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Technical Information

Atmospheric Occurrence of Particle-associated Nitrotriphenylenes via Gas-phase Radical-initiated Reactions Observed in South Osaka, Japan

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ABSTRACT Nitrotriphenylenes (NTPs), which include the highly mutagenic isomer 2-nitrotriphenylene (2-NTP), have been detected in airborne particles. From a public hygienic point of view, it is necessary to study the environmental occurrence of NTPs in detail. In this study, concentrations of five nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) including NTPs in airborne particles and of nitrogen oxides (NO_x ; $\text{NO}+\text{NO}_2$) and carbon monoxide (CO), at a location in South Osaka, Japan, were measured at 3 h intervals. It was found that the diurnal variations in the concentrations of 1-nitropyrene (1-NP), NO_x , and CO were similar, being high early in the morning and late in the evening. This finding indicates that the occurrence of 1-NP is affected significantly by primary emissions, particularly by automotive emissions. The concentration change in 1-nitrotriphenylene was similar to that of 2-nitropyrene produced by an atmospheric OH radical-initiated reaction. On the contrary, the variations in the concentrations of 2-nitrofluoranthene (2-NF) and 2-NTP were significantly different from those of the other nitro-PAHs, i.e., their concentrations increased during the nighttime, suggesting that neither 2-NF nor 2-NTP was emitted from the primary sources, but were formed via the NO_3 radical-initiated nitration of the parent fluoranthene and triphenylene (TP) in the atmosphere. Based on the ambient concentration of 2-NTP and the reported rate constant for the reaction of TP with NO_3 radicals, the yield of 2-NTP from the gas-phase NO_3 radical-initiated reaction of TP was estimated to be 23%.

KEY WORDS PAH, Nitroarene, Triphenylene, Secondary formation, Airborne particles

1. INTRODUCTION

Most nitrated polycyclic aromatic hydrocarbons (nitro-PAHs), a class of polycyclic aromatic compounds (PACs), exhibit direct-acting mutagenicity or carcinogenicity (Durant *et al.*, 1996). Some of them have been detected in particulate matters in the ambient air (Bamford and Baker, 2003) or combustion exhaust (Schuetzle *et al.*, 1982). For example, 1-nitropyrene (1-NP) has been detected in both diesel exhaust particles (Schuetzle, 1983) and airborne particles (Feilberg *et al.*, 2001). Although 1-NP can be formed from gas-particle phase heterogeneous reactions on a specific substrate such as mineral dust aerosols (Kameda *et al.*, 2016) or under the high NO_2 condition (Nguyen *et al.*, 2009; Miet *et al.*, 2004;

Finlayson-Pitts and Pitts, 2000), atmospheric 1-NP is believed to originate predominantly from combustion processes (Bamford and Baker, 2003; Feilberg *et al.*, 2001). In contrast, several types of nitro-PAHs are formed via gas-phase reactions of semi-volatile PAHs. For example, 2-nitropyrene (2-NP) and 2-nitrofluoranthene (2-NF) are formed by the gas-phase OH radical-initiated reactions of pyrene (PYR) and fluoranthene (FLRA) in the presence of NO₂ (Wilson *et al.*, 2020; Atkinson and Arey, 1994; Atkinson *et al.*, 1990; Arey *et al.*, 1986). The reaction proceeds by the initial addition of the OH radicals to PYR or FLRA, followed by the addition of NO₂ and loss of H₂O. A similar mechanism for the gas-phase NO₃ radical reaction with FLRA produces 2-NF upon the loss of HNO₃ (Atkinson and Arey, 1994; Atkinson *et al.*, 1990; Arey *et al.*, 1986). Triphenylene (TP), which is less volatile than FLRA (Finlayson-Pitts and Pitts, 2000), also reacts with OH and/or NO₃ radicals in the gas-phase, resulting in nitrotriphenylenes (NTPs) (Zimmermann *et al.*, 2012; Kameda *et al.*, 2006), which include the strong mutagenic isomer 2-nitrotriphenylene (2-NTP) (Ishii *et al.*, 2001, 2000). The rate constants for the gas-phase reactions of TP with OH or NO₃ radicals have been determined by a relative-rate technique in a CCl₄ liquid-phase system (Kameda *et al.*, 2013). Because strongly mutagenic 2-NTP has been found in the air at concentrations comparable to those of 1-NP and 2-NF, which are the most abundant airborne nitro-PAHs (Zimmermann *et al.*, 2012; Kameda *et al.*, 2006; Kawanaka *et al.*, 2005; Kameda *et al.*, 2004; Ishii *et al.*, 2001; Ishii *et al.*, 2000), its contribution to the mutagenicity of airborne particles is expected to be significant. However, it is difficult to understand the factors influencing the formation and behaviour of atmospheric NTPs, because they are produced from not only the gas-phase radical-initiated reactions but also gas-solid-phase heterogeneous reactions of TP with NO₂/NO₃/N₂O₅ (Yang *et al.*, 2013; Ishii *et al.*, 2000) and combustion of organic matters such as fossil fuels (Zimmermann *et al.*, 2012; Kameda *et al.*, 2006). From a public hygienic point of view, the acquisition of more detailed data about the environmental occurrence of NTPs is of great importance.

