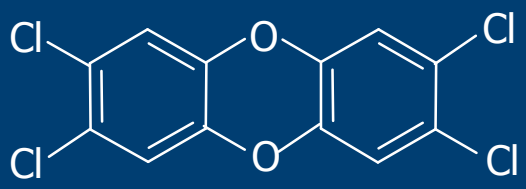
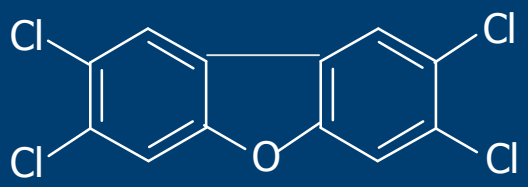
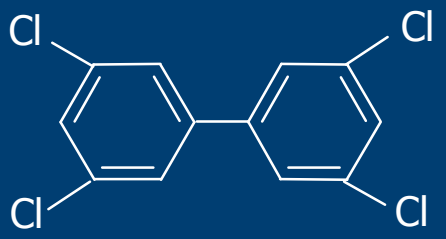
‘Dioxin-like’ Toxicity



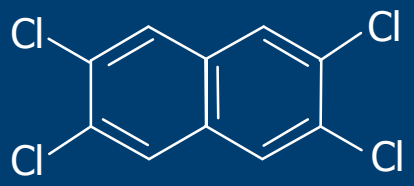
Dibenzo-p-dioxins



Dibenzofurans



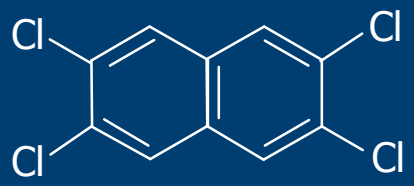
Polychlorinated biphenyls (PCBs)



Polychlorinated naphthalenes (PCNs)

Polychlorinated naphthalenes (PCNs)

- Chlorinated aromatic hydrocarbons
- Commercial mixtures; 75 congeners



Widely Used

- Production 1910-1980s
- Protective coating materials, dielectric fluids, cutting oils, engine oil additives, flame retardants, fungicides
- PCB formulations at ppm concentrations

Potential sources

- coal combustion, municipal solid waste incineration, metallurgical processes, chlor-alkali processes, impurities in PCB mixtures

PCN Bioaccumulation

- Mich./Great Lakes fish, bird eggs (Kannan et al. 2000, 2001)
- Great Lakes foodwebs (Helm et al 2008; Hanari et al. 2004)
- People (Lunden and Noren 1998)

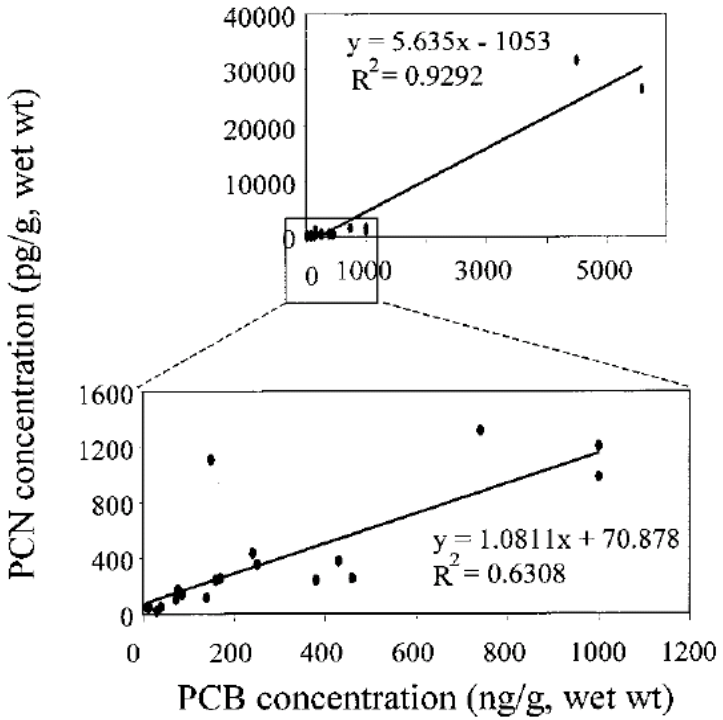


FIGURE 2. Relationship between PCB and PCN concentrations in fishes from Michigan waters.

