

Changes in Concentration Levels of Polycyclic Aromatic Compounds Associated with Airborne Particulate Matter in Downtown Tokyo after Introducing Government Diesel Vehicle Controls

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ABSTRACT

The effectiveness of the government regulation on tail-pipe emission for diesel vehicles issued in 2003 in Tokyo was evaluated in this study. Variations in annual average concentrations of polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs associated with airborne particulate matter were investigated in connection with the variation in airborne elemental carbon (EC) concentration in downtown Tokyo, Japan in 2006-2007 and in 1997-1998. The annual average concentrations of EC, seven different PAHs, and 1-nitropyrene were found to have decreased significantly from 1997-1998 to 2006-2007. The most prominent decrease in atmospheric concentration was observed for 1-nitropyrene, which is a representative nitro-PAH originating from diesel vehicles. This indicated that the government control has worked to considerably reduce both atmospheric mutagens and airborne particulate matter. In contrast, the concentrations of two nitro-PAHs, 2-nitrofluoranthene and 2-nitropyrene, remained the same. These nitro-PAHs are known to be formed by atmospheric nitration of their parent PAHs, and this result suggested factors other than the concentration of parent PAHs and NO₂ affects the degree of atmospheric formation of nitro-PAHs.

Key words: PAHs, Nitro-PAHs, Airborne particulate matter, Diesel vehicle, Elemental carbon

1. INTRODUCTION

Air pollution caused by vehicle emissions has been

of great concern in terms of the increasing number of lung cancer patients. Lung cancer is currently the leading cause of death in Japan. Particulate matter (PM) is regarded as an extremely important pollutant especially in urban areas since it contains various mutagenic or carcinogenic polycyclic aromatic compounds (PACs), some of which are found both in diesel engines and in airborne PM (Kakimoto *et al.*, 2002; Hayakawa *et al.*, 1995; Murahashi *et al.*, 1995). Among the mutagenic PACs, two groups are well known. One group is the polycyclic aromatic hydrocarbons (PAHs), such as benzo[*a*]pyrene, which exhibit mutagenicity expressed by metabolic activation (Nisbet and LaGoy, 1992). PAHs are formed during combustion of organic compounds and a considerable fraction of them, especially those with high molecular weight, aggregate on PM generated during the combustion processes of organic compounds due to their low vapor pressure (Mastral and Callen, 2000). The other PAC group is the nitro-PAHs, which show direct-acting and stronger mutagenicity (Rosenkranz and Mermelstein, 1983). Some nitro-PAHs are also believed to be formed in the combustion process especially at high temperature, such as in diesel engines because an elevated concentration of nitrogen oxides is attained under such conditions (Tang *et al.*, 2005). Such nitro-PAHs, represented by 1-nitropyrene (1-NP), have been identified and determined both in airborne PM (Tang *et al.*, 2005; Kakimoto *et al.*, 2002; Hayakawa *et al.*, 1995; Murahashi *et al.*, 1995) and diesel exhaust particulate (DEP) (Schuetzle, 1983). There are also some nitro-PAHs that are believed to be formed via atmospheric reactions of parent PAHs with nitrogen oxides (Phoungphouang and Arey, 2003; Ishii *et al.*, 2001; Enya *et al.*,

1997; Arey *et al.*, 1986; Zielinska *et al.*, 1986; Pitts *et al.*, 1978). For example, it is believed that 2-nitrofluoranthene (2-NF) and 2-nitropyrene (2-NP) are produced in the atmosphere via the reactions of fluoranthene or pyrene with NO_2 , which are initiated by OH radicals in the daytime or by NO_3 radicals in the nighttime (Arey *et al.*, 1986; Zielinska *et al.*, 1986).

In 2003, additional regulations to those already in place from the national government were enforced by the Tokyo metropolitan government on emissions for diesel vehicles used in Tokyo. As a result, the diesel vehicles not meeting this standard were to be replaced with newer low-emission models or have PM reduction devices installed, such as a diesel particulate filter (DPF) (Yokota, 2007; Tokyo Metropolitan Government, 2006). In recent years, the concentration of suspended particulate matter (SPM, particles with a 100% cut-off aerodynamic diameter $< 10 \mu\text{m}$) has been decreasing in downtown Tokyo according to government environmental monitoring data. However, there are limited reports on the change in concentration levels of individual pollutants associated with airborne PM since implementation of the government diesel vehicle controls. Above all, the change in mutagenic PAC concentration is of great importance from a public health point of view.

