Environ Geol (2007) 52:123–129
DOI 10.1007/s00254-006-0465-0

ORIGINAL ARTICLE

Vertical profile of polycyclic aromatic hydrocarbons in a sediment core from a reservoir in Osaka City

Miho Ishitake · Hiroshi Moriwaki · Kenshi Katahira · Osamu Yamamoto · Kenshiro Tsuruho · Hideo Yamazaki · Shusaku Yoshikawa

Received: 29 July 2006 / Accepted: 1 August 2006 / Published online: 20 September 2006

Abstract Concentrations of polycyclic aromatic hydrocarbons (PAHs) were measured in a dated sediment core from a reservoir at Osaka City, Southwest Japan. The sediment core consisted of deposits collected over a period of almost 70 years whose PAH content would serve as a historical record of atmospheric environment at Osaka City. Total PAH concentrations varied from 4.2 to 26 mg kg^{-1} dry wt, and peaked in the 1940s, reflecting the occurrence of a large fire due to air attacks during World War II. The results indicated that warfare had the largest impact on atmospheric environment in Osaka City. Total PAH concentrations decreased in the post-war period except for a small peak. In the 1950s, there was a downward trend from the 1970s to the present. These trends can be ascribed to the growth of industrial activities and the regulation of atmospheric pollutant emissions, respectively.

M. Ishitake (✉) · S. Yoshikawa
Department of Biology and Geosciences,
Graduate School of Science, Osaka City University,
3-3-138, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan
e-mail: ishitake@scas.co.jp

H. Moriwaki · K. Katahira · O. Yamamoto ·
K. Tsuruho
Osaka City Institute of Public Health and Environmental Sciences, 8-34 Tojo-cho, Tennouji-ku,
Osaka 543-0026, Japan

H. Yamazaki
Department of Life Science,
School of Science and Engineering, Kinki University,
3-4-1 Kowakae, Higashi-Osaka 577-8502, Japan

Keywords Polycyclic aromatic hydrocarbons · Reservoir sediment · Osaka City · World War II · Climatology

Introduction

Osaka City is one of the largest commercial and industrial cities in Japan. The population of Osaka City is almost 2.6 million. The number of factories was over 20,000 in 2004. Air pollution here has been a problem since the 1880s. Osaka offers therefore an important opportunity to explore the historical trend of the urban atmospheric environment in Japan.

Measurement of molecular markers in sediment core samples from a reservoir has already proven a very useful technique for studying historical trends in the atmospheric environment (Kumata et al. 2000). In the current study, concentrations of polycyclic aromatic hydrocarbons (PAHs) were measured in a sediment core sample from Nagaike Pond, a reservoir located in the south of Osaka City (Fig. 1).

Polycyclic aromatic hydrocarbons are ubiquitous contaminants of great environmental concern. They are produced by incomplete combustion of organic matter and contained in petroleum products such as crude oil, gasoline and asphalt. It is important to identify the sources and the behaviour of PAHs in the environment because they are toxic and carcinogenic (Boström et al. 2000). Their persistence in the environment allows PAHs to be a valuable recorder of anthropogenic pollution (Mastral and Callen 2000). Nagaike Pond has no surface inflow or outflow and the sediment consists mostly of stormwater runoff and airborne deposits. The core is a deposit of sediments from 1930s to 2000s. Dating was performed using the

method of ^{137}Cs and ^{210}Pb profiles (Katahira et al. 2006). The vertical profile of PAHs in the sediment core reflects the historical trends of the atmospheric environment in Osaka City over the past 70 years.

The objectives of this study were to determine historical changes in the metropolitan atmospheric environment over the past 70 years and to explore how temporal changes in human activities and historical events affect the environment. In a previous study the historical trends of PAHs from 1620s to 1970s in another reservoir sediment core from Osaka City were explained. The event having the greatest impact on the atmospheric environment during almost 350 years was World War II (Moriwaki et al. 2005). It was particular interest in the present study to determine the historical trends of PAHs in Osaka City from 1970s to 2000s, and to find out whether trends similar to those of the previous study could be demonstrated.

