PERGAMON

Methyl- and dimethyl-/ethyl-nitronaphthalenes measured in ambient air in Southern California

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Abstract

Naphthalene and alkylnaphthalenes are abundant semi-volatile polycyclic aromatic hydrocarbons (PAHs) present in ambient air as a result of emissions from combustion sources. At ambient temperatures, these PAHs can undergo atmospheric gas-phase reactions with hydroxyl (OH) radicals. We report here on environmental chamber reactions simulating ambient photooxidation of volatilized diesel fuel PAHs and demonstrate for the first time that dimethylnitronaphthalenes and/or ethylnitronaphthalenes identified as formed from the OH radical-initiated reactions of alkyl-PAHs present in diesel fuel are also present in ambient air samples collected in Southern California.
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1. Introduction

Methylnaphthalenes (MNs), dimethylnaphthalenes (DMNs) and ethylnaphthalenes (ENs) are semi-volatile polycyclic aromatic hydrocarbons (PAHs) emitted into the atmosphere from a variety of incomplete combustion sources, including diesel engines (Williams et al., 1986; Nelson, 1989; Zielinska et al., 1996; Marr et al., 1999). Unburned diesel fuel PAHs are likely to contribute significantly to the alkylnaphthalenes observed in urban areas (Williams et al., 1986; Tancell et al., 1995). The MNs, ENs and 9 of the 10 isomers of DMNs have been measured in ambient air [1,8-DMN is not present in ambient air (Phousongphouang and Arey, 2002, 2003a) nor in diesel fuel (Bundt et al., 1991)]. At ambient temperatures, these alkylnaphthalenes exist primarily in the gas-phase and their major atmospheric loss process is by daytime gas-phase reaction with the hydroxyl (OH) radical (Atkinson, 2000). Previous studies reported atmospheric lifetimes of the alkylnaphthalenes due to the gas-phase reactions with the OH radical of about 2 h for the DMNs and 3–4 h for the MNs and ENs (Phousongphouang and Arey, 2002). The products of PAH atmospheric reactions include mutagenic nitrated derivatives (Arey et al., 1992; Sasaki et al., 1995; Gupta et al., 1996; Ciccioli et al., 1996; Arey, 1998; Cecinato et al., 2001; Feilberg et al., 2002). All 14 isomers of methylnitronaphthalenes (MNNs) have been reported in ambient air samples (Arey and Zielinska, 1989; Zielinska et al., 1989; Gupta et al., 1996), but dimethylnitronaphthalenes (DMNNs) and ethylnitronaphthalenes (ENNs) have not previously been reported.

We report here on environmental chamber reactions simulating ambient photooxidation of volatilized diesel fuel PAHs and demonstrate for the first time that DMNNs and/or ENNs identified as formed from the OH radical-initiated reactions of alkyl-PAHs present in diesel fuel are also present in ambient air.

2. Experimental

PAHs were separated from whole diesel fuel using a Silica open column and typically 200 mg were volatilized

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into the 70001 all-Teflon environmental chamber. Simulated atmospheric reactions of the diesel fuel PAHs with OH radicals were carried out as described previously using photolysis of CH_3ONO as the OH radical source (Arey et al., 1992; Sasaki et al., 1995). After reaction, the chamber contents were sampled onto polyurethane foam plugs (PUFs), followed by Soxhlet extraction in dichloromethane and fractionation by high performance liquid chromatography (HPLC) using a Silica column (Arey et al., 1992; Sasaki et al., 1995). The HPLC fraction containing the nitro-PAHs was analyzed by gas chromatography/mass spectrometry (GC/MS) on a DB-5MS column with negative ion methane chemical ionization and selected ion monitoring (NCI-SIM).

Ambient measurements were carried out in Southern California, USA during the summer of 2002 in Los Angeles (an urban site) and Riverside (a downwind receptor site). Four time intervals per day (07:00–10:30, 11:00–14:30, 15:00–18:30 and 19:00–6:30) were sampled for one 5-day period each in Los Angeles (12–16 August 2002) and Riverside (26–30 August 2002). Samples of volatile PAHs were collected onto replicate Tenax-TA solid adsorbent cartridges at $200\,cm^3\,min^{-1}$ for the daytime samples and $100\,cm^3\,min^{-1}$ for the nighttime samples. Semi-volatile PAHs and nitro-PAHs were collected onto PUFs at a flow rate of $\sim 0.6\,m^3\,min^{-1}$.