(Kannan et al. 2000)

Relative Potencies of PCNs and Coplanar PCBs

TABLE 3. Concentrations (pg/g, wet wt) of Dioxin-like PCBs and PCNs in Double-Crested Cormorants and Herring Gulls from the Great Lakes in May 1998[a]

		double-crested cormorants			herring gulls		
	TEF	Little Charity Is.	Scarecrow Is.	Taquamenon Is.	Little Charity Is.	Scarecrow Is.	Taquamenon Is.
lipid (%)		4.6 (4–5.2)	6 (5.6–6.5)	5.8 (5.3–6.6)	8.9 (8.1–9.6)	10.2 (9.8–10.6)	11.3 (10.7–11.9)
				Coplanar PCBs			
77	0.000018	580 (280–920)	280 (250–310)	320 (130–510)	260 (160–360)	360 (210–500)	200 (73–340)
126	0.022	1500 (880–2200)	1100 (750–1500)	1300 (660–2400)	1460 (590–2300)	940 (340–1600)	2300 (135–4400)
169	0.00047	220 (140–340)	180 (160–210)	270 (130–450)	370 (150–580)	43 (27–58)	570 (27–1110)
105	0.00000035	40 (31–53)	32 (29–34)	34 (18–60)	52 (23–81)	71 (68–74)	97 (7.1–190)
118	0.000008	130 (110–170)	110 (95–120)	110 (72–190)	140 (59–220)	230 (230)	260 (21–510)
156	0.000055	11 (8.2–16)	9.5 (8.9–10.4)	12 (6.8–20)	16 (8.5–23)	29 (29)	33 (3–62)
				Dioxin-like PCNs			
54	0.00017	2.6 (1.4–3.9)	1.3 (0.7–2.3)	1.3 (0.31–2)	<0.1	<0.1	0.48 (<0.1–0.48)
56	0.000049	1.3 (0.47–2.9)	0.75 (0.46–1.1)	0.51 (0.16–1)	3.3 (0.5–6.1)	0.98 (0.87–1.1)	0.4 (0.13–0.68)
57	0.0000037	12 (6–21)	9.7 (6.7–15)	13 (1.9–23)	<0.1	0.63 (0.87–1.1)	0.94 (<0.1–0.94)
60	1.42E–05	280 (150–520)	290 (130–550)	300 (98–600)	9.5 (7–12)	38 (17–58)	21 (6.3–35)
63	0.002	6.5 (3.6–12)	4.2 (2.9–6.3)	5 (1–8)	0.27 (<0.1–0.27)	0.64 (0.61–0.68)	0.27 (0.24–0.31)
66	0.0024	400 (160–770)	330 (190–500)	310 (120–620)	530 (390–660)	350 (270–420)	630 (60–1190)
68	0.0015	38 (20–70)	31 (19–51)	37 (11–69)	3.3 (2.4–4.2)	5.8 (3.6–8)	3.3 (0.6–6)
69	0.002	72 (30–140)	88 (30–190)	59 (20–110)	2.3 (2–2.6)	7.6 (5.1–10)	4.2 (1.5–7)
70	0.0095	1.1 (0.61–1.6)	0.31 (0.22–0.41)	0.51 (0.51)	0.76 (<0.1–0.76)	0.48 (<0.1–0.48)	0.60 (0.23–0.97)
73	0.001	3.7 (0.92–6.7)	1.7 (1.5–2)	1.6 (1.3–2.2)	12 (3.2–22)	0.72 (<0.1–0.72)	4.5 (0.89–8.2)

[a] Concentrations of PCB congeners 105, 118, and 156 are in ng/g,wet wt. Congeners 64 and 67 elicit dioxin like activity, but they coelute with congeners 68 and 66, respectively. Congeners 71 and 72 are active, but their potencies relative to TCDD are uncertain. H4IIE-TEFs for PCNs were from refs *9*, *10*, or *12*. H4IIE-TEFs for PCBs were from ref *22*.