In the present study, we sampled airborne particles at a point in South Osaka, Japan at 3-hr intervals, and determined the particle-associated NTPs, other typical nitro-PAHs, and gaseous atmospheric pollutants simul-

taneously in order to understand the factors controlling the occurrence and concentrations of atmospheric NTPs.

2. MATERIALS AND METHODS

2.1 Sampling of Airborne Particles

Airborne particulates were collected on quartz fiber filters (Advantec MFS, QR100) using high-volume air samplers (Kimoto Electrics, Model 120) on the rooftop of a three-story building (approximately 10 m above the ground level) at Osaka Prefecture University in Sakai, Osaka, Japan (34°55'N, 135°51'E). The sampling site was located in a slightly polluted residential area in South Osaka, which can be regarded as a typical suburban area in Japan. Vehicular traffic on moderately busy roads, Route 310 and Hanwa-Highway, 200 m and 2 km away from the sampling site, respectively, was the only substantial source of air pollutants; no other significant potential stationary source of air pollution was present near the site. Air samples were collected at intervals of 3 h over two 27-hr periods: (I) September 4 and 5, 2001 and (II) November 28 and 29, 2001. The average air collection rate of the air samplers was 1.5 m³ min⁻¹ and no cut-off stage was employed. The filter samples were stored at 253 K until they were subjected to the analysis.

2.2 Chemical Analysis of Nitro-PAHs

The filter samples were cut into fine pieces, and all the fine pieces were put into 200 mL of benzene/ethanol (3/1, v/v). Soluble organic fractions (SOF) was extracted by sonication for 15 min twice, then the extract solution was filtered to remove solid substances with cellulose acetate filter (Advantec MFS, No.2). The filtrate was washed with 100 mL of 5% sodium hydroxide, 100 mL of 20% (v/v) sulfuric acid and 100 mL of water. After evaporating the organic layer to ca. 5 mL and filtered with a 0.22 μm membrane filter, the solvent was gently removed with a nitrogen stream. A 0.5 mL sample solution was obtained by adding methanol to the residue. An aliquot of the sample solution was injected into the HPLC system. The HPLC system with column-switching and chemiluminescence detection was employed for nitro-PAHs quantification as reported previously (Kameda *et al.*, 2006; Kameda *et al.*, 2004). Although nitro-PAHs are not fluorescent,

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they are metal-catalytically reduced to strongly fluorescent amino-PAHs in the HPLC system, enabling a sensitive and selective detection of nitro-PAHs by the chemiluminescence detector. For the calibration curves of the standard nitro-PAHs, the chemiluminescence intensities were proportional to the concentrations of the compounds up to 2000 fmol per injection, and the calibration curves showed good linearity ($r > 0.999$). The quantification limits of the HPLC system employed for 1-NP, 2-NP, 2-NF, 1-nitrotriphenylene (1-NTP), and 2-NTP were 2, 20, 10, 75, and 60 fmol, respectively ($S/N = 3$). Chemical structures of the target nitro-PAHs in this study are summarized in Table 1 with the information of their atmospheric sources.

