x star
6/7/05 John Bing sent
to CRL Lab Person
to look at

EPA mtg w/ PRB
Chicago Office
6/3/05

Sources of PCBs to the Kalamazoo River

June 3, 2005

Kalamazoo River Study Group

RRSG - agrees w/ ~~what~~ amt of PCB
Cause overclaw but
disagrees with what
happened after went over
dam. QEA ~~[illegible]~~ Report for Eaton
Samp PCBs varied downstream out to Lake Michigan

EPA Region 5 Records Ctr.
284900

Per Jeff - Tammy's thoughts on

- Was a source of 1254
- ~~It~~ can't all be explained by weathering
-

Agenda

- Overview of PCB Sources in the Watershed
- Evidence of PCB Discharges
  - PCB Chemistry 209;
  - Evidence of Aroclor 1254 discharges; and
  - Morrow Lake.
- So, where did the Aroclor 1254 come from?
- Conclusions

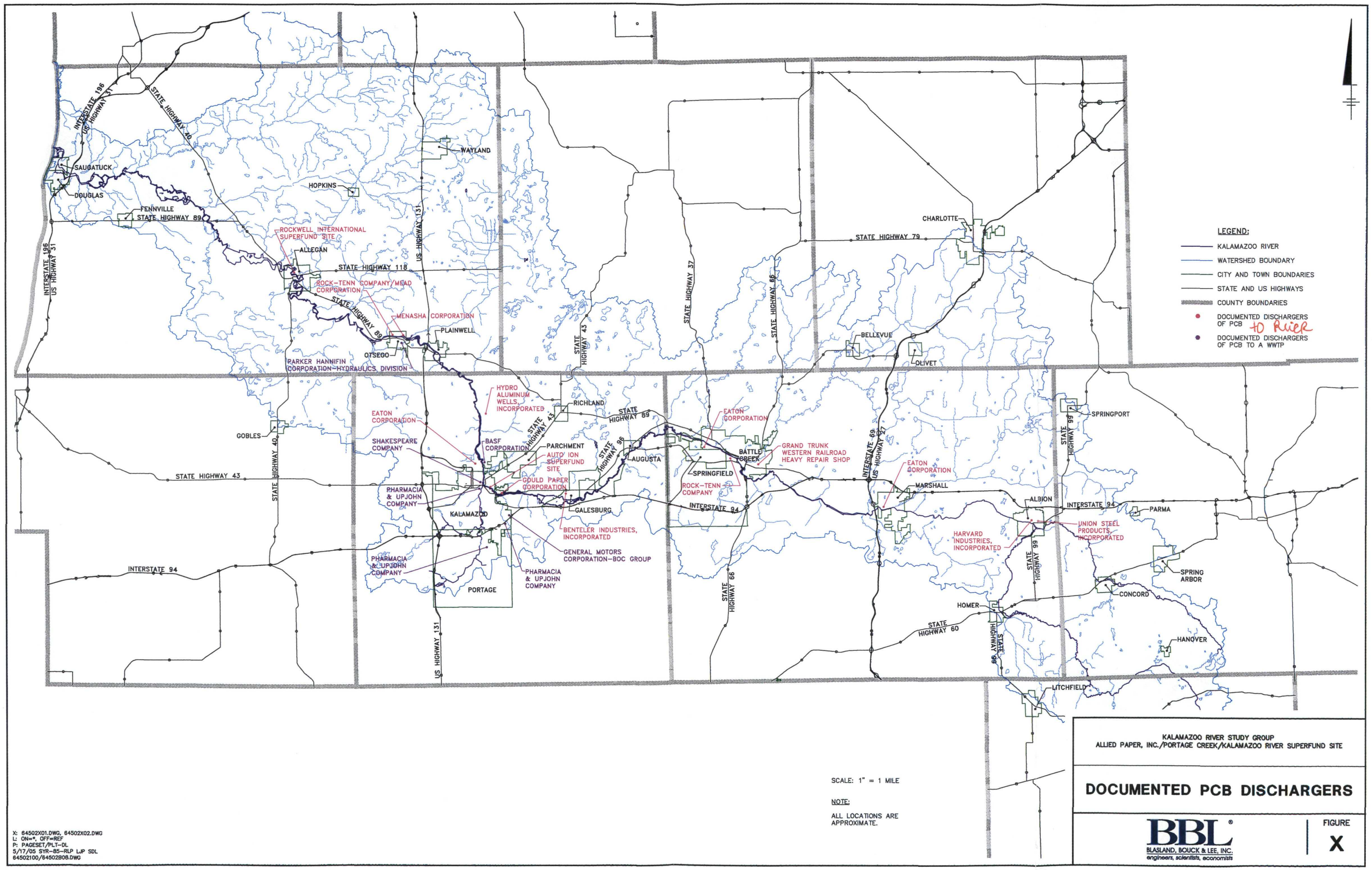
End-Uses of PCBs by Type

Reference: Durfee, et al., 1976.

End-Use	1016	1221	1232	1242	1248	1254	1260	1262	1268	PCTs
Existing Sales										
Capacitors	XX	X		XX through 1971		X				
Transformers				X		XX	X through 1971			
Sales Phased-Out										
Heat transfer				X						
Hydraulics/lubricants										
• hydraulic fluids			X	X	X	X	X			
• vacuum pumps					X	X				
• gas-transmission turbines		X		X						
Plasticizers										
• rubbers		X	X	XX	X	X			X	
• synthetic resins					X	X	X	X	X	XX
• carbonless paper				XX						
Miscellaneous Industrial										
• adhesives		X	X	XX	X	X				XX
• wax extenders				XX		X			X	XX
• dedusting agents						X	X			
• inks						X				XX
• cutting oils						X				
• pesticide extenders						X				
• sealants & caulking compounds										XX

Notes:
(1) X denotes use of a given Aroclor in a specific end-use, while XX denotes principal use.
(2) PCTs denote seres 25, 44, & 54 Aroclors.

Source: Monsanto Industrial Chemical Co.



KALAMAZOO RIVER STUDY GROUP
ALLIED PAPER, INC./PORTAGE CREEK/KALAMAZOO RIVER SUPERFUND SITE

DOCUMENTED PCB DISCHARGERS

BBL®
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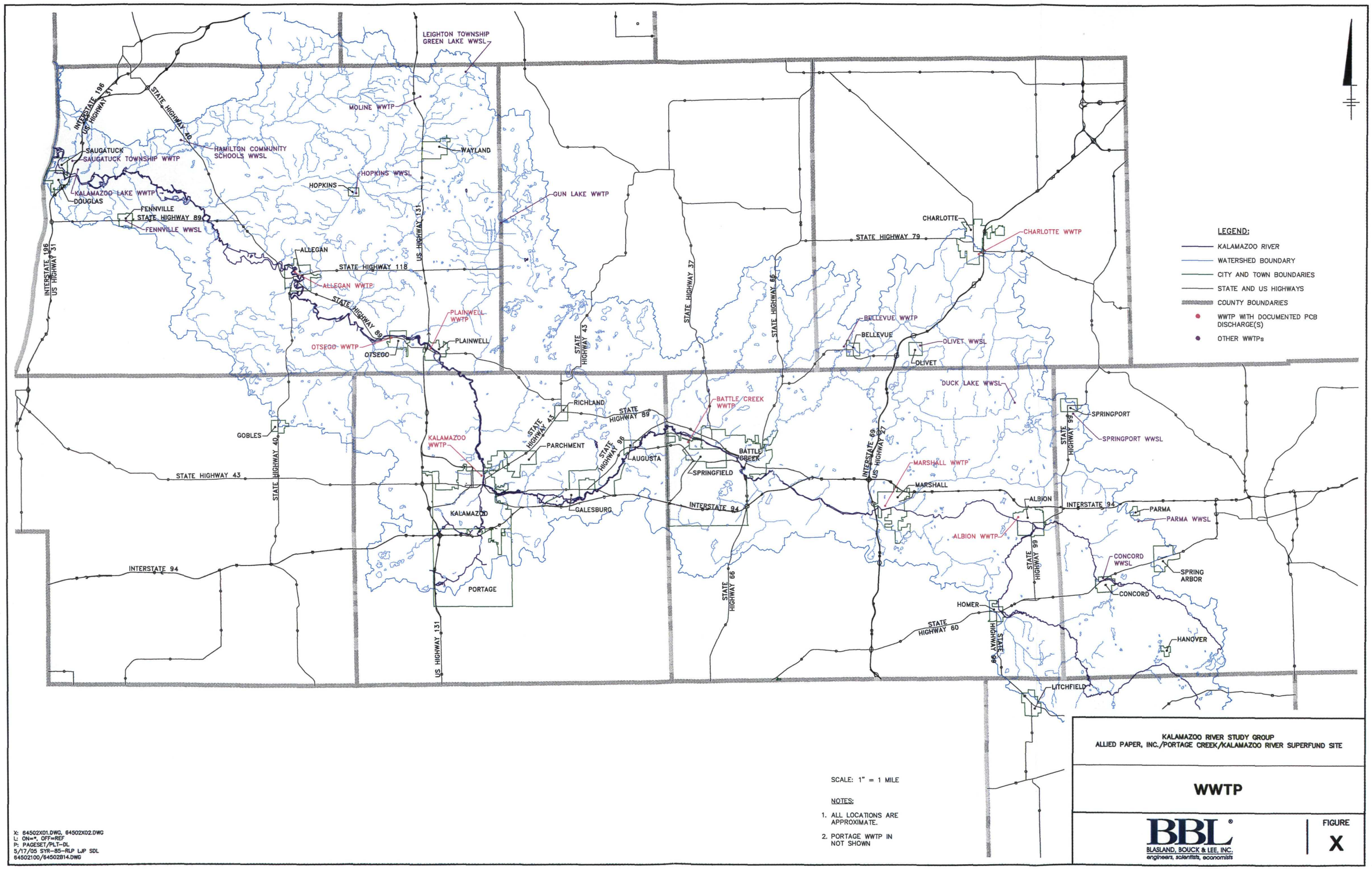
engineers, scientists, economists

FIGURE
X

X: 64502X01.DWG, 64502X02.DWG
L: ON=*, OFF=REF
P: PAGESET/PLT-DL
5/17/05 SYR-BS-RLP LJP SDL
64502100/64502B08.DWG



SCALE: 1" = 1 MILE

NOTES:

1. ALL LOCATIONS ARE APPROXIMATE.
2. PORTAGE WWTP IN NOT SHOWN

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WWTP

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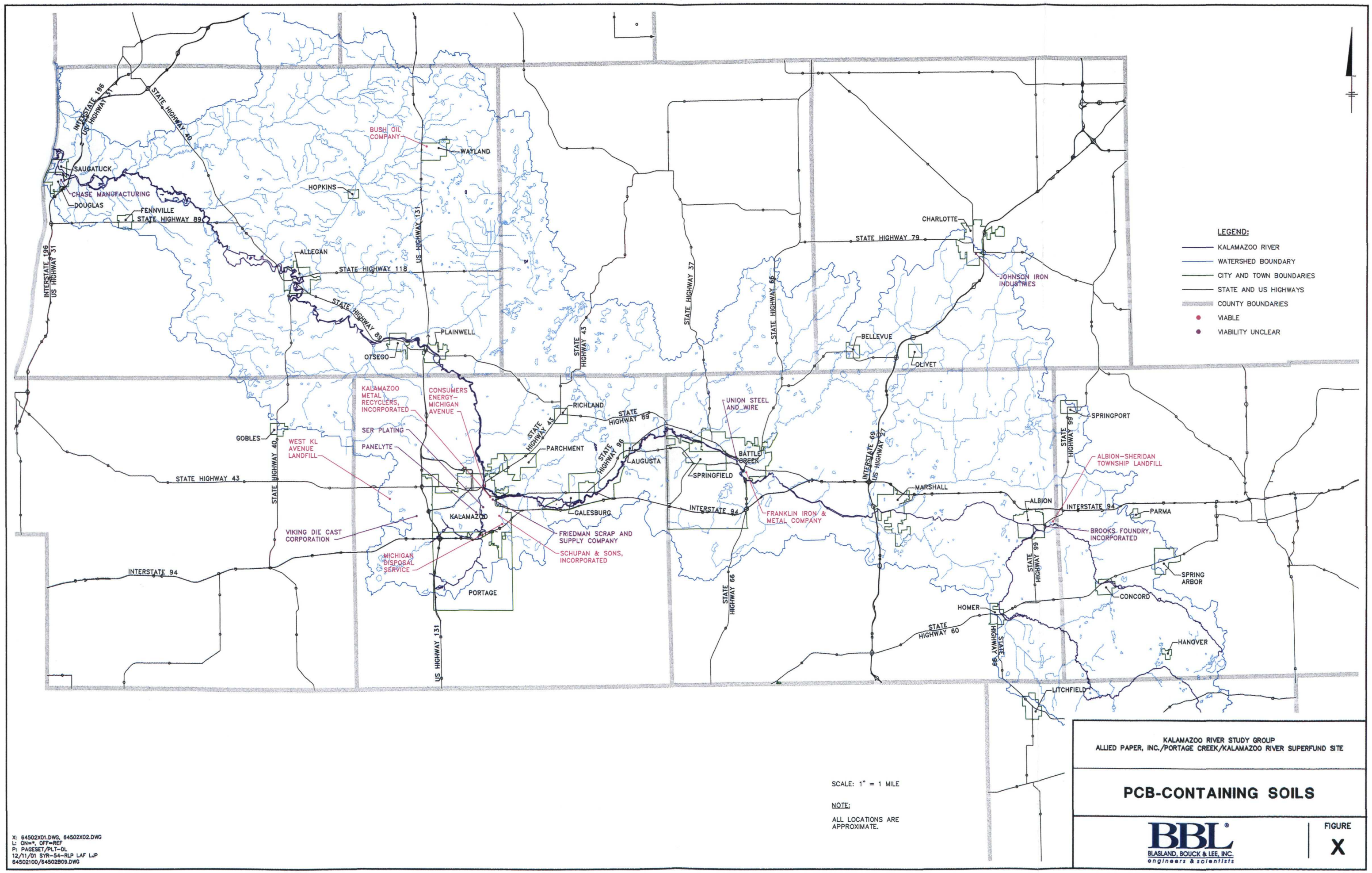
FIGURE
X

X: 64502X01.DWG, 64502X02.DWG
L: ON=*, OFF=REF
P: PAGESET/PLT-DL
5/17/05 SYR-85-RLP LJP SDL
64502100/64502B14.DWG

Detections of PCB at POTWs

- Battle Creek WWTP:
  - Effluent 0.16-0.39 ug/L; 1971-1972 samples
  - Sludge 2.8 mg/kg – dry weight; 1973
- Kalamazoo Water Reclamation Plant
  - Effluent 0.11 – 4.7 ug/L; 1990-1994
  - DSE – WAR Building Ash up to 12 mg/kg; 1990-1991
- Marshall WWTP
  - Effluent PCB detected in 1973 sample
- Plainwell WWTP:
  - Effluent 0.017 - 0.031 µg/L; 1985.
- Portage WWTP:
  - Effluent 1.9 µg/L; 1971



SCALE: 1" = 1 MILE

NOTE:

ALL LOCATIONS ARE APPROXIMATE.

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PCB-CONTAINING SOILS

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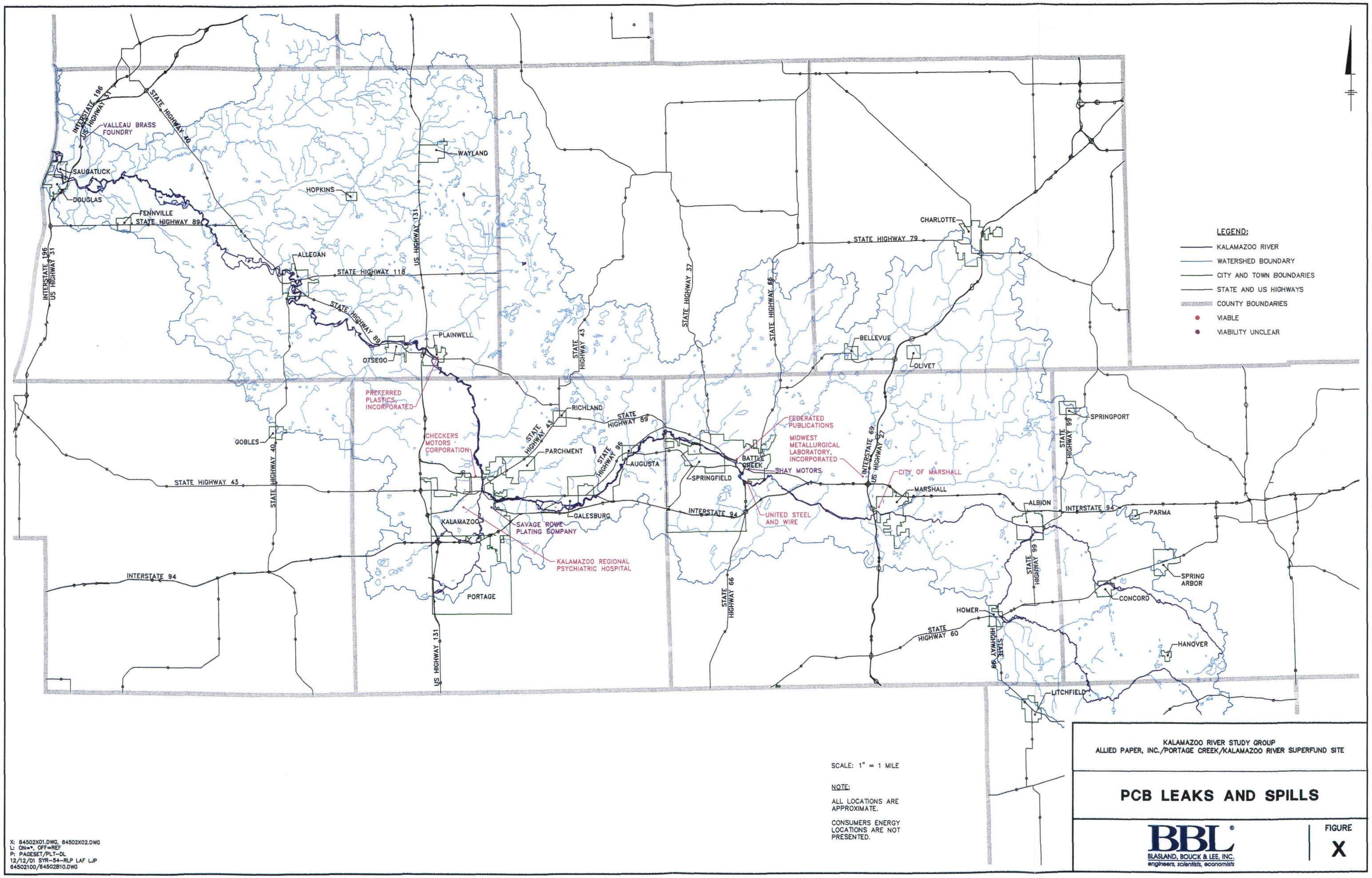
FIGURE
X

X: 64502X01.DWG, 64502X02.DWG
L: ON=*, OFF=REF
P: PAGESET/PLT-DL
12/11/01 SYR-54-RLP LAF LJP
64502100/64502B09.DWG



SCALE: 1" = 1 MILE

NOTE:

ALL LOCATIONS ARE APPROXIMATE.

