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Comparison of Point and Nonpoint Sources of Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans to Sediments of the Housatonic River

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Sediment samples were collected from the Housatonic River, a river known to be contaminated with polychlorinated biphenyls from a point source. Samples were analyzed via high-resolution gas chromatography/high-resolution mass spectrometry. These samples are shown to contain polychlorinated dibenzo-*p*-dioxins and dibenzofurans from both point and nonpoint sources. Analysis of concentrations, homolog profiles, and use of principal component analysis allow the point source input of PCDD/F to be differentiated from nonpoint atmospheric input.

Introduction

There is ample evidence that polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are ubiquitous in the environment. These compounds are classified as congeners, isomers, and homologs. Congeners have the same structural backbone (i.e., dioxin or furan) but differ in the number and/or position of chlorination sites; isomers have the same backbone and number of chlorines, differing only in the position of the chlorines. A homolog (or congener class) represents all the isomers at a single level of chlorination.

PCDD and PCDF have been found in the sediment of many lakes including a remote isolated lake (*1, 2*), the ambient atmosphere (*3, 4*), fish (*5, 6*), Arctic seals (*7*), and human adipose tissue (*8, 9*). Various combustion processes represent major sources of these compounds to the environment. Processes such as municipal waste incineration produce a varying mix of the different PCDD/F congeners which are emitted to the atmosphere along with the combustion effluent (*2*). PCDD/F are transported throughout the environment by the atmosphere, with both dry and wet depositional processes transferring them into the aquatic environment. It has been shown that although combustion produces a wide range of concentrations and congeners, by the time combustion-produced PCDD/F reach sediment, transformations have taken place that produce a very distinctive homolog profile (*4*).

A second source of PCDD/F to the environment is the production of these compounds as unintentional byproducts of chemical manufacturing processes. The PCDD/F are subsequently distributed to the environment with the product or its waste stream. Examples of this class include PCDD/F contamination associated with polychlorinated biphenyl (PCB) production (*10, 11*), paper pulp bleaching (*12*), or pentachlorophenol production (*13*). These sources will often produce a specific mix of congeners rather than the wide variety of congeners produced during combustion.

To monitor the behavior of PCDD/F in the environment, it is important to follow them from their sources to their sinks. However, multiple sources are more difficult to follow. Either a specific congener unique to one of the sources must be monitored or a statistical procedure which can compare patterns of isomers must be used. These patterns (homolog or congener profiles) represent the proportional amount of the various homologs or congeners produced by different sources.

The Housatonic River provides a unique opportunity to demonstrate the power of principal component analysis in sorting out the relative importance of point and nonpoint sources to a single system. The Housatonic River flows south for approximately 150 river miles through a series of impoundments in Western Massachusetts and Western Connecticut into Long Island Sound, draining a total of about 2000 square miles (Figure 1). This puts much of the river's watershed downwind of the industrial New York metropolitan area. Therefore, it would be expected that atmospheric transport and deposition of combustion-generated PCDD/F would show up in the sediment of this river. Previous work has shown that much of the river is contaminated with PCB from a point source at concentrations up to 60 ppm (*14*). Given that PCDF are common contaminants in PCB, it is likely that PCDF from the PCB point source would be present in the river's sediment. There are also several paper mills that discharge into the river, providing a potential PCDD input. Thus, sediments from this river offer a unique opportunity to use statistical analyses to compare the environmental importance of PCDD and PCDF from these potential point sources with the nonpoint atmospheric input. Comparison of the concentrations, homolog profiles, and congener profiles of PCDD/F in sediments taken from the Housatonic River with sediments taken from other lakes near the Housatonic but not contaminated from the point source(s) enable us to determine the relative importance of point and nonpoint PCDD/F sources. In addition, this is the first report on the extent of the PCDD/F contamination of the Housatonic River.