2.3 Gas Analysis

During the sampling period, typical gaseous pollutants, namely, NO_x (NO and NO_2), and CO were monitored with a chemiluminescence NO_x analyzer (Thermo Electron, MODEL 42s) and an NDIR CO analyzer (Thermo Electron, MODEL 48), respectively.

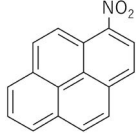
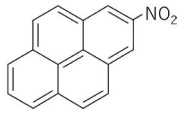
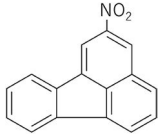
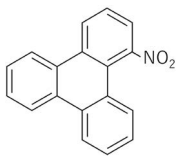
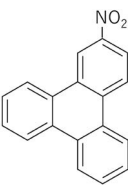
2.4 Chemicals

1-NP was obtained from Sigma-Aldrich Co; 1-NTP and 2-NTP were obtained from Hayashi Pure Chemical Ind. Ltd. and ChemBridge Co., respectively; and 2-NF and 2-NP were purchased from Chiron AS. All the solvents and other chemicals used were HPLC or analytical grades from Wako Pure Chemical Ind., Ltd.

3. RESULTS AND DISCUSSION

Table 2 shows the concentrations of selected inorganic gases and nitro-PAHs in 3-hr averaged samples of the airborne particles obtained in this study. The diurnal change of 1-NP in airborne particles collected between November 28 and 29 (abbreviated as Nov 28–29) is shown in Fig. 1a with the concentrations of NO_x ($=\text{NO}+\text{NO}_2$) and CO , which were measured during the same period of time. The concentrations of NO_x and CO were in the ranges from 13 to 53 ppbv and from 0.6 to 1.3 ppmv, respectively. These concentrations can be regarded as normal for residential areas with slight pollution in Japan (Morikawa *et al.*, 1997) and the observed concentrations of 1-NP associated with airborne particles (29–96 fmol m^{-3}) were comparable to values reported by other researchers in Japan

Table 1. Structures of nitro-PAHs observed in this study and their atmospheric sources.

Nitro-PAHs	Atmospheric Sources
 1-nitropyrene (1-NP)	Primary emission from combustion sources Gas-solid-phase heterogeneous reaction (minor contribution)
 2-nitropyrene (2-NP)	Gas-phase OH radical-initiated reaction
 2-nitrofluoranthene (2-NF)	Gas-phase OH radical-initiated reaction Gas-phase NO_3 radical-initiated reaction
 1-nitrotriphenylene (1-NTP)	Primary emission from combustion sources Gas-solid-phase heterogeneous reaction Gas-phase OH radical-initiated reaction
 2-nitrotriphenylene (2-NTP)	Primary emission from combustion sources Gas-solid-phase heterogeneous reaction Gas-phase OH radical-initiated reaction Gas-phase NO_3 radical-initiated reaction

(Kamiya *et al.*, 2017; Kojima *et al.*, 2010a; Ishii *et al.*, 2001), Hong Kong (Ma *et al.*, 2016), New Zealand (Kalisa *et al.*, 2019), and Czech Republic (Nežiková *et al.*, 2020). The diurnal variations in concentrations of particle-associated 2-NF, 2-NP, 1-NTP, and 2-NTP on Nov 28–29 are shown in Fig. 1b. The concentration of 2-NF ranged from 33 fmol m^{-3} for the sample collected between 12:00 and 15:00 (abbreviated as 12:00) to 412 fmol m^{-3} for the sample collected at 0:00. The concentration of the 2-NF obtained in this study is substantially the same as the previously reported levels in Japan (Kamiya *et al.*, 2017; Kojima *et al.*, 2010a; Kojima *et al.*, 2010b), France (Albinet *et al.*, 2007), and Italy (Di Filippo *et al.*, 2010). The concentration of 2-NTP

Table 2. Concentrations of selected inorganic gases and nitro-PAHs in 3-hr averaged samples of the airborne particles collected in Osaka, Japan on September 4–5, 2001 and November 28–29, 2001.

