

Diurnal Cycle of PAHs, Nitro-PAHs, and oxy-PAHs in a High Oxidation Capacity Marine Background Atmosphere

MANOLIS TSAPAKIS[†] AND EURIPIDES G. STEPHANOU*

Environmental Chemical Processes Laboratory (ECPL),
Department of Chemistry, University of Crete,
EL-71003 Voutes-Heraklion, Greece

Received May 17, 2007. Revised manuscript received August 31, 2007. Accepted September 11, 2007.

To improve our understanding of the formation and fate of nitro-PAHs, which contribute to the toxicity of ambient particles, the diurnal variation of their ambient concentration was studied concurrently with the corresponding PAH, OH radical, ozone, and oxy-PAH concentration, during an intensive field campaign at an eastern Mediterranean marine background location (Finokalia, Island of Crete) in August, 2001. The gas-phase PAH and OH radical concentrations maximized at noon. Gas-phase PAH concentrations were correlated ($p < 0.001$) with ambient temperatures. The gas-phase OH-radical-initiated PAH reaction was identified as the major process contributing to the ambient burden of nitro-PAHs. 2-Nitrofluoranthene and 2-nitropyrene were the most abundant particle-associated nitro-PAHs. A well-defined diurnal pattern was identified for both compounds exhibiting a maximum during midday followed by a rapid decrease. 9,10-Anthracenedione and 9-fluorenone, the most abundant oxy-PAHs, did not present a diurnal variation of concentration.

Introduction

Several physical and chemical processes such as gas-particle phase distribution and transformation reactions determine the levels of PAHs in the atmosphere (1). The fate of PAHs in the atmosphere has been extensively studied (2–5). Most of the studies were carried out on a 24-h or a monthly or seasonal sampling scale. Information gathered from measurements of the seasonal variation of the atmospheric concentration of PAHs was useful to point out critical parameters (e.g., long-range transport) which govern their occurrence in various regions worldwide. However, a long sampling period (e.g., 24 h) suffers from substantial weaknesses. Changes in ambient temperature, wind direction, wind speed, air humidity, and oxidant and analyte concentrations during the sampling period could substantially influence the observed levels of atmospheric PAHs (6–9).

Intensive sampling is suitable to study the occurrence and fate of the short-lived highly toxic compounds such as nitro-PAHs and oxy-PAHs (10). Nitro-PAHs are emitted in the atmosphere by primary sources (11) or formed by gas-phase PAHs reacting with hydroxyl (OH) radicals during the

daytime and nitrate (NO₃) radicals during the nighttime, in the presence of NO_x (12–14). Nitro-PAH isomer patterns present in direct emissions are significantly different from those resulting from atmospheric reactions, reflecting thus their formation pathways. During incomplete combustion processes, 1-nitropyrene (1-NP) and 3-nitrofluoranthene (3-NF), formed by electrophilic nitration, are the most abundant compounds found in diesel fuel particulate material (11). Conversely, gas-phase reaction pathways involve OH radical attack at the sites of highest electron density, with subsequent NO₂ addition followed by a loss of water (11). The most abundant nitroarenes produced by this mechanism are 2-nitrofluoranthene (2-NF) and 2-nitropyrene (2-NP) (11). Equivalent to the OH reaction, the attack of the NO₃ radical forms a fluoranthene–NO₃ adduct, followed by the ortho addition of NO₂ and subsequent loss of HNO₃ (11). This reaction is notably selective, forming only 2-NF. In the atmosphere, the gas-phase reactions of PAHs with OH and NO₃ radicals form 2-NF, which is the most abundant particle-associated nitro-PAH (10, 15).

Oxygenated PAH compounds (oxy-PAHs) such as aromatic ketones, aromatic aldehydes, quinones, and carboxylic acids have been identified in various environmental samples (16–18). Oxy-PAHs are mainly emitted from combustion processes; however, they are also produced by heterogeneous reactions of particulate associated PAHs with ozone (11, 16).

Nitro-PAHs and oxy-PAHs are potent mutagens (19) contributing to an increase in the mutagenic activity of airborne matter. The objective of the present study was to perform simultaneous field measurements of the diurnal atmospheric cycle of gaseous PAH's, OH radicals (20), and nitro-PAHs in order to expand the current knowledge of the atmospheric formation of nitro-PAHs. In addition, measurements of ozone and oxy-PAH ambient concentrations were also included to improve the understanding of PAH behavior in a high oxidation capacity area such as the eastern Mediterranean (21).

