



Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: [www.elsevier.com/locate/envpol](http://www.elsevier.com/locate/envpol)

## Spatial and vertical distributions of sedimentary halogenated polycyclic aromatic hydrocarbons in moderately polluted areas of Asia

Takeshi Ohura<sup>a,\*</sup>, Hiroyuki Sakakibara<sup>b</sup>, Izumi Watanabe<sup>c</sup>, Won Joon Shim<sup>d</sup>, Pathmalal M. Manage<sup>e</sup>, Keerth S. Guruge<sup>f</sup>

<sup>a</sup> Faculty of Agriculture, Meijo University, 1-501 Shiogamaguchi, Nagoya 468-8502, Japan

<sup>b</sup> Faculty of Agriculture, University of Miyazaki, 1-1 Gakuen Kibana-dai Nishi, Miyazaki 889-8526, Japan

<sup>c</sup> United Graduate School of Agriculture, Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu 183-8509, Japan

<sup>d</sup> Oil and POPs Research Group, Korea Institute of Ocean Science and Technology, 391 Jangmok-myon, Geoje-shi 656-834, South Korea

<sup>e</sup> Faculty of Applied Science, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka

<sup>f</sup> Pathology and Pathophysiology Research Division, National Institute of Animal Health, National Agriculture and Food Research Organization, Kannondai 3-1-5, Tsukuba 305-0856, Japan

### ARTICLE INFO

#### Article history:

Received 17 September 2014

Received in revised form

27 October 2014

Accepted 30 October 2014

Available online 12 November 2014

#### Keywords:

☐ CIPAHs

PAHs

Elements

Sediment

Indicator

### ABSTRACT

The sedimentary halogenated (chlorinated and brominated) polycyclic aromatic hydrocarbons (Cl/BrPAHs), PAHs, and elements were analyzed to investigate contamination processes and sources. Assessments were conducted in sediments from three sites: surface sediments from the Yellow Sea and sediment cores from Kandy Lake and Negombo Lagoon, Sri Lanka. Most of CIPAHs targeted were detected in all sediments. Spatial distributions of total CIPAH concentrations in the Yellow Sea showed the presence of multiple hot spots that differed from those of total PAHs. In Kandy and Negombo sediments, total CIPAH concentrations were slightly higher in surface layers than in bottom layers; the opposite trend was observed for PAHs. Principal component analysis showed that the clusters of most CIPAHs were similar to those of anthropogenically derived elements, but were far from those of PAHs. Consequently, CIPAHs in sediments appear to be persistent contaminants, which may make them appropriate as indicators of anthropogenic sources.

© 2014 Elsevier Ltd. All rights reserved.

### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are of great environmental concern because of their potential toxicity; for example, they may have mutagenic, carcinogenic, and endocrine disrupting properties (Baek et al., 1991; Bostrom et al., 2002; Ball and Truskewycz, 2013). Because most biologically toxic PAHs are hydrophobic and non-biodegradable, they are highly persistent in the environment (Meador et al., 1995; Wild and Jones, 1995). The occurrence of PAHs in aquatic environments is affected by inputs from the surrounding environment, including from atmospheric deposition, riverine inputs, municipal runoff, and accidental oil spills (Arzayus et al., 2001; Lima et al., 2005; Boonyatumanond et al., 2006). PAHs have also been known to be produced by incomplete combustion processes of organic materials and fossil fuels; PAHs are therefore frequently used as a marker to evaluate

anthropogenic pollution (Mastral and Callén, 2000; Ravindra et al., 2008; Kim et al., 2013). Highly populated regions with a high amount of anthropogenic activity are likely to be highly polluted with PAHs, and the extent of PAH pollution reflects the history of pollution associated with anthropogenic activities.

Halogenated PAHs, e.g., chlorinated PAHs (CIPAHs) and brominated PAHs (BrPAHs), are currently of interest in the study of PAH derivatives as new classes of environmental contaminants (Ohura, 2007; Sun et al., 2013). Studies on atmospheric CIPAHs have been conducted by a number of researchers; these studies have produced knowledge about the specific behavior of CIPAHs. For example, concentrations of relatively high-molecular-weight CIPAHs, i.e. particulate CIPAHs, in the air are significantly correlated with corresponding parent PAH concentrations (Ohura et al., 2008, 2013a). This finding indicates that they are produced from common emission sources. However, there are few reports on the occurrence of CIPAHs in sediments (Horii et al., 2009; Sun et al., 2011). Horii et al. (2009) reported that all target CIPAHs were detected in sediments from industrialized areas, total levels of which had a range of 580–8800 pg/g. The profiles of individual

\* Corresponding author.

E-mail address: [ohura@meijo-u.ac.jp](mailto:ohura@meijo-u.ac.jp) (T. Ohura).

CIPAHs in sediments were quite different between sediment samples, while sedimentary PAH profiles were similar between samples. This suggests that differences in profiles reflect differences in emission sources.

The Yellow Sea contains semi-enclosed areas, the continental shelf, and shallow seas, and is surrounded by various industrial cities in China and Korea. The rapid industrialization and population increase in the coastal area has caused an increase in the inflow of hazardous compounds to the Yellow Sea, resulting in sedimentation and an increase in ecological risk. Indeed, historical surveys of PAHs and elements in sediment cores from the Yellow Sea reflect the economic development in China and the corresponding increase in consumption of fossil resources (Wu et al., 2001; Hu et al., 2008; Zhang et al., 2009; Li et al., 2012). Sri Lanka has also undergone rapid industrialization since the 1980s; as a result, a number of critical environmental problems and issues have recently come about. In particular, Sri Lanka has experienced increases in air pollution resulting from an increase in vehicle emissions (Pathiratne et al., 2007). The concentrations of PAHs in sediments from Beira Lake in downtown Colombo, the capital of Sri Lanka, were in the range of 152–569 ng/g with an average of 329 ng/g (Pathiratne et al., 2007). The mean concentration was somewhat consistent with those of the Yellow Sea (280 ng/g) (Hu et al., 2008), Masan Bay, Korea (353 ng/g) (Khim et al., 1999), the Yalujiang River, China (290 ng/g) (Wu et al., 2003), and Lake Manzala, Egypt (363 ng/g on median concentration) (Barakat et al., 2012); these levels could be classified as moderately contaminated compared with San Francisco Bay, USA (2653–27,680 ng/g) (Pereira et al., 1996), and Pialassa Baiona, Italy (3032–87,150 ng/g) (Guerra, 2012).

The aims of this study were to evaluate the spatial and vertical distributions of CIPAHs, BrPAHs, PAHs, and elements in sediments collected from the Yellow Sea and from two water bodies in Sri Lanka. To our knowledge, this is the first study in which these contaminants were investigated simultaneously in sediments. Furthermore, we evaluated the sedimentary behavior, potential sources, and ecological risks of CIPAHs in comparison with those of PAHs and elements, and discuss the specificity in the sediments.

