

# Toxaphene, the Underestimated Pesticide P197

## Differentiating between sources of toxaphene transported to Lake Winnipeg during the 1997 Red River Flood

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### Introduction

In 1997, the Red River valley experienced its worst flood in over 100 years. A number of factors contributed to the severity of the flood including above average snow accumulation, a blizzard during the snowmelt period and high soil moisture conditions. At the peak of the flood, discharge was estimated to be 3,850 m<sup>3</sup>/s on April 18, 1997 at Grand Forks ND, 3,740 m<sup>3</sup>/s on May 2, 1997 at Emerson MB, and 4,587 m<sup>3</sup>/s on May 4, 1997 at Winnipeg MB<sup>1</sup>. The flood resulted in the evacuation of over 103,000 people (75,000 in the US and 28,000 in Manitoba), destruction of physical property and potentially short-term and long-term impacts on water quality, particularly from contaminants mobilized during the flood<sup>1</sup>.

Numerous sources of contamination were identified during the flood. In Manitoba, the Red River exceeded its banks, spreading to a maximum width of 40 km, flooding farm properties, urban households, a rural town (St. Agathe MB), and farmland; each with their own retinue of contamination. In the United States an agricultural storage facility in Grand Forks ND was compromised during the flood. Water and a layer of sunflower oil sampled from the basement of this facility were found to be heavily contaminated with both toxaphene and lindane ( $\gamma$ -HCH) (US EPA, Denver CO, 1997).

We present here results which show that a pulse of undegraded technical toxaphene, corresponding to approximately 46 kg, was introduced into the Red River at Grand Forks over a 15 day period. This new source of toxaphene was subsequently transported down the Red River where it has accumulated in the sediment and biota of Lake Winnipeg. Almost 14 months after the flood the mean concentration of  $\Sigma$ CHB (sum of hexa to nonachlorobornanes) in walleye, one of the top predators in Lake Winnipeg, was 9x higher than the pre-flood levels measured in fish collected in October 1996.

### Materials and Methods

*Sample collection and analysis.* 18-L water samples were collected from the floodway and Selkirk a minimum of every 2-3 days from April 28, 1997 until June 2, 1997, then weekly at the Selkirk site for the month of June and then monthly until the middle of October. Extracts of the filtered water and suspended sediments were analyzed for toxaphene 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  $\sim$ 12000. Argon (UHP) was used as the moderating gas and perfluorokerosene as the mass calibrant. Optimum sensitivity was obtained at a gas pressure of  $\sim$ 2 x 10<sup>-4</sup> torr as measured by the source ion gauge. The electron energy was adjusted for maximum sensitivity ( $\sim$ 180 eV), the accelerating voltage was

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5.3 kV and the ion source temperature was 120°C. The SIM program and GC conditions used have been described previously<sup>2</sup>.

### Results and Discussion

While maximum concentrations of  $\Sigma$ CBz,  $\Sigma$ DDT,  $\Sigma$ CHLOR and  $\Sigma$ PCB occurred in Selkirk water at peak flow (between May 2 and 7), both  $\Sigma$ HCH (predominantly  $\gamma$ -HCH) and  $\Sigma$ CHB (see Figure 1) reached maximum concentrations several days after peak flow on May 16 and May 20, respectively. Based on information provided by the U.S. EPA (Denver CO, personal communication) this delayed maximum can most likely be attributed to the release of toxaphene and lindane from the AGSCO storage facility in Grand Forks ND. When the contaminated oil and water was discovered in the basement of this storage facility on April 29, 1997, 8 days after peak flow had occurred in the area, concentrations of toxaphene and lindane in the oil were 170,000  $\mu$ g/L and 21,000  $\mu$ g/L, respectively. Contaminated water was found in a nearby drainage ditch, suggesting that the toxaphene and lindane were being removed from the basement.

