Search for Chlorobornanes in River Sediments: Part 1

Christoffer Rappe, Peter Haglund, Rolf Andersson, and Hans-Rudolf Buser*

Institute of Environmental Chemistry, Umeå University, SE-901 87 Umeå, Sweden.
* Swiss Federal Research Station, CH-8820 Wädenswil, Switzerland.

Introduction

At Dioxin '95 in Edmonton, Swackhamer, et al. (1) reported on the accumulation of chlorobornanes in sediments in the Great Lakes. These authors claim that "it appears that the common notion that [chlorobornanes] in the Great Lakes is due mostly to long-range transport and atmospheric deposition of [chlorobornanes] is incorrect. Significant quantities of non-atmospheric [chlorobornanes] have been and are currently accumulating in Great Lakes sediments." The primary researcher of that paper has speculated that pulp mills or other forest product industry operations are likely sources of anthropogenic chlorobornanes. At Dioxin '97, Rappe et al. (2) reported on the analyses of sediment samples collected outside a Swedish pulp mill on the shore of the Baltic Sea. Unlike the trend observed for pulp mill related compounds (PCDDs, PCDFs, R-PCDFs and AOX) -- decreasing as a function of distance from the mill --, no similar trend was observed for chlorobornanes in these sediments, thereby refuting the notion that pulp mills are a source of chlorobornanes. This present study sought to determine the recent role, if any, of pulp mills on the presence of chlorobornanes in sediments.

Materials and Methods

We collected and analyzed nine sediment samples. Seven of these samples, including one duplicate, were from the Wisconsin River, WI, USA, and two were from Beaver Dam Creek, Ontario, Canada. The samples were collected upstream and downstream of four pulp mills, three on the Wisconsin River and one on Beaver Dam Creek. Two of the mills on the Wisconsin River (Port Edwards and Nekoosa) are operated by the same company and share a single common discharge into the river. At least three of the mills are bleached kraft mills. The nine sediment samples were collected using a petite ponar dredge sampler from the upper portion (0-5 cm) of the sediment column. The samples were acidified with sulfuric acid after removing leaves, twigs, gravel and other debris. The samples then were shipped on ice to the analytical laboratory in Umeå, Sweden. A 10-g aliquot of each sample was used for analysis. Determination of loss of ignition (LOI), extraction, clean-up, and instrumental analysis using on-column injection by HRGC-ECNI-MS are described elsewhere (3-6).

Results and Discussion

The concentrations for the hexa- through decachlorobornanes in the sediments are given in Table 1. Samples WR-1 and WR-2 were taken below the Port Edwards/Nekoosa mills' combined discharge. Samples WR-3 and WR-4 were taken above the Port Edwards/Nekoosa mills' discharge and below another pulp mill. Samples WR-5 and WR-6 (and the duplicate) were taken above the upstream mill. Samples BDC-1 and BDC-2 were taken above and below the Beaver Dam Creek pulp mill, respectively. Only heptachlorobornanes were detected in some of the samples; and those were at very low concentrations (0.02 - 0.03 ng/g d.m.). All other chlorobornanes were below the detection limit (0.02 - 0.1 ng/g d.m.).

Figure 1 shows the ECNI SIM chromatograms (m/z 343) for the heptachlorobornanes from three Wisconsin River sediment samples. The first eluting peak shown in two of these chromatograms is HpSed (7). In the sample taken above all three mills (WR-6), the HpSed concentration was 0.03 ng/g d.m.; in the sample taken below the upper most mill and above Port Edwards/Nekoosa (WR-4), the HpSed concentration was 0.02 ng/g d.m.; and HpSed was not detected in the sample collected below Port Edwards/Nekoosa (WR-1). The second eluting peak is inside the elution window for heptachlorobornanes, eluting a few seconds earlier than toxicant B. This peak was disregarded as a heptachlorobornane, due to the constantly lower values for the (F+2)/(F+4) isotopic ratio (0.65, instead of the theoretical value of 0.80).

In Beaver Dam Creek, no chlorobornanes were detected (see Table 1); but we found a much higher concentration of the same unknown compound that was found and disregarded as a heptachlorobornane in the Wisconsin River samples. Figure 2 shows partial ECNI mass spectra of this compound in the samples from above (BDC-1) and below (BDC-2) the Beaver Dam Creek mill's discharge. The mass spectra exhibit a pentachloro isotopic cluster, which shows that the unknown compound cannot be a heptachlorobornane. Because this unknown compound was observed above and below the mill, and at the same concentrations based on LOI, it is unrelated to the mill's operations.

In the two samples from Beaver Dam Creek, complex envelopes suggesting a multitude of closely eluting compounds was observed in the SIM chromatograms, especially in those for the octa- through decachlorobornanes. The mass spectra of these compounds show a great similarity with what has been reported by Schmid and Müller for chlorinated paraffins (8).

