption of similar diffusion rates for both contaminants,

12   it would indicate that Freon 12 concentrations in the air are higher

13   over the central basin and lower over the eastern basin with the opposite

14   holding true for Freon 11.

15   Based on the observed means of Freon 12 and Freon 11 (Table 1)

16   and assuming an uniform distribution of both throughout the lake and a

17   lake volume of 470 km^3 (Sly, 1976), the total amounts in the lake

18   were calculated as approximately 35×10^3 kg Freon 12 and 18×10^3 kg

19   Freon 11, respectively. These amounts are equivalent to 0.3 per cent

20   of the estimated annual production in the U.S. Great Lakes basin of

21   Freon 12 and 0.2 per cent of that of Freon 11 (Table 3).

22   The amount of Freon in Lake Erie, as calculated from the

23   observed concentrations, compares reasonably well with that calculated

24   from the potential flux of this gas from the air into the water.

25

1   Background concentrations of Freon 11 in air over North America were

2   reported as approximately 100×10^{-12} g.m^{-3} with urban areas

3   frequently showing levels of up to 10 to 100 times higher (Singh et

4   al., 1977; Wilkniss et al., 1975).   As large urban areas are

5   situated to the west and northwest of Lake Erie, upwind from the

6   prevailing westerly winds (Simons, 1976), the concentration of Freon 11

7   is estimated to be 500×10^{-12} g.m^{-3} in the overlying air.   Given a

8   lake surface of 25×10^3 km^2 (Rainey, 1967), the amount of Freon 11

9   in the lake is calculated to 11×10^3 kg, according to the procedure

10   by Liss and Slater (1974).

11

12   <u>Chlorocarbons</u>

13   Three chlorocarbons, chloroform, carbon tetrachloride, and

14   trichloroethane, were observed in most water samples from both cruises.

15   Chloroform has been recognized as a widespread contaminant of drinking

16   water (Shackleford and Keith, 1976) and is thought to arise primarily

17   from the chlorination of raw and wastewaters (Morris and Baum, 1978).

18   Lawrence (1978) and Noack and Doerr (1978) investigated haloform and

19   potential haloform concentrations in several water sources and under

20   varied conditions and confirmed that potential haloform concentrations

21   are related to the concentrations of humic materials in such natural

22   waters.   In addition, chloroform and, to a lesser degree, carbon

23   tetrachloride, are formed by the disinfection of wastewater with

24   chlorine.   Comparatively little is known about the origin of trichloro-

25   ethane in lake water.   In addition to the above-mentioned sources, each

1 of these compounds can enter the aquatic environment from direct

2 discharges from manufacturing and use processes, as well as from the

3 atmosphere, as reviewed by Giger (1977). In order to relate these

4 possible sources to the concentrations observed, it is of interest

5 to compare the relevant production and use figures with the

6 concentrations and quantities observed as shown in Table 3.

7 A large survey of halomethanes in raw and finished drinking

8 water by Symons et al. (1975) reported the absence of $CHCl_3$ and

9 CCl_4 from raw water for Cleveland, Ohio, taken from Lake Erie.

10 However, such findings can now be augmented by our results, as

11 our detection limits and most concentrations observed are lower than

12 the limits of the above survey (50 $ng \cdot l^{-1}$ of $CHCl_3$ or CCl_4).

13

14 Chloroform

15 The distribution of chloroform in 1978 is represented in

16 Figure 3. Most stations showed levels of 10 to 19 $ng \cdot l^{-1}$ with little

17 variation to either higher or lower concentrations. This result

18 appears somewhat surprising in view of the known formation of chloroform

19 by wastewater chlorination, which is commonly practised in the larger

20 urban areas. No localized effects can be seen in the observed

21 distribution of chloroform. Only partial data on chloroform are

22 available for the 1977 cruise. Such data, however, appear to be

23 quite similar to those of 1978, indicating no significant difference

24 between the two sampling periods.