Materials and methods

Sediment sample

Located in a highly urbanised area of Osaka City, Nagaike Pond (Fig. 1) was built at the beginning of the 1930s its present shape is rectangular (120 × 50 m).

A sediment core was collected using an acrylic tube (110 cm length × 10 cm i.d.) in September 2001. The columner section of the sediment core is shown in Fig. 2. At a length of about 105 cm, the core consisted mainly of silt with an abundance of charcoal and plant material fragments. The banded structures from 35 to 105 cm were differently coloured clays. The core was cut into 3.0 cm sections using a silicon slicer. In the upper 36 cm, the width of the slice varied depending on lithofacies. Each section was dried at room temperature and stored in a cool and dark place until it was used for analysis.

The dating of the sediment core from Nagaike Pond was estimated by using the depth profile of ^{137}Cs and ^{210}Pb activity in another sediment core from Nagaike Pond, which was sampled at the same time to estimate the sedimentation rate (Katahira et al. 2006). Profiles of ^{137}Cs activity in sediment cores in Japan usually have only one peak, which was caused by atmospheric nuclear weapons testing when it was at its height in 1963 (e.g. Peirson 1971 and Hirose et al. 1987).

The bottom of each core dated back to the period when Nagaike Pond was altered into its present shape during the mid-1930s.

The concentrations of heavy metals (Cu, Zn and Pb) were measured in both the present core under consideration and the core from the earlier study. Comparisons of the vertical profiles of Cu, Zn, and Pb concentrations of the two samples were used. In addition, Murakami and Inoue (2004) previously reported that charcoal fragments concentrated at a depth of 75–80 cm in a sediment core from the same reservoir were due to air attacks, and a section of their sample was found to correspond to the mid-1940s.

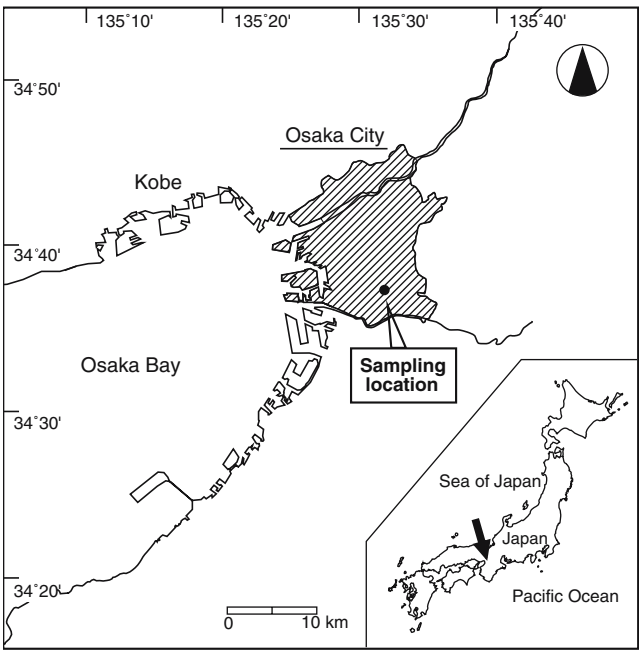

Fig. 1 Sampling location of this study

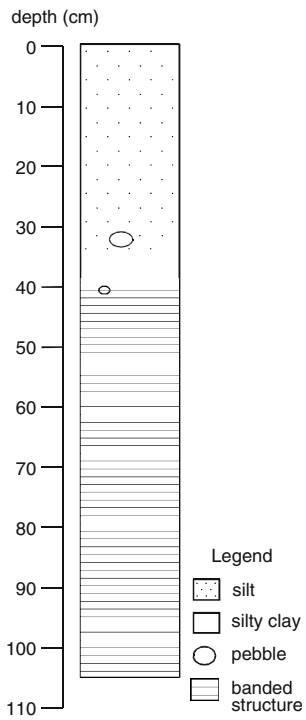

Fig. 2 Columnar section of the sediment core from Nagaike pond

Chemical analysis

Polycyclic aromatic hydrocarbons analysis was performed according to a modification of the procedure reported by Moriwaki et al. (2004). Extraction of PAHs from the sediment was performed according to a modification of the procedure reported by Tsuji et al. (1985) as summarized briefly below.

