Search for Chlorobornanes in River Sediments: Part 2

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Introduction

The United States EPA, in collaboration with Indiana University, collected twenty sediment samples from the Wisconsin River in July, 1997. We obtained split samples of the sediments and report the results of our analyses of those samples for chlorobornanes in this paper.

Materials and Methods

Collection of all samples was conducted by representatives of Indiana University. We were provided splits of the samples. Seven were grab samples and 13 were composites of two to three individual cores. Two core samples were collected from a depth in excess of 10 cm. The remaining cores were collected from a depth of 0-10 cm. Two of the samples were collected from the same vicinity as two samples collected in our independent sediment study (1). The samples were acidified with H_2SO_4 and shipped to the analytical laboratory in Umeå, Sweden. Determination of loss of ignition (LOI), extraction, clean-up, and instrumental analysis using on-column injection by HRGC-ECNI-MS followed the procedures described elsewhere (2-5).

Results and Discussion

Table 1 lists the hexa- through decachlorobornane concentrations, the LOI and the recovery for 19 of the 20 split sediment samples. (One sample (#15) broke during transport and could not be replaced). We numbered these samples and provide the Global Positioning System (GPS) coordinates for each sample location as provided to us. In addition, we segregated and ordered the samples to correspond to the three pulp mills located on the Wisconsin River and described in our other studies presented at this conference (1, 6). Specifically, seven EPA samples were collected above an upstream pulp mill (Samples 1, 2, 3, 3D, 4, 5, and 6); six samples were collected below this upstream mill and above two mills operated by the same company and that share a single common discharge (Port Edwards/Nekoosa) (Samples 7-12); and seven samples were collected below Port Edwards/Nekoosa (Samples 13, 14, 15, 16, 17, 17D, and 18).

Table 1. Summary of sample locations, chlorobornane concentrations (ng/g dry matter), loss of ignition (LOI) and recovery (REC) data for EPA/Indiana University sediments

Sample #	GPS Coordinates		ng/g dry matter						
	North Latitude	West Longitude	hexa	hepta	octa	nona	deca	LOI %	REC %
Samples Above Upstream Mill									
1	44°27'12.81890"	89°41'15.49057"	nd¤	nd	nd	nd	nd	0.58	73
2	44°27'06.42430"	89°41'14.81407"	nd	nd	nd	nd	nd	0.34	79
3	44°27'09.42637"	89°41'49.54144"	nd	nd	nd	nd	nd	0.29	74
3D*	44°27'09.42637"	89°41'49.54144"	nd	nd	nd	nd	nd	0.27	47
4	44°26'59.27785"	89°42'20.04763"	nd	0.02	nd	nd	nd	1.00	65
5	44°26'55.40775"	89°43'04.48419"	nd	0.02	nd	nd	nd	3.00	88
6	44°26'44.20029"	89°43'26.00452"	nd	0.04	nd	nd	nd	3.92	49
Samples Below Upstream Mill and Above Port Edwards/Nekoosa									
7	44°23'04.45971"	89°50'09.85572"	0.15	0.10	0.04	nd	nd	8.60	58
8	44°23'03.92116"	89°50'09.20545"	nd	0.10	0.07	nd	nd	6.67	43
9	44°22'39.88093"	89°50'45.29601"	nd	nd	0.15	nd	nd	7.55	80
10	44°22'41.34882"	89°50'42.40994"	nd	nd	nd	nd	nd	2.49	58
11	44°22'27.07667"	89°51'01.11678"	nd	0.01	nd	nd	nd	1.54	79
12	44°22'27.16962"	89°51'04.93753"	0.08	0.20	0.36	nd	nd	11.8	87
Samples Below Port Edwards/Nekoosa									
13	44°18'24.11584"	89°53'51.43723"	nd	nd	nd	nd	nd	0.80	67
14	44°18'20.75683"	89°53'40.60521"	nd	nd	nd	nd	nd	0.69	67
15	44°18'12.29686"	89°53'36.44534"	-	-	-	-	-	-	-
16	44°18'05.63457"	89°53'33.26406"	nd	nd	nd	nd	nd	0.87	52
17	44°17'59.16219"	89°53'29.89591"	0.08	0.06	0.06	nd	nd	4.16	64
17D	44°17'59.16219"	89°53'29.89591"	0.33	0.30	0.41	nd	nd	9.86	85
18	44°17'47.97651"	89°53'31.31449"	nd	nd	nd	nd	nd	0.44	71

* D= deep sample (> 10 cm). ¤ nd= not detected at the limit of detection (0.02-0.07, 0.03, 0.02-0.04, 0.02-0.05, 0.03-0.07 for the hexa-, hepta-, octa-, nona-, and decachlorobornanes, respectively.

In the seven samples taken above the upstream mill, only heptachlorobornanes were detected at trace levels (0.02-0.04 ng/g) in three samples. In the six samples below the upstream mill and above the Port Edwards/Nekoosa mills, we detected hexa-, hepta- and/or octachlorobornanes in all but one sample at a total concentration of up to 0.64 ng/g. In the seven samples taken below the Port Edwards/Nekoosa mills, we detected hexa-, hepta- and octachlorobornanes only in the surface and deep sediment samples from one particular location (see Samples 17 and 17D). In the deep sediment sample from this location, the concentrations for all those homologues are 4-7 times greater than for the surface sediment sample at this location (see, Figure 1), and the highest in the entire study (total concentration of ~ 1 ng/g). All other samples below Port Edwards/Nekoosa, including the three samples collected nearest the Port Edwards/Nekoosa mills, had no detectable chlorobornanes.

