

Chapter 8

Recent Trends in Atmospheric Concentrations of Polycyclic Aromatic Hydrocarbons and Nitropolycyclic Aromatic Hydrocarbons in Japanese Cities

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Abstract Total suspended particulate matter (TSP) was collected during the summer and winter in Japanese cities (Sapporo, Kanazawa, Tokyo, Sagamihara, and Kitakyushu) from 1997 to 2014. Polycyclic aromatic hydrocarbons (PAHs) with four to six rings and two nitropolycyclic aromatic hydrocarbons (NPAHs), 1-nitropyrene and 6-nitrobenzo[*a*]pyrene, were determined. A comparison between PAH and NPAH concentrations and [NPAH]/[PAH] ratios revealed the following characteristics:

1. Commercial cities (Sapporo, Kanazawa, Tokyo, and Sagamihara): the concentrations of PAHs and NPAHs were high at the beginning of the sampling period and then steadily decreased, with NPAHs decreasing more than PAHs. The major contributor was automobiles, but their contributions decreased significantly as a result of the effective regulation control of particulate matter and NO_x emitted from automobiles.
2. Iron-manufacturing cities (Kitakyushu and Muroran): PAH concentrations did not decrease, though concentrations of NPAHs decreased. The major contributor of PAHs was iron manufacturing which uses a large amount of coal.

Keywords Polycyclic aromatic hydrocarbons · Nitropolycyclic aromatic hydrocarbons · Japanese urban atmospheric pollution · Recent pollution trends · Emission source

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8.1 Introduction

In the 1970s and 1980s, urban air pollution in Japanese cities became serious, and automobiles were considered to be the major contributor with many kinds of pollutants such as carbon dioxide, sulfur oxides, nitrogen oxides, polycyclic aromatic hydrocarbons (PAHs), and nitropolycyclic aromatic hydrocarbons (NPAHs). Automobiles were identified as the main source of atmospheric PAHs and NPAHs in Kanazawa, a commercial city in Japan, as seen by the parallel between variations in diurnal PAH and NPAH concentrations and traffic volume (Fig. 8.1) (Hayakawa et al. 1995; Murahashi et al. 1995). The Japanese government gradually reinforced controls on nitrogen oxides (NO_x) and PM emitted from automobiles starting in the 1990s (Ministry of Land, Infrastructure Transport and Tourism 2017). As a result, a decrease in PAH and NPAH concentrations was observed (Kojima et al. 2010; Hama et al. 2012; Suzuki et al. 2015; Inomata et al. 2016). In this chapter, the changes in atmospheric concentrations and sources of PAHs and NPAHs during the period from 1997 to 2014 were clarified to obtain a more accurate picture of the effect of government emission controls on the allowable emissions from automobiles.

Total suspended particulate matter (TSP) was collected in Sapporo, Kanazawa, Tokyo, Sagamihara, and Kitakyushu (Fig. 8.2). Sapporo and Kanazawa, the respective capital cities of Hokkaido and Ishikawa Prefecture, are commercial cities though the former has a population about five times larger. Tokyo, having the largest population, is the capital of Japan, and Sagamihara is a typical satellite city of Tokyo. Both are commercial cities. Kitakyushu is one of the major iron-manufacturing cities in Japan. TSP samples in each city were collected for 2 weeks in winter (January–February) and summer (July–August) by using high-volume air