## 2. Material and methods

### 2.1. Sample collection

Sixteen surface sediment samples in the Yellow Sea were collected from the Korean ocean dumping site which received the sewage and waste sludge. The top 2 cm of surface sediments were collected from 77 to 82 m below the surface of the Yellow Sea in September, 2004 using a van Veen grab sampler. The sampling sites were located near the center of the Yellow Sea (approximately 150 km off the coast of South Korea), and were distributed at regular intervals (Fig. 1). Two sediment cores were collected in 2004 using a HR columnar type bottom sampler (length 50 cm, inner diameter 11 cm; Rigo Co. Ltd., Saitama, Japan) from each sampling site in Sri Lanka: one site was located approximately 1 km inside the inlet of Negombo Lagoon, and the other was located at the center of lake in Kandy (Kandy Lake) (Fig. 1). Detailed information of the sampling sites was listed in Table S1. The Negombo Lagoon is a shallow estuarine lagoon linked to the sea by a narrow channel near the city of Negombo, on the West Coast of Sri Lanka. Kandy Lake is a freshwater man-made lake located in the city of Kandy,

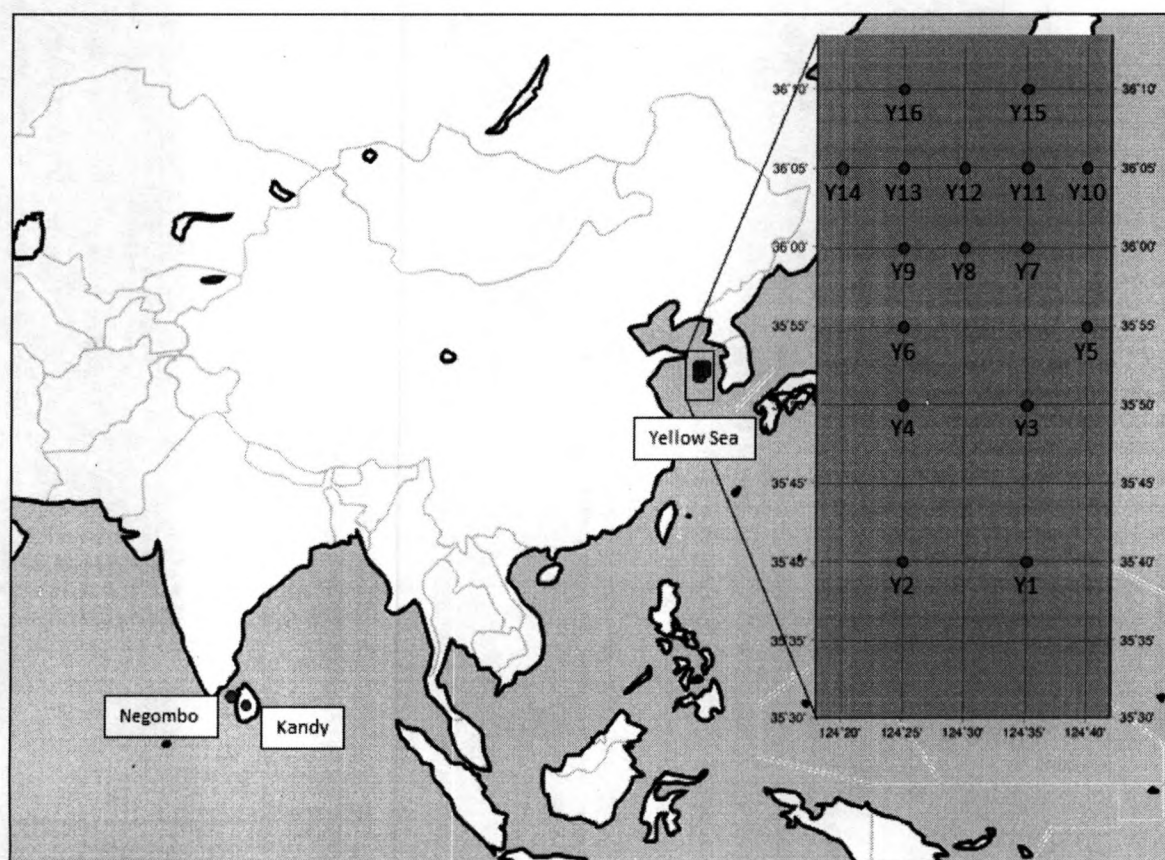


Fig. 1. Sampling sites in the study area.

which is the second largest city in Sri Lanka. The sediment cores were sliced at 3-cm increments. Sediment samples were freeze dried and stored at  $-20^{\circ}\text{C}$  in the dark until analysis.

## 2.2. Materials

The target compounds were 20 species of CIPAHs and 11 species of BrPAHs, and 16 US Environmental Protection Agency priority PAHs. Details of the synthesis and preparation conditions for CIPAHs and BrPAHs are described in previous reports (Ohura et al., 2005, 2008, 2009). The PAH standard solution for target PAHs was purchased from Sigma–Aldrich (St. Louis, MO). The individual halogenated PAH standards were dissolved in isooctane (Dojindo Laboratories, Kumamoto, Japan), and the standard solutions for target CIPAHs and BrPAHs was prepared by combining the individual CIPAH and BrPAH standard solutions, respectively. The solvents used for extraction and clean-up were residual-pesticide-analysis grade (Wako Pure Chemical Industries, Osaka, Japan).

The 20 CIPAHs measured in this study were: 9-chlorofluorene (9-ClFlu), 9-chlorophenanthrene (9-ClPhe), 1,9-dichlorophenanthrene (1,9-Cl<sub>2</sub>Phe), 3,9-dichlorophenanthrene (3,9-Cl<sub>2</sub>Phe), 9,10-dichlorophenanthrene (9,10-Cl<sub>2</sub>Phe), 3,9,10-trichlorophenanthrene (3,9,10-Cl<sub>3</sub>Phe), 2-chloroanthracene (2-ClAnt), 9-chloroanthracene (9-ClAnt), 9,10-dichloroanthracene (9,10-Cl<sub>2</sub>Ant), 3-chlorofluoranthene (3-ClFluor), 8-chlorofluoranthene (8-ClFluor), 3,4-dichlorofluoranthene (3,4-Cl<sub>2</sub>Fluor), 3,8-dichlorofluoranthene (3,8-Cl<sub>2</sub>Fluor), 5,7-dichlorofluoranthene (5,7-Cl<sub>2</sub>Fluor), 1-chloropyrene (1-ClPy), 6-chlorochrysene (6-ClChry), 6,12-dichlorochrysene (6,12-Cl<sub>2</sub>Chry), 7-chlorobenz[a]anthracene (7-ClBaA), 7,12-dichlorobenz[a]anthracene (7,12-Cl<sub>2</sub>BaA), and 6-chlorobenzo[a]pyrene (6-ClBaP). The 11 BrPAHs used in this study are abbreviated as follows: 2-bromofluorene (2-BrFlu), 9-bromophenanthrene (9-BrPhe), 9-bromoanthracene (9-BrAnt), 9,10-dibromoanthracene (9,10-Br<sub>2</sub>Ant), 1-bromopyrene (1-BrPy), 7-benz[a]anthracene (7-BrBaA), 4,7-dibromobenz[a]anthracene (4,7-Cl<sub>2</sub>BaA), 5,7-dibromobenz[a]anthracene (5,7-Cl<sub>2</sub>BaA), 7,11-dibromobenz[a]anthracene (7,11-Cl<sub>2</sub>BaA), 7,12-dibromobenz[a]anthracene (7,12-Cl<sub>2</sub>BaA), and 6-bromobenzo[a]pyrene (6-BrBaP). The 16 PAHs used in this study are abbreviated as follows: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluor), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), dibenzo[a,h]anthracene (DBaA), and benzo[ghi]perylene (BghiP). We also measured 25 elements: Li, Mg, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Mo, Ag, Cd, In, Sb, Cs, Ba, Tl, and Pb.

## 2.3. Sample extraction

For the analysis of target aromatics, each sediment sample (approximately 5–10 g in dry weight) was spiked with surrogate standards fluoranthene-d<sub>10</sub> (Fluor-d<sub>10</sub>, 38.0 ng) and perylene-d<sub>12</sub> (Pery-d<sub>12</sub>, 35.8 ng), and extracted by soxhlet with 300 mL of dichloromethane. The extracts of sediment samples were concentrated to approximately 100  $\mu\text{L}$  using a rotary evaporator and a gentle stream of N<sub>2</sub> at 40  $^{\circ}\text{C}$ , and solvent exchanged to n-hexane. The solution was cleaned up using pretreated silica gel columns (Sep-Pak silica, 690 mg sorbent, Waters, Milford, MA) with 10 mL of n-hexane. The eluted solution was concentrated to 200  $\mu\text{L}$  under a gentle stream of N<sub>2</sub> at 40  $^{\circ}\text{C}$ , then spiked with a recovery standard (phenanthrene-d<sub>10</sub>, 31.4 ng). During processing, the solutions were protected from light to prevent photochemical degradation of the analytes.

