

Application of Equilibrium Partitioning Approach for the Assessment of Polychlorinated Biphenyls (PCBs) Contamination in Sediments from Kyeonggi Bay, Namyang Bay, and Lake Shihwa, West Coast of Korea

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To assess present status of polychlorinated biphenyls (PCBs) contamination in Kyeonggi Bay, Namyang Bay, and Lake Shihwa, 63 sediment samples were analyzed and applied to equilibrium partitioning approach. Sediment quality criteria (SQC) for exposure to Kanechlor mixture (KC-mix) was calculated as a value of 16 $\mu\text{g/g}$ -organic carbon (OC). Two sites (Sites K18 and K19) within Incheon North Harbor (INH) with total PCBs concentrations 48 and 38 $\mu\text{g/g}$ -OC, respectively, exceeded SQC, indicating a potential of adverse biological effects. The advantage and disadvantage of equilibrium partitioning approach has been discussed.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are highly persistent compounds which have been widely used as dielectric fluids in capacitors and transformers, resin, wax extenders, flame retardents, dedusting agents, adhesives, inks, pesticides, formulation of cutting and lubricating oils due to the properties of thermal and chemical stability, resistance to chemical corrosion, and general inertness (Safe, 1990). Although PCBs have a useful properties as industrial materials, they were banned in 1973 in Japan, 1979 in U.S.A., in late 1980's in Europe because PCBs cause carcinogenesis, immunotoxic responses and reproductive problems (Safe *et al.*, 1985). Commonly used PCBs mixtures were Aroclor 1242, 1248, 1254, 1260 in the United States, Kanechlor 300 (KC-300), KC-400, KC-500, KC-600 in Japan, Clophen in Germany, Phenochlor in France, and Chlorofen in Poland.

Sediments are the major sink of hydrophobic contaminants such as PCBs (Smith *et al.*, 1988). In recent years, several approaches have been used to develop sediment quality criteria (SQC) by using AET (apparent effects threshold), SLC (screening level concentration), and SQT (sediment quality triad) approaches (Chapman, 1986; Adams *et al.*, 1992; Environment Canada, 1992).

Equilibrium partitioning (EqP) is one of the

recent approaches (Pavlou and Weston, 1983), which have been reviewed by Di Toro *et al.* (1991). This approach was applied by Webster and Ridgway (1994) to develop a SQC for non-ionic contaminants in England. Based on the assumption of EqP of hydrophobic contaminants between sediment and pore water, it is possible to establish criteria in terms of a contaminant concentration in sediment above which adverse biological effects may be expected to occur. This approach can be considered as a valuable tool to assess the sediment quality (Webster and Ridgway, 1994).

There has been no standard value, guideline, even criteria on PCBs in sediments from Korean coastal areas. This work was aimed to establish SQC for PCBs and assess the present contamination of PCBs in sediments from the West coast of Korea. In the present study, the SQC by EqP approach were proposed for the exposure to KC preparations and applied to the field.

MATERIALS AND METHODS

Sample collection

The Han River, the largest one in Korea borders on Kyeonggi Bay. Incheon harbor, the second biggest one in Korea borders is also located at Kyeonggi Bay which has a tidal flat and tidal