After 0.20 g sediment samples were extracted by ultrasonic agitation, a 30 min extraction was carried out in a centrifuge tube with ethanol (4.0 ml) and toluene (16 ml). The tube was then centrifuged at 3,000 rpm for 10 min. This step was repeated twice, after which the supernatants were combined and concentrated to 1.0 ml using a rotary evaporator, and then dried under a stream of N_2. The obtained residue was then dissolved in *n*-hexane (2.0 ml) and the hexane solution was loaded onto a Sep-Pak Plus silica cartridge (Waters). The cartridge was eluted into a glass tube with 10 ml of a hexane-toluene mixture (90:10, v/v) and the eluent was dried by a nitrogen purge and dissolved in 0.50 ml of acetonitrile. A 10 µl volume of the internal methanol solution (benzo(*a*)pyrene-d_{12} 10 mg/l) was added, after which a 10 µl aliquot was injected into a liquid chromatography–mass spectrometry system. The following 12 PAHs were detected and determined in this study: phenanthrene (Phe), anthracene (An), fluoranthene (Flu), pyrene (Py), benzo(*a*)anthracene (BaA), chrycene (Chr), benzo(*b*)fluoranthene (BbF), benzo(*k*)fluoranthene (BkF), benzo(*a*)pyrene (BaP), benzo(*e*)pyrene (BeP), benzo(*ghi*)perylene (BghiP), and indeno(1,2,3-*cd*)pyrene (IP). For the recovery evaluation of PAHs by this method, the procedure was carried out after the sediment core sample (0.20 g at the depth of 72–75 cm) was spiked with 100 ng of the PAHs. Pairs of BaA and Chr or BaP and BeP were treated as a single species in calculations. The mean recovery ($n = 3$) was calculated from the difference between concentrations obtained from the spiked and the non-spiked sediment. The limits of detection for PAHs by this method, defined as three times the standard deviation of the concentration obtained from recovery tests, varied from 0.06 mg kg^{-1} for An to 0.9 mg kg^{-1} for BkF.

Results and discussion

PAH concentrations

The concentrations of PAHs in the sediment core from Nagaike Pond are shown in Table 1, and the vertical profile of total PAH concentration is shown in Fig. 3.

Total PAH concentrations in the sediment core varied from 4.2 to 26 mg kg^{-1} dry wt, and the average of total PAH concentrations was 13 mg kg^{-1} dry wt. The levels of total PAH concentrations in the sediment core were about as high as those reported of a sediment core from a reservoir situated in the centre of Tokyo (7.5–30 mg kg^{-1} dry wt; Kumata et al. 2000). (Tokyo is the largest city in Japan and 500 km from Osaka. PAHs analysis of the reservoir at Tokyo used a different method this study.)

The vertical profiles of individual PAHs showed trends similar to those of total PAHs. In most samples, the highest concentrations were Fl, BkF or Py.

The dating of the sediment core was segmented into four sections by type of fossil fuel primarily in use and other significant occurrences in the history of the city (Fig. 3). At a depth of 81–105 cm, the first section is from 1930s to 1940s. Coal was used as the primary fuel during this period. Total PAH concentrations in this period were in the range of 9.7 to 14 mg kg^{-1}. Okuda et al. (2000) reported that PAHs during the 1930s in Japan were due to combustion of organic materials. Osaka City had been troubled by problems of atmospheric pollution since the 1880s due to the use of soft coal in factories, which in 1932 led to the establishment of statutory controls on particulates. The main source of PAHs at this time must thus have been the combustion of coal.

