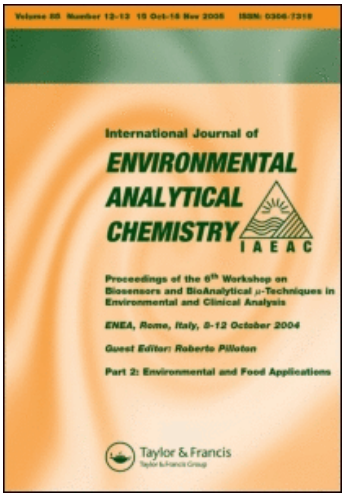

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Determination of particle-associated hydroxynitropyrenes with correction for chemical degradation on a quartz fibre filter during high volume air sampling

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A correction method for the determination of atmospheric monohydroxylated derivatives of 1-nitropyrene (hydroxy-1-nitropyrenes, OHNPs) based on their degradation rates during high volume air sampling was established. OHNPs adsorbed directly on a quartz fibre filter (QFF) or on airborne particles collected on a QFF were exposed to ambient air passively or actively in a high volume air sampling system. The influence of ozone flux and exposure time on the degree of degradation of OHNPs was investigated. Up to 50% of OHNPs degraded over 1 h of exposure to ambient air containing ~60 ppbv of ozone in the active system. The degradation rate constants of OHNPs were found to correlate with the number of ozone molecules passing through the QFF in a unit time (N_{O3}) during high volume air sampling. The chemical loss of OHNPs under high volume air sampling conditions was successfully evaluated by the exposure time and the pseudo-first-order rate constant for OHNP degradation estimated from the correlation with N_{O3}. Concentrations of 3-, 6-, and 8-hydroxy-1-nitropyrenes in airborne particles collected in Osaka, Japan were determined using the established correction method.

Keywords: polycyclic aromatic hydrocarbons; nitropyrene; airborne particles; sampling artifact; ozone; oxidation

1. Introduction

Polycyclic aromatic compounds (PACs), including polycyclic aromatic hydrocarbons (PAHs) and nitrated polycyclic aromatic hydrocarbons (NPAHs), are a class of atmospheric mutagens/carcinogens. In recent years, several kinds of PAHs and their derivatives have also been found to act as endocrine disruptors that may cause dysfunction of human and wildlife endocrine systems, abnormalities associated with developing reproductive systems and deficiencies in immune systems. 1-Nitropyrene (1-NP) is a representative NPAH formed through combustion processes of fossil fuel, such as diesel fuel combustion, and one of the most abundant NPAHs in the atmosphere [1,2]. We recently found that the hydroxylated derivatives of 1-NP (3-, 6-, and 8-hydroxy-1-nitropyrenes; 3-, 6-, and 8-OHNPs) show estrogenic, antiestrogenic and antiandrogenic activities in yeast two-hybrid assay systems [3]. 8-OHNP in particular exhibits strong

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antiestrogenic and antiandrogenic activities, e.g. 1.0×10^{-6} M of 8-OHNP inhibited 32 and 90% of β-galactosidase activity induced by 1.0×10^{-9} M of 17β-estradiol and 1.0×10^{-8} M of 5α-dihydrotestosterone in the assay systems, respectively. Gibson *et al.* [4] previously reported that OHNPs were observed in ambient airborne particles. However, the details of their sources or sinks in the atmosphere are still uncertain. In order to clarify the health impacts of OHNPs on humans, their monitoring in the atmosphere is urgently required.

Most of the OHNPs in the atmosphere are expected to be distributed in the particle phase, because the vapour pressure of OHNPs should be lower than that of the parent 1-NP due to hydrogen bonds derived from hydroxyl groups in their structures. Therefore, it is necessary to collect airborne particles for determination of atmospheric OHNPs. Many reports indicated that particle-associated PACs may degrade on glass- or quartz fibre filters (GFF and QFF) during the collection of airborne particles due to oxidation reactions with oxidants such as O_3, OH radical, NO_3 radical, etc. [5–8]. Since OHNPs have reductive phenolic hydroxyl groups in their structures, they are expected to decompose more easily than the parent PACs during high volume air sampling. The heterogeneous chemical reaction of PACs with O_3 is an especially important decomposition process of particle-associated PACs in the atmosphere [9–11]. In fact, O_3 can be regarded as a tracer for atmospheric oxidising power that drives the chemical degradation of PACs during air sampling [8]. It is commonly accepted that the substrate material on which PACs are deposited also affects the degradation of PACs by the reaction with O_3. For example, the decomposition of PACs on GFF and QFF occurs more easily than on Teflon filters [9]. On the other hand, PACs adsorbed onto airborne particles, especially soot-rich particles, are protected from chemical transformations [12,13].

