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Estimates of Lead, Cadmium, and PCB Loading to the Lower Fox River and Lower Green Bay

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Introduction

In 1987 the Green Bay portion of Lake Michigan was identified as the study area for a mass balance study. This study is evaluating the feasibility of using a mass balance concept as a management tool for the control of toxic substances in large complex ecosystems. In a mass balance, the quantities of contaminants entering the system, minus the quantities stored, transformed, or degraded within the system, must equal the quantity leaving the system. For this study, lead (Pb), cadmium (Cd), dieldrin, and polychlorinated biphenyl (PCB) were selected as representative toxic substances. Individual PCB congeners (compounds) were included since the physical, chemical, and biological properties of each of the 209 possible congeners are different.

Between fall 1988 and spring 1990, a comprehensive monitoring program determined the inputs, outputs, and quantities of the 4 pollutants in the Green Bay ecosystem. Some of these data were used in developing the Pb, Cd, and PCB loading estimates that are reported in this Findings article. These estimates are from the urban area that drains to the Lower Fox River and Green Bay below the DePere Dam. These loadings will be used as inputs to a physical/chemical transport model, which is one component of the mass balance study. This study will end in late 1992.

Study Area

The study area covered in this Findings article consisted of the total urban area that drains to the Lower Fox River and Green Bay below the DePere Dam (13,670 ha--10,902 ha to the Lower Fox River and 2,770 ha directly to Green Bay) (Fig. 1). The East River Priority Watershed Project comprises 11,716 ha of the study area (D'Antuono 1992). An additional 1,954 ha is within the watersheds of Ashwaubenon and Dutchman creeks.

Methods

Previous studies had determined relationships between Pb, Cd, and PCB loads in stormwater runoff and different urban land uses in the Milwaukee area. Because of the high costs of monitoring urban stormwater, these studies were used as the basis for evaluating the significance of the urban area associated with the Lower Fox River/Green Bay as a source of toxic substances to Green Bay. Dieldrin has not been detected in Fox River samples and has seldom been detected in other urban stormwater runoff studies. It was assumed that significant amounts of dieldrin would not be present in runoff from the Green Bay urban area; therefore, dieldrin loads were not determined.

A detailed land use inventory was conducted and annual Pb and Cd loads were calculated in the East River Priority Watershed Project by summing the loads from the appropriate storm sewer drainage areas. The same unit area loads were used to calculate total loads for the area in the watersheds of the Ashwaubenon and Dutchman Creeks.

To determine the significance of the urban area as a source of PCBs, loads were estimated in 2 steps. An initial screening was made using total PCB concentrations measured in stormwater collected in 1973 from 21 sites in the Milwaukee area (Bannerman et al. 1979). In this study, PCBs

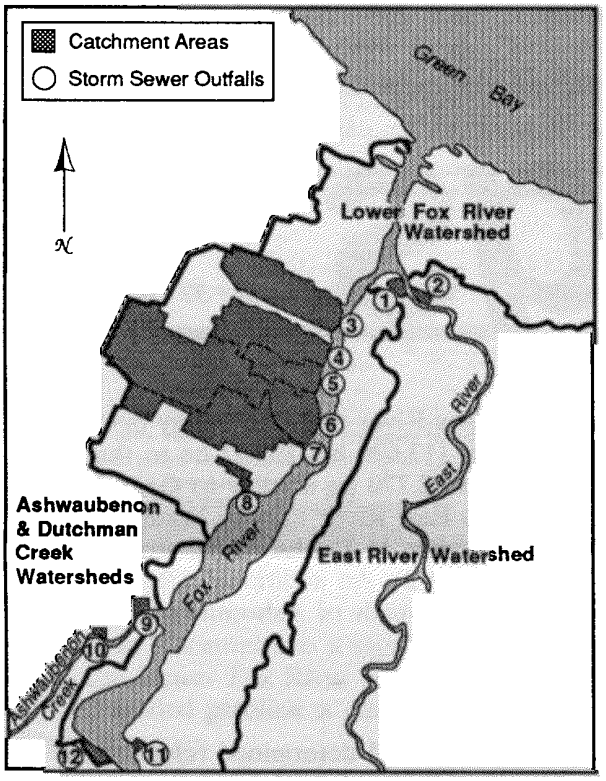

Figure 1. Location of urban subwatersheds, storm sewer drainage areas, and catch basins sampled for PCB residues.

were only detected in samples associated with industrial areas. The average and highest concentrations from these areas (2.0 μg/L and 7.9 μg/L, respectively) were used to calculate PCB loads for the Green Bay study area. Applying these values to estimates of the annual runoff from metropolitan Green Bay industrial areas resulted in annual total PCB loads of 12-47 kg. The high end of this range could account for 10% of the 540-1,200 kg annual load of PCBs at the mouth of the Fox River (Marti 1984); therefore, further evaluation of potential PCB loads was necessary.