(Kannan et al. 2001)

PCNs contributed 2-3% of the sum dioxin toxic equivalents (TEQ) in bird eggs collected far from local sources in the Great Lakes

TABLE 4. Mean 2,3,7,8-Tetrachlorodibenzo-*p*-Dioxin Equivalents (pg/g, wet wt) of PCBs, PCNs, PCDDs, and PCDFs in Double-Crested Cormorants and Herring Gulls Collected from the Great Lakes in May 1998

	double crested cormorants			herring gulls		
	Little Charity Is.	Scarecrow Is.	Taquamenon Is.	Little Charity Is.	Scarecrow Is.	Taquamenon Is.
PCBs	33 (60)	25 (71)	28 (73)	32 (60)	21 (58)	51 (73)
PCNs	1.1 (2)	1 (3)	0.89 (2)	1.3 (2)	0.85 (2)	1.5 (2)
PCDDs	13 (24)	3.2 (9)	6.3 (17)	19 (36)	11 (30)	15 (22)
PCDFs	7.8 (14)	6 (17)	3.1 (8)	0.92 (2)	3.4 (10)	2.4 (3)
total	55	35	38	53	36	70

(Kannan et al. 2001)

PCN contribution to sum TEQ similar or greater than PCB contribution in fish collected from the Detroit River

TABLE 2. Mean Concentrations of Dioxin-Like PCN Congeners and Their 2,3,7,8-TCDD Equivalents (pg/g, Wet Wt) in Fishes from Michigan Waters

		wholebody						fillet									
		Detroit River (3)[a]		Lake Superior (2)		Siskiwit Lake (1)		Lake Superior (2)		Siskiwit Lake (3)		Lake Huron (2)		Lake Michigan (1)		inland waterbodies (8)	
congener	TEF[e]	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs
40	0.000016	ND[f]	ND	ND	ND	ND	ND	ND	ND	0.03	<0.0001	0.91	<0.0001	ND	ND	0.18	<0.0001
54	0.00017	420	0.07	5.8	0.001	ND	ND	2.95	0.0005	0.74	0.0001	10	0.0017	8.1	0.001	2.2	0.0004
63	0.002	330	0.66	3.9	0.008	0.69	0.0014	2.94	0.006	0.54	0.001	20	0.034	8.1	0.016	1.4	0.003
66/67[b]	0.0023	890	2.1	29	0.066	87	0.2	31	0.071	13	0.029	180	0.41	110	0.25	6	0.014
68[c]	0.00015	1300	0.19	12	0.002	19	0.002	8.9	0.001	5.5	0.0008	45	0.007	43	0.006	4.2	0.0006
69	0.002	2400	4.7	21	0.042	43	0.09	14	0.028	7.7	0.015	77	0.15	58	0.12	9.3	0.019
70	0.00059	ND	ND	0.69	0.0004	ND	ND	0.43	0.0003	0.29	0.0002	1.8	0.001	0.64	0.0004	ND	ND
71/72[d]	0.000007	3000	0.02	13	<0.0001	11	<0.0001	7.8	<0.0001	4.9	<0.0001	43	0.0003	47	0.0003	14	0.0001
73	0.001	80	0.08	3.1	0.003	2.2	0.002	2.9	0.003	0.63	0.0006	8.2	0.008	4.8	0.005	0.37	0.0004
total			**7.8**		**0.12**		**0.29**		**0.11**		**0.047**		**0.63**		**0.4**		**0.04**

[a] Values in parentheses indicate the number of samples. [b] TEF for 66/67 represents mean TEF of each congener. [c] Congener 68 coelutes with 64, but the TEF value is available only for congener 68. [d] Congener 71 is inactive (ref *21*), but a mixture of 71/72 was active (ref *20*). [e] TEFs for PCNs are from ref *20* and *21*. [f] ND = not detected; <0.0001 indicates that the congeners were detected but at attogram levels.