In this study, the variations of annual concentration levels of PAHs and nitro-PAHs associated with airborne PM in downtown Tokyo before and after the regulation became effective (i.e. 1997-2006) were investigated. Airborne elemental carbon (EC) was also investigated, as it is an excellent indicator of diesel emissions. These studies would help reveal the effectiveness of the regulation in reducing atmospheric mutagenic PACs. A comparison with the concentration changes at neighboring suburban sites was also made with respect to the same pollutants for further evaluation of the effectiveness of the regulation.

2. EXPERIMENTAL

2.1 Sampling of Airborne PM

Airborne PM was collected on a quartz fiber filter ($8 \times 10 \text{ inch}^2$, Pallflex Product, 2500QATUP) using a high-volume air sampler (HV-1000F, Sibata Co.) equipped with an impactor stage to eliminate any particle larger than $10 \mu\text{m}$ in aerodynamic diameter. The flow rate was 0.5 or $1.1 \text{ m}^3 \text{ min}^{-1}$ and samples were collected on the rooftop of the building at each site (A, B, C and D in Fig. 1). After collection, the filter samples were dried at room temperature, and weighed to determine the concentration of the PM. All filters were then stored at -30°C until being submitt-

ed for analysis. Sites A and B were located in typical urban areas that included busy roads with a traffic density of 40,000-80,000 cars per day. Sites C and D were located in representative suburban areas of Tokyo. Twenty-four-hour sampling programs were carried out on 4-6 days in each month of May, September, and January in 1997-1998 (site A) and in 2006-2007 (site B), in January 2001 (sites A and C), and in October 2005 (sites B and D). The change in concentration levels of SPM, EC and PACs from before to after the regulation became effective were analyzed by comparing the concentrations in 1997-1998 (site A) and 2006-2007 (site B). Although comparing the concentrations at different sampling sites is not an ideal way to evaluate the effectiveness of the newly issued regulation on emission from diesel vehicle in Tokyo, the air quality at the two sampling sites in this study is expected to be almost the same for the following reasons. First, as described later (Results and Discussion), SPM concentrations at the two sites are almost the same during the last ten years (Fig. 1). Second, both sites can be regarded as urban background sites that are not significantly influenced by direct emissions from the traffic roads because the actual points of the sampling were more than 100 m away from the traffic roadside to avoid the exclusive impact from particular traffic roads. Finally, as described later (Results and Discussion), no significant difference in the concentration of PACs was observed between the urban and suburban sites (e.g. sites A and C) which

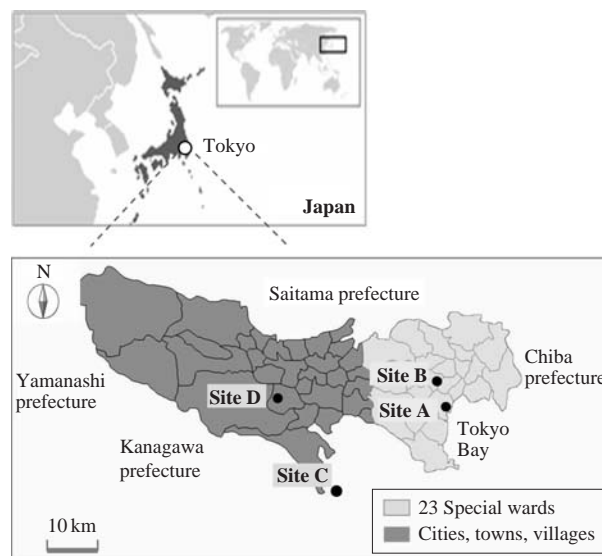


Fig. 1. The sampling sites: Site A, Minato-ku (National Institute of Public Health); Site B, Shinjuku-ku (Waseda University); Site C, Midori-ku, Yokohama (Tokyo Institute of Technology); Site D, Hino, Tokyo (Tokyo Metropolitan University).

are more than 20 km distant from each other (Fig. 5), indicating that the concentration level of PACs at site A and B only approximately 5 km distant from each other should also be the same. Considering these facts, the differences in concentrations of these compounds from 1997-1998 (site A) to 2006-2007 (site B) are suitable to evaluate changes in the air quality induced by the regulation in Tokyo although it's the second best way.