CONSUMERS ENERGY LOCATIONS ARE NOT PRESENTED.

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PCB LEAKS AND SPILLS

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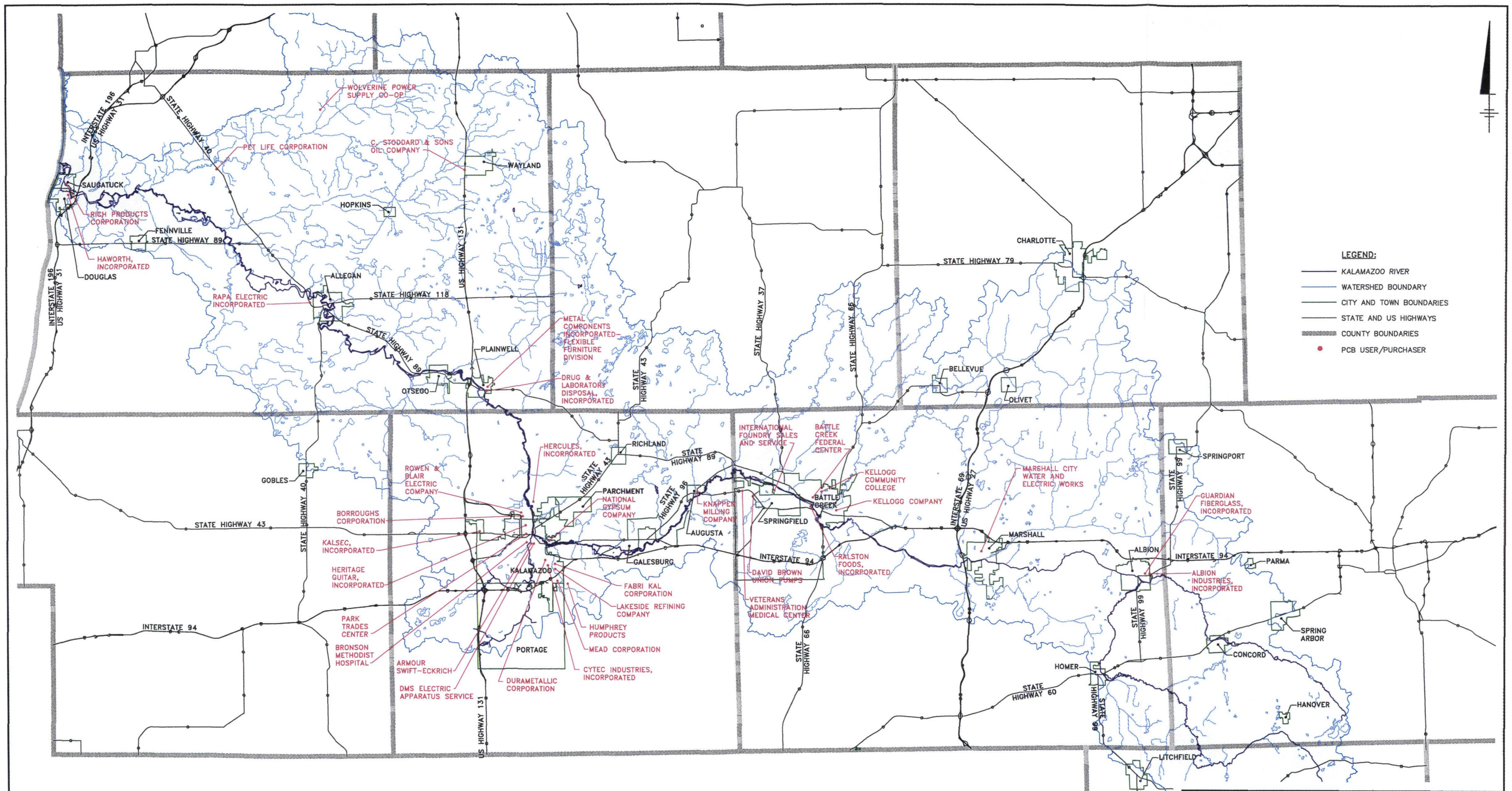
FIGURE
X

X: 64502X01.DWG, 64502X02.DWG
L: ON=*, OFF=REF
P: PAGESET/PLT-DL
12/12/01 SYR-54-RLP LAF LJP
64502100/64502B10.DWG



SCALE: 1" = 1 MILE

NOTE:

ALL LOCATIONS ARE APPROXIMATE.

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OTHER PCB USERS

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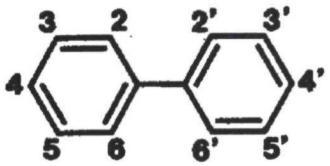
FIGURE
X

X: 64502X01.DWG, 64502X02.DWG
L: ON=*, OFF=REF
P: PAGESET/PLT-DL
5/17/05 SYR-54-RLP LJP SDL
64502100/64502B13.DWG

PCB Chemistry- 209 compounds (a.k.a. congeners)



Reference: Wade, 1986.

Chlorine Substitution	Number of Possible Isomers
Mono-	3
Di-	12
Tri-	24
Tetra-	42
Penta-	46
Hexa-	42
Hepta-	24
Octa-	12
Nona-	3
Deca-	1
Total:	209

PCB Environmental Chemistry

- More chlorine, less soluble
- Less soluble, more bioaccumulative
- More chlorine, more bioaccumulative

Average Composition (wt. %) of Some Aroclors

Reference: Erickson, 1997.

Homolog (chlorines)	Aroclor 1221	1232[a]	1016	1242	1248	1254	1260
0	10						
1	50	26	2	1			
2	35	29	19	13	1		
3	4	24	57	45	22	1	
4	1	15	22	31	49	15	
5				10	27	53	12
6					2	26	42
7						4	38
8							7
9							1

less soluble more bioaccumulative

more soluble less bioaccumulative

penta-hexa biphenyls

70% of 1242 contains 3+4 chlorines

79% of 1254 contains 5+6 chlorines

[a] Five percent unidentified (biphenyl?).

Source: From Brinkman, U. A. Th. and De Kok, *Halogenated Biphenyls, Terphenyls, Napthalenes, Dibenzodioxins and Related Products*, Kimbrough, R. D., Ed., Elsevier Biomedical Press, New York, 1980, 1. With permission.

PCB Environmental Chemistry- Primary "Weathering" Processes

- Dissolution - removes low molecular-weight PCB from solid phase (e.g. sediment, residuals). Can make lighter Aroclors appear heavier.

- Anaerobic dechlorination – removes chlorine from the PCB molecule (e.g transforms penta-CB to tetra-CB to tri-CB). Can make heavy Aroclors appear lighter.

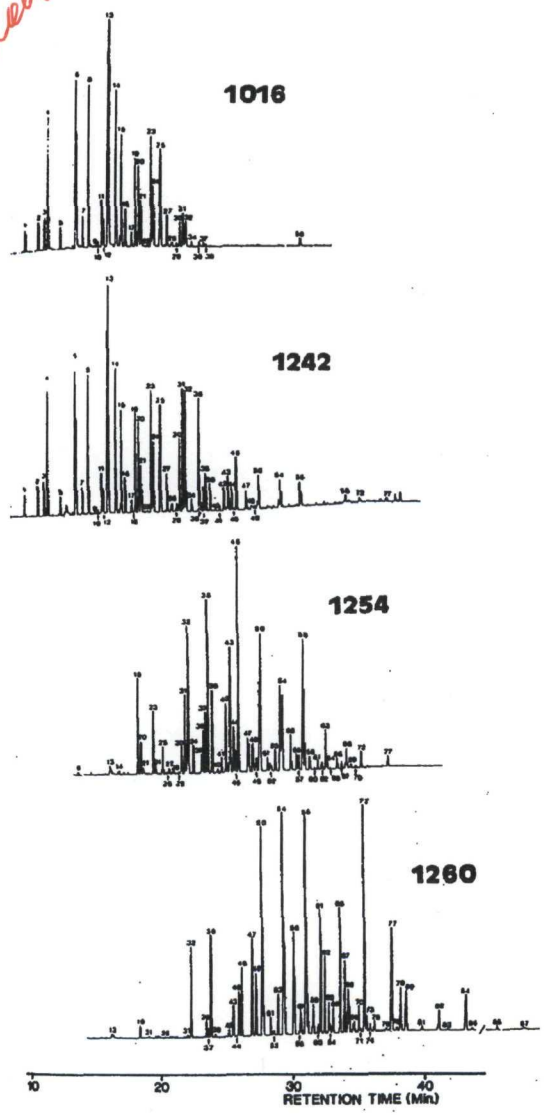
BBL - apply generalizations apply to specific different environments

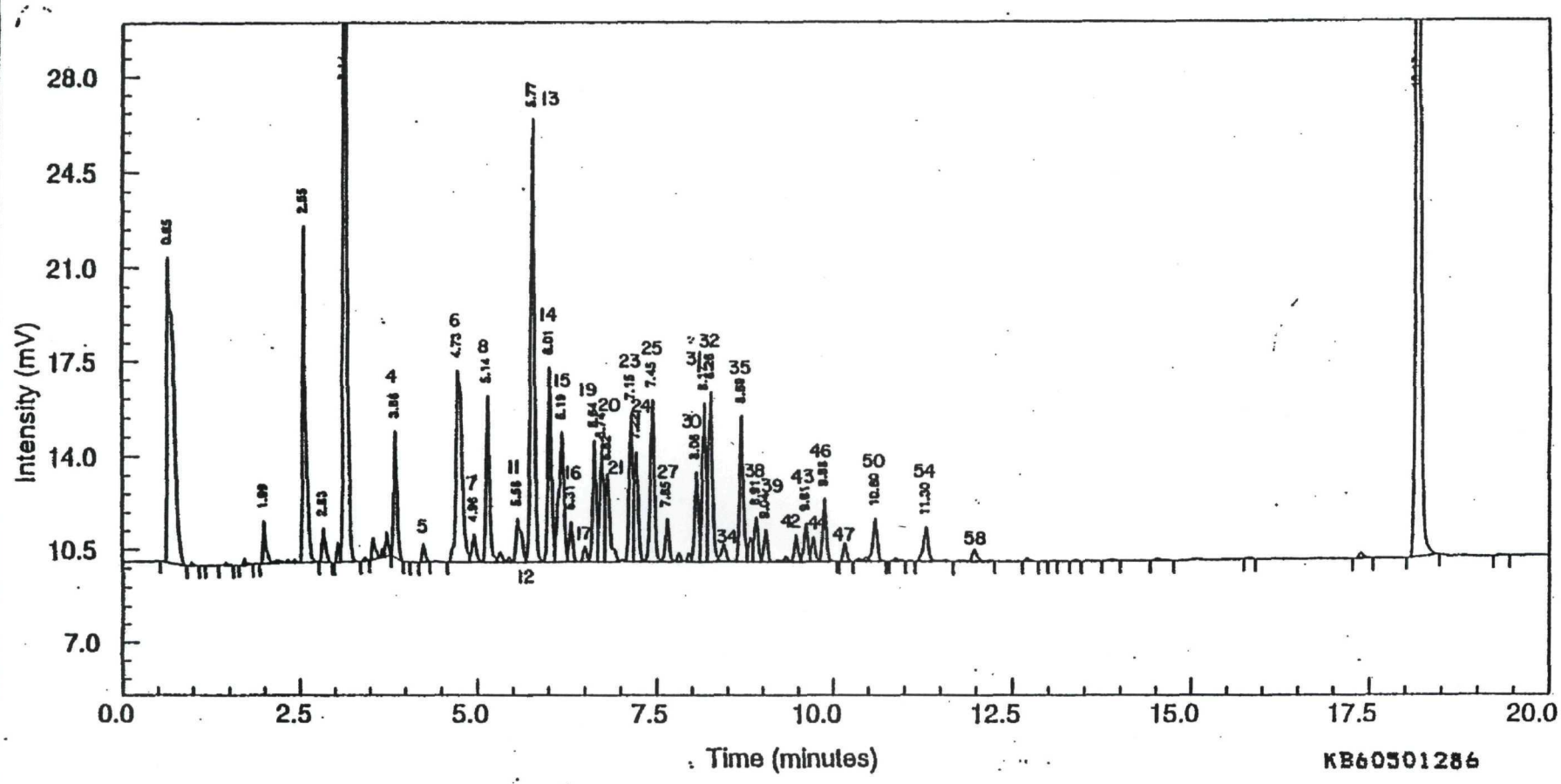
Bryant mare pond 1989 1984

8270 1242

ECD Chromatograms of Aroclor 1016, 1242, 1254, and 1260 on a Single SE-54 Column

Reference: Schulz, et al., 1989.





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ENGINEERS & SCIENTISTS

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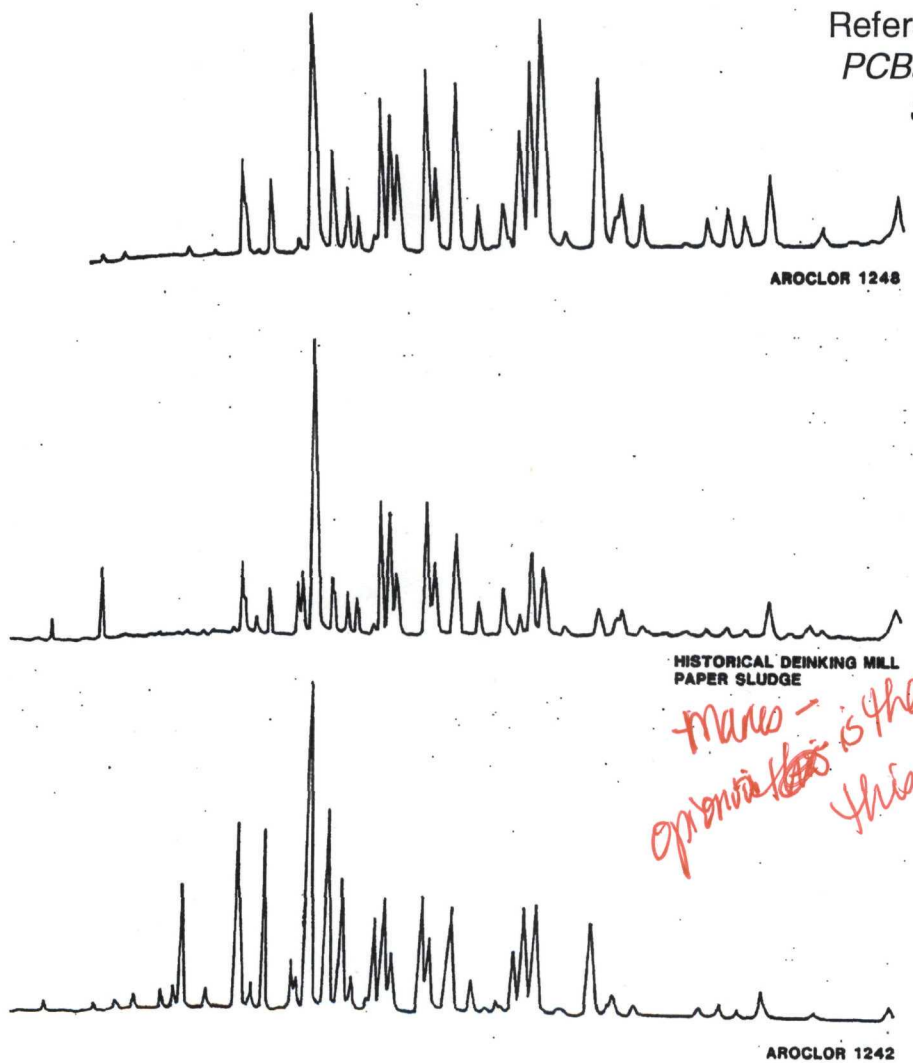
KALAMAZOO RIVER SUPERFUND SITE

AROCLOR 1242
ANALYZED BY
RTX-5 COLUMN

FIGURE
3

Comparison of Capillary-Column Chromatograms for Historical Deinking Mill Paper Sludge

Reference: BBL, *The Determination of PCBs in Pulp and Paper Effluents and Sludges: A Review of Regulatory Methods*, 1994.



undelineated dissolution

Mano - opinion is that this is weathered 1242 NOT 1248

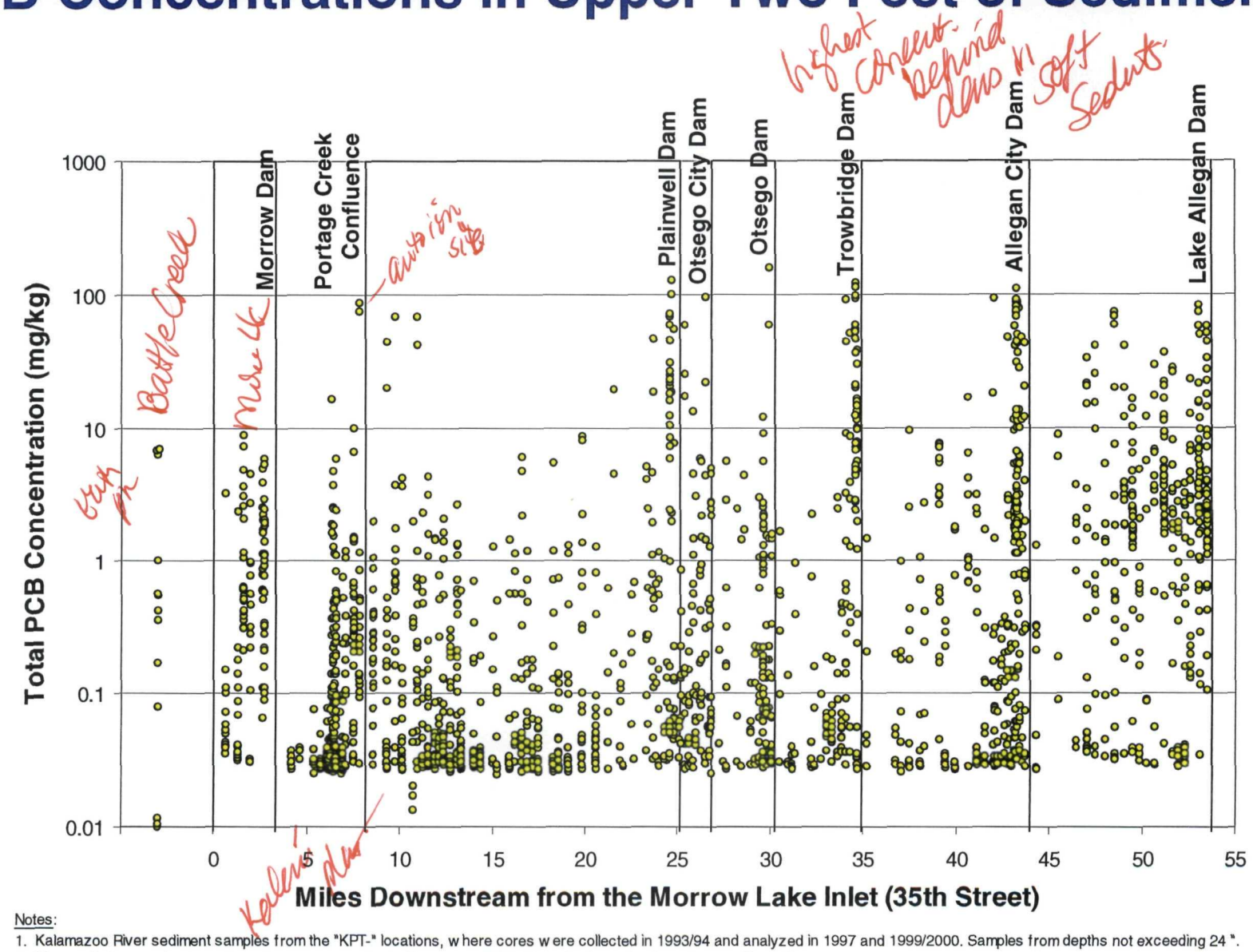
6+
11 9 105

What's in the Sediment?