In this study, we investigated the effect of O_3 flux, i.e. the number of O_3 molecules passing through QFF in a unit time (N_{O3}/molecules min^{-1}), on the loss of OHNPs under high volume air sampling. We also established a correction method for the determination of atmospheric particle-associated OHNPs. This was accomplished by the calculation of the decomposed fraction of OHNPs on airborne particles during high volume air sampling based on the degradation rate and exposure time.

2. Experimental

2.1 *Reagents and chemicals*

3-, 6- and 8-OHNPs and deuterated 3-OHNP (3-OHNP-d_8) were synthesised according to the previously reported procedure [14]. Briefly, acetoxypyrene, which was prepared from pyrene by treatment with lead tetraacetate in benzene/acetic acid (9/1, v/v), was nitrated using concentrated HNO_3 in acetic acid. The obtained mixture of three isomers of acetoxynitropyrenes was treated with CH_3ONa in methanol/THF (1/1, v/v) to obtain a mixture of OHNPs. Each OHNP isomer was purified by preparative normal phase HPLC (SUPELCO, Supelcosil PLC-SI, 21.2 mm ID $\times$ 250 mm, eluted with CH_2Cl_2 containing 0.5 mM CH_3COOH at 10 mL/min). To identify the synthetic compounds, their GC-MS and proton NMR spectra were compared with literature data [14,15]. 1-NP and deuterated 1-NP (1-NP-d_9) were obtained from Sigma-Aldrich Co. and C/D/N Isotopes, respectively. All solvents and other chemicals used were HPLC or analytical grades from Wako Pure Chemical Ind.

2.2 *Chemical analysis of OHNPs by HPLC*

The filter samples were cut into fine pieces before extraction. The soluble organic fractions (SOF) from the filter samples were extracted twice with 100 mL of ethanol under sonication for 20 min. The extract solution was filtered with a cellulose acetate filter to remove solid residue, followed by adding 100 μL of dimethyl sulphoxide (DMSO) into the filtrate to avoid complete dryness of the solvent during the concentration steps. After concentration using a rotary evaporator to ca. 5 mL and filtration with a 0.45 or 0.22 μm membrane filter, the samples were concentrated to 100 μL under a nitrogen stream to leave only DMSO, and then 400 μL of methanol was added. An aliquot of each of the sample solutions was subjected to HPLC analysis. An HPLC system with column-switching and chemiluminescence detection [16–18] was employed for OHNPs and 1-NP analysis, with several modifications to the column type and size in the previously reported system [19]. Briefly, the system consists of four HPLC pumps, a 6-port switching valve, a clean up column (GL Sciences, Inertsil ODS-P, 3.0 mm ID × 250 mm), separation columns (GL Sciences, Inertsil ODS-EP, 3.0 mm ID × 250 mm or Inertsil ODS-3, 3.0 mm ID × 250 mm × 2), a reducer column (Jasco, NPpak-RS, 4.6 mm ID × 10 mm), a trapping column (GL Sciences, Inertsil ODS-3, 4.0 mm ID × 30 mm), and a chemiluminescence detector (Soma Optics, S-3400). The chemiluminescence reagent solution was an acetonitrile solution containing 0.03 mmol L^{-1} bis(2,4,6-trichlorophenyl)oxalate and 15 mmol L^{-1} H_2O_2. Mobile phases were methanol/water (3 : 1, v/v) for the clean up and reduction of OHNPs and/or 1-NP, and acetonitrile/imidazole-perchloric acid buffer (45 : 55, v/v) for the separation. The reduction of OHNPs and 1-NP into the corresponding amino compounds, which are strongly fluorescent, was performed at 373 K in the reducer column. In order to exclude interfering compounds, specific fractions for the analytes eluted from the clean up column were introduced into the separation column: two different injections were necessary to determine all the OHNP isomers for a sample. The injection volume was 20 μL. To clarify the origin of the peaks observed in the HPLC chromatograms, the SOF sample washed with 5% NaOH/water was also analysed by the HPLC system. For the calibration curves of the standard OHNPs, the chemiluminescence intensities were proportional to the concentrations of the three compounds in the range from 10 to 2000 fmol per injection, and the calibration curves showed good linearity ($r^2 > 0.999$). Quantification limit of the HPLC system employed for each OHNP was 2 fmol (S/N = 10).

