

Chlorinated Bornanes (Toxaphene) in Yukon Lakes: Atmospheric or Non-Atmospheric Source

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INTRODUCTION

Toxaphene was introduced in the USA in 1945 by Hercules Co. as a new insecticide to control a variety of insect pests. Two thirds of the total production was used for insect control on cotton¹. In Canada and the US, toxaphene was also used extensively in fish eradication programs. This practice, however, was discontinued in the mid 1960s when it was found that toxaphene was extremely persistent and that lakes could not be successfully restocked for years after treatment². Prior to its ban in 1982 by the US EPA¹, toxaphene was the most extensively used pesticide in the USA and many other parts of the world with maximum usage occurring in the mid 1970s after the ban of DDT.

With the exception of Hanson lake, which was treated with toxaphene as a piscicide in the early 1960s, no evidence of any past release of Σ CHBs into Yukon Lakes or into the upper Yukon River system exists. Elevated Σ CHBs levels found in fish tissues from several of the large lakes in the system have thus been attributed to an atmospheric source, rather than a local one, and a longer than normal food chain^{3,4}.

We present here results which show that the higher levels of Σ CHBs observed in some Yukon Lakes, can also be attributed to the use of toxaphene as an additional active ingredient in the insecticidal DDT mixtures used by the military for insect control⁵. Although brief mention is made in the literature regarding this practice¹, no records documenting the quantities of toxaphene added to the DDT mixtures, and the dates and sites where these mixtures were applied, could be found.

MATERIALS AND METHODS

Sediment Extraction and Dating. Sediment cores, collected using a KB corer (10 or 16 cm diameter), were sliced at 1 cm increments and kept at -10°C. Extractions were performed as described by Muir *et al.*⁶. Excess ²¹⁰Pb and ¹³⁷Cs profiles were used to calculate the median age of each core slice¹¹.

Mass Spectrometry. Samples were analysed using high resolution gas chromatography electron capture negative ion high resolution mass spectrometry (HRGC/ECNI/HRMS) in the selected ion mode on a Kratos Concept mass spectrometer controlled using a Mach 3 data system. Analyses were performed at a resolving power of ~12000. Argon (UHP) was used as the moderating gas and perfluorokerosene as the mass calibrant. Optimum sensitivity was obtained at a gas pressure of ~2 x 10⁻⁴ torr as measured by the source ion gauge. The electron energy was adjusted for maximum sensitivity (~180 eV), the accelerating voltage was 5.3 kV and the ion source temperature was 120°C. The SIM program and GC conditions used have been described previously⁸.

RESULTS AND DISCUSSION

The ECNI selective ion chromatograms of Σ CHBs in representative slices of sediment cores from five different Yukon Lakes are shown in Figure 1. The chromatographic pattern of Σ CHBs in the Hanson Lake sediment consists primarily of two congeners, a hexa- and a heptachlorinated bornane. Stern *et al.* have shown that these two congeners, referred to as Hx-Sed (B6-923) and Hp-Sed (B7-1001), respectively, are predominant in the sediment of lakes which have been exposed to non-atmospheric sources of toxaphene⁹. Hx- and Hp-Sed are also the predominant CHB congeners in sediments from Watson and Fox Lake suggesting contamination by a non-atmospheric source even though no evidence documenting past release of Σ CHBs to either of these lakes could be found. Hx- and Hp-Sed are present in the Lake Laberge sediment, but at levels similar to that which is associated with atmospheric deposition. In the Kusawa lake sediment, the Σ CHB profile is consistent with inputs associated with atmospheric deposition only.

Σ CHB and Σ DDT sediment concentration profiles are shown in Figure 2. Peak concentrations of Σ DDT in Watson lake sediments are seen in the slices corresponding to the period 1955 to 1958. These high concentrations are consistent with extensive aerial spraying of DDT in the Watson Lake area over this period. The observed Σ CHB profile is very similar to that observed for Σ DDT and is not consistent with what would be expected based solely on atmospheric deposition¹⁰ (i.e. peak levels occurring in the early to mid 1970s). Peak Σ DDT concentrations in the Fox Lake sediment core was observed in the slices representing a 10 year time period from 1958 to 1968. Maximum concentrations in the Lake Laberge sediment core, occurred a somewhat earlier time period from 1940 to 1946. Like that of Watson Lake, the historical profile of Σ CHB observed in the Laberge and Fox Lake sediment cores are not consistent with what would be expected if contamination was due solely to atmospheric deposition. The higher than expected Σ CHB levels observed in the sediment core slices representing the period from 1953 to 1964 in the Laberge core and from 1947 to 1958 in the Fox Lake core overlap with the periods representing the historical usage of Σ DDT. The approximately 10 fold increase in Σ CHB levels from the mid 1940s to the early 1950s in the Laberge sediment core suggests that the practice of adding toxaphene as an additional active ingredient in the insecticidal DDT mixtures did not begin until the early 1950s. The historical profiles and low levels of both Σ DDT and Σ CHB in the Kusawa sediment core are consistent with an atmospheric source only. Both Fox Lake and Lake Laberge, unlike Kusawa Lake, are located close to Whitehorse and the Alaska Highway and therefore, would almost certainly have been exposed to the huge quantities of the insecticidal DDT mixtures which were sprayed primarily in the Whitehorse area, over the period from 1949 to 1969.