25 The chloroform means of each station were compared to the means

Fig. 3
near here

1   of the other contaminants (Table 2). Both with Freon 12 and Freon 11,

2   insignificant correlation coefficients of 0.02 and 0.14, respectively,

3   were obtained for the chloroform concentrations in 1978. The

4   correlation coefficients of chloroform with carbon tetrachloride and

5   with trichloroethylene were much higher for the same year. In particular,

6   the coefficient for trichloroethylene and chloroform of 0.37 is

7   significant at the 99.9% confidence limit and indicates a basically

8   similar distribution pattern of these two contaminants.

9

10   Carbon tetrachloride and Trichloroethylene

11   Carbon tetrachloride and trichloroethylene have frequently been

12   observed in environmental samples. Numerous accounts establish their

13   widespread presence in both marine and freshwater systems, as reviewed

14   by Giger (1977). As evident from a comparison of Figures 4 and 5, in

15   Lake Erie both compounds show similar distribution patterns. Carbon

16   tetrachloride (Figure 4) was observed at most stations in levels up to

17   19 $ng \cdot \ell^{-1}$, similar to chloroform. However, in contrast to chloroform,

18   large areas with elevated levels were observed in the vicinities of

19   Sandusky and Cleveland in the central basin and to the northeast of

20   Erie, Pennsylvania in the eastern basin of Lake Erie. The distribution

21   of carbon tetrachloride in the eastern basin appears to show particularly

22   high concentrations covering an area between Erie and Westfield,

23   Pennsylvania, and the deepest sounding.

24   The distribution pattern of trichloroethylene during the cruise

25   period in 1978 is shown in Figure 5. High levels of this contaminant

Figure 5
near here

1   were observed in the vicinity of Erie, Pennsylvania, extending parallel

2   to the southern shore to the centre of the eastern basin, followed by

3   a rapid decline to very low levels in the northern and eastern part of

4   the eastern basin. As with carbon tetrachloride, also trichloroethylene

5   concentrations were higher in the areas to the east and north of

6   Sandusky and Cleveland, respectively. In addition, a large zone of

7   intermediate trichloroethylene levels was observed in the central part

8   of the central basin. This zone appears to have somewhat higher

9   concentrations near the southern shore of Lake Erie close to Ashtabula,

10 Ohio.

11 Apart from the Ashtabula area of the central basin, the visual

12 comparison of the distributions of carbon tetrachloride and trichloro-

13 ethylene shows a striking similarity. The correlation coefficient of

14 both compounds for the 1978 period of 0.67 is significant at the

15 99.9% confidence limit and is the highest observed (Table 2).

16 The distribution of trichloroethylene during the sampling period

17 in 1977 was similar to that of 1978, except for the central part of the

18 central basin where more uniform low levels were recorded. Elevated

19 levels were found in the southwestern part of the central basin and

20 throughout the eastern basin of Lake Erie. Overall, the trichloroethylene

21 mean, increased from 11 ± 9 ng·ℓ^{-1} in 1977 to 20 ± 13 ng·ℓ^{-1} in 1978

22 (Table 1) but shows an insignificant correlation of 0.12. In contrast,

23 the carbon tetrachloride mean level declined from 37 ± 20 ng·ℓ^{-1} in

24 1977 to 19 ± 11 ng·ℓ^{-1} in 1978. Furthermore, the station means of

25 1977 were relatively uniform with a zone of high values reaching from

1. Erie, Pennsylvania in northwesterly direction to Long Point and

2. extending from there to approximately Long. 81°W. Higher concentra-

3. tions of carbon tetrachloride were also observed at two central

4. stations in the eastern basin; however, no significantly higher levels

5. were found in the area between Sandusky and Cleveland as was the case

6. for trichloroethylene.

7.   Finally, it is of interest to consider any possible association

8. of carbon tetrachloride or trichloroethylene with either one or both

9. of the Freons. The highest correlation coefficient observed in that

10. respect, 0.59, is that of trichloroethylene with Freon 11 in 1977

11. (Table 2). This value is in strong contrast to the extremely low

12. correlation coefficient of 0.03 for the same compounds in 1978.

13. Similarly, the correlation of Freon 11 with carbon tetrachloride of

14. only 0.02 in 1977 changes to 0.23 in 1978. However, the correlation

15. coefficients of Freon 12 with carbon tetrachloride of 0.44 in 1977

16. and 0.31 in 1978 are both significant at the 99% confidence level,

17. while insignificant correlations are found for Freon 12 and trichloro-

18. ethylene for both years.