The second section, at a depth of 75–81 cm, dates back to World War II. Total PAH concentrations were highest in the sediment layer of 1945. Osaka City was a target of air attacks in 1945 during World War II. Therefore, the peak of total PAH concentrations during the mid-1940s were due to a large fire caused by the air attacks. In 1940s the area around of Nagaike Pond was residential, and most houses in Japan were of wooden construction. Furthermore, the historical record (Osaka City 1994) states that houses around Nagaike Pond were struck by bombs during air attacks. Combustion of wood is therefore thought that the main source of PAHs during World War II. This view is supported by the observation of Murakami and Inoue (2004) of a large amount of charcoal fragments in a sediment core from Nagaike Pond. Moreover, as described later, a similar spike increase in PAHs was observed in a sediment core sampled at another site in Osaka City (Moriwaki et al. 2005). Thus the period considered to have the greatest influence on PAH production around Nagaike Pond in the past 70 years is thus the World War II because there was no other significant event capable of causing the high level of PAH contribution except World War II bombings and subsequent fires. The third section is from 1946s to

Table 1 Concentrations (mg kg^{-1} dry wt) of PAHs in the sediment core from Nagaike Pond

Depth (cm)	Year	Phe	An	Flu	Py	BaA + Chr	BbF	BkF	BaP + BeP	BghiP	Ip	Total PAHs
0–5	2000	0.51	0.034	0.70	0.71	0.61	0.40	0.55	0.41	0.25	0.24	4.4
5–15	1995	0.36	0.032	0.70	0.70	0.67	0.35	0.51	0.40	0.23	0.23	4.2
15–21	1995	0.70	0.092	1.5	1.5	1.5	0.78	1.0	0.79	0.43	0.38	8.6
21–25	1983	0.65	0.054	1.1	1.1	1.0	0.61	0.80	0.61	0.34	0.31	6.6
25–26	1981	0.61	0.076	0.99	1.0	1.3	0.72	0.98	0.76	0.47	0.44	7.4
26–31	1978	0.83	0.078	1.8	1.7	1.8	1.2	1.7	1.2	0.70	0.60	12
31–34	1973	0.74	0.069	1.6	1.7	1.8	1.1	1.5	1.2	0.74	0.70	11
34–36	1963	1.0	0.11	2.1	2.1	2.0	1.1	1.6	1.1	0.70	0.64	12
36–39	1961	1.3	0.10	2.9	2.8	2.2	1.4	1.7	1.3	0.74	0.67	15
39–42	1960	1.1	0.16	2.2	2.3	2.0	1.4	1.7	1.2	0.84	0.76	14
42–45	1958	1.6	0.26	3.2	3.6	3.3	2.0	2.9	2.1	1.3	1.4	22
45–48	1957	1.0	0.10	1.9	1.9	2.4	1.4	1.9	1.3	1.0	0.89	14
48–51	1955	1.4	0.16	2.8	2.6	3.3	1.9	2.7	2.0	1.4	1.2	19
51–54	1953	1.3	0.17	2.6	2.6	3.5	2.3	3.3	2.3	1.7	1.4	21
54–57	1951	0.94	0.10	1.7	1.8	2.2	1.3	2.1	1.4	1.1	1.0	14
57–60	1951	1.0	0.13	1.8	1.8	2.5	1.4	2.0	1.4	1.1	0.99	14
60–63	1950	0.79	0.11	1.8	1.9	2.6	1.4	2.2	1.6	1.1	0.98	14
63–66	1949	0.95	0.13	1.8	1.7	2.3	1.1	1.9	1.4	1.1	0.95	13
66–69	1948	0.91	0.12	1.6	1.8	2.2	1.3	1.9	1.4	1.0	0.92	13
69–72	1947	1.1	0.14	2.4	2.4	3.4	1.8	2.8	2.1	1.5	1.2	19
72–75	1946	0.94	0.17	1.9	2.0	3.2	1.9	2.9	2.2	1.7	1.3	18
75–78	1945	1.1	0.26	2.7	3.1	4.6	2.5	4.4	3.1	1.5	2.2	26
78–81	1945	1.3	0.29	3.2	3.4	4.8	2.8	4.3	2.9	1.7	1.8	26
81–84	1943	0.75	0.13	1.7	1.8	1.4	1.0	2.0	1.2	1.4	0.89	12
84–87	1941	0.74	0.10	1.4	1.5	1.6	0.72	1.4	0.86	1.4	0.64	10
87–90	1940	0.81	0.13	1.7	1.8	2.0	0.89	1.6	1.0	1.5	0.72	12
90–93	1939	0.70	0.11	1.3	1.6	1.8	0.92	1.6	0.95	1.5	0.68	11
93–96	1938	0.73	0.11	1.7	1.8	2.1	1.1	1.7	1.2	1.7	0.80	13
96–99	1937	0.80	0.15	1.9	2.0	2.3	1.1	1.9	1.3	1.7	0.79	14
99–102	1936	0.70	0.12	1.6	1.6	1.9	0.92	1.6	1.0	1.6	0.74	12
102–105	1935	0.55	0.080	1.3	1.2	1.6	0.74	1.2	0.88	1.6	0.60	9.7

