

# OCCURENCE AND PROFILES OF CHLORINATED AND BROMINATED PAHS IN SEDIMENTS FROM INDUSTRIAL AREAS IN JAPAN AND THE UNITED STATES

Horii Y<sup>1</sup>, Ohura T<sup>2</sup>, Yamashita N<sup>3</sup>, Kannan K<sup>4</sup>

<sup>1</sup>Center for Environmental Science in Saitama, Kisai-mashi 347-0115, Japan; <sup>2</sup>University of Shizuoka, Shizuoka 422-8526, Japan; <sup>3</sup>National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8569, Japan; <sup>4</sup>Wadsworth Center, New York State Department of Health, PO Box 509, Albany, NY 12201-0509, USA

## Abstract

Chlorinated and brominated polycyclic aromatic hydrocarbons (Cl-/Br-PAHs) are widespread environmental pollutants in the urban environment. Nevertheless, there is little information available regarding the occurrence and profiles of Cl-/Br-PAHs in environmental matrices. In this study, the concentrations and profiles of 20 CIPAHs, 11 BrPAHs, and 16 U.S.EPA priority PAHs were determined in sediments from waterbodies near industrialized areas: Tokyo Bay, Japan; the Saginaw River watershed, Michigan, USA; a former chlor-alkali plant, Georgia, USA; and the New Bedford Harbor Superfund site, Massachusetts, USA. Blue mussels from the latter site were measured. We calculated dioxin-like toxic equivalents (TEQs) of Cl-/Br-PAHs. The concentrations and TEQs of Cl-/Br-PAHs in sediments were compared with previously reported concentrations of TEQs of PCDD/Fs, PCBs, and PCNs in Tokyo Bay and in Saginaw River watershed, to enable an understanding of distribution and potential toxic effects of complex mixture of organohalogen compounds.

## Introduction

Chlorinated and brominated polycyclic aromatic hydrocarbons (Cl-/Br-PAHs) are a class of halogenated aromatic hydrocarbons (HAHs) found in the urban atmosphere. CIPAHs are structurally similar to polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (PCBs). Although the environmental chemistry of HAHs has been studied in detail for over three decades, given these compounds' potential for persistence, bioaccumulation, and toxic effects, little is known about the fates and effects of CIPAHs. Due to the lack of purified, individual Cl-/Br-PAH standards, the environmental chemistry and toxicity of these compounds have not been examined in detail. Recent synthesis of individual Cl-/Br-PAHs (3-5 aromatic rings) in our laboratory, has, however, made the congener-specific analysis possible<sup>1,2</sup>. The sources of CIPAHs can be related to various reactions in which chlorine and aromatic precursors exist (e.g., automobile exhaust, chlor-alkali processes, municipal waste incineration). The distribution of individual Cl-/Br-PAHs in waste incinerators<sup>3</sup>, and in environmental samples from an electronic waste recycling facility and a chemical-industrial complex in China<sup>4</sup>, have been reported in earlier studies. In terms of the toxicity, a recent study of our research group showed that several CIPAHs elicit dioxin-like toxic potencies in an *in vitro* bioassay<sup>5</sup>.

Despite the widespread occurrence of CIPAHs in the atmosphere, little is known about their occurrence and profiles in aquatic environments. PAHs persist in ecosystems for many years, owing to their low water solubility and their propensity for absorption to solid particles<sup>6</sup>. Chlorination of PAHs is expected to increase the stability of these compounds in the environment<sup>7</sup>. In this study, concentrations and profiles of 20 CIPAHs, 11 BrPAHs, and 16 U.S.EPA priority PAHs were determined in sediment samples collected around industrialized areas: Tokyo Bay, Japan, the Saginaw River watershed, Michigan, a former chlor-alkali plant, Georgia, and New Bedford Harbor, Massachusetts. Mussels from the latter site were also measured. A dated sediment core collected from Tokyo Bay was analyzed to examine historical trends and fluxes of CIPAHs and parent PAHs since the 1950s. We calculated dioxin-like toxic equivalents (TEQs) of Cl-/Br-PAHs in sediment samples. The concentrations and TEQs of Cl-/Br-PAHs in sediments were compared with previously reported concentrations of TEQs of PCDD/Fs, PCBs, and PCNs in Tokyo Bay<sup>8</sup> and in Saginaw River watershed<sup>9</sup>, to enable an understanding of distribution and potential toxic effects of complex mixtures of organohalogen compounds.