Experimental Section

Sampling and Measurements. The variation of atmospheric concentration of PAHs, nitro-PAHs, and oxy-PAHs in the gas and particle phases was studied at the background coastal site of Finokalia on the Island of Crete (35°19' N, 25°40' E; 130 m above sea level) in the eastern Mediterranean (Figure S1, Supporting Information). Details on the sampling area geography and meteorology have been previously reported (21, 22). The three-day intensive campaign started on August 17, 2001, and was terminated on August 21, 2001. The sampling interval time was 4 h, and the sample volume collected was 100–125 m³. Samples were collected using a modified high-volume (Hi-Vol) sampler. An oxidant denuder was used to minimize PAH degradation during sampling (9).

Atmospheric OH concentrations were measured at the sampling station every 30 s and averaged over 5 min intervals using chemical ionization mass spectrometry (20). The detection limit for OH was calculated to be $2.4 \times 10^5 \text{ cm}^{-3}$ (2 σ) on the basis of signal count statistics. Details regarding the method and OH levels during the intensive field campaign have been published elsewhere (20).

Meteorological data, including air temperature (T), wind speed (WS), wind direction (WD), solar radiation (SR), ozone levels (O₃), and black carbon (BC) were measured at Finokalia station during the sampling campaign. Backward trajectories of air masses were calculated using an atmospheric circulation model, HYSPLIT 4 (23), developed by the National Oceanic and Atmospheric Administration (NOAA), U.S.A.

* Corresponding author phone: +30 2810545028; fax +30 2810545001; e-mail: stephanou@chemistry.uoc.gr.

[†] Present address: Institute of Oceanography, Hellenic Center of Marine Research, Gournes Peditados, EL-71003 Heraklion, Greece.

TABLE 1. Ambient Conditions during Intensive Sampling Period^a

parameter	average (stdev)		
	August 18, 2001	August 20, 2001	August 21, 2001
T (°C)	24.1 (0.8)	24.7 (1.3)	26.0 (2.1)
RH (%)	74.8 (8.6)	65.1 (7.3)	46.8 (11.6)
WD (deg)	272.8 (10.7)	262.4 (11.2)	264.1 (21.6)
WS (m s ⁻¹)	11.9 (1.4)	12.6 (0.4)	11.9 (1.9)
SR (watt m ⁻²)	320.7 (335.0)	283.3 (346.8)	297.2 (357.7)
BC (μg m ⁻³)	1.2 (0.3)	0.9 (0.1)	1.1 (0.2)
O ₃ (ppbv)	54.8 (1.9)	56.2 (3.9)	64.8 (4.7)

^a Abbreviations: stdev, standard deviation; T, temperature; RH, relative humidity; WD, wind direction; WS, wind speed; SR, solar radiation; BC, black carbon content; O₃, ozone.

(<http://www.arl.noaa.gov/ready.html>). These trajectories (72 h back) were defined at constant air pressure (850 hPa, 1200–1400 m, varying height according to season and atmospheric temperature).

Sample Analysis and Quality Assurance. The protocol followed for PAH analysis has been described in detail elsewhere (24). Identification of nitro-PAHs was carried out with a Finnigan GCQ ion trap tandem mass spectrometer following a method previously reported (25). Optimization of the Finnigan GCQ system was carried out using a series of standard solutions according to a method published earlier (26). The optimum values for six instrumental parameters were as follows: isolation time, 12 ms; excitation voltage, 1.5 V; excitation time, 15 ms; “q” value, 0.3; ion source temperature, 240 °C; and electron energy, 70 eV. Oxy-PAHs were analyzed by GC/MS in the selective ion monitoring mode (27).

The identification of each compound was based on the use of the mass spectra of reference standards. Relative response factors were determined each time prior to sample analysis by using a standard mixture containing the reported analytes and three internal standards. Field and laboratory blank samples were routinely analyzed in order to evaluate analytical bias and precision. The detailed procedure is presented in the Supporting Information (see S.I. Quality Assurance).