Date	Time ^a (JST)	Nitro-PAHs ^b					Inorganic gases	
		1-NP	2-NP	2-NF	1-NTP	2-NTP	CO ^c	NO _x ^d
September 4–5, 2001	12:00	17	4	26	N.A.	9	0.3	37
	15:00	22	18	11	N.A.	13	0.3	54
	18:00	43	35	108	N.A.	16	0.6	47
	21:00	34	52	187	N.A.	16	0.7	44
	0:00	33	27	369	N.A.	31	0.6	48
	3:00	28	17	293	N.A.	31	0.5	44
	6:00	54	N.A.	553	N.A.	36	0.7	66
	9:00	17	3	176	N.A.	22	0.4	32
	12:00	40	1	63	N.A.	17	0.3	28
Mean	32	20	199	N.A.	21	0.5	45	
November 28–29, 2001	12:00	87	N.A.	33	N.A.	10	0.6	13
	15:00	29	21	64	22	16	0.7	22
	18:00	82	86	168	72	23	1.1	46
	21:00	96	61	272	32	31	1.3	53
	0:00	41	49	412	12	43	1.0	35
	3:00	37	34	313	8	26	0.8	20
	6:00	59	76	239	12	27	1.1	35
	9:00	47	26	81	8	20	0.8	17
	12:00	43	52	201	33	20	0.9	43
Mean	58	51	198	25	24	0.9	32	

Abbreviations of compounds: see text and Table 1.

NA: not available

^aStart of sample collection

^bGiven in unit of fmol m⁻³

^cGiven in unit of ppmv

^dGiven in unit of ppbv

was also the lowest (10 fmol m⁻³) at 12:00 and reached the maximum (43 fmol m⁻³) at 0:00. On the contrary, the highest concentrations of 1-NTP and 2-NP were observed at 18:00. The concentrations of 1-NTP and 2-NP were in the ranges from 8 to 72 fmol m⁻³ and from 21 to 86 fmol m⁻³, respectively. The observed concentration of 2-NP in airborne particles was slightly higher than that measured previously in Japan (Kamiya *et al.*, 2017; Murahashi *et al.*, 1999), France (Ringuet *et al.*, 2012), and Italy (Di Filippo *et al.*, 2010). While the concentrations of 1-NTP and 2-NTP obtained in this study were lower than previously reported levels in Tokyo, Japan (Ishii *et al.*, 2001; Ishii *et al.*, 2000), these values were slightly higher than those reported in Riverside, CA and Mexico City, Mexico (Zimmermann *et al.*, 2012). The diurnal variations in the concentrations

of NO_x, CO, and 1-NP, which are primarily emitted from the combustion processes, were similar, i.e., their concentrations increased early in the morning and late in the evening. However, the concentrations of 2-NF and 2-NTP were low during the daytime and high at night. The opposite diurnal variability of 2-NF and 2-NTP compared with the diurnal variability of the primary emitted chemicals clearly indicates that 2-NF and 2-NTP did not originate from the primary combustion sources, but were formed by the atmospheric nitration of the parent FLRA and TP, respectively. 2-NF was found to be produced from the gas-phase reactions initiated by NO₃ or OH radicals in the presence of NO_x (Atkinson and Arey, 1994; Atkinson *et al.*, 1990; Arey *et al.*, 1986). At night, the atmospheric concentration of OH radicals, which are produced from photochemi-

