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Relation	



PAHs concentration and toxicity in organic solvent extracts of atmospheric particulate matters and sea sediments

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Abstract

The concentration of polycyclic aromatic hydrocarbons (PAHs) and the toxicity to marine bacteria (*Vibrio fischeri*) were measured for the organic solvent extracts of sea sediments collected from an urban watershed area (Hiroshima Bay) of Japan and compared with the concentrations and toxicity of atmospheric particulate matters. Among atmospheric particulate matters, the PAHs concentration was highest in FPM collected during cold seasons. The concentrations of sea sediments were 0.01-0.001 times those of atmospheric particulate matters. $1/EC_{50}$ was 1-10 L g⁻¹ PM for atmospheric particulate matters and 0.1-1 L g⁻¹ dry solids for sea sediments. These results imply that toxic substances from atmospheric PM are diluted several tens or hundreds times in sea sediments. The ratio of the $1/EC_{50}$ to PAHs concentration (($1/EC_{50}$)/16PAHs) was stable for all sea sediments (0.1-1 L μg⁻¹ 16PAHs) and was the same in the order of the magnitude as that of FPM and CPM. The ratio of sediments collected from the west was more similar to that of CPM while that of the east was to FPM, possibly because of hydraulic differences among water bodies. The PAHs concentration pattern analyses (principal component analysis and isomer ratio analysis) were conducted and from the results. PAHs pattern of sea sediments was fairly different from that of FPM and CPM. Comparison to previously conducted PAHs analyses suggested that biomass burning residues comprised a major portion of these other sources.

Keywords

atmospheric particulate matter; PAHs; sea sediment; toxicity; *Vibrio fischeri*

40 INTRODUCTION

41 The load of toxic chemical substances runoff from urban areas has become a serious problem. These toxic
42 chemicals include polycyclic aromatic hydrocarbons (PAHs), which are a group of organic compounds
43 composed of two or more fused benzene rings that have been linked to carcinogenicity and mutagenicity
44 (Dipple 1985; Vinggaard et al., 2000; Xue et al., 2005). PAHs primarily originate from the incomplete
45 combustion of fossil fuels, which results in their emission into the atmosphere and subsequently into
46 water environments. In our previous studies (Ozaki et al., 2006, 2007, 2009; Iwasaki et al., 2009; Kojima
47 et al., 2010), the behaviours of PAHs were extensively investigated in Hiroshima Bay.

48 In this study, the concentration of polycyclic aromatic hydrocarbons (PAHs) and their toxicity to marine
49 bacteria (*Vibrio fischeri*) were measured based on the organic solvent extracts of sea sediments collected
50 from the Hiroshima Bay and compared with those of atmospheric particulate matters. Many researchers
51 have extensively investigated atmospheric and aquatic PAHs pollution (Radke et al., 1988; Rodge et al.,
52 1998; Fernandez et al., 2000; Schauer et al., 2001; Yunker et al., 2002; Dickhut et al., 2000; Soclo et al.
53 2000; Kovouras et al. 2001; Martins et al. 2002; Pengchai et al. 2004; Colombo et al., 2006); however,
54 the relationship between PAHs concentration and the risks they pose is still unclear. One difficulty is that
55 the majority of PAHs are emitted from many different incomplete combustion processes, which makes
56 determining the relationship between toxicity and each specific chemical complicated. Also, each PAHs
57 pattern of different sources is not so clearly differentiated.

58 When evaluating the toxicity of sediments, chemical analyses of PAHs would help determine the
59 magnitude of anthropogenic contamination and provide estimates of their concentration. However, such
60 analyses do not provide information about the effects of the contaminants on living organisms.
61 Conversely, toxicity bioassays provide information about the biological impacts of contaminants, but no

1 indication of the causes of the observed toxicities. To evaluate the environmental impact of sediment
2 contaminants, both chemical and biological analyses are needed (Salizzato et al., 1998; Brack et al., 1999;
3 Papadopoulou and Samara, 2002; Olajire et al., 2005; Abbondanzi et al., 2006; Bihari et al., 2007).
4 This study focused on atmospheric particles and sea sediments. The PAHs concentration patterns and
5 toxicities in the same region were compared between the atmospheric particles collected in 2002~2003
6 and 2009 and the coastal sea sediments collected in 2004. Both are the major, spatial and temporal
7 averaged stages and coastal sea sediments are considered to be a major final sink of PAHs. Hence,
8 investigation of the similarities or differences in the toxicity and PAHs concentrations of organic extracts
9 of atmospheric particulate matters and sediments can enable an effective discussion of the sources and
10 pathways of PAHs and other related toxic substances.