Following spiking with naphthalene-d_8 and 1-methylnaphthalene-d_{10} to serve as internal standards, the Tenax samples were thermally desorbed onto a DB-1701 column and analyzed by electron impact (EI) GC/MS-SIM (Phousongphouang and Arey, 2002). Each of the 8 Tenax samples per day were analyzed individually, while the PUFs were composited according to time interval prior to analysis. The PUFs were spiked with 1-nitronaphthalene-d_7 as an internal standard and then extracted, fractionated by HPLC, and analyzed by GC/MS-NCI as described above for the chamber reactions.

The instrumentation used was: Hewlett-Packard (HP) 1050 HPLC, HP-5971A-MSD for EI GC/MS and an Agilent 5973-MSD for GC/MS-NCI.

3. Results and discussion

The top panels of Figs. 1 and 2 show mass chromatograms for the MNNs (m/z 187) and DMNNs and/or ENNs (m/z 201), respectively, from the OH radical-initiated reaction of the volatilized diesel fuel PAHs. The pattern of MNNs formed (see Fig. 1 for identification of the 11 individual peaks observed) matches what has previously been observed from the OH radical-initiated reactions of 1-MN and 2-MN (with initial 2-MN concentrations twice that of 1-MN, reflecting typical ambient air measurements (Gupta et al., 1996; Arey, 1998)). The identity of the diesel fuel product peaks in Fig. 2 (top) as DMMNs and/or ENNs
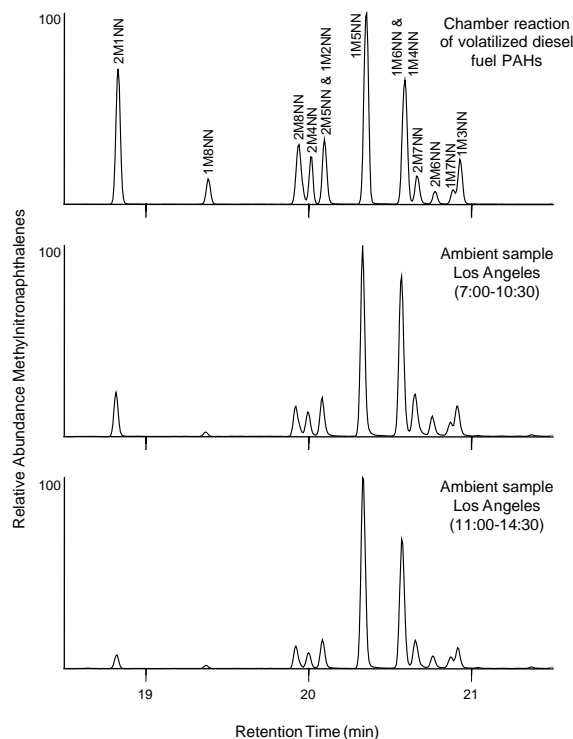

Fig. 1. Mass chromatograms for the methylnitronaphthalenes (m/z 187) observed by GC/MS NCI-SIM analysis of: (top) sample from the OH radical-initiated chamber reaction of the PAHs present in volatilized diesel fuel; (center) composite of early morning (7–10:30) ambient air samples collected in Los Angeles during 12–16 August 2002; (bottom) composite of mid-day (11–14:30) ambient air samples collected in Los Angeles during 12–16 August 2002.

is based upon the selectivity provided by HPLC fractionation and GC/MS-NCI analysis, and was further confirmed from additional chamber reactions of volatilized diesel fuel PAHs with the nitrate radical in which full EI mass spectra showing abundant molecular ions and characteristic fragmentation patterns (Arey and Zielinska, 1989) were obtained (Reisen and Arey, in preparation).