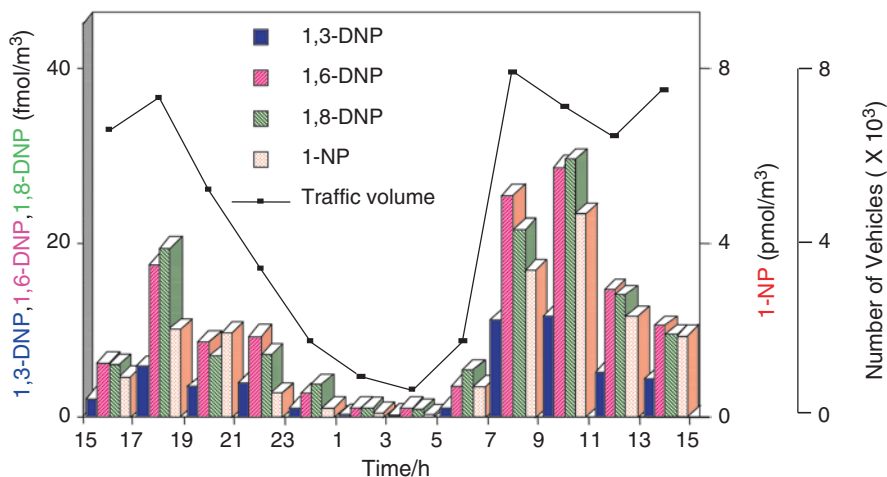


Fig. 8.1 Diurnal variations of 1,3-, 1,6-, and 1,8-dinitropyrenes (DNPs) and 1-NP in urban air sampling site of downtown Kanazawa; sampling period: February 2–3, 1993

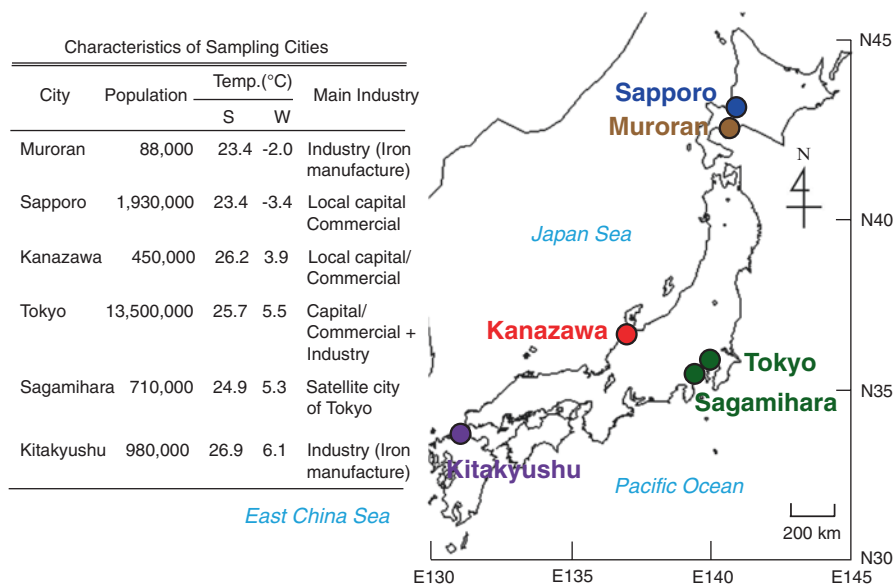


Fig. 8.2 Airborne particulate sampling cities in Japan

samplers. Nine PAHs, fluoranthene (FR), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), BaP, benzo[*ghi*]perylene (BghiPe), and indeno[1,2,3-*cd*]pyrene (IDP), were determined by using an HPLC equipped with a fluorescence detector. Two NPAHs, 1-nitropyrene (1-NP) and 6-nitrobenz[*a*]pyrene (6-NBaP), were determined using an HPLC equipped with a fluorescence detector.

8.2 Long-Term Changes in PAH and NPAH Concentrations from 1997 to 2014

In Sapporo, Kanazawa, and Tokyo, the highest mean Σ PAH concentrations observed were in the range between 5.1 and 8.0 ng/m³ in winter 1997 or 1999. Subsequently, in Sapporo, Kanazawa, and Tokyo, the respective concentrations decreased to 1/6 (summer), 1/3 (winter) and 1/3 (summer), and 1/2 (winter) of the initial concentrations with seasonal differences (winter > summer). However, TSP concentrations did not show any statistical decrease in these cities. In Kitakyushu, the initial mean Σ PAH concentrations (3.0 ng/m³ in summer 1997 and 4.6 ng/m³ in winter 1997) were at the levels similar to those of the other Japanese cities and remained at similar levels until a sudden increase in 2014, despite a low TSP concentration (Hayakawa et al. 2017). The variations in BaP, as a representative PAH, in the five cities are shown in Fig. 8.3. In Sapporo, Kanazawa, and Tokyo, the highest mean

