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## Distributions of nitrated polycyclic aromatic hydrocarbons in the sediment of Osaka Bay, Japan

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## ABSTRACT

The distributions of 15 nitrated polycyclic aromatic hydrocarbons (NPAHs) in sediments collected at 44 sites throughout Osaka Bay, Japan were examined. The highest total NPAHs, with a concentration of 1949 ng/kg dry weight, were detected near the city of Amagasaki. Some sites near the cities of Osaka, Kishiwada, and Sakai registered ng/kg levels of NPAHs, but individual NPAH concentrations were relatively lower than those in previous studies. The sources were estimated using principal component analysis, and NPAHs were derived from exhaust gases of automobiles and industries at some sites. However, our results suggest that it is difficult to estimate the source, especially in coastal areas near big cities and large industrial areas, because the generation pathways between parent polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs are slightly different, and the ratio of PAHs and NPAHs could not be accurately reflect the characters of sources in sediments especially at coastal areas with large-scale industrial zones.

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## 1. Introduction

Because nitrated polycyclic aromatic hydrocarbons (NPAHs) are recognized as probable mutagens and/or carcinogens (Landvik et al., 2007; Watt et al., 2007), their occurrence in various environmental matrices are currently under investigation (Bamford et al., 2003; Delhomme et al., 2007). NPAH compounds are formed either 1) during the incomplete combustion of organic compounds such as diesel and gasoline (Nielsen, 1984), which is the primary source, or 2) by the reaction of parent polycyclic aromatic hydrocarbons (PAHs) with nitrogen oxides in ambient air (Atkinson and Arey, 1994) which is the secondary sources. NPAHs are highly persistent in the atmosphere and are transported from their original sources to distant places by their absorbing to particulate matter (Bamford et al., 2003). There are already several reports on the distribution and behavior of NPAHs in ambient atmosphere (Bamford et al., 2003; Schauer et al., 2004; Delhomme et al., 2007; Hien et al., 2007; Albinet et al., 2008) and surface soil (Watanabe et al., 2003). In most instances, persistent chemicals from the atmosphere such as NPAHs, reach aquatic ecosystems either directly or as fallout from

rain. However, literature on the distribution of NPAHs in freshwater and seawater environments is scarce, with a few reports on water (Chondo et al., 2013; Zhang et al., 2014) and sediment (Sato et al., 1985; Lübcke-von Varel et al., 2011, 2012; Huang et al., 2014) samples from fresh water areas, and some more reports on water (Murahashi et al., 2001) and sediment (Fernandez et al., 1992; Ozaki et al., 2010) samples from coastal areas. Most of those previous investigations in aquatic environments were limited to a few target NPAHs.

Osaka Bay has an area of 1450 km<sup>2</sup>, is located at the eastern end of the Seto Inland Sea, and is enclosed by Osaka and Hyogo Prefectures, which are a couple of the most densely populated areas in Japan. The cities of Osaka and Sakai in Osaka Prefecture have populations of 2,700,000 and 840,000, respectively, and the city of Kobe in Hyogo Prefecture has a population of 1,540,000. Osaka Bay is surrounded by the island of Honshu and Awaji Island, and is classified as an enclosed coastal sea with only two narrow entrances. This limits water exchange in the bay, and possibly leads to increase risk of marine pollution with heavy traffic together with the presence of large industrial plants. We have already reported on the polluted conditions regarding NPAHs in bivalves (Uno et al., 2011), endocrine disrupting chemicals in sediments (Koyama et al., 2013) and polychaetes (Nurulnadia et al., 2014), and parent and alkylated PAHs in sediments (Miki et al., 2014) and bivalves (Ito et al., 2015).