For analysis of elements, each sediment sample (approximately 0.1 g in weight) was digested with 2.0 mL of nitric acid, 0.5 mL of

hydrogen peroxide, and 0.5 mL of hydrogen fluoride using a double-sealed decomposition Teflon vessel at room temperature for 30 min, then placed in a microwave oven at 100 W for 15 min. The mixture solvent was further digested on a hot plate at 150  $^{\circ}\text{C}$  for 90 min. The solution was filtered through a cellulose filter (5C, Advantec, Tokyo, Japan) and diluted to 25 mL with 5% nitric acid. The prepared solutions were stored in Teflon tubes until analysis.

## 2.4. Chemical analysis

Aromatic compounds (CIPAHs, BrPAHs, and PAHs) were analyzed on a gas chromatograph (Agilent HP7890A; Agilent Technologies, Santa Clara, CA) interfaced with a tandem quadrupole mass spectrometer (GC/MS/MS, Waters Quattro micro GC; Waters), operating in EI mode (70 eV). Briefly, the analytical conditions were as follows: for all target CIPAHs, BrPAHs, and PAHs, injection temperature was 250  $^{\circ}\text{C}$  and 5  $\mu\text{L}$  of extracts were injected into the system in pulsed split-less mode with a pulse time of 2 min and pulsed pressure of 20 psi. A DB-5ms capillary column (30 m  $\times$  0.25 mm inner diameter  $\times$  0.25  $\mu\text{m}$  film thickness; Agilent) was used. A constant flow of helium at 1.0 mL/min was used as the carrier gas. The GC column temperature was programmed to increase from 100 (initial equilibrium time 1 min) to 200  $^{\circ}\text{C}$  at a rate of 25  $^{\circ}\text{C}/\text{min}$ , from 200 to 300  $^{\circ}\text{C}$  at a rate of 5  $^{\circ}\text{C}/\text{min}$ , then maintained at 300  $^{\circ}\text{C}$  for 5 min. GC interface and ionization source temperatures were both 300  $^{\circ}\text{C}$  and the system operated in MS/MS mode using Ar as collision gas at a pressure of  $2.8 \times 10^{-3}$  mbar in the collision cell. The detailed analytical conditions, including multiple reaction monitoring conditions for each compound, are described elsewhere (Ohura et al., 2013b).

The analysis of elements was carried out using inductively coupled plasma-mass spectrometry (ICP/MS, HP7500C; Agilent) under the following conditions: RF power: 1600 W, carrier gas (Ar) flow rate: 1.12 L/min, peristaltic pump speed: 0.1 rps.

## 2.5. Quality assurance/quality control

For GC/MS/MS analysis, the procedural blank samples were routinely analyzed after every five samples; no interferences were detected in the blanks. The recovery efficiencies were checked using surrogate standards (Fluor-d<sub>10</sub> and Pery-d<sub>12</sub>) added to all field samples; average recoveries of Fluor-d<sub>10</sub> and Pery-d<sub>12</sub> were  $115 \pm 38\%$  and  $93 \pm 27\%$ , respectively. The instrumental detection limits of target aromatic compounds were equivalent to three times the standard deviation of the peak area of diluted standard solutions, which had a range of 6.1 pg (6,12-Cl<sub>2</sub>Chry) to 185 pg (1-BrPy). The quantification of each target compound was performed by MassLynx software (Waters); retention time (within  $\pm 0.1$  min of the standard value) and intensity of corresponding monitored ions (within  $\pm 30\%$  of the standard value) were then checked as qualitative criteria. Correlation analysis (parametric Pearson correlation test) and principal component analysis (PCA) were performed using statistical analysis software (Excel Tokei, Tokyo, Japan).

Quality control methods for ICP/MS analysis used in this study have been previously confirmed and described elsewhere (Suzuki et al., 2007). Results of elemental analyses are expressed on a dry weight basis.

## 3. Results and discussion

### 3.1. Spatial distributions of sedimentary contaminants

The Yellow Sea is subject to industrial discharges and partially treated domestic effluents; these inputs have increased in recent years because of population growth and industrialization, and rapid

economic development and contamination of the Yellow Sea is a significant concern. To date, there are many reports on the levels of various contaminants in surface sediments and sediment cores from coastal and offshore areas of the Yellow Sea (Wu et al., 2001; Hu et al., 2008; Zhang et al., 2009; Jiao et al., 2012; Li et al., 2012). Here, we provide the first report of Cl/BrPAH contamination of surface sediments in the Yellow Sea.

Eighteen of the 20 target CIPAHs were detected in the sediments. The average, standard deviation, minimum, and maximum concentrations of the sum of CIPAHs detected are summarized in Table 1, and the box plot is represented in Fig. S1 in Supplementary material. The concentrations of individual CIPAHs are listed in Table S2. The mean concentration of total CIPAHs was 731 pg/g, which is similar to the concentration observed in core samples from Tokyo Bay (584 pg/g) (Horii et al., 2009), but is approximately 40 times lower than the concentration in surface sediments from the Muzhou River Watershed in Shenzhen, South China (27.6 ng/g) (Sun et al., 2011). Of the individual CIPAHs, 6-CiBaP was the most abundant, with an average concentration of 246 pg/g, followed by 1-CiPy (159 pg/g), 8-CiFluor (65 pg/g), and 3-CiFluor (55 pg/g) (Table S2). The order in which the concentrations of individual CIPAH species occurred was similar to that observed for CIPAHs associated with ambient particles (Kitazawa et al., 2006) and in fly ash samples from waste incinerators from South Korea (Horii et al., 2008), and CIPAHs in sediments from Tokyo Bay (Horii et al., 2009).

Only five of 11 target BrPAH species were detected in the sediments, and the total concentrations was 33 pg/g on average (Table 1 and Fig. S1). The mean concentration of BrPAHs in sediments from Shenzhen was 53 ng/g (Sun et al., 2011), which is approximately three orders of magnitude higher than that observed in Yellow Sea sediments in this study. Additionally, although relatively low-molecular-weight BrPAHs, such as 1-BrPy and 9-BrFlu, were detected, high-molecular-weight BrPAHs, such as Cl<sub>2</sub>BaA and 6-BrBaP, were not detected. This trend is quite different from that observed in surveys of ambient particles in Japan (Ohura et al., 2009). This implies that sedimentary BrPAHs could be difficult to account for the atmospheric deposition because BrPAHs are susceptible to photodegradation in comparison to CIPAHs (Ohura et al., 2009).

All target PAHs were detected in the sediments, the total concentrations of which had a range of 169–4492 ng/g, with a mean of 518 ng/g (Table 1 and Fig. S1). The mean concentration was similar to that of sediments in coastal areas of the Yellow Sea (472 ng/g) (Jiao et al., 2012), and Tokyo Bay (690 ng/g) (Horii et al., 2009). The mean concentration of total PAHs was approximately three orders of magnitude higher than that of total CIPAHs; this ratio is similar to that observed in airborne particles in a suburban area of Shanghai, China (Ma et al., 2013). A previous study conducted in the Yellow Sea indicated that atmospheric deposition was the primary source of sedimentary PAHs (Liu et al., 2012). These facts suggested that the concentrations of sedimentary CIPAHs in the Yellow Sea would have no small effect on circumjacent CIPAH air pollution. Therefore, CIPAH contaminants in historical samples, such as sediment cores, may be an appropriate indicator reflecting historical air pollution.

All target elements were detected in the sediments; the concentrations of individual elements are listed in Table S2. The mean concentrations of Cu, Zn, and Pb (anthropogenically derived elements) were 86, 206, and 61 μg/g, respectively; these concentrations are somewhat consistent with those observed in sediments from Masan Bay, southeastern Korea (Jeong et al., 2006). The values of the ratio of maximum to minimum concentrations of individual heavy metals were in the range of 1.2 (Ga) to 29 (In), and over half of the targets had a ratio of <5. This consistency was specific for elements, and was quite different from the maximum:minimum concentration ratios of CIPAHs, BrPAHs, and PAHs. This indicates that sedimentary accumulation and removal processes vary between elements and such aromatic contaminants.

