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Long term trends in atmospheric concentrations of polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons: A study of Japanese cities from 1997 to 2014☆

Kazuichi Hayakawa [a, *], Ning Tang [a, b], Edward Gou Nagato [a], Akira Toriba [b], Shigekatsu Sakai [c], Fumio Kano [d], Sumio Goto [e], Osamu Endo [e], Kei-ichi Arashidani [f], Hitoshi Kakimoto [g]

[a] Institute of Nature and Environmental Technology, Kanazawa University, Kakuma-machi, Kanazawa, Ishikawa 920-1192, Japan
[b] Institute of Medical, Pharmaceutical and Health Sciences, Kanazawa University, Kakuma-machi, Kanazawa, Ishikawa 920-1192, Japan
[c] Hokkaido Prefectural Environmental Science Research Center, Kita 19 jo-nishi 12, Sapporo, Hokkaido 060-0819, Japan
[d] Tokyo Metropolitan Institute of Public Health, 3-24-1, Hyakunin-cho, Shinjuku-ku, Tokyo 169-0073, Japan
[e] Azabu University, 1-17-71 Fuchinobe, Chuo-ku, Sagamihara, Kanagawa 252-5201, Japan
[f] School of Health Science, University of Occupational and Environmental Health, Japan, 1-1 Isegaoka, Yahata-nishi-ku, Kitakyushu, Fukuoka 807-8555, Japan
[g] Ishikawa Prefectural Institute of Environment and Health, 1-11 Taiyogaoka, Kanazawa, Ishikawa 920-1154, Japan

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ABSTRACT

Total suspended particulate matter (TSP) was collected during the summer and winter in five Japanese cities spanning Hokkaido to Kyushu (Sapporo, Kanazawa, Tokyo, Sagamihara and Kitakyushu) from 1997 to 2014. Nine polycyclic aromatic hydrocarbons (PAHs) with four to six rings, including pyrene (Pyr) and benzo[*a*]pyrene (BaP), were identified using high-performance liquid chromatography (HPLC) with fluorescence detection. Two nitropolycyclic aromatic hydrocarbons (NPAHs), 1-nitropyrene (1-NP) and 6-nitrobenzo[*a*]pyrene (6-NBaP), were identified by HPLC with chemiluminescence detection. A comparison of PAH and NPAH concentrations and [NPAH]/[PAH] ratios such as [1-NP]/[Pyr] and [6-NBaP]/[BaP] revealed the following characteristics in the five cities: (1) In 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 faster than PAHs. The large initial [1-NP]/[Pyr] ratios suggest that the major contributor was automobiles but subsequent decreases in this ratio suggest decreased automobile contributions. (2) By contrast, PAH concentrations in Kitakyushu did not decrease during the sampling period, though concentrations of NPAHs decreased. The consistently smaller [1-NP]/[Pyr] ratio and larger [6-NBaP]/[BaP] ratio in Kitakyushu suggests that the major contributor of PAHs was not automobiles but iron manufacturing which uses a large amount of coal. The sudden increase in atmospheric PAH concentrations in the winter of 2014 may also be due to iron manufacturing.

1. Introduction

The combustion of fossil fuels and biomass produces many kinds of air pollutants such as carbon dioxide, sulfur oxides, nitrogen oxides, polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs). Several NPAHs such as 2-nitropyrene and 2-nitrofluoranthene are secondary formation products from parent PAHs in the urban atmosphere (Arey et al., 1986; Atkinson and Arey, 1994). These PAHs and NPAHs are found in airborne particulate matter (PM), especially fine particulate matter ($PM_{2.5}$) which have a diameter of no more than 2.5 μm. Among these compounds, the International Agency for Research on Cancer (IARC) has classified benzo[*a*]pyrene (BaP) as a Group 1 compound (carcinogenic to humans), while dibenz[*a,h*]anthracene, 6-nitrochrysene (6-NC) and 1-nitropyrene (1-NP) are classified as Group 2A compounds (probably carcinogenic to humans) (IARC,

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* Corresponding author.
E-mail address: hayakawa@p.kanazawa-u.ac.jp (K. Hayakawa).

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2017). Moreover, 1,3-, 1,6-, 1,8-dinitropyrenes (DNPs) and 1-NP show strong direct-acting mutagenicity (Ames et al., 1975; Epstein et al., 1979) and several PAHs and NPAHs show endocrine-disrupting and reactive oxygen species-producing activities (Hayakawa et al., 2007; Motoyama et al., 2009). Recently, outdoor air pollution as well as PM have been classified into Group 1 (IARC, 2013).

The Japan Society for Atmospheric Environment (JSAE) reported that since the 1980s, the major contributor to air pollution in Japanese commercial cities has shifted from factories to automobiles (JSAE, 2007). In one study, both a cluster analysis and factor analysis indicated that the dominant source of the atmospheric PAHs and NPAHs was automobile emissions, especially diesel-engine vehicles in Japanese commercial cities such as Tokyo, Sapporo and Kanazawa (Tang et al., 2005). Similar results in Japan were obtained in Tokyo (Chetwittayachan et al., 2002), Nagasaki (Wada et al., 2001) and Niigata (Kawata et al., 1997). Furthermore, the use of NPAH to PAH concentration ratios can be a useful proxy in determining the source of the NPAHs such as 1-NP and 6-nitrobenzo[*a*]pyrene (6-NBaP), as their production is largely temperature dependent and sources such as diesel combustion, coal combustion and biomass combustion show very different [NPAH]/[PAH] ratios (Yang et al., 2010). In Japan, it has been demonstrated that [1-NP]/[Pyr] ratios in cities are much higher than in Northern Chinese cities, where large amounts of coal are consumed for winter heating (Tang et al., 2005) and that [6-NBaP]/[BaP] is larger in automobile emissions than from coal and biomass burning systems (Yang et al., 2010), thus indicating that the major source of PAHs and NPAHs are from automobiles. These PAHs and NPAHs originating from automobiles in urban areas have decreased the air quality of suburban areas as well, given the high mobility of these contaminants (Kakimoto et al., 2002).