Concentrations of NPAHs distributed in marine areas are likely to be extremely low compared with parent PAHs, and, in fact, our previous study showed very low concentrations of NPAHs in bivalves (Uno et

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al., 2011). Therefore, investigations on NPAHs require sensitive analytical methods, even for sediment samples, which possibly accumulate these hydrophobic chemicals. Because of the toxicities of the NPAHs, they may affect aquatic organisms, and thus information about their distributions in aquatic environments becomes important. In the present study, the distributions of NPAHs in sediments at 44 sites throughout Osaka Bay were studied. Because we have reported on the distributions of parent and alkylated PAHs in sediments collected at the same sampling sites already (Miki et al., 2014), the present study focused on comparing the differences in distributions among parent, nitrated, and alkylated PAHs. In addition, we tried to estimate the source of NPAHs based on their distribution patterns.

## 2. Material and methods

### 2.1. Collection of sediments

Sediment samples were collected from 44 sites in Osaka Bay, which are the same sampling sites sampled in our previous study of PAH distributions (Miki et al., 2014). Samplings were conducted on four occasions: April 2000 (Sites 1–5 and 7–22 in Fig. 1), May 2001 (Sites 23–28), May 2002 (Site 6), and October 2006 (Sites C1–C20 excluding the vacant sites in the present study of C8, C11, C15, and C16). Sediment samples were collected using a Smith-McIntyre grab sampler from aboard the R.V. Shirafuji Maru (National Research Institute of Fisheries and Environment of Inland Sea, Japan) at Sites 1–28, and using an Ekman-Berge grab sampler from the shoreline at Sites C1–C20 (minus C8, C11, C15, and C16). All sediments were dried at 60 °C for 12 h, and then were sorted by passage through a sieve with a mesh size of 1 mm. The sediments that passed through the sieve were stored at –20 °C until analysis.

### 2.2. Reagents

The standards of the NPAHs were purchased from Tokyo Kasei Kogyo Co., Japan [1-nitronaphthalene (1-NNap), 2-nitronaphthalene (2-NNap), 1,5-dinitronaphthalene (1,5-DNap), and 2-nitrofluorene (2-NFle)]; Sigma-Aldrich, USA [2,7-dinitrofluorene (2,7-DFle), 1-nitropyrene (1-NPyr), 3-nitrofluoranthene (3-NFla), and 6-nitrochrysene (6-NChr)]; AccuStandard Inc., USA [3-nitrophenanthrenes (3-NPhe), 9-nitrophenanthrene (9-NPhe), 1,3-dinitropyrene (1,3-DPyr), 1,6-dinitropyrene (1,6-DPyr), 1,8-

dinitropyrene (1,8-DPyr), and 7-nitrobenzo(a)anthracene (7-NBaA)]; Dr. Ehrenstorfer GmbH, Germany [4-nitropyrene(4-NPyr)]; and C/D/N Isotopes Inc., Canada [(1-nitropyrene- $d_9$ )]. The solvent as dichloromethane, hexane, acetone, and diethyl ether were all pesticide grade, while methanol and acetonitrile were HPLC grade (Wako Pure Chemical Industries Ltd., Japan). Other chemicals used, such as Wakogel® (C-100, silica gel), anhydrous sodium sulfate, sodium hydrogen sulfide (NaSH), acetic anhydride, ammonium acetate, and formic acid, were purchased from Wako.

### 2.3. NPAHs analysis

The NPAHs were analyzed following the procedure in our previous study (Uno et al., 2011). Sediment was ultrasonically extracted dichloromethane-methanol (3:1, v/v) and extracts were dried using gentle stream of nitrogen gas. After drying, the residue was immediately dissolved in hexane, and cleaned-up in silica gel column packed in a Pasteur pipette. The target chemicals were eluted using 60% acetone-hexane (v/v) and then, reduced to amino PAHs (APAHs) by NaSH. The reduced target chemicals were extracted with diethyl ether, and completely dried under a nitrogen gas, and dissolved in acetonitrile. Then, APAHs were acetylated by acetic anhydride. The derivatives of the NPAHs were analyzed with a liquid chromatography tandem mass spectrometry (LC-MS/MS) with an electrospray ionization (ESI).