Experimental Section

Materials. All solvents used were pesticide grade or better from J. T. Baker (Philipsburg, NJ). Tridecane was obtained from the Aldrich Chemical Co. (Milwaukee, WI). Silica gel, neutral alumina, and Celite 545 were from Fisher Chemical (Pittsburgh, PA) and super-A activated carbon was purchased from the Anderson Development Co. (Adrian, MI). White quartz sand was from Sigma (St. Louis, MO). All 2,3,7,8-substituted PCDD/F were obtained from Cambridge Isotope Laboratories (Woburn, MA) except for the octachlorodioxin and octachlorofuran standards, which were obtained from Accustandard (New Haven, CT). Nine ^{13}C-labeled 2,3,7,8-substituted PCDD/F were also purchased from Cambridge Isotope Laboratories with two additional ^{13}C standards from U.S. EPA Chemicals Repository (Research Triangle Park, NC).

Sampling. Sediment samples were collected from Housatonic River depositional zones created by dams.

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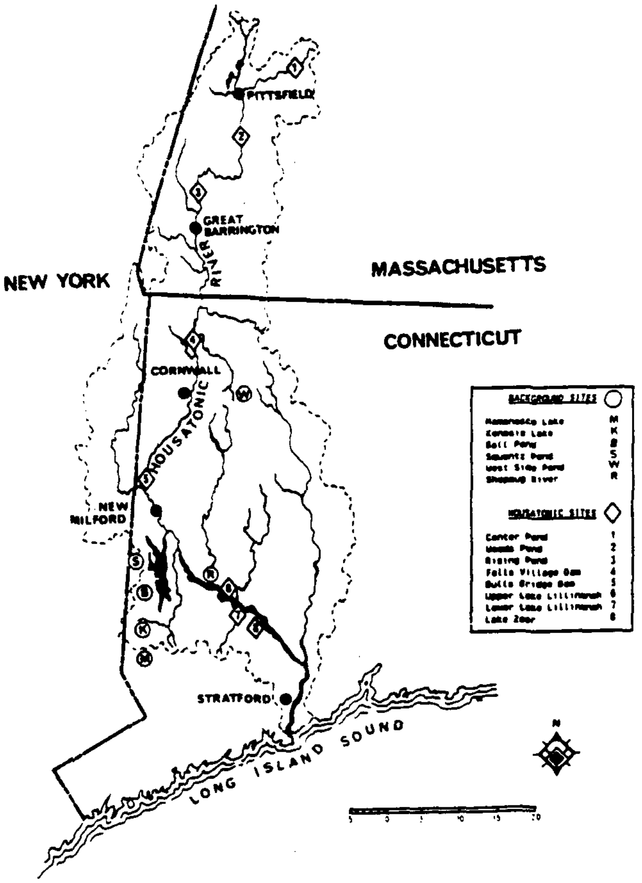

Figure 1. Map of the Housatonic River Watershed showing sampling locations.

Table I. Sample Location Information

location	site code	no. of samples	% organic
Background Sites			
Mamanasco Lake	M	2	32
Kenosia Lake	K	2	19
Ball Pond	B	2	29
Squantz Pond	S	2	11
West Side Pond	W	2	29
Shepaug River	R	1	5
Housatonic Sites (Downstream Order)			
Center Pond	1	3	8
Woods Pond	2	3	17
Rising Pond	3	3	3
Falls Village Dam	4	2	3
Bulls Bridge Dam	5	2	5
Upper Lake Lillinonah	6	1	5
Lower Lake Lillinonah	7	3	14
Lake Zoar	8	2	14

These zones included the areas which showed high PCB concentrations in the report by Frink *et al.* (*14*). Additional sediment samples were collected from lakes near the Housatonic River to serve as atmospheric background comparisons. Most locations were sampled in duplicate; some were sampled in triplicate. Sample locations along with site codes are listed in Table I. Sediment samples were taken with an Eckman dredge, which was rinsed with acetone between samples. The collected sediments were stored in clean glass jars and frozen until analyzed.