2.2 Materials

Benzo[*a*]pyrene (BaP), benzo[*k*]fluoranthene (BkF), and indeno[1,2,3-*cd*]pyrene (IP) were obtained from Wako Pure Chemical Industries. Pyrene (PY), benzo[*ghi*]perylene (BghiP), and perylene (PER) were obtained from Aldrich Chemical Co. Fluoranthene (FL) and 1-nitropyrene (1-NP) were obtained from Tokyo Kasei Kogyo. 2-nitrofluoranthene (2-NF) and 2-nitropyrene (2-NP) were obtained from Chiron AS. All the chemicals were used without further purification.

2.3 Analysis of PAHs and Nitro-PAHs

A section of each filter was cut into small pieces and put in a flask followed by addition of an internal standard. Then both PAHs and nitro-PAHs were extracted ultrasonically for 20 min twice with dichloromethane (DCM) and the extract solution was filtered to remove solid material. The filtrate was concentrated to dryness under a flow of N₂. For PAH analysis, the residue was dissolved in 500 μ L of DCM and the solution was cleaned by solid phase extraction (SPE) with silica gel as the solid phase (Discovery SPE DSC-Si Silica, Supelco). The extract solution was concentrated to dryness under a flow of N₂ flow and the residue re-dissolved in 500 μ L of acetonitrile. This sample solution was analyzed by HPLC. For nitro-PAH analysis, the residue was dissolved in 2 mL of DCM, and the solution was cleaned by SPE with alumina-acidic and alumina-basic solid phases (Bond Elut JR-AL-A and JR-AL-B, Varian). The extract solution was then concentrated to dryness under a flow of N₂ followed by dissolution in 300 μ L of ethanol/water (3/1, v/v). This sample solution was analyzed by HPLC.

PAHs were determined by HPLC with fluorescence detection. The system consisted of the detector (RF-10A_{XL}, Shimadzu), a pump (LC-10AD, Shimadzu), a system controller (SCL-10A, Shimadzu), a degasser (DGU-20A₅, Shimadzu), a column oven (CTO-10Avp, Shimadzu), and a column (3.0 mm i.d. \times 250 mm, Pegasil ODS, Senshu Pak). The mobile phase was acetonitrile/water (8/2, v/v). The flow rate was 0.5 mL min⁻¹. The time program of the fluorescence detector was set to detect at the optimum excitation and emission wavelength for each target PAH.

For nitro-PAH analysis, the in-line reduction and chemiluminescence detection method using HPLC was employed, following a previously reported method (Murahashi and Hayakawa, 1997). The system consisted of a chemiluminescence detector (CLD-10A, Shimadzu), four pumps (LC-10ADvp and LC-10ATvp, Shimadzu), a six-port switching valve (FCV-12AH, Shimadzu), a column oven (CTO-10ACvp, Shimadzu), and a system controller (CBM-20A, Shimadzu). Two separation columns (3.0 mm i.d. \times 250 mm, 201TP54, Vydac and 5C₁₈-MS-II, Nakalai Tesque), a concentration column (2.0 mm i.d. \times 5 mm, Cadenza CD-C18, Imtakt), and a reducing column (4.0 mm i.d. \times 10 mm, NPPak-R, Jasco) were employed. The mobile phase for first separation and reduction of nitro-PAHs was 75% ethanol-acetate buffer (pH 5.5), and that for the second separation was acetonitrile/imidazole-perchloric acid buffer (pH 7.6) (1 : 1, v/v). Each flow rate was 0.5 mL min⁻¹. The mobile phase for concentration was 10 mM ascorbic acid in water, and the flow rate was 2 mL min⁻¹ when necessary. The chemiluminescence reagent solution was 8 mM H₂O₂ and 0.64 mM bis (2,4,6-trichlorophenyl)oxalate in acetonitrile.

2.4 Analysis of EC

EC was determined by the thermal oxidation method (Tanner *et al.*, 1982) using CHN-CORDER (MT-3, Yanako). Carbonaceous components that were oxidized over a copper oxide catalyst under helium flow below 550°C were considered as organic carbon (OC). The remainders of the carbonaceous components, oxidized above 950°C in helium flow containing 10% oxygen, were assigned as EC.