The spatial distribution of each pollutant could provide useful information with which to evaluate sedimentary processes. Fig. 2A shows the spatial distributions of total CIPAH, total PAH, and Pb concentrations of sediments in the Yellow Sea. A common trend in the distributions of those contaminants is the presence of an extremely highly polluted site located in the northwestern part of the study area. This suggests that this site could be polluted by dumping activities including these contaminants. Indeed, Leipe et al. have reported that sediments of historical dump site area are significantly enhanced in heavy metals such as Pb and Zn, and PAHs (Leipe et al., 2005). A site that was highly polluted by CIPAHs was observed in the southeast. Interestingly, the compositions of individual CIPAHs varied between two highly polluted sites (Y1/Y3 and Y9/Y13, Fig. 2B): the most abundant species at sites Y1/Y3 and Y9/Y13 were 6-CiBaP and 1-CiPy, respectively. On the other hand, the composition of individual PAHs in among Y1, Y3 and Y9 were almost same despite the concentration levels were quite different (Fig. 2B). Such distinct differences of distribution between CIPAHs and PAHs in the sediments imply the presence of specific sources for CIPAHs. Consequently, sedimentary CIPAHs may be specific indicators of contaminant sources.

### 3.2. Temporal trends in sedimentary contaminants

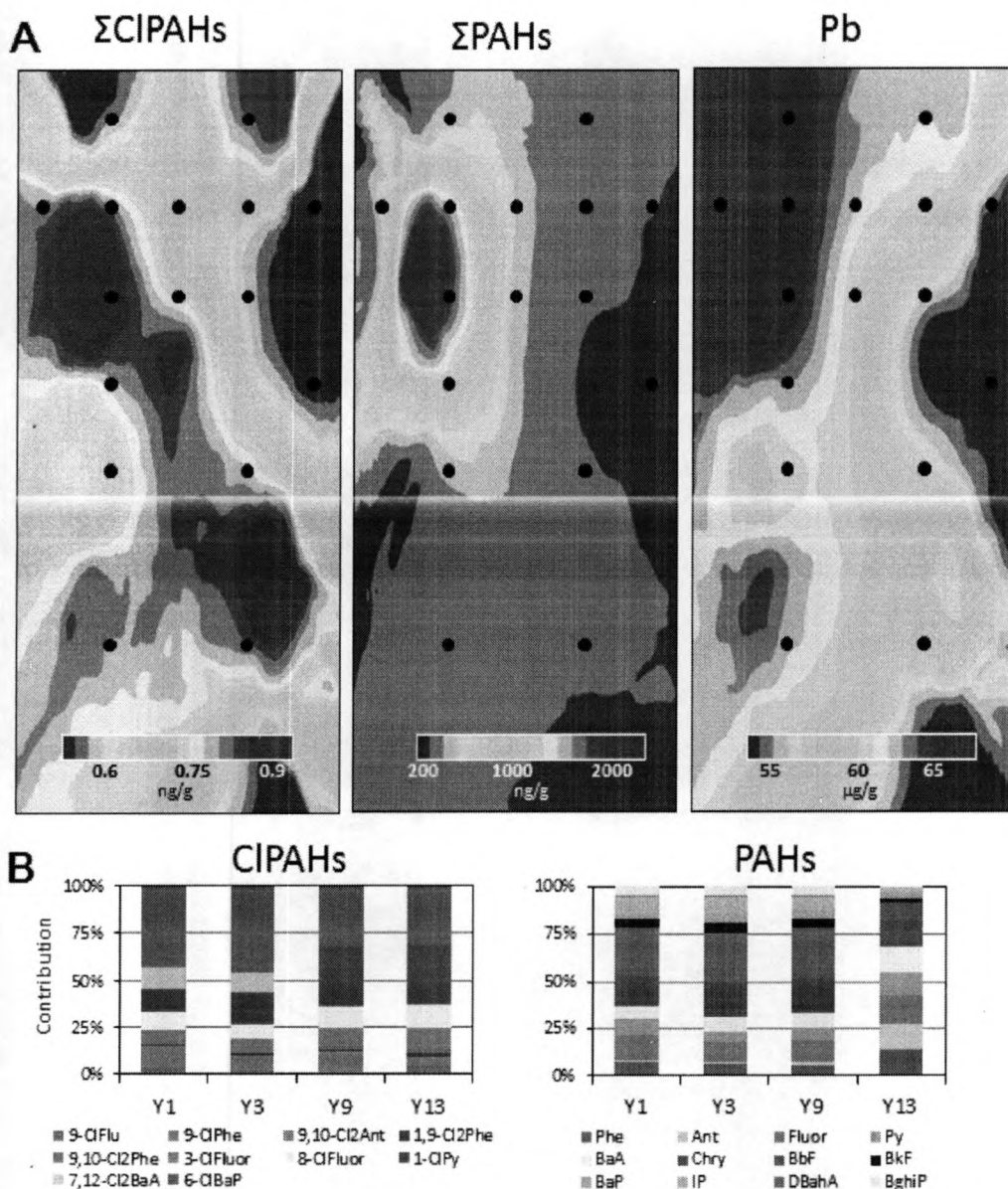
Investigating contaminants in sediment core samples could be helpful in understanding historical trends in pollution. As indicated above, CIPAHs in sediments are capable of being a novel contaminant indicator because of their persistence in sediments. Here, we investigated the concentrations of CIPAHs, BrPAHs, PAHs, and elements in sediment core samples from two locations in Sri Lanka.

Most target CIPAHs were detected in sediment core samples from both sites in Sri Lanka. The mean concentrations of total CIPAHs in sediment cores from Negombo Lagoon and Kandy Lake were 761 and 1147 pg/g, respectively (Table 1 and Fig. S1), and the total CIPAH concentration tended to increase from the bottom to the top of the core (Fig. 3). The possible sources were evaluated by the ratios of CIPAH isomers. Although distinct diagnostic ratios of CIPAHs reflecting their origin have not been identified, as they have for PAHs, we have previously demonstrated that the 6-CiBaP/3-CiFluor ratio has the potential to be applied as a specific indicator of CIPAHs (Horii et al., 2008). The ratio that is used to represent a

**Table 1**

The mean, standard deviation (SD), minimum (min), and maximum (max) concentrations of total CIPAHs (pg/g), total BrPAHs (pg/g), and total PAHs (ng/g) detected in surface sediments (Yellow Sea site) and sediment core (Negombo and Kandy sites) samples.

	Yellow sea				Negombo				Kandy			
	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max
ΣCIPAHs	731.4	194.4	290.2	1129.8	761.0	474.3	320.3	1797.8	1147.2	473.5	551.9	2381.2
ΣBrPAHs	32.7	54.4	5.5	248.3	46.6	35.4	15.3	104.3	58.0	42.7	20.2	159.9
ΣPAHs	517.8	994.9	168.8	4492.0	618.3	397.8	348.3	1503.5	2000.9	410.1	1378.5	3044.6



**Fig. 2.** Spatial distributions of total CIPAHs, total PAHs, and Pb concentrations in surface sediments in the Yellow Sea (A), and the compositions of individual CIPAH at sites Y1, Y3, Y9 and Y13 (B). The notations of sites were represented in Fig. 1.

potential emission source (3.74, the ratio observed in fly ash) is represented as a dashed line in Fig. 3. In the samples from Negombo Lagoon, the ratios do not vary significantly and are relatively close to the ratio of fly ash throughout the cores. In contrast, the ratios in cores from Kandy Lake tended to decrease towards the top, and the ratios in the upper samples (approximately 0–24 cm) were consistent with that of fly ash. The compositions of CIPAHs were also quite different between the sediment cores from the two sites. In Negombo Lagoon, four-ring CIPAHs were dominant throughout the cores. Conversely, in Kandy Lake sediments, the occurrence of four-ring CIPAHs decreased towards the bottom, while the compositions of upper layers were similar to those in Negombo Lagoon sediments. These findings suggest the following: (i) incineration processes are likely to have caused CIPAH contamination in recent years, (ii) impacts of high-molecular-weight CIPAHs, such as 7,12-Cl<sub>2</sub>BaA and 6-ClBaP, were more significant in the past in Kandy Lake, (iii) sediments in Kandy Lake may be more susceptible to diverse sources of CIPAHs than are Negombo Lagoon sediments.