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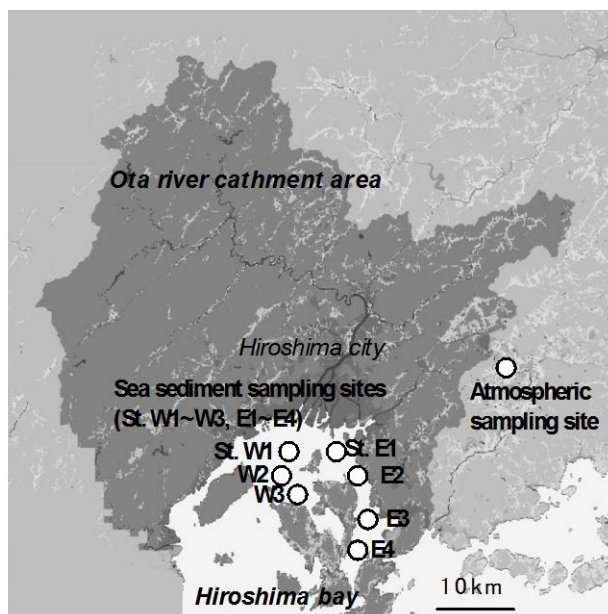
12 **EXPERIMENTAL METHODS**

13 **Air and sea sediment samples**

14 The atmospheric particulate matter (PM) sampling site was located at the Saijo campus of Hiroshima
15 University in Higashihiroshima, Japan (34°23'11" N, 132°43'00" E), which is located 3 km southwest of
16 the city center. Sampling devices were placed on the roof of an eight storey building on campus (height:
17 30 m). Atmospheric PM was collected using a high volume air sampler with an impactor system followed
18 by a glass fiber filter. The impactor system trapped particles with a diameter > 7 μm (coarse particulate
19 matter; CPM), which were then sieved so that only particles of 0.6–7 μm (fine particulate matter; FPM)
20 were collected on a glass fiber filter. Samples were collected during warm (September and October 2002
21 and Aug. 2009; n=13 for FPM and 8 for CPM) and cold seasons (December 2002, Jan. 2003 and Dec.
22 2009; n=10 for FPM and 3 for CPM).

23 The atmospheric and sea sediment sample locations are shown in **Figure 1** along with their watershed
24 area. The watershed area was located in the southwest region of Japan (34° N, 132° E). The area is 1,710
25 km² and includes Hiroshima City. The total population of the watershed area is 9.8×10^5 (population
26 density: 570 person km⁻²). The area of Hiroshima Bay is 230 km², and the maximum depth is 28 m.
27 Samples were collected from seven sampling points (St. W1-W3 (Sediment West) and E1-E4 (Sediment
28 East)) in September and November of 2004 using a core sampler. Core samples were cut into 2 cm slices
29 and freeze dried. Samples were subsequently homogenized and particles larger than 2 mm were removed
30 by sieving. The PAHs in the first three (6 cm) slices measured resulting in three samples per station, and a
31 total of 21 samples. Chemical and mechanical analyses were conducted for the top sediments (top 2 cm
32 slices). C, H, N, and S contents were measured with a CHNS/O analyzer (2400 series-II; Perkin Elmer
33 Co. Ltd.). Sediments were passed over sieves with different meshing to quantify the grain size fractions
34 <5 μm and <75 μm.

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39 **PAHs extraction and analysis**
Figure 1. Sampling locations.

1 For particulate PAHs, a sample was extracted with dichloromethane (DCM) in an ultrasonic water bath,
 2 and the extract was concentrated into 2 mL by N₂-gas. After concentration, the PAH concentration was
 3 analyzed using a gas chromatograph equipped with a mass selective detector (GC-17A/MS-QP5050;
 4 SHIMADZU Co.). The details of the extraction and analysis are shown elsewhere (Iwasaki et al., 2009).
 5 Sixteen unsubstituted PAHs were measured (**Table 1**). The detection limit was set at the level of 3 in the
 6 SN ratio. Instrument detection limits (IDL) ranged from 0.1 ~1 pg for each species. Within this level, the
 7 coefficient of variation of each of the compounds was less than 20%. The quality of extraction was
 8 checked using dried marine sediments (HS-3B, National Research Council of Canada Institute for Marine
 9 Biosciences), and the diesel particulate matter (NIST SRM2975). The recovery averaged 50 ~ 80% for
 10 the marine sediments and 40~60% for the diesel particulate matter for all PAHs, and the repetition error
 11 was 5 ~ 10%.

12
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Table 1. List of measured PAHs and their instrumental detection limits.

Name	Abbreviation	IDL* (pg)	Name	Abbreviation	IDL* (pg)
Acenaphthylene	Acty	0.10	Chrysene	Chr	0.10
Acenaphthene	Acen	0.10	Benzo(b)fluoranthene	B(b)F	0.14
Fluorene	Flu	0.23	Benzo(k)fluoranthene	B(k)F	0.45
Phenanthrene	Phe	0.10	Benzo(e)pyrene	B(e)P	0.10
Anthracene	Ant	0.10	Benzo(a)pyrene	B(a)P	0.50
Fluoranthene	Flt	0.10	Dibenzo(ah)anthracene	D(ah)A	0.74
Pyrene	Pyr	0.10	Benzo(ghi)perylene	B(ghi)P	0.38
Benzo(a)anthracene	B(a)A	0.10	Indeno(123-cd)pyrene	Ind	0.43

*IDL: Instrument detection limit (pg injected)