- Morrow Lake Dam – Lake Allegan Dam
  - Submerged Sediment - 64,000 lbs. of PCB
  - Exposed Sediment - 55,000 lbs. of PCB
  - Majority Aroclor 1242-like (tri- & tetra- chlorobiphenyls)
  - Localized exceptions of Aroclor 1254 dominated

119 lbs of PCBs

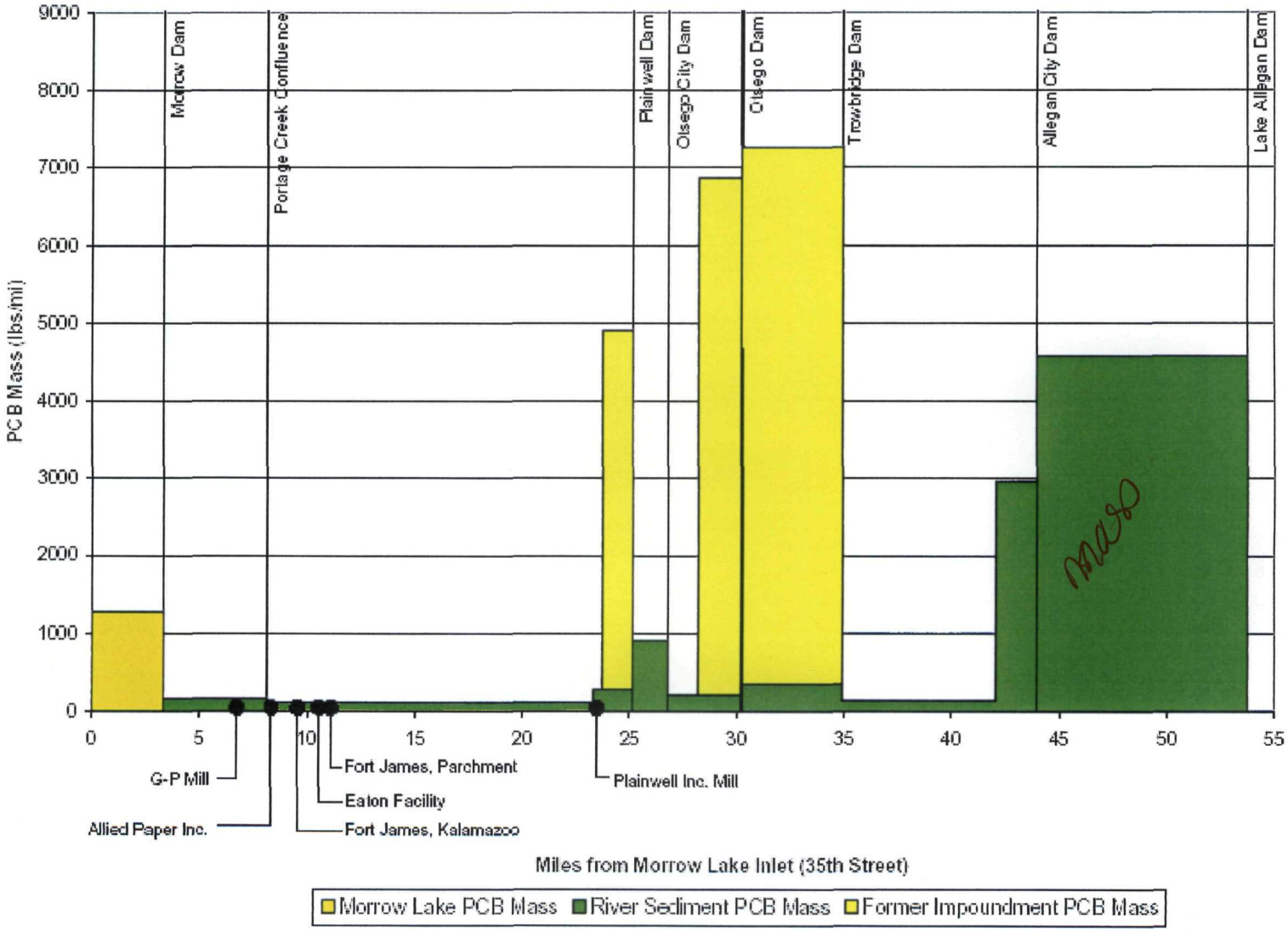
PCB Concentrations in Upper Two Feet of Sediment



Notes:

1. Kalamazoo River sediment samples from the "KPT-" locations, where cores were collected in 1993/94 and analyzed in 1997 and 1999/2000. Samples from depths not exceeding 24".
2. Morrow Lake samples from 16 sediment cores collected in summer 2000. Samples from depths not exceeding 24".
3. Includes samples from finely-sectioned cores collected in 2000. Samples from depths not exceeding 24".

PCB Distribution in the Kalamazoo River



PCB Composition Variations

KPT25-1	
Depth(in)	PCB(ppm)
0-2	0.22 J
2-6	ND(0.060)

KPT25-4	
Depth(in)	PCB(ppm)
0-3	0.12

KPT25-5	
Depth(in)	PCB(ppm)
0-2	0.051 J
2-6	0.042 J
6-11.5	0.11 J/0.10 J

KPT25-6	
Depth(in)	PCB(ppm)
0-2	0.13 J
2-6	1.2
6-12	0.15
12-24	0.072/0.098

KPT25-7	
Depth(in)	PCB(ppm)
0-2	0.027 J
2-6	0.73
6-12	0.47
12-24	0.24

KPT25-8	
Depth(in)	PCB(ppm)
0-2	69
2-6	42
6-12	0.64
12-24	0.20/0.29

KPT23-1	
Depth(in)	PCB(ppm)
0-2	0.21 J
2-10	1.8

KPT23-2	
Depth(in)	PCB(ppm)
0-2	1.2 J
2-6	0.81
6-9	0.99 J

KPT23-4	
Depth(in)	PCB(ppm)
0-2	0.59 J
2-7	0.26

KPT23-5	
Depth(in)	PCB(ppm)
0-2	0.68 J
2-6	0.39
6-12	0.71 J
12-17	0.54/0.87

KPT23-6	
Depth(in)	PCB(ppm)
0-2	0.67
2-6	0.79
6-12	3.7
12-20	67

KPT23-7	
Depth(in)	PCB(ppm)
0-2	0.16 J
2-6	ND(0.12)
6-12	ND(0.076)
12-24	ND(0.061)/ND(0.061)

KPT24-1	
Depth(in)	PCB(ppm)
0-2	ND(0.053)
2-12	ND(0.053)
12-27	0.046 J/0.11 J

KPT24-2	
Depth(in)	PCB(ppm)
0-2	0.031 J
2-6	ND(0.056)
6-12	ND(0.057)
12-24	0.031 J

KPT24-3	
Depth(in)	PCB(ppm)
0-2	0.16 J
2-6	0.063
6-12	0.037 J
12-19	ND(0.063)/ND(0.064)

KPT24-5	
Depth(in)	PCB(ppm)
0-2	0.091 J
2-6	0.046 J
6-12	0.13 J/0.036 J

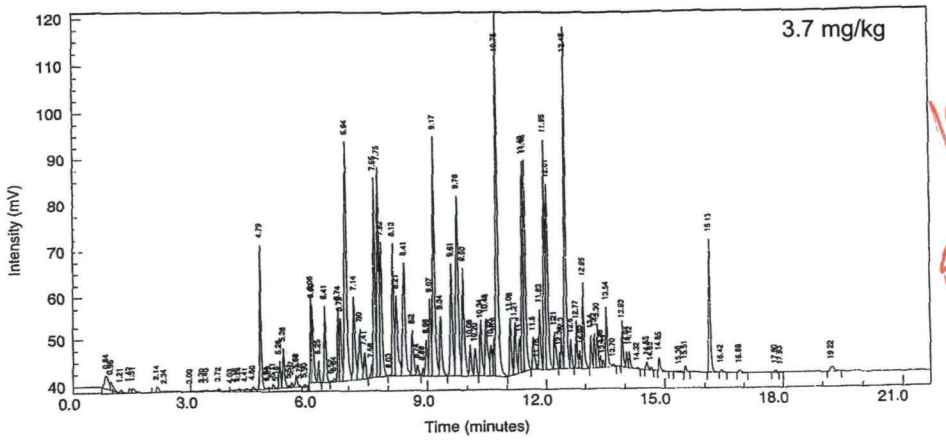
KPT24-6	
Depth(in)	PCB(ppm)
0-2	0.034 J
2-6	ND(0.063)
6-10	0.042 J

KPT24-7	
Depth(in)	PCB(ppm)
0-2	ND(0.052)
2-6	ND(0.058)
6-11	0.031 J

KPT24-8	
Depth(in)	PCB(ppm)
0-2	4.2 J
2-12	4.9/2.4
12-24	0.12

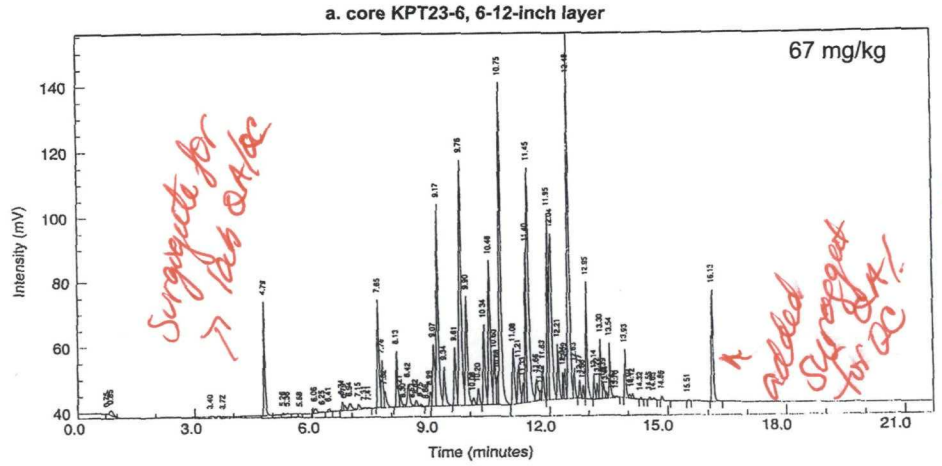
Chromatograms and Standards for Sediment Samples Near Eaton Corporation Kalamazoo Facility