Similar to the diesel fuel PAH reactions, the ambient samples (see middle and bottom mass chromatograms on figures) also show 11 MNN peaks and about 30 peaks in the m/z 201 mass chromatograms (from a possible 56 isomers of DMNNs and ENNs). The alkylnitronaphthalenes observed in these ambient samples can be rationalized based on the gas-phase chemistry of the alkylnaphthalenes emitted from vehicles at this heavily traffic impacted site.

Table 1 gives the averaged naphthalene and alkylnaphthalenes concentrations for the two sampling intervals shown in Figs. 1 and 2. The site in Los Angeles was near the intersection of the 10 and 110 freeways and

it is likely that the PAHs measured are almost entirely the result of vehicle emissions. The relative abundances of the alkylnaphthalenes found in the ambient samples were similar to the diesel fuel PAHs with 2-MN > 1-MN, and with 1,6-, 1,7-, 2,6- and 2,7-DMNs among the most
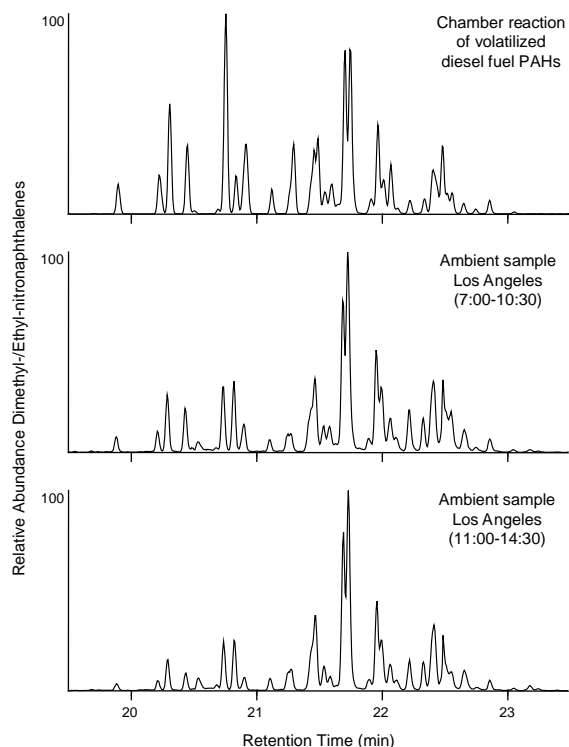

Fig. 2. Mass chromatograms for the dimethylnitronaphthalenes and/or ethylnitronaphthalenes (m/z 201) observed by GC/MS NCI-SIM analysis of: (top) sample from the OH radical-initiated chamber reaction of the PAHs present in volatilized diesel fuel; (center) composite of early morning (7–10:30) ambient air samples collected in Los Angeles during 12–16 August 2002; (bottom) composite of mid-day (11–14:30) ambient air samples collected in Los Angeles during 12–16 August 2002.

abundant DMN isomers. Thus the patterns of the nitro-alkyl-PAHs formed from the chamber reaction (top mass chromatograms in figures) should be similar to those of the ambient samples (lower mass chromatograms) if the major source of the nitro-alkyl-PAHs is gas-phase OH radical-initiated reactions of diesel-derived alkyl-PAHs. Data from Table 1 can be used to verify that, as anticipated, ambient OH radical reactions of the gas-phase PAHs occurred in Los Angeles. While the decrease in the PAH concentrations during the 11–14:30 samples relative to the early morning samples will reflect dilution from an increasing mixing height, it will also reflect atmospheric reactions during this period of highest OH radical concentration (George et al., 1999). Indeed the relative decreases measured during the 11–14:30 samples generally follow the OH radical rate constants of the PAHs, being lowest for naphthalene (61% decrease) and greatest for the DMNs (81% decrease), the most reactive of the alkyl-PAHs measured (Phousongphouang and Arey, 2002). The increased ratio of the nitro-PAHs to the parent PAHs during the 11–14:30 samples is also consistent with the nitro-PAHs being formed by OH radical-initiated reactions, with the percent formation of the DMNNs + ENNs reaching over 1% in the midday samples (see Table 1). The samples collected at the downwind Riverside site had consistently higher nitro-PAH/PAH ratios reflecting formation of nitro-PAHs during transport (Reisen and Arey, in preparation).