The Green Bay metropolitan area was reviewed to identify industries typically associated with PCB usage. This review identified storm sewers where catch basin residues could be sampled (Fig. 1). Since the objective of this portion of the mass balance study was to determine the significance of urban stormwater runoff as a source of PCBs, the catch basin residues were only analyzed for total PCB (Aroclor 1242, 1254, or 1260). These analyses were conducted at the State Laboratory of Hygiene using packed column gas chromatography. PCB concentrations in the catch basin residues were used along with land use and sediment load estimates to calculate annual PCB loads for the study area.

Results and Discussion

The calculated Pb and Cd loads are summarized in Table 1. Since the primary urban source of Pb is automobile exhaust, the largest Pb loads are associated with freeways and other areas with heavy traffic. Freeways accounted for only 3% of the watershed land area; however, they produced 52% of the annual Pb load. Likewise, industrial storage yards and parking areas contributed 22% of the annual Pb load from 8% of the land area.

While there was no single predominate Cd source, the largest unit area loads were associated with industrial and commercial land use.

Residue samples were obtained in May 1989 from 10 of the 12 storm sewer catch basins (Table 2). Two sites contained no sediment. Industrial land use was present in all the sampled storm sewer drainage areas. However, because of the size of several of the drainage areas (Sites 3-7), a significant amount of residential land use was also present.

Assuming that PCB loads are a function of both sediment load and land use, these larger drainage areas should have accumulated PCBs in catch basin residues. Industrial land use has average unit area sediment loads about 3x those for residential land use (768 kg/ha and 233 kg/ha, respectively). Thus, even in the sample areas with large residential areas, industrial areas accounted for an average of 47% of the sediment, with only 24% of the land area (Table 2). Also, the industrial areas are generally located lower in the drainage areas, closer to the catch basins. The fact that PCBs were below the Level of Detection (LOD)

Table 1. Annual Pb and Cd loadings to the Lower Fox River and Green Bay.

	Low. Fox R.			Low East R.			Dir To Bay		
	Area	Pb	Cd	Area	Pb	Cd	Area	Pb	Cd
Land Use	ha	-----kg----		ha	-----kg----		ha	-----kg----	
Residential	1,440	71	3.1	1,926	79	4.2	650	27	1 2
Commercial	260	82	2.4	223	80	2.2	77	23	0 8
Industrial	776	325	4.3	162	79	1.2	118	50	0.7
Institutional	82	19	0.3	91	12	0.3	65	9	0.2
Park/Open	954	5	0.0	2,900	18	1 1	1,789	10	0.1
Freeway	237	586	1.4	125	310	0.7	71	176	0 4
Undefined	1,725	105	3.7	NA	NA	NA	NA	NA	NA
Total	5,474	1,193	15.2	5,427	578	9.7	2,770	295	3.4

in 5 of the catch basin residues indicates that the industries in these drainage areas were probably not PCB sources.

For the catch basin residue samples with PCBs below the Level of Detection, PCB loads were calculated using the <LOD results as both 0.0 μg/g and as equal to the LOD (either 0.15 μg/g or 0.05 μg/g). While this procedure is not statistically correct, it provides a range of values that can be used to evaluate the importance of urban areas as sources of PCBs. Using the LOD for values that were <LOD provides a "worst case" estimate. Using this approach, the average total PCB concentrations in the catch basin residues were 0.11 μg/g for <LOD = 0.0 μg/g and 0.145 μg/g for <LOD = LOD.

These catch basin residue concentrations were used to calculate the annual PCB loads from the study area. Two different procedures were used to extrapolate drainage areas represented by the catch basin residues to the entire study area. First, average unit area loads for the sampled area were determined. These unit area loads were then extrapolated to the study area. This extrapolation method resulted in annual PCB loads from the Fox River of 0.65-0.82 kg. If the direct drainage to Green Bay is included, annual urban PCB loads are 0.82-1.03 kg (Table 3). The results of the catch basin residue analyses including the determination of average unit area loads are summarized in Table 2.

