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In surface waters

By:

Klaus Kaiser & M.E. Comba
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Volatile halocarbons as indicators of industrial pollution in surface waters

Klaus L.E. Kaiser and M.E. Comba

**Nearshore-Offshore Interactions, Lakes Research Branch,
National Water Research Institute, PO Box 5050, Burlington, Ontario, Canada**

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Abstract

Increased levels of volatile halocarbons in surface waters, in particular such compounds as di-, tri-, and tetrachloro-ethanes, -ethylenes, and -methanes are typically associated with increased levels of other organic and inorganic contaminants from industrial origins. As there are comparatively simple sample collection, processing and analytical methods available, their determination can help to reduce the cost of surveys to find hotspots and/or sources of contamination. This work reviews some recent findings and relates them to other environmental data and conditions.

Introduction

Highly volatile halocarbons, which exist under normal conditions as gases or low boiling liquids, have been recognized as important indicators of environmental contamination by industrial effluents. For example, trichloromethane (chloroform) is a typical byproduct of pulp and paper bleaching with elemental chlorine. Thus it is a common constituent of adsorbable organic halogen (AOX) which has been implicated as the contributor to a wide variety of deleterious effects on fish and other biota in rivers and lakes receiving such effluents (Munkittrick *et al.*, 1992; Servos *et al.*, 1992). Other volatile halocarbons, such as carbon tetrachloride and tetrachloroethylene have been found to enter surface waters in liquid form to act as carriers of other, far more persistent and lipophilic compounds, such as hexachlorobenzene and octachlorostyrene (Oliver and Kaiser, 1986). In other work, a common association of industrial solvents, such as trichloroethane (TCA) and trichloroethylene (TCE) with polychlorinated biphenyls (PCB), polynuclear aromatic hydrocarbons (PAH) and other types of industrial compounds has been shown (Comba and Kaiser, 1985).

Apart from their association with other contaminants, some volatile halocarbons are known to have chronic effects on certain fish species at the low microgram per litre levels (Loekle *et al.*, 1983). Such chronic effects are produced at concentrations significantly lower than might be expected from their acute toxicities (Loekle, 1987). However, some of the more sensitive bioassay methods corroborate the sensory perception by fish of, for example, TCE levels in the 10 to 20 $\mu\text{g}/\text{L}$ range (Diamond *et al.*, 1990; Kaiser and McKinnon, unpublished results). Furthermore, several of the chloroalkenes are known mucous membrane irritants (Kaiser and McKinnon, 1993) and enzyme inducers.

The volatility and chemical inertness of halocarbons with a chain length of one to three carbon atoms makes them amenable to headspace analytical methods. When coupled with gas chromatography and electron capture detection, this methods allows simple, fast and sensitive determinations at the ng/L level (Comba and Kaiser, 1983). Furthermore, the avoidance of matrix effects and field versatility of the processing system makes it suitable for surveys of both rivers and lakes using either stationary or mobile facilities (Kaiser and Valdmanis, 1979; Comba *et al.*, 1993). This feature can be exploited to determine the spatial and temporal evolution of effluent plumes and currents in receiving waters (Fogelqvist *et al.* 1982; Kaiser and Valdmanis, 1979; Kaiser and Comba, 1983, 1986a, 1986b; Kaiser *et al.*, 1983).

This report provides an overview of volatile halocarbon levels in surface waters of the Laurentian Great Lakes basin their relevance to other contaminants and water quality observations and management in general.

Experimental

The experimental procedures and conditions have been described in detail (Comba and Kaiser, 1983; Kaiser and Oliver 1976). Therefore, only a brief description is given here.

Water samples of 250 mL are taken with an inverted bottle sampler at 1 m depth by hand. The bottles are filled completely, capped and stored cool and out of sunlight until processing. Processing is preferably done within a few hours from sample collection. The samples are transferred to 125 mL elongated separatory funnels, drained to a 100 mL volume and the funnel inverted. The overlying headspace of the still cold sample (25 mL) is then quickly evacuated through the funnel stopcock and the funnel closed again. The sample is then heated for several minutes to a temperature of 90 °C which partitions dissolved gases and volatile contaminants into the evacuated headspace. The headspace contents are then transferred into an evacuated 15 mL vial equipped with a rubber septum and Teflon valve cap which is cooled with liquid nitrogen to condense the headspace contents. Vials with samples thus processed can be stored without deterioration for several weeks. Direct injection of such headspace samples by capillary gas chromatography with electron capture detector allows determination of a number of volatile halocarbons at the low ng/L levels. At somewhat higher concentrations and with the use of a mass selective detector, also some non-halogenated compounds, such as benzene, toluene and xylenes are amenable to this type of analysis (Gough *et al.*, 1993).