## Materials and Methods

**Samples and Chemicals.** A sediment core was collected in July 2004 from Tokyo Bay, Japan (N35°34'58", E139°54'57"), near a site studied previously<sup>8, 10</sup>, using an acrylic tube (120 cm long and 11 cm i.d.). The

sediment core (90 cm length), sliced at 2-cm increment (n=12), was analyzed. The sedimentation rate for the core, estimated using  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  profiles, was ~15 mm/yr. Surface sediments (0-5 cm) were collected from the New Bedford Harbor Superfund site (n=2)<sup>11</sup>, the Saginaw River watershed (Saginaw River, Saginaw Bay, and Tittabawassee River (n=10)<sup>9</sup>, and a former chlor-alkali plant near the city of Brunswick, Georgia (n=3)<sup>12</sup> in the U.S. during 2004-2006. In addition to sediments, blue mussels (*Mytilus edulis*) collected during 1993-1997 from New Bedford Harbor (n=4) were analyzed. All of sediment and mussel samples examined were kept below -20°C prior to analysis. All of the sampling sites are known to be contaminated with PAHs, PCBs, and/or PCDD/Fs.

Twenty individual ClPAHs, representing mono- through tri-chloro PAHs, were measured in this study; they included chlorofluorene (ClFle), chlorophenanthrene (ClPhe), chloroanthracene (ClAnt), chlorofluoranthene (ClFlu), chloropyrene (ClPyr), chlorochrysene (ClChr), chlorobenz[a]anthracene (ClBaA), and chlorobenz[a]pyrene (ClBaP). In addition, 11 individual BrPAHs representing mono- and di-bromoPAHs were measured, included bromofluorene (BrFle), bromophenanthrene (BrPhe), bromoanthracene (BrAnt), bromopyrene (BrPyr), bromobenz[a]anthracene (BrBaA), and bromobenz[a]pyrene (BrBaP). Standards of 2-ClAnt, 9-ClAnt, and 9,10-Br<sub>2</sub>Ant were purchased from Aldrich (St. Louis, MO). Standards of 9-BrAnt, 9-BrPhe, and 7-BrBaA were purchased from Tokyo Chemical Industry (Tokyo, Japan). 9-ClPhe was obtained from Acros Organics (Geel, Belgium). The remaining Cl-/Br-PAHs were synthesized at the University of Shizuoka (Shizuoka, Japan). The purities of the synthesized standards of ClPAHs were >95%, confirmed by gas chromatography-mass spectrometric analysis; GC-MS<sup>1,2</sup>.

