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Polychlorinated Biphenyls in Selected Sites in Pasig River and Laguna Lake in the Philippines Before and After a Big Flood Event Investigated Under the UNU East Asia Regional POPs Monitoring Project

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Abstract This paper reports the results of the 2009 United Nations University (UNU) East Asia Regional Monitoring of the Coastal Hydrosphere Project implemented in the Philippines. The monitoring activity focused on the concentrations of 16 specific congeners of Polychlorinated Biphenyls in selected sites in Pasig River and Laguna Lake for two sampling periods in August and in November, 2009. The results show that the total concentrations of PCBs detected in the sampling sites in August increased during the November sampling from 0.9–12.2 to 6.1–32 ng/L in Pasig River and from 0.1–0.9 to 2.9–10.8 ng/L in Laguna Lake. The increase in PCB concentrations on second sampling is attributed to the increase in contaminated sediments in the river sites and to the overflow of contaminated water in the lake sites; both of which could have been caused by the flooding event that occurred in September 2009.

Keywords Polychlorinated biphenyls · River and lake pollution · Flooding event · UNU POPs monitoring

The Environmental Monitoring and Governance in East Asian Hydrosphere is a program of the United Nations University (UNU) in Tokyo to build the capacity of selected laboratories in East Asia to conduct environmental monitoring. Many participating countries in this program are signatory to the Stockholm Convention, the agreement among countries to take actions to eliminate Persistent Organic Pollutants (POPs) in the global environment by 2028 (Stockholm Convention 2001). Polychlorinated biphenyls (PCBs), a type of POPs, had been found to suppress the immune system, disturb the behavior and reproduction in birds, fish and mammals, and potentially cause cancer in humans (McFarland and Clarke 1989). The monitoring and destruction of PCBs stockpiles is a major concern of the participating countries related to the Stockholm Convention; hence, developing the capability to confirm and quantify PCBs in the environment was implemented by the UNU project in 2009. The capacity building project focused on the accurate determination of PCB congeners by Gas Chromatography/Mass Spectrometry (GCMS) and selected a simple matrix (river water) and a simple sampling method (grab sampling of one liter surface water) that can be implemented in all participating countries.

In the Philippines, most electric utilities which existed before 1980 used PCBs as transformer oil (DENR 2006). It was reported that some operators of service facilities for retro filling and repair of transformers in the Greater Manila Area (GMA), unaware of the hazards of PCBs, and disposed used transformer oils in their facilities (DENR 2006). With the identified possible sources of PCBs pollution in the GMA, it is important to investigate the PCBs contamination in major water bodies surrounding GMA.

Materials and Methods

Surface water samples were collected in Pasig River, Manila Bay and in Laguna Lake. Table 1 shows the details of the locations of the sampling sites. The first sampling was done on August 13 and 18 during the rainy season and the second sampling at the beginning of the dry season on November 13 and 18 in the year 2009.

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Table 1 Details of the location of sampling sites

Sampling site	Location	Latitude Longitude	Sampling site	Location	Latitude Longitude
Sta. 1	Manila Bay, 2.5 km from the mouth of Pasig River	N14°35′27″ E120°57′00″	Sta 5	Marikina Bridge on the main tributary of Pasig River	N14°38′07″ E121°05′61′
Sta. 2	Jones Bridge, Manila, on the main tributary of Pasig River	N14°35′42.5″ E120°58′37″	Sta 6	Taguig, in Laguna Lake	N14°30′ 03′ E121°05′42″
Sta. 3	Sanchez Bridge, San Juan River, a big river joining the main tributary of Pasig River	N14°35′ 65″ E121°01′ 56′,	Sta 7	Sucat, near a power plant in Laguna Lake	N14°27′ 12′ E121°04′11″
Sta. 4	Guadalupe Bridge, Makati on the main tributary of Pasig River	N14°11′ 00″ E121°00″00″	Sta 8	Sta Rosa, near mouth of Sta Rosa River in Laguna Lake	N14°18′ 24′ E121°07′ 52″