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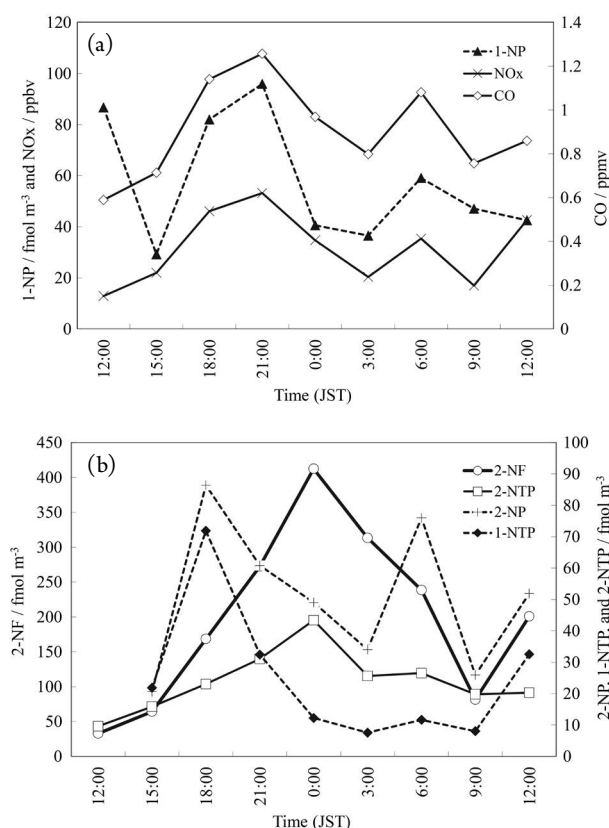


Fig. 1. Diurnal variations in the concentrations of 1-NP (solid triangle), NO_x (cross), and CO (open diamond) (a), and 1-NTP (solid diamond), 2-NTP (open square), 2-NF (open circle), and 2-NP (plus) (b) in south Osaka, Japan on November 28–29, 2001.

cal processes, is reduced almost to zero. On the contrary, NO₃ radicals generally increase after sunset, and play a significant role in the atmospheric nighttime reactions. The nighttime increase in the 2-NF concentration observed in this study suggests the significance of the gas-phase NO₃ radical-initiated nitration of FLRA. The increase in 2-NF during the nighttime could also be partly attributed to the transportation of the air mass containing 2-NF secondarily produced from the OH radical-initiated reaction of FLRA during the daytime. However, the concentration of 2-NP, which is probably not formed by an NO₃ radical-initiated reaction but by an OH radical-initiated reaction (Atkinson and Arey, 1994) in the gas-phase, did not increase during the nighttime. This supports the idea that a significant part of 2-NF was produced by the reaction of FLRA with NO₃ radicals in the gas phase, at least over the duration of the sampling in this study. 2-NTP was previously reported to be formed by a gas-

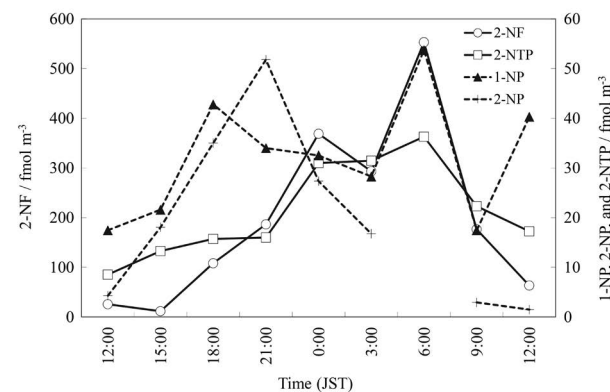


Fig. 2. Diurnal variations in the concentrations of 1-NP (solid triangle), 2-NP (plus), 2-NTP (open square), and 2-NF (open circle) in south Osaka, Japan on September 4–5, 2001.

