AROCLOR MIXTURES: PATTERN RECOGNITION IN ENVIRONMETNAL AND BIOLOGICAL MATRICES

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Introduction

Polychlorinated biphenyls (PCBs) were first synthesized in the early 1880s by Schmidt and Schultz.[1] The term 'Aroclor' is trade name for PCB mixtures manufactured by the Monsanto Company in the United States. The most common Aroclors produced were Aroclor 1016, Aroclor 1221, Aroclor 1232, Aroclor 1242, Aroclor 1248, Aroclor 1254, and Aroclor 1260[2-4]. Over a million tons of PCBs were produced from 1929 through mid-1970s and used in variety of industries.[3] Wide spread use of PCBs lead to environmental contamination and health effects in wildlife and humans. [5,6] Due to recalcitrant properties, bioaccumulation, biomagnification in food chain and harmful health effects of these compounds, the production of PCBs were banned in the United States in the mid-1970s.[5] Although the production of PCBs were restricted about four decades ago, PCBs continue to cause environmental health problems.[5,6] Earlier studies measured PCBs in environmental and biological samples primarily based on total PCBs (sum of PCB congeners measured). Little emphasis was given on the quantitation of PCBs as Aroclor mixtures in the environmental and biological samples. Identification of Aroclors in the samples will help in tracking the contamination sources of the Aroclor mixture. In this study an attempt has been made to recognize Aroclor signatures in environmental and biological samples using various Aroclors such as Aroclor 1016, Aroclor 1221, Aroclor 1232, Aroclor 1242, Aroclor 1248, Aroclor 1254, Aroclor 1260, and Aroclor 1268. The gas chromatography equipped with HP-5 capillary column and an electron capture detector (GC-ECD) was used for separation and quantification of PCBs.

Materials and methods

Aroclor standards (Aroclor 1016, Arcolor 1232, Aroclor 1242, Aroclor 1248, Aroclor 1260 and Arcolor 1268) (100 µg/mL in hexane) were obtained from UltraScientific, North Kingstown, RI, USA. Standard Reference Material (SRM)-2262 containing representative PCB congeners (*mono* to *deca*chlorobiphenyls) was obtained from National Institute of Standards and Technology (NIST), Gaithersburg, Maryland, USA. The standards were diluted using clean hexane. Individual Arcolor mixture concentration was 4 ng/µL and individual PCB congener concentration in SRM solution was 80 pg/µL. The standards were injected into an Agilent Technologies 7890A gas chromatograph equipped with ^{63}Ni electron capture detector (ECD). The column oven temperature was programmed as follows: Initial temperature 90°C held at 1 min. The oven temperature was raised to 180°C at the rate of 5°C/minute with hold time of 0 min. Ramp 2: the oven temperature was raised to 280°C at the rate of 2°C/minute with final hold time of 13 minutes Ultra high purity helium and nitrogen were used as carrier and makeup gas respectively. Helium flow rate was 1 mL/min. Injector and detector temperatures were 270°C and 330°C respectively. The GC-ECD was calibrated using the NIST SRM-2262.

Environmental (sediment) and biological samples (pine needle, freshwater mussel, shrimp and fish) were selected and analyzed to identify the presence of Aroclor mixtures. Sediment samples were selected from three locations, Savannah River, Savannah, GA, Kentucky Lake, and New York. Selected biological samples (extract) included pine needle (superfund site), mussel (KY Lake), freshwater drum, shad, gizzard shad, sunfish (KY Lake), largemouth bass (KY Lake, Lower most Tennessee River) and Shrimp, Fish (Savannah River, Savannah, GA), These samples extracts were analyzed into a GC-ECD. SAS statistical analysis software was used to perform cluster analysis of various PCB congeners to identify Aroclor mixtures.