TABLE 3. Mean Concentrations of Non- and Mono-Ortho-PCB Congeners and Their H4IIE-in Vitro Bioassay TEF Based 2,3,7,8-TCDD Equivalents (pg/g, Wet Wt) in Fishes from Michigan Waters

		wholebody						fillet									
		Detroit River (3)[b]		Lake Superior (2)		Siskiwit Lake (1)		Lake Superior (2)		Siskiwit Lake (3)		Lake Huron (2)		Lake Michigan (1)		inland waterbodies (8)	
congener	H4IIE-TEF[a]	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs
77	1.8E-05	3980	0.07	290	0.005	60	0.001	475	0.009	46	0.001	1600	0.029	3810	0.07	88	0.002
126	2.2E-02	256	5.60	120	2.7	97	2.1	72	1.58	17	0.37	220	4.76	430	9.46	13	0.283
169	4.7E-04	24	0.01	35	0.02	110	0.05	16	0.007	19	0.009	41	0.019	43	0.02	1.3	0.001
105	8E-06	50 900	0.41	8700	0.07	9400	0.08	8300	0.067	1400	0.011	20 000	0.16	32900	0.26	2500	0.02
118	3.5E-07	119 000	0.05	21 600	0.01	23 900	0.01	17 300	0.007	3200	0.001	41 800	0.017	64 800	0.03	7100	0.003
156	5.5E-05	13 700	0.69	2500	0.13	4800	0.24	1800	0.09	570	0.028	4180	0.209	6300	0.32	880	0.044
total			**6.9**		**2.9**		**2.5**		**1.8**		**0.42**		**5.2**		**10**		**0.352**

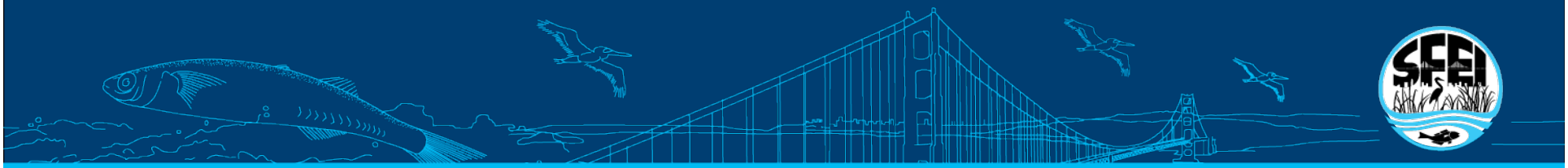
[a] H4IIE-TEFs for PCBs are from ref *31*. [b] Values in parentheses indicate the number of samples.

Concern for San Francisco Bay?

- Few data available; chemical analysis challenging
- Potential association between PCNs and PCBs?
- Dioxin-like chemical

Analysis of PCNs will tell us:

- Significance of PCNs as dioxin-like chemical in SF Bay
- Bioaccumulation behavior relative to PCBs



FIVE YEAR PLAN FOR RMP DIOXIN WORK

Sample Design Element	Questions Addressed	2008	2009	2010	2011	2012	Total by Element
Sport fish	1,2,4,6		$22,000			$22,000	$44,000
Bird eggs	2,4,					$10,000	$10,000
Surface sediment	2,3 6	$57,000	$57,000			$57,000	$171,000
In-Bay surface water	3,6		$20,000		$20,000		$40,000
Sediment cores	3,4,6	$57,000					$57,000
Trib. loadings, Delta outflow	5,6		$34,000 (Small Trib)	$34,000 (Small Trib) $34,000 (Delta outflow)	$34,000 (Small Trib) $34,000 (Guadalupe)		$170,000
Atmospheric deposition	5,6		$25,000				$25,000
One-box model	6			$20,000			$20,000
Foodweb model	6					$20,000	$20,000
QA/QC lab intercomparison			$20,000				$20,000
Total by Year		$114,000	$178,000	$88,000	$88,000	$109,000	$577,000

PCNs in Sport Fish ($4,500)

- 2009 sport fish (S&T monitoring)
- White croaker, 2 composites @ 3 sites (6 total)
- Dioxins funded, dioxin-like PCBs not funded
- Exposure risk to fish-eating wildlife, people

PCNs in Cormorant Eggs ($4,500)

- 2009 Cormorant eggs (S&T monitoring)
- PCNs in 2 comps/site (6 total)
- No dioxin or coplanar PCB analysis planned for 2009; could analyze archives in future