Analysis. The extraction and mass spectrometric analytical procedures have been reported in detail elsewhere (*15, 16*) and are described briefly below. The frozen sediment was thawed, 10 g of sediment was mixed with 50 g of sand and layered on top of 5 g of silica gel in a cellulose

isotopically labeled PCDD/F standards and extracted using a Dean-Stark Soxhlet for 16 h with toluene. The extracts were acid/base-washed, reduced in volume, and passed through two stages of adsorption column chromatography: first, a neutral alumina column eluted with hexane, followed by 8% methylene chloride in hexane, before collecting a 60% methylene chloride in hexane fraction; then, an activated carbon dispersed on Celite-545 column, eluted with hexane, 1:1 methylene chloride: cyclohexane, and 75:20:5 methylene chloride:methanol: benzene before collecting a back-eluted toluene fraction. The purpose of these adsorption chromatography columns was to remove compounds which interfere in the high-resolution gas chromatography/high-resolution mass spectrometric (HRGC/HRMS) analysis. Ten microliters of two ^{13}C standards in tridecane was added to the final fraction as a recovery standard, and the extract was then concentrated to a final volume of 20 μL for analysis by HRGC/HRMS. The organic content of each sediment sample was determined on a separate portion. Each sample was dried to a constant weight, the samples were then heated in a muffle furnace to 550 °C, and the loss upon ignition was determined. This loss upon ignition was used as the percent organic content. Although this is not an ideal way to determine organic content, it does give an estimate that is useful for the discussion of the results.

The sample extracts were analyzed with a HRGC/HRMS system consisting of a Hewlett-Packard 5890 GC (HP; Avondale, PA) interfaced to a Kratos Concept 1S mass spectrometer (Kratos; Manchester, England). A 60 m × 0.32 mm J&W DB-5 capillary column with 0.25-μm film thickness (J&W; Folsom, CA) was used with a 2-μL splitless injection. The temperature program was as follows: 200 °C for 2 min, 5 °C/min to 220 °C and hold for 16 min, 5 °C/min to 235 °C and hold for 7 min, 5 °C/min to 330 °C and hold for 5 min. The MS was operated in the electron impact mode with 35 eV ionizing potential, 250 °C source temperature, and 8 KV accelerating voltage. PCDD/F with four or more chlorines were monitored with selected-ion monitoring. Four groups of eight ions each (two ions for each homolog, both native and ^{13}C) and one group of six ions (there was no [^{13}C]octachlorofuran) at a resolution of at least 10 000 were monitored. Chromatographic peaks were determined to be PCDD/F based on retention times (as compared to a sample containing all congeners) and the proper intensity ratio for the two ions monitored.

Quantification. Response factors for the native PCDD/F standards relative to the internal standards were determined in a series of calibration runs on the HRGC/HRMS. Measured response factors within a homolog were averaged to develop a response factor to be used on all the isomers of a given homolog. Homolog abbreviations are as follow: D4, D5, D6, D7, and D8 for tetrachloro-, pentachloro-, hexachloro-, heptachloro-, and octachlorodioxins, respectively; F4, F5, F6, F7, and F8 for the tetrachloro-, pentachloro-, hexachloro-, heptachloro-, and octachlorofurans. The instrumental conditions do not yield complete isomer specificity, due to coeluting isomers. Therefore, the congener-specific data is retention time based on peak number within a homolog without reference to the specific isomers contained within that peak. There were 14 D4 peaks, 12 D5 peaks, 7 D6 peaks, 2 D7 peaks, 1 D8 peak, 17 F4 peaks, 14 F5 peaks, 14 F6 peaks, 4 F7

Table II. Variability Data Demonstrated with Lake Lillinonah Samples[a]

(A) Variability of GC/MS Peaks within the D6 Homolog[b]

GC/MS peak	A (1st)	A (2nd)	B	C
D6-1	42	41	43	30
D6-2	18	21	15	13
D6-3	68	74	66	50
D6-4	4.7	n.d.	0.9	0.9
D6-5	6.6	5.8	4.5	4.5
D6-6	20	22	16	14
D6-7	14	20	15	12