2.3 *Airborne particle collection for the exposure experiment of OHNPs*

Prior to the evaluation of the degradation of OHNPs on airborne particles during high volume air sampling, ambient particles were collected on the QFF every 3 hours at the rooftop level of a three-story building approximately 10 m above ground level at Osaka Prefecture University, Sakai, Osaka, Japan (34°55′N, 135°51′E). This sampling site is located in a polluted residential area. Traffic on moderately busy roads Route 310 and Hanwa-Highway is the only substantial source of air pollutants throughout the year and no large potential stationary source of airborne particles is located near the site. Sampling was conducted using a high volume air sampler (Kimoto Electric, Model 120) having no cut-off stage with the QFF (Advantec MFS, QR100), i.e. total suspended particulate matters (TSP) were collected, at a flow rate of 1500 L min^{-1} during 12–16 May 2003. The mass of ambient particles was determined by measuring the weight of the QFF, before and

after sample collection, after equilibrium weight was attained for each filter stored in desiccators at constant relative humidity of ca. 40% under 295 ± 3 K, resulting in 14 ± 6 mg (mean $\pm$ S.D., $n = 36$). All the QFF samples were stored at 253 K until subjected to the exposure experiments or analysis.

2.4 *Passive exposure of OHNPs to indoor air on QFF and on airborne particles*

Ten pmol of 3-, 6- and 8-OHNPs dissolved in methanol were uniformly deposited on a QFF directly by the following procedure: 2 mL of the stock solution (5 nM) was evenly dribbled onto the QFF with a microsyringe, and then the solvent was evaporated at room temperature in the dark. The air-dried QFF was passively exposed to indoor air containing trace levels of O_3 (less than 1 ppbv) for 1 and 18 hours in the dark at room temperature. In order to avoid interference of OHNPs originally contained in the airborne particulate samples with the HPLC analysis, 10 pmol of 3-OHNP-d_8 dissolved in methanol was deposited onto airborne particles collected on a QFF as described above. 3-OHNP-d_8 adsorbed on airborne particles was also exposed to indoor air for 24 hours according to the same procedure. The remaining OHNPs and 3-OHNP-d_8 were analysed by HPLC after extraction from the QFF or airborne particle samples as described above.

2.5 *Active exposure of 3-OHNP-d_8 to ambient air on airborne particles under the high volume air sampling condition*

Decomposition of 3-OHNP-d_8 on airborne particles during high volume air sampling was evaluated according to the following procedure. Ten pmol of 3-OHNP-d_8 and 1-NP-d_9, which was added in order to determine the recovery during the sample pretreatment, dissolved in methanol were uniformly deposited on airborne particles that were collected on a QFF as described above. After being installed in a high volume air sampler, the QFF was exposed to ambient air containing up to 60 ppbv of O_3 at a flow rate of 1500 L min^{-1} for 1–9 hours. The remaining 3-OHNP-d_8 and 1-NP-d_9 were analysed by HPLC after extraction from the airborne particles as mentioned above. To clarify the unexpected formation of 3-OHNP-d_8 by oxidation of 1-NP-d_9 during the high volume air sampling, the active exposure of 1-NP-d_9 in the flow system was also performed independently.

2.6 *Airborne particle collection for the determination of the atmospheric particle-associated OHNPs with the correction method*

TSP were collected every 3 hours at the same site, as is described in Section 2.3. Sampling was conducted using a high-volume air sampler with a QFF at a flow rate of 1500 L min^{-1} during 26–27 November 2001 for 24 hours. A total of 8 samples were prepared. The filter samples onto which 0.5 mL of 10 nM 3-OHNP-d_8 solution was added as an internal standard were subjected to the extraction process.

2.7 *Measurement of gases*

The concentration of O_3 in the air was monitored using a UV spectrophotometric O_3 analyser (Dylec, Model 1150) or obtained by public environment monitoring stations in Sakai, Osaka, Japan.

3. Results

3.1 *Chemical analysis of OHNPs by HPLC*

HPLC chromatograms of authentic and extracted OHNPs from airborne particles are shown in Figure 1(a) and (b), respectively. 3-, 6-, and 8-Hydroxy-1-aminopyrenes (3-, 6-, and 8-OHAPs) and 3-OHAP-d_8, which are the reduced compounds of the corresponding OHNPs, were successfully detected with good separation for each peak by a HPLC/chemiluminescence detection system. Figure 1(c) shows a chromatogram of an SOF sample analysed by the HPLC/chemiluminescence detection system without the reducer column in the system. In the case without the reduction, the OHAP peaks were completely eliminated from the chromatogram because OHNPs were not reduced into their corresponding fluorescent OHAPs in the HPLC system. After washing the SOF with 5% NaOH/water, the peaks derived from acidic OHNPs having phenolic hydroxyl groups also disappeared from the chromatogram (Figure 1(d)). These results ensure that the peaks, the retention times of which are consistent with those of the authentic OHAPs, originate from OHNPs that have nitro and phenolic hydroxyl groups in their structures.