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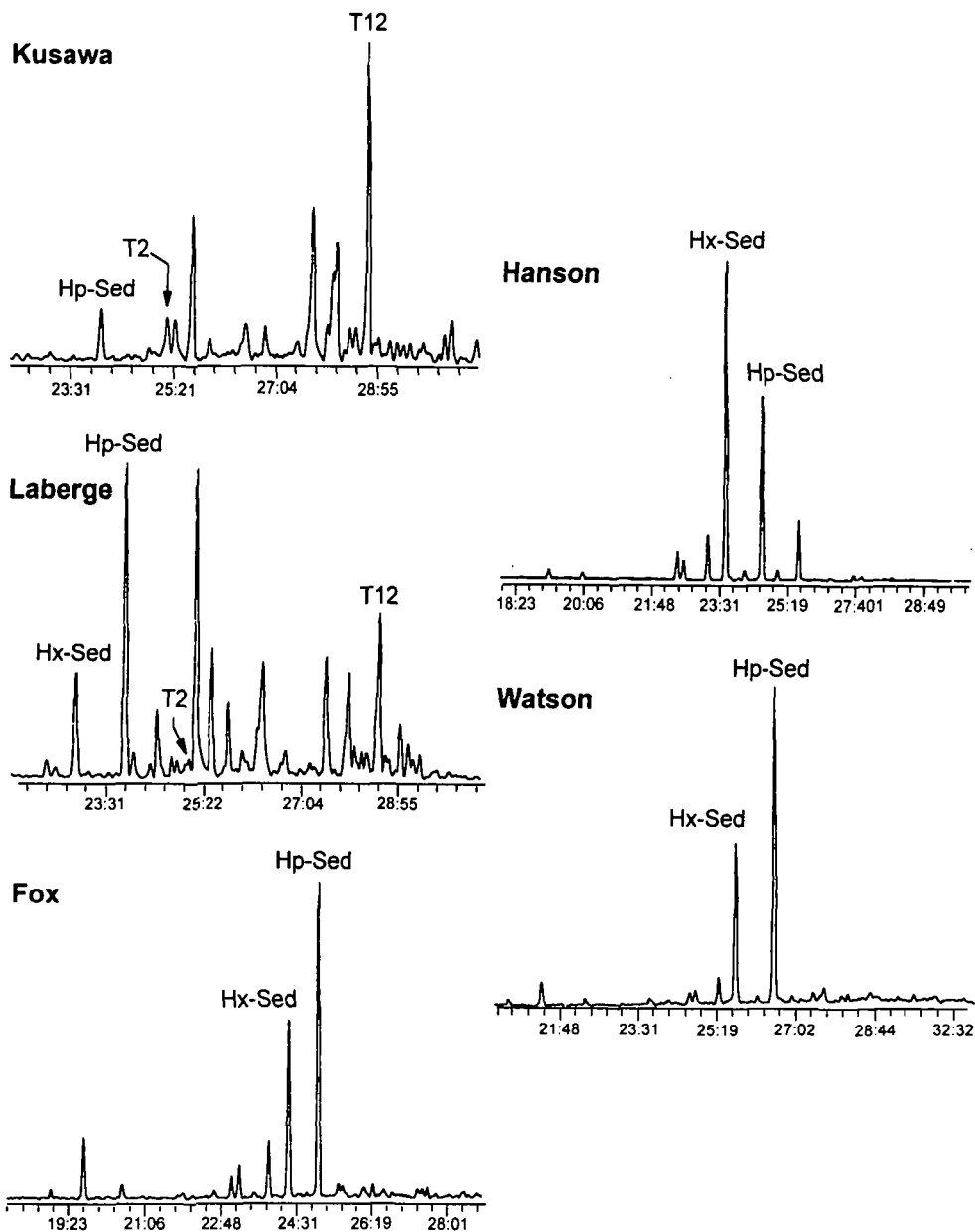


Figure 1. ECNI selected ion chromatograms of Σ CHBs in sediment core slices from five Yukon Lakes. Hanson Lake was treated with toxaphene as a piscicide in the early 1960s.