(B) Variability of the Different Homologs[c]

homolog	A (1st)	A (2nd)	B	C
D4	41	36	34	32
D5	44	34	34	36
D6	170	180	160	120
D7	580	620	610	480
D8	2500	2900	2700	2300
F4	940	1100	750	820
F5	440	640	510	570
F6	290	290	280	220
F7	270	300	280	220
F8	100	130	150	110

[a] Sample A was analyzed in duplicate. [b] Concentration of peak in pptr. [c] Concentration of homolog in pptr.

peaks, and 1 F8 peak, for a total of 86 separately determined concentrations. These peak number-specific data are more useful for the pattern recognition used in the comparison of sources than in limiting the data analysis to the 2,3,7,8-substituted congeners. The method does yield exact data for the 2,3,7,8-substituted congeners, for regulatory concerns, all of which have ^{13}C standards.

The mass spectrometer consistently detected individual PCDD/F standards at concentrations of less than 50 fg injected. Combining this high sensitivity with the large concentration factor, generated by reducing the extract to a final volume of 20 μL, allowed the detection limits for individual peaks to be below 0.1 pptr.

Quality Assurance

One method blank was analyzed with every three samples. D8 was a consistent contaminant in the method blank at a level which, on average, would correspond to a 25 pptr concentration in the samples. Other congeners were only occasionally present and at much lower concentrations when present. Method blank concentrations were not subtracted from sample concentrations in the data. The sampling locations at which multiple samples were collected showed individual congener concentrations to be within 50% of each other for most congeners at most locations. An example of this variability is shown in Table II with the data obtained from the Lake Lillinonah sampling site. There is good agreement both for the concentrations determined for individual GC/MS peaks and for the overall homolog concentrations. This amount of variability is an acceptable precision, given the low concentrations of PCDD/F measured in these samples.

Results and Discussion

Table III shows the average concentration of each homolog in the sediment samples taken from each site. Clearly the Woods Pond (site code 2) samples are different from all of the other samples in both pattern and total concentration. The PCB point source is between Center Pond and Woods Pond (site codes 1 and 2, respectively). It is most likely, therefore, that this point source is creating a major impact on the dioxin and furan concentrations in the Woods Pond sediment samples. It appears that there is some increase in concentrations further downstream as compared to the background levels, but whether this increase is the result of the point source remains to be determined. Examination of these downstream increases are discussed below.

First, consider the organic content of the sediments. It is possible that the small increases in concentration downstream are the result of a higher organic content in the sediment, which would better adsorb dioxins and furans. This factor is taken into account in Figures 2 and 3, which show the average homolog level at each site normalized to the organic content of the sediment at that site. Note that the background sites have consistently low levels of PCDD/F homologs except for the Shepaug River, site R, a Housatonic tributary which enters above site 6. There are dramatic concentration increases between sites 1 and 2 and decreases between sites 2 and 3 in the Housatonic sites. This shows the impact of the point source, which is located between sites 1 and 2, on the PCDD/F sediment concentrations. The dam which creates Woods Pond appears to restrict the movement of the contaminated sediment downstream, resulting in the decrease in PCDD/F concentrations between sites 2 and 3. That site 3 still appears to have somewhat elevated concentrations may indicate that some of the contaminated sediment has bypassed the dam and been transported downstream. Further downstream, the levels first fall and then start to rise again. Although the method of determining organic content is not ideal, it is unlikely that a better method would yield sufficiently different results to alter this interpretation of the data. A legitimate question is whether these increased levels at the downstream sites are also the result of the point source (with better sedimentation zones than sites 3–5) or are they from some other source? Alternate sources could include a focused nonpoint atmospheric input or other point sources (including those of downstream tributaries).

This question can be answered by examining the relationships between the various congeners/homologs. This can be done using homolog profiles, which shown the relative concentrations of each homolog in a given sample and by using principal component analysis to statistically compare all of the samples. Average homolog profiles for six of the sites are shown in Figure 4. These sites are categorized as background sites and Housatonic sites. It should be noted that Center Pond is listed with the background sites because, being upstream of the point source and close to the river source, it should reflect an atmospheric source.