3.2 *Passive exposure of OHNPs to indoor air on QFF and airborne particles*

Figure 2 shows the time course of the remaining fractions of OHNPs directly deposited on QFF, i.e. OHNPs on the 'naked' QFF, during passive exposure to indoor air. The mean OHNP recoveries from unexposed filters (exposure time: 0 h) were 70–85%. The mean recoveries of OHNPs after passive exposure to indoor air for 1 and 18 hours were 26–38 and 2–5%, respectively. No significant difference in the degradation was observed among the three OHNP isomers at the same exposure time. In addition, it was possible to uniquely identify 3-OHNP-d_8 from the peaks of OHNP isomers originally contained in ambient airborne samples using the HPLC system. Hereafter, therefore, we evaluated the degradation for 3-OHNP-d_8 as a representative OHNP. The loss of 3-OHNP-d_8 deposited on airborne particles, i.e. 3-OHNP-d_8 on the 'particle-loaded' QFF, was not significant even after 24 hours of exposure (mean recovery $\pm$ S.D.: $79 \pm 12\%$, $n = 4$) in the passive mode.

3.3 *Active exposure of 3-OHNP-d_8 to ambient air on airborne particles during high volume air sampling*

Figure 3 shows the recovery of 3-OHNP-d_8 from the airborne particles after active exposure to the ambient air for 1–9 hours. The mean concentrations of O_3 during the exposures were not entirely identical. The recovery of 1-NP-d_9 was stable during the exposure to ambient air under the high volume sampling condition (mean recovery $\pm$ S.D.: $93 \pm 10\%$, $n = 25$). In contrast, 3-OHNP-d_8 was easily decomposed in the active mode even on the airborne particles. The mean recovery of 3-OHNP-d_8 was less than 20% after 9 hours of exposure. Formation of 3-OHNP-d_8 by oxidation of 1-NP-d_9 on the airborne particles was not observed in the active mode.

4. Discussion

O_3 is one of the most powerful oxidants in the atmosphere. The effect of O_3 concentration on the loss of PACs under high volume air sampling conditions has been investigated

