Bull Environ Contam Toxicol (2009) 83:899–902
DOI 10.1007/s00128-009-9874-6

Determination of Polychlorinated Biphenyl Congeners in Water and Sediment in North West Persian Gulf, Iran

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Received: 9 April 2009 / Accepted: 9 September 2009

Abstract Polychlorinated biphenyl (PCB) was detected as isomer groups (congener numbers 28, 52, 101, 118, 138, 153 and 180) in the coastal water and sediment of four stations around Shadegan wetland protected area in the northwestern part of the Persian Gulf. Total PCB concentration range was 8–375 ng/L in water and 3.4–50.2 μg/g in sediment. Concentration of different congeners and chromatogram indicates that the source of PCB in this area can be Clophen A60; it used for long time in Iranian electronic industries. Other chlorinated hydrocarbons such as lindane, DDT and their metabolites were also present in the samples.

Keywords Polychlorinated biphenyl · Clophen · Persian Gulf · Iran

Polychlorinated biphenyls (PCBs) are a class of non-polar, non-flammable industrial fluids with good thermal and chemical stability consisting of 209 congeners (Erickson 1997; Loveridge et al. 2007; Hu et al. 2009). Because of their electrical insulating properties, PCBs have been used as dielectric fluids in transformers and capacitors, as heat-transfer and hydraulic fluids, as plasticizers in paint, copying papers, adhesives, sealant, and plastics, and as a component in lubricating and cutting oils.

PCBs are anthropogenic contaminants of long-term environmental concern. PCBs were used in open systems from 1929, when worldwide commercial production began, until 1972. From 1950 to 1980, PCBs were also used in closed systems, such as transformers and capacitors, as well as for underground mining (hydraulic fluids). PCB accumulation in the biotic environment is widespread and highly conservative (Erickson 1997; NRC 1979).

Imam Khomeini Port is the biggest port in Iran, making Musa Khoor the most economically important area of the North West Persian Gulf. The Mahshahr Port is one of the major crude oil export terminals of Iran and is the site of many factory and petrochemical complexes. Several articles published in field of determination, monitoring and assessment of Polychlorinated biphenyls (Blanco-Penedo et al. 2008; Fu et al. 2008; Li et al. 2007; Loveridge et al. 2007). But there has not been any literature work done about level of PCBs in Persian Gulf.

The propose of this study was examination of the presence of PCBs in Musa Khoor, located in the north west of the Persian Gulf, Iran. This region occurs in the southern part of Shadegan wetland protected area.

Materials and Methods

Chemicals and solvents were pesticide grade for residue analysis and purchased from Merck (Darmstadt, Germany). A mixture of 7 PCB congeners ranging from tri- to hepta-chlorobiphenyls in isooctane was used as the PCB standard for this study (Table 1). Before extraction, octachloronaphthalene (OCN) as internal standards (IS) were added to

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Table 1 PCBs analyzed in this study

No.	IUPAC No.	Structure
1	28	2, 4, 4′
2	52	2, 2′, 5, 5′
3	101	2, 2′, 4, 5, 5′
4	118	2, 3′, 4, 4′, 5
5	138	2, 2′, 3, 4, 4′, 5′
6	153	2, 2′, 4, 4′, 5, 5′
7	180	2, 2′, 3, 4, 4′, 5, 5′

the samples. PCB stock solutions standards were prepared using dichloromethane (DCM) and *n*-hexane and storing in a freezer −20°C in glass bottles with PTFE-faced screw caps.

Samples were collected from four stations in Shadegan wetland protected area in the northwestern part of the Persian Gulf. From the west to east, sampling stations are denoted Imam Khomeini Port (IKP), Majidieh Khoor (MK), Mahshahr Port (MP) and Musa Khoor Estuary (MKE). Sea water samples (2 L) were collected using a shallow water sampler (hydro bios, Germany). The samples stored in cool (4°C), dark place and before being sent to the laboratory for extraction (Csuros 1997).

Surface coastal sediments were collected from bottom accumulation. One to three replicates were collected from each sampling station. Samples from each station were collected in autumn and spring, homogenized and stored frozen until extraction.