The homolog profiles for the background sites are remarkably similar from sample to sample in that the octachlorodioxin (D8) concentration in each sample is much higher than any of the other homologs. This type of homolog profile is quite similar to those reported by Czuczwa *et al.* (*1, 2*) in Great Lakes sediment and is most likely the result of the atmospheric transformations discussed by Eitzer and Hites (*3, 4*) and Koester and Hites (*17, 18*). These workers discuss how atmospheric transformations tend to enrich the D8 homolog. The PCDD/F can exist in the atmosphere either in the vapor phase or bound to particles. The D8 homolog has the lowest vapor pressure of any PCDD/F (*19*), thus there is less partitioning into the vapor phase of the particulate bound material.

Table III. Average Homolog Concentrations at Each Sample Location (in pg/g

code	D4	D5	D6	D7	D8	F4	F5	F6	F7	F8	total
M	1.9	2.1	9.6	39	670	11	6.6	8.2	13	10	770
K	1.3	1.2	7.3	30	340	11	9.7	15	11	9.0	430
B	20	3.3	32	81	650	19	15	19	23	19	880
S	1.3	1.8	12	46	650	31	6.7	11	13	8.9	780
W	8.7	37	38	63	220	60	44	41	37	26	570
R	12	4.5	44	89	380	240	93	36	31	19	950
1	1.3	1.6	5.2	20	86	11	10	6.7	8.6	7.4	160
2	320	460	1 240	4 720	20 800	27 600	13 900	7 540	3 830	1 540	82 000
3	15	9.5	53	180	890	600	290	350	140	69	2 600
4	5.5	3.5	14	46	190	120	84	34	30	14	530
5	5.4	5.8	20	58	240	170	140	45	39	16	740
6	11	7.7	35	100	450	290	110	43	39	19	1 100
7	35	36	160	560	2 550	870	540	270	260	130	5 400
8	18	23	120	350	1 960	470	340	230	280	88	3 900

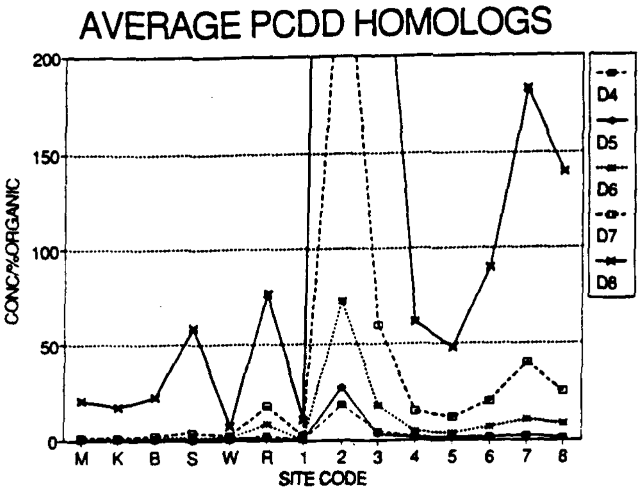

Figure 2. Average concentration of the PCDD homologs at each sample location normalized to the sediment samples organic content in percent.

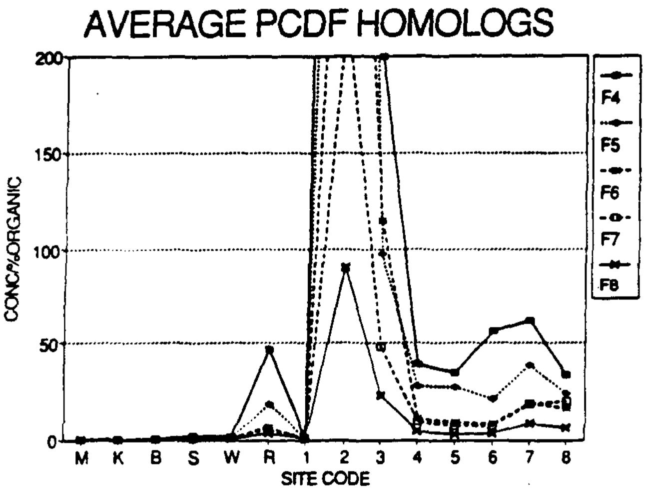

Figure 3. Average concentration of the PCDF homologs at each sample location normalized to the sediment samples organic content in percent.