Results and discussion

Table 1 to 7 shows PCB congener composition (percent) in sediment (8A- from coastal region of Savannah, GA, KY-1-SD-2 sediment from Kentucky Lake, fish (LMB-HBS, largemouth bass collected near Hancock Biological Station, LMB-LTR-largemouth bass collected from Lower most Tennessee River, DRUM-KYL- freshwater

drum collected from Kentucky Lake), shrimp (collected from coastal waters of Savannah, GA) in comparison with the congener composition in Aroclor 1016, 1232, 1242, 1248, 1254, 1260 and 1268. Percent composition allows us to see Aroclor fingerprint in the environmental and biological samples. Observation of PCB congener composition in comparison to the congener distributing the samples indicate the presence two or more Aroclors contributing to the contamination in the environmental as well as biological tissues.

Table 1. PCB congener composition (%) in sediment, fish tissues and shrimp samples in comparison with the composition in Aroclor 1016.

PCBs	SED 8-A	KY-1 SD-2	LMB-HBS	LMB-LTR	DRUM-KYL	Shrimp-3	S-2	AROLCOR 1016(ng/mL)
8	3.70	0.00	0.22	0.97	0.15	5.80	1.51	8.10
18	14.27	0.00	0.51	0.86	2.13	6.68	0.00	9.30
52	13.92	26.19	5.46	7.94	7.79	10.26	0.00	4.60
101	5.52	22.11	10.78	8.61	0.00	7.46	13.75	0.00
153	4.35	2.38	14.60	9.84	23.10	9.59	0.00	0.00
170	1.09	0.00	3.65	2.81	0.00	0.00	0.67	0.00
201	0.00	0.00	0.24	0.52	0.26	0.00	5.31	0.00
206	0.61	0.00	0.16	0.99	0.08	0.00	21.46	0.00

Table 2. PCB congener composition (%) in sediment, fish tissues and shrimp samples in comparison with the composition in Aroclor 1232.

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PCBs	SED 8-A	KY-1 SD-2	LMB-HBS	LMB-LTR	DRUM-KYL	Shrimp-3	S-2	AROCLOR 1232(ng/mL)
8	3.70	0.00	0.22	0.97	0.15	5.80	1.51	10.00
18	14.27	0.00	0.51	0.86	2.13	6.68	0.00	5.10
52	13.92	26.19	5.46	7.94	7.79	10.26	0.00	2.30
101	5.52	22.11	10.78	8.61	0.00	7.46	13.75	0.50
153	4.35	2.38	14.60	9.84	23.10	9.59	0.00	0.00
170	1.09	0.00	3.65	2.81	0.00	0.00	0.67	0.00
201	0.00	0.00	0.24	0.52	0.26	0.00	5.31	0.00
206	0.61	0.00	0.16	0.99	0.08	0.00	21.46	0.00

Table 3. PCB congener composition (%) in sediment, fish tissues and shrimp samples in comparison with the composition in Aroclor 1242.

PCBs	SED 8-A	KY-1 SD-2	LMB-HBS	LMB-LTR	DRUM-KYL	Shrimp-3	S-2	AROCLOR 1242(ng/mL)
8	3.70	0.00	0.22	0.97	0.15	5.80	1.51	7.60
18	14.27	0.00	0.51	0.86	2.13	6.68	0.00	8.90
52	13.92	26.19	5.46	7.94	7.79	10.26	0.00	4.60
101	5.52	22.11	10.78	8.61	0.00	7.46	13.75	1.60
153	4.35	2.38	14.60	9.84	23.10	9.59	0.00	0.30

170	1.09	0.00	3.65	2.81	0.00	0.00	0.67	0.00
201	0.00	0.00	0.24	0.52	0.26	0.00	5.31	0.00
206	0.61	0.00	0.16	0.99	0.08	0.00	21.46	0.00

Table 4. PCB congener composition (%) in sediment, fish tissues and shrimp samples in comparison with the composition in Aroclor 1248.