In response to this worsened air pollution, the Japanese government started several countermeasures analogous to the US Clean Air Act passed in 1978. The Japanese government gradually enforced 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, the average atmospheric concentrations of 1-NP were 68 fmol/m^3 (17 pg/m^3) in Tokyo during the period between 1997 and 1998, and 26 fmol/m^3 (6.4 pg/m^3) during the period between 2006 and 2007. This decrease in 1-NP concentration (38% of the initial concentration) was larger than that of suspended PM (84% of the initial concentration) and PAHs (62% of the initial concentration) (Kojima et al., 2010). Also at two different sites in Tokyo, atmospheric PAH and NPAH concentrations in 2013 were 45–79% and 36–84%, respectively, of those in 2006 (Suzuki et al., 2015). In Kanazawa, PAH and NPAH concentrations decreased to 24–34% and 11–12% of the initial respective concentrations during the period from 1999 to 2010 (Hama et al., 2012). However, these observations were limited to a few cities. To more accurately assess the effect of government emission controls on urban air pollution from automobiles across Japan, it is necessary to look at PAH and NPAH data for a longer period across a wider geographic range, while covering the induction of various pollution curbing laws enforced since the 1990s.

Since the completion of the above studies we have continued to collect TSP samples in Japanese cities during the summer and winter up to 2014, during which we changed two of the sampling cities (Toyama to Kitakyushu in 1997 and Tokyo to Sagamihara in 2007). The purpose of the present study then is to clarify the changes in long term atmospheric concentrations and sources of PAHs and NPAHs in these Japanese cities during the period from 1997 to 2014 with relation to legislative events in Japan.

2. Materials and methods

2.1. Chemicals

The US Environmental Protection Agency 610 PAH mix, a mixture of 16 PAHs was purchased from Supelco (Bellefonte, PA, USA). Two internal standards for PAHs, pyrene-d_{10} (Pyr-d_{10}) and benzo[*a*]pyrene-d_{12} (BaP-d_{12}), were purchased from Wako Pure Chemicals (Osaka, Japan). 1-NP, 6-nitrobenzo[*a*]pyrene (6-NBaP) and 2-fluoro-7-nitrofluorene (FNF; an internal standard for NPAH analysis) were purchased from Chiron AS (Trondheim, Norway). Standard solutions of PAHs and NPAHs were prepared by dissolving each standard compound in ethanol. The internal standard solutions were prepared by dissolving Pyr-d_{10}, BaP-d_{12} and FNF in ethanol as well. All other chemicals used were of reagent analytical grade.

2.2. Atmospheric PM sampling

TSP samples were collected in Sapporo, Kanazawa, Tokyo, Sagamihara and Kitakyushu (Fig. 1) from 1997 to 2014. Sapporo and Kanazawa, the capital cities of Hokkaido and Ishikawa Prefecture, respectively, are commercial cities, though the former has a population about 5 times larger. Tokyo, having the largest population, is the capital of Japan and Sagamihara is a satellite city of Tokyo. Both are commercial cities. Kitakyushu is one of the major iron manufacturing cities in Japan. These cities span a wide geography across Japan and their characteristics (population, temperature and main industry) are summarized in Table 1. The sampling sites were in residential areas not far from downtown except for Kanazawa, where the sampling site was along two major traffic roads in a residential area.

TSP samples in each city were collected for two weeks in the winter (January–February) and the summer (July–August) using high-volume air samplers (Kimoto Electric Company Limited, Osaka, Japan and Sibata Scientific Technology Limited, Saitama, Japan) at a flow rate of 1000 L/min and fitted with a quartz fibre filter (8 × 10 inches, 2500QAT-UP, Pallflex Products, CT, USA). The filters were changed every day. Filters were prepared by drying them over two nights in a desiccator in the dark, were weighed and

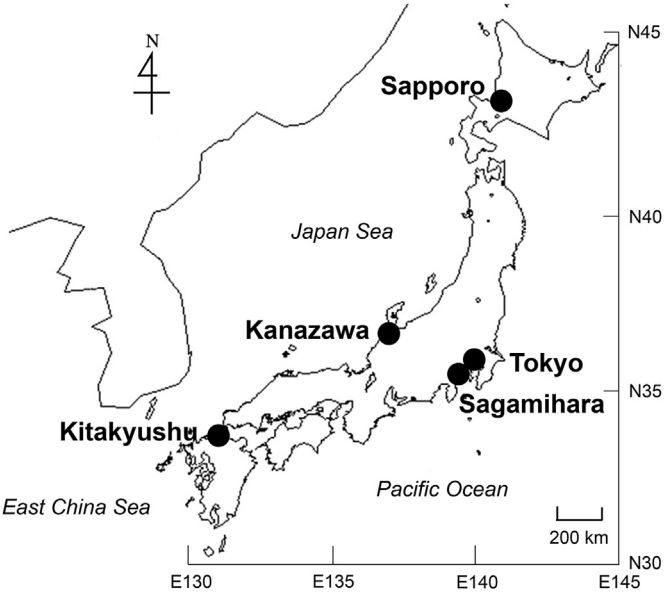

Fig. 1. Airborne particulate sampling cities in Japan.