Upstream



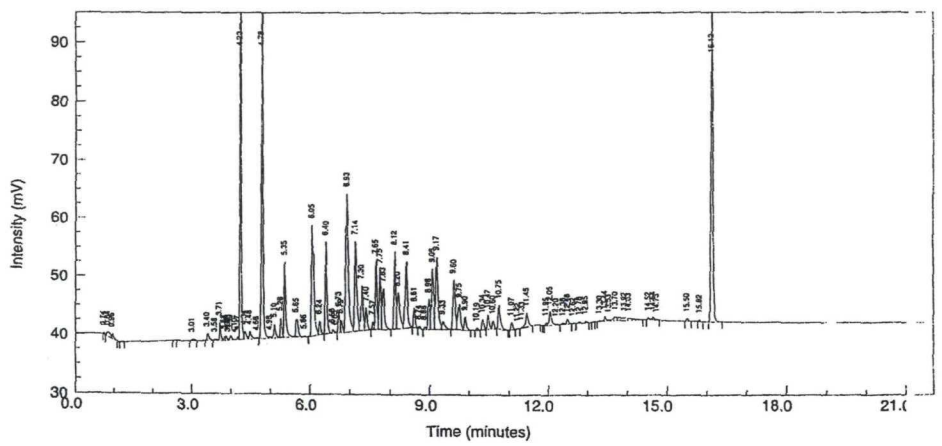
a. core KPT23-6, 6-12-inch layer

lab = porto
SD 1242
SD 1254

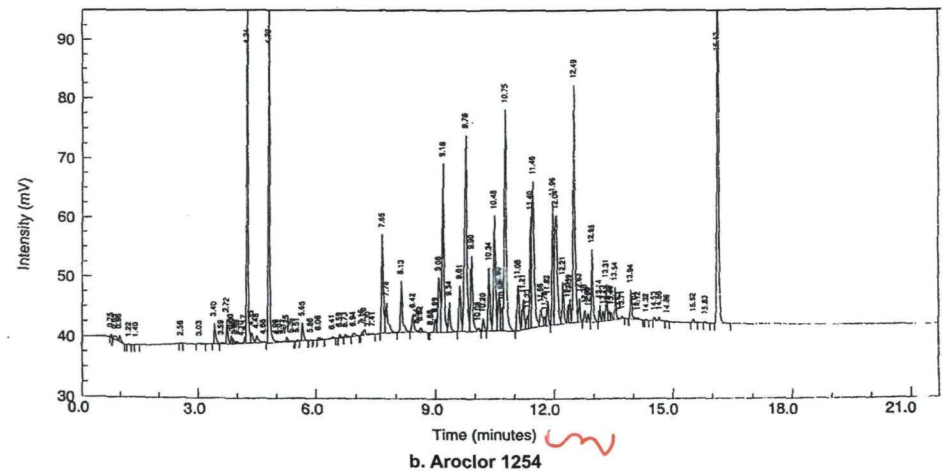


b. core KPT23-6, 12-20-inch layer

lab-quantitation
SD 1254

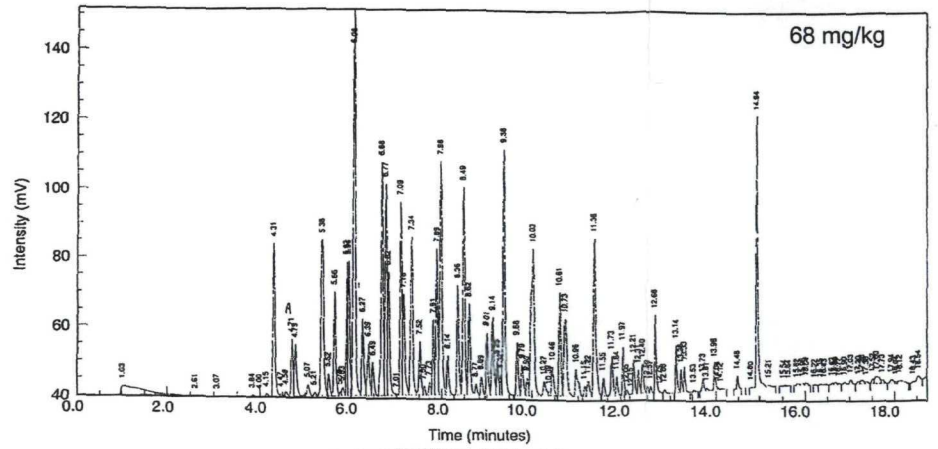


a. Aroclor 1242

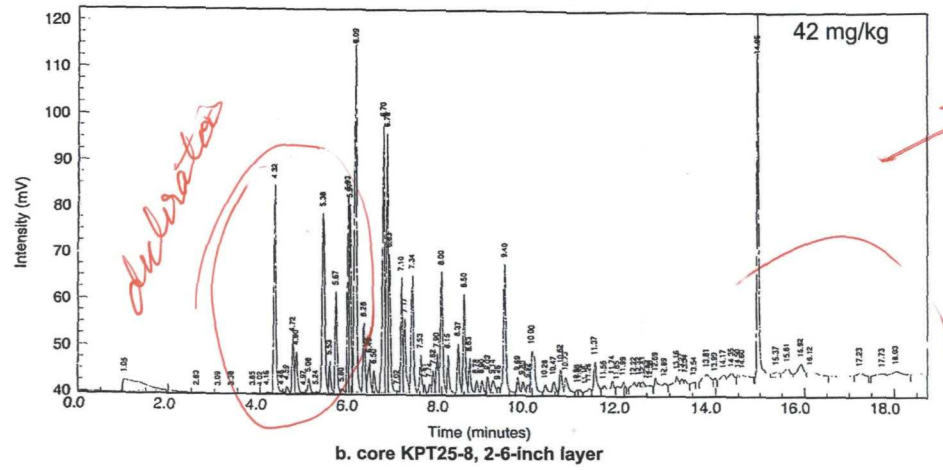


b. Aroclor 1254

Downstream

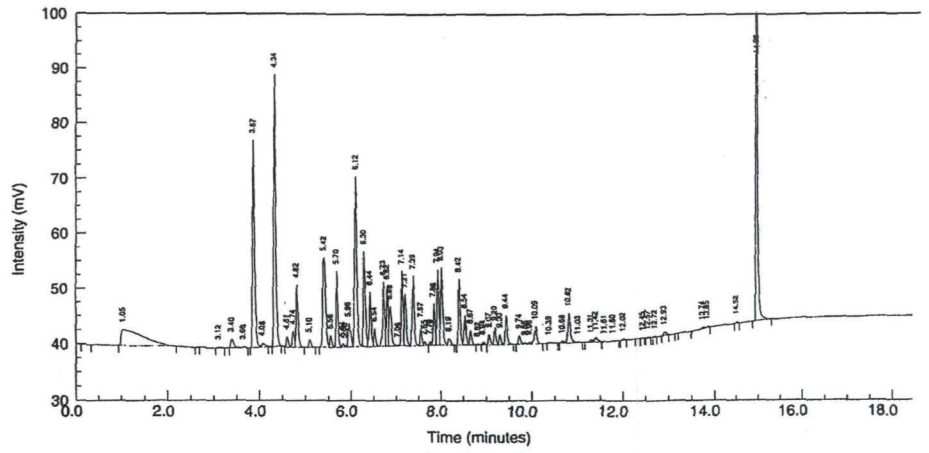


a. core KPT25-8, 0-2-inch layer

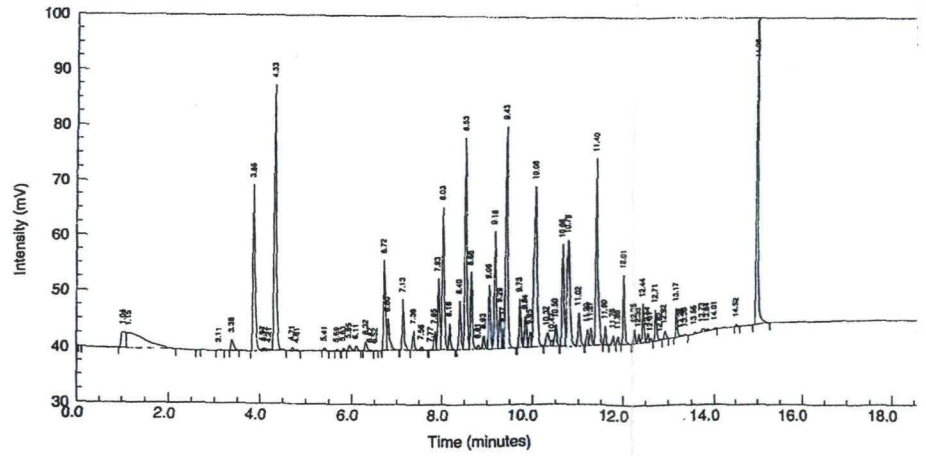


b. core KPT25-8, 2-6-inch layer

Aroclor 1248 or 1254
100% 1242
predominately 1242



a. Aroclor 1242



b. Aroclor 1254

04/27/05 SYR-D85-DJH
64502100/64502g05.cdr

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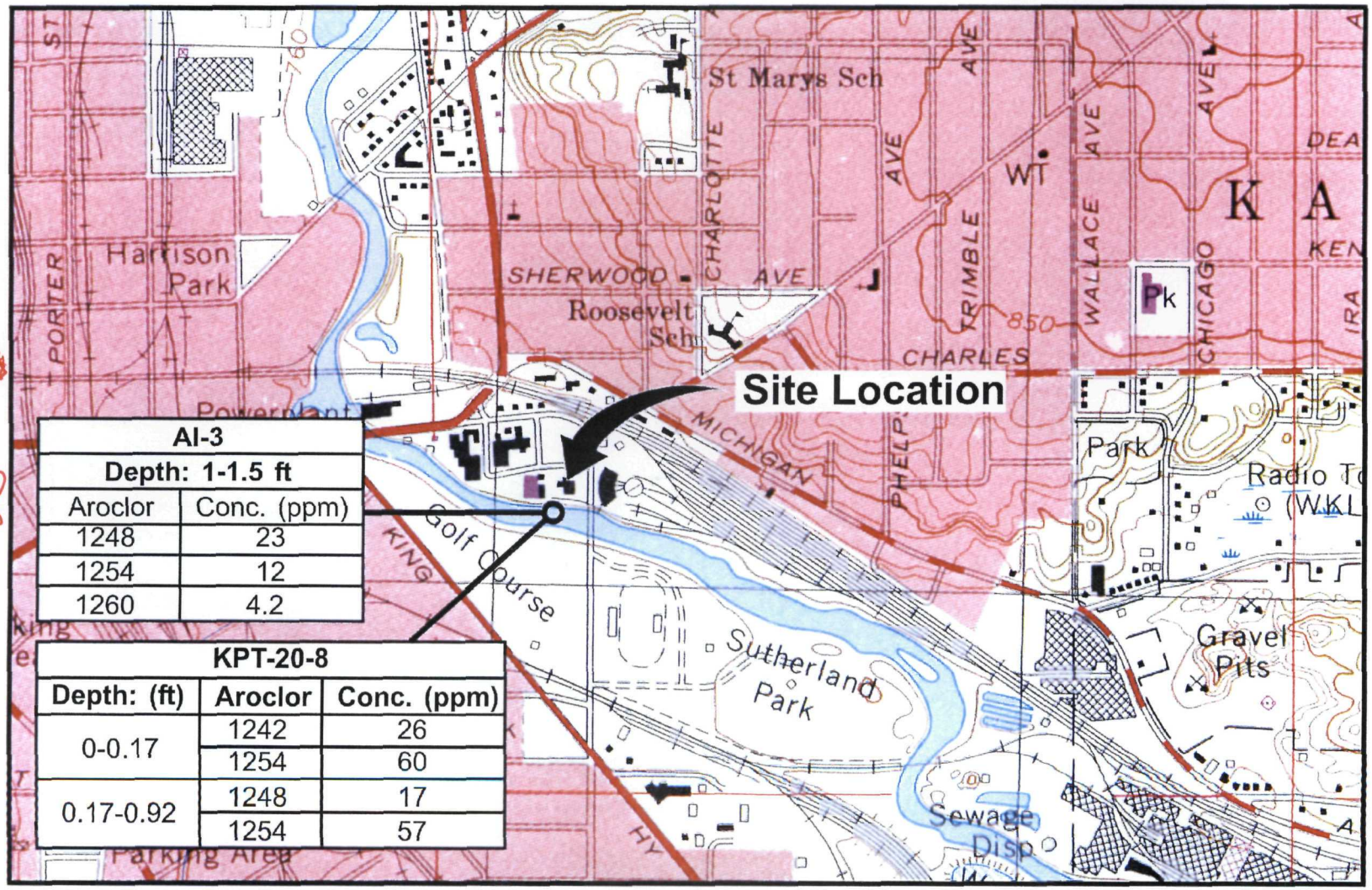
Auto Ion Superfund Site

portage creek

drain sludge

RI

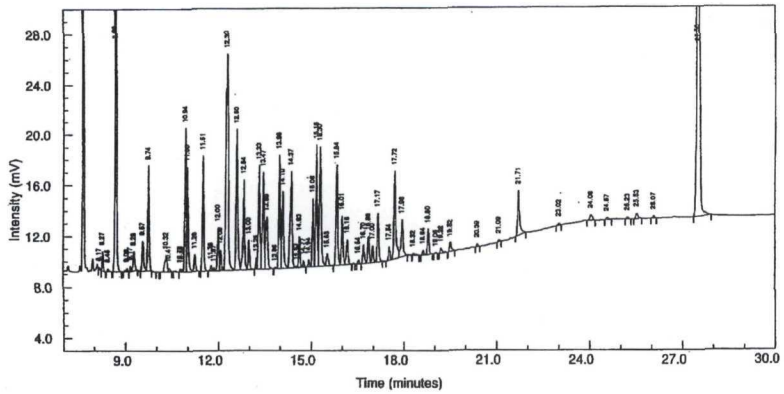


Al-3	
Depth: 1-1.5 ft	
Aroclor	Conc. (ppm)
1248	23
1254	12
1260	4.2

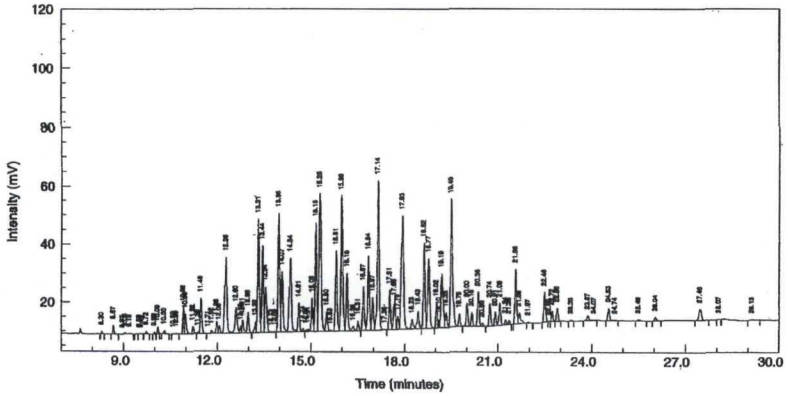
KPT-20-8		
Depth: (ft)	Aroclor	Conc. (ppm)
0-0.17	1242	26
	1254	60
0.17-0.92	1248	17
	1254	57

Auto Ion Superfund Site

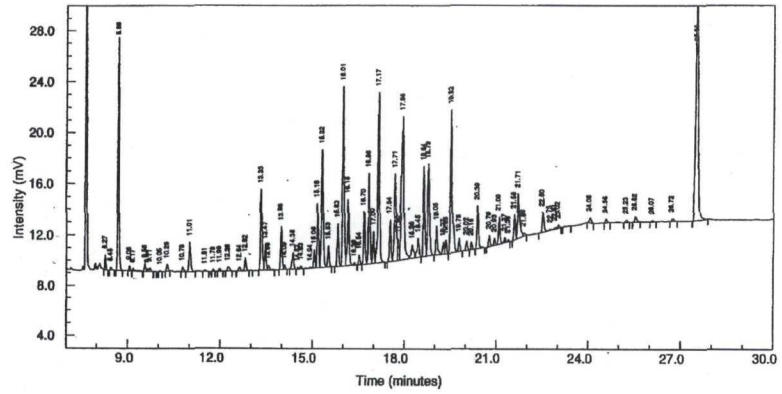
Aroclor 1242



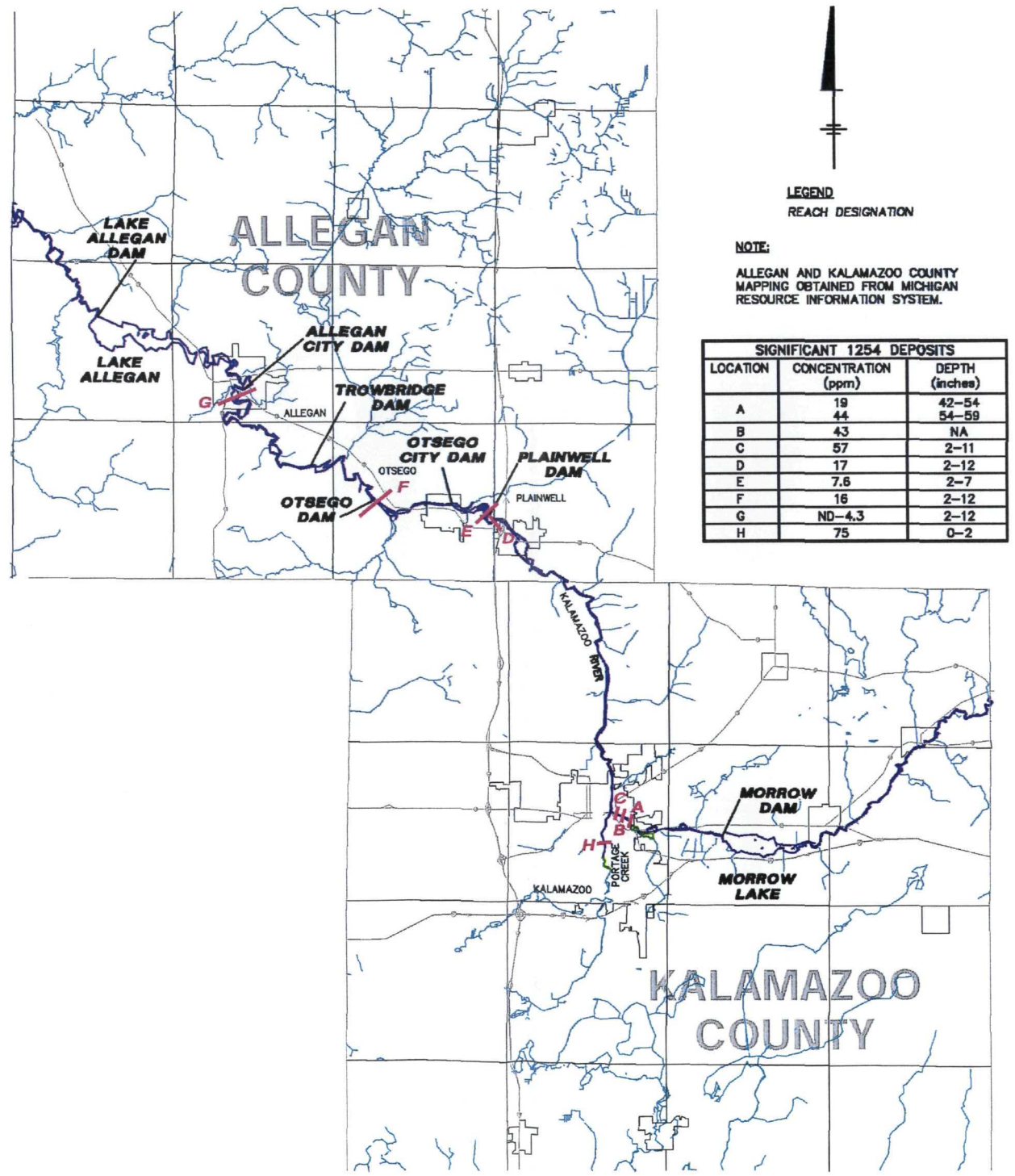
Sample AI-3
(1- to 1.5-foot interval)



Aroclor 1254



Sediments with Aroclor 1254-Like Composition Examples



LEGEND

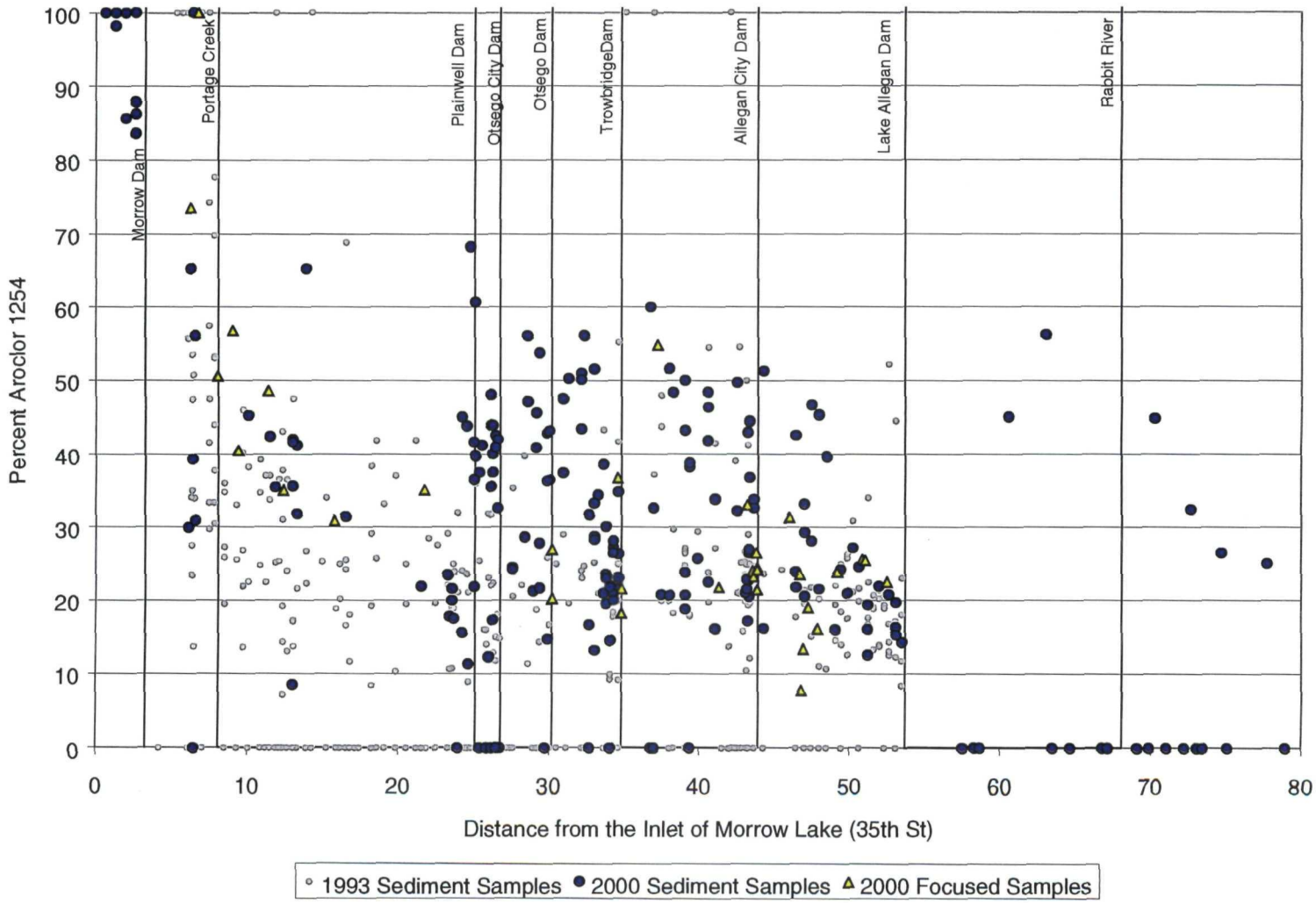
REACH DESIGNATION

NOTE:

ALLEGAN AND KALAMAZOO COUNTY MAPPING OBTAINED FROM MICHIGAN RESOURCE INFORMATION SYSTEM.