PCBs	SED 8-A	KY-1 SD-2	LMB-HBS	LMB-LTR	DRUM-KYL	Shrimp-3	S-2	AROCLOR 1248(ng/mL)
8	3.70	0.00	0.22	0.97	0.15	5.80	1.51	0.80
18	14.27	0.00	0.51	0.86	2.13	6.68	0.00	4.70
52	13.92	26.19	5.46	7.94	7.79	10.26	0.00	7.50
101	5.52	22.11	10.78	8.61	0.00	7.46	13.75	2.90
153	4.35	2.38	14.60	9.84	23.10	9.59	0.00	0.30
170	1.09	0.00	3.65	2.81	0.00	0.00	0.67	0.00
201	0.00	0.00	0.24	0.52	0.26	0.00	5.31	0.00
206	0.61	0.00	0.16	0.99	0.08	0.00	21.46	0.00

Table 5. PCB congener composition (%) in sediment, fish tissues and shrimp samples in comparison with the composition in Aroclor 1254

PCBs	SED 8-A	KY-1 SD-2	LMB-HBS	LMB-LTR	DRUM-KYL	Shrimp-3	S-2	AROCLOR 1254(ng/mL)
8	3.70	0.00	0.22	0.97	0.15	5.80	1.51	0.00
18	14.27	0.00	0.51	0.86	2.13	6.68	0.00	0.00
52	13.92	26.19	5.46	7.94	7.79	10.26	0.00	5.90
101	5.52	22.11	10.78	8.61	0.00	7.46	13.75	9.40
153	4.35	2.38	14.60	9.84	23.10	9.59	0.00	5.40
170	1.09	0.00	3.65	2.81	0.00	0.00	0.67	1.00
201	0.00	0.00	0.24	0.52	0.26	0.00	5.31	0.20
206	0.61	0.00	0.16	0.99	0.08	0.00	21.46	0.00

Table 6. PCB congener composition (%) in sediment, fish tissues and shrimp samples in comparison with the composition in Aroclor 1260.

PCBs	SED 8-A	KY-1 SD-2	LMB-HBS	LMB-LTR	DRUM-KYL	Shrimp-3	S-2	AROCLOR 1260 (ng/mL)
8	3.70	0.00	0.22	0.97	0.15	5.80	1.51	0.00
18	14.27	0.00	0.51	0.86	2.13	6.68	0.00	0.00
52	13.92	26.19	5.46	7.94	7.79	10.26	0.00	0.20
101	5.52	22.11	10.78	8.61	0.00	7.46	13.75	3.10
153	4.35	2.38	14.60	9.84	23.10	9.59	0.00	9.90
170	1.09	0.00	3.65	2.81	0.00	0.00	0.67	5.00

201	0.00	0.00	0.24	0.52	0.26	0.00	5.31	0.40
206	0.61	0.00	0.16	0.99	0.08	0.00	21.46	0.50

Table 7. PCB congener composition (%) in sediment, fish tissues and shrimp samples in comparison with the composition in Aroclor 1268.

PCBs	SED 8-A	KY-1 SD-2	LMB-HBS	LMB-LTR	DRUM-KYL	Shrimp-3	S-2	AROCLOR 1268(ng/mL)
8	3.70	0.00	0.22	0.97	0.15	5.80	1.51	0.00
18	14.27	0.00	0.51	0.86	2.13	6.68	0.00	0.00
52	13.92	26.19	5.46	7.94	7.79	10.26	0.00	0.00
101	5.52	22.11	10.78	8.61	0.00	7.46	13.75	0.00
153	4.35	2.38	14.60	9.84	23.10	9.59	0.00	0.00
170	1.09	0.00	3.65	2.81	0.00	0.00	0.67	0.00
201	0.00	0.00	0.24	0.52	0.26	0.00	5.31	1.40
206	0.61	0.00	0.16	0.99	0.08	0.00	21.46	30.00

The tables show presence of multiple Aroclors in environmental and biological samples. Among the various samples examined, S-2 (pine needle) sample from a Superfund site revealed higher percentage of *octa-, nona-, and deca* chloro biphenyls which is signature of Aroclor 1268. Sediment samples from Savannah, GA (Atlantic coast) contained congeners representing Aroclor 1016, 1232, 1242 and 1248. Presence of multiple Aroclor signatures in the environmental and biological samples (except S-2) indicated non-point source of contamination in these samples. Pine needle sample (S-2) from Brunswick, GA revealed point-source contamination. This study provides evidence that environmental and biological samples are exposed to some specific Aroclor mixtures.

References

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