3. RESULTS AND DISCUSSION

The variation in annual concentration of SPM at sites A and B, located in urban downtown Tokyo, were provided by government pollution-monitoring stations

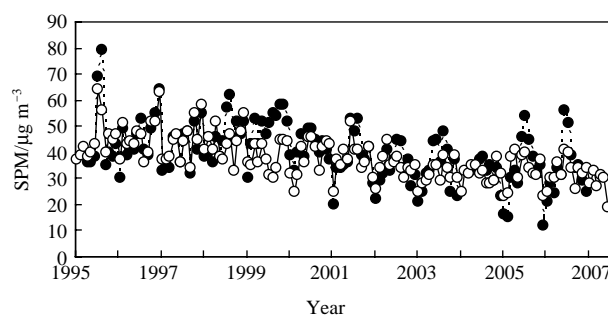


Fig. 2. Annual variation in concentration of SPM at site A (solid circles) and B (open circles).

located close to each site, at Shirokane Station in Minato Ward (site A) and Honcho Station in Shinjuku Ward (site B). The SPM concentrations at the two sites were almost the same, and slightly decreased over the ten-year period studied (Fig. 2). The annual means of SPM concentration in 1997 and 2006 at site B were $44 \mu\text{g m}^{-3}$ and $33 \mu\text{g m}^{-3}$, respectively. This decrease suggests an improvement in the purification techniques for exhaust from combustion processes, such as in vehicles or power plants. Fig. 3 compares the annual mean concentrations of CO, NO_x ($\text{NO} + \text{NO}_2$), Oxidant (O_x), SPM, EC, PAHs, and nitro-PAHs from 1997-

1998 (site A) to 2006-2007 (site B). O_x concentrations were based on the ultraviolet absorption method (APOA-370, Horiba). The SPM and gaseous concentrations were obtained by recalculating the data provided from the Honcho environmental monitoring station in Shinjuku Ward (site B). The P value is the statistical difference level calculated by a two-sided t-test. The SPM concentration slightly decreased from $34 \mu\text{g m}^{-3}$ in 1997-1998 to $29 \mu\text{g m}^{-3}$ in 2006-2007, in parallel with the results shown in Fig. 2. Similarly, the mean concentrations of NO_x and O_x also slightly decreased. In contrast to our results, the annual mean

