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Factors affecting atmospheric 1-, 2-nitropyrenes and 2-nitrofluoranthene in winter at Noto peninsula, a remote background site, Japan

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HIGHLIGHTS

- Trace levels of three atmospheric nitroarenes (NPAHs) were determined.
- We described the long-range transport of atmospheric NPAHs in East Asia.
- NPAHs at a background site of Japan in winter probably largely come from China.

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ABSTRACT

Airborne particulates were collected at a background site (Wajima Air Monitoring Station; WAMS) on the Noto Peninsula, Japan from January 2006 to December 2007. 1-, 2-nitropyrenes (1-, 2-NPs) and 2-nitrofluoranthene (2-NFR), in the particulates were determined with a sensitive HPLC method with chemiluminescence detection. The average concentrations were higher in winter than in summer. A meteorological analysis indicated that the air samples collected in winter were transported mainly from Northeast China over the Japan Sea. Both the concentration ratios of 2-NFR to 1-NP and 1-NP to pyrene were similar to those in Shenyang in Northeast China which located along the air transportation route to WAMS, but not in Kanazawa which near WAMS. These results strongly suggest that most of the atmospheric 1-, 2-NPs and 2-NFR at WAMS in winter were long range transported from Northeast China.

1. Introduction

Among air pollutants, polycyclic aromatic hydrocarbons (PAHs) and their nitrated derivatives (nitropolycyclic aromatic hydrocarbons, NPAHs) are well-known to be carcinogenic and/or mutagenic (Ames et al., 1975; Epstein et al., 1979; Pedersen et al., 2004, 2005; Landvik et al., 2007; Øvrevik et al., 2010). The International Agency for Research on Cancer has categorized benzo[*a*]pyrene (BaP) and 1-nitropyrene (1-NP) in group 1 (carcinogenic to humans) and 2A (probably carcinogenic to humans), respectively (IARC, 2012, in press). Atmospheric PAHs and most NPAHs, such as 1-NP, mainly originate from imperfect combustion of organic matter such as petroleum, coal and biomass. For example, urban atmospheric concentrations of 1,3-, 1,6- and 1,8-dinitoropyrenes and 1-NP are strongly correlated with traffic volume (Hayakawa et al., 1995), and a 1-NP metabolite in human urine is strongly correlated with exposure to diesel exhaust (Toriba et al., 2007). In addition, some NPAHs such as 2-nitrofluoranthene (2-NFR) and 2-nitropyrene (2-NP) are formed in the atmosphere. Hydroxyl radical-initiated reactions contribute to the formation of 2-NFR and 2-NP while nitrate radical-initiated reactions contribute to the formation of 2-NFR only in nighttime (Arey et al., 1986, 1989; Sweetman et al., 1986). Therefore, PAHs and NPAHs need to be monitored because of their health risks to humans.

Today, Northeast Asia is the most industrially active region in the world. However, this has led to serious environmental pollution. Our studies in this region over the past 15 years have shown that the main contributors to the atmospheric PAHs and NPAHs were automobiles, especially diesel-engine vehicles in Japanese cities (Tokyo, Sapporo, Kanazawa and Toyama) and Seoul, Korea,

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and coal combustion processes in Shenyang, Fushun and Tieling, China, and Vladivostok, Russia. Atmospheric concentrations of PAHs were 3–180 times higher in Chinese and Russian cities than in Japanese and Korean cities (Kakimoto et al., 2000, 2002; Tang et al., 2002, 2005; Hattori et al., 2007), mainly because of the large consumption of coal in China and Eastern Russia (Chen et al., 2005; Tang et al., 2005). Furthermore, PAHs as well as acid rain and Asian Dust (Yellow Sand) were long-range transported from the Asian continent to Japan during the winter heating period of North China (Tamamura et al., 2007; Yang et al., 2007). The long-range transport of air masses from the Asian Continent to Japan can be explained by the atmospheric pressure pattern of Northeast Asia in cold seasons (Terada et al., 2002). Because NPAHs are highly-reactive (Fan et al., 1996; Feilberg and Nielsen, 2000; Miet et al., 2009a,b,c; Kameda et al., 2011; Zhang et al., 2011; Liu et al., 2012; Ringuet et al., 2012a), and because several of their derivatives, such as hydroxylated NPAHs, are considered toxic (Kameda et al., 2008), monitoring atmospheric NPAHs is important to clarify how they transported from Northeast Asia to other areas. In order to predict movements of atmospheric particulates from Northeast Asia, it is helpful to monitor background sites such as the Noto Peninsula, Japan (Tsapakis and Stephanou, 2007; Yang et al., 2007). In the past, we did not monitor atmospheric NPAHs on the Noto Peninsula because their concentrations were too low to be detected by our conventional HPLC-chemiluminescence detection (CLD) system (Murahashi and Hayakawa, 1997; Murahashi et al., 1999; Tang et al., 2003). Recently, we developed a more sensitive system for measuring trace levels of NPAHs by modifying the conventional system (Hayakawa et al., 2011).