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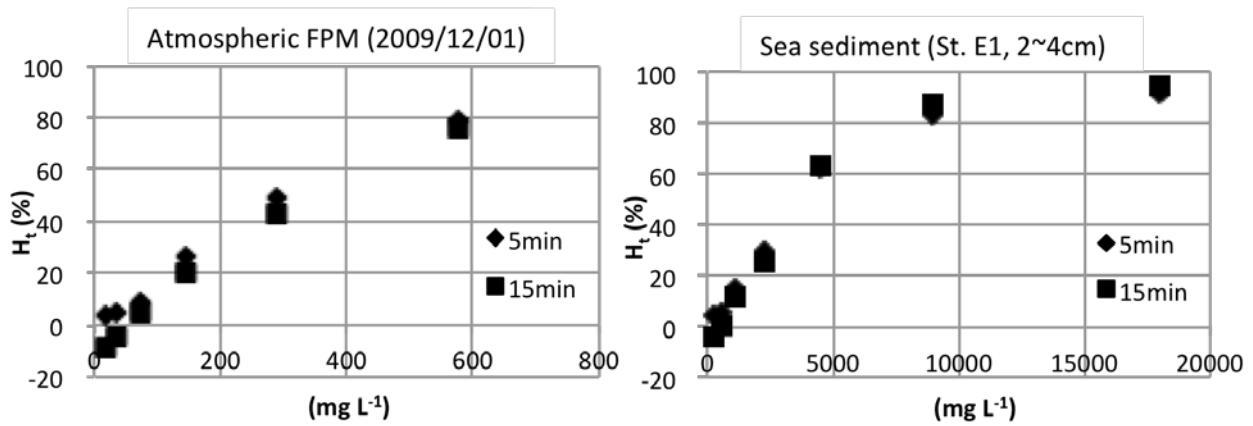
16 Toxicity measurements with *Vibrio fischeri*

17 The toxicity of organic solvents extracts from the solids were measured based on the attenuation of
 18 luminescence of the marine luminescent bacteria *Vibrio fischeri* (NRRRL B-11177). To accomplish this,
 19 sample solids were extracted with DCM using a method similar to that used for PAHs. The solvents were
 20 subsequently transferred to dimethyl sulfoxide (DMSO), which is less toxic to bacteria, by N₂-gas. Next,
 21 the toxicity was measured using the ISO 11348-1(2007) method. Briefly, the bacteria were supplied in a
 22 standard freeze-dried state by Strategic Diagnostics Inc. and then cultivated with the designated substrates
 23 prior to the experiments. The luminescence was measured using a luminescence microplate reader
 24 (LP-5000; Microtech-Nichion Co. Ltd.). The DMSO concentration was set at 5% for all dilution series, at
 25 which level the background DMSO toxicity was negligible. However, residual DCM in the transferred
 26 DMSO solution may exert toxicity, thereby hindering the evaluations. Accordingly, these effects were
 27 checked prior to the analyses using DCM blank solution and the level of the toxicity after transfer was
 28 found to be negligible (<5%). The recovery ratio of the extracts following the transfer from DCM to
 29 DMSO was investigated for several pure reagents of targeted PAHs (phenanthrene (3-rings), pyrene
 30 (4-rings), and benzo(a)pyrene (5-rings)). The solvent concentration was determined based on the
 31 excitation-emission spectra of each chemical. The obtained recovery ratio was almost 100% for all three
 32 compounds.

33 The inactivation ratio was determined by the luminescence attenuation after the 15 minutes exposure to
 34 the sample solution, and the EC50 was determined from the results by the dilution series of exposures.

35 **Figure 2** shows an example of the results of toxicity testing of atmospheric FPM and sea sediment. The
 36 luminescence inhibitory effect (H_i), Γ, and EC50 and 20 calculated from the Γ value are shown for t=5
 37 and 15min (EC50 and 20 concentrations were calculated from power law of the concentration (C) and Γ
 38 (Γ=a Cⁿ)). EC50 concentration was expressed as the amount of particulate matter or dry solid of sea
 39 sediments subjected to extraction with DCM in a liter of toxicity testing solution.

40



(mg L ⁻¹)	Mean	95% confidence interval
T=5min EC50	2.8x10 ²	(2.0x10 ² , 4.6x10 ²)
EC20	1.0x10 ²	(0.8x10 ² , 1.4x10 ²)
T=15min EC50	3.2x10 ²	(2.7x10 ² , 3.9x10 ²)
EC20	1.5x10 ²	(1.3x10 ² , 1.8x10 ²)

(mg L ⁻¹)	Mean	95% confidence interval
T=5min EC50	3.3x10 ³	(2.6x10 ³ , 4.1x10 ³)
EC20	1.2x10 ³	(0.9x10 ³ , 1.5x10 ³)
T=15min EC50	3.8x10 ³	(2.9x10 ³ , 5.1x10 ³)
EC20	2.0x10 ³	(1.4x10 ³ , 2.6x10 ³)

1
2 **Figure 2.** Examples of the toxicity of atmospheric PM and sea sediment extracts by DCM to *V. fischeri*.
3