To determine if the toxaphene in Red river water and suspended sediment samples consisted of a new or old source, Hx-Sed and Hp-Sed (or B6-923 and B7-1001, respectively<sup>3</sup>) concentrations were plotted as a percent of  $\Sigma$ CHB in the sample over the flood period. These two congeners are considered to be the dead-end metabolites of technical toxaphene in the environment<sup>4</sup> and, therefore, a lower ratio of Hx-Sed + Hp-Sed to total toxaphene should indicate a newer source (undegraded). This is in fact what was found. The ratio ranged from 4 to 13 during the flood period and 16 to 22 during the summer and fall after the flood. The higher ratio after peak flow suggested that an older source of toxaphene was being remobilized and probably represented a typical summer loading. The lower ratio indicates that a new source of toxaphene was released as a pulse during the flood, most likely from the compromised storage facility in Grand Forks ND. Suspended sediment ratios for these congeners were also lower during the flood period (~3-6) relative to the ratios measured in late June to mid-July (~10-13).

The ECNI selective ion chromatograms of ECHB in Lake Winnipeg and Red River water at Selkirk (Figure 2) also imply that a new source of toxaphene was released during the flood. The ECHB profiles of water collected during the flood event (April 28 - May 26, 1997) were found to be very similar to that of the technical toxaphene. Conversely, the profiles observed in the water samples collected after the flood event (June 26- Oct 16, 1997) and in Lake Winnipeg water in September 1998, showed a shift to the lower chlorinated congeners with Hx-Sed and Hp-Sed peaks predominating. Similar results were obtained for the suspended sediments (not shown). Surficial sediments collected from the south basin of Lake Winnipeg in March 1998 showed a profile consistent with a mixture of the degraded and non-degraded toxaphene, while in surface sediments collected prior to the flood (1994), Hx-Sed and Hp-Sed were by far the most predominant congeners present.

### References

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- 2) D.B. Donald, D.B., G.A. Stern, D.C.G. Muir, B..R. Fowler, B.M. Miskimmin, R. Bailey, *Environ. Sci. Technol.* **1998**, 32, 1391-1397.
- 3) P. Andrews and W. Vetter, *Chemosphere* 1995, 31, 3879-3886.
- 4) G.A. Stern, M. Loewen, B. Miskimmin, D. Muir, J.B. Westmore, *Environ. Sci. Technol.* **1996**, 30, 2251-2258.

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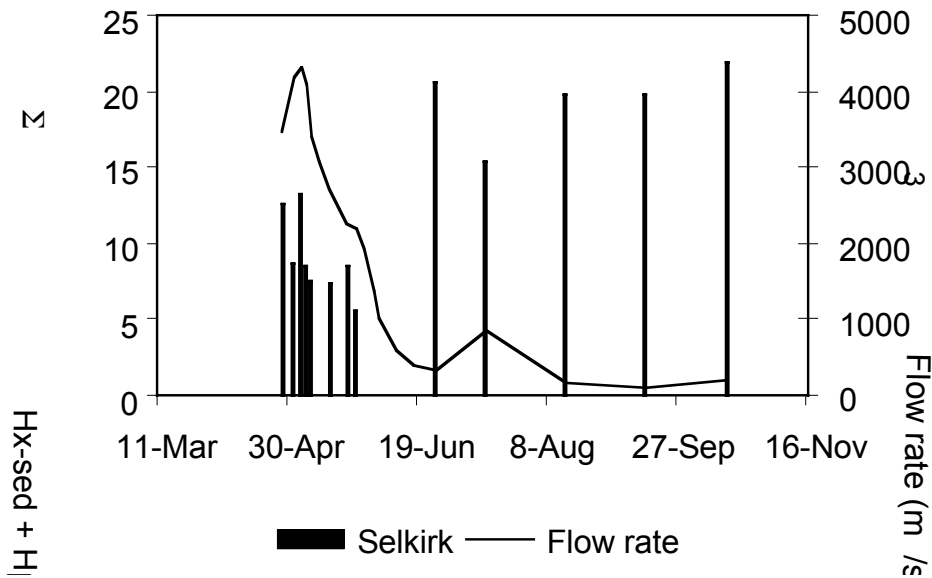


Figure 1. Concentrations of  $\Sigma$ CHB (top) and the sum of Hx- and Hp-Sed as a ratio of  $\Sigma$ CHB (bottom) in water collected from the Red River at Selkirk and the Floodway in 1997 plotted against flow rate. Flow rate data was obtained from Environment Canada at stations best corresponding to our sampling sites.