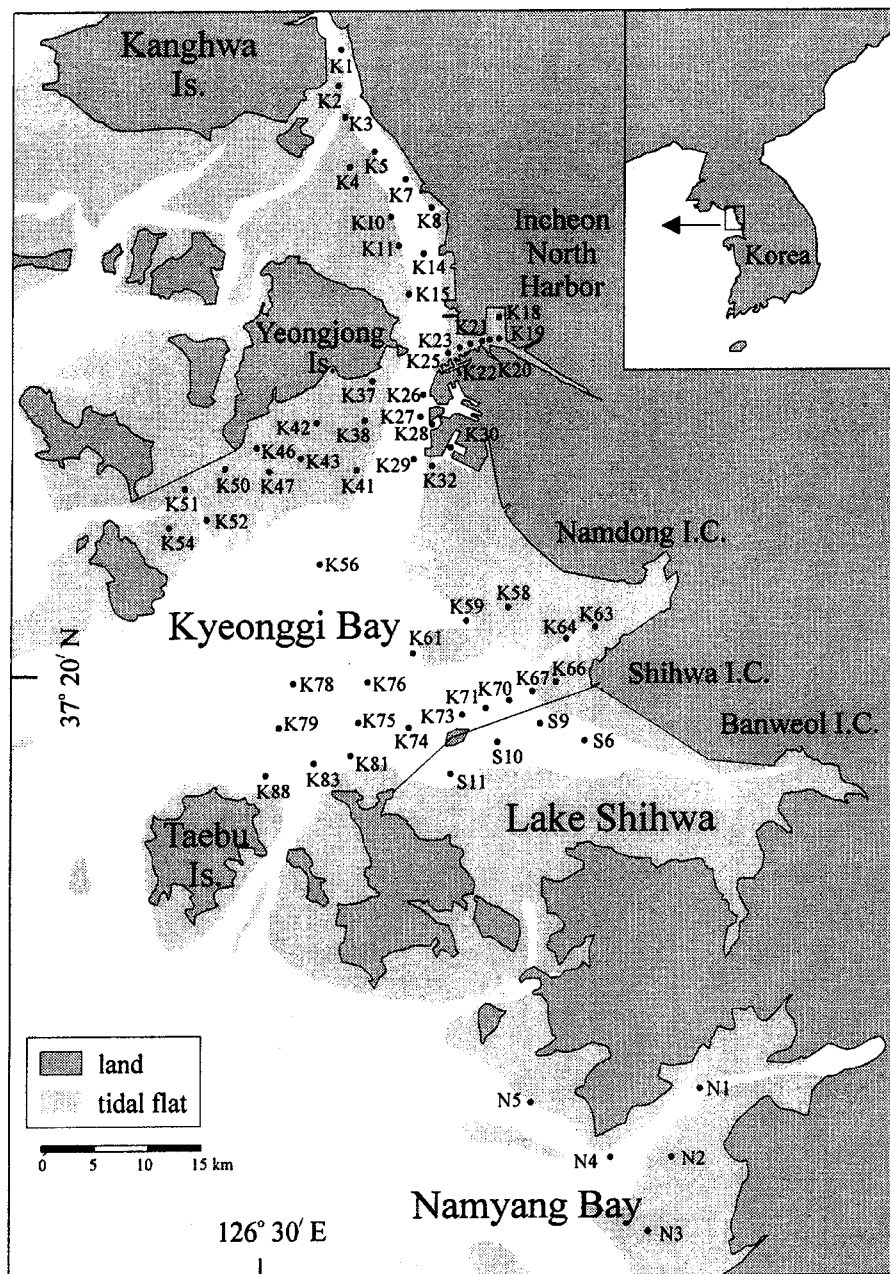


Fig. 1. Location map of sediment sampling sites.

difference as high as 8 m. Kyeonggi Bay is influenced by sewage input from the Han River. A lot of factories are located in the vicinity of Incheon North Harbor (INH). In addition, intensive shipping activities are also common in the region. Lake Shihwa has received direct input of anthropogenic contaminants from Shihwa and Banweol industrial complexes. On the other hand, Namyang Bay remains natural. Fig. 1 shows a map of study area where sediments were collected. Sampling sites were selected preferentially at muddy areas to diminish the effects of grain size and/or carbon

content on hydrophobic contaminants. Sampling depth was largely within 10 m. A van Veen grab sampler of 0.1 m² was used to collect 63 surface sediment samples from Kyeonggi Bay in Dec. 1995, Namyang Bay in Feb. 1996, and Lake Shihwa in Feb. 1996. For the PCBs analysis, materials from the top 1–3 cm were taken with a metal scoop and aluminum foil, and frozen at –20°C until analysis. Separate samples were also taken for grain size distribution and organic carbon determination.

Chemical analyses

Grain size was determined by dry- and wet-sieving method (Galehouse, 1971; Ingram, 1971). Total organic carbon (TOC) contents were determined by the method of Wong *et al.* (1993). One gram of freeze-dried sediment samples were acid-treated with 10% HCl for removal of carbonate carbon. After termination of acid reaction, samples were dried at 60°C. TOC were determined with CHNS analyzer (CHNS-962, LECO). PCBs in sediment samples were analyzed by following the method of Ramesh *et al.* (1991). 20–40 g air-dried sediments were extracted for 1h with 200-ml acetone and the extract was transferred to 100-ml hexane, followed by concentration with KD (Kunderna Danish) concentrator. Concentrated 10-ml extracts were treated with sulfuric acid 5 times for the clean-up and subsequently copper granule twice for removing interference of elemental sulfur. Separation between polar and non-polar organochlorine compounds and further clean-up were proceeded by 12 g florisil column. 120 ml of *n*-hexane was eluted to separate PCBs fraction. One more sulfuric acid and copper treatments were carried out to ensure complete clean-up after the final volume of each fraction was adjusted to 5 ml under gentle nitrogen stream.