We have successfully used this procedure for a number of years under a variety of conditions, such as on shipboard, in the cargo space of small trucks, in motel rooms and with a portable generator in other field situations. Although there are now commercial instruments available for this kind of analysis, we continue to use our system developed over 10 years ago.

Results and Discussion

Chloroethylenes

The two most commonly observed chloroethylenes in water are the tri- and tetrachloro congeners. In Canada, their annual usages are in the order of 1.5×10^6 kg and 7.5×10^6 kg, respectively. In Great Lakes' surface waters, such as the St. Clair, Detroit, Niagara and St. Lawrence Rivers, concentrations of trichloroethylene (TCE) and tetrachloroethylene (TECE) are generally in the low, i.e., 10 to 50 ng/L range. Exceptions with higher values were found at the mouth of certain tributaries receiving industrial effluents or below direct outfalls into the main streams, where levels up to 1000 ng/L TECE and up to 90000 ng/L TCE have been observed (Lum *et al.*, 1986). In the lakes, higher levels are generally restricted to embayments and the nearshore zones. The water of tributaries and outfalls with a temperature warmer than that of the receiving water stays at or rises to its surface and can be clearly identified for considerable distances into the lake. For example, zones so identified extended up to 20 km into Lake St. Clair (Kaiser and Comba, 1986a) and up to 40 km into Lake Erie (Kaiser and Valdmanis, 1979), as shown in Figure 1. TECE pathways and fate in Lake St. Clair were later modelled with the TOXFATE model (Halfon, 1986).

Fig. 1. Trichloroethylene plumes in Lake Erie, from Kaiser and Valdmanis (1979).

In early fall, smaller tributaries cool down faster than the receiving lakes waters. Under those conditions, the colder, hence more dense tributary or effluent water quickly sinks to the bottom of the lake or embayment. Good examples for such situations have been observed in Jackfish Bay of Lake Superior (Figure 2). Prolonged exposure of sediments with higher concentrations of halocarbon compounds can lead to their adsorption into organic matter and their subsequent slow release into the hypolimnion.

Fig. 2. Chloroform in bottom water of Jackfish Bay during October, from Comba *et al.* (1993).

Haloforns

Haloforns, chemicals of the general formula CHX_3 , where $\text{X} = \text{Cl}$ or Br , are common byproducts of the chlorination of potable or waste waters. The reaction of natural or manmade organic materials with chlorine to form chloroform (CHCl_3) has been well documented. Dependent on the conditions of chlorination (primarily pH and temperature), and the bromide ion content of the water, bromo analogs of chloroform, namely CHBrCl_2 , CHBr_2Cl and CHBr_3 are formed in a constant ratio with chloroform. The constant ratio of chloroform to bromodichloromethane can be used to compute the concentration of chloroform attributable to the chlorination process. By taking the difference between the total (measured) and computed chloroform concentrations (derived from CHBrCl_2), the amount of "industrial source chloroform", i.e., chloroform which is not a byproduct of potable water chlorination can be determined. In the Great Lakes basin, we observed the $\text{CHCl}_3/\text{CHBrCl}_2$ ratios for potable water typically in the 1.5 to 3.5 range.

In the nearshore areas of Lake Ontario, particularly between the mouths of Twelve Mile Creek (Ontario) and Oak Orchard Creek (New York), distinct plumes of industrial chloroform were found in surface waters (Comba and Kaiser, 1984). Figure 3 shows such a nearshore plume of approximately 50 km length and 5 km width.

Fig. 3. Industrial source chloroform in nearshore Lake Ontario water along the Niagara frontier, from Comba and Kaiser (1984).