The concentrations of PCBs in water were determined following the analytical procedure prescribed by UNU for all the project participants (*UNU and Shimadzu Manual for PCBs Analysis, 2009*). Water sample contained in a 1 liter sampling bottle was transferred into a 2 L separatory funnel containing 50 g of sodium chloride. Surrogate labeled PCBs (100 µL of 20 ng/mL mixed surrogate solution, Cambridge Isotope Laboratories Cat No. EC 4189-A) was added. The sample bottle was rinsed with 100 mL hexane; the hexane rinse was added to the sample in the separatory funnel. The sample was mixed and the layers were allowed to separate. The extraction of water layer with 100 mL hexane was repeated. The hexane layers were combined in an Erlenmeyer flask and dried with anhydrous sodium sulfate. The extract was transferred in a rotary evaporator flask and concentrated in a rotary evaporator with heating at 40°C and vacuum pressure of 60 cm Hg until the volume of the extract was 5 mL. A solid phase extraction cartridge (44 % H_2SO_4 Silica Gel cartridge) was cleaned with 50 mL hexane. The hexane extract was transferred into the cleaned cartridge and the PCBs were eluted with 20 mL hexane into a recovery flask. The solvent was evaporated in the rotary evaporator until the volume is 1 mL. The extract was transferred into a 2 mL graduated centrifuge tube and 100 µL of the internal standard perylene-d12 (20 ng/mL in isooctane) was added. The extract was concentrated to a volume of 100 µL by blowing with Nitrogen at 40°C. The sample was mixed in a vortex mixer and transferred into a 100 µL glass insert in a GCMS vial for GCMS analysis.

The GCMS analysis was done using a Shimadzu GCMS QP 2010 (Electron Impact Ionization and Selected Ion Mode) equipped with Auto injector AOC-20i and a capillary column (RTX-PCB, 59.6 m long, 0.25 µm thickness, 0.25 mm diameter). The injector port was set at 280°C, the ion source at 200°C and the interface temperature at 280°C with helium as carrier gas at a constant linear velocity of 32.6 cm/s. Sixteen PCB congeners (PCB#1, PCB#4&10, PCB#8, PCB#18, PCB #37, PCB#44, PCB#74, PCB#99 + 150, PCB#118,PCB#153, PCB#156, PCB#189, PCB#195, PCB#194, PCB#206 and PCB#209) were analyzed using a column temperature program (constant at 110°C for 3 min, ramp increases of 10°C/min up to 210°C, 3°C/min to 310°C and 5°C/min to 320°C and held constant at 320°C for 10 min). Surrogate labeled PCB congeners (Cambridge Isotope Laboratories Cat No.EC 4189-A) were used as internal standards and perylene-d_{12} (Cambridge Isotope Laboratories Cat No.DLM-366-1.2) as recovery standard in quantitation of the PCBs. Calibration standards were prepared for mono and di PCBs (0.5–200 ng/mL) and for tri-deca PCBs (0.25–100 ng/mL) using mixed PCBs standard solution (Cambridge Isotope Laboratories Cat. No. EC5434). Each calibration standard solution contained 20 ng/mL mixed surrogate solution and 10 ng/mL perylene d-$_{12}$ recovery standard.

Results and Discussion

The % recoveries of the spiked samples (1 ng/L tri to decachlorinated biphenyls (CBs), 2 ng/L mono and di- CBs) from different batches of analysis are shown in Table 2. The average % recoveries for native mono to tri- CBs are very low; indicating that losses of these PCB congeners occur; possibly during the drying of the extract due to the high volatility of these PCBs. The % recoveries of the surrogate PCBs in the spiked and in the test samples showed the same trend as the % recoveries of the native PCB congeners.

The quantitation limits (LOQs), calculated as 10 s of repeated injection (n = 10) of the standard solution of lowest concentration (0.25 ng/mL tri-deca CBs, 0.5 ng/mL mono and di CBs) are shown in Table 3. PCB concentrations less than the LOQs were not reported.

Table 2 % Recoveries of PCB congeners in the spiked and test samples

PCB congeners from spiked samples	% Recovery (n = 7)	PCB congeners from spiked samples	% Recovery (n = 7)
Mono-CB (PCB#1)	4	Penta-CB (PCB#118)	74
Di-CB (PCB#4&10)	34	Hexa-CB (PCB#153)	79
Di-CB (PCB#8)	50	Hexa-CB (PCB#156)	82
Tri-CB (PCB#18)	21	Hepta-CB (PCB#189)	70
Tri-CB (PCB#37)	26	Octa-CB (PCB#195)	78
Tetra-CB (PCB#44)	61	Octa-CB (PCB#194)	70
Tetra-CB (PCB#74)	56	Nona-CB (PCB#206)	72
Penta-CB (PCB#99+150)	45	Deca-CB (PCB#209)	76
Surrogate PCBs from spiked samples	% Recovery (n = 7)	Surrogate PCBs from spiked samples	% Recovery (n = 7)
13C Mono(13C PCB#3)	7.0	13C Hexa (13C PCB#153)	63
13C Di (13C PCB#15)	24	13C Hepta(13C PCB#180)	68
13C Tri (13C PCB#28)	33	13C Octa(13C PCB#194)	69
13C Tetra (13C PCB#52)	38	13C Nona(13C PCB#208)	66
13C Penta (13C PCB#118)	64	13C Deca(13C PCB#209)	66
Surrogate PCBs from test samples	% Recovery (n = 32)	Surrogate PCBs from test samples	% Recovery (n = 32)
13C Mono(13C PCB#3)	15	13C Hexa (13C PCB#153)	75
13C Di (13C PCB#15)	34	13C Hepta(13C PCB#180)	79
13C Tri (13C PCB#28)	50	13C Octa(13C PCB#194)	77
13C Tetra (13C PCB#52)	51	13C Nona(13C PCB#208)	76
13C Penta (13C PCB#118)	75	13C Deca(13C PCB#209)	75