solid phase heterogeneous reaction (Yang *et al.*, 2013; Ishii *et al.*, 2000) or a gas-phase homogeneous reaction (Kameda *et al.*, 2006) of the parent TP. Although both reactions, namely, the reaction of the TP deposited on a solid-surface with NO₃/NO₂/N₂O₅ and that of the gas-phase TP with OH radicals in the presence of NO₂, yield 2-NTP, these processes can also yield abundant amounts of 1-NTP (Yang *et al.*, 2013; Zimmermann *et al.*, 2012; Kameda *et al.*, 2006; Ishii *et al.*, 2000). However, the gas-phase reaction of TP with NO₃/NO₂/N₂O₅ produces almost only 2-NTP (Kameda *et al.*, 2006). Therefore, the observed diurnal variation in 2-NTP in this study, which was similar to that of 2-NF and different from that of 1-NTP, strongly suggests that a significant part of 2-NTP in airborne particles collected during the sampling period was formed from the gas-phase NO₃ radical-initiated reaction of TP in the atmosphere. We have previously demonstrated that the correlation between the atmospheric concentrations of 2-NTP and 2-NF ($r = 0.70$, significance level $p < 0.001$) was significantly better than the correlation between 2-NTP and 2-NP ($r = 0.38$, $p < 0.001$) (Kameda *et al.*, 2005). These correlation coefficients were based on more than 90 data sets. This result also supports the view that NO₃ chemistry can yield atmospheric 2-NTP.

Changes in the concentrations of 1-NTP were accompanied by similar changes in the concentration of 2-NP (Fig. 1b). When the concentration of 2-NP increased, the increase was probably because of only the OH chemistry. Therefore, atmospheric 1-NTP was assumed to be formed mainly by an OH radical-initiated reaction; however, some part of it may have come from direct emis-

sions from combustion processes.

The diurnal changes in the nitro-PAH concentrations in airborne particles collected on September 4–5 (abbreviated as Sept 4–5) (Fig. 2) and Nov 28–29 (Fig. 1) were similar, i.e., the concentrations of 1-NP and 2-NP were low in both daytime and nighttime, whereas those of 2-NF and 2-NTP were elevated in the nighttime. The 1-NTP concentration could not be determined during for the Sept 4–5 period owing to the lack of the sample amount.

When all the data obtained on Sept 4–5 and Nov 28–29 were combined, the 2-NF concentration increased linearly with an increase in the 2-NTP concentration ($r = 0.91$, $p < 0.001$), although the x -intercept value was significant (Fig. 3a). When the daytime (6:00–15:00) and nighttime (18:00–3:00) data were plotted separately, the x -intercept was significant in the daytime (Fig. 3b), but almost zero in night (Fig. 3c). This result implies that the potential sources of 2-NTP, for example, direct emissions, existed during the daytime and that the nighttime formation pathways of 2-NTP and 2-NF were the same or almost similar. The mean value of the observed concentration ratio of $[2\text{-NF}]_{\text{obs}}/[2\text{-NTP}]_{\text{obs}}$ during the nighttime determined by a least-square analysis was 10.1. The rate of the atmospheric concentration change of 2-NF and 2-NTP can be given by the following equations based on their rate of formation by the NO_3 radical-initiated reaction:

$$d[2\text{-NF}]/dt = y_{2\text{NF}} k_{\text{FLRA-NO}_3} [\text{NO}_3] [\text{FLRA}] - k_{\text{loss-2NF}} [2\text{-NF}] \quad (1)$$

$$d[2\text{-NTP}]/dt = y_{2\text{NTP}} k_{\text{TP-NO}_3} [\text{NO}_3] [\text{TP}] - k_{\text{loss-2NTP}} [2\text{-NTP}] \quad (2)$$