4 RESULTS AND DISCUSSION

5 PAHs concentrations of atmospheric PM and sea sediments

6 **Table 2** shows the results of concentrations of the sum of sixteen PAHs (16PAHs) in atmospheric PM and
7 **Table 3** shows the PAHs concentration determined from sea sediments along with the results of the basic
8 chemical and mechanical analyses. Among the PM concentrations, FPM concentration in warm season
9 was substantially fluctuated ($39.64 \pm 36.00 \mu\text{g m}^{-3}$). This was due to their being two exceptionally high
10 concentrations ($131.25 \mu\text{g m}^{-3}$: 2009/08/09; $93.40 \mu\text{g m}^{-3}$: 2002/10/05) in the FPM warm measurements.
11 When those readings were excluded, the concentration of PAHs in the FPM was calculated to be
12 $26.76 \pm 17.63 \mu\text{g m}^{-3}$. Comparison of the 16PAHs concentrations in FPM and CPM revealed that they were
13 higher for FPM. Investigation of the seasonal fluctuations revealed that the 16PAHs concentrations were
14 higher for cold seasons in FPM. These tendencies are commonly observed in atmospheric PAHs
15 measurements. Analysis of the 16PAHs in PM revealed that FPM concentrations were substantially higher
16 than those of CPM. Seasonal fluctuations were not observed in the concentration of PAHs of the CPM.
17 **Figure 3** shows the concentration patterns of the PAHs (ng g^{-1}) in atmospheric PM and sea sediments.
18 The concentrations of the sea sediments were 0.01–0.001 times those of the atmospheric particulate
19 matters. Additionally, the PAHs concentrations were higher in Sediment East samples than Sediment West
20 samples. This was likely a result of water flow in the bay. Specifically, the western area is more open to
21 the outer sea area, whereas the east is relatively enclosed by other islands (**Figure 1**), which may cause
22 pollutants to be retained to a greater degree in the eastern portion of the bay. The concentrations of C, H,
23 N and S were also found to be higher in Sediment East samples than Sediment West samples (**Table 3**).

24
25 **Table 2.** Atmospheric PMs and PAHs concentrations.

	FPM warm	CPM warm	FPM cold	CPM cold
PM $\mu\text{g m}^{-3}$	39.64 ± 36.00	4.83 ± 2.49	23.02 ± 11.58	10.69 ± 4.52
16PAHs ng m^{-3}	1.28 ± 0.82	0.11 ± 0.05	2.62 ± 1.76	0.19 ± 0.14

26
27
28 **Table 3.** Chemical and mechanical analysis of sea sediments and PAHs concentrations.

	Water depth (m)	Water content (%)	CHN contents				Grain size distribution			16PAHs ng g^{-1}
			C (%)	H (%)	N (%)	S (%)	Clay (<5 μm) (%)	Silt (5~75 μm) (%)	Sand (75 μm ~2mm) (%)	
Sed. West	18~28	92.2 ± 0.4	2.8 ± 0.2	1.04 ± 0.04	0.31 ± 0.04	0.5 ± 0.02	24.1 ± 3.7	75.8 ± 3.5	0.1 ± 0.1	227 ± 139
Sed. East	11~22	87.7 ± 7.1	3.5 ± 0.4	1.19 ± 0.07	0.35 ± 0.04	0.85 ± 0.07	29.2 ± 4.7	70.8 ± 4.7	0.1 ± 0.1	824 ± 255

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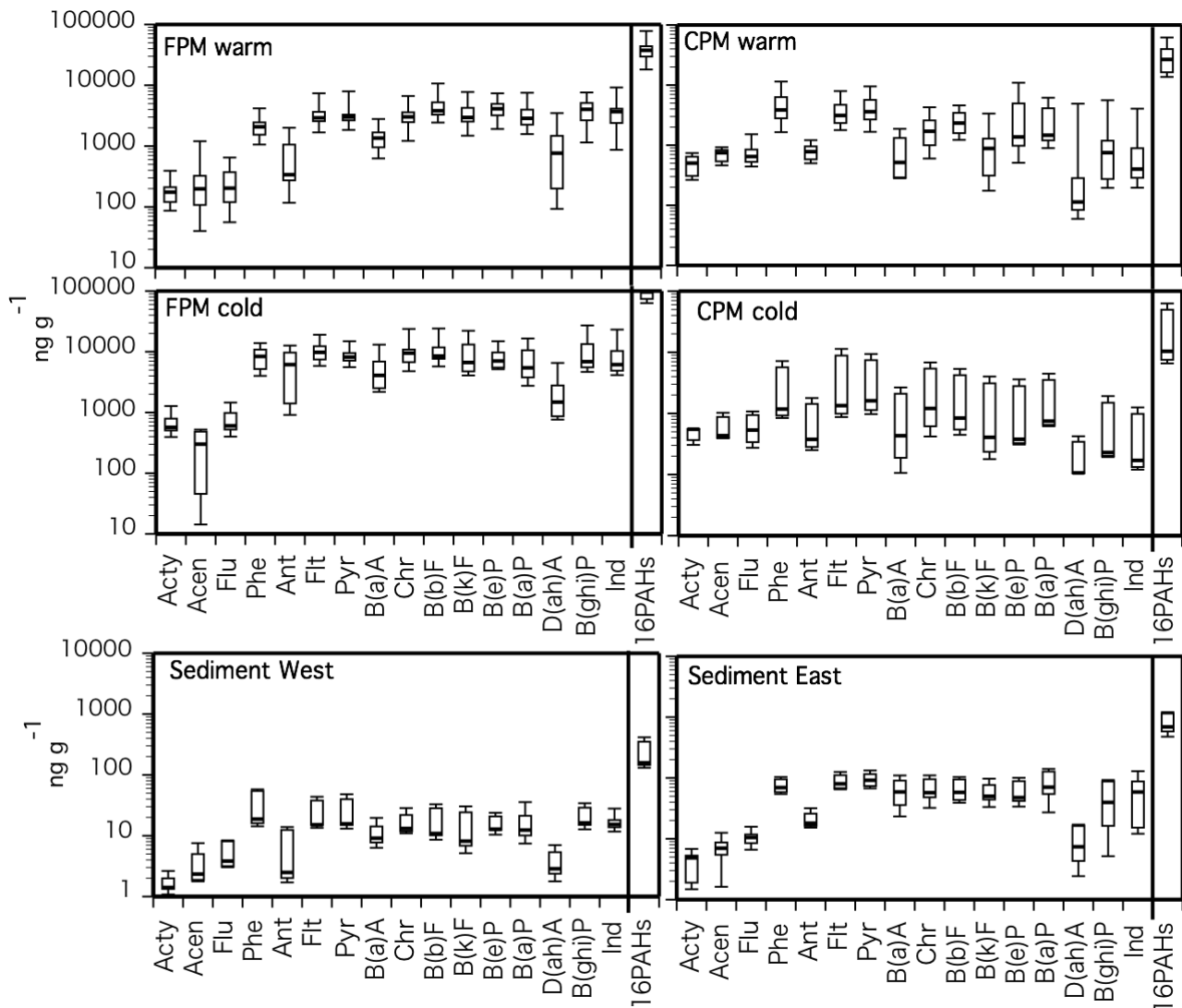