Other volatile halocarbons

Besides those mentioned above, the headspace analysis of many surface waters reveals the presence of varying levels of other methane derivatives, such as CCl_4 and the chlorofluorocarbon CCl_2F_2 , ethane derivatives, such as 1,1,1- and 1,1,2-trichloroethane, vinylchloride, and occasionally some propane derivatives. Commonly, their levels are at or near background concentrations of 1 to 10 ng/L, but higher levels have been observed in lakes and rivers, particularly for 1,1,1-trichloroethane, a widely used degreasing solvent (Kaiser and Comba, 1986a). In contrast to most other halocarbons, higher levels of the chlorofluorocarbons are usually derived from atmospheric washout rather than from direct aqueous sources.

Conclusions

The headspace analysis of surface waters has proven to be a simple tool to determine ng/L levels of a variety of highly volatile halocarbons in the one to three carbon range. The samples should be processed soon after collection to isolate the compounds in a gaseous matrix, but this work can be done rapidly with a simple methodology.

The obtained data are useful in several ways: They highlight areas of inputs to receiving waters and, because of their general association with other contaminants are useful pointers for other more detailed sampling and analysis.

Under conditions of steady point source inputs, volatile halocarbons can be used as tracers of plumes and currents in lakes and rivers. In this way, they can assist physical limnology and system modelling by providing nearly synoptic data on large water bodies.

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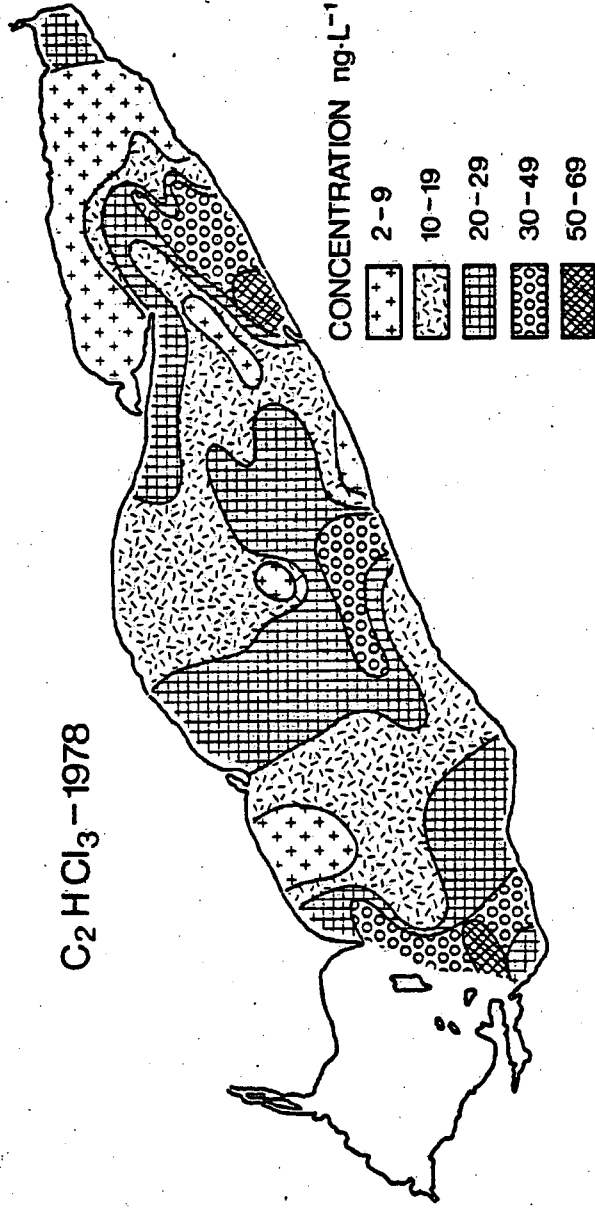