Water samples were extracted with dichloromethane using a separatory funnel. A 100 g portion of sediment samples was frozen at –20°C, freeze-dried, ground, and homogenized. Dried samples were extracted with DCM using an ultrasonic bath (US EPA 1991). Samples were further purified with a simple column chromatographic partition.

A chromatography column was prepared using a 50 mL burette in which a piece of glass wool was added near the stopcock to maintain the packing. Then the column was filled with *n*-hexane and 10 mL of silica was transferred into the column gradually while the column was knocked to compact the particles. Subsequently, 10 mL of alumina and, on top, 3 g anhydrous granulated sodium sulphate were added to prevent disturbance of the first layer when solvents were poured into the column. The DCM extract was concentrated to 1 mL by evaporation with nitrogen blow down. Concentrates were reconstituted to a final volume of 100 μL before further analysis (Albro et al. 1977, 1981; Kannan et al. 1987; Ayris 1997).

One microliter of each sample was injected into a gas chromatograph (GC-14A, Shimadzu, Kyoto), coupled with a Shimadzu QP-XP1100 Mass Selective Detector that was equipped with a fused silica capillary column (Agilent Technology DB-5MS, 60 meter long, 0.32 mm i.d., Ft. = 0.25 μm). Data were acquired in the electron impact (EI) mode (70 eV) using the total ion current (TIC) technique.

The injector and detector were maintained at 290°C and the oven temperature was programmed to increase from 50 to 205°C at a rate of 15°C/min and from 205 to 300°C at a rate of 2°C/min before being held at 300°C for 10 min. The initial holding time at 50°C was also 5 min (Duinker and Hillebrand 1983; Kannan et al. 1987; Ayris et al. 1997).

The United State Environmental Protection Agency (US EPA) guidelines were used to assess whether the data for the samples were of acceptable quality (US EPA 1991).

The types of quality control (QC) checks and the frequency at which checks were performed such as use of replicate samples, duplicate and triplicate. Duplicate analyses for PCBs were average 18%. Detection limit was 2 ng/L for water and 0.1 μg/g for sediment.

Instrument and extraction blanks were used and were analyzed daily. All solvents were checked for organic contamination. The average recovery for water and sediment samples was 86.1 ± 17.8% and 92.2 ± 9.9%, respectively, %RSD = 8.4.

Results and Discussion

The concentrations of PCBs in the water and sediment are summarized in Tables 2 and 3, respectively. The total (sum of 7 congeners) concentration of PCBs in water were from 8 to 375 ng/L and the average value was 93.25 ng/L.

The total concentrations of PCBs in sediment were from 3.4 to 50.2 μg/g and the average value was 18.22 μg/g.

The majority of samples show a preferential accumulation in the coastal sediment, as can also be observed by comparing the median.

Table 2 Concentrations (ng/L) of PCBs in autumn (A) and spring (S) in water samples

Station	Season	PCB congener							
		28	52	101	118	138	153	180	ΣPCB
IKP	A	ND	3	7	6	13	16	7	52
IKP	S	ND	4	4	3	6	9	6	32
MK	A	17	29	51	42	81	102	53	375
MK	S	9	8	18	21	36	31	17	140
MP	A	8	6	2	7	10	19	11	63
MP	S	2	5	ND	12	21	6	16	62
MKE	A	ND	2	ND	ND	2	4	ND	8
MKE	S	ND	ND	ND	2	6	6	ND	14

Table 3 Concentrations (μg/g, dry weight) of PCBs in autumn (A) and spring(S) in sediment samples

Station	Season	PCB congener							
		28	52	101	118	138	153	180	ΣPCB
IKP	A	0.1	ND	0.2	0.4	0.8	0.9	1	3.4
IKP	S	0.2	0.2	0.3	0.6	1.6	1.2	1.1	5.2
MK	A	1.9	1	4.1	7	8.7	13.6	5.2	41.5
MK	S	1.6	1.2	4.4	8	10.2	18.4	6.4	50.2
MP	A	0.4	0.2	2.1	2.8	4.1	1	4.4	15
MP	S	0.1	0.4	1	3.3	3.7	4.2	5	17.7
MKE	A	ND	0.6	0.7	1.2	1.4	1.1	1.6	6.6
MKE	S	0.2	0.8	0.6	0.9	1.1	1.2	1.4	6.2