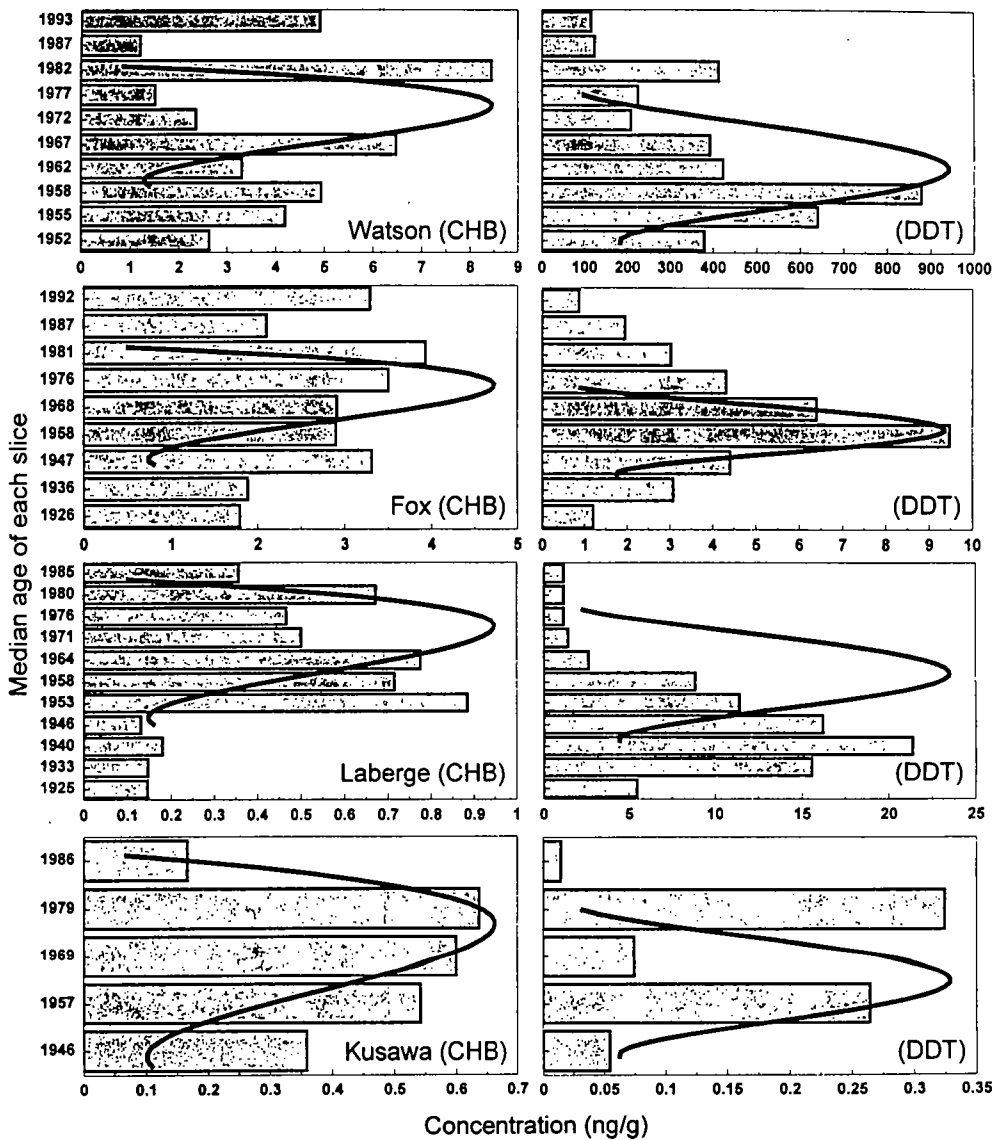


Figure 2. Concentration profiles (ng/g, dry wt.) of Σ CHB and Σ DDT in sediment cores from four Yukon Lakes. The curves correspond to the atmospheric input functions of Σ CHB and Σ DDT derived by Rapaport and Eisenreich¹⁰.