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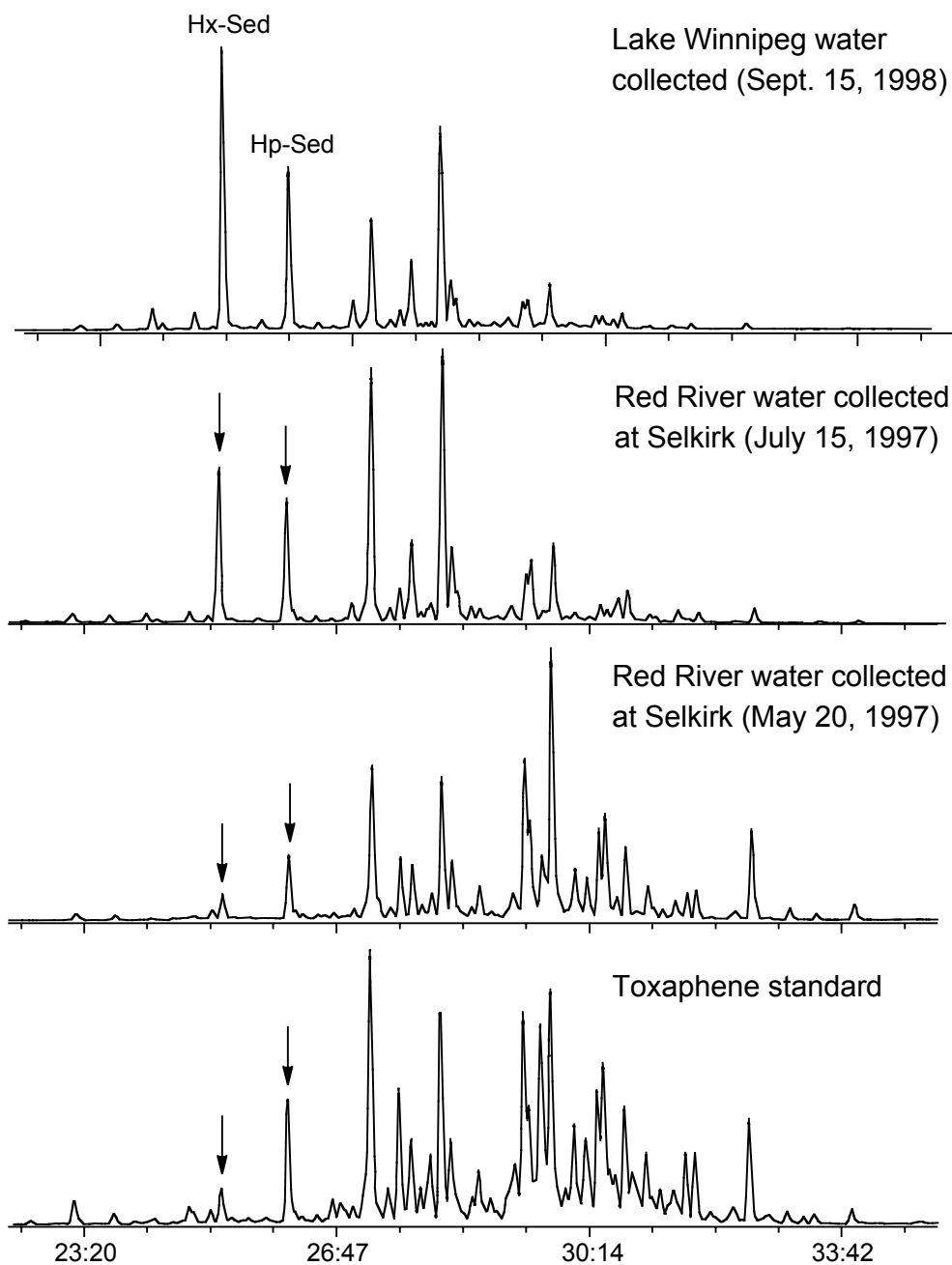


Figure 2. Electron capture negative ion selected ion chromatograms of  $\Sigma\text{CHB}$  (sum  $\text{Cl}_6\text{-Cl}_9$ ) in Lake Winnipeg and Red River (at Selkirk) water and technical toxaphene.