Figure 3. PAHs concentrations (in ng g^{-1}) of atmospheric PMs and sea sediments.

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4 Toxicity of the organic solvent extracts of atmospheric PM and sea sediments

5 The toxicity ($1/\text{EC}_{50}$ (L g^{-1})) is shown in **Table 4** and the relationship between PAHs concentrations and
6 toxicity are shown in **Figure 4**. The $1/\text{EC}_{50}$ values of atmospheric PM ranged from 1-10 L g^{-1} PM for
7 FPM and CPM, and was 0.1-1 L g^{-1} dry solids for sea sediments. These results imply that toxic
8 substances from atmospheric PM are diluted several tens or hundreds times in sea sediments. To examine
9 the relationship between PAHs concentrations and toxicity, the ratio of the $1/\text{EC}_{50}$ to the 16PAHs was
10 calculated ($(1/\text{EC}_{50})/16\text{PAHs}$). The geometric mean of the ratio was 0.089 and $0.54 \text{ L } \mu\text{g}^{-1}$ 16PAHs for
11 FPM and CPM, respectively. For sea sediments, the ratio was 1.01 and $0.18 \text{ L } \mu\text{g}^{-1}$ 16PAHs for Sediment
12 West and Sediment East samples, respectively. Since direct PAHs toxicity was not that high when
13 compared with the direct toxicity against *V. fischeri* (their contributions accounted for less than 1% for all
14 samples), the total toxicity of the solvent extracts was not directly related to the PAHs or their derivatives.
15 Nevertheless, the accordance in the order was observed between atmospheric particles and sea sediments,
16 which implies a connection between the atmospheric emission stage and final sedimentation stage.
17 **Figure 5** shows the relation between PAHs concentrations and $1/\text{EC}_{50}$. The ratio was found to be similar
18 between the FPM and Sediment East samples, as well as between CPM and Sediment West samples.
19 These findings suggest that the toxic substances in the Sediment West samples are primarily from CPM,
20 while those the Sediment East samples are primarily from FPM. Accordingly, the composition and
21 properties of the sources of pollutants in the sea sediments resemble those of atmospheric PM. It should
22 be noted that there are many types of toxic substances that affect the luminescence of the bacteria in the
23 assay conducted in this study, and the contribution of PAHs to the effects of the toxic substances may not
24 be dominant. It is known that naturally occurring sulfur is an influential factor that influences such testing
25 (Jacobs et al., 1992; Svenson et al., 1996; Brack et al., 1999). However, sulfur was not removed in the
26 present study because of the concern that the removal process could affect the results of the toxicity test.