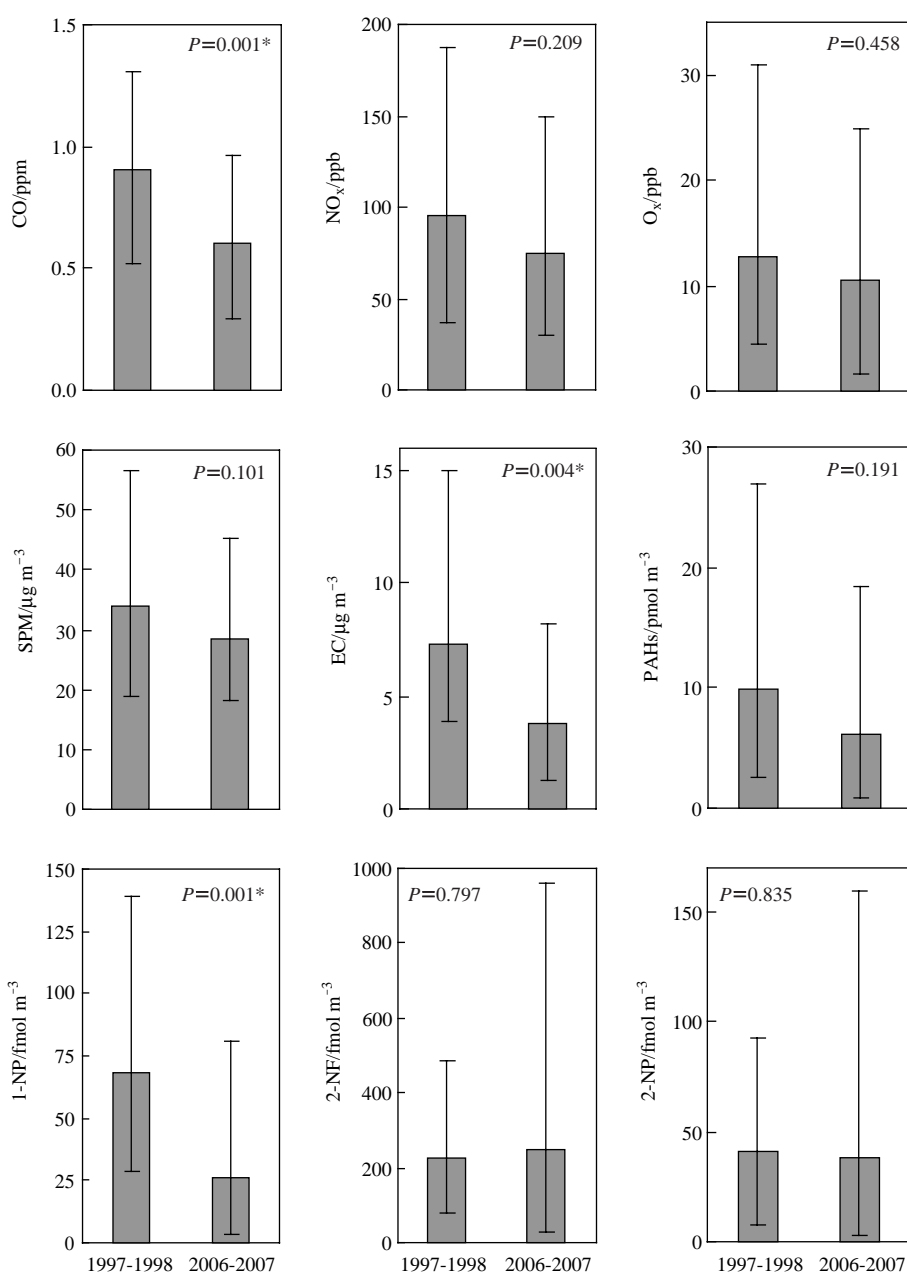


Fig. 3. Comparison of annual mean concentrations of CO, NO_x , O_3 , SPM, EC, selected PAHs, and nitro-PAHs in 1997-1998 (site A) and in 2006-2007 (site B), and the statistical difference level (P , two-sided t-test). The PAH concentration is the sum of the concentrations of FL, PY, BkF, BaP, BghiP, IP, and PER. The column and error bar represent the annual mean concentration and the concentration range, respectively. Asterisks indicate a significant difference between the two sites ($P < 0.05$).

concentration of O_x in Japan, including downtown Tokyo, has recently been reported to be constant or slightly increased in contrast to SPM and other gaseous pollutants such as CO and NO_x , which are the major primary emissions from combustion (Tokyo Metropolitan Government, 2006; Ohara and Sakata, 2003). However, in our study the decrease was not statistically significant ($P < 0.05$) and the P value was much higher than those for primary emissions such as CO, PAHs and 1-NP, this could be due to the O_x concentration covering a wide range of values in this study and could explain the discrepancy with the previous research.

Our results also showed that the annual mean concentrations of EC, primary PAHs and nitro-PAHs associated with airborne PM were much lower in 2006-2007 than in 1997-1998. The decrease in the atmospheric concentration of 1-nitropyrene (1-NP) and EC was particularly remarkable and statistically significant ($P < 0.01$). A comparison of the annual-mean concen-

tration ratios of SPM, PAHs, EC, and 1-NP in 2006-2007 to that in 1997-1998 showed they were in order $SPM > PAHs > EC > 1-NP$ (Table 1). The slight decrease of the mean SPM concentration compared with EC, PAHs, and 1-NP could be due to the variety of emission sources for airborne PM over and above primary combustion. Secondary aerosol formation from the oxidation of volatile organic compounds (VOCs) would also contribute significantly to changes in airborne PM concentration (Carreras-Sospedra *et al.*, 2005; Eatough *et al.*, 2003). The decrease in 1-NP concentration was the most significant, a possible explanation for this is the simultaneous reduction of both PM and NO_x from diesel engines, where the higher-temperature combustion required for nitro-PAH formation from PAHs and NO_x takes place (Tang *et al.*, 2005). Over the time period of this study there were no large climate events, such as precipitation or wind. Even if the climate events influenced the atmospheric concentration of SPM, they did not influence the composition of primary emissions associated with airborne PM. Thus it was concluded that the regulation for DEP, which came into effect in Tokyo in 2003, led to a significant decrease of these compounds.