where $y_{2\text{NF}}$ and $y_{2\text{NTP}}$ are, respectively, the yields of 2-NF and 2-NTP from the gas-phase reactions of FLRA and TP with NO_3 radicals; $k_{\text{FLRA-NO}_3}$ and $k_{\text{TP-NO}_3}$ are the rate constants of the reactions; $k_{\text{loss-2NF}}$ and $k_{\text{loss-2NTP}}$ are, respectively, the rate constants for the atmospheric loss processes of 2-NF and 2-NTP such as photolysis and oxidation; and $[\text{FLRA}]$ and $[\text{TP}]$ are the gas-phase concentrations of FLRA and TP, respectively. Under steady state conditions, both these rates are equal to zero. Therefore, the ratio of the loss rate constant $k_{\text{loss-2NTP}}/k_{\text{loss-2NF}}$ can be expressed as follows:

$$k_{\text{loss-2NTP}}/k_{\text{loss-2NF}} = y_{2\text{NTP}} k_{\text{TP-NO}_3} [\text{TP}] [2\text{-NF}]_{\text{ss}} / y_{2\text{NF}} k_{\text{FLRA-NO}_3} [\text{FLRA}] [2\text{-NTP}]_{\text{ss}} \quad (3)$$

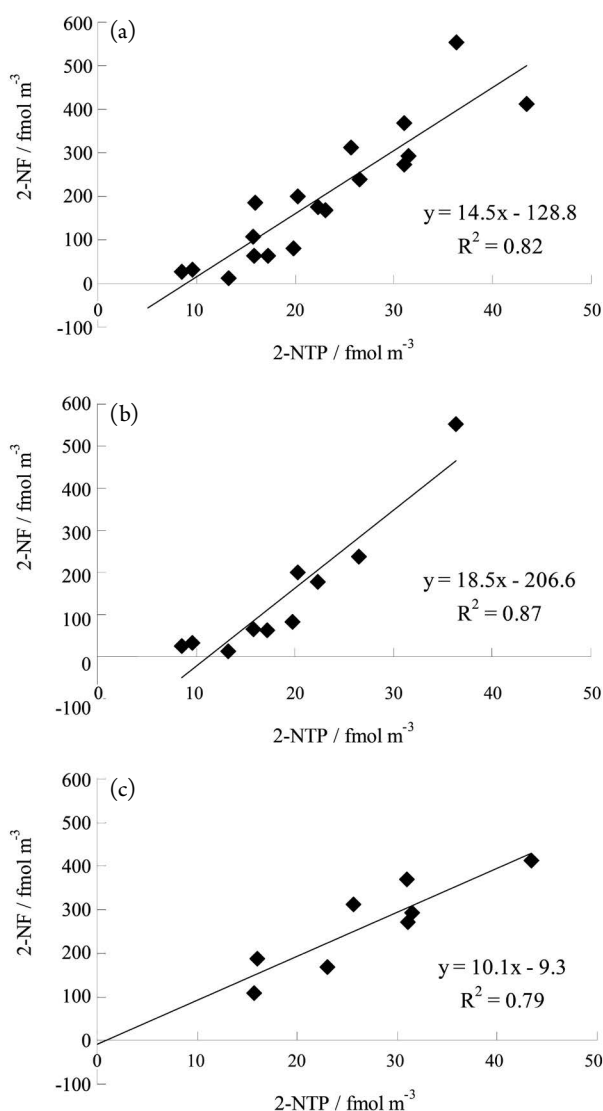


Fig. 3. Relations between atmospheric concentrations of 2-NF and 2-NTP in south Osaka, Japan measured September 4–5 and November 28–29, 2001. (a) All data; (b) daytime data (6:00–15:00) only; (c) nighttime data (18:00–3:00) only.