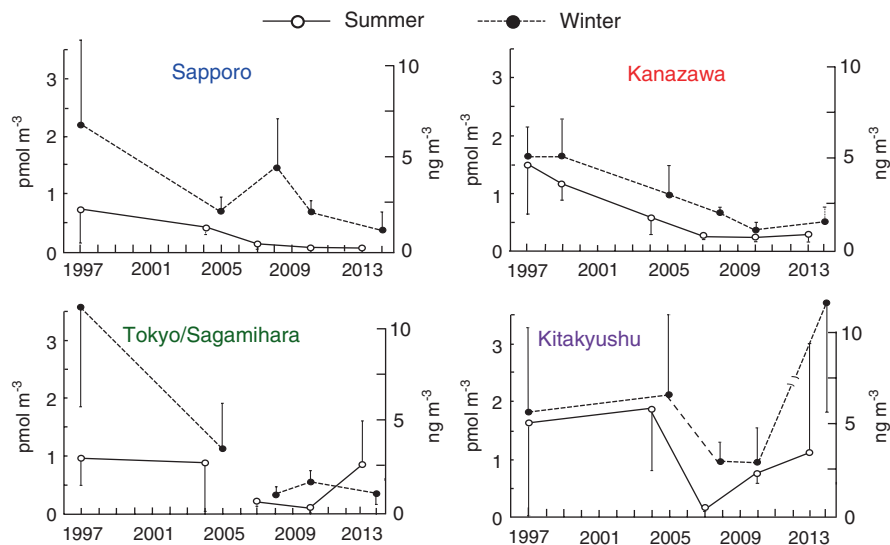


Fig. 8.3 Atmospheric BaP concentrations

BaP concentrations observed were in the range between 0.48 and 0.91 ng/m³ in the winter of 1997 or 1999. Subsequently, in Sapporo, Kanazawa, and Tokyo, the concentrations decreased significantly with seasonal differences (winter > summer). In Kitakyushu, the initial BaP concentrations (0.40 ng/m³ in summer 1997 and 0.45 ng/m³ in winter 1997) were at the levels similar to those of the other Japanese cities and increased suddenly to 1.72 ng/m³ in winter 2014.

In Sapporo, Kanazawa, and Tokyo, the highest winter Σ NPAH concentrations ranged from 70 to 141 pg/m³ and were observed during the winters of 1997 and 1999. Subsequently, in Sapporo, Kanazawa, and Tokyo, the concentrations decreased more significantly than those of PAHs. The rates of decrease were faster in the first stage (during 1997–2005) than in the second stage (2007–2014). However, Kitakyushu showed different patterns. The initial mean Σ NPAH concentrations in summer and winter were much lower than those of the other three Japanese cities. The subsequent summer concentration seemed to decrease, but the winter concentration did not (Hayakawa et al. 2017). Variations in 1-NP, as a representative NPAH, in the five cities are shown in Fig. 8.4. In Sapporo, Kanazawa, and Tokyo, the highest winter 1-NP concentrations ranged from 70 to 141 pg/m³ and were observed in winter 1997. Subsequently, the concentrations decreased more significantly than those of BaP and faster in the first stage (during 1997–2005) than in the second stage (2007–2014). However, Kitakyushu showed initial mean 1-NP concentrations in both summer and winter that were much lower than those of the other three Japanese cities. While the summer concentration seemed to subsequently decrease, the winter concentration did not.