**Chemical Analysis.** The analytical methods for Cl-/Br-PAHs are similar to those described earlier<sup>3,4</sup>. Briefly, sediment samples were extracted using a mixture of dichloromethane (DCM) and *n*-hexane (3:1, v/v) for 16 h in a Soxhlet apparatus. One hundred nanograms of deuterated PAHs (naphthalene, acenaphthene, phenanthrene and chrysene) were spiked onto samples before extraction. The extracts were concentrated to 2 mL, purified and fractionated using activated silica gel column (2 g) chromatography. The target compounds were eluted with 20 mL of 20% DCM in *n*-hexane (F2) after passage of 7 mL of *n*-hexane (F1) through the column. The F2 fraction contained Cl-/Br-PAHs and PAHs; this fraction was concentrated to 1 mL. An aliquot of F2 fraction was used for PAH analysis, and the remaining extract was further purified with a disposable cartridge packed with 0.2 g of a 1:40 w/w mixture of activated carbon (G-60, 60-100 mesh; Sigma-Aldrich, St. Louis, MO) and silica gel (grade 644, 100-200 mesh, 150Å, Sigma-Aldrich) for Cl-/Br-PAH analysis. The cartridge was eluted with 50 mL of 20% DCM in *n*-hexane (F2-1). Then the cartridge was reversed and eluted with 100 mL of toluene (F2-2). The F2-2 fraction that contained Cl-/Br-PAHs was concentrated to 100 µL. Concentrations of Cl-/Br-PAHs were determined by high-resolution gas chromatography- high resolution mass spectrometry (HRGC-HRMS; AutoSpec Ultima, Micromass, Manchester, UK). Ion source and MS interface temperatures were held at 280°C. Gas chromatographic separation was accomplished by means of a 30-m DB-5 fused silica capillary column (0.25 mm id, 0.25 µm film thickness; Agilent, Foster City, CA). Two microliters of the extract were injected in splitless mode at 280°C. The column oven temperature was programmed from 80°C (1 min) to 140°C at a rate of 15°C/min, and to 300°C at 5°C/min; this was held for 5 min. The ions monitored for Cl-/Br-PAHs are reported in earlier studies<sup>2</sup>. Concentrations of PAHs were determined by a GC-MS (Agilent 6890GC and 5973MSD, Agilent Technologies). Details of PAH analysis were described in previous report<sup>3</sup>.

**Quality Assurance/Quality Control.** The recovery rates of ClPAHs through the carbon column clean-up were 102±8% (n=3 determinations). Procedural blanks (n=6) were analyzed with every batch of samples, to monitor for procedural contamination. A trace level of 3,9-ClPhe was detected in some procedural blanks. The limit of quantification (LOQ) was set to be three times the signal-to-noise ratio, or three times the blank levels. Recoveries of deuterated PAHs spiked into samples were 56 ± 9% for naphthalene, 75 ± 9% for acenaphthene, 98 ± 13% for phenanthrene, and 125 ± 17% for chrysene. Sample concentrations were determined from external calibration curves. Quality control standards for ClPAHs and PAHs were analyzed after every five samples, to monitor for instrument stability. Peaks in samples were identified as ClPAHs if the retention time matched that of corresponding standard to within ±0.1 min, and if the ratio between first and second ions was within ±15% of the theoretical ratio.

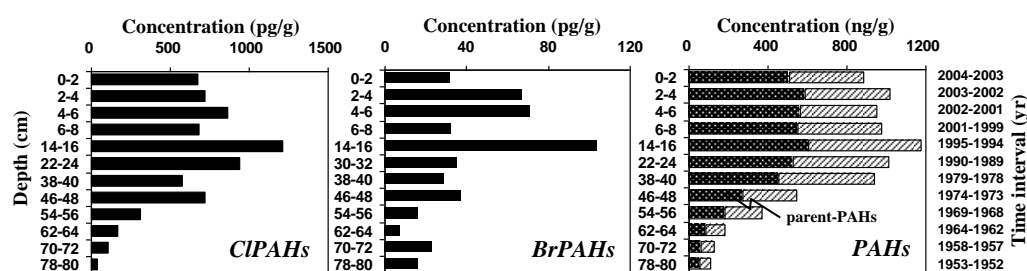
## Results and Discussion

The mean value and range of concentrations for sum of 20 CIPAHs ( $\Sigma$ CIPAHs), sum of 11 BrPAHs ( $\Sigma$ BrPAHs), 8 parent PAHs (Flu, Ant, Phe, Flu, Pyr, Chr, BaA, and BaP =  $\Sigma$ parent-PAHs), and 16 PAHs ( $\Sigma$ PAHs) in sediment and mussel samples examined are summarized in Table 1. The concentrations in sediment samples and mussel samples are reported on a dry weight basis and a lipid weight basis, respectively.