Fig. 1

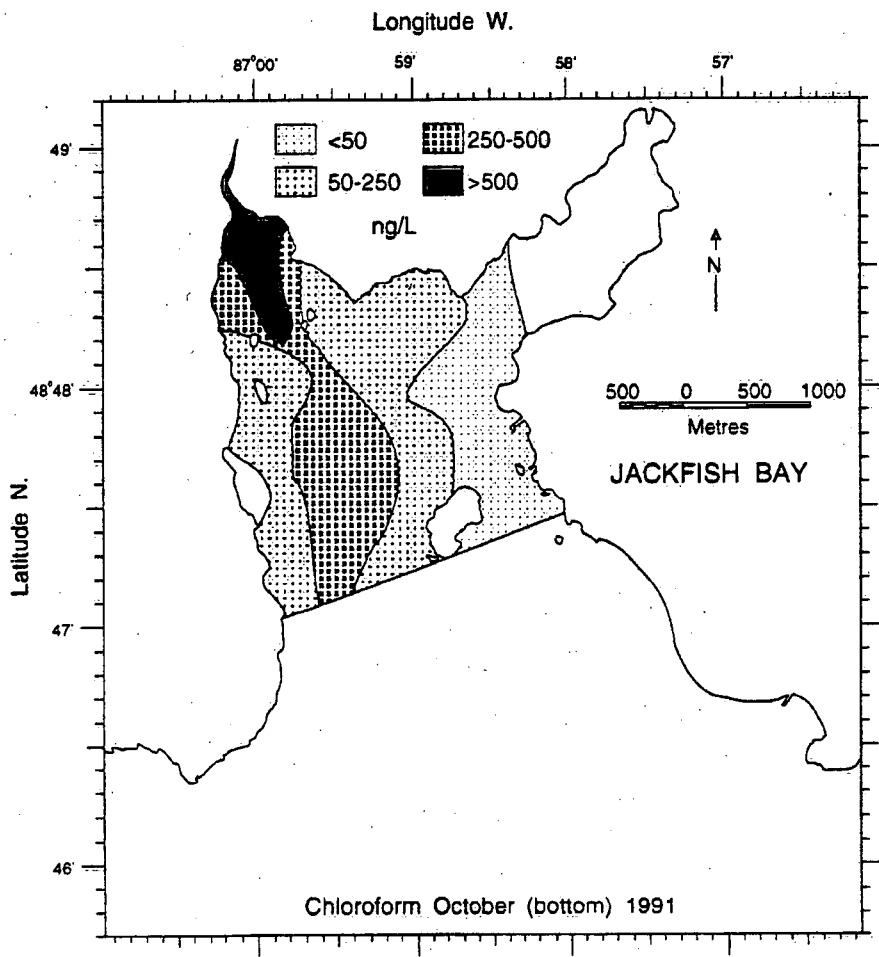


Fig. 2

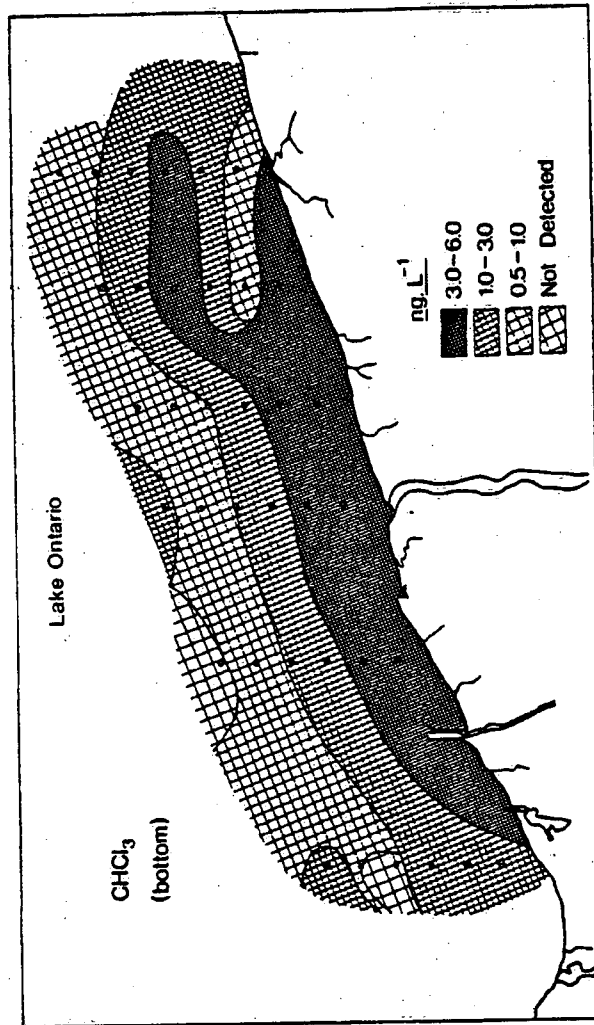


Fig. 3

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