SIGNIFICANT 1254 DEPOSITS		
LOCATION	CONCENTRATION (ppm)	DEPTH (inches)
A	19 44	42–54 54–59
B	43	NA
C	57	2–11
D	17	2–12
E	7.6	2–7
F	16	2–12
G	ND–4.3	2–12
H	75	0–2

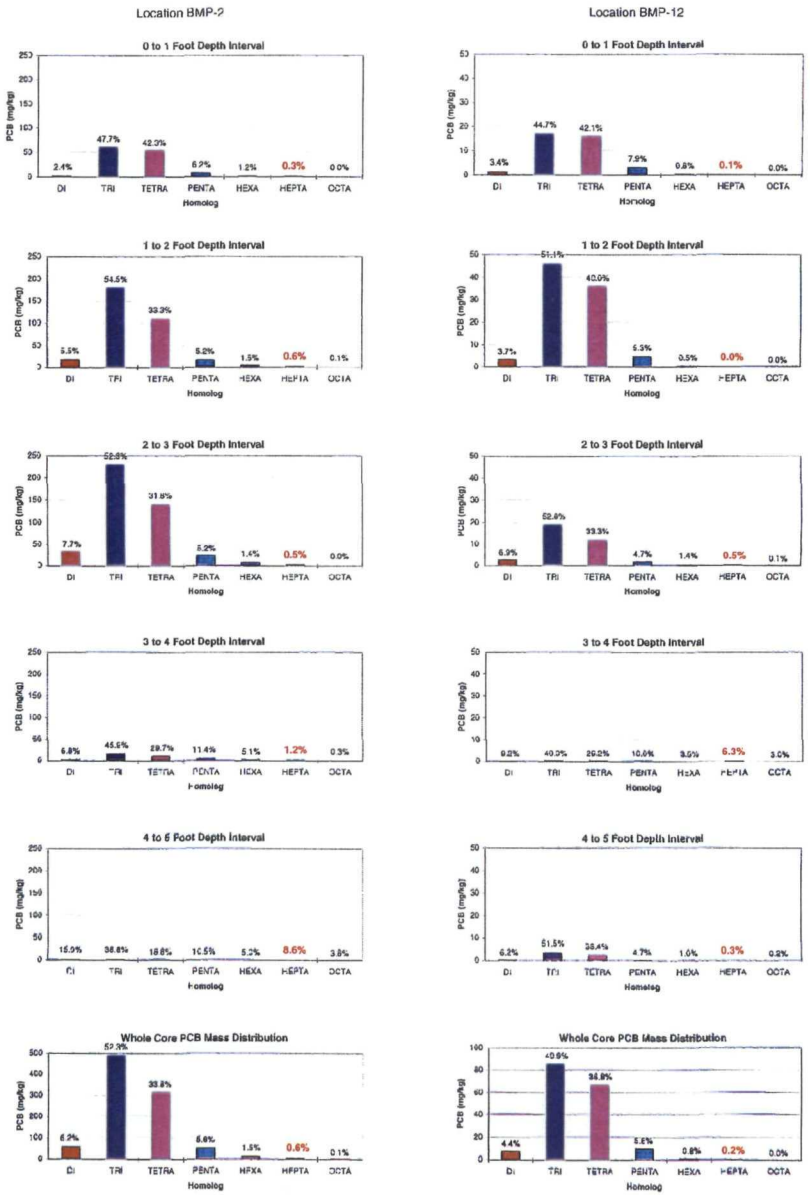
Percent of Total PCB Quantified as Aroclor 1254 in Surficial Sediment



PCB Composition of Residual Samples from Kalamazoo River Operable Units and Kalamazoo River Sediment Samples

Location	n	Percent of Total Detected PCB Mass Quantitated by Aroclor						
		% 1016	% 1242	% 1248	% 1254	% 1260	% 1016 +1242+1248	% 1254+1260
Operable Units								
12th Street Landfill	35	8.1	45.6	41.5	3.1	1.6	95.3	4.7
King Highway Landfill	105	0.0	88.6	11.2	0.1	0.1	99.8	0.2
A-Site	55	0.0	89.2	8.7	1.8	0.3	97.9	2.1
Willow Boulevard	32	1.2	91.9	5.9	0.4	0.5	99.1	0.9
Allied Paper, Inc.	111	11.3	86.0	2.4	0.3	0.1	99.6	0.4
River Segments								
Morrow Lake	51	0.0	0.0	1.8	89.6	8.6	1.8	98.2
Morrow Dam to Portage Creek	199	0.0	36.5	8.7	52.7	2.0	45.2	54.7
Portage Creek to Main Street, Plainwell	331	0.0	58.3	9.5	29.8	1.8	67.8	31.6
Main Street Plainwell to Plainwell Dam	58	0.0	78.0	11.9	10.3	0.0	89.9	10.3
Plainwell Dam to Otsego City Dam	63	0.0	80.9	1.9	17.0	0.2	82.8	17.2
Otsego City Dam to Otsego Dam	81	0.0	58.8	29.3	10.9	1.0	88.1	11.9
Otsego Dam to Trowbridge Dam	87	0.0	69.0	8.5	22.1	0.4	77.5	22.5
Trowbridge Dam to Allegan City Line	85	0.0	44.1	23.9	19.2	12.8	68.0	32.0
Allegan City Line to Allegan City Dam	140	0.0	89.8	2.4	7.8	0.1	92.2	7.9
Lake Allegan	228	0.0	87.0	3.8	9.2	0.1	90.8	9.3
Former Impoundment Exposed Sediment								
Plainwell	125	0.3	2.8	77.8	14.3	4.8	80.9	19.1
Otsego	122	18.3	20.7	35.7	23.6	1.7	74.7	25.3
Trowbridge	194	9.1	3.2	66.2	16.5	5.0	78.5	21.5

Homolog Distribution in Bryant Mill Pond Sediment Samples



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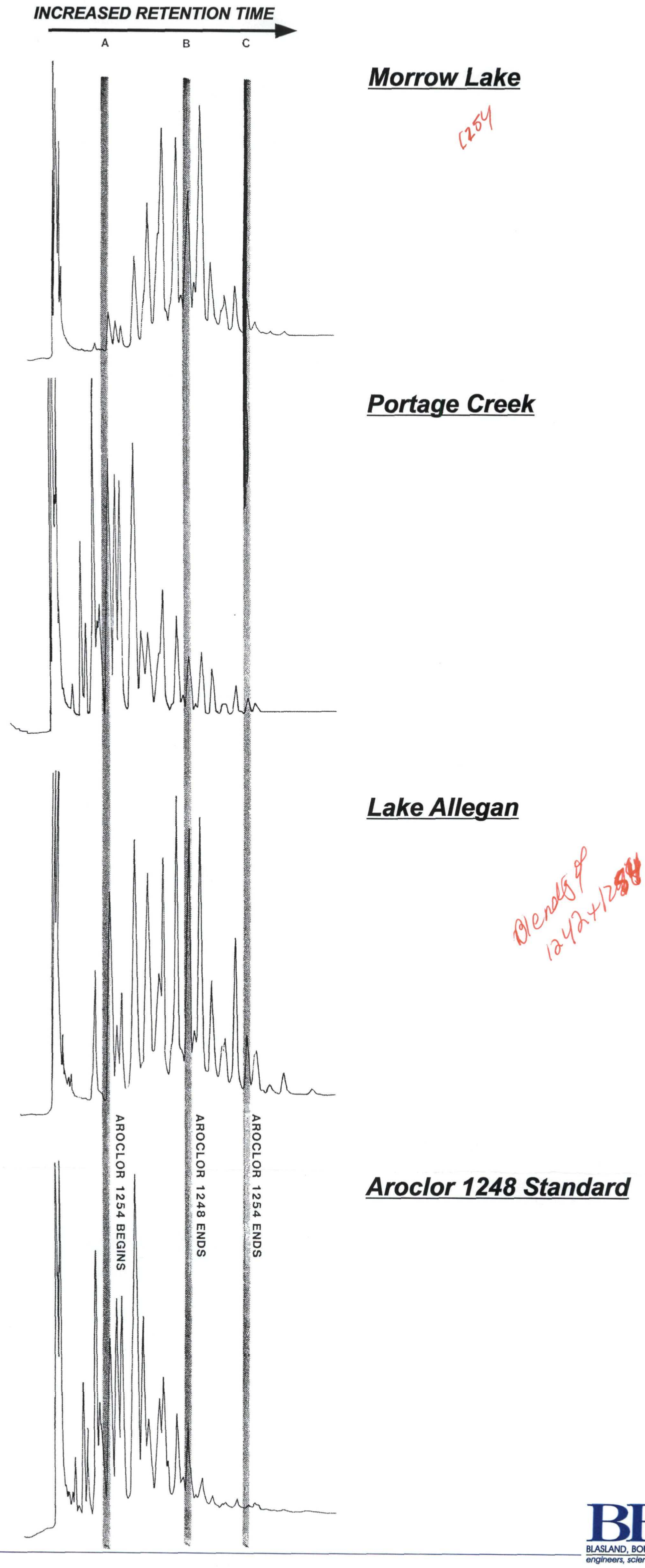
Comparison of Fish Chromatograms from The Kalamazoo River



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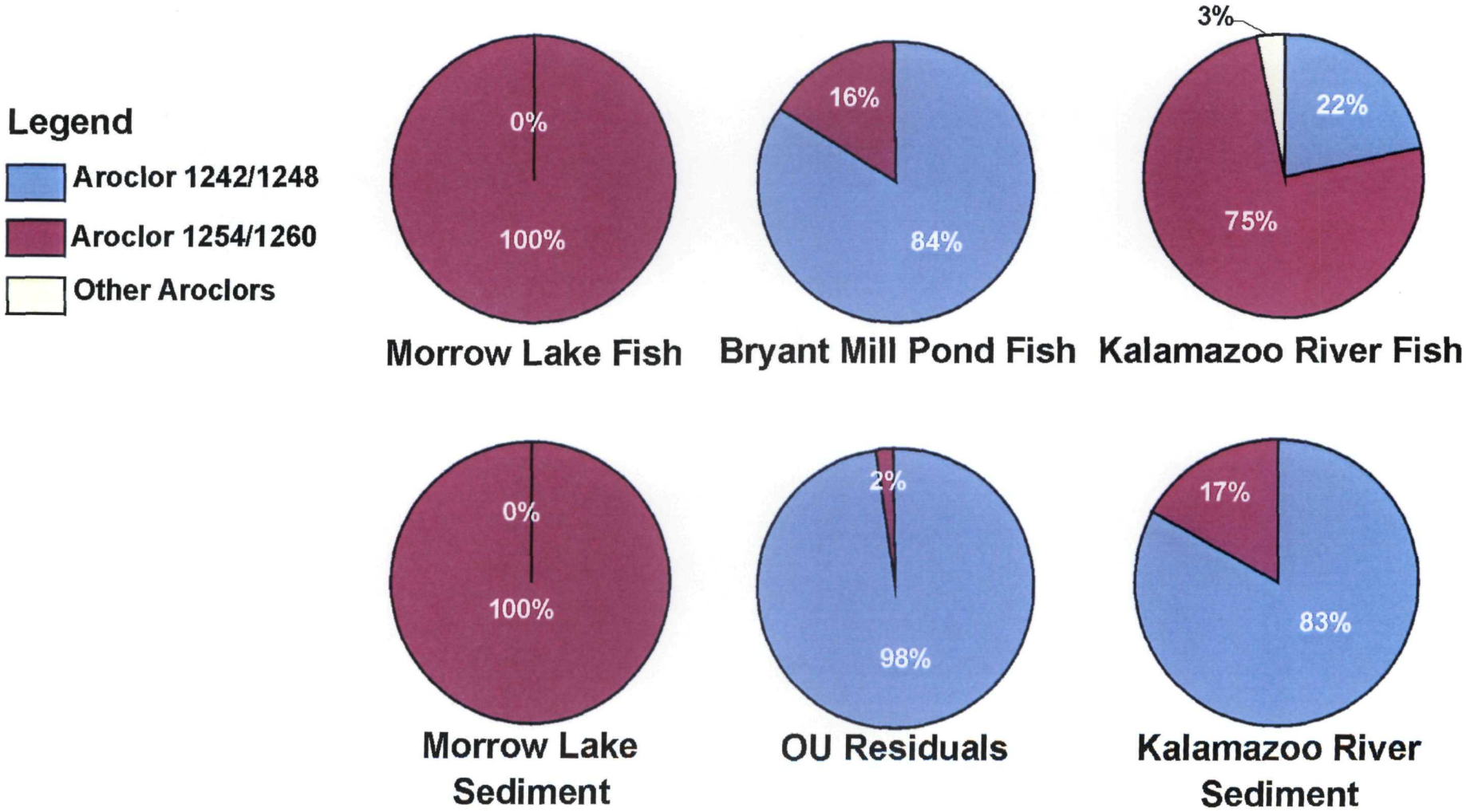
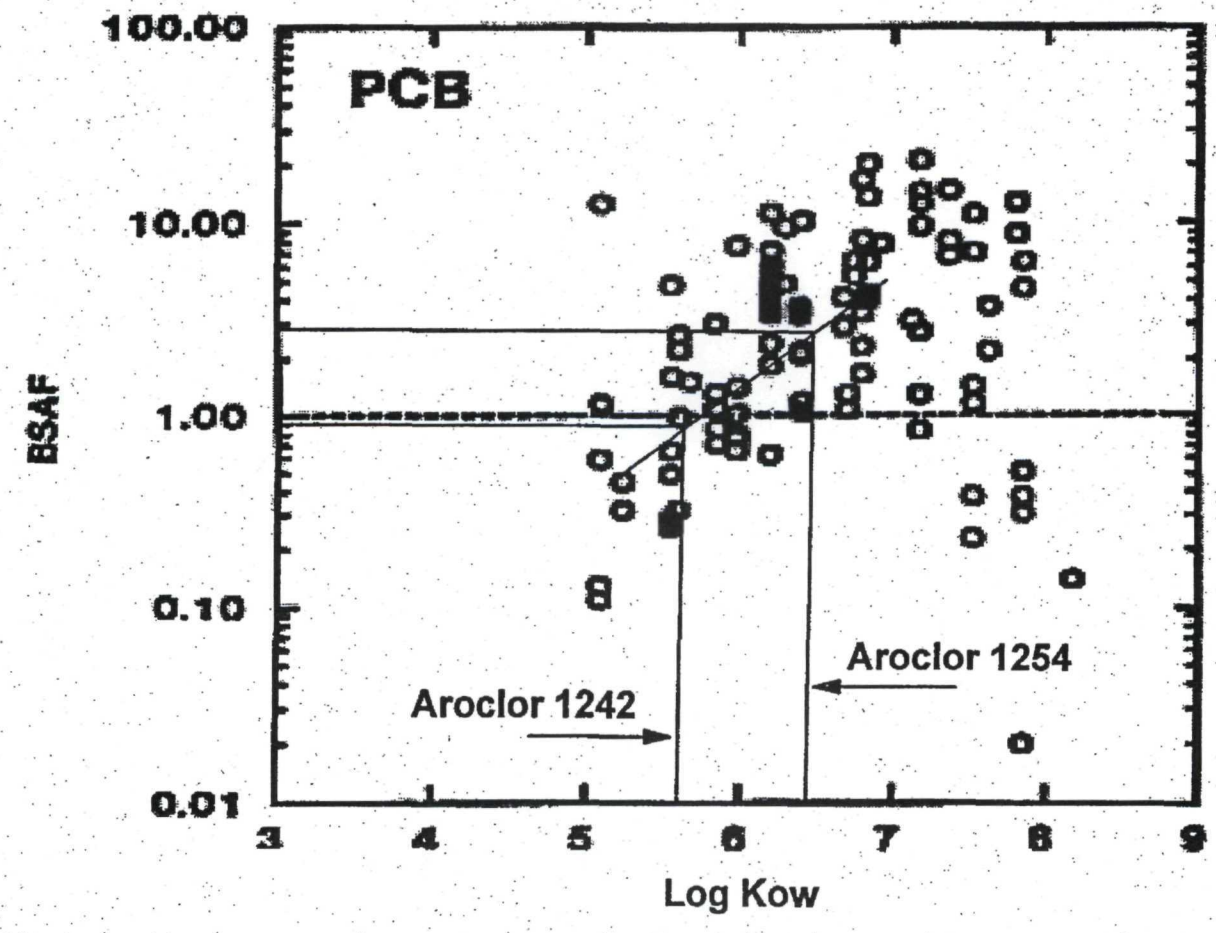
Comparison of "Aroclor Composition" in Fish and Sediment PCBs



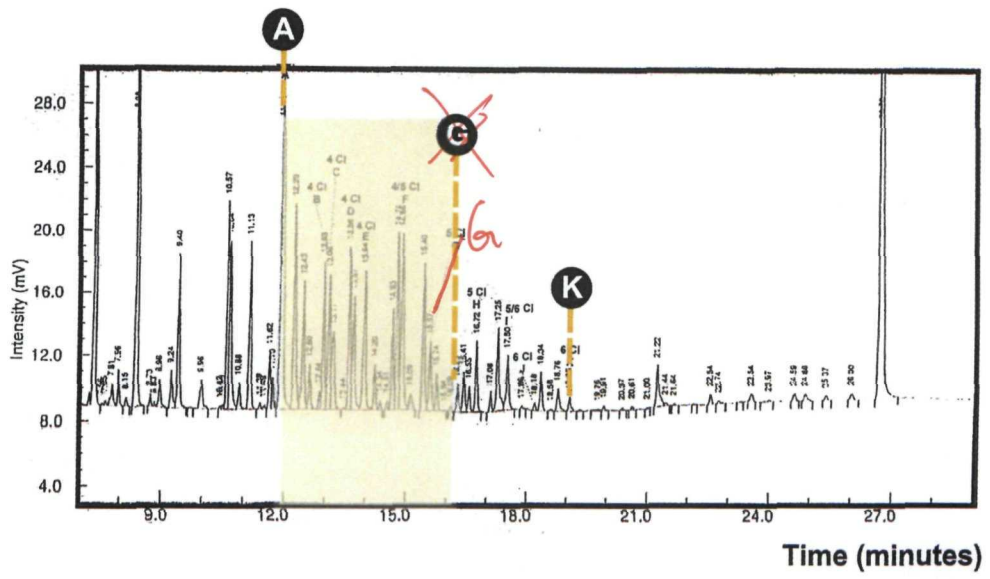
Relationship Between Biota to Sediment Accumulation Factors (BSAFs) and the Logarithm of Octanol-Water Partition Coefficients (Log Kow)