Therefore, there is less potential for vapor-phase photodegradation. In contrast, particle-adsorbed PCDD/F are protected from photodegradation (*17*). The reduced vapor-phase partitioning of the D8 and the concomitant reduction in photodegradation causes this homolog to become enriched on the particle as compared to the other homologs. Finally, particle deposition dominates over vapor deposition (*5*, *17*), transferring the D8-enhanced particles to the sediment. The fact that the background sites here have profiles matching those seen by other workers indicates that the background sites are likely representative of the nonpoint atmospheric source.

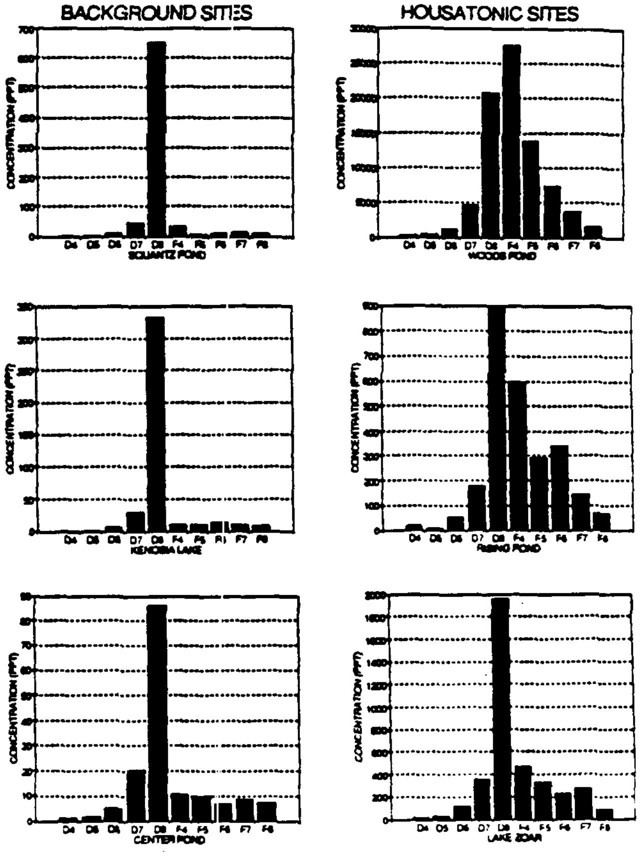

Figure 4. Average homolog profiles of sediments taken from six sample locations.

The Housatonic sites, however, show elevated levels of PCDF homologs, particularly the F4, F5, and F6 homologs. This is most pronounced in the Woods Pond samples in which F4 actually exceeds D8. Since PCDF are known contaminants of PCB (*10*, *11*), it is quite likely that the elevated PCDF originate from the PCB point source. The proportional increase in PCDF diminishes as samples are taken further downstream from Woods Pond, which indicates a reduced impact of the point source on the downstream sediments. This change in relative proportion of the various homologs (and congeners) can be examined further with principal component analysis.

The complete data set consisting of the 86 separately determined chromatographic peaks for each of the 30 samples was normalized to the total PCDD/F concentration. Normalization is necessary to examine how the

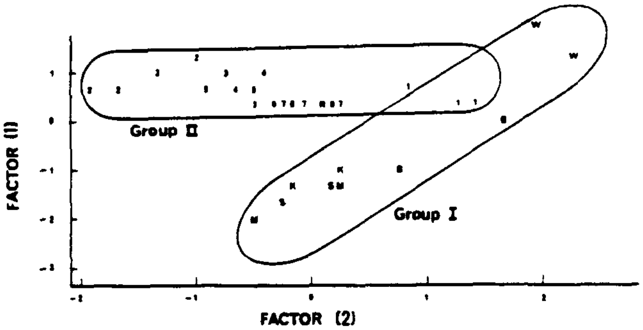

Figure 5. Plot of the first two principal components of the homolog data normalized to the total PCDD/F concentration.