1950s, at a depth of 41–75 cm. After the war, total PAH concentrations steadily decreased from 1946 to 1951, but increased again in the 1950s. Industrial activity in the 1950s was very energetic as a result of rapid economic growth, and the consumption of coal was levelling off as that of oil increased in Japan. Both oil and coal are considered to be the sources of PAHs during this period.

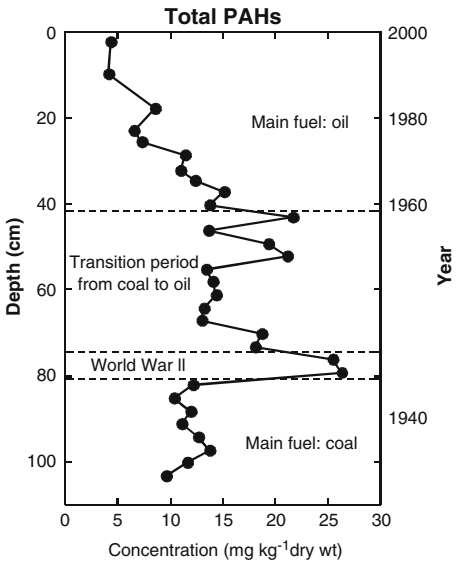

Fig. 3 Vertical profile of total PAH concentrations in the sediment core from Nagaike Pond

At a depth of 0–41 cm, the last section corresponds to the period from 1960s to 2000s. Total PAH concentrations decrease in this period. The sample at a depth of 5–15 cm exhibited the lowest concentration (4.2 mg kg^{-1}) in this sediment core. The reduction in PAH concentrations was partly due to improvements in emission controls and may be linked to the decrease in oil consumption caused by the oil crisis in the 1970s (The Institute of Energy Economics, Japan 1997). Furthermore, the enactment of the Air Pollution Control Law in 1968 also influenced the decrease of PAHs. Total PAH concentrations have remained stable from the 1980s to the present. This may be due to the balance maintained between a gentle increase in the fossil fuel consumption and controls placed on PAHs production through legal measures and technological advances. Kawaraya (1998) reported that atmospheric PAH concentrations in Osaka City have

decreased since the 1970s. Moreover, PAH concentrations in the sediment core from a reservoir in Tokyo indicated a similar pattern to Nagaike Pond. PAH concentrations exhibited a peak in the 1950s and decreased during the decades that followed (Kumata et al. 2000).

PAH compositions

Changes in PAH patterns may reflect changes in the sources of PAHs, such as coal, wood, gas, and petroleum combustion, and the effect of combustion conditions. Many studies have examined PAHs sources from changes in PAH composition (e.g. Blokzijl and Guicherit 1972; Gschwend and Hites 1981). The use of ratios of PAH components of the same molecular mass has been established as a method of inferring PAHs sources (Yunker et al. 1996). PAHs of molecular mass 178 are commonly used to distinguish between coal or wood and petroleum sources (e.g. Gschwend and Hites 1981, Sicre et al. 1987 and Yunker et al. 2002). The ratio of anthracene to anthracene plus phenanthrene (An/An + Phe) (Fig. 4) is one of the important contributors. An An/An + Phe ratio greater than 0.10 suggests combustion source of coal or wood, whereas one less than 0.10 implies a petroleum source. Nevertheless, the ratio the limit between two processes are not precise (Yunker et al. 1996 and Baumard et al. 1998). An/An + Phe ratios in the sediment core are shown in Fig. 4. An/An + Phe ratios were in the range from 0.12 to 0.15 in the first section, i.e. prior to the war, which indicates that the PAH source during this period was mainly wood and coal combustion. At 0.18–0.19, the ratio during World War II was highest. PAH sources were estimated to be due to wood combustion as a result of buildings burned down in air attacks because most buildings of this age were wooden. This conclusion is supported by previous observation of the amount of charcoal fragments in another core taken at Nagaike Pond (Murakami and Inoue 2004). After World War II, An/An + Phe the ratio gradually decreased until it exhibited the lowest value at the top of the core. This would be due to the fuel conversion from coal to oil, and it is thought that the source of PAHs from the 1960s to 2000s was mainly oil combustion.