Both PCBs congeners 138 and 153 were found in all water samples at concentrations as high as 81 and 102 ng/L, respectively. Incidentally, both of these concentrations were observed in the all sediment samples (refer to Table 3). This level of PCB 153 is also the highest PCB congener detected in all samples. The total PCB concentrations in the sediment samples ranged from 3.4 to 50.2 μg/g and the average value was 18.22 μg/g. The highest concentration of total PCBs was observed in sampling station 2 Majidieh Khoor, which is near to industrial waste disposal site.

The results show that low chlorine PCBs (e.g. isomer 28 trichloro biphenyl) were in low concentrations because of better degradation. Level of the ∑PCBs in Musa Khoor compare with other areas – Japan, United States and Sweden – are summarized in Tables 4 and 5.

Table 4 Level of PCBs in water samples around the world

Area	Concentration (ng/L)	Reference
Japan	1–100	WHO (1976)
US, Lake Michigan	100–450	Erickson (1997)
US/Canada	1–20	Strachan and Eisenreich (1990)
Northwest Persian Gulf	8–375	Present study

Table 5 Level of PCBs in sediment samples around the world

Area	Concentration (μg/g, dry wt)	Reference
Japan, polluted area	2700	Kimbrough (1980)
Sweden	4–170	NRC (1979)
US/Canada	0.03–0.2	Strachan and Eisenreich (1990)
Northwest Persian Gulf	3.4–50.2	Present study

PCBs were used in lubricants, softening agents, transformers, capacitors and many other industrial appliances until 1980s, and PCB concentrations in the semi-enclosed basin such as the Persian Gulf are influenced by many factors, including direct discharges, the tide level, the presence of currents and sediment remobilization, etc. as a result generally not explain about the time and main pollution source (Duinker and Hillebrand 1983).

The seawater is not a final reservoir of pollutants but a dynamic compartment where PCBs concentration depends on the net balance of inputs (atmospheric depositions, sediment re-suspension, and direct revering contributions) and losses (volatilization, bubble bursting, photo decomposition, particle settlement) consequently it is hard to find a direct relationship between the different potential sources and the final concentration at the interface.

The relationship between PCBs in water and sediments and the main meteorological parameters (temperature, wind speed, solar irradiation) have been investigated, but no statistically significant results have been found, probably due to the concurrence of many factors or the spread of samples. The chromatograms indicated that other persistence organic pollutants (POPs) chlorinated hydrocarbons such as lindane, DDT and their metabolites are detectable in these samples.

Levels of PCBs, on sediments, were found in approximately similar concentrations in the different sediment analyzed, except for MKE where the levels were lower. Lower levels in the MKE are most likely explained by the effect of waves and tide wash out PCB in Musa Khoor.

Persistent organic pollutants, which have been heavily used globally in agriculture and industry, are found in the Musa Khoor predominantly due to long range transport from areas of use with the atmosphere, Persian Gulf currents, and Karoon River; on the other hands PCBs entered the Musa Khoor from leakages, dumped sewage sludge and industrial discharges. PCBs are one the most important contaminant among POPs, so information about their type and concentration in different environment is necessary for development and planning.

In conclusion, evidence presented in this paper shows that: (a) concentration of PCBs in coastal water and sediment of North West Persian Gulf (Iranian part) is higher than similar place in Japan, Europe and North America. (b) The concentration has been found at contaminated sites in Majidieh Khoor is high enough to require bioremediation. (c) Sediments in the bottom of the Musa Khoor are considered to produce point loadings of organochlorine contaminants. (d) Comparison of literature data (Verschueren 1996) and concentration of different congeners and chromatogram indicates that the main source of PCB in this area can be Clophen A60; it used for long time in Iran Transfo Company (the main Iranian transformer manufacture).