**Table 1. Mean and range (in parentheses) of concentrations of CIPAHs, BrPAHs, and PAHs in sediment (ng/g dry wt) and mussels (ng/g lipid wt) investigated.**

	Tokyo Bay sediment core n=12	Saginaw River watershed sediment n=10	Former chlor-alkali plant sediment n=3	New Bedford Harbor sediment n=2	New Bedford Harbor mussel n=4
$\Sigma$ 20CIPAHs	0.62 (0.036-1.2)	1.1 (0.049-2.5)	8.8 (0.58-24)	1.9	21 (14-29)
$\Sigma$ 11BrPAHs	0.037 (0.007-0.10)	0.19 (0.008-0.69)	1.6 (0.21-3.5)	0.89	8.7 (1.0-19)
$\Sigma$ 8parent-PAHs	371 (52-605)	1970 (28-5340)	1740 (898-3370)	17800	22400 (15300-32700)
$\Sigma$ 16PAHs	690 (109-1170)	2970 (50-7590)	2840 (1360-5670)	29600	28700 (17200-42000)

**Tokyo Bay.** Chlorinated and brominated PAHs were found throughout the sediment core, at total concentrations ranging from 36 to 1210 pg/g and from 7.46 to 104 pg/g, respectively (Table 1). The highest concentration of  $\Sigma$ Cl-/Br-PAHs was found in the 14-16 cm section of the core, corresponding to the mid-1990s (Fig. 1). The concentrations of  $\Sigma$ CIPAH increased with decreasing depth of up to 14-16 cm (1994-1995), then gradually decreased upto the surface layer corresponding to the year 2004 (673 pg/g). The vertical profiles of  $\Sigma$ BrPAH were similar to those for CIPAHs whereas concentrations of BrPAHs were 10-fold lower that the concentrations of CIPAHs. The concentrations of  $\Sigma$ PAHs and  $\Sigma$ parent-PAHs were the highest in the 14-16 cm section of the core, at concentrations of 1200 ng/g and 610 ng/g, respectively.  $\Sigma$ PAH and  $\Sigma$ parent-PAH concentrations decreased with increasing depth; the lowest concentrations were found in the bottom-most sediment section analyzed. The concentrations of  $\Sigma$ PAHs were three orders of magnitude higher than the concentrations of  $\Sigma$ CIPAHs. We examined the relationship between CIPAH concentrations and corresponding parent PAH concentrations, in the sediment core. A significant positive correlation ( $p < 0.01$ ) was found between ClFlu, ClPyr, ClBaA, ClBaP, and  $\Sigma$ CIPAHs and the corresponding parent PAHs. The positive correlation found in this study is similar to a correlation previously reported for urban air<sup>13</sup>. A positive correlation between CIPAH and the corresponding parent PAH suggests that direct chlorination of parent PAH compound is the major pathway of formation of CIPAHs.



**Fig. 1. Vertical profiles in concentrations (pg/g) for CIPAHs, BrPAHs, and PAHs, along with time interval represented, in Tokyo Bay sediment core.**

The annual fluxes of Cl-/Br-PAHs and PAHs were calculated based on the total concentration, sedimentation rate, and dry bulk densities. The annual fluxes ranged from 0.029 to 0.57 ng/cm<sup>2</sup>/yr for CIPAHs, 0.005 to 0.045 ng/cm<sup>2</sup>/yr for BrPAHs, and from 85 to 609 ng/cm<sup>2</sup>/yr for PAHs. Annual fluxes of PCDDs, PCDFs, PCBs, and PCNs in the Tokyo Bay sediment core, previously reported by Yamashita et al. (2000)<sup>10</sup>, were compared with the CIPAH fluxes. The highest flux of CIPAHs (0.57 ng/cm<sup>2</sup>/yr) was approximately 30-fold lower than the highest flux of PCDD/Fs in 1973-1981 (17.3 ng/cm<sup>2</sup>/yr), and 120-fold lower than that of PCBs (69

ng/cm<sup>2</sup>/yr). The highest flux of PAHs was approximately 10-30 times higher than the highest fluxes of PCDD/Fs and PCBs.