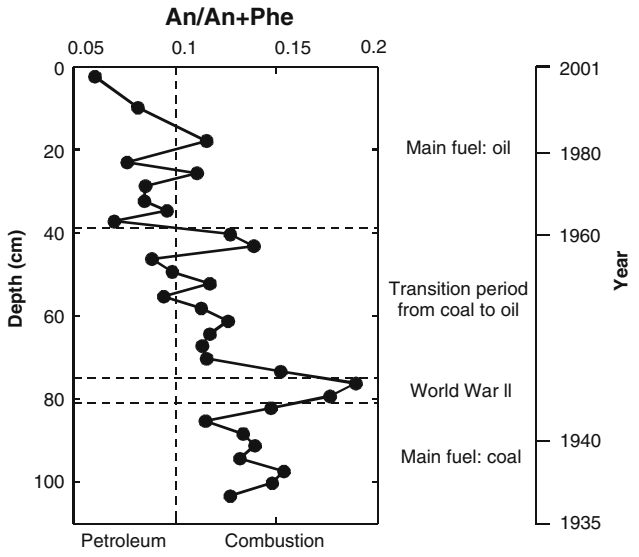

Fig. 4 Ratio of anthracene to anthracene plus phenanthrene (An/An + Phe) in the sediment core from Nagaike Pond

Comparison of sediment cores from Nagaike Pond and Osaka Castle outer moat

Osaka Castle is at the city's centre, 6.0 km north of Nagaike Pond. Moriwaki et al. (2005) analyzed PAHs in a sediment core from the outer moat of Osaka Castle. The vertical profiles of total PAH concentrations in the sediment cores from Nagaike Pond and the outer moat of Osaka Castle are shown in Fig. 5. Total PAH concentrations in the sediment core from Osaka Castle began to increase at a depth of about 100 cm and showed a peak at a depth of about 50 cm corresponding to the mid-1940s. This spiked peak of total PAH concentrations could be due to a combustion occurring as a result of the air attacks during World War II. Both samples showed the peak in the 1940s. The massive fire due to World War II air attacks occurred on a wide scale in Osaka City (Fig. 6), and the areas around both sampling sites suffered severe damage because of air attacks. Osaka City was exposed to air attacks from 1941 to 1945; in particular, the air attacks of 1945 were the largest (Osaka City 1994).

Total PAH concentrations in World War II segments in the sediment core from Nagaike Pond were about 2.5-fold greater than the average excluding World War II values, while those in the sediment core from Osaka Castle during World War II were about 4-fold greater than the average of this core. This difference might be due to conditions at the sampling sites. Nagaike Pond was surrounded by urban and residential areas during the 1940s. On the other hand, there was a weapon factory nearby Osaka Castle that was completely destroyed by fire in the air attacks of 1945 (Osaka City 1994). The Osaka Castle sediment core may reflect a greater combustion source near this sampling point.