The observed concentrations (0.02 - 0.03 ng/g d.m.) are in the same range or lower than the concentrations for chlorobornanes reported by Stern, et al. (9) for three Arctic lakes in Canada. These concentrations also are much lower than the values previously reported from our Baltic Sea study (2). No increase in the concentrations of chlorobornanes was found in sediments downstream of the four pulp mills. In fact, a decrease was observed in the only chlorobornane detected. No chlorobornanes except HpSed were detected in any samples from the Wisconsin River or Beaver Dam Creek. Finally, the HpSed was lower below the upper most pulp mill than above that mill, and was not quantifiable at all below the Port Edwards/Nekoosa mills, confirming our earlier Baltic Sea study and refuting the hypothesis that pulp mills are currently a source of chlorobornanes.

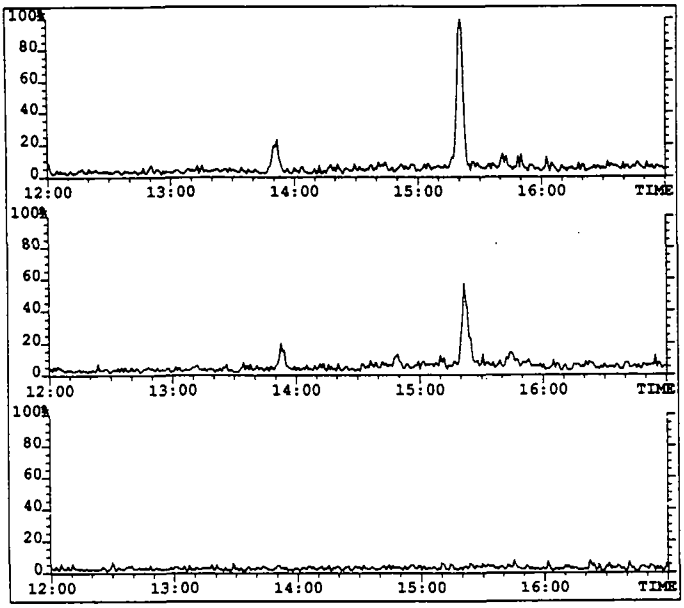

Figure 1. ECNI SIM chromatograms (m/z 307) showing presence of HpSed (ret. time 13.3 min) and an unknown compound (ret. time 15.4 min) for samples WR-6 (above the upstream mill), WR-4 (below the upstream mill and above Port Edwards/Nekoosa), and WR-1 (below Port Edwards/Nekoosa).

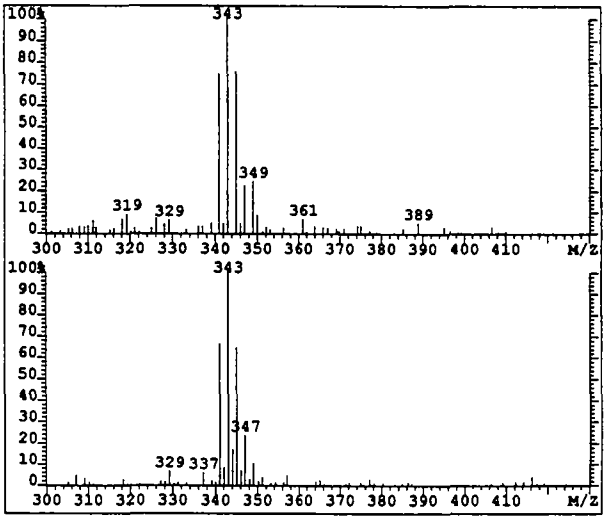

Figure 2. Partial ECNI mass spectra (m/z 300-430) of the unknown compound observed in sample BDC-1 (top) and BDC-2 (bottom).

Table 1: Summary of chlorobornane concentrations (ng/g dry matter), loss of ignition and recovery data for Wisconsin River and Beaver Dam Creek sediments

Sample Code	Location	hexa	hepta	octa	nona	deca	LOI %	REC %
WR-1	Below Port Edwards/Nekoosa	nd	nd	nd	nd	nd	0.53	52
WR-2	Below Port Edwards/Nekoosa	nd	nd	nd	nd	nd	0.58	49
WR-3	Between Upstream Mill and PE/N	nd	nd	nd	nd	nd	0.40	53
WR-4	Between Upstream Mill and PE/N	nd	0.02	nd	nd	nd	1.54	70
WR-5	Above Upstream Mill	nd	nd	nd	nd	nd	0.47	48
WR-6	Above Upstream Mill	nd	0.03	nd	nd	nd	2.76	56
WR-6 DUP	Above Upstream Mill	nd	0.03	nd	nd	nd	3.03	39
BDC-1	Above Beaver Dam Creek Mill	nd	nd	nd	nd	nd	2.96	63
BDC-2	Below Beaver Dam Creek Mill	nd	nd	nd	nd	nd	18.6	37

REC= Recovery. DUP= Duplicate. PE/N= Port Edwards/Nekoosa. nd= not detected at the limit of detection (0.02-0.1, 0.02-0.05, 0.02, 0.02, 0.02-0.1 for the hexa-, hepta-, octa-, nona- and decachlorobornanes, respectively).

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