Quantitative analyses of PCBs congeners in sediments and biota were accomplished by gas chromatography equipped with a ⁶³Ni electron capture detector (Hewlett Packard 5890 Series II) using a DB-1 silica capillary column (J & W Scientific Co. Ltd., USA: 30 m (length) × 0.25 mm (inner diameter) (0.25 μm (film width))). Helium was used as a carrier gas and nitrogen as a make-up gas. GC condition was programmed as follows; injector and detector temperatures were held at 250°C, 280°C, respectively. Oven temperature was initially kept at 60°C for 1 min., and increased to 160°C at the rate of 20°C per min., and held at 160°C for 10 min., and raised to 260°C at the rate of 2°C per min., and finally kept at 260°C for 20 min. Thus, total elapsed time for one injection was 86 min.

The triplicate recovery tests of total PCBs (T-PCBs) with sediment yielded 103% (±0.3), showing that the quantity is very reproducible. In each batch, detection limits of T-PCBs were defined as twice concentration of the corresponding blank peaks, and totally determined to 0.99 (±1.18) ng/g dry wt (n=13). A procedural blank was run with every batch to check the artifact.

Individual PCB congeners in sample were

quantified by comparing their retention times and peak areas to PCBs standard (KC-mixture; an equivalent mixture of KC 300, 400, 500, 600). The concentrations of T-PCBs were computed as the summation of the concentrations of all identifiable individual congeners. Coelutes were calculated on the basis of their original percentage in KC-mixture. All concentrations were corrected for blank values but not for recovery percentage.

Calculation of sediment quality criteria (SQC)

Partitioning of contaminants between sediment particle and pore water can be expressed as a function of each concentration of two compartments at equilibrium state, and this equilibrium constant is commonly expressed as:

$$K_d = C_s / C_{TW}$$

where K_d refers to partition coefficient between sediment particle and interstitial water, and C_s and C_{TW} correspond to concentrations in the sediment and in the interstitial water, respectively. It is possible to introduce K_{oc} , partition coefficient between water and organic materials in the sediment, based on the assumption that partitioning of hydrophobic pollutants between water and sediment depends on total organic carbon contents in the sediments (Karickhoff, 1981). The modified partition coefficient is defined as follows;

$$K_{oc} = C_s / C_{TW} / TOC$$

$\text{Log } K_{oc} = 0.989 \text{ Log } K_{ow} - 0.346$ ($r^2 = 1.00$); with aromatic and polynuclear aromatic hydrocarbon

where K_{oc} and K_{ow} are carbon normalized partition coefficient and octanol-water partition coefficient, respectively, and TOC means total organic carbon content in sediment. Consequently, C_{soc} can be expressed by replacing C_{TW} with C_{woc} as:

$$C_{soc} = K_{oc} \times C_{woc} \times TOC$$

where C_{soc} refers to the concentration derived from water quality criteria (WQC) with the assumption of EqP, thereby, K_{oc} is the organic carbon normalized partition coefficient, C_{woc} is the concentration, and OC is organic carbon content in sediment. Based on this relationship, tolerance levels in sediment can be defined as the corresponding sediment concentration at which the concentration in interstitial water is at the limit of WQC.

Table 1. Relationships between T-PCBs concentrations and environmental factors

	TOC (%) ¹	Mz (ϕ) ²	Mud (%) ³
T-PCBs (ng/g)	r=0.81 p<0.01 n=34	r=0.20 p>0.01 n=36	r=0.23 p>0.01 n=36

¹Total organic carbon²Mean grain size³Mud=silt+clay

RESULTS AND DISCUSSION

The concentrations of T-PCBs were significantly correlated to organic carbon contents (Table 1). Other environmental factors which may influence PCBs distributions in sediments such as mean grain size and mud contents were investigated but they didn't show any correlation, indicating they are not important factors in PCBs distribution. There is no information on the occurrence, source, and nature of PCBs contamination in coastal areas of Korea. The best way to trace PCBs contamination is the comparison of peak pattern of PCB congeners between sediment and commercial PCBs preparations exposed though some PCB congeners are easily degraded in the environment. Generally, an equivalent mixture of PCBs preparations is used as a standard to calculate total PCBs concentration in environmental samples when no specific information is available for PCBs contamination. The