### 2.4. Measurements with LC-MS/MS-ESI

LC-MS/MS was carried out with an Agilent 1200 LC system (Agilent Technologies, USA) coupled to an API-2000 triple stage quadrupole mass spectrometer equipped with an ESI source (Applied Biosystems, USA), employed in positive mode. Details of the HPLC and MS/MS analysis condition were identical to those described in Uno et al. (2011). The target chemicals were the derivatives of 15 NPAHs: 1- and 2-NNaps; 1,5-DNap; 2-NFle; 2,7-DFle; 3- and 9-NPhe; 1- and 4-NPyr; 3-NFla; 6-NChr; and 1,3-, 1,6-, and 1,8-DPyr. The derivatives of the NPAHs were separated individually by a liquid chromatography system using a column of Inertsil® C8-3 (4.6 mm i.d. × 150 mm, 5 μm of particle size, GL Sciences, Inc. Japan). The mean recovery rates for each NPAH were above 75%. Analysis was conducted in duplicate (n = 2). The errors of all the analysis data were within ±20% for the duplicates, the results of which are presented as an average.

### 2.5. Statistical analysis and data treatment

Principal components analysis (PCA) was performed on the concentrations individual NPAHs detected in the sediments at all sites, and performed with the R programming language (<http://www.r-project.org/>). The distribution pattern of total NPAHs were constructed and shown by Microsoft Excel 2013 (Fig. 2).

## 3. Results and discussion

### 3.1. Distribution of total NPAHs

Concentrations of the total NPAHs ( $\sum$  NPAHs), which consists of the concentrations of the 15 target compounds, ranged from 116 to 1949 ng/kg dry weight and tend to be remarkably higher near the shoreline and on the eastern side of the Bay (Fig. 2). Especially, high concentrations of  $\sum$  NPAHs were detected at Site C20 near the city of Amagasaki in Hyogo Prefecture (1949 ng/kg dry weight) and at C1, C3, and C4 near the city of Osaka (1575, 1129, and 1059 ng/kg dry weight, respectively), C14 near the city of Kishiwada (1528 ng/kg dry weight), and C7 near city of Sakai (1053 ng/kg dry weight), in Osaka Prefecture. Because those sites are located near the Gulf or Kobe Lines of the Hanshin Expressway, which experience heavy traffic, the NPAHs in the exhaust gas from automobiles might contribute to the

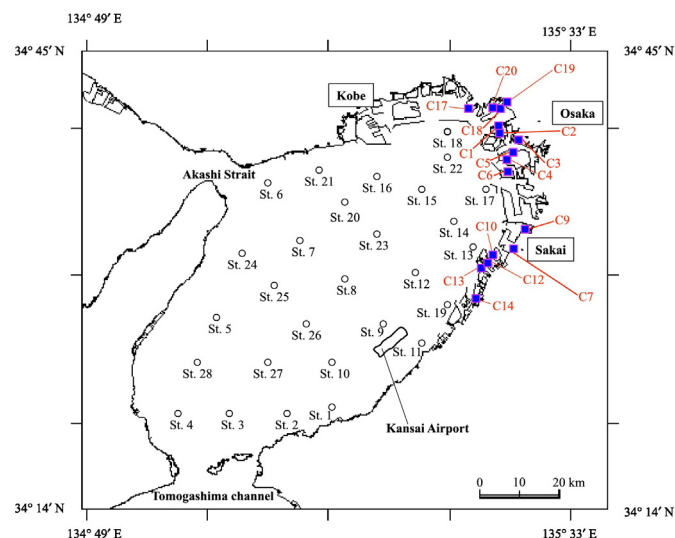


Fig. 1. Sampling sites in Osaka Bay. Circles indicate the sites where samples were collected from aboard the research vessel. Squares indicate the sites where samples were collected from the shoreline. St. means site.

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