Table 3 MDL and LOQ of PCB congeners (pg/L)

Compound name	MDL	LOQ	Compound name	MDL	LOQ	Compound name	MDL	LOQ
PCB#1	12	40	PCB#44	30	99	PCB#156	25	84
PCB#4&10)	20	65	PCB#74	29	96	PCB#189	35	118
PCB#8	21	69	PCB#99+150	51	169	PCB#195	65	217
PCB#18	19	62	PCB#118	49	163	PCB#194	71	235
PCB#37	15	50	PCB#153	36	120	PCB#206	138	460
						PCB#209	54	179

The reported concentrations for the detected PCB congeners in the sample were corrected for the % recoveries of the corresponding surrogates in the sample.

During the first sampling, the total PCB concentration (sum of all detected PCB congeners detected from the sample) was highest in Sta.3 in San Juan River (12,200 pg/L) and the lowest in Sta.5 (900 pg/L) among the sites in Pasig River (Fig. 1). The PCB concentration in water could be due to the enhanced mobility of suspended PCB contaminated particulates in the river (Vellux and Endicott 1994, Bremle and Laarson 1997). PCBs, a mixture of very lipophilic compounds, will partition in water and transported in this phase in a river and the transported proportions between PCB in aqueous phase and PCB associated with suspended particles depend on the amount of suspended sedimentary particles that are rich in organic matter (Chevreuil et al. 1987). The high PCB concentration during the rainy season in San Juan River, a wide but slow flowing river that collects the wastewater from many creeks in the GMA, could be partly due to re-suspension of accumulated PCB contaminated sediments in the river bed. In Laguna Lake, the less mobility of suspended particulates and the dilution of the concentration by the large amount of water, contributed to the much smaller PCB concentrations detected in Sta.6, Sta.7 and Sta.8. On September 29 a typhoon (internationally coded Ketsana) hit the Philippines, heavy rainfall and floodwaters inundated the land surface and flushed pollution from GMA. The water samples from most sampling sites on second sampling in November showed higher concentrations of PCBs. However, the PCB concentrations in Sta. 2 and Sta. 4 on the main tributary of Pasig River decreased and this could be

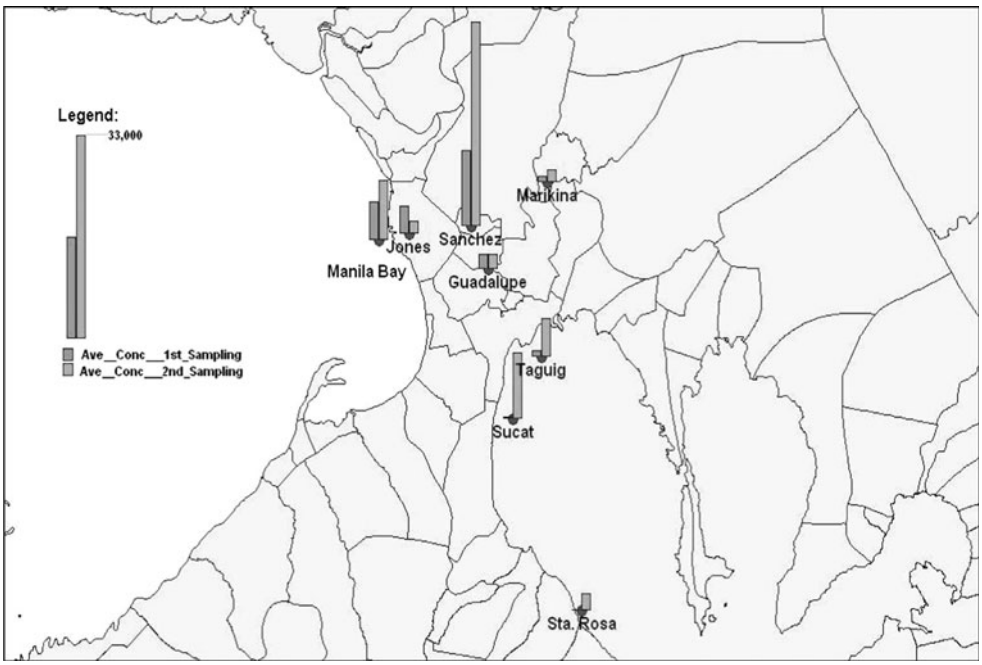

Fig. 1 Total PCB concentrations (pg/L) in water samples from sampling sites on 1st and 2nd samplings

