Contamination sources of PCBs in the marine sediments of Ulsan Bay, Korea

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Introduction

The city of Ulsan is a heavily industrialized harbor located in the southeastern part of Korea. In Ulsan, there are two huge shipbuilding yards, complex industrial bases including petrochemical plants, pulp mills, smelteries, etc. The levels of PCBs are widely investigated in many environmentally important areas of the world because of their harmful biological effects [1-4] and considerable persistency in the environment[5,6]. In Korea, however, rare research reports are available about the distributions of PCBs although Korea has already been heavily industrialized. We reported the PCBs levels of surface soils of Ulsan and Masan areas of Korea[7] from which we obtained the evidence that PCBs are still in using and widespread in Korea.

The objective of this study is to investigate the contamination levels and sources of polychlorinated biphenyls (PCBs) in the marine sediments of Ulsan Bay, Korea.

Materials and Methods

The marine sediments were collected using a grab sampler in October 1997 from Ulsan Bay. The 16 sampling sites are illustrated in Fig. 1. Sediment samples were dried at room temperature and passed through a 2-mm mesh sieve and then stored in the brown airtight bottles until analysis.

The extraction and clean-up procedures of PCBs from sediments is as follows: About 50 g of each dried sediment sample was taken in a reflux equipment and then the samples were extracted for 2 hours with 150 mL of 1N-KOH/EtOH solution. After the solution was cooled

to about 50°C, 100 mL of n-hexane was added and shook gently by hand. The extract was filtered with a filter paper and transferred the extract to a separatory funnel. The contents in the Erlenmeyer flask of the reflux equipment was rinsed twice with 50 mL of n-hexane, then poured the extracts into the separatory funnel. After adding 50 mL of hexane-washed water, shook well with a flask shaker, and took the hexane phase (PCBs extracts) after two phases were completely separated. The PCBs extracts were cleaned up with concentrated H_2SO_4, concentrated with a Snyder and Kuderna-Danish condenser to 20 mL, then under nitrogen gas purging to 3 mL, and then clean up them again with silica gel and Florisil column which were covered with anhydrous Na_2SO_4. The PCBs extract was eluted through a silica gel column using 250 mL of n-hexane at a rate of 1 drop/sec, and then concentrating the hexane eluate to about 1 mL with a stream of nitrogen gas. The recoveries of PCBs standards in these columns were about 95%. Identification for PCBs in the final samples were accomplished using HP6890 gas chromatorgraph (Hewlett Packard, U.S.A.) equipped with an electron capture detector (^{63}Ni). A 0.2 mm i.d. × 25 m length capillary column (Ultra 1, cross-linked methyl silicon gum) was held at 80°C for 5 min, then the temperature was increased at a rate of 30°C/min to 190°C, keep at 190°C for 1 min, and then further increased at a rate of 6°C/min to a final temperature of 275°C. Identification of contaminated PCBs sources to the marine sediments of Ulsan Bay was done by comparing patterns with those of commercial Aroclor 1260, 1254, 1248, 1242, 1232, 1221, 1016 and their mixtures.

Results and Discussion

The sampling sites and major sources of PCBs obtained by applying the "congener pattern matching" method are listed in Table 1. The congener patterns compared with the 1:1 mixtures of Aroclor 1254+1260 standards and those of from site 15, 11 and 5 are illustrated in Fig. 2. The maximum total PCBs from the marine sediments of Ulsan Bay is around 200 ng/g dry weight at the site number 16. The major source of PCBs contaminated at this site is Aroclor 1254 and 1260. This finding is believed to be reasonable because huge shipbuilding yards, in which a great amount of paints for ships are consumed, are located at the sampling sites 5, 15 and 16. The other major source of PCBs is Aroclor 1248. This trend is the same throughout most of the marine sediments we observed in this bay.

Highest levels of total PCBs in the marine sediments of Ulsan Bay were observed at sites 1, 15 and 16. These sites are very narrow area or almost separated from outer ocean by breakwaters. Thus, PCBs discharged from the industrial sources such as shipbuilding yards are hard to neither transported nor distributed to the outer sea. These circumstances cause the PCBs to accumulate heavily at these sites. The congener patterns of PCBs obtained from these three sites are also well matched with that of the 1:1 mixture of Aroclor 1254 and 1260.

These two Aroclors are usually found in various industrial products such as paints, special lubricants, electric wires, polyethylene and polyvinyl resins, rubbers, etc., which are manufactured near these sampling sites.