individual congeners in KC preparations were quantified (Boonyathumanondh *et al.*, 1995). The relative percentages of PCBs homolog compositions in KC preparations and sediments are shown in Table 2. The compositions of PCBs homologs in contaminated sediments were similar to those of KC mixture. Sediment quality criteria or guideline values by various studies including EqP approach have been suggested for Aroclor preparations (Environment Canada, 1992). However, the SQC by equilibrium partitioning approach are unavailable for KC preparations. United States environmental protection agency (US EPA) has developed WQC to ensure that aqueous concentrations of contaminants should be within acceptable limits for the protection of aquatic organisms (US EPA, 1987). WQC for PCBs from US EPA was applied to calculate SQC in this study because there is no chronic WQC for PCBs in Korea. SQC for the exposure to KC preparations were derived by EqP approach (Table 3). The SQC values of each KC preparation were different because octanol-water partition coefficients (K_{ow}) are different between KC preparations. The SQC value of KC-600, the most chlorinated one among KC preparations, showed one order of magnitude higher than that of KC-300, the least chlorinated one among KC preparations, because highly chlorinated congeners possessed higher K_{ow} values. US EPA discriminated WQC in salt water

Table 2. The relative percentages of PCBs homolog compositions in KC preparations and sediments

No. of Cl	KC preparation					sediment				
	KC-300	KC-400	KC-500	KC-600	KC-mix	K18	K19	K20	K21	K22
di-CBs	16	0.91	0.45	0.47	4.5	4.3	4.6	4.3	3.0	6.6
tri-CBs	56	22	2.1	1.5	20	29	22	27	26	23
tetra-CBs	23	54	15	2.1	24	22	22	22	27	19
penta-CBs	3.9	21	57	12	23	19	20	20	18	18
hexa-CBs	0.67	1.9	24	38	16	16	16	18	15	20
hepta-CBs	0.14	0.31	2.1	35	9.2	6.5	13	7.5	8.0	11
octa-CBs	0.041	0.1	0.24	11	2.8	2.4	2.3	2.3	2.1	3.0
nona-CBs	0	0.024	0.075	0.45	0.14	0.39	0.71	0.16	0.10	0.31

Table 3. The SQC of T-PCBs by equilibrium partitioning approach

	KC-300	KC-400	KC-500	KC-600	KC-mix
Log K_{ow} ^a	5.58	5.96	6.40	6.87	6.14
Log K_{oc} ^b	5.18	5.55	5.99	6.45	5.73
WQC ($\mu\text{g/L}$) ^c	0.03	0.03	0.03	0.03	0.03
SQC of T-PCBs ($\mu\text{g/g-C}$)	4.5	11	29	85	16
SQC at 1% OC (ng/g)	45	110	290	850	160

^aLog K_{ow} values were calculated as a mean of values which multiplied the values of homolog K_{ow} by their homolog CB% in each KC preparations (Hwaker and Connell, 1988).^bValues were calculated by regression equation (Karickhoff, 1981).^cMarine chronic criteria from US EPA (1987).

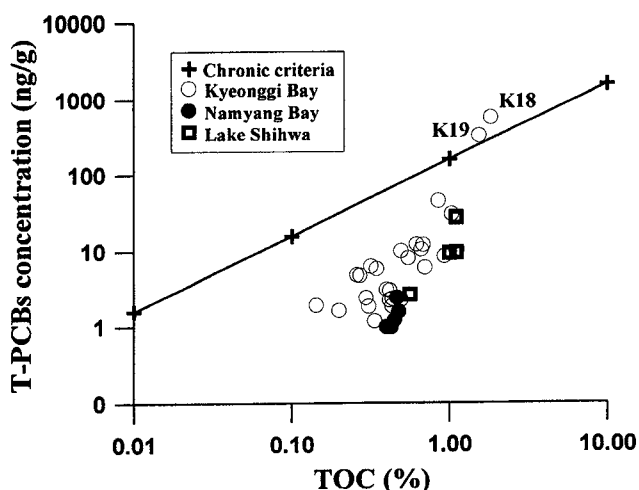


Fig. 2. Plot of TOC vs. T-PCBs concentrations. Chronic SQC for KC-mixture were applied to assess the sediment quality.