Results

Air masses reaching the sampling station at Finokalia during the intensive field campaign had a similar origin, predominantly from the northeast (Figure S1, Supporting Information). The atmospheric conditions (Table 1) during the study period were relatively stable: ambient average temperature varied from 24.1 to 26.0 °C (Table 1); wind direction and speed varied from 262.4° to 272.8° and 11.9 m s⁻¹ to 12.6 m s⁻¹, respectively. The ozone concentration levels varied from 50.6 to 71.5 ppbv, with an average of 58.3 ppbv. OH radical concentration levels showed a strong diurnal variation with high maxima (approximately 2 × 10⁷ molecules cm⁻³) occurring around 13:30 Eastern European Summer Time (EEST). The nocturnal concentration values were below the detection limit. Daily 24-h average concentrations varied between 3.6 and 6.7 × 10⁶ cm⁻³ (20).

Occurrence of PAHs. The total PAH concentration in the gas and particulate phases varied from 22.6 to 97.4 ng m⁻³ and from 0.6 to 1.8 ng m⁻³, respectively (Table S1, Supporting Information). The concentration levels measured during the intensive study period fall within the range of seasonal PAH concentrations measured previously in the area (24). Phenanthrene was the most abundant member, and its gas-phase concentration varied from 10.0 to 58.6 ng m⁻³ (Table S1, Supporting Information). The diurnal variation of gaseous

and particulate PAH concentrations, for the 3-day intensive campaign, are shown in Figure 1. The gaseous concentration of PAHs exhibited their maxima during the daytime (Figure 1). The averaged night and day concentrations were 25.6 and 49.6 ng m⁻³ (August 17–18, 2001), 30.3 and 45.7 ng m⁻³ (August 19–20, 2001), and 34.3 and 88.4 ng m⁻³ (August 20–21, 2001). The absence of a distinct diurnal pattern was observed for particulate PAHs (Figure 1).

Long-range transport, ground evaporation, chemical reactions, and deposition processes are the most important factors contributing to the ambient atmospheric concentration patterns of gaseous and particulate PAHs, especially in remote areas (28). In addition, due to the semivolatile character of PAHs, changes in ambient temperature might substantially influence their gas/particle partitioning (24). Air mass back-trajectory analysis during the measurement period (August 18–21, 2001) showed that air masses reaching the sampling station were of similar origin, predominantly from northeasterly directions (Figure S1, Supporting Information). Consequently, the observed diurnal changes in PAH concentrations could not be related to significant changes in air mass origin.

The diurnal variation of particulate PAHs observed in this study could be explained, to some extent, by changes in specific atmospheric variables (Table 2). A statistically significant negative correlation ($p < 0.05$ – 0.001) was observed between ambient temperature and high-molecular-weight (HMW) PAHs (228–276 amu: Chr/T, chrysene/triphenylene; BbF, benzo[b]fluoranthene; BkF, benzo[k]fluoranthene; BeP, benzo[e]pyrene; BaP, benzo[a]pyrene; IP, indeno[1,2,3-cd]pyrene; Table 2). No correlation was observed between temperature and low-molecular-weight (LMW) particulate PAHs (166–202: Fl, fluorene; Phe, phenanthrene; An, anthracene; Fluo, fluoranthene; Py, pyrene; Cy[cd]Py, cyclopentane[cd]pyrene; BaA, benzo[a]anthracene; Table 2). LMW PAHs exist mainly in the gas phase (Table S1, Supporting Information), and their very low fraction measured in particles is likely to be nonexchangeable. Conversely, Chr/T, BbF, BkF, BeP, BaP, and IP are mainly associated with particles (Table S1). Thus, an increase in ambient temperature resulted in an increase in their evaporation from particles (Table 2).

The relative atmospheric humidity varied from 32.2 to 83.9% with an average value of 63.9%. The correlation between particulate concentrations of PAH members and relative humidity was not significant (Table 2). Previous studies have pointed out that an increase in humidity leads to an enhancement of PAH photodecomposition (29, 30). The decomposition rate depends on the radiation intensity (30) as well as on the physicochemical properties of the particles (29). Under typical atmospheric conditions (temperature 20 °C and solar radiation 1 cal cm⁻² min⁻¹), the half-life varies from 0.3 to 0.5 h for Cy[cd]Py and BaP, respectively (30). Despite the high temperature (23.1–28.8 °C) and the intense solar radiation (1.26 cal cm⁻² min⁻¹) occurring during the study period (Table 1), the concentration of particulate PAHs did not present any significant variation (Table 2). Only Py, BeP, and IP were slightly correlated ($p < 0.1$) with solar radiation (Table 2). The photolytic half-life of PAHs was found to be highly dependent on the physical and chemical characteristics of the substrate (30, 31). It has been shown that the adsorption of reactive PAHs on black carbon protects them from light (29). A significant positive correlation ($p < 0.05$ – 0.001 ; Table 2) was observed between pyrogenic PAHs (Cy[cd]Py, BaA, Chr/T, BbF, BkF, BeP, BaP, and IP; Table 2) and black carbon particle content (Table 2), implying their association with it. The common origin of black carbon and pyrogenic PAHs has also been previously reported (32, 33). Similar results to those reported here were also