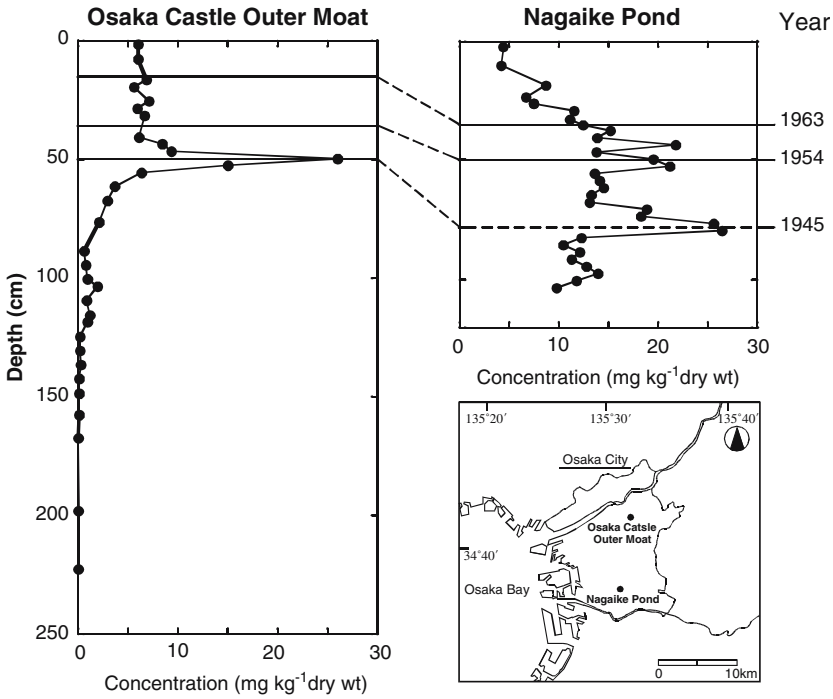

Fig. 5 Vertical profiles of total PAH concentration in the sediment cores from Nagaike Pond and Osaka Castle Outer Moat. Total PAH concentrations in the sediment core from Osaka Castle Outer Moat were from Moriwaki et al. (2005)

Conclusions

The greatest changes of the atmospheric environment in Osaka City during the past 70 years were caused by World War II. Furthermore, regulatory controls of industrial emissions have a positive correlation to PAH concentrations contained in dust in the metropolitan atmosphere. The source of PAHs during World War II in the city is postulated to be the combustion of wooden structures. Comparison of the vertical profile of PAH concentrations in the sediment core with that from another reservoir in the city indicates that both sediment cores have recorded combustion caused by the war. From the 1960s to 2000s the main source of PAHs in the air has been petroleum combustion. Loading of PAHs to the atmosphere decreased during this period, and the total concentration of PAHs is presently at its lowest level in the last 70 years.

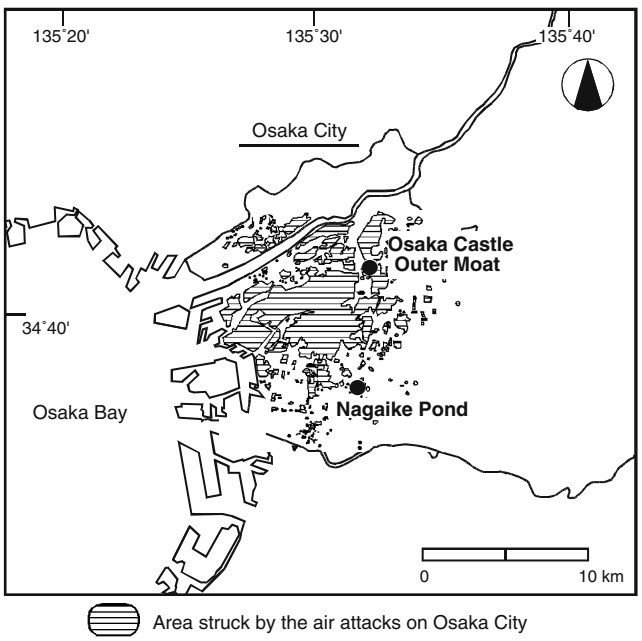

Fig. 6 The distribution map of the area struck by World War II air attacks in Osaka City

Acknowledgments The authors are grateful to Dr. Mitamura of Osaka City University for his invaluable comments and advice. Thanks to the staff of the laboratory of natural history of anthropogene at Osaka City University for their advice.