Figures 8.3 and 8.4 showed that air pollution caused by PAHs and NPAHs has improved in Sapporo, Kanazawa, and Tokyo, especially in the first stage but not in

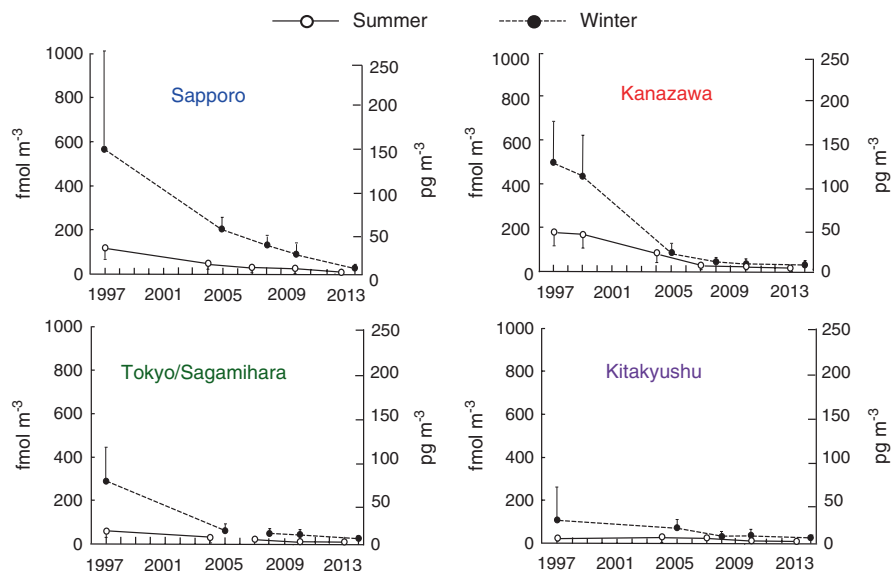


Fig. 8.4 Atmospheric 1-NP concentrations

Kitakyushu. The most important difference between Japanese cities and the other Far Eastern Asian countries is that pollution levels of PAHs and NPAHs in China and Far Eastern Russia were much higher than those in Japan by 1–2 orders of magnitude or more (Tang et al. 2002, 2005; Hattori et al. 2007).

8.3 Source Estimation

We previously reported that the concentration ratio of NPAH to corresponding PAH ([NPAH]/[PAH]) in TSP becomes larger with an increase in combustion temperature (Tang et al. 2005; Hama et al. 2012). This is because the formation of NO₂ and the mono- and di-nitration of PAHs depends on the combustion temperature. Depending on the combustion temperature and differences between coal-burning stoves (1100–1200 °C) and automobile engines (2700–3000 °C), the [1-NP]/[Pyr] value of PM from coal stoves ($8 \times 10^{-4} - 6 \times 10^{-3}$) was much smaller than that of PM from automobile engines (0.36) as seen in Fig. 8.5 (Yang et al. 2010).

The diurnal variations in atmospheric PAH and NPAH concentrations were in parallel with traffic volume in Kanazawa, a typical local commercial city in Japan (Hayakawa et al. 1995), suggesting automobiles were the main contributors (Hama et al. 2012). Figure 8.6 shows changes in [1-NP]/[Pyr] ratios for the five Japanese cities from 1997 to 2014 with a single value for Muroran in winter 2009. At the beginning of the study, Kanazawa showed the largest summer and winter [1-NP]/[Pyr] ratios (0.18 and 0.20, respectively). From the average [1-NP]/[Pyr] ratio (0.35)

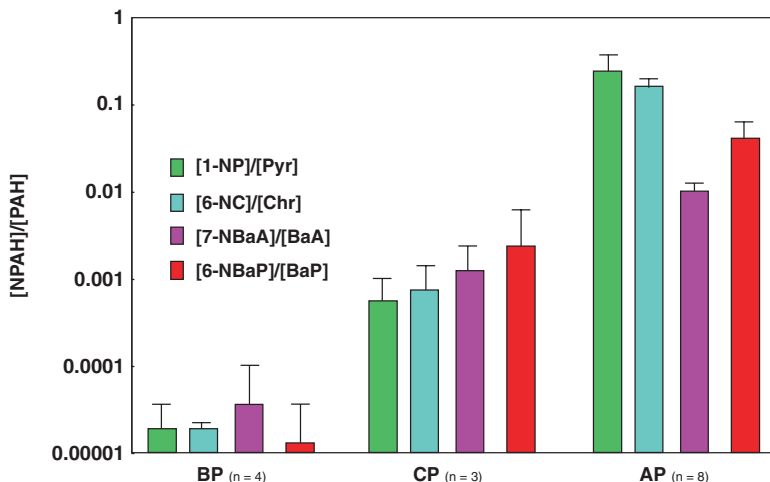


Fig. 8.5 [NPAH]/[PAH] ratios of automobile engine exhaust particulates (AP), coal-burning particulates (CP), and biomass-burning particulates (BP)