In contrast to the decrease observed in direct emissions such as PAHs and 1-NP, the concentrations of nitro-PAHs, which are likely formed by atmospheric reaction of PAHs with NO_2 (e.g. 2-NF), remained the same or even slightly increased (Fig. 3). The concentration ratios for these secondary formed nitro-PAHs to 1-NP or BkF (nitro-PAH/1-NP or nitro-PAH/BkF ratio) also significantly increased ($P < 0.05$) compared with those in 1997-1998, with the exception of 2-NP/BkF (Fig. 4). This indicated that atmospheric nitro-PAH formation was influenced by not only the concentration of the parent PAHs and NO_2 but also other factors such as concentration of OH radicals, NO_3 radicals, and

Table 1. The annual mean atmospheric concentration and the ratios of SPM, PAHs, EC and 1-NP from 2006-2007 compared with those from 1997-1998.

Pollutant	Mean concentration		Ratio ^a
	1997-1998	2006-2007	
SPM [$\mu\text{g}/\text{m}^3$]	34	29	0.84
EC [$\mu\text{g}/\text{m}^3$]	7.3	3.8	0.51
PAHs ^b [pmol/ m^3]	9.9	6.2	0.62
BkF ^c [pmol/ m^3]	0.90	0.51	0.57
1-NP ^d [fmol/ m^3]	68	26	0.38

^aThe annual-mean concentration ratio from 2006-2007 compared with that from 1997-1998.

^bThe sum of fluoranthene, pyrene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, indeno[1,2,3-cd]pyrene, and perylene.

^cBenzo[k]fluoranthene.

^d1-Nitropyrene.

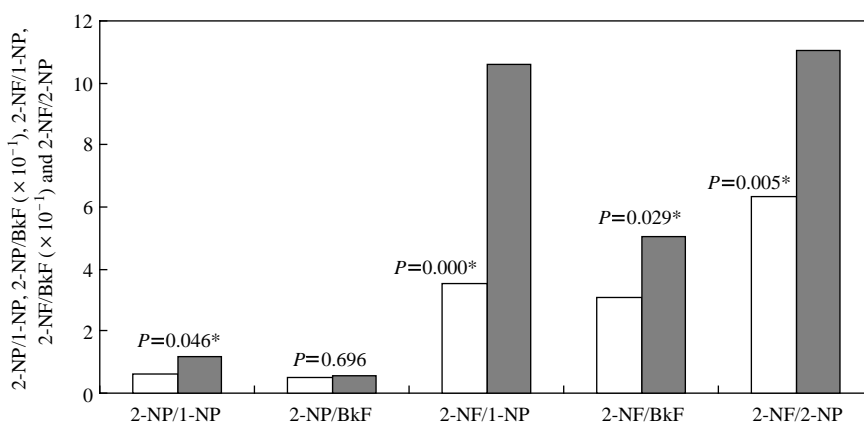


Fig. 4. The concentration ratios of PACs observed in 1997-1998 (site A, white bar) and in 2006-2007 (site B, gray bar), and the statistical difference level (P , two-sided t-test). Asterisks indicate a significant difference between the two sites ($P < 0.05$).

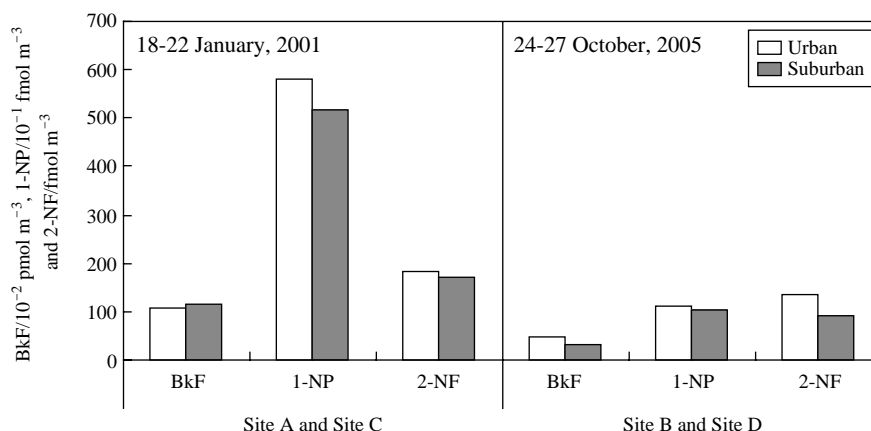


Fig. 5. The average concentrations of BkF, 1-NP, and 2-NF in urban and suburban area observed in 18-22 January 2001 (sites A and C) and in 24-27 October 2005 (sites B and D).