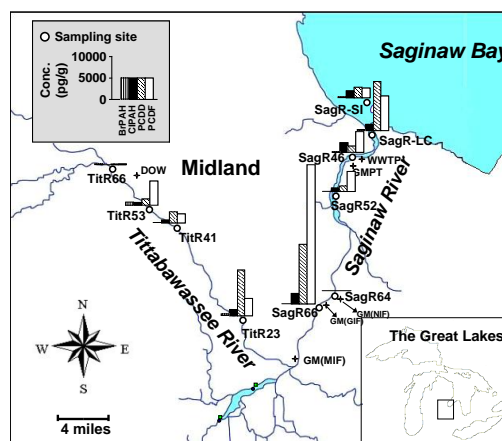
**Saginaw River Watershed.** Concentrations of  $\Sigma$ CIPAHs and  $\Sigma$ BrPAHs in sediment from the Saginaw River and Saginaw Bay, and the Tittabawassee River, varied from 49 to 2490 pg/g and from 7.9 to 687 pg/g, respectively (Table 1). The mean concentration of  $\Sigma$ CIPAHs in the Saginaw River and Saginaw Bay (1440 pg/g) was two-fold higher than the mean concentration measured in the Tittabawassee River (702 pg/g). The Saginaw River and Bay receive discharges from 87 industrial facilities and 127 wastewater treatment plants. Recently, Kannan et al. (2008)<sup>9</sup> reported the distribution of PCBs, PCDDs, and PCDFs in sediments and floodplain soils collected from the Saginaw River watershed. A few selected sediment samples were analyzed for CIPAHs in the present study to enable comparison of concentrations of CIPAHs with concentrations of other organochlorine compounds. The mean concentration of CIPAHs found in this study (1140 pg/g) was 10-fold lower than the mean concentration of PCDD/Fs (11000 pg/g), and two-fold higher than the mean concentrations of coplanar PCBs (438 pg/g) (Fig. 2). The mean concentrations decreased in the order: PAHs >

PCDFs > PCDDs > CIPAHs > coplanar PCBs > BrPAHs. In general, PCDFs were the dominant organochlorine compounds in the Saginaw River watershed. CIPAHs determined in this study were correlated with the concentrations of PCDD/Fs in the same samples ( $p < 0.05$ ), but they were not correlated with parent PAHs. As has been reported for dioxins<sup>14</sup>, low-temperature combustion processes and formation as unwanted byproducts during the production of various chlorinated chemicals can be additional sources of CIPAHs in the environment.

**Chlor-alkali Plant.** The highest concentration of CIPAHs found in our study (24100 pg/g) was from a marsh sediment collected near a former chlor-alkali plant (Table 1). As a result of multi-industrial operations from 1955 to 1994, the site and the adjacent brackish marsh have been severely contaminated by metals and organics (mercury and PCBs)<sup>15</sup>. The strikingly wide variation in  $\Sigma$ CIPAH concentrations found among the three samples that we analyzed (577-24100 pg/g) could reflect the disturbances caused by recent dredging activities at the site. The high concentration of CIPAHs found in one sample from the vicinity of chlor-alkali plant suggests that the chlor-alkali process is a source of CIPAHs in the environment.

**New Bedford Harbor.** High mean concentration of CIPAHs (1880 pg/g) was found in sediment from the New Bedford Harbor (Table 1). In addition to sediment, blue mussels collected from New Bedford Harbor were analyzed for CIPAHs. The concentration of CIPAHs in mussels ranged from 14 to 28 ng/g lipid wt; this range was three orders of magnitude lower than the range for the parent PAHs.