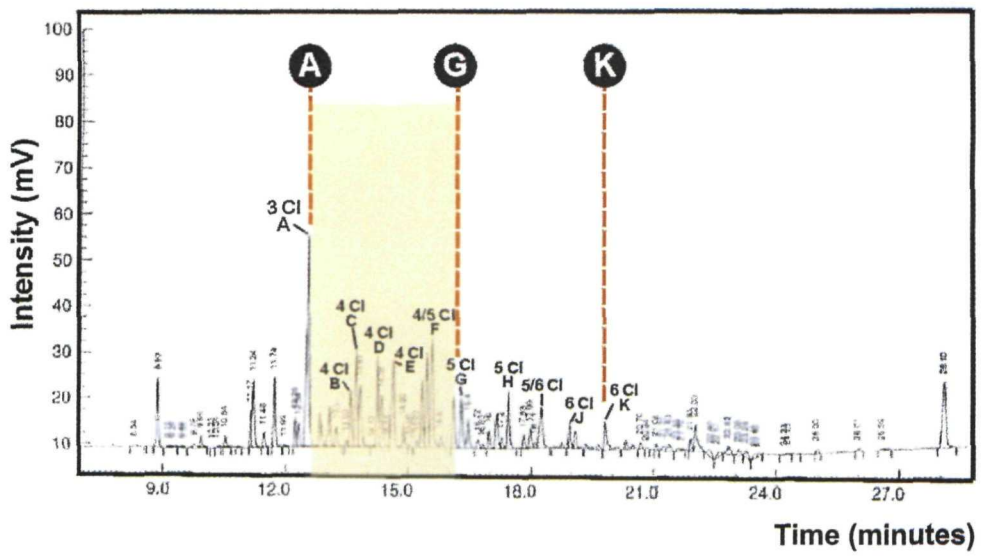
PCB in Fish

Composite of 3 fish
Single Sucker

Aroclor 1242

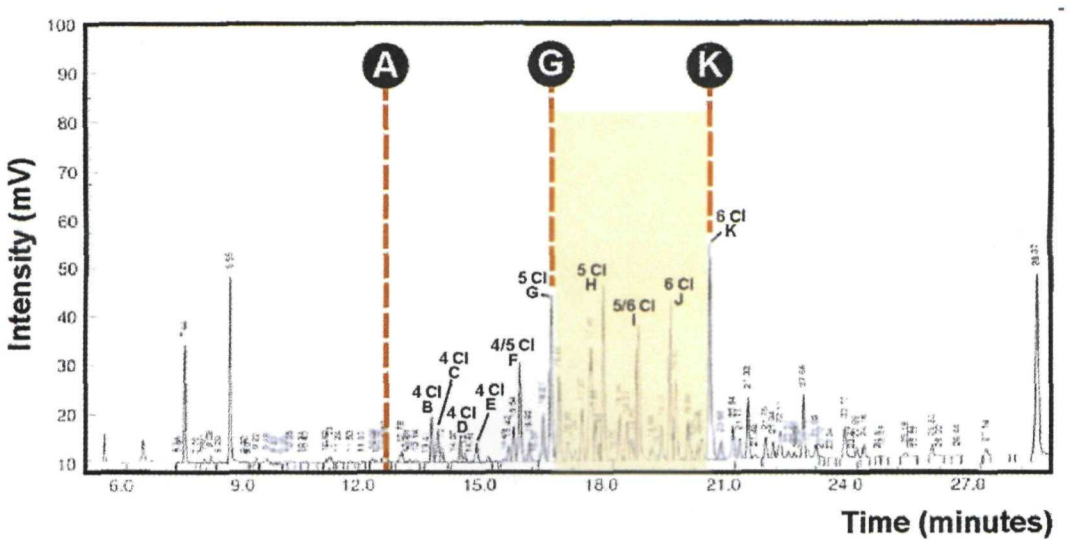


Bryant Mill Pond (2.4 ppm)

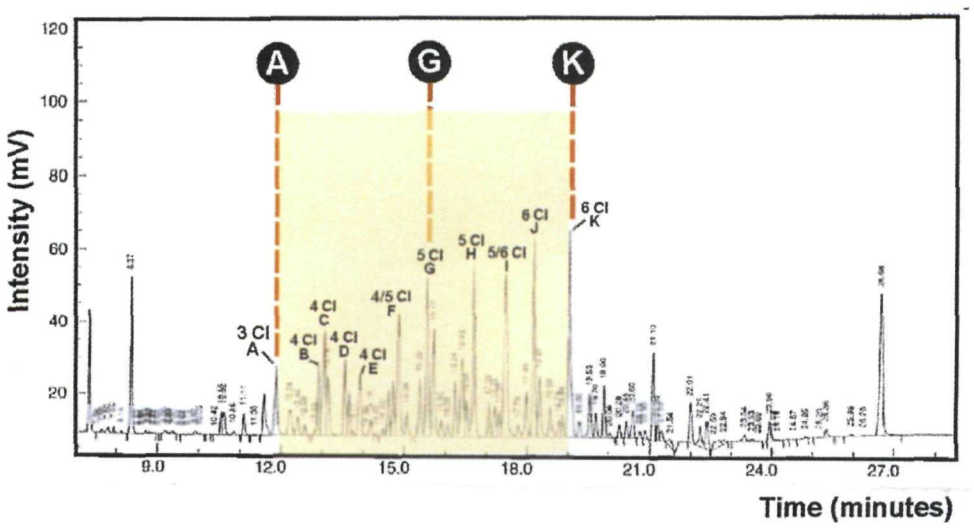


pre-remediation

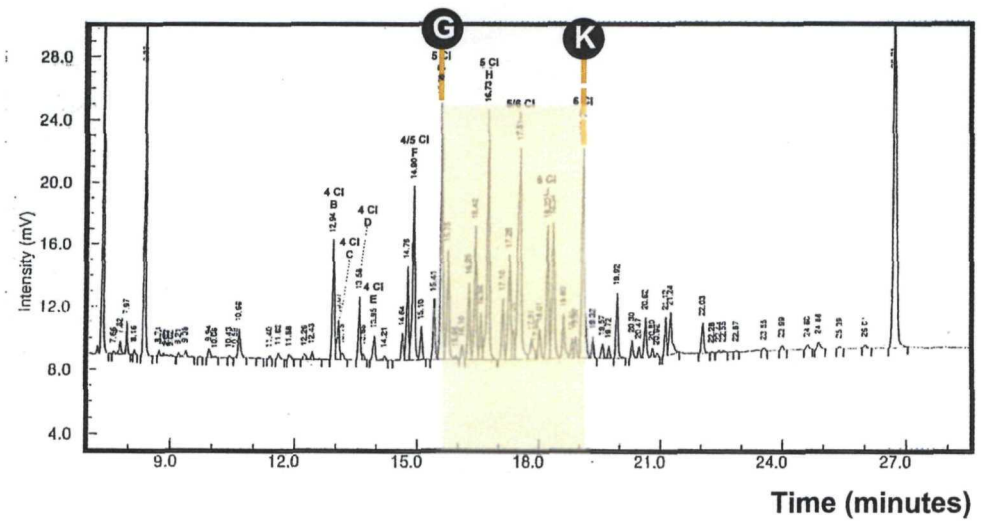
Morrow Lake (0.7 ppm)



Trowbridge Impoundment (1.2 ppm)



Aroclor 1254



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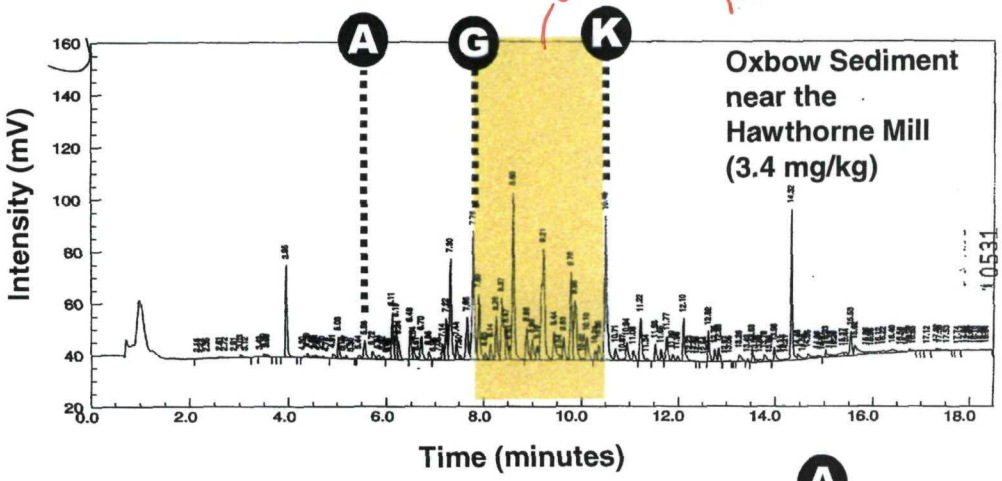
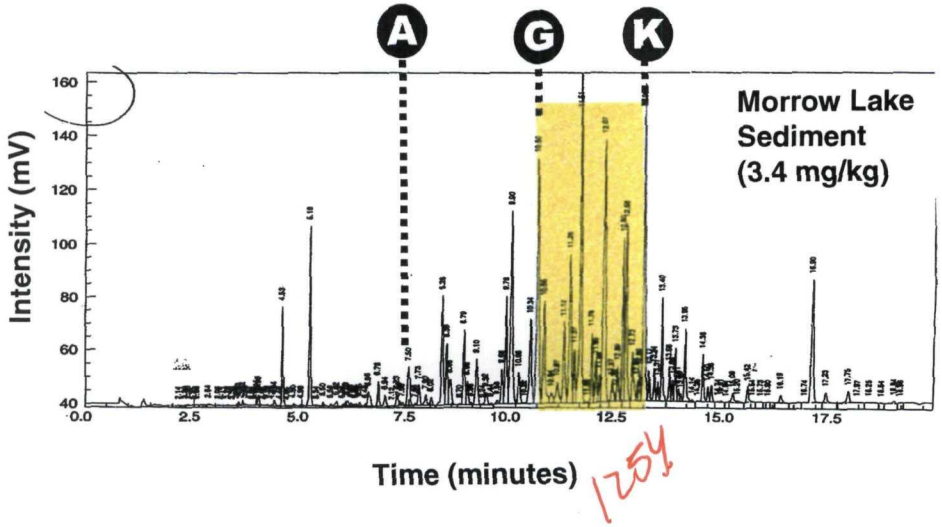
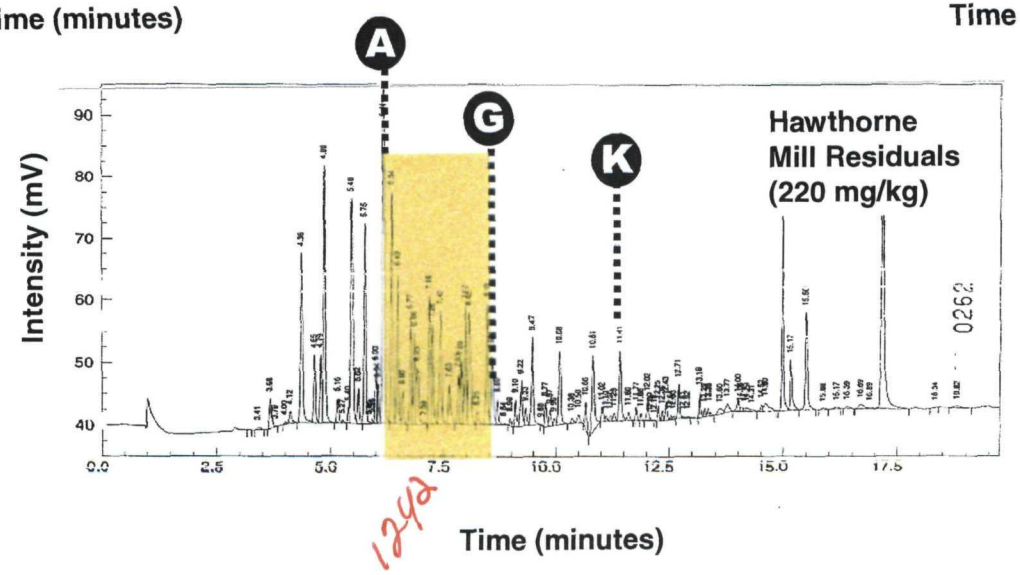
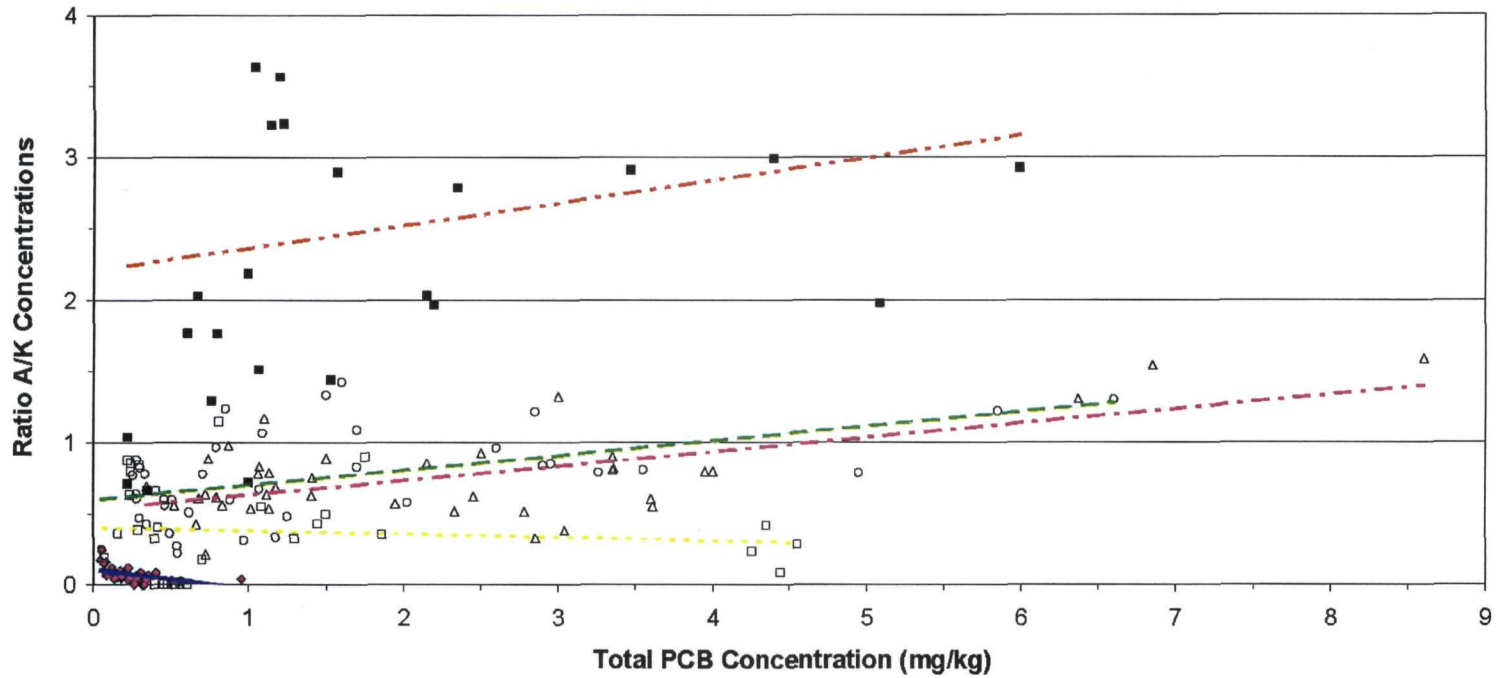
PCB Chromatograms for Morrow Lake Sediment Samples From Near the Hawthorne Mill

sediment looks like 1254 instead









LEGEND

- Morrow Lake
- Bryant Mill Pond
- Lake Allegan
- Plainwell Dam
- Near Saugatuck
- Linear Regression Line - Morrow Lake ($r^2 = 0.25$)
- Linear Regression Line - Bryant Mill Pond ($r^2 = 0.017$)
- Linear Regression Line - Lake Allegan ($r^2 = 0.26$)
- Linear Regression Line - Plainwell Dam ($r^2 = 0.38$)
- Linear Regression Line - Near Saugatuck ($r^2 = 0.010$)

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NOTE:
Peak A = 2,4',5 & 2,4,4'-Trichlorobiphenyls
Peak K = 2,3,3',4,5,6 & 2,2',3,4,4',5' & 2,3,3',4,4',6-Hexachlorobiphenyls

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REMEDIAL INVESTIGATION REPORT