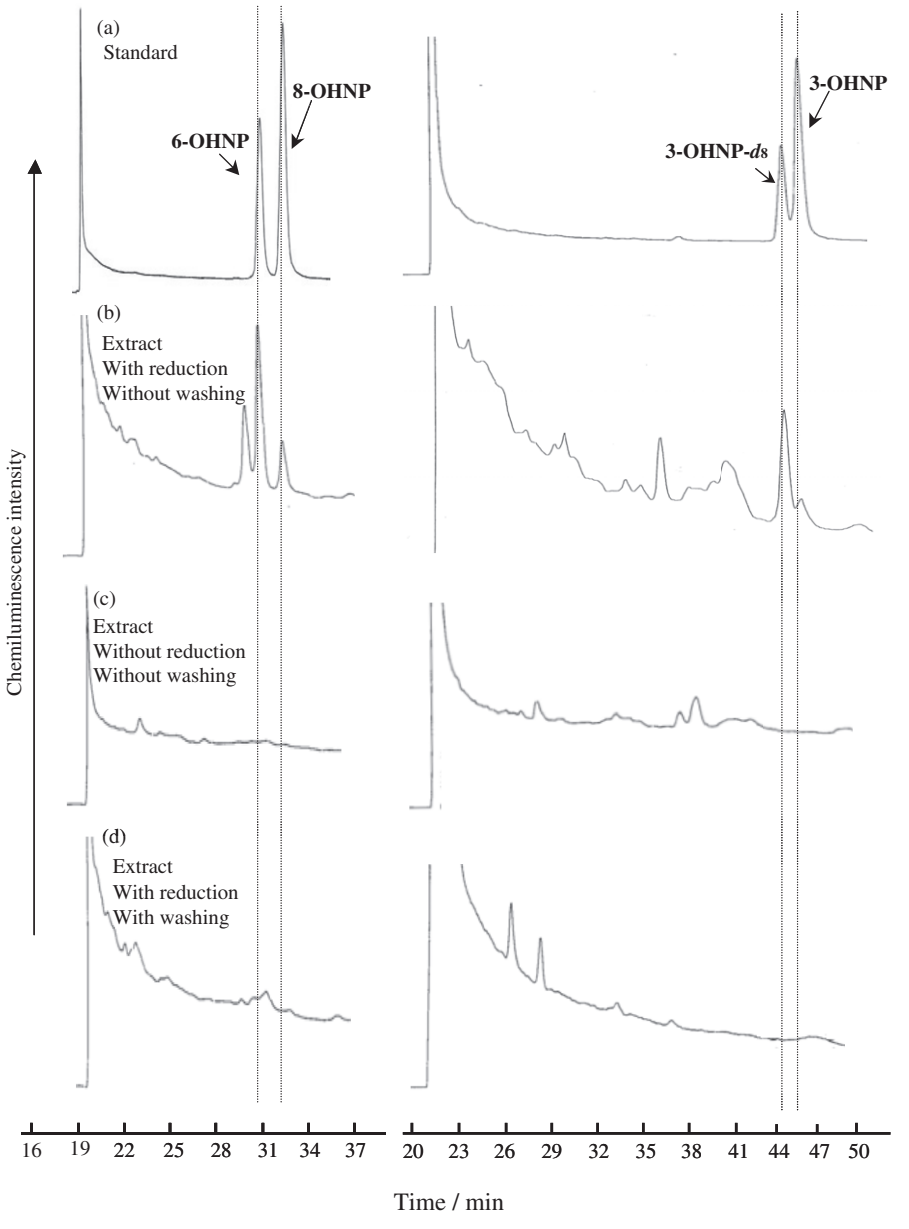

Figure 1. Typical chromatograms from the HPLC-chemiluminescence detection system for standard solution of 6-, 8-, and 3-OHNPs and 3-OHNP-d_8 (internal standard) and soluble organic fraction (SOF) of airborne particles. OHNPs were reduced into their corresponding amino compounds in the HPLC system, and then were detected by the chemiluminescence detector. (a) Authentic standard of the OHNPs, (b) SOF of airborne particles, (c) SOF of airborne particles without the reduction process, (d) SOF of airborne particles with washing process with 5% NaOH solution. In the case without the reduction or with the washing process, the peaks of the compounds were eliminated from the chromatograms (see text for details). Amounts of authentic OHNPs determined: 268 fmol (3-OHNP); 230 fmol (6-OHNP); 335 fmol (8-OHNP); 183 fmol (3-OHNP-d_8). Amounts of OHNPs from the SOF: 35 fmol (3-OHNP); 239 fmol (6-OHNP); 70 fmol (8-OHNP). Quantification limit of the HPLC system employed for each OHNP was 2 fmol (S/N = 10). Injection volume: 20 μL.

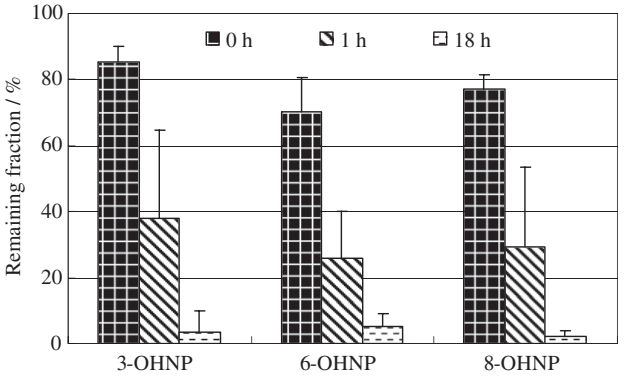

Figure 2. Decays of the remaining fractions of OHNPs directly deposited on quartz fibre filters during passive exposure to indoor air. Error bars represent one standard deviation of the average ($n = 3$, 10, and 8 for 0, 1, and 18 h exposure, respectively).

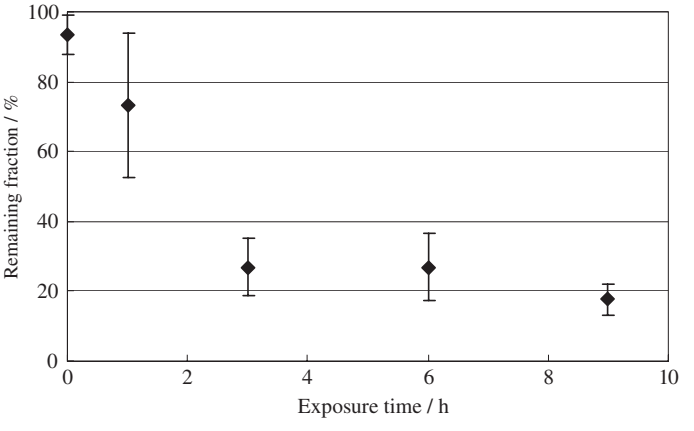

Figure 3. Decays of the remaining fractions of 3-OHNP-d_8 on airborne particles deposited on quartz fibre filters under the high volume air sampling condition at various O_3 concentrations. Data are represented as the mean ± S.D. ($n = 3$ except for 0 and 1 h exposure; $n = 4$ and 12 for 0 and 1 h exposure, respectively).

in numerous studies, and the lifetime or residual fraction of the PACs was found to be inversely correlated with O_3 concentration [8,20,21]. The decomposition of 3-OHNP-d_8 on airborne particles during high volume air sampling was also strongly expected to be attributable to oxidation reactions by O_3, although a possibility of contribution of other atmospheric oxidants such as OH and NO_3 radicals to the chemical degradation of 3-OHNP-d_8 can not be completely excluded. In this study, therefore, we evaluated the relationship between the degradation of 3-OHNP-d_8 on airborne particles and O_3 flux (N_{O3}/molecules min^{-1}). This was calculated from the mean concentration of O_3 in the ambient air and the flow rate during the air sampling.