The five species of three to four-ring BrPAHs were detected in cores as shown in the Yellow Sea (Table S2). The mean concentrations of total BrPAHs in core samples from Negombo Lagoon and Kandy Lake were 47 and 58 pg/g, respectively, which were slightly higher than that in Yellow Sea sediments, despite the inclusion of deeper sediments (Table 1 and Fig. S1). The concentrations of individual BrPAH compounds occurred in the following order at both Sri Lankan sites: 1-BrPy > 9,10-Br2Ant > 9-BrPhe ≈ 2-BrFlu; this order was quite different from that observed in Yellow Sea sediments. The differences may be the result of differences in contamination history and differences in contaminant sources between the two areas.

The concentrations of PAHs in the cores were also investigated. The mean concentrations of total PAHs in sediment cores from Negombo Lagoon and Kandy Lake were 618 and 2001 ng/g, respectively (Table 1 and Fig. S1). In studies of historical trends in sedimentary PAH concentrations from around the world, an increase in concentrations from deeper segments to the surface is

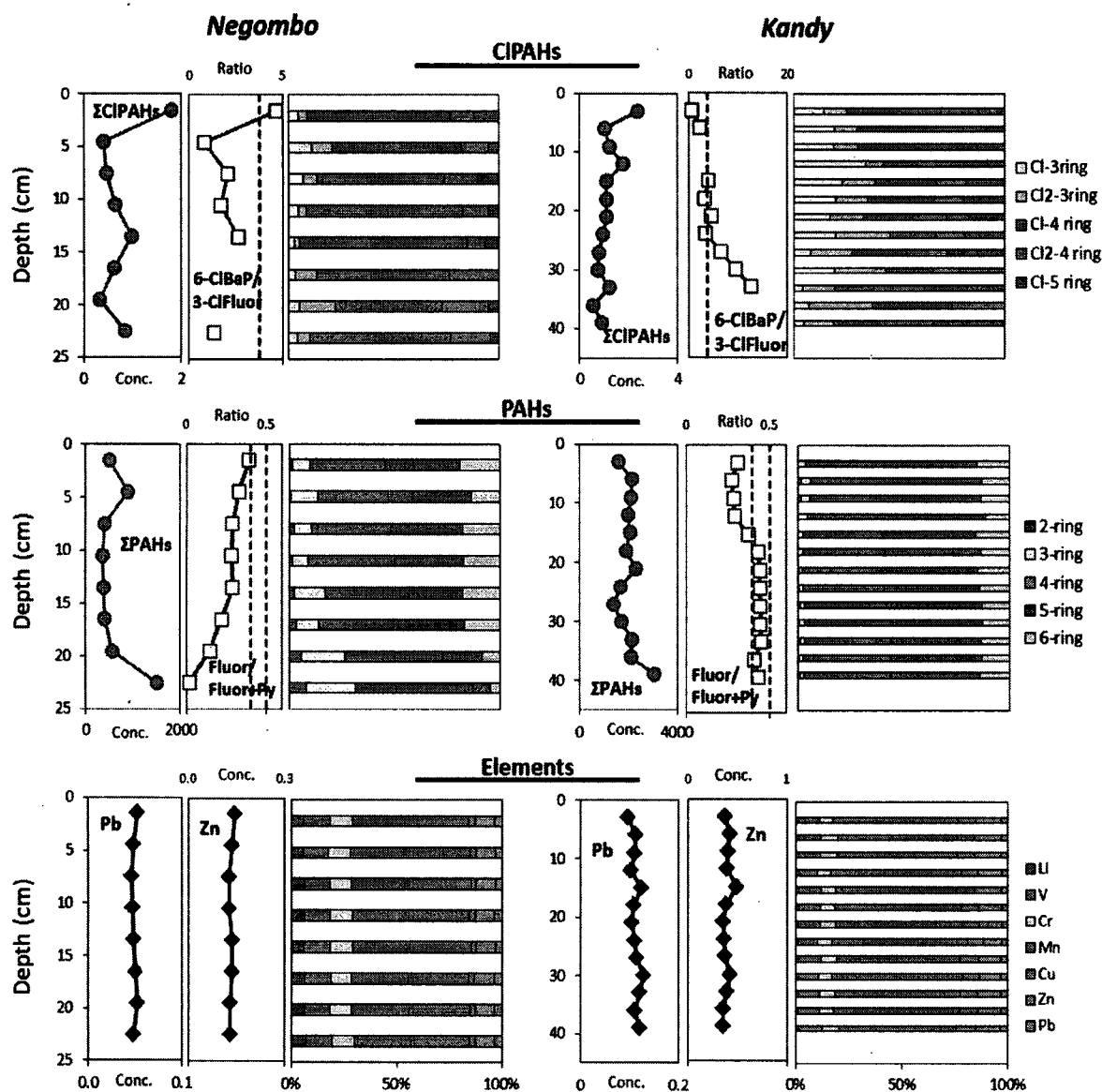


Fig. 3. Vertical profiles of total CIPAHs (ng/g), total PAHs (ng/g), Pb (mg/g), and Zn (mg/g) concentrations, diagnostic ratios of CIPAHs and PAHs, compositions of each aromatic ring, and typical trace elements in sediment cores from Negombo Lagoon and Kandy Lake. The dashed lines shown in diagnostic ratios profiles of CIPAHs represent the value defined as fly ash (3.74), and the dashed lines shown in diagnostic ratios profiles of PAHs represent values defined as the range of petroleum combustion (0.4–0.5).

generally observed. However, no such trend was observed in these cores. Total sedimentary PAH concentrations in Negombo Lagoon decreased from the bottom to the top of the core, while the concentrations in Kandy Lakes sediments varied throughout the core with relatively high concentrations (Fig. 3). A previous study showed that the concentration profile of CIPAHs in Tokyo bay sediment core was similar to that of PAHs, and suggested that they could be related to common sources (Horii et al., 2009). So those possible sources in Sri Lanka sediment cores were estimated from the PAH diagnostic ratio. The concentration ratio of Fluor/(Fluor + Py), a commonly used indicator of coal combustion, also varied between the two cores. The ratios <0.4, 0.4–0.5, and >0.5 have been characterized as indicators of petroleum resources, petroleum combustion (liquid fossil fuel combustion), and grass, wood or coal combustion, respectively (Yunker et al., 2002). In this study, the Fluor/(Fluor + Py) ratios increased from the top to the bottom of the sediment core in Negombo Lagoon, while the ratios

in Kandy Lake sediments were somewhat constant throughout the core (Fig. 3). This indicates that the primary source of sedimentary PAHs could have changed from petrogenic inputs to petroleum combustion in recent years in Nagombo, whereas the source in Kandy Lake remains petroleum combustion, likely representing the effects of accelerated industrialization and urbanization, and associated heavy motor traffic. Negombo Lagoon is also the site of extensive fishing activities, for which small motor boats are used; these may represent a major source of PAHs through the direct disposal of unburned waste diesel and oil into the lagoon. Serious pollution of Kandy Lake waters is expected because it is subject to the discharge of waste into waterways feeding the lake. Recent studies have shown that concentrations of perfluoroalkyl acids and nonylphenol in the surface water of Kandy Lake were a few times higher than those in Negombo Lagoon (Guruge et al., 2007, 2011). Additionally, the compositions of heavy-molecular-weight PAHs (more than five-ring PAHs) increased in the upper layers of

Negombo sediments, which is consistent with Kandy Lake sediments (Fig. 3). That is, it could be said that the significant sources impacting pollution in Negombo Lagoon are changing, which close in on those of Kandy Lake.