Total PCBs levels from sites 3, 4, 6-10, and 12-14 are relatively low, around 10 ng/g dry weight, which tells us that these sites are far from the point sources of PCBs. We can see from Fig. 1 that these sites are not narrow and open to the ocean, and waters from the Taehwa River can enhance the PCBs to be transported. Low total PCBs levels at site 3 indicates that sediments from Taehwa River were not contributed much to the PCBs levels in the sediments of Ulsan Bay. Sites 13 and 14 are very far from other sites thus total levels are very low and congener patterns are not matched with any of the commercial standards or their mixtures of Aroclors.

Site 5 is near a big shipbuilding yard so total PCBs level is relatively higher than the other sites around this site and congener pattern is much similar to that of 1:1 mixture of the Aroclor 1254 and 1260 which is readily observed from paints used for applying large ships. Site 2 also show middle levels of total PCBs due to the topographical effect, that is, this site is narrow enclosed area so the effect of water streams from the Taehwa River is relatively low.

We found, from this study, that major fractions of PCBs in the sediments are congeners contained in the Aroclor 1254 and 1260 (Table 1). This tells that PCBs used and discharged into Ulsan Bay are homologues containing 5-6 chlorine atoms per biphenyl molecule.

Table 1. Sampling sites in Fig. 1, levels and major sources of PCBs at each site

Site	Levels*	Major sources*	Site	Levels	Major sources
1	High	AC 1254+1260	9	Low	AC 1248+1254+1260
2	Middle	AC 1254+1260 major	10	Low	AC 1248+1254+1260
3	Low	Unmatched*	11	Middle	AC 1254+1260
4	Low	AC 1254+1260	12	Low	AC 1254 major
5	Middle	AC 1254+1260	13	Low	Unmatched
6	Low	AC 1248+1254+1260	14	Low	Unmatched
7	Low	Unmatched	15	High	AC 1254+1260
8	Low	AC 1254+1260	16	High	AC 1254+1260

* AC: Aroclor mixture standard; Unmatched: hard to find similar congener mixture patterns;

* Total PCBs levels (ng/g dry weight): High (~200), Middle (~50), Low (~10)

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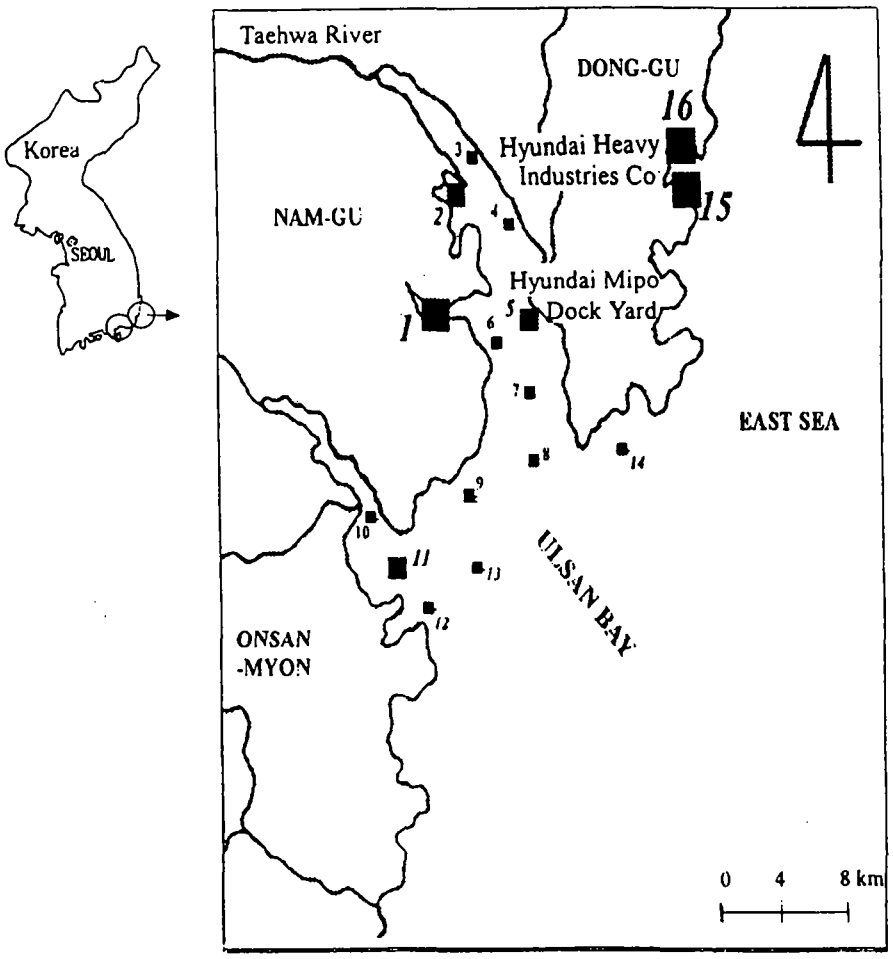