Figure 4 shows the dependence of N_{O3} on the remaining 3-OHNP-d_8 on the airborne particles deposited on the QFF after 1 hour of active exposure. The recovery of 3-OHNP-d_8 from airborne particles clearly decayed with increasing N_{O3} ($r = 0.91$, $p < 0.01$).

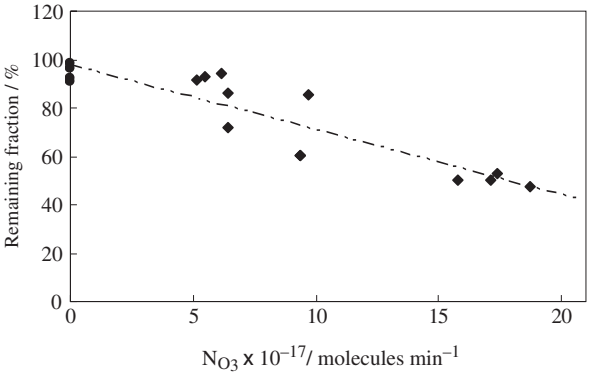

Figure 4. Remaining fraction of 3-OHNP-d_8 deposited on airborne particles after 1 h of exposure to ambient air under the high volume air sampling condition plotted against gas phase O_3 flux; number of molecules passing through the quartz fibre filter per minute (N_{O3}/molecules min^{-1}). The remaining fractions of 3-OHNP-d_8 at 0 molecules min^{-1} of N_{O3} were obtained from the 3-OHNP-d_8 recoveries from unexposed airborne particles to ambient air (circles).

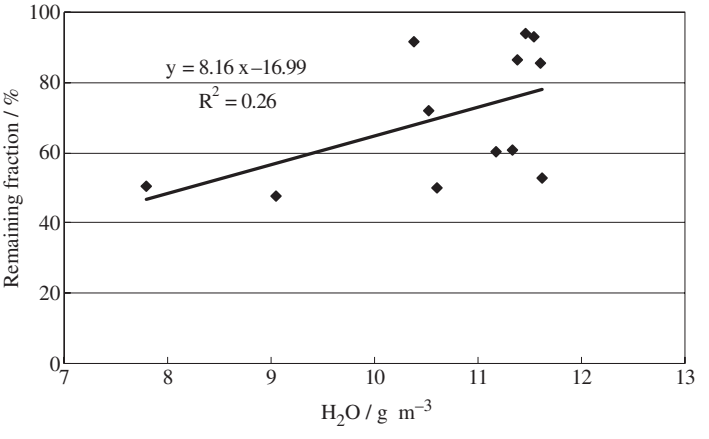

Figure 5. Plot of remaining fraction of 3-OHNP-d_8 on airborne particles deposited on quartz fibre filters after 1 h of active exposure versus water vapour concentration in ambient air.

The loss of PAHs on atmospheric soot particles with respect to the effects of humidity and ambient temperature have been evaluated previously [22]. In the present study, a clear relationship between the humidity in the ambient air and the remaining fraction of 3-OHNP-d_8 on QFF during high volume air sampling was not observed (Figure 5). Contrariwise, the recovery of 3-OHNP-d_8 increased with decreasing ambient temperature during the air sampling (Figure 6). The data points were classified into three categories according to N_{O3} as shown in Figure 6. Both the remaining 3-OHNP-d_8 fraction and the inverse of the temperature seem to be low in the high N_{O3} group, but clear temperature dependence on the remaining 3-OHNP-d_8 was not observed within each N_{O3} category. The O_3 concentration in the atmosphere was usually high in the daytime when the ambient temperature and solar intensity were also high because of active photochemical