Among the congeners detected in the samples from this study were HxSed and HpSed. Further, a number of hepta- and octachlorobornanes, including a major unknown octachloro congener, were identified.

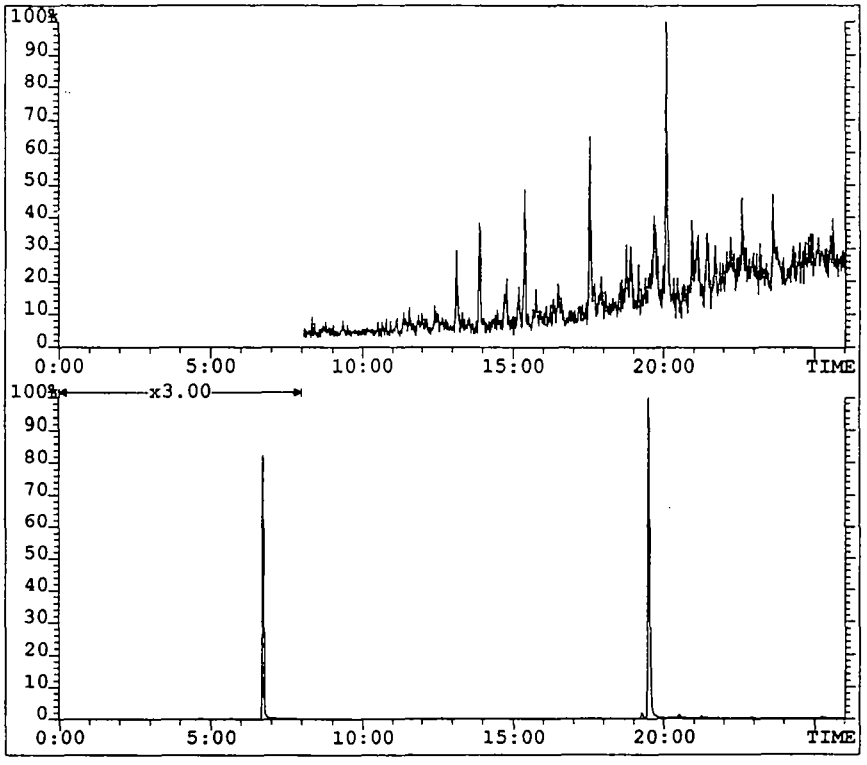

Figure 1. Combined ECNI SIM (m/z 307, 343, 377) chromatograms showing the elution of some hexa- through octachlorobornanes (upper panel) and ECNI SIM (m/z 259, 406) for the internal standards $^{13}C_6$-γ-HCH and $^{13}C_6$-PCB #180 (lower panel) in Sample 17.

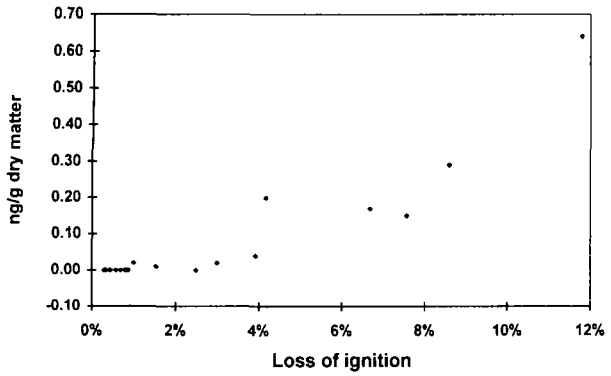

Figure 2. Total concentrations (ng/g d.m.) plotted versus LOI values (%) for the EPA surface sediment samples from the Wisconsin River.

Two samples in this study (Samples 6 and 12, Table 1) were collected in the same vicinity as two samples collected in our independent study (Samples WR-6 and WR-4, respectively; see Ref. 1). The results for Sample 6 in this study and for WR-6 in our other study closely agree. Specifically, both contain only heptachlorobornanes at low levels (0.04 and 0.03 ng/g, respectively). However, Sample 12 from this study and WR-4 from our other study appear to differ significantly. Specifically, Sample 12 from this study contains detectable, but low, concentrations of hexa-, hepta- and octachlorobornanes at a total level of 0.64 ng/g, while the corresponding Sample WR-4 from our other study contains only heptachlorobornanes at ca. 10% of the level found in this study. The apparent difference in concentration between these samples parallels the difference in LOI for these samples (11.8% in this study versus 1.54% in our other study). Generally, the samples with detectable chlorobornanes had higher LOI values than those samples with no detectable chlorobornanes (see Figure 2). Therefore, the concentrations of chlorobornanes seem to parallel the organic content of the sediments. This is most likely due to a preferred association of chlorobornanes to organic matter.

Acknowledgment

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