The vertical profiles of Pb and Zn, which are typical anthropogenically derived elements, are shown in Fig. 3. They exhibited uniform vertical concentration profiles at both sites, which was different from the results observed for CIPAHs and PAHs. Uniform distributions of trace elements such as Co, Zn, and Cd, but not terrigenous materials such as Al, Fe, and K, have been observed in other lake sediment cores, suggesting that these predominantly originate from natural sources, and may also suggest that their inputs to the lakes have been constant over the measured time scale (Mikac et al., 2011). Additionally, the cause of the differences in vertical profiles between elements and CIPAHs/PAHs might be the result of the partial degradation of CIPAHs/PAHs in sediments.

### 3.3. Source apportionment of CIPAHs in the sediment

To investigate the relationships between the studied contaminants, correlations between individual concentrations were analyzed. Significant correlations ( $p < 0.05$ ) between individual CIPAH concentrations were not widely observed, whereas highly significant correlations ( $p < 0.01$ ) were observed between the concentrations of PAH with more than four rings at each sampling site (Table S3–S5). No significant correlation was observed between total CIPAH and total PAH concentrations at any site (Fig. 4). In the air, individual and total concentrations of particulate CIPAHs and PAHs have frequently been observed to be significantly correlated with each other (Kitazawa et al., 2006; Ma et al., 2013; Ohura et al., 2013a). It is thought that this is the result of common emission sources and similar atmospheric behaviors of those compounds. Therefore, the differences in CIPAH and PAH sedimentary concentrations observed in this study suggest that the origin, and sedimentary inflow processes vary between CIPAHs and PAHs. Additionally, the sedimentary Cu, Zn, and Pb concentrations, which are defined as indicators of anthropogenic activities such as fossil fuel burning, metal manufacturing, and ship building, were

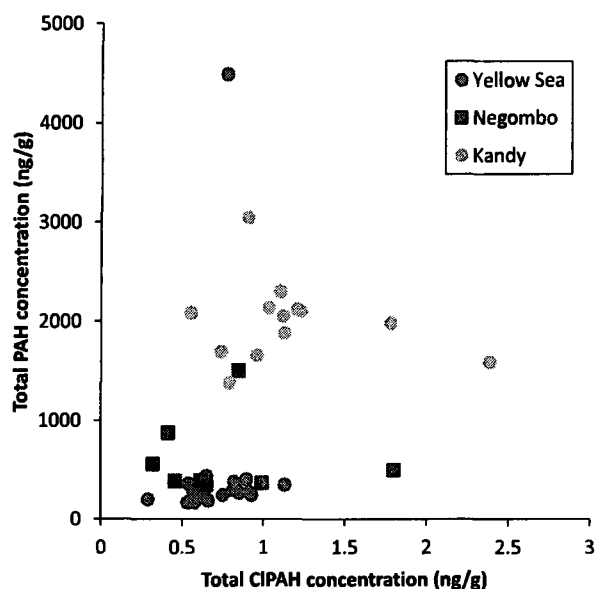


Fig. 4. Relationships between total CIPAH and PAH concentrations at each sampling site.

significantly correlated ( $p < 0.05$ ) with those of total CIPAHs, but not with those of total PAHs (Table S3–S5).

Principal component analysis (PCA) was also performed for certain compounds used in the cluster analysis at each site to clarify the relationships between compounds. The loading plot of each sampling site is shown in Fig. 5A–C. For the samples from the Yellow Sea, the three factors accounted for 78.7% of the variability in the data (Fig. 5A). Factor 1 explains 44.7% of total variance, which showed high loadings on a group of PAHs, including BaA, BaP, BghiP, and IP, which are associated with coal combustion (the loading of each compound is shown in Table S6). Factor 2 explains 20.5% of total variance, which showed high loadings on group of elements, including Cu, Zn, and As, which are associated with anthropogenic sources (Nriagu and Pacyna, 1988). Factor 3 explains 13.5% of total variance, which showed high loadings on a group of CIPAHs, including 9-ClPhe, 3-ClFluor, and 6-ClBaP, whereas most PAHs were associated with each other with negative scores. For the samples from Negombo Lagoon, the three factors accounted for 76.0% of the variability in the data (Fig. 5B). Factor 1 explains 42.9% of total variance, which showed high loadings on a group of PAHs, including BaP, IP, and BghiP, and metals, including Cr, Zn, and As. Factor 2 explains 20.7% of total variance, which showed high loadings on a group of CIPAHs, including 7-ClBaA, 7,12-Cl<sub>2</sub>BaA, and 6-ClBaP. Factor 3 explains 12.4% of total variance, which showed moderately high loadings on 1-ClPy and Pb, whereas a group of PAHs showed negative scores as in the Yellow Sea samples. For the samples from Kandy Lake, the three factors accounted for 71.6% of the variability in the data (Fig. 5C). Factor 1 explains 35.9% of total variance, which showed high loadings on a group of elements, including Ti, Pb, and Cu. Factor 2 explains 21.9% of total variance, which also showed high loadings on a group of metals, including Zn and As. Factor 3 explains 13.8% of total variance, which showed high loadings on a group of PAHs, including Phe, Fluor, and Py. However, the score plots showed specific patterns arising from contaminant characteristics of the sediments. In the samples from the Yellow Sea, the score of the Y13 site was distinguished from those of other samples (Fig. 5D). Site Y13 was highly polluted by PAHs (Fig. 2). Indeed, the influence of PAH contamination in Y13 is also supported by the results of the loading plot (Fig. 5A). Additionally, the scores from Negombo Lagoon show that the extent of contamination tended to be higher in the upper layers (N<sub>0</sub>–3) (Fig. 5E). In Kandy Lake, the score plot shows that the samples from upper layers (K<sub>2</sub>–5 to K<sub>11</sub>–14) may have been subjected to CIPAH contamination, whereas the bottom (K<sub>31</sub>–34 to K<sub>37</sub>–40) and middle layers (K<sub>14</sub>–17 to K<sub>29</sub>–31) were relatively susceptible to PAH and elemental contamination, respectively (Fig. 5F). These findings indicate that the sources and contaminant processes of CIPAHs may be similar to those of elements, rather than to those of PAHs because most of the corresponding loadings were clustered in the PCA. Additionally, contamination by CIPAH may have occurred relatively recently.

### 3.4. Ecotoxicological risk

To evaluate the potential ecotoxicological risk in sediments, we calculated effects range low (ERL) and effects range median (ERM) values from adverse biological effects for various PAH compounds (Long et al., 1995). The evaluation was performed on the concentrations of PAHs and elements; the evaluation did not include CIPAHs and BrPAHs because the guidelines of such halogenated PAHs have been not estimated at all. Additionally, evaluation of sediments from the Yellow Sea was performed using average concentration values, and sediments from Negombo Lagoon and Kandy Lake were evaluated using the concentrations present in each top layer sample, to standardize sediment condition. The ERL and ERM