Table 2. The concentration ratios of 2-NF to 1-NP and BkF at four sampling sites in January and October.

	January				October	
	1998 (n=5)	2001 (n=5)	2001 (n=5)	2007 (n=6)	2005 (n=4)	2005 (n=4)
	Site A (Urban)	Site A (Urban)	Site C (Suburban)	Site B (Urban)	Site B (Urban)	Site D (Suburban)
2-NF/1-NP	3.0	3.0	3.2	9.9	12	10
2-NF/BkF	0.16	0.16	0.18	0.45	0.27	0.34

other oxidants. Our results are consistent with a previous report that investigated diurnal changes of nitro-PAHs (Kameda *et al.*, 2004a).

In addition, the mean 2-NF/2-NP ratio significantly increased ($P < 0.01$) (Fig. 4). 2-NF is known to be formed via both OH and NO_3 radical initiated reactions of the parent PAH, FL (Arey *et al.*, 1986). In comparison, 2-NP is formed only via OH radical-initiated reaction of PY (Zielinska *et al.*, 1986). The relative importance of these two pathways for nitro-PAH formation can be determined from the 2-NF/2-NP ratio; several reports have utilized this index to discuss the occurrence of radical initiated-formation (Kameda *et al.*, 2004a; Bamford and Baker, 2003; Feilberg *et al.*, 2001). The increase in the 2-NF/2-NP ratio between 1997-1998 and 2006-2007 indicates that the NO_3 radical-initiated nitration of PAHs has become more important. However, it has been reported that a 2-NF/2-NP ratio of 5-10 shows the OH-initiated reaction dominates when gas-phase concentrations of FL and PY are comparable, whereas the ratio will be more than 100 when the NO_3 -initiated reaction dominates (Bamford and Baker, 2003; Feilberg *et al.*, 2001). In this study, the mean 2-NF/2-NP ratios in 1997-1998 and in 2006-2007 were 6.3 and 11.4, respectively. Thus, although the relative importance of the NO_3

radical-initiated nitration of PAHs has increased, the OH radical-initiated reaction is still the major pathway for atmospheric formation of these nitro-PAHs.

As mentioned above, the Tokyo metropolitan government regulation on PM in diesel vehicle emissions resulted in changes, not only in the atmospheric concentration, but also in the composition of mutagenic PACs (indicated by 2-NF/BkF and 2-NF/1-NP ratios) associated with airborne PM in downtown Tokyo. Emission controls were also applied in neighboring prefectures such as Saitama, Chiba, and Kanagawa. Thus, the influence of the regulation was also examined at sites C and D (Fig. 1), which were located in suburban areas with lower population density than downtown Tokyo. The concentration levels of primary emissions from vehicles have been reported to be lower in suburban areas than in urban areas (Kameda *et al.*, 2004b; Bamford and Baker, 2003; Hayakawa *et al.*, 2002). However, no significant difference ($P < 0.05$) in the mean concentrations of PACs was observed between the urban and suburban sites in either January 2001 (sites A and C) or October 2005 (sites B and D) (Fig. 4). Table 2 shows the mean 2-NF/BkF and 2-NF/1-NP ratios at four sampling sites in January and October. Even though the climate conditions in October are somewhat different to those in January, the mean

2-NF/1-NP and 2-NF/BkF ratios tended to increase after the implementation of control in 2003. These results indicate that emission control affected the chemical composition of airborne PM not only in urban Tokyo but also in the surrounding area.

4. CONCLUSIONS

This study revealed the effectiveness of the recently issued regulation on vehicle emissions as follows: 1. The government emission control, which began for vehicles in Tokyo in 2003, has worked effectively to remarkably decrease the atmospheric concentrations of primary emissions, especially those from diesel-vehicles, such as 1-NP and EC; 2. The annual mean concentration of secondary-formed nitro-PAHs, 2-NF and 2-NP, has remained the same level suggesting other factor(s) than the concentration of parent PAHs and NO₂ affect the degree of atmospheric formation of nitro-PAHs; 3. The 2-NF/2-NP ratio has clearly increased, indicating that the degree of atmospheric formation of nitro-PAHs by the NO₃ radical-initiated reaction is elevated.

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