References

Baumard P, Budzonski H, Garrigues P (1998) Polycyclic aromatic hydrocarbons in sediments and mussels of the western Mediterranean Sea. Environ Toxicol Chem 17:765–776

Blokzijl PJ, Guicherit R (1972) The occurrence of polynuclear aromatic hydrocarbons (PAH) in outdoor air. TNO-news 1972, Nov 653–660

Boström CE, Gerde P, Hanberg A, Jernström B, Johansson C, Kyrklund T, Rannug A, Törnqvist M, Victorin K, Westerholm R (2000) Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. Environ Health Perspect 110:451–488

Gschwend PM, Hites RA (1981) Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the

northeastern United States. Geochim Cosmochim Acta 45:2359–2367

Hirose K, Aoyama M, Katsuragi Y, Sugiyama Y (1987) Annual deposition of Sr-90, Cs-137 and Pu-239, 240 from the 1961–1980 Nuclear Explosions: a Simple Model. J Meteorol Soc Jpn 65:259–277

Katahira K, Ishitake M, Moriwaki H, Yoshikawa S, Yamamoto O, Fujita T, Yamazaki H (2006) Method for the estimation of the past illegal dumping recorded in a sediment core. Water Air Soil Pollut (in press)

Kawaraya T (1998) Trend and dustribution of polycyclic aromatic hydrocarbon in Osaka from 1967 to 1994. Seikatsu Eisei 42:229–232

Kumata H, Sanada Y, Takada H, Ueno T (2000) Historical trends of *N*-cyclohexyl-2-benzothiazolamine, 2-(4-morpholinyl)benzothiazole, and other anthropogenic contaminants in the urban reservoir sediment core. Environ Sci Technol 34:246–253

Mastral AM, Callen MS (2000) Review on polycyclic aromatic hydrocarbon (PAH) emissions from energy generation. Environ Sci Technol 34:3051–3057

Moriwaki H, Ishitake M, Yoshikawa S, Miyakoda H, Alary JF (2004) Determination of polycyclic aromatic hydrocarbons in sediment by liquid chromatography-atmospheric pressure photo ionization-mass spectrometry. Anal Sci 20:375–377

Moriwaki H, Katahira K, Yamamoto O, Fukuyama J, Kamiura T, Yamazaki H, Yoshikawa S (2005) Historical trends of polycyclic aromatic hydrocarbons in the reservoir sediment core at Osaka. Atmos Environ 39:1019–1025

Murakami A, Inoue J (2004) History of fossil fuel combustion during the last 100 years in and around Osaka City, Japan: changes of the spheroidal carbonaceous particles (SCPs) recorded in a moat and in pond sediments. Quaternary Res 43:265–274

Okuda K, Nakada N, Isobe T, Nishiyama H, Sanada Y, Sato F, Takada H (2000) Endocrine disruptors in a sediment core collected from Tokyo Bay—the historical trends during the past 50 years. Bull Coast Oceanogr 37:15–24

Osaka City (1994) Shinshu-Osakashishi 7, 1068, 33p

Peirson DH (1971) Worldwide deposition of long-lived fission products from nuclear explosions. Nature 234:79

Sicre MA, Marty JC, Saliot A, Aparicio X, Grimalt J, Albaiges J (1987) Aliphatic and aromatic hydrocarbons in different sized aerosols over the Mediterranean Sea: occurrence and origin. Atmos Environ 21:2247–2259

The Institute of Energy Economics, Japan (1997) EDMC/energy and economy statistical report, 304p

Tsuji I, Koide K, Moriyama H, Tanabe K, Matsusita H (1985) Analysis of polynuclear aromatic hydrocarbons in shellfishes, seabottom sediments and sea water by high performance liquid chromatography. J Food Hyg Soc Jpn 26:50–55

Yunker MB, Snowdon LR, Macdonald RW, Smith JN, Fowler MG, Skibo DN, McLaughlin FA, Danyushevskaya AI, Petrova VI, Ivanov GI (1996) Polycyclic aromatic hydrocarbon composition and potential sources for sediment samples from the Beaufort and Barents Seas. Environ Sci Technol 30:1310–1320

Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, 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