In the present study, we used this system to analyze total suspended particulates (TSP) on the Noto Peninsula over an approximately two-year period. We determined the concentrations of 1-NP, which is a typical NPAH that is mainly produced by combustion systems, especially diesel-engine vehicles, and 2-NP and 2-NFR, which are typical NPAHs formed in the atmosphere. We also determined the concentrations of PAHs in the same samples to better understand the seasonal variations of NPAHs and their major sources in winter.

2. Materials and methods

2.1. Sampling

TSP were collected at Kanazawa University Wajima Air Monitoring Station (WAMS: Nisifutamata-machi, Wajima City, Ishikawa Prefecture, Japan; 37°23′ N, 136°54′; 60 m above sea level), which locates in Noto Peninsula, 2.1 km south from the Japan Sea coast (Fig. 1). This station is the former National Wajima Acid Rain Monitoring Station of the Ministry of the Environmental Agency, Japan. No major emission sources of PAHs and NPAHs are near the station. TSP were collected by a high volume air sampler (AH-600, Shibata Sci. Tech. Ltd., Saitama, Japan) with a quartz fiber filter (8 in. - × 10 in., 2500QAT-UP, Pallflex Products, Putnam, CT, USA) at a flow rate of 700 L min^{-1} continuously from January 13, 2006 to December 28, 2007. According to previous reports (Yang et al., 2007), result of preliminary test and other information, the filters were changed newly every week to minimalize secondary formation of NPAHs. The description of the sampling design is presented in Supplementary Material Section 1. After being dried in a desiccator in the dark, the used filters were weighed and then kept in a refrigerator (−20 °C) until use. The quartz fiber filters used for collecting particulate-bound PAHs and NPAHs were pre-heated at 600 °C for 4 h before using it to lower their PAHs and NPAHs blank values. Field blanks, which accompanied samples to the sampling sites, were used to determine any background contamination. Three filters were selected randomly from the same lot number filters. No contamination was found during traveling of blank samples.

2.2. Chemicals

1-NP and 2-NFR were purchased from Aldrich Company Inc. (Milwaukee, WI, USA). 2-NP was kindly supplied by Professor Akihisa Hirayama, Kyoto Pharmaceutical University. Deuterated 1-NP (1-NP-d_9), internal standard for NPAHs, was purchased from CDN Isotopes Inc. (Pointe-Claire, Quebec, Canada). All other chemicals used were of analytical reagent grade.

2.3. Sample preparation

Sample preparation method was the same as in our previous report (Hayakawa et al., 2011). In order to remove interfering matter originated from the filter, only one-fourth of the filter was used to extract NPAHs. The filter was cut into small pieces in a flask and 100 μL of 1-NP-d_9 standard solution was added to the flask as an internal standard. Then, NPAHs were extracted ultrasonically twice with benzene/ethanol (3:1, v/v). The solution was washed successively with sodium hydroxide solution, sulfuric acid solution and water. After filtering the organic solution with an HLC-DISK membrane (pore size 0.45 μm, Kanto Chemical Co., Tokyo, Japan), the solution was evaporated to dryness. The residue was dissolved in 1.0 mL of ethanol, and then an aliquot (100 μL) of the solution was injected into the HPLC-CLD system.

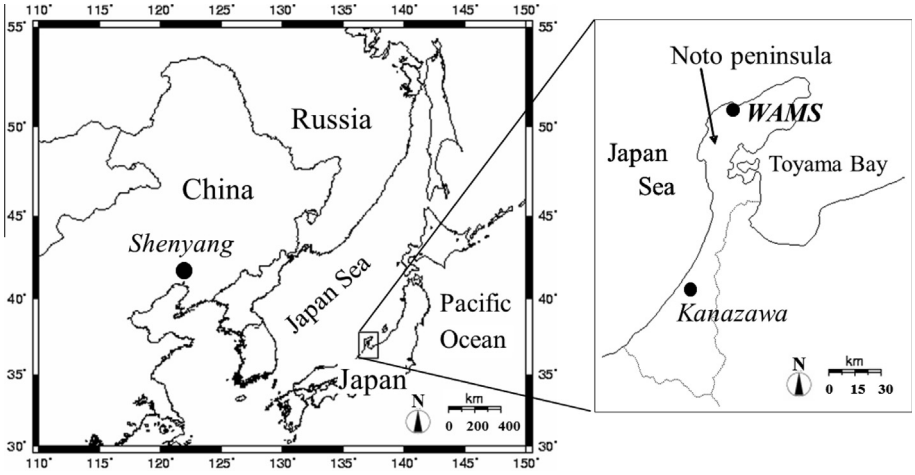

Fig. 1. Location of sampling site. WAMS: Nisifutamata-machi, Wajima City, Ishikawa Prefecture, Japan; 37°23′ N, 136°54′ E; 60 m above sea level.

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