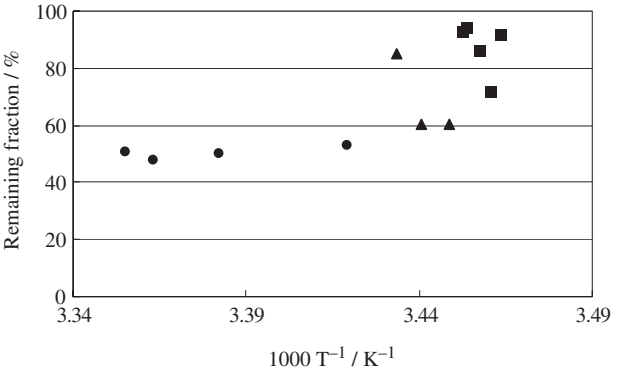

Figure 6. Plot of remaining fraction of 3-OHNP-d_8 on airborne particles deposited on quartz fibre filters after 1 h of active exposure under various O_3 flux (N_{O3}) conditions versus inverse of ambient temperature: circles, $N_{O3} = (15.8–18.7) \times 10^{17}$ molecules min^{-1}; triangles, $N_{O3} = (9.35–9.68) \times 10^{17}$ molecules min^{-1}; squares, $N_{O3} = (5.16–5.48) \times 10^{17}$ molecules min^{-1}.

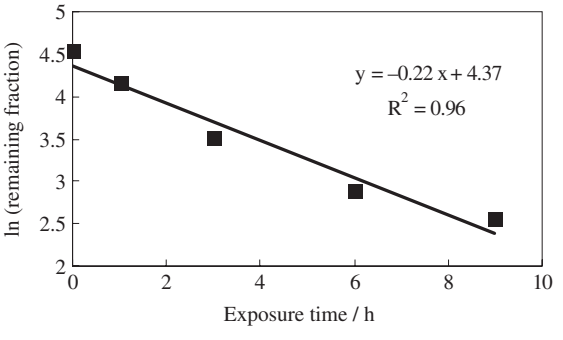

Figure 7. Logarithmic decay of 3-OHNP-d_8 exposed to ambient air under the high volume air sampling condition at 1.0×10^{18} molecules min^{-1} of O_3 flux (N_{O3}, mean $N_{O3} \pm$ S.D.: $(1.0 \pm 0.1) \times 10^{18}$ molecules min^{-1}). The time-dependence decay displays clear single exponential behaviour.

reactions contributing to O_3 formation. The result obtained implies that there is no significant relationship between the ambient temperature and the remaining 3-OHNP-d_8 during high volume air sampling. A similar result was observed in the previous report [8].

In order to understand the relationship between OHNP degradation and exposure time at the same O_3 concentration, the results obtained under the N_{O3} of 1.0×10^{18} molecules min^{-1} are shown in Figure 7. A linear relationship was observed between the logarithm of the residual fraction of 3-OHNP-d_8 and exposure time under similar N_{O3} conditions ($r^2 = 0.96$, $p < 0.01$), indicating a first-order reaction with respect to 3-OHNP-d_8 concentration. Therefore, the pseudo-first-order reaction constant for the decay of 3-OHNP-d_8 deposited on the airborne particles on QFF can be obtained for each exposure assuming a constant N_{O3}. Perraudin *et al.* [23] also reported that the plots for the reaction of PAHs adsorbed on different types of particles with O_3 exhibit an exponential decay over time under constant O_3 concentration and determined the pseudo-first-order rate

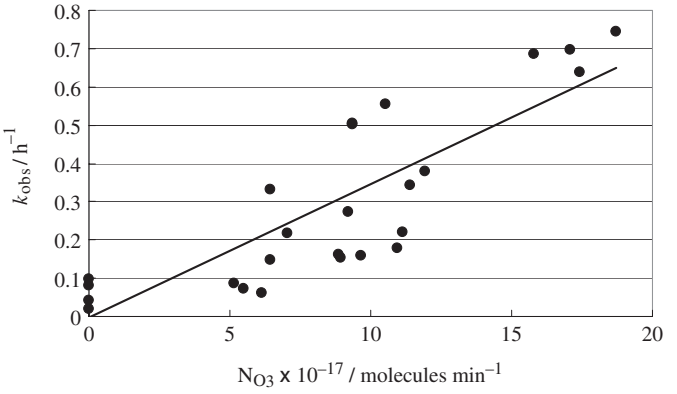

Figure 8. Observed pseudo-first-order rate constants (k_{obs}) for reactions of O_3 with 3-OHNP-d_8 adsorbed on airborne particles plotted against the number of O_3 molecules passing through the quartz fibre filter per minute (N_{O3}/molecules min^{-1}). k_{obs} is expressed as a function of N_{O3}; $k_{obs} = 0.034$ ($N_{O3} \times 10^{-17}$) -0.003. The slope of the regression line has an error of $\pm 6\%$.