**Profiles of Cl-Br-PAHs.** Among individual CIPAHs, 6-ClBaP was a predominant CIPAH in sediment from Tokyo Bay and chlor-alkali plant, followed in abundance by 1-CiPyr (Fig. 3). In general, CIPAH profiles found in the Tokyo Bay sediment core were similar to the profiles previously reported for incineration ash and urban air samples<sup>3, 16</sup>, which had high 6-ClBaP and 1-CiPyr. In sediment from Saginaw River watershed, 6-ClBaP (16%) was followed in abundance by 6,12-Cl<sub>2</sub>Chr (13%), 3,8-Cl<sub>2</sub>Flu (13%), and 7,12-Cl<sub>2</sub>BaA (11.6%) (Fig. 2). The differences in the profiles of CIPAHs between sediments from the Saginaw River and Tokyo Bay suggest existence of multiple sources. Biodegradation of CIPAHs can alter the distribution profiles of CIPAHs in sediment. Environmental stability and biodegradation rates of PAHs are related to molecular size (number of aromatic rings); for instance, the half-life of three-ring phenanthrene in soil and sediment (16-126 days) is shorter than the half-life of five-ring BaP (229-1400 days)<sup>17</sup>. We also measured CIPAHs in mussels. Whereas



**Fig. 2. Spatial distribution of total concentrations (pg/g) of Cl-Br-PAHs in surface sediment collected from Saginaw River watershed, compared with the concentrations previously reported for PCDD/Fs (Kannan et al. 2008)**

high-molecular-weight CIPAHs were predominant in sediment, low-molecular-weight CIPAHs (3-4 rings) were predominant in the mussels (Fig. 3). This may indicate lower bioavailability or strong sorption to sediments of high-molecular-weight CIPAHs. Among individual BrPAHs, 1-BrPyr was a predominant BrPAH in most of sediments analyzed. The profiles in sediment were different from those in urban air (Ohura 2009) and waste incineration (Horii 2008) whereas similar profiles of CIPAHs found in sediment and the suspected sources. This suggests that urban air particle and waste incineration could not be a major source of BrPAHs in sediment, and/or environmental stability and biostability of BrPAHs could easily alter the distribution profiles of BrPAHs in aquatic environment.

In general, the profiles of CIPAHs were similar between our sediment and profiles reported for urban air; potential emission sources of CIPAHs are waste incineration and chlor-alkali processes.

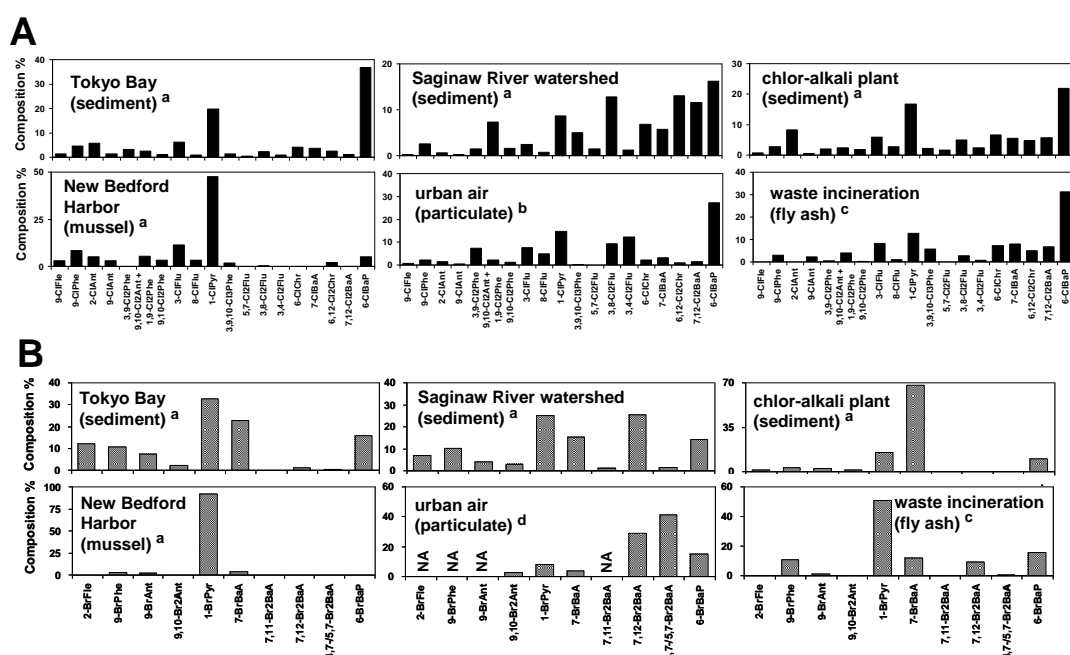


Fig. 3. Profiles of individual CIPAHs (A) and BrPAHs (B) to total concentrations in selected environmental matrices. <sup>a</sup> Data from this study. <sup>b</sup> Data from Ohura et al. (2008). <sup>c</sup> Data from Horii et al. (2008). <sup>d</sup> Data from Ohura et al. (2009).