Looking in detail at the specific MNN isomer distributions, it is clear that 2M1NN and 1M8NN (Fig. 1) are significantly lower in the ambient samples than seen from the chamber reaction. The photolysis rates of several MNNs have recently been measured and the photolysis lifetimes of 2M1NN and 1M8NN estimated at 10 and 8 min, respectively, in comparison with 22–133 min for the other MNNs (Phousongphouang and Arey, 2003b). Because of the short reaction times, photolysis of the MNNs during the chamber reaction in which they were produced was negligible (Phousongphouang and Arey, 2002, 2003b).

Table 1
Naphthalene and alkylnaphthalenes concentration and percent of nitrated parent PAH for samples collected 12–16 August 2002 in Los Angeles, California, USA

Sampling times	PAHs (ng/m³)				Percent nitrated		
	Naphthalene	1-MN + 2-MN	1-EN + 2-EN	DMNs	%NNs[a]	%MNNs[b]	%(DMNNs + ENNs)[c]
7–10:30	390	239	6.5	29.4	0.13	0.10	0.38
11–14:30	152	65	2.1	5.6	0.32	0.36	1.29

[a] $\sum$(1-NN + 2-NN)/naphthalene.
[b] $\sum$(14 isomers of $xMyNN$)/$\sum$(1-MN + 2-MN), assumes NCI response of all $xMyNN$ isomers is similar to that of 2M1NN.
[c] $\sum$(isomers of DMNNs and/or ENNs)/$\sum$(nine isomers of DMNs + 1-EN + 2-EN), assumes NCI response of all nitro-isomers of 201 Da is similar to that of 2M1NN.

Thus the differences in the profile of the MNNs chamber reaction products and the MNNs in the ambient samples can be attributed to ambient photolysis, which is their major atmospheric loss process (Phousongphouang and Arey, 2003b).

For the molecular weight 201 species, the obvious difference between the chamber reaction products and the ambient samples is the lower abundances of peaks in the early portion of the ambient sample chromatograms (see Fig. 2). For the MNNs and nitronaphthalenes, photolysis rates showed a distinct trend with ortho- (2M1NN) and peri- (1M8NN) substituted MNNs having the highest rates and with MNNs with NO_2 on the α-carbon of the naphthalene structure being more reactive than those with the NO_2 group on the β-carbon (Feilberg et al., 1999; Phousongphouang and Arey, 2003b). As may be seen from the MNN chromatogram in Fig. 1, elution is earliest for ortho- and peri-substituted isomers and latest for isomers with the NO_2 on the β-carbon (e.g., 1M3NN and 1M7NN). Therefore, it is likely that ambient photolysis of DMNNs and/or ENNs also accounts for the differences between the chamber 201 m/z mass chromatograms and those of the ambient samples.

To our knowledge, this is the first time that DMNNs and ENNs have been reported in ambient air, and we attribute their presence in Los Angeles air samples mainly to OH radical-initiated formation from the parent alkyl-PAHs. Nitrate radical reactions may also produce nitro-PAHs (Ciccioli et al., 1996; Arey, 1998), but at the Los Angeles sampling site the rapid reaction of NO_3 radical with NO emissions from vehicles (as well as daytime NO_3 radical photolysis) will preclude NO_3 radical reactions.

NNs and MNNs are bacterial and human cell mutagens (Gupta et al., 1996; Sasaki et al., 1997, 1999), and it is expected that DMNNs and ENNs will also be mutagens. It should be noted that although the DMNs/ENs concentrations are lower than those of naphthalene and the MNs (see Table 1), the relative abundances of the nitro-derivatives were more similar. During this study in Los Angeles, nitronaphthalene concentrations ranged from 202 to 494 pg/m³, methylnitronaphthalene concentrations from 108 to 244 pg/m³ and dimethyl- and ethyl-nitronaphthalene concentrations from 49 to 128 pg/m³. Therefore, further work is warranted to identify the specific DMNN/ENN isomers present in ambient air, their concentrations in other urban areas, their gas/particle partitioning and their potential health effects.

Acknowledgements

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