constants for the decomposition reactions at several O_3 concentrations. The pseudo-first-order rate constants k_{obs} obtained from the logarithmic plot of the remaining 3-OHNP-d_8 with the exposure time in the present study were plotted versus N_{O3} in Figure 8, clearly highlighting that the k_{obs} values were proportional to N_{O3} ($k_{obs} = 0.034$ ($N_{O3} \times 10^{-17}$) – 0.003, $r^2 = 0.73$, $p < 0.01$). Perraudin *et al.* [23] also showed that a similar proportional relationship between the pseudo-first-order rate constants for PAHs decay and the O_3 concentrations exists. Donaldson *et al.* [24] reported that the reaction of PAHs with O_3 on the surface of organic substrates is consistent with a Langmuir-Hinshelwood surface mechanism. The dependence of the pseudo-first-order rate constants k on the gas-phase O_3 concentration is given by

$$k = A[O_3(g)]/(B + [O_3(g)])$$

where A is the product of the maximum number of surface sites available to O_3 and the second-order rate constant for the reaction of PAH with O_3, and B represents the ratio of desorption to adsorption rate constants of O_3. This equation indicates that k exhibits a linear dependence versus the gas-phase O_3 concentration under the $[O_3] \ll B$ condition. Kahan *et al.* [25] showed that the constants B for various PAHs are calculated to be $\sim 10^{15}$ molecules cm^{-3} for the reaction with O_3 on the surface of organic films, which is significantly higher than the ambient O_3 concentration ($\sim 10^{12}$ molecules cm^{-3}). From the linear least-squares fitting line between k_{obs} and N_{O3} obtained in Figure 8, the k_{obs} under any N_{O3} condition can be predicted.

The residual fraction of 3-OHNP-d_8 on a QFF, y (%), after exposure to ambient air under high volume air sampling is expressed as the following equation:

$$y = 100e^{-k_{obs}t} \quad (1)$$

where t is the exposure time. Therefore, assuming that the atmospheric concentration of OHNP is constant during the sample collection, the total ratio of remaining fraction R

Table 1. Atmospheric concentrations of hydroxy-1-nitropyrenes, 1-nitropyrene, and O_3 during 26–27 November 2001 at Sakai, Osaka, Japan.

Compounds	Mean ($n=8$)	Range
3-OHNP[a]	5	2–12[c]
6-OHNP[a]	42	17–73[c]
8-OHNP[a]	50	28–85[c]
1-NP[a]	27	9–48
O_3[b]	27	20–35

Notes: OHNP = hydroxy-1-nitropyrene; 1-NP = 1-nitropyrene.
[a]Given in units of fmol m^{-3}.
[b]Given in units of ppbv. Concentration was revalued to a 3-hour mean, which is coincident with the sampling period of airborne particles.
[c]Each 3-hour mean concentration has an error derived from the error of the slope of the linear regression line in Figure 8. See the caption of Figure 8 for details.

to decomposed fraction D from $t=0$ to $t=T$ is given by:

$$R/D = \left(\int_0^T 100e^{-K_{\mathrm{obs}}t}\,\mathrm{dt}\right)/\left(100T - \int_0^T 100e^{-K_{\mathrm{obs}}t}\,\mathrm{dt}\right). \quad (2)$$

It is possible to determine the concentrations of OHNPs in the airborne particles before decomposition by the correction based on this relationship.

The concentrations of 3-, 6-, and 8-OHNPs in airborne particles collected on the QFF at Sakai, Osaka, Japan were determined using the correction method proposed in this study. The mean concentrations of atmospheric 3-, 6-, and 8-OHNPs were 5, 42 and 50 fmol m^{-3} on 26–27 November 2001, respectively (Table 1). The mean measured values of 3-, 6-, and 8-OHNPs before the correction, 3, 25, and 29 fmol m^{-3}, respectively, were ca. 60% of the corrected concentrations. The mean concentration of 1-NP in the airborne particles was 27 fmol m^{-3} on the same sampling day, lower than those of 6- and 8-OHNPs. Gibson *et al.* [4] reported that the atmospheric concentration of OHNPs at a remote site on Bermuda was much higher than that of 1-NP, which is generally emitted from combustion sources. Our result is consistent with this study. These observations suggest that atmospheric secondary formation processes are operating as an atmospheric source of OHNPs. It is critical to clarify the atmospheric occurrence of OHNPs including their sources and sinks to evaluate their health impact on humans.

5. Conclusion

A correction method for the determination of atmospheric OHNPs based on their degradation rates during high volume air sampling was established. The degradation rate constants of OHNPs were found to correlate with the number of ozone molecules passing through the quartz fibre filter in a unit time during high volume air sampling. The chemical loss of OHNPs under high volume air sampling conditions was successfully evaluated by the exposure time and the pseudo-first-order rate constant for OHNP degradation estimated from the correlation. Concentrations of 3-, 6-, and 8-OHNPs in airborne particles collected in Osaka, Japan were determined using the established

correction method, and were comparable to that of 1-NP, a representative atmospheric NPAH.

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