relationships between the different variables change, otherwise the principal component analysis will be driven by the large total concentration differences. This normalized data set represents the fractional portion of the total PCDD/F concentration of each chromatographic peak in each sample. Next, a principal component analysis was performed on this normalized data set by the SYSTAT data analysis package (Systat Inc.; Evanston, IL). Figure 5 plots the first two principal components (factors) of this analysis with each sample's location on this plot indicated by its site code. These two principal components represent 45% of the total variance of the data set. Throughout the figure, multiple samples taken from the same site occur in the same region of the plot, thus indicating that the analytical variability in the data is not creating a problem with the principal component analysis.

Two trends are readily visible in the data. The first trend occurs for the background samples (letter codes) labeled Group I on the figure, which appear to lie on a line which runs from the lower left section of the plot to the upper right section, with the bulk of these samples clumped to the lower left. These background samples should be representative of atmospheric profiles. It is possible that the spread of samples along this line is indicative of the distance to major sources. The samples at the lower left of this group are closer to the New York City industrial area. Although Center Pond (code 1) is closer to the lower left samples than it is to the West Side Pond samples (code W), it is possible that this reflects its proximity to the industrial area of Pittsfield, MA. The West Side Pond samples would, therefore, be the furthest from any major atmospheric source.

The second trend, labeled Group II in the figure, is seen in the Housatonic sediment samples. Here the samples start within the atmospheric envelope at Center Pond and then shift to the upper left corner of the plot. This shift, between sites 1 and 2, would be indicative of the point source contamination. As the sediment samples are taken in a downstream progression (moving towards the higher numbers), the samples location on this principal component plot move toward the atmospheric envelope described previously. The sediment samples from these lower reaches of the Housatonic, therefore, have profiles which reflect a predominantly atmospheric input.

It is useful to simplify the data set for analysis by working strictly with the homolog data as discussed by Cash and Breen (*20*). The reduced number of variables allows easier examination of those variables (10 homolog variables rather than 86 individual peaks). The component loadings, which are the coefficients of each variable on the vector representing the given principal component, are also easily tabulated for examination. These loadings can range from +1 to −1, and comparison of the loadings within a principal component enables a determination of which variables have the greatest influence on a particular principal component.

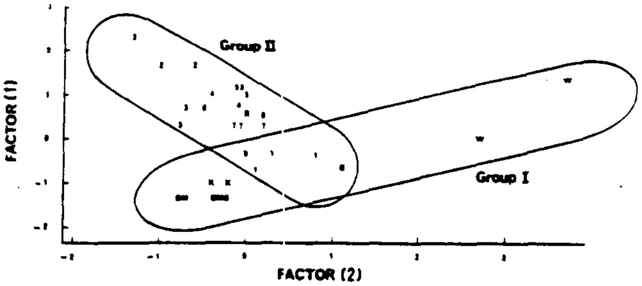

Figure 6. Plot of the first two principal components of the congener-specific data normalized to the total PCDD/F concentration.

Table IV. Component Loadings from Principal Components Analysis of Normalized Homolog Data

	component loading	
homolog	factor(1)	factor(2)
D4	0.332	0.385
D5	0.583	0.497
D5	0.590	0.652
D7	0.592	0.584
D8	−0.853	0.488
F4	0.511	−0.710
F5	0.492	−0.534
F6	0.644	−0.509
F7	0.856	−0.100
F8	0.749	0.411

In Figure 6 the first two principal components are shown for a principal component analysis performed on normalized homolog data (all isomers of a given homolog summed prior to normalization to the total concentration). In this analysis, these two principal components account for 78% of the total variance. The component loadings for these two factors are tabulated in Table IV. The same two trends are seen in Figure 6 as in Figure 5; one trend, again labeled Group I, appears to be of atmospheric origin, and one trend, labeled Group II, appears to be from the point source. Note that for factor(1), which accounts for 40% of the total variance, all the loadings are positive numbers except for D8, which is strongly negative. This indicates that this principal component is primarily based on the D8 homolog. As can be seen in Figure 6, this factor produces much of the sample spread on this plot for the first trend discussed, the atmospheric background group. The larger positive numbers occur for samples at West Side Pond and Center Pond, and more negative values of this component occur for the samples closer to the New York City area. This would, therefore, appear to indicate that the D8 proportion of the profile decreases with distance from the atmospheric sources (if the New York City area is the major atmospheric source to the Housatonic).