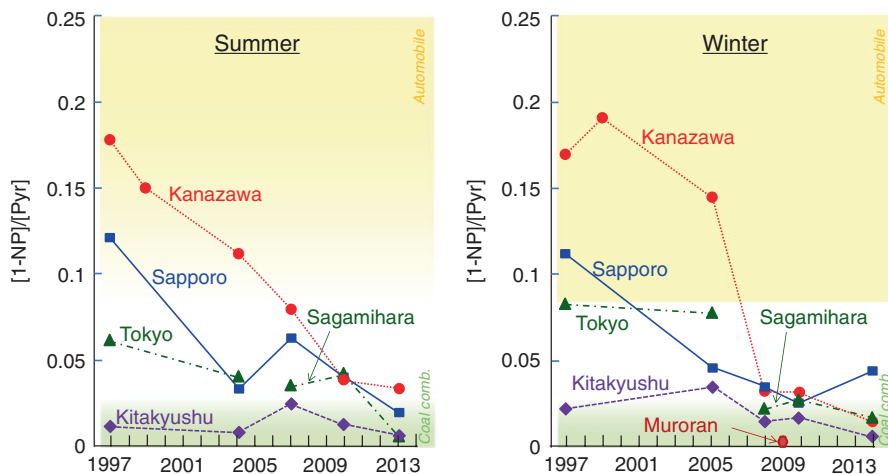


Fig. 8.6 Variation in [1-NP]/[Pyr] ratios

of PM exhausted from diesel engines, the contribution of automobiles to atmospheric PAHs and NPAHs was calculated to be between 47 and 57%. These values decreased significantly to 0.03 ($p < 0.01$) and 0.013 ($p < 0.01$), respectively, in 2013/2014.

Sapporo showed the largest [1-NP]/[Pyr] ratios (0.12 in both summer and winter) in 1997. They decreased to 0.019 and 0.043 ($p < 0.01$) by 2013/2014. The recent small [1-NP]/[Pyr] ratios suggest that the contribution of automobiles decreased significantly.

8.4 The Effect of Regulations on Atmospheric PAH/NPAH Levels

In Japan, during the period between 1995 and 2014, the registered number of cars increased from 44,680,000 to 60,670,000, while the registered number of trucks/buses, which consisted mainly of diesel-engine vehicles, decreased from 20,670,000 to 14,850,000. This alone does not explain the significant decreases in atmospheric NPAH concentrations shown in Fig. 8.4. Automobile mileage was also improved through innovations in engine performance and oil quality (Japan Automobile Manufacturers Association 2017). This might be another reason. Recently, the Japanese government enforced legislation limiting the values of NO_x and PM from new diesel vehicles through a step-by-step procedure starting in 1993. Emissions of CO, HC, and NO_x from new gasoline car in 2000, 2001, and 2002 (Shin-tanki kisei) were similarly restricted. Figure 8.7 shows the change of the regulation values of NO_x and PM emitted from new diesel vehicles of three weight categories, < 1.7 tons, 1.7–3.5 tons, and >3.5 tons, as an example of automobile categories. The regulation values of NO_x and PM from diesel-engine automobiles (≤ 3.5 tons) decreased significantly to 13.7–29.4% and 2.8–3.8% of the original levels before 1997. Because TSP contains not only PM exhausted from automobiles but also soils and particulates from the road surface, the decreases in Pyr and BaP may be explained primarily by decreases in regulation values of PM from automobiles (Fig. 8.7). Considering that the formation of NPAHs depends on $[\text{PM}]$ and $[\text{NO}_2]$, it is reasonable that atmospheric concentrations of 1-NP and 6-NBaP decreased faster than

