Search for Chlorobornanes in Influents and Effluents from Pulp and Paper and Related Industry Facilities

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, thereby refuting the notion that pulp mills are a source of chlorobornanes.

In two other studies presented at this conference (3, 4), we analyzed chlorobornanes in sediments from the Wisconsin River, Wisconsin, USA, and Beaver Dam Creek, Ontario, Canada, in order to evaluate recent and historic levels of these compounds. In this study, we sampled and analyzed influents and effluents from eight different forest industry related facilities, including three bleached kraft pulp mills, in order to determine whether these operations are a source of chlorobornanes and other toxaphene-related compounds.

Materials and Methods

We sampled influent and effluent from eight forest industry related facilities in the midwest United States and Canada. See Table 1. Influent and effluent samples were taken from two pulp mills in Wisconsin (Port Edwards and Nekoosa) and one in Thorold, Canada. The Port Edwards and Nekoosa pulp mills are operated by the same company and utilize common input and have a single common discharge system. As a result, one influent sample and one effluent sample were collected and are representative of both mills (Port Edwards/Nekoosa). Influent

and effluent samples also were taken from (i) two hardboard manufacturing facilities (Bemidji, MN and Phillips, WI); (ii) a tissue facility (Gary, IN); (iii) a containerboard plant (Sheboygan, WI); (iv) a packaging plant (Circleville, OH); and, (v) a chemical plant (Columbus, OH).

All influent samples were collected by grab sampling. All effluent sampling was done on a time averaged (18-24 h) basis using an ISCO autosampler taking approximately 150 ml every 30 minutes. Composite samples were acidified immediately and shipped on ice to the analytical laboratory in Umeå, Sweden. The procedures for extraction, clean-up, and instrumental analysis using on-column injection by HRGC-ECNI-MS are described elsewhere (5-7).

Results and Discussion

Table 1 shows the analytical results for all influent and effluent samples for the hexa-, hepta-, octa-, nona- and decachlorobornanes. None of the samples contained detectable levels of these compounds with detection limits of 0.2 - 1.4 ng/L. Figure 1 shows ECNI SIM chromatograms of a representative sample. The absence of peaks in the chlorobornane SIM chromatogram (upper panel) verifies the effectiveness of the clean up procedures. The chromatogram in the lower panel shows the elution of the internal and recovery standards ($^{13}C_6$-γ-HCH and $^{13}C_{12}$-PCB #180, respectively).

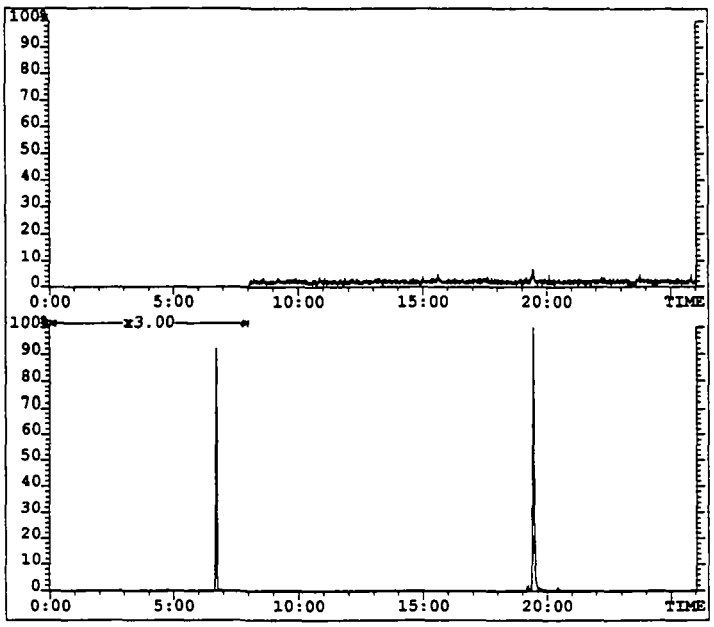

Figure 1. Combined ECNI SIM (m/z 307, 343, 377, 413, 445) chromatogram for chlorobornanes and related compounds (upper panel) and ECNI SIM (m/z 259, 406) chromatogram for the internal and recovery standards ($^{13}C_6$-K-HCH and $^{13}C_6$-PCB #180) (lower panel).

Table 1: Summary of chlorobornane concentrations (ng/L) and recovery (REC) data for influents and effluents from pulp and paper and related industry facilities

Facility Location	Facility Type	Sample Type	hexa	hepta	octa	nona	deca	REC %
Port Edwards/Nekoosa, WI, USA	Pulp Mill	Influent	nd*	nd	nd	nd	nd	54
		Effluent	nd	nd	nd	nd	nd	61
Thorold, Ontario, Canada	Pulp Mill	Influent	nd	nd	nd	nd	nd	80
		Effluent	nd	nd	nd	nd	nd	78
Phillips, WI; USA	Hardboard	Influent	nd	nd	nd	nd	nd	54
		Effluent	nd	nd	nd	nd	nd	155
Bemidji, MN, USA	Hardboard	Influent	nd	nd	nd	nd	nd	89
		Effluent	nd	nd	nd	nd	nd	36
Gary, IN, USA	Tissue	Influent	nd	nd	nd	nd	nd	59
		Effluent	nd	nd	nd	nd	nd	78
Sheboygan, WI, USA	Container board	Influent	nd	nd	nd	nd	nd	53
		Effluent	nd	nd	nd	nd	nd	55
Columbus, OH, USA	Chemical	Influent	nd	nd	nd	nd	nd	55
		Effluent	nd	nd	nd	nd	nd	48
Circleville, OH, USA	Packaging	Influent	nd	nd	nd	nd	nd	58
		Effluent	nd	nd	nd	nd	nd	27

* nd= not detected at the limit of detection (0.05-1.0, 0.2-0.6, 0.2-0.5, 0.2-0.5, 0.4-1.4 for the hexa-, hepta-, octa-, nona- and decachlorobornanes, respectively).

On the basis of this study, none of these forest product related facilities, including the three pulp mills, are a source of chlorobornanes.

Acknowledgment

This research project was sponsored by Georgia-Pacific Corporation, Atlanta, GA, USA.

References

1. Swackhamer D, Pearson R, Eisenreich S and Long D; *Organohalogen Compds.* **1995**, 26, 319
2. Rappe C, Haglund R, Buser H-R and Müller MD; *Organohalogen Compds.* **1997**, 31, 233.
3. Rappe C, Haglund P, Andersson R and Buser H-R; *Abstract submitted to DIOXIN '98.*
4. Rappe C, Haglund P, Andersson R and Buser H-R; *Abstract submitted to DIOXIN '98.*
5. Haglund P, Buser H-R, Andersson R, Wågman N and Rappe C; *Abstract submitted to DIOXIN '98.*
6. Buser H-R and Müller MD; *Environ. Sci. Technol.* **1994**, 28, 119.
7. Wågman N, Buser H-R, Haglund P and Rappe C; *Abstract submitted to DIOXIN '98.*