The second procedure involved estimates of the sediment load from the study area. Since PCBs are associated with urban areas, only the sediment load originating from the urban portion of the study area was important. Sediment loads by land use type were available for the East River portion of the study area (D'Antuono 1992). Sediment loads for Ashwaubenon and Dutchman creeks were estimated using the same procedures used in the East River watershed. The total sediment load based on the urban watershed area that drains to the Lower Fox River below the DePere Dam (including the portion in the watersheds of Ashwaubenon and Dutchman creeks) was 2.0 x 10^6 kg/yr. Using this annual sediment load and the average PCB concentration in the catch basin residues gave an annual PCB load to the Fox River of 0.22-0.29 kg. Including the urban area that drains directly to Green Bay increased to 0.25-0.33 kg the annual PCB load from the entire study area.

Table 2. *Annual PCB loads and unit area loads from storm sewer drainage areas based on PCB concentrations in catch basin residues and estimated sediment loads. The PCB loads represent the total load from the storm sewer area, not broken down by land use.*

Site*	Total Area ha	Prin. Land Uses Type	%	Sediment Load %	Total kg	PCB** μg/g	kg	kg/ha
						---x10^{-3}---		
1	9.09	Inst	62	55	4,368	<0.15	0.66	0.072
		Comm	38	45				
2	9.61	Ind	88	95	7,554	0 39	2 95	0.306
3	118 85	Res	65	48	40,033	0.51	20 42	0.171
		Ind	16	36				
4	110.42	Res	58	35	32,489	<0.05	1.62	0 014
		Ind	19	47				
5	44.31	Res	47	37	21,022	<0 05	1 05	0.023
		Ind	37	58				
6	310.24	Res	73	57	72,939	<0.05	3.65	0.011
		Ind	11	37				
7	145 89	Ind	36	59	73,220	No Sediment		
		Res	25	9				
		Comm	20	31				
8	9.36	Ind	93	98	7,215	No Sediment		
9	11 05	Ind	NA	NA	7,296	0.06	0.44	0.039
10	10.57	Ind	NA	NA	6,979	<0.05	0.35	0 033
11	4 21	Ind	43	72	2,218	0.08	0.18	0.042
		Park	31	0				
		Comm	26	28				
12	7.56	Ind	69	99	5,049	0.06	0.30	0.040
Avg.		If <LOD = LOD					0.145	0.075
		If <LOD = 0.0 μg/g					0.11	0.060

* Site numbers correspond to numbers on Figure 1.
** If concentration <LOD, load is based on <LOD=LOD.

The results of these different approaches to calculate annual PCB loads to the Lower Fox River and Lower Green Bay are compared in Table 3. While the 2 procedures based on the catch basin samples differ by a factor of about 3, they are both 2 orders of magnitude lower than the loads estimated by extrapolating the 1973 Milwaukee area runoff concentration data.

In 1990 additional PCB stormwater runoff data from the Milwaukee area became available (Bannerman, pers. comm.). The median total PCB concentration for 50 samples was 0.02 μg/L. Using this value resulted in an annual PCB load of 0.12 kg, which compared favorably to the loads calculated using catch basin PCB concentrations.

Table 3. Comparison of annual PCB loads by different calculation methods.

Method & Area (ha)	Sediment kg x 10^6	PCB µg/g	PCB kg/ha x 10^{-3}	PCB kg
Catch Basin				
10,902 *	--	0.11-0.145	0.060-0.075	0.65-0.82
13,672 **	--	0.11-0.145	0.060-0.075	0.82-1.03
Priority Watershed				
10,902	2.00	0.11-0.145	--	0.22-0.29
13,672	2.31	0.11-0.145	--	0.25-0.33
Extrapolation		µg/L	kg/ha x 10^{-3}	kg
1,214 ***	--	2.0-7.9+	--	12-47
	--	0.02++	--	0.12

* Urban area below DePere dam tributary to Fox River
** Includes urban area tributary directly to Green Bay
*** Industrial Land Area Only
\+ Data from 1973 Milwaukee monitoring
++ Data from 1990 Milwaukee monitoring

Conclusions

- Urban stormwater is a significant source of Pb to the Lower Fox River and Lower Green Bay. As leaded gasoline is eliminated, Pb loads should decrease.
- Urban Cd loads do not appear to be significant.
- Urban stormwater runoff is presently not a significant source of PCBs to the Lower Fox River. These loads have probably decreased since the early 1970s.
- Given the agreement between the different load calculation methods, the results are more credible than indicated initially by the limited field data.

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