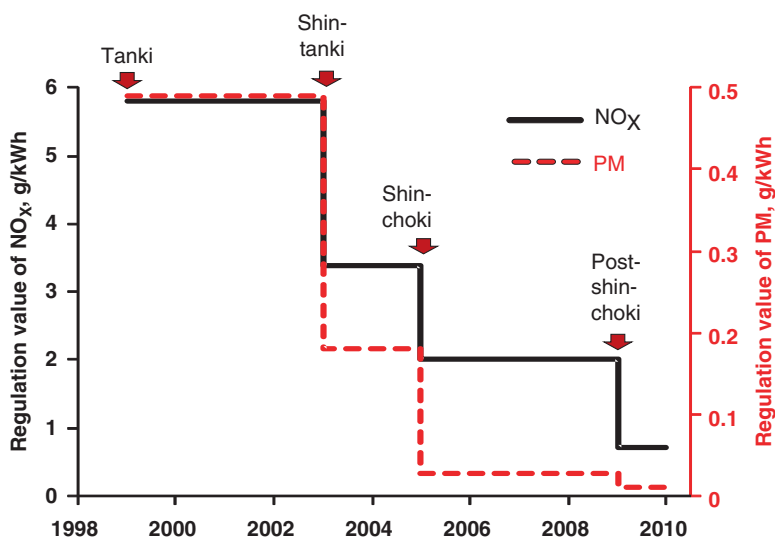


Fig. 8.7 Japanese regulation of NO_x and PM emissions from new diesel-engine vehicle regulation names: Tanki, short-term; Shin-tanki, new short-term; Shin-choki, new long-term; Post shin-tanki, post new short-term

those of Pyr and BaP, respectively. The rapid decrease in atmospheric concentrations of PAHs and NPAHs (Figs. 8.3 and 8.4) means that governmental control of PM and NO_x emission from automobiles has dramatically improved urban air pollution caused by automobiles in Japanese commercial cities (Kakimoto et al. 2000, 2002; Kashiwakura et al. 2008, 2009).

By contrast, Kitakyushu showed a different [1-NP]/[Pyr] profile. The values were very low during the monitoring period. The values were below 0.0004 in 2013/2014 (Fig. 8.6). Similarly, in another recent study of Muroran, which is a typical iron-manufacturing city in Japan, the [1-NP]/[Pyr] ratio was also very small (3.1×10^{-3}) in the winter of 2009. A coke-oven iron-manufacturing plant, which consumes a large amount of coal, was found to be the major contributor of PAHs in the city (Hayakawa et al. 2016). Like Muroran, Kitakyushu is also a major iron-manufacturing city.

8.5 Conclusion

An analysis of long-term concentrations of atmospheric PAHs and NPAHs, as well as [NPAH]/[PAH] ratios in five Japanese cities from Hokkaido to Kyushu from 1997 to 2014, led to two conclusions:

1. Commercial cities [Sapporo, Kanazawa, Tokyo, and Sagami-hara]: the concentrations of PAHs and NPAHs were high in the 1990s and then decreased. NPAHs decreased faster than PAHs. The major source was automobiles at the beginning, but the contribution of automobiles decreased significantly after the enforcement of regulations aimed at curbing automobile emissions.
2. Iron-manufacturing cities [Kitakyushu and Muroran]: the concentrations of PAHs did not decrease, while the concentrations of NPAHs decreased. The major PAH contributor was from iron manufacturing.

From the comparison of Japanese cities (Chap. 8) and the other East Asian countries (Chap. 9), it must be emphasized that the pollution levels of PAHs and NPAHs in Japanese urban air were much lower than those in China and Russia and that the major sources are different. Automobiles are the major contributor in Japanese commercial cities such as Sapporo, Tokyo, Kanazawa, and Busan. While iron manufacturing, which consumes a large amount of coal, is the major contributor in Kitakyushu and Muroran, winter coal heating is the major contributor in Shenyang, Beijing, and Vladivostok. In the automobile cities, the concentration of NPAHs relative to the concentration of PAHs was higher in East Asian countries. This means that there will be differences between locales that require differing countermeasures (Hayakawa 2016).

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