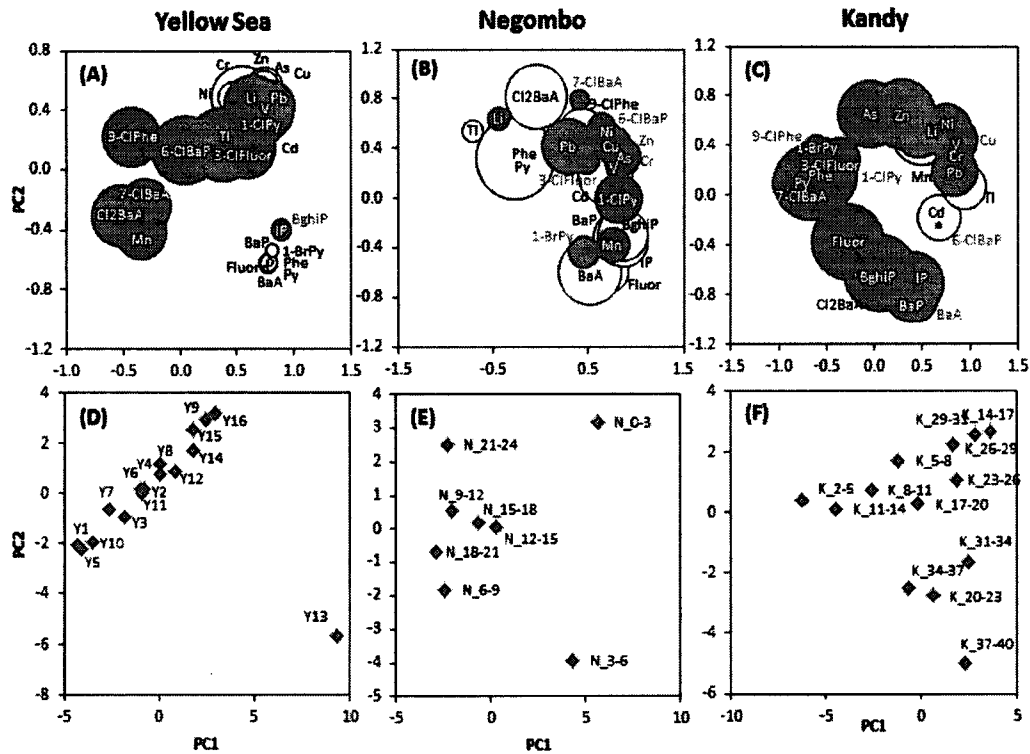


Fig. 5. Loading plots (A–C) and score plots (D–F) of typical CIPAHs, PAHs, and elements at each sampling site. Loading values of principal component 3 in loading plots are represented by the circle size. Blue and open circles shown in loading plots represent positive and negative scores in principal component 3, respectively. The numbers shown in score plots represent the sampling sites in the Yellow Sea and the depth of core samples in Negombo Lagoon and Kandy Lake. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

values and sedimentary concentrations of appropriate toxicants are listed in Table S7. Fig. 6 shows the relative intensities of each element and of PAHs with the same number of rings in sediment samples; in this figure, the ERL and ERM values are represented by 0 and 100 on the y-axis, respectively. The index for elements indicate characteristic variations of each sample; high toxicities were observed in sediments of the Yellow Sea for Cr, and in Kandy

Lake for Cu and Zn, while the risks associated with PAHs were low in all sediments. The risks associated with PAHs tended to decrease with an increase in the number of aromatic rings. A relatively high contribution of low-molecular-weight PAHs (<4-ring PAHs) has been considered to indicate a petrogenic source origin. In contrast, a high contribution of high-molecular-weight PAHs (more than four-ring PAHs) indicates a pyrolytic source origin. Considering the

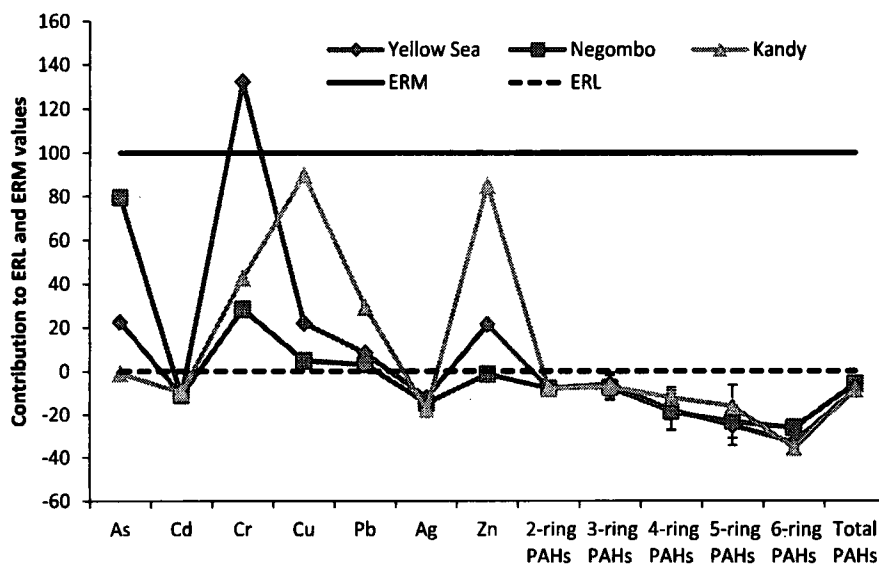


Fig. 6. Relative intensity of effects range low and effects range medium values for corresponding components in each sediment sample.



biological impacts of PAHs in these areas, more attention should be paid to petrogenic contaminants than to pyrolytic ones.

#### 4. Conclusion

This study reports the spatial and vertical distributions of halogenated PAHs in the sediments at differential sites in Asia. The spatial distributions of total CIPAHs concentrations in the Yellow Sea showed the specific hot spots that are different from those of PAHs. The vertical distributions of CIPAHs were investigated in the sediments at two sites in Sri Lanka. In the both sites, the concentrations of total CIPAHs showed relatively similar trends, which were higher in surface layers than in bottom layers. However the total PAHs concentrations showed the profiles quite different from those of CIPAHs. That is, the characteristic is common, but limited surveys, was that the concentration profiles varied between CIPAHs and PAHs. These facts suggest that there is a distinct difference in sources and/or contaminant processes including decay processes such as photo- and biodegradation between CIPAHs and PAHs in the sediments. There are only a few reports that CIPAHs were investigated in sediments. Therefore the occurrences, behaviors and sources of CIPAHs in sediment remain unclear rather than those of PAHs. Further studies that investigate the sedimentary CIPAHs will be needed to accurately evaluate their biological impacts.

#### Acknowledgments

This work was supported in part by the Ministry of Education, Culture, Sports, Science and Technology, Grant-in-Aid for Scientific Research (B) (No. 23310011) and Scientific Research (C) (No. 26340015).

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2014.10.028>.