Fig. 1. Locations of sampling sites for the marine sediments in Ulsan Bay, Korea

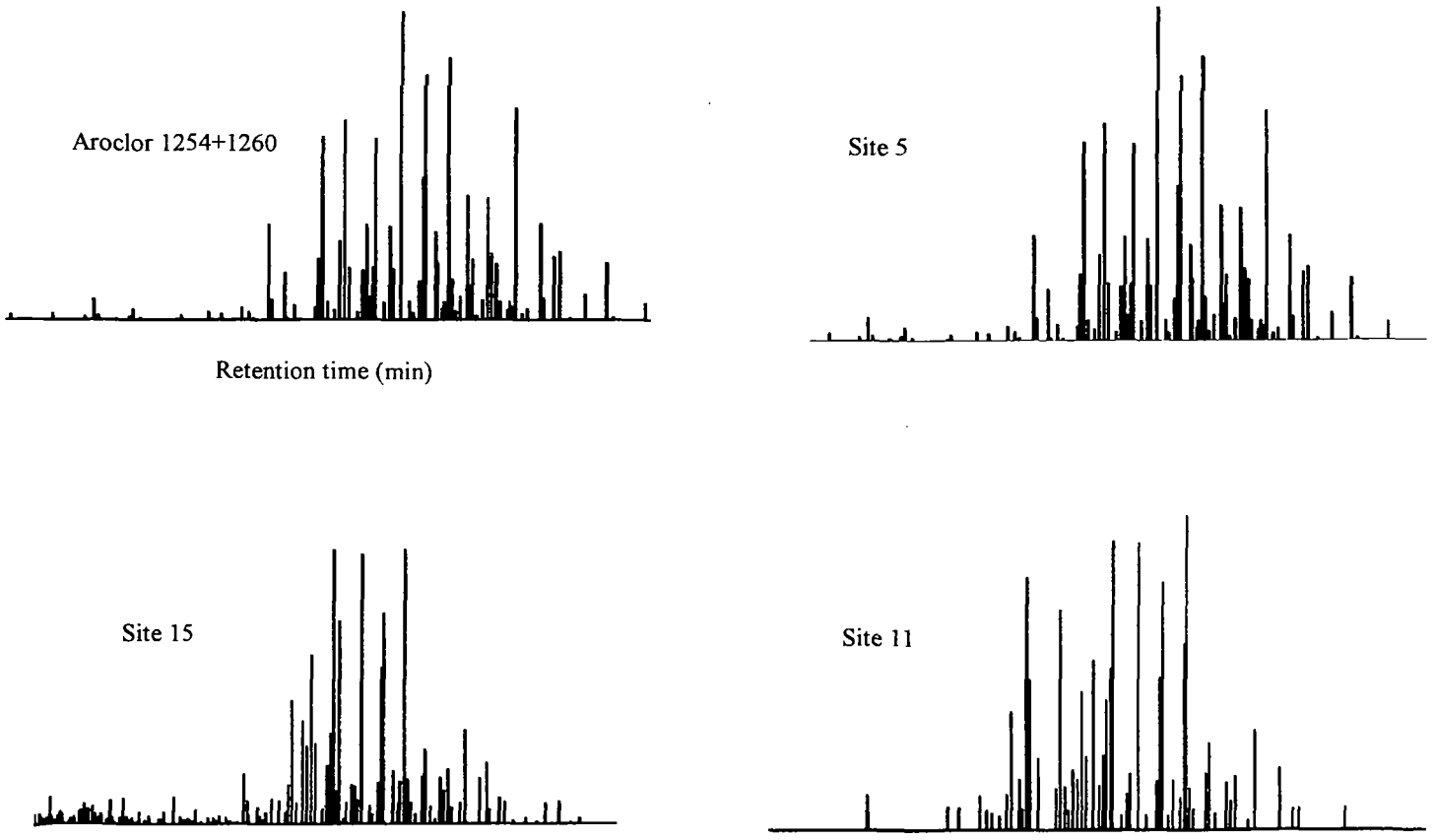

Fig. 2. Congeners patterns of PCBs standard and marine sediment samples from site 15, 11 and 5 of Ulsan Bay, Korea