19.   In general, it may be concluded that the Freons are most likely

20. to enter the aquatic system from the atmosphere, while the chlorocarbons

21. are interpreted as entering primarily from discrete point sources

22. associated with large urban and industrial outfalls along the southern

23. shore of Lake Erie.

24.

25.

1 ACKNOWLEDGEMENTS

2   We thank Mr. H. Huneault of the Toxic Substances Section, the

3 crew of CSS LIMNOS, and the staff of the Technical Operations Section

4 of NWRI for their cooperation and assistance in the collection of the

5 samples.

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TABLE 1. Station means, standard deviations, relative standard deviations, and ranges of Freon 12, Freon 11, chloroform, carbon tetrachloride, and trichloroethylene in the eastern and central basins of Lake Erie, 1977 and 1978, concentrations in $ng \cdot \ell^{-1}$.

Compound	1977				1978		
	N [a]	$\bar{x}$ [b] $\pm$ s [c]	(%) [d]	Range	N	$\bar{x} \pm$ s (%)	Range
Freon 12	91	73 ± 36	(49)	10-190	94	76 ± 38 (50)	16-255
Freon 11	90	46 ± 40	(87)	6-185	94	34 ± 26 (76)	6-168
$CHCl_3$	-	-		-	90	15 ± 4 (27)	5-34
CCl_4	85	37 ± 20	(54)	9-110	95	19 ± 11 (48)	4-53
C_2HCl_3	96	11 ± 9	(82)	3-48	96	20 ± 13 (65)	5-63

a) Number of station means
b) Mean
c) Standard deviation
d) Relative standard deviation

- 22 -

TABLE 2. Correlation coefficients of the station means.

	Freon 12 (1978)	Freon 11 (1977)	Freon 11 (1978)	$CHCl_3$ (1978)	CCl_4 (1977)	CCl_4 (1978)	C_2HCl_3 (1977)	C_2HCl_3 (1978)
Freon 12 (1977)	.35	.31	.09	.10	.44	–	.10	–
Freon 12 (1978)		–	.09	.02	–	.31	–	.13
Freon 11 (1977)			.38	–	.02	–	.59	–
Freon 11 (1978)				.14	–	.23	–	.03
$CHCl_3$ (1978)					–	.20	–	.37
CCl_4 (1977)						.18	.03	–
CCl_4 (1978)							–	.67
C_2HCl_3 (1977)								.12

TABLE 3. Production rates and estimated quantities in Lake Erie (1978) of Freon 12, Freon 11, $CHCl_3$, CCl_4, and C_2HCl_3, in 10^3 kg.

Compound	Annual Production			Quantities in Lake Erie
	World[a]	U.S. Total[c]	U.S. Great Lakes Basin[f]	
Freon 12	570,000	219,000	11,000	35
Freon 11	485,000	153,000	9,000	18
$CHCl_3$	245,000		500	7.1
CCl_4	1,000,000 1,700,000 [b]	522,000 390,000 [d] 680,000 [e]	2,500	8.9
C_2HCl_3	1,010,100		2,000	9.4

a) Pearson and McConnell (1975)

b) Lovelock et al. (1973)

c) OCPDB (1978)

d) Estimated from Altshuller (1976)

e) Estimated from Lovelock et al. (1973)

f) Estimated as approximately 1/20 of total U.S. or 1/50 of world production

LIST OF FIGURES

FREON 12 – 1978

CONCENTRATION ng·L^{-1}

▓	5-49
▓	50-99
▓	100-199

FIG. 1

FREON 11 – 1978

CONCENTRATION ng·L^{-1}

2–24
25–49
50–99
100–149

FIG. 2

CHCl$_3$ – 1978

CONCENTRATION ng·L^{-1}

	4-9
	10-19
	20-29
	30-39
	40-49

FIG. 3

CCl₄ - 1978

CONCENTRATION ng·L⁻¹
- 2-9
- 10-19
- 20-29
- 30-39
- 40-49

FIG. 4

$C_2 H Cl_3 - 1978$

CONCENTRATION $ng \cdot L^{-1}$
- 2-9
- 10-19
- 20-29
- 30-49
- 50-69

FIG. 5