where $[2\text{-NF}]_{\text{ss}}$ and $[2\text{-NTP}]_{\text{ss}}$ are the steady state concentrations of 2-NF and 2-NTP, respectively. The concentrations of particle-associated FLRA and TP at the sampling site were reported to be comparable (Kameda *et al.*, 2004). Significantly less literature is currently available on the gas-particle distribution of TP. Lammel *et al.* (2010a, 2010b) reported the particle-phase mass fractions of TP (θ_{TP}) and FLRA (θ_{FLRA}) to be 0.52–0.63 and 0.07–0.12, respectively, at ambient temperatures of 289.4–309.0 K. Therefore, assuming that the particle-phase concentrations of TP and FLRA were the same,

the gas-phase concentration ratio $[TP]/[FLRA]$ was estimated to be ~ 0.08 using the mean θ_{TP} and θ_{FLRA} values. The reaction rate constant $k_{FLRA-NO_3}$ was determined to be $5.1 \times 10^{-28} [NO_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and y_{2NF} was determined to be 24% (Atkinson and Arey, 1994). Although the reaction rate constant k_{TP-NO_3} was determined to be $0.66 \times 10^{-28} [NO_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ (Kameda *et al.*, 2013), the yield of 2-NTP from the gas-phase NO_3 radical-initiated reaction has not been obtained. The relative loss rate $k_{\text{loss-2NTP}}/k_{\text{loss-2NF}}$ was estimated to be ~ 0.1 based on the ambient concentrations of TP, FLRA, 2-NTP, and 2-NF, the rate constant for the reaction of TP with OH radicals, and the rate constant for the reaction of FLRA with OH radicals assuming the steady state condition as well as Eq (3) (Kameda *et al.*, 2013). Therefore, using the reported reaction rate constants and assuming that $[2-NF]_{ss}/[2-NTP]_{ss} = 10.1$, $k_{\text{loss-2NTP}}/k_{\text{loss-2NF}} = 0.1$, and $[TP]/[FLRA] = 0.08$, Eq (3) gives the yield y_{2NTP} of 23%. The yield of 2-NTP from the reaction of TP with $NO_3/NO_2/N_2O_5$ in CCl_4 was determined to be 35% (Kameda *et al.*, 2006). The nitro-isomer profiles of the reactions of several PAHs with $NO_3/NO_2/N_2O_5$ in CCl_4 were similar to those in the gas-phase NO_3 radical-initiated reactions (Phou-songphouang and Arey, 2003; Zielinska *et al.*, 1986). In those studies, the yield was higher than 20% for several types of nitro-PAH isomers in the gas-phase NO_3 radical-initiated nitration, which is in agreement with our estimation of the yield of 2-NTP. The abundance of 2-NTP in the atmosphere, in spite of the low reactivity of the parent TP (Kameda *et al.*, 2013; Nielsen, 1984), may be attributed not only to the high stability of 2-NTP (i.e. the small $k_{\text{loss-2NTP}}$ value) but also to the high yield of 2-NTP from the gas-phase NO_3 radical-initiated reaction of TP.

4. CONCLUSIONS

In this study, diurnal concentrations of NTPs in airborne particles at a location in South Osaka, Japan were monitored at 3-hr intervals over two 27-hr periods. The concentration change in 1-NTP was very similar to that of 2-NP produced by an atmospheric OH radical-initiated reaction. On the contrary, the variations in the concentrations of 2-NF and 2-NTP were significantly different from those of other nitro-PAHs, i.e., they increased during the nighttime, suggesting

that 2-NF and 2-NTP were formed via the NO_3 radical-initiated nitration of the parent FLRA and TP in the atmosphere. Based on the ambient concentration of 2-NTP and the reported rate constant for the reaction of TP with NO_3 radicals, the yield of 2-NTP from the gas-phase NO_3 radical-initiated reaction of TP was newly determined to be 23%. This high yield may be one of the reasons for the high concentration of 2-NTP in the atmosphere. Although the observation period in this study was not recent, the results obtained in this study on the secondary formation of NTPs via the radical-initiated reactions can be considered to be general and independent of the observation year. Despite the strong mutagenicity of 2-NTP, very few studies have been performed to measure its concentration in the atmosphere. Although, in this study, we successfully estimated one of the factors that led to the high concentration of 2-NTP, further elucidation of the atmospheric behavior including the occurrence and loss processes of NTPs is desired.

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