#### References

- Arzayus, K.M., Dickhut, R.M., Canuel, E.A., 2001. Fate of atmospherically deposited polycyclic aromatic hydrocarbons (PAHs) in Chesapeake Bay. *Environ. Sci. Technol.* 35, 2178–2183.
- Baek, S.O., Field, R.A., Goldstone, M.E., Kirk, P.W., Lester, J.N., Perry, R., 1991. A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior. *Water Air Soil Pollut.* 60, 279–300.
- Ball, A., Truskeywicz, A., 2013. Polyaromatic hydrocarbon exposure: an ecological impact ambiguity. *Environ. Sci. Pollut. Res. Int.* 20, 4311–4326.
- Barakat, A.O., Mostafa, A., El-Sayed, N.B., Wade, T.L., Sweet, S.T., 2012. Polycyclic aromatic hydrocarbons (PAHs) in surface sediments of Lake Manzala, Egypt. *Soil Sediment Contam. Int. J.* 22, 315–331.
- Boonyatumanond, R., Wattayakorn, G., Togo, A., Takada, H., 2006. Distribution and origins of polycyclic aromatic hydrocarbons (PAHs) in riverine, estuarine, and marine sediments in Thailand. *Mar. Pollut. Bull.* 52, 942–956.
- Bostrom, C.E., Gerde, P., Hanberg, A., Jernstrom, B., Johansson, C., Kyrklund, T., Rannug, A., Tornqvist, M., Victorin, K., Westerholm, R., 2002. Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. *Environ. Health Perspect.* 110 (Suppl. 3), 451–488.
- Guerra, R., 2012. Polycyclic aromatic hydrocarbons, polychlorinated biphenyls and trace metals in sediments from a coastal lagoon (Northern Adriatic, Italy). *Water Air Soil Pollut.* 223, 85–98.
- Guruge, K.S., Horii, Y., Yamashita, N., 2011. Profiles of nonylphenol isomers in surface waters from Sri Lanka. *Mar. Pollut. Bull.* 62, 870–873.
- Guruge, K.S., Taniyasu, S., Yamashita, N., Manage, P.M., 2007. Occurrence of perfluorinated acids and fluorotelomers in waters from Sri Lanka. *Mar. Pollut. Bull.* 54, 1667–1672.
- Horii, Y., Ohura, T., Yamashita, N., Kannan, K., 2009. Chlorinated polycyclic aromatic hydrocarbons in sediments from industrial areas in Japan and the United States. *Arch. Environ. Contam. Toxicol.* 57, 651–660.
- Horii, Y., Ok, G., Ohura, T., Kannan, K., 2008. Occurrence and profiles of chlorinated and brominated polycyclic aromatic hydrocarbons in waste incinerators. *Environ. Sci. Technol.* 42, 1904–1909.
- Hu, J., Liu, W.X., Chen, J.L., Fan, Y.S., Xing, B.S., Kang, H., Tao, S., 2008. Distribution and property of polycyclic aromatic hydrocarbons in littoral surface sediments from the Yellow Sea, China. *J. Environ. Sci. Health A Toxic Hazard. Subst. Environ. Eng.* 43, 382–389.
- Jeong, K.S., Cho, J.H., Lee, J.H., Kim, K.H., 2006. Accumulation history of anthropogenic heavy metals (Cu, Zn, and Pb) in Masan Bay sediments, southeastern Korea: a role of chemical front in the water column. *Geosci. J.* 10, 445–455.
- Jiao, W., Wang, T., Khim, J., Luo, W., Hu, W., Naile, J., Giesy, J., Lu, Y., 2012. PAHs in surface sediments from coastal and estuarine areas of the northern Bohai and Yellow Seas, China. *Environ. Geochem. Health* 34, 445–456.
- Khim, J.S., Kannan, K., Villeneuve, D.L., Koh, C.H., Giesy, J.P., 1999. Characterization and distribution of trace organic contaminants in sediment from Masan Bay, Korea. 1. Instrumental analysis. *Environ. Sci. Technol.* 33, 4199–4205.
- Kim, K.-H., Jahan, S.A., Kabir, E., Brown, R.J.C., 2013. A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. *Environ. Int.* 60, 71–80.
- Kitazawa, A., Amagai, T., Ohura, T., 2006. Temporal trends and relationships of particulate chlorinated polycyclic aromatic hydrocarbons and their parent compounds in urban air. *Environ. Sci. Technol.* 40, 4592–4598.
- Leipe, T., Kersten, M., Heise, S., Pohl, C., Witt, G., Liehr, G., Zettler, M., Tauber, F., 2005. Ecotoxicity assessment of natural attenuation effects at a historical dumping site in the western Baltic Sea. *Mar. Pollut. Bull.* 50, 446–459.
- Li, X., Liu, L., Wang, Y., Luo, G., Chen, X., Yang, X., Gao, B., He, X., 2012. Integrated assessment of heavy metal contamination in sediments from a coastal industrial basin, NE China. *PLoS One* 7, e39690.
- Lima, A.L.C., Farrington, J.W., Reddy, C.M., 2005. Combustion-derived polycyclic aromatic hydrocarbons in the environment—a review. *Environ. Forensics* 6, 109–131.
- Liu, L.-Y., Wang, J.-Z., Wei, G.-L., Guan, Y.-F., Zeng, E.Y., 2012. Polycyclic aromatic hydrocarbons (PAHs) in continental shelf sediment of China: implications for anthropogenic influences on coastal marine environment. *Environ. Pollut.* 167, 155–162.
- Long, E., Macdonald, D., Smith, S., Calder, F., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environ. Manag.* 19, 81–97.
- Ma, J., Chen, Z., Wu, M., Feng, J., Horii, Y., Ohura, T., Kannan, K., 2013. Airborne PM2.5/PM10-associated chlorinated polycyclic aromatic hydrocarbons and their parent compounds in a suburban area in Shanghai, China. *Environ. Sci. Technol.* 47, 7615–7623.
- Mastral, A.M., Callén, M.S., 2000. A review on polycyclic aromatic hydrocarbon (PAH) emissions from energy generation. *Environ. Sci. Technol.* 34, 3051–3057.
- Meador, J.P., Stein, J.E., Reichert, W.L., Varanasi, U., 1995. Bioaccumulation of polycyclic aromatic hydrocarbons by marine organisms. *Rev. Environ. Contam. Toxicol.* 143, 79–165.
- Mikac, I., Fiket, Z., Terzic, S., Baresic, J., Mikac, N., Ahel, M., 2011. Chemical indicators of anthropogenic impacts in sediments of the pristine karst lakes. *Chemosphere* 84, 1140–1149.
- Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* 333, 134–139.
- Ohura, T., 2007. Environmental behavior, sources, and effects of chlorinated polycyclic aromatic hydrocarbons. *ScientificWorldJournal* 7, 372–380.
- Ohura, T., Fujima, S., Amagai, T., Shinomiya, M., 2008. Chlorinated polycyclic aromatic hydrocarbons in the atmosphere: seasonal levels, gas-particle partitioning, and origin. *Environ. Sci. Technol.* 42, 3296–3302.
- Ohura, T., Horii, Y., Kojima, M., Kamiya, Y., 2013a. Diurnal variability of chlorinated polycyclic aromatic hydrocarbons in urban air. *Jpn. Atmos. Environ.* 81, 84–91.
- Ohura, T., Kitazawa, A., Amagai, T., Makino, M., 2005. Occurrence, profiles, and photostabilities of chlorinated polycyclic aromatic hydrocarbons associated with particulates in urban air. *Environ. Sci. Technol.* 39, 85–91.
- Ohura, T., Sawada, K., Amagai, T., Shinomiya, M., 2009. Discovery of novel halogenated polycyclic aromatic hydrocarbons in urban particulate matters: occurrence, photostability, and AhR activity. *Environ. Sci. Technol.* 43, 2269–2275.
- Ohura, T., Yamamoto, T., Higashino, K., Sasaki, Y., 2013b. Halogenated PAH contamination in urban soils. In: Lichtfouse, E., Schwarzbauer, J., Robert, D. (Eds.), *Green Materials for Energy, Products and Depollution*. Springer, Netherlands, pp. 449–466.
- Pathiratne, K.A.S., De Silva, O.C.P., Hehemann, D., Atkinson, I., Wei, R., 2007. Occurrence and distribution of polycyclic aromatic hydrocarbons (PAHs) in Bolgoda and beira lakes, Sri Lanka. *Bull. Environ. Contam. Toxicol.* 79, 135–140.
- Pereira, W.E., Hostettler, F.D., Rapp, J.B., 1996. Distributions and fate of chlorinated pesticides, biomarkers and polycyclic aromatic hydrocarbons in sediments along a contamination gradient from a point-source in San Francisco Bay, California. *Mar. Environ. Res.* 41, 299–314.
- Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmos. Environ.* 42, 2895–2921.
- Sun, J.L., Ni, H.G., Zeng, H., 2011. Occurrence of chlorinated and brominated polycyclic aromatic hydrocarbons in surface sediments in Shenzhen, South China and its relationship to urbanization. *J. Environ. Monit.* 13, 2775–2781.
- Sun, J.L., Zeng, H., Ni, H.G., 2013. Halogenated polycyclic aromatic hydrocarbons in the environment. *Chemosphere* 90, 1751–1759.
- Suzuki, Y., Watanabe, I., Oshida, T., Chen, Y.-J., Lin, L.-K., Wang, Y.-H., Yang, K.-C., Kuno, K., 2007. Accumulation of trace elements used in semiconductor industry in Formosan squirrel, as a bio-indicator of their exposure, living in Taiwan. *Chemosphere* 68, 1270–1279.

- Wild, S.R., Jones, K.C., 1995. Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget. *Environ. Pollut.* 88, 91–108.
- Wu, Y., Zhang, J., Mi, T.-z., Li, B., 2001. Occurrence of n-alkanes and polycyclic aromatic hydrocarbons in the core sediments of the Yellow Sea. *Mar. Chem.* 76, 1–15.
- Wu, Y., Zhang, J., Zhu, Z., 2003. Polycyclic aromatic hydrocarbons in the sediments of the Yalujiang Estuary, North China. *Mar. Pollut. Bull.* 46, 619–625.
- Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* 33, 489–515.
- Zhang, P., Song, J., Fang, J., Liu, Z., Li, X., Yuan, H., 2009. One century record of contamination by polycyclic aromatic hydrocarbons and polychlorinated biphenyls in core sediments from the southern Yellow Sea. *J. Environ. Sci.* 21, 1080–1088.