from freshwater. However, PCBs preparations-specific WQC are still not available. Tolerance level against exposure to KC-mix, 16 $\mu\text{g/g-OC}$, was applied to examine the sediment quality of Kyeonggi Bay, Namyang Bay, and Lake Shihwa because the pattern of PCBs congeners in contaminated sediments was similar to those of KC-mixture. The plot of organic carbon content vs. T-PCBs concentrations along with chronic SQC guide line was illustrated in Fig. 2. The sites K18 (48 $\mu\text{g/g-OC}$) and K19 (38 $\mu\text{g/g-OC}$) contained T-PCBs concentrations that may cause potentially biological harmful effects. T-PCBs concentrations at K18 and K19 were also higher than those of 2.9 $\mu\text{g/g-OC}$ developed by the EqP approach. Chapman (1987) reported SQC for T-PCBs, based on FDA action level, BCFs, chronic WQC, and BSAFs. Long *et al.* (1995) suggested effect range-low (ERL) and effect range-medium (ERM) as an integrated SQC of the various assessments such as the spiked sediment toxicity test, EqP model, field studies of sediment toxicity test and alteration of community. The concentrations of T-PCBs at Sites K18 and K19 (580 and 330 ng/g) were also higher than 65 ng/g by Chapman (1987), and 22.7 ng/g and 180 ng/g corresponding to the ERL and ERM, respectively, by Long *et al.* (1995).

The advantage and disadvantage of each approach have been discussed (Chapman, 1987; Lyman, 1987; Pavlou, 1987). The EqP approach, as stated by Pavlou and Weston (1983) also has many assumptions. This approach assumes equilibrium

state between pore water and sediments. EqP approach also assumes that contaminants in interstitial water are the only source of exposure of organisms. This ignores the potential for direct transfer of contaminants through food chain and other media such as sediment. The SQC by EqP may not sufficiently protect benthic species because benthic species could be exposed to xenobiotics through both water and food uptake/sediment contact. This potential could be offset by recent BSAFs (biota-sediment accumulation factors) studies (Boese *et al.*, 1995 and 1996). Both synergism and antagonism among contaminants occur in field sediment, however, single chemical study such as EqP approach would not integrate these kinds of interactions. Another practical problem with EqP approach could result from the variability and reliability of partitioning coefficient. The SQC by EqP are affected the K_{oc} value. But the values of K_{oc} are influenced by several variables, including mineralogical composition, sediment texture, and dissolved organic carbon contents. Inaccuracy of K_{oc} leads to a difference in the SQC by a factor of 10 or more. A lack of chronic WQC for many contaminants is one of the limitations of EqP approach. For example, PCBs are a family of 209 compounds with different numbers and positions of chlorine on the phenyl rings. Each congener has different toxicity as well as different physico-chemical property. Until now, the WQC for PCBs was 0.014 $\mu\text{g/L}$ for fresh water and 0.03 $\mu\text{g/L}$ for marine water, irrespective of PCBs preparations. This fact causes a serious fallacy when the SQC for each commercial PCBs preparation (Aroclor or KC series) with different toxicity are calculated with same WQC. The PCB congeners with higher hydrophobicity possess more potential of biomagnification as well as increased persistency in organisms. The results from SQC by EqP approach showed that the SQC for more toxic KC-600, which is composed of mainly higher CBs (more heavily chlorinated CBs), was one order of magnitude higher than those for less toxic KC-300, which has lower percentage of higher CBs, as if KC-600 is less harmful than KC-300. This reversed SQC resulted from the same WQC for PCBs in spite of the 10 times difference in K_{oc} values between KC-300 and KC-600. The SQC for PCBs preparations with higher percentage of heavily chlorinated congeners such as KC-600 should be established at lower level compared to KC-300. Therefore, any

attempt to develop SQC for each PCBs preparation is meaningless unless a reasonable SQC could be established through preparations with different toxicity. For the SQC by EqP at the present time, it's the best to establish the SQC for the mixture of PCBs preparations like Aroclor mixture or KC mixture rather than each one. K_{oc} should be modified to make up for the problem of variability and reliability through the chemical-specific relationship.

The advantages of EqP approach are 1) inexpensive method compared to other approach, 2) utilization of existing WQC, 3) easy application to wide range of organisms and regions. Although EqP approach has many limitations, there is a growing need to develop numerical SQC. EqP approach together with burden effect approach (bioassay) contributes to developing numerical SQC. The SQC by EqP can be considered as one of the numerical guideline values for the legislation and legal action. However, additional researches including BSAFs, SLC, AET, SQT, and new approaches are needed to establish the reasonable and integrated SQC in the Korean.

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