Toxic congeners of PCBs are available in marine environments; the ΣPCB concentration range was between 8 and 375 ng/L in water and 3.4–50.2 μg/g in the sediment and highest PCBs concentration were found in sediments consequently there can be dangerous. The significance of POPs on the health of organisms in Musa Khoor is unknown at present however PCBs and other chlorinated hydrocarbons definitely are harmful for aquatic environments, so identification and determination of POPs is necessary in this area.

Further research should be directed towards quantifying the relation between the concentration of petroleum hydrocarbons and PCB for the reason that chlorinated hydrocarbons can extract naturally in sea water surface layers, specially in case of Musa Khoor because there is one of the most oil polluted area in Persian Gulf.

References

Albro PW, Haseman JK, Clemmer TA, Corbett BJ (1977) Identification of the individual polychlorinated biphenyls in a mixture of gas-liquid chromatography. J Chromatogr 136:141–146

Albro PW, Corbett JT, Schroeder JL (1981) Quantitative characterization of polychlorinated biphenyl mixtures (Aroclors® 1248, 1254 and 1260) by gas chromatography using capillary columns. J Chromatogr 205:103–111

Ayris S, Marco Currado G, Smith D, Harrad S (1997) GC/MS procedures for the determination of PCBs in environmental matrices. Chemosphere 35:905–917

Blanco-Penedo I, López-Alonso M, Miranda M, Benedito JL, Shore RF (2008) Organochlorine pesticide and polychlorinated biphenyl in calves from north-west Spain. Bull Environ Contam Toxicol 81:583–587

Csuros M (1997) Environmental sampling and analysis. Lewis, Boca Raton

Duinker JC, Hillebrand MTJ (1983) Characterization of PCB components in Clophen formulations by capillary GC-MS and GC-ECD techniques. Environ Sci Technol 17:449–456

Erickson MD (1997) Analytical chemistry of PCB. Lewis, Boca Raton

Fu S, Cheng H, Liu Y, Zhang L, Yang Z, Li K, Xia X, Xu X (2008) Polychlorinated biphenyls residues in the soil in Linfen, China. Bull Environ Contam Toxicol 81:594–598

Hu G-J, Chen S-L, Zhao Y-G, Sun C, Li J, Wang H (2009) Persistent toxic substances in agricultural soils of Lishui county, Jiangsu province, China. Bull Environ Contam Toxicol 82:48–54

Kannan N, Tanabe S, Wakimoto T, Trtsukawa R (1987) Coplanar polychlorinated biphenyls in Aroclor and Kanechlor mixtures. J Assoc Off Anal Chem 70:451–454

Kimbrough RD (1980) Environmental pollution of air, water and soil. In: Halogenated biphenyls, terphenyls, naphthalenes, dibenzodioxins and related products. Elsevier/North-Holland/Biomedical Press, New York, pp 77–80

Li K, Yin HW, Zheng MH, Rong ZY, Jia LJ (2007) Polychlorinated dibenzo-p-dioxins, dibenzofurans and dioxin like biphenyls in sediments from the Suzhou creek, China. Bull Environ Contam Toxicol 79:432–436

Loveridge AR, Bishop CA, Elliott JE, Kennedy CJ (2007) Polychlorinated biphenyls and organochlorine pesticides bioaccumulated in green frogs, *Rana clamitans*, from the lower Fraser valley, British Columbia, Canada. Bull Environ Contam Toxicol 79: 315–318

NRC (1979) Polychlorinated biphenyls. National Research council, Washington, DC

Strachan WM, Eisenreich SJ (1990) Mass balance accounting of chemicals in the Great Lakes. In: Kurtz DA (ed) Long range transport of pesticides. Lewis, Boca Raton Chap. 19

US EPA (1991) Test method for evaluating of solid waste – SW 846. US Environmental Protection Agency, Cincinnati

Verschueren K (1996) Handbook of environmental data on organic chemicals, 3rd edn. Van Nostrand Reinhold, New York

WHO (1976) Polychlorinated biphenyls and terphenyls environmental health criteria 2. World Heath Organization, Geneva