This can be visualized by comparing the Center Pond and Squantz Pond profiles in Figure 4. The sample with the larger positive value for factor(1) (Center Pond) has the D8 homolog representing a smaller fraction of the total. If New York City is the major atmospheric source, then samples further from the source have less D8 influence. Though West Side Pond is closer to New York than Center Pond, it has a more positive value for factor(1), but this anomaly could be because of the proximity of Center Pond to Pittsfield (a minor source as compared to New York

City), leaving West Side Pond as the sample furthest from atmospheric sources. This type of trend is the opposite of that reported by the previous workers as discussed above (*3*, *4*, *17*, *18*), which appeared to show an increase in D8 with distance from the atmospheric sources for air samples. Perhaps, this is a local-scale event (all sediment samples are within 100 miles of each other) while the earlier reports were of a larger scale. Alternatively, it is possible that weather patterns (which were not examined) would indicate that the air masses which pass over West Side Pond and Center Pond come from different areas than those which pass over the lower parts of the Housatonic River Watershed. A third possibility is that there is some alternative source (other than the atmosphere) to these samples which produces this trend.

A second pattern is observed in the loadings for factor-(2) which accounts for 26% of the total variance. In this factor, F4, F5, and F6 are strongly negative; F7 is slightly negative; and all other loadings are positive. Thus, these four furan homologs are important to this factor. In Figure 6, the second trend is almost a flat line along factor(2), with the numbers increasing in a left to right direction (downstream direction) except for the Center Pond samples (code 1). This factor, therefore, appears to be caused by the point source contamination in the same manner as previously discussed. The four furan homologs which are reponsible for this factor are most prevalent (have the largest negative numbers) in these point source-impacted samples. Recalling the PCB nature of the point source, and that PCDF are characteristic PCB contaminants (*10*, *11*), it again reinforces our conclusion that this point source contamination has a PCDF contamination associated with it. The plot shows the decrease in point source character of the PCDD/F with distance downstream, indicating that the transport of point source contaminated sediment is retarded by each of the Housatonic River's Dams.

Both of the principal component plots show the Shepaug River sample (site code R) being just outside of the atmospheric envelope. This is most likely the result of the sample being taken too close to the entry of this river into the Housatonic, in an area where there was mixing between the rivers, so that the profiles are essentially a mix of site code 6 and atmospheric input. This would explain the sample's position in the second trend, a position closer to the atmospheric envelope in character than samples taken further downstream from where the Shepaug enters the Housatonic. It is also possible that there is a small alternate source to this river slightly shifting its profile from the atmospheric background.

Neither of these principal component plots show the existence of a third trend. This reduces the likelihood that the downstream concentration increase discussed previously is the result of an additional point source because an additional point source (if one were present) should have unique pattern characteristics that would be observed in the principal component plots. It is, however, still possible that a point source could still be present with its impact obscured by the other sources.

Conclusions

This paper reports for the first time on PCDD/F contamination of the Housatonic River. The river sediment indicates that there are two major sources of PCDD/F to the Housatonic, a point source between Woods Pond and Center Pond and a nonpoint atmospheric input. This paper demonstrates the power of statistical analyses in sorting out the contributions of these two sources to the river; the point sources being the major PCDD/F contributor to the upper portion of the river, while the nonpoint sources are the major contributor to the lower sections. In additon, it is seen that the point source is primarily composed of furan homologs, while the atmospheric source is dominated by the D8 homolog. Application of the statistical techniques demonstrated here should prove useful in monitoring the environmental behavior of PCDD/F in other areas which have been impacted by multiple sources.

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