attributed to the effect of the purging of the PCB contaminated sediments by the high flood water flow in the main river tributary. The total PCB concentrations in samples from Sta. 6 and Sta.7 in Laguna Lake on the second sampling were significantly higher ($p < 0.05$.by t test of means) than the concentrations on the first sampling. The increase in PCB concentrations in the lake could be contributed both by the overflow of Pasig River and run-off from the land area surrounding the lake. However, the high total PCB concentration detected at Sta.7 (10,900 pg/L) near a retired power plant suggests that a point source could be a major contributor to the contamination at this site.

The profiles of the PCB congeners found in water samples from Sta. 3 and from Sta.1 collected during the first and second samplings are similar, indicating that the PCB contamination from the San Juan River tributary greatly influences the types of PCB congeners in the site at Manila Bay (Fig. 2). On the first sampling, the major PCB congeners found in the sample from Sta. 3 were hexa-CB, penta-CB and tetra- CB, PCB congeners known to be present in some commercial PCB mixtures historically used as transformer oil. Higher concentrations of di-CB, tri-CB and tetra-CBs detected in the samples collected on second sampling could be due to leaching out of the more soluble congeners from PCB contaminated sediments by the large volume of flood waters. The PCB congeners detected in Sta. 6 and Sta. 7 in Laguna Lake during the second sampling were predominantly the more water soluble tri-CB, di-CB and mono CB, which could have been contributed mainly by the overflow of water during the flooding. Sta. 8 near a river mouth in Laguna Lake showed

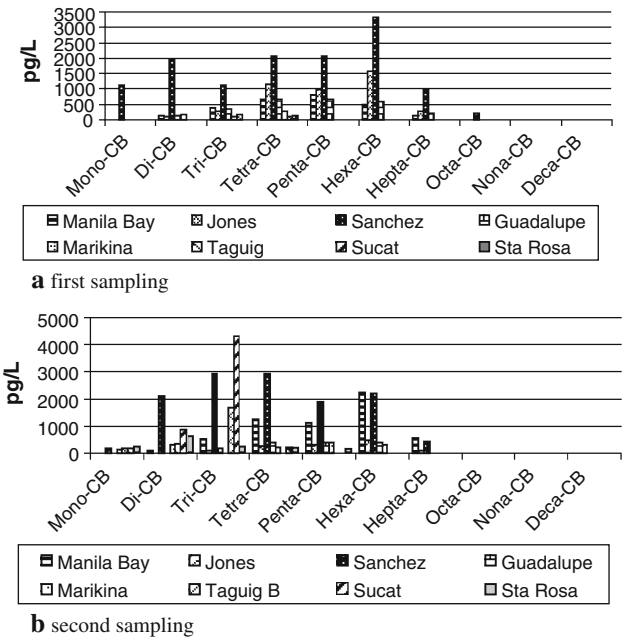

Fig. 2 Concentrations of PCB congeners in water samples

a profile similar to that found in Pasig River, indicating that the source of PCBs could be river sediments contaminated with high chlorinated PCBs.

Compared to total PCB concentrations found in other water bodies, the concentrations found in the study sites in Pasig River and Laguna Lake are much higher as shown in Table 4. The Global Atmospheric Passive Sampling (GAPS) study of POPs in 2005 found that one of the highest total PCB concentrations in air (316–2,826 pg/m3) among 57 global sampling sites was from a site in Quezon

Table 4 Total PCB concentrations detected in different water bodies

Location	Total PCBs (ng/L)	Reference	Location	Total PCBs (ng/L)	Reference
Pearl River Delta	0.12–1.47	Guan et al. (2009)	Hongkong Coast	0.266–0.433	Worl et al. (2006)
ChaoPhraya, Mekong Rivers	0.26–4.82	Boonyatumanond and Thongkreang (2010)	Manila Bay	6.1–9.8	This study
Pasig River	0.9–32.8	This study	Venice Lagoon	0.036–1.8	Moret et al. (2005)
			Laguna Lake	3.0–10.9	This study

City in GMA (Pozo et al. 2006). The mussel watch in Asia (Monirith et al. 2003) showed that the mean total PCB concentration in mussels collected from Manila Bay (290 ng/g) is much higher than the average total PCB concentrations in mussels from Vietnam (160 ng/g), Malaysia (56 ng/g), Indonesia (87 ng/g) and China (120 ng/g).

The analytical method of the UNU monitoring project on PCBs applied to water samples from Pasig River and Laguna Lake confirmed the high PCB pollution in GMA and showed the changes in the PCB pollution of the water bodies due to a major flooding event in the city environment.

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