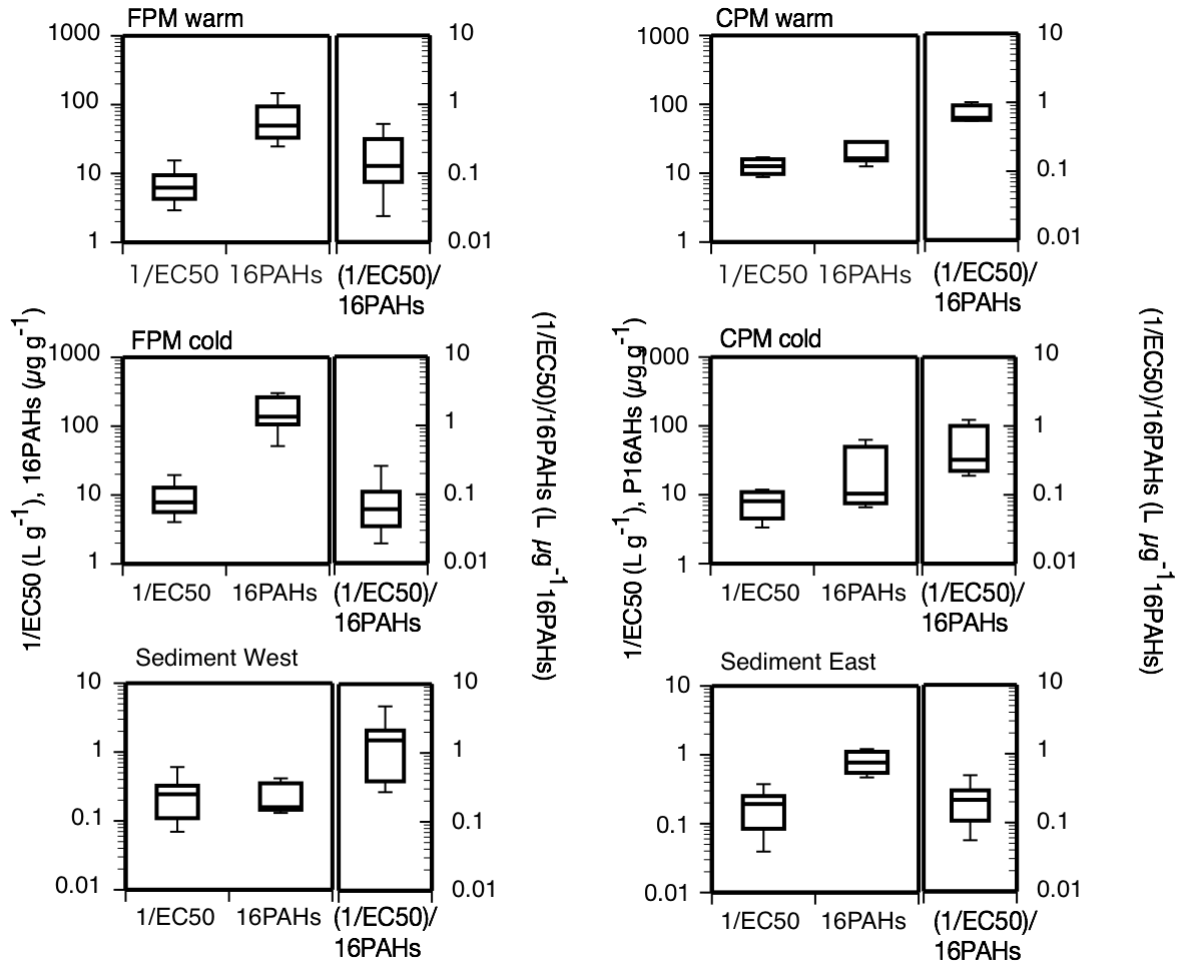
1 As a result, classification of the effects of sulfur should be considered in future studies.

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Table 4. 1/EC50 of organic extracts of atmospheric PMs and sea sediments.

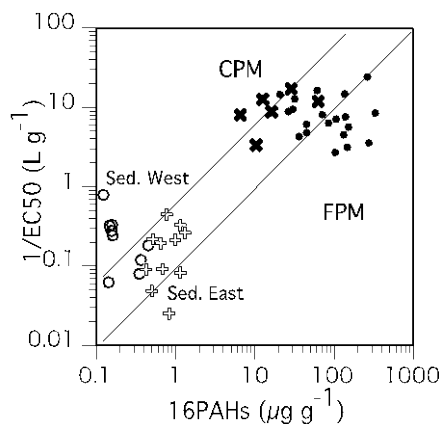
	FPM warm	FPM cold	CPM warm	CPM cold	Sed. West	Sed. East
Mean ± sd	7.66 ± 4.68	12.81 ± 4.12	9.67 ± 6.16	7.77 ± 4.27	0.27 ± 0.22	0.18 ± 0.13
Geometric mean	6.50	12.35	8.29	6.85	0.20	0.14

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Figure 4. Relation of 1/EC50 and 16PAHs concentration.