A/K PCB CONCENTRATION RATIO VS TOTAL PCB - 1993 FISH DATA

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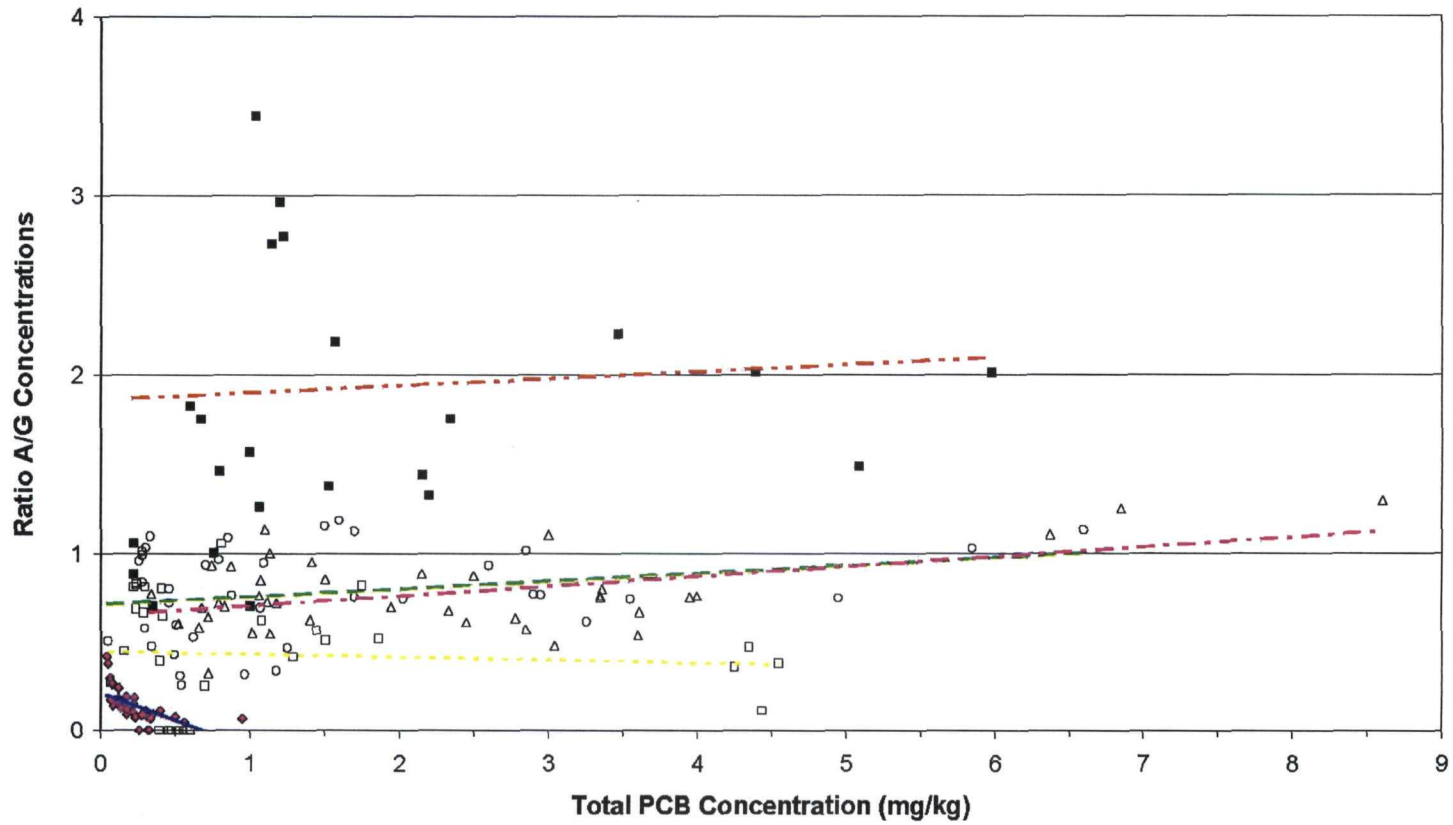
FIGURE 9



LEGEND

- Morrow Lake
- Bryant Mill Pond
- Lake Allegan
- Plainwell Dam
- Near Saugatuck
- Linear Regression Line - Morrow Lake ($r^2 = 0.34$)
- Linear Regression Line - Bryant Mill Pond ($r^2 = 0.0025$)
- Linear Regression Line - Lake Allegan ($r^2 = 0.069$)
- Linear Regression Line - Plainwell Dam ($r^2 = 0.24$)
- Linear Regression Line - Near Saugatuck ($r^2 = 0.0047$)

NOTE:
Peak A = 2,4',5 & 2,4,4'-Trichlorobiphenyls
Peak G = 2,2',3,4',5 & 2,2',4,5,5'-Pentachlorobiphenyls

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REMEDIAL INVESTIGATION REPORT

A/G PCB CONCENTRATION RATIO VS TOTAL PCB - 1993 FISH DATA

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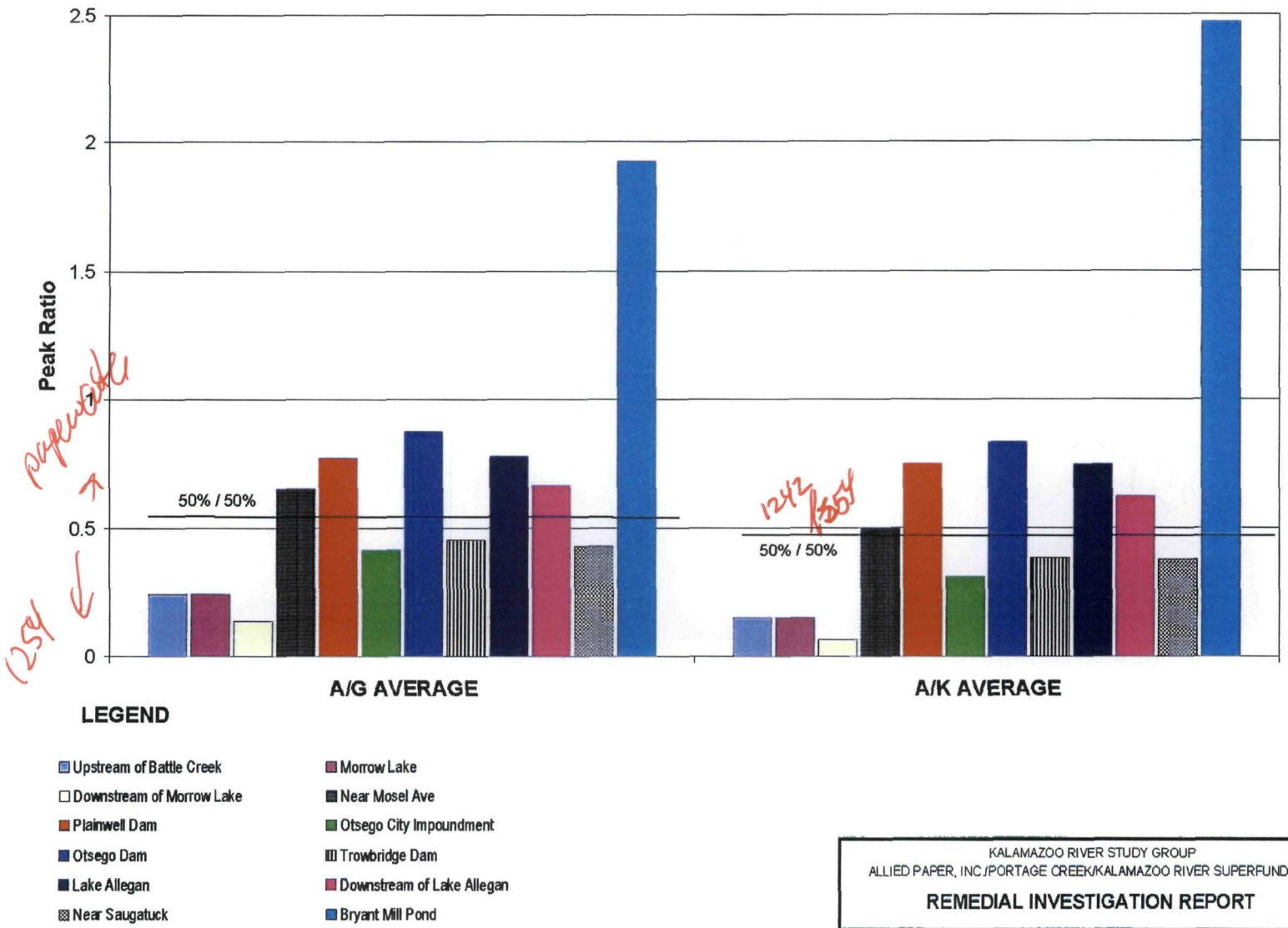
FIGURE 8



Kresgbais for ½ PCB's in fish are from sources other than aroclor

DRAFT FOR STATE AND FEDERAL REVIEW

NOTE:
Peak A = 2,4',5 & 2,4,4'-Trichlorobiphenyls
Peak G = 2,2',3,4',5 & 2,2',4,5,5'-Pentachlorobiphenyls
Peak K = 2,3,3',4,5,6 & 2,2',3,4,4',5' & 2,3,3',4,4',6-Hexachlorobiphenyls

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REMEDIAL INVESTIGATION REPORT

PCB CHROMATOGRAM PEAKS A/G AND A/K PCB CONCENTRATION RATIO AVERAGES - 1993 FISH DATA

BBL BLASLAND, BOUCK & LEE, INC. engineers & scientists

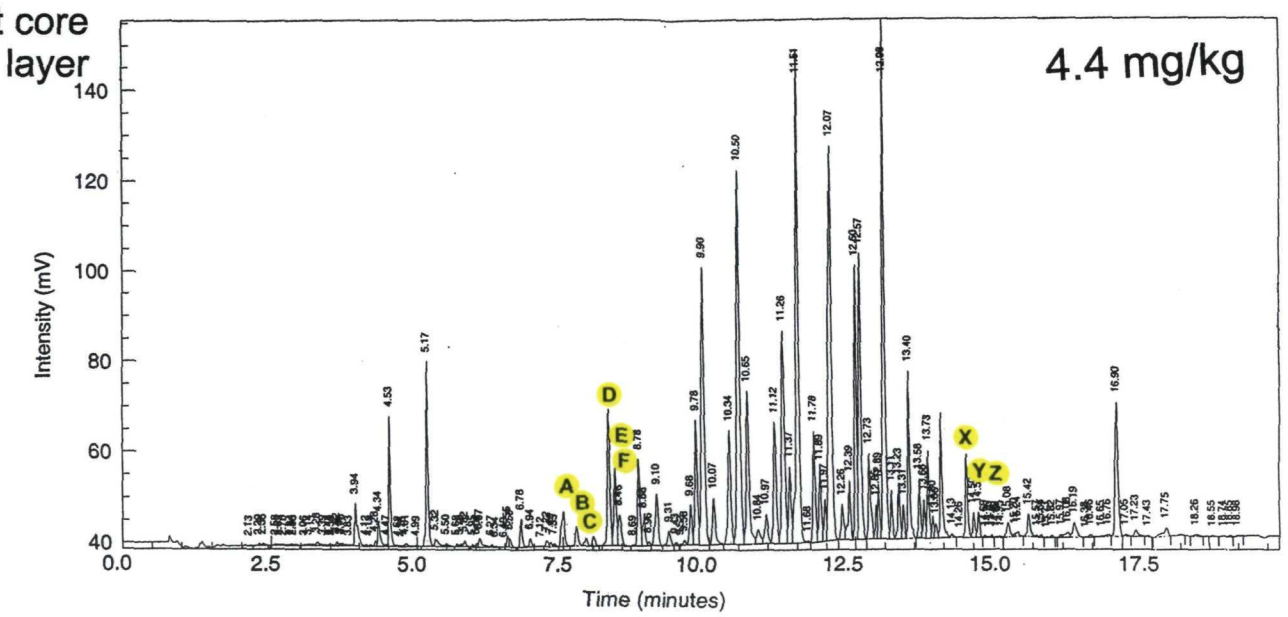
FIGURE 10

Morrow Lake

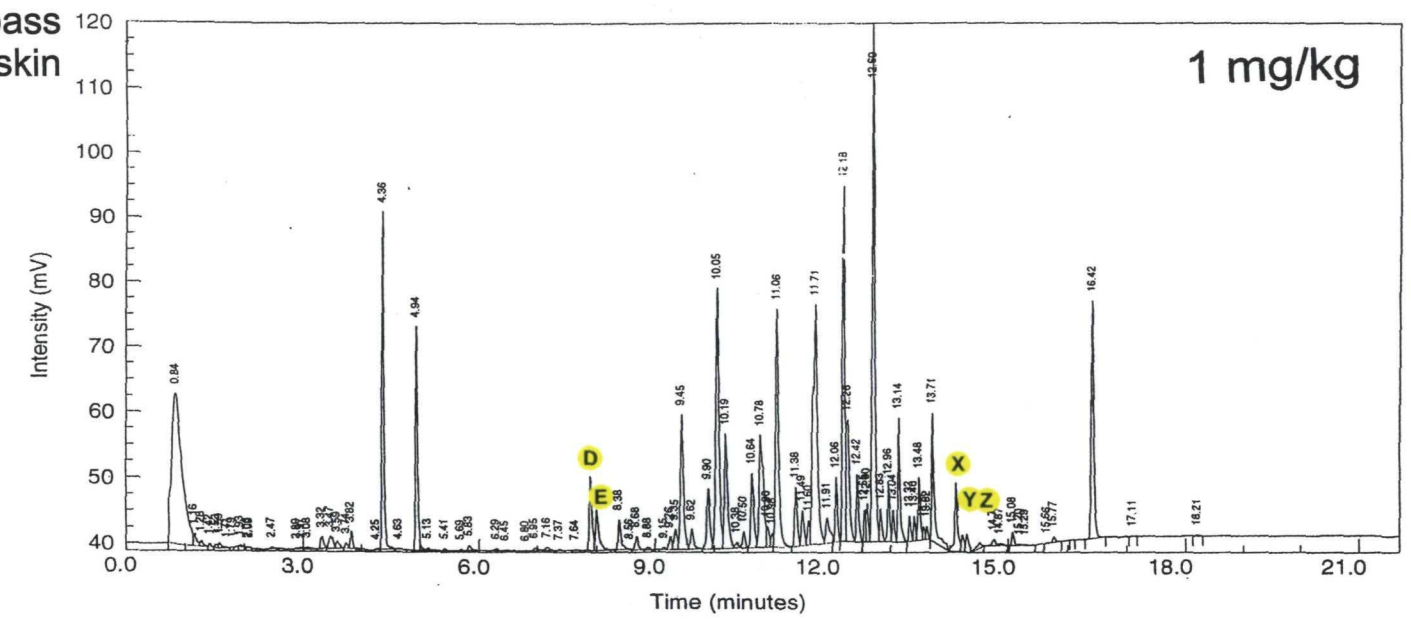
- Sediments contain approx. 4,000 lbs of Aroclor 1254-like PCB.
- According to Connolly (1997), Morrow Lake retains 22% of the entering particles.
- Therefore, roughly 15,000 lbs of PCB transported over the dam.

PCB Chromatograms for Morrow Lake Sediment and 1999 Fish

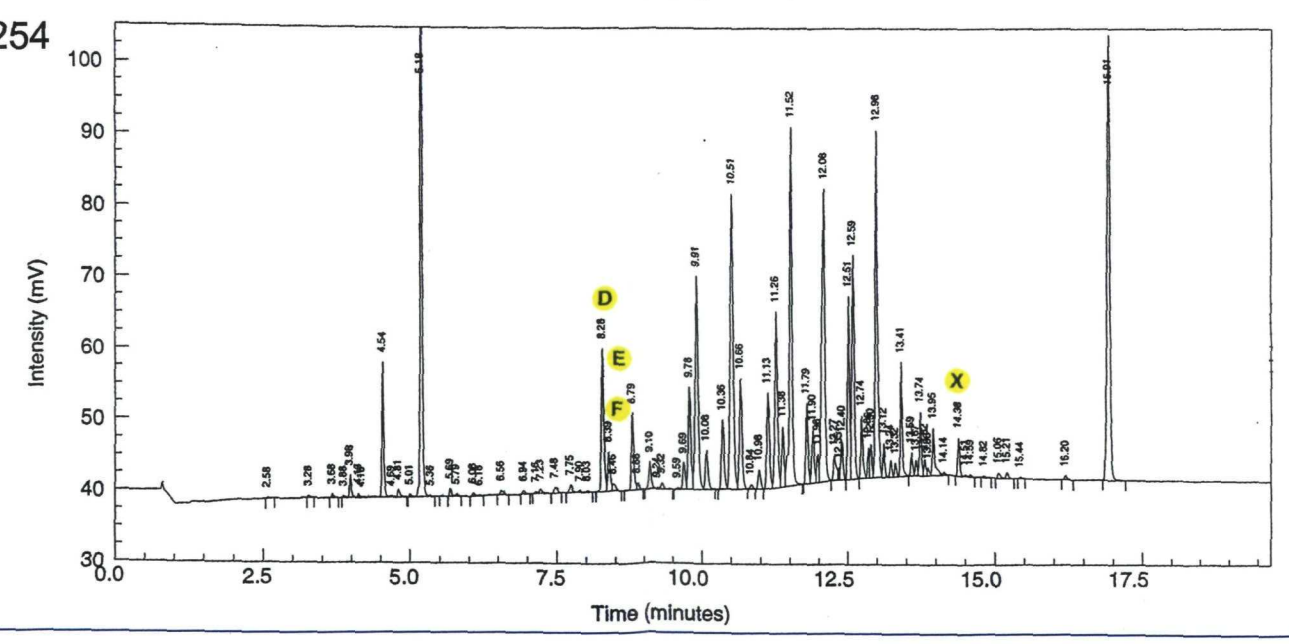
a. Sediment core ML3-3, 12-24-inch layer



b. Smallmouth bass fillet, without skin



c. Aroclor 1254



PCB Sources- Who are they?