**Dioxin-like Toxic Potential.** Relative potencies (RePs) of Cl-/Br-PAHs recently reported by Horii et al. (2009)<sup>5</sup> were used to estimate dioxin-like toxic equivalents (TEQs) in the sediment samples analyzed here. Potencies of individual Cl-/Br-PAHs, relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, ranged from  $2.3 \times 10^{-5}$  for 5,7-Br<sub>2</sub>BaA to  $6.3 \times 10^{-6}$  for 7-ClBaA. The calculated total TEQ concentrations contributed by CIPAHs varied from  $<0.016$  to 1.3 fg-TEQ/g (Tokyo Bay sediment) and from 0.08 to 6.0 fg-TEQ/g (Saginaw River sediment) (Table 2). For BrPAHs, it was  $<0.005$ -0.21 fg-TEQ/g in Tokyo Bay and 0.01-3.1 fg-TEQ/g in Saginaw River. The greatest TEQ concentration, 55 fg-TEQ/g, was calculated for sediment

Table 2. Mean and maximum (in parentheses) values of TEQs (fg-TEQ/g) for Cl-/Br-PAHs in sediments, compared with TEQ values previously reported for other

	Tokyo Bay	Saginaw River watershed	Chlor-alkali plant
CIPAHs	1.1 (1.3)	2.4 (6.0)	18 (55)
BrPAHs	0.13 (0.21)	0.77 (3.1)	16 (25)
PCDDs	47,200 <sup>a</sup>	33,000 <sup>b</sup>	
PCDFs	157,000 <sup>a</sup>	660,000 <sup>b</sup>	
PCBs	622 <sup>a</sup>	1,100 <sup>b</sup>	
PCNs	277 <sup>a</sup>		

<sup>a</sup> Data from Kannan et al. (2000) <sup>b</sup> Data from Kannan et al. (2008)

collected near the former chlor-alkali plant. The reported TEQ concentrations of PCDD/Fs, PCBs, and PCNs in the Tokyo Bay sediment<sup>8</sup> and in Saginaw River sediments<sup>9</sup> were compared with the TEQs of Cl-/Br-PAHs. The Cl-/Br-PAH-TEQs determined in our study were approximately 5-6 orders of magnitude lower than the TEQs reported for PCDD/Fs, and 3-4 orders of magnitude lower than the TEQs of PCBs and PCNs. In other words, sum of Cl-/Br-PAHs in sediment accounted for 0.0005-0.0006% of the total TEQs, whereas CIPAHs in urban air have been reported to account for 0.5% of the total TEQs<sup>5</sup>. PCDFs were the predominant contributors to TEQs in Saginaw River sediments (>99%)<sup>9</sup>. Among Cl-/Br-PAHs, 6-ClChr accounted for 56% of the TEQs contributed by Cl-/Br-PAHs and were the predominant contributor in the sediment samples, followed by 7-BrBaA (32%). It should be noted that RePs of several other CIPAHs present in sediment samples are not available; information regarding concentrations of highly substituted chlorinated PAHs, in particular, in environmental matrixes is limited. Previous studies showed the existence of highly chlorinated PAHs (more than three chlorine atoms) in fly ash<sup>3</sup> and in road-tunnel air<sup>18</sup> and RePs of some CIPAHs increased with increasing chlorination of PAHs (e.g. phenanthrene and fluoranthene)<sup>5</sup>. Further studies should focus on the analysis of more highly substituted chloro-PAHs, and determination of their toxicities, in environmental samples.

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