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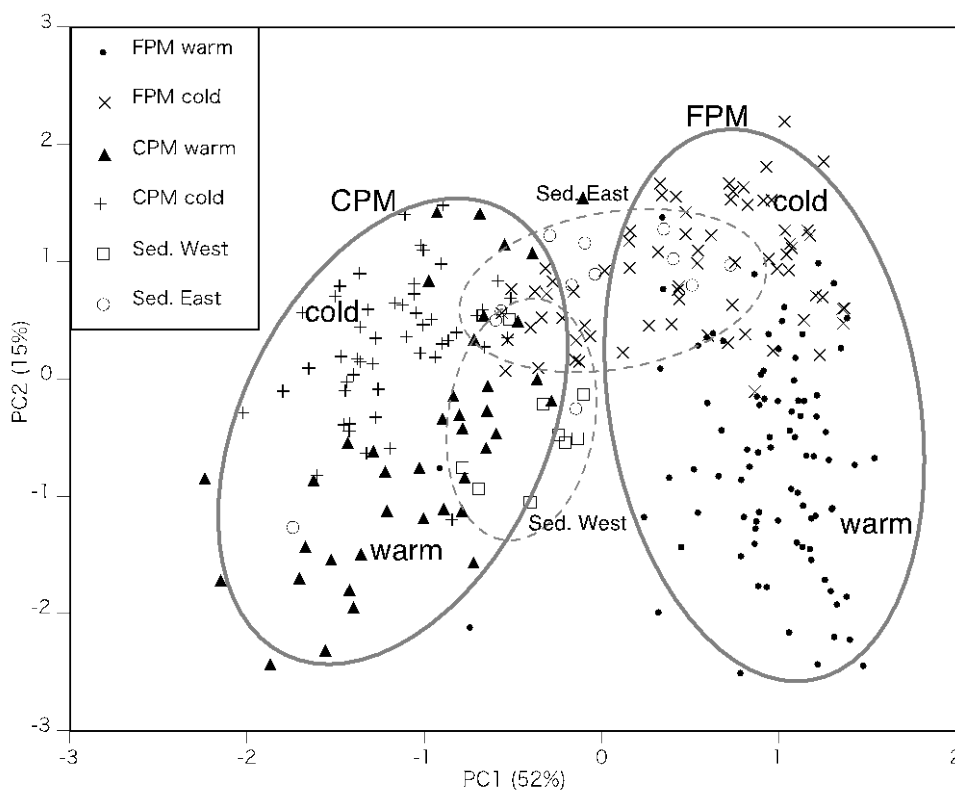
Figure 5. 1/EC50 vs. 16PAHs concentrations for atmospheric PMs and sea sediments.

12 Analysis of PAHs concentration patterns

13 Principal component analysis (PCA) was conducted to compare the similarities of atmospheric particles
14 and sea sediments based on patterns of PAHs concentrations. To enable comprehensive comparison of the
15 atmospheric PM, consecutive measurements made from August 2004 to September 2005 at the same
16 sampling station by our group were summarized (Warm: n=92, Jun.–Aug. 2005, Cold: n=63, Dec. 2004

1 –Feb. 2005; Kojima et al., 2010). (The ratios measured for this study were similar to them). PCA analysis
 2 was performed based on 15PAHs because dibenzo(ah)anthracene was excluded because of a lack of the
 3 data for many samples due to under detection limit. Prior to PCA analysis, the concentration of each
 4 compound was normalized to the total PAHs concentration to remove the effect of the absolute
 5 concentration. The first and second principal components described 52% and 15% of the variability,
 6 respectively (**Figure 6**). FPM and CPM formed different clusters, and warm and cold samples were
 7 further segmented within each cluster. Contrary to the (1/EC50)/16PAHs ratios, Sediment East and
 8 Sediment West samples were not included solely in the FPM or CPM clusters. Rather, Sediment West
 9 samples were somewhat similar to CPM, while Sediment East samples fell between the CPM cold and
 10 FPM cold clusters. Overall, the results of PCA suggested that sediment PAHs originate from a mixture of
 11 FPM and CPM.

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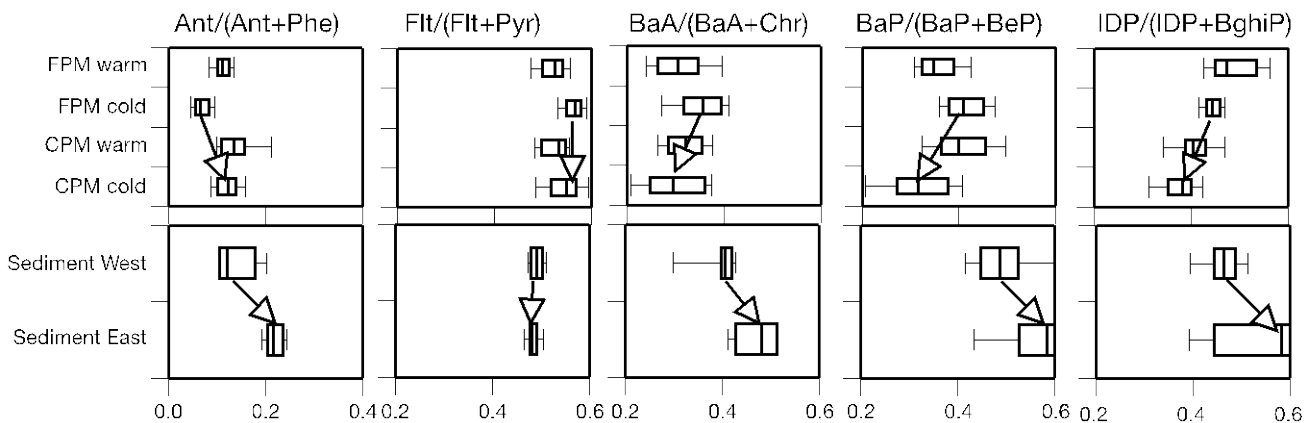
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14 **Figure 6.** Plot of principal component 1 vs. 2 for the principal component analysis of PAHs in
 15 atmospheric PMs and sea sediments.