- Morrow Lake
- Downstream of Morrow Lake and Upstream of Plainwell

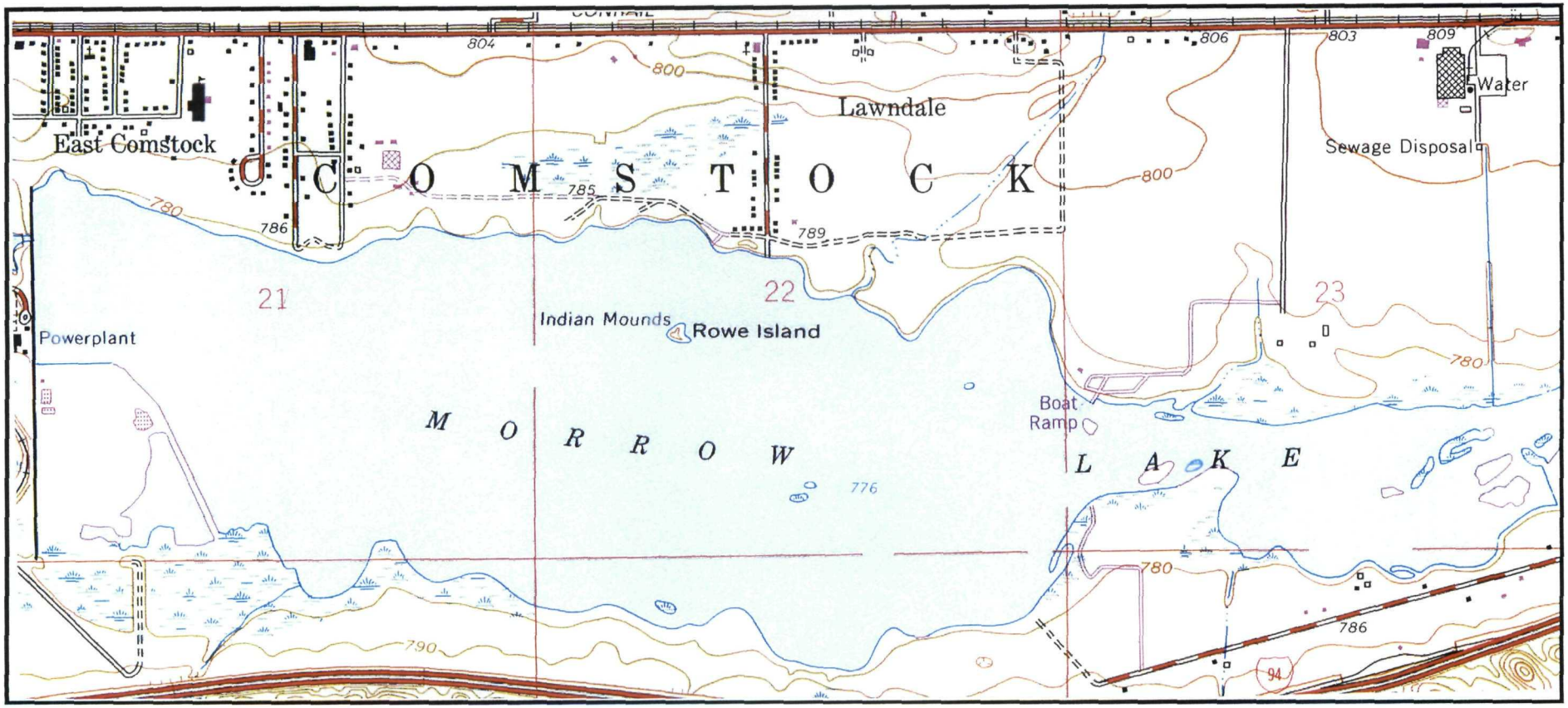
General Signal Corporation/Benteler Industries, Inc., Comstock Township

- Measured PCB concentrations up to 164 mg/kg in the drainage ditch leading to Morrow Lake. Aroclors 1248, 1254, and 1260 used to quantify.

- In 1990, the MDEQ asked Benteler to cease all discharges to the ditch due to possibility that "large storm water flows could transport PCB in the ditch to the Kalamazoo River."

- PCB spills in plant evident from PCB measured in concrete flooring. 289 cy of concrete was removed, remaining floor was decontaminated or decontaminated/encapsulated.

General Signal Corporation/Benteler Industries, Inc., Comstock Township



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Eaton Corporation

- Battle Creek:
  - Made engine valves; and
  - 1.4 µg/L – 1972 water sample in ditch.
- Kalamazoo:
  - Made heavy-duty truck transmissions.

Eaton - Wood Block Flooring

- Kalamazoo
  - In 1984, Eaton initiated a program of PCB sampling of the wooden tile blocks that make up most of the work area;
  - Over 70 tile blocks were sampled. PCB were detected up to 743 ppm; and
  - Approximately 1,500 to 2,000 ft^2 of wood block flooring with PCB greater than 50 ppm were removed.

- Battle Creek
  - About 9.1 acres of the Battle Creek facility were wood block flooring; and
  - Based on laboratory analysis of the wood block, approximately 20% of the block (1.8 acres) had PCB concentrations greater than 50 ppm.

Reference: McLaughlin, 2001.

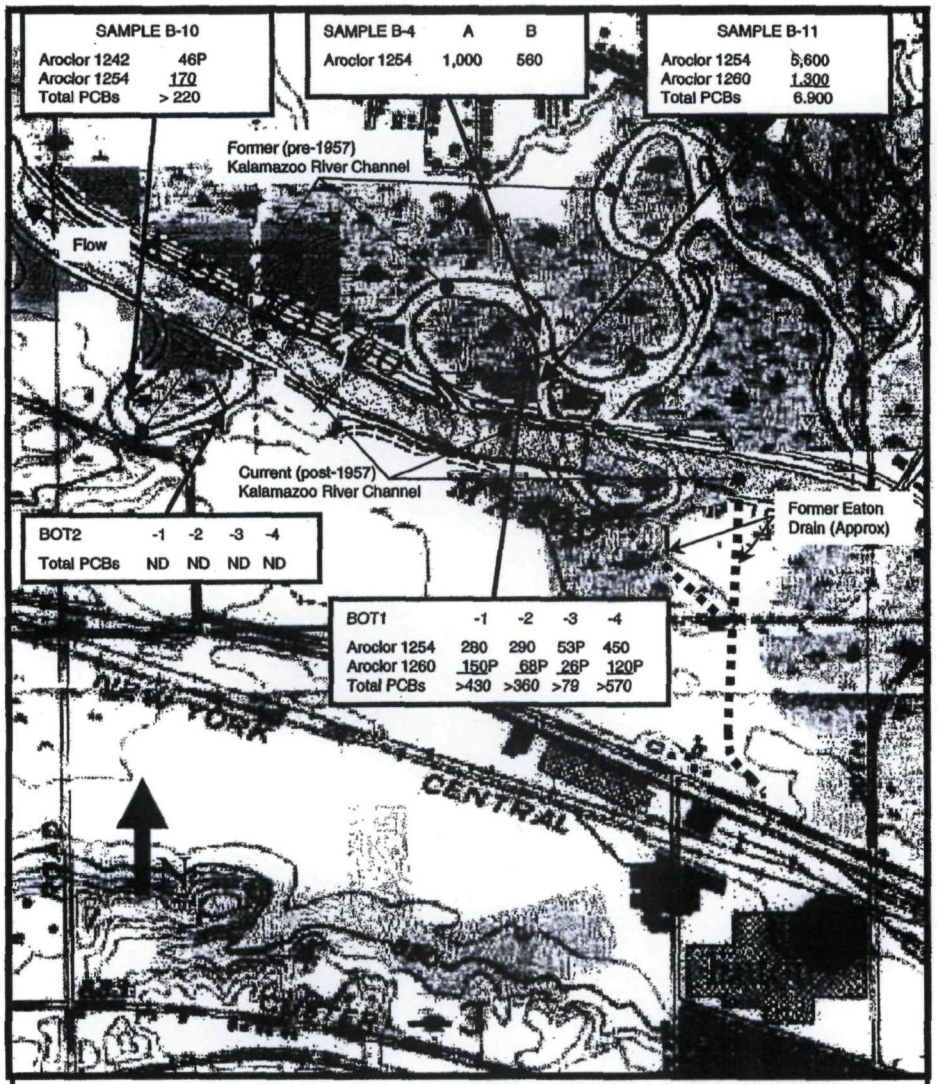
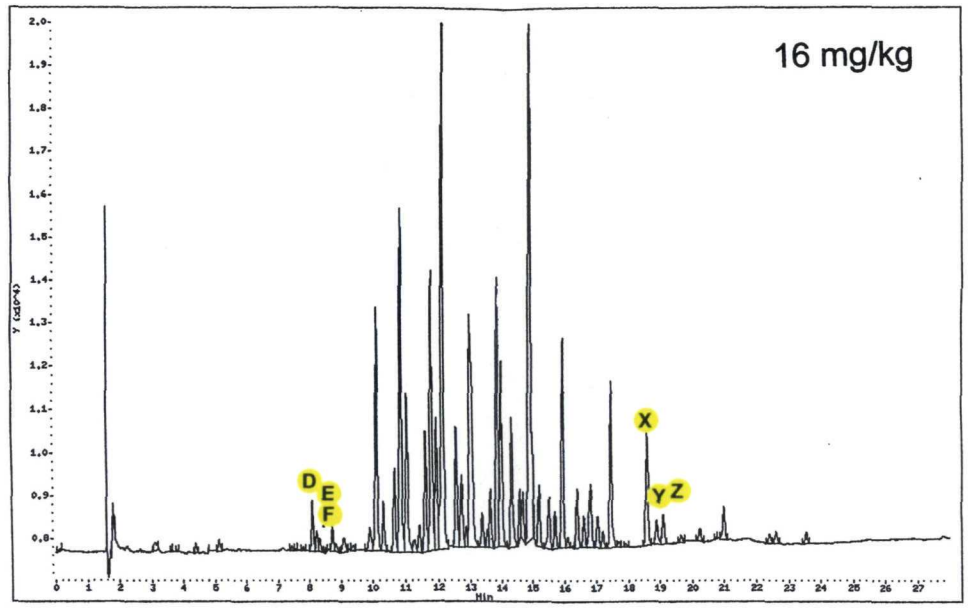


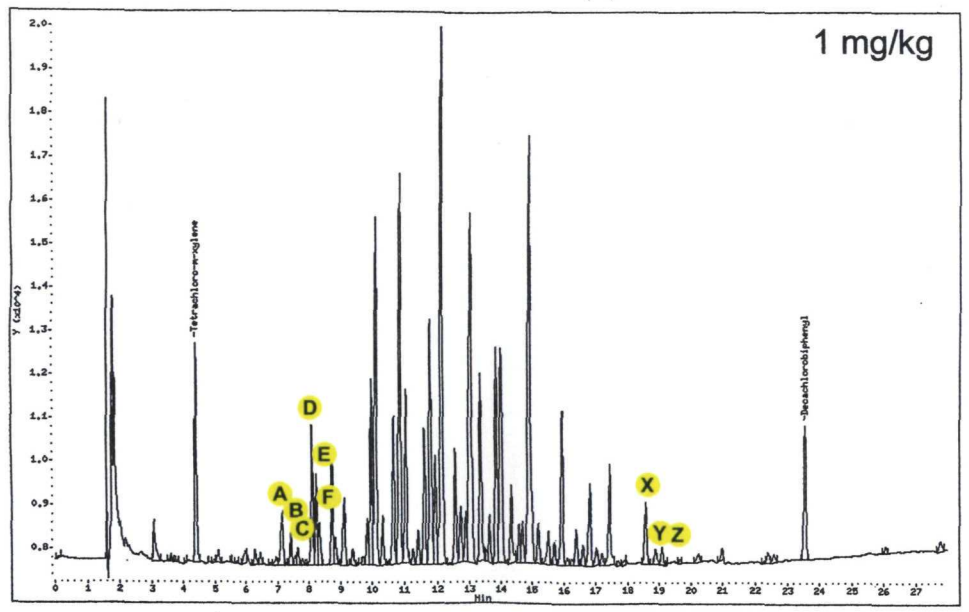
Figure 2. SAMPLE LOCATION MAP—OXBOWS
EATON BATTLE CREEK (SPRINGFIELD)

PCB Chromatograms for Eaton Battle Creek Outfall and Former River Channel Upstream of Morrow Lake

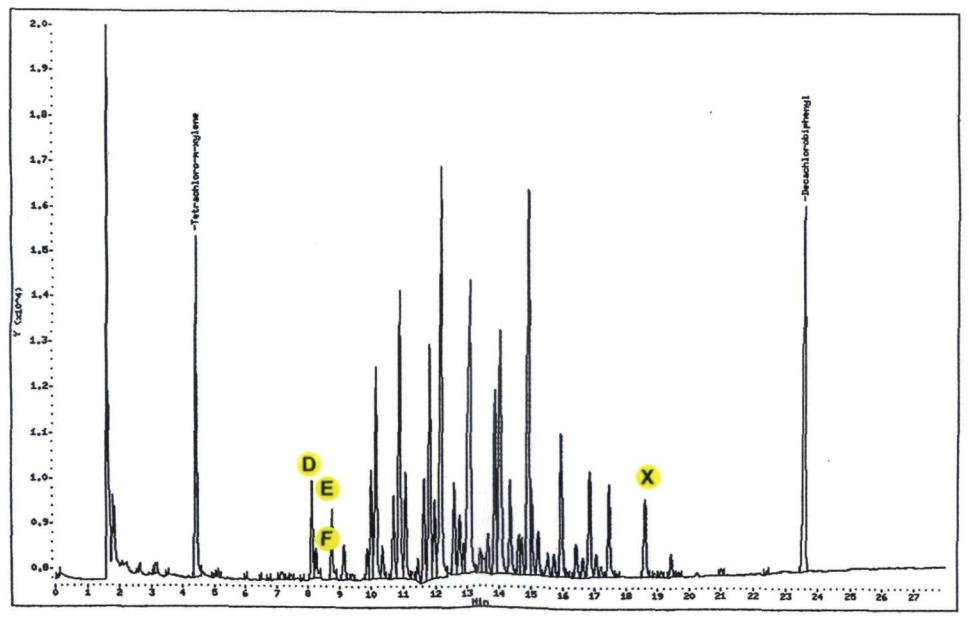
a. Eaton outfall sample B-5



b. Former river channel sample B-4A



c. Aroclor 1254



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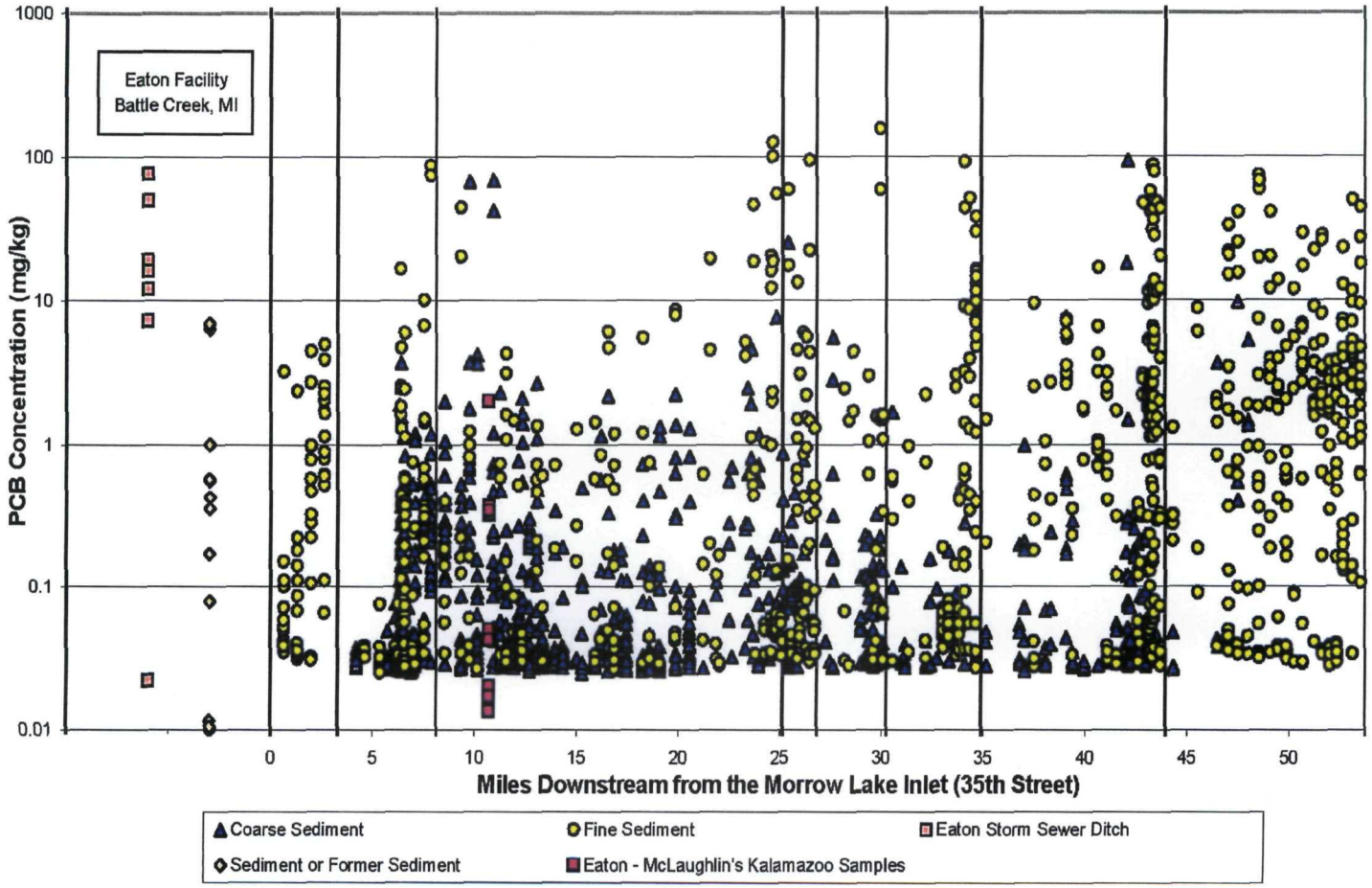
Comparison of McLaughlin's Eaton Battle Creek and Kalamazoo Samples to KRSG Sediment Samples



Notes:

1. Kalamazoo River sediment samples were from the "KPT-" locations, where cores were collected in 1993/1994 and analyzed in 1997 and 1999/2000. Samples were from depths not exceeding 24 inches.
2. Morrow Lake samples were from 16 sediment cores collected in summer 2000. Samples were from depths not exceeding 24 inches.
3. Eaton samples collected by SCS Engineers in 2001. Samples were from depths not exceeding 24 inches

Readily available documentation shows:

- Twelve industrial facilities discharged PCB to the Kalamazoo River;
- Six industrial facilities discharged PCB to a WWTP that discharges to the Kalamazoo River;
- Eight WWTPs discharged PCB to the Kalamazoo River;
- 10 facilities had PCB spills or leaks;
- Nine companies with PCB contaminated soils; and,
- more than 26 others used PCBs

Reference standards 1254/1248. Reference standards not same mix b/c diff. process used to make 42+54 – Tammy – seen more variability in 1254 standard than any other standard

Reference standards for 1254 – more variability

Stand. for 1242

Conclusions

* Tammy (CH2M Hill) agrees from lab

- Multiple sources of PCB;
- No evidence of massive NAPL loading of PCB;
- Aroclor 1254 responsible for half the fish PCB;
- Fish PCB can't be explained by weathering of Aroclor 1242; all – Tammy agreeded
- Aroclor 1242 does not weather to produce Aroclor-like PCB
- Aroclor 1254 was apparently widely used and released in the watershed
- Significant amount of Aroclor 1254 came over the Morrow Lake Dam; and
- There is a significant orphan share at the Site.

* Per Jim – another reason to use sediment not fish for determining source