16

17 For further comparison, five widely applied isomer ratios were calculated (**Figure 7**). Although the values
 18 of the ratios themselves differed between atmospheric particles and sea sediments, the similarities and
 19 differences between the changes from FPM -> CPM and Sediment West samples -> Sediment East
 20 samples can be discussed (arrows in **Figure 7**). Three ratios (BaA/(BaA+Chr), BaP/(BaP+BeP) and
 21 IDP/(IDP+BghiP)) were more similar to CPM in Sediment West samples, while they were more similar
 22 to FPM in Sediment East samples. For Flt/(Flt+Pyr), the values differed substantially between the
 23 atmospheric PM (both FPM and CPM) and sea sediment, while the values were similar between FPM and
 24 CPM, and between Sediment East and Sediment West samples. Based on these observations,
 25 Flt/(Flt+Pyr) is not a good marker for distinguishing FPM and CPM, and the PAHs of sea sediments
 26 cannot be said to come directly from atmospheric PM. The Ant/(Ant+Phe) showed a trend opposite to
 27 that of the other three ratios. Specifically, the ratio was higher for the CPM than the FPM, but that of
 28 Sediment East samples was higher than Sediment West samples. Based on these results, comparison of
 29 FPM/CPM to sediments collected from the west/east revealed that trends in Sediment West samples and
 30 CPM were similar, as were those in Sediment East samples and FPM (if the opposite result of
 31 Ant/(Ant+Phe) is ruled out). However, the absolute values were fairly different between atmospheric PM
 32 and sea sediments, indicating that pollutants in sea sediments do not simply come from atmospheric PM.

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1
2 **Figure 7.** Isomer ratios of atmospheric PMs and sea sediments.

3
4 Yunker et al. (2002) classified the isomer ratio values of different sources (e.g. combustion/petroleum).
5 According to their classification, the Ant/(Ant+Phe) ratios were higher for combustion sources than for
6 petroleum; therefore, contaminants in Sediment East samples in the present study are attributed more to
7 combustion sources. Similarly, the other ratios of pollutants in sea sediments observed in this study are
8 indicative of combustion sources. Flt/(Flt+Pyr) is considered an indicator for classification of biomass
9 and fossil fuel (petroleum) combustion, with a ratio of <0.4 indicating petroleum, 0.4–0.5 reflecting
10 petroleum combustion, and >0.5 corresponding to biomass combustion. In the present study, the
11 Flt/(Flt+Pyr) sediment ratios were around 0.5, suggesting an even mixture of petroleum and biomass
12 combustion led to contamination of the sediments.

13 Overall, the results indicated that the PAHs in the sediments in Hiroshima Bay primarily originated from
14 combustion of petroleum and biomass. The substantial differences in the ratios of sediments and
15 atmospheric PM suggest that the sediment PAHs originate from atmospheric PM as well as other
16 pathways. Nevertheless, the (1/EC50)/16PAHs ratio was similar to that of atmospheric PM, which
17 suggests that the toxic composition of other hidden sources would be similar to that of atmospheric PM.
18 Biomass burning residues may possibly be a major source of contaminant flow into sea sediments. One
19 possible pathway is that biomass is burned in an open area, resulting in some contaminants being
20 dispersed into air, but the majority remaining on the ground. These residues are then directly discharged
21 into water bodies as runoff following rainfall events.

22
23 **CONCLUSIONS**

24 In this study, the concentration of polycyclic aromatic hydrocarbons (PAHs) and the toxicity to marine
25 bacteria (*V. fischeri*) were measured for organic solvent extracts of sea sediments collected in an urban
26 watershed area (Hiroshima Bay) in Japan and compared with those of atmospheric particulate matters.
27 For atmospheric particulate matters, the PAHs concentrations were highest for the FPM during cold
28 seasons. The PAHs concentrations of sea sediments were 0.01 to 0.001 times those of atmospheric
29 particulate materials. The 1/EC50 of atmospheric particulate matters was in the order of 1 to 10 L g⁻¹ PM
30 for FPM and CPM, and 0.1 to 1 L g⁻¹ dry solids for sea sediments. These results imply that toxic
31 substances from atmospheric particulate matters are diluted several tens or hundreds of times in sea
32 sediments.

33 To consider the effects of the toxicity related to PAHs, the ratio of 1/EC50 to the PAHs concentrations
34 ((1/EC50)/16PAHs) were calculated. These ratios were stable for all the sea sediments (0.1-1 L μg⁻¹
35 16PAHs) and same in the order of magnitude as those of FPM and CPM. Finally, the PAHs patterns of
36 the sea sediments were compared with those of FPM and CPM using PCA and isomer ratio analysis.
37 Several ratios of sea sediments differed considerably from those of FPM or CPM, and the toxicity of sea
38 sediments was considered to be a result of a mixture of atmospheric particulate matters and other sources
39 including PAHs. Comparison to previously conducted PAHs analyses suggested that biomass burning
40 residues comprised a major portion of these other sources.

41
42 **ACKNOWLEDGEMENT**

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