TABLE 2. Correlation Statistics of Particulate PAHs with Ambient Parameters^a

PAH member	T	>WS	SR	BC	O ₃	OH
Fl	ns	ns	ns	(-) ^b	ns	ns
Phe	ns	ns	ns	ns	ns	ns
An	ns	ns	ns	ns	ns	ns
Fluo	ns	ns	ns	ns	ns	ns
Py	ns	ns	(-) ^b	ns	ns	(-) ^b
Cy[cd]Py	ns	ns	ns	(+) ^d	ns	ns
BaA	ns	ns	ns	(+) ^c	ns	ns
Chr/T	(-) ^c	ns	ns	(+) ^d	ns	ns
BbF	(-) ^c	ns	ns	(+) ^c	ns	ns
BkF	(-) ^c	ns	ns	(+) ^c	ns	ns
BeP	(-) ^c	ns	(-) ^b	(+) ^d	ns	ns
BaP	(-) ^c	ns	ns	(+) ^d	ns	ns
IP	(-) ^d	ns	(+) ^c	(+) ^d	ns	(-) ^c

^a Abbreviations: T, temperature; WD, wind direction; WS, wind speed; SR, solar radiation; BC, black carbon content; O₃, ozone; Fl, fluorene; Phe, phenanthrene; An, anthracene; Fluo, fluoranthene; Py, pyrene; Cy[cd]Py, cyclopentane[cd]pyrene; BaA, benzo[a]anthracene; Chr/T, chrysene/triphenylene; BbF, benzo[b]fluoranthene; BkF, benzo[k]fluoranthene; BeP, benzo[e]pyrene; BaP, benzo[a]pyrene; IP, indeno[1,2,3-cd]pyrene. ^b $p < 0.1$. ^c $p < 0.05$. ^d $p < 0.001$, ns: non significant.

TABLE 3. Correlation Statistics of Gas PAHs with Ambient Parameters^a

PAH member	T	WS	SR	O ₃	OH
Fl	(+) ^d	ns	(+) ^d	ns	(+) ^d
Phe	(+) ^d	ns	(+) ^c	ns	(+) ^b
An	(+) ^d	ns	ns	ns	ns
Fluo	(+) ^d	ns	(+) ^d	ns	(+) ^d
Py	(+) ^d	ns	(+) ^d	(+) ^c	(+) ^c
Cy[cd]Py	ns	ns	ns	ns	ns
BaA	ns	ns	ns	ns	ns
Chr/T	ns	ns	ns	(+) ^c	ns
BbF	ns	ns	ns	ns	ns
BkF	ns	ns	ns	ns	ns
BeP	ns	ns	ns	ns	ns
BaP	ns	ns	ns	ns	ns

^a See Table 2 for abbreviations. ^b $p < 0.1$. ^c $p < 0.05$. ^d $p < 0.001$, ns: non significant.

imply that, although, on a seasonal basis, long-range transport is the main source of PAHs (24), the diurnal variation of PAH concentration during this campaign is driven by temperature. Similar results were also observed in Chesapeake Bay (33). The positive correlation observed between solar radiation and the concentration of LMW PAHs could also be attributed to the temperature variation driven by solar radiation (Table 3).

No correlation was observed between wind speed and gas-phase PAHs (Table 3). Wind speed is a crucial parameter in many atmospheric processes (mixing layer, deposition process, and evaporation and absorption from the ground and sea surface) governing semivolatile organic compound concentrations in the atmosphere. However, although certain studies have pointed out that wind speed is an important parameter controlling gas-phase semivolatile organic compound concentration, other studies have not identified any significant dependence (4, 33, 38). It should also be noted that a lack of correlation does not necessarily mean a lack of dependence. Other parameters such as temperature or reaction with OH radicals could mask this dependence. In the present study, an absence of significant correlation was observed between most gaseous PAH members and the ozone concentration (Table 3). Only Py and Chr/T presented a positive correlation ($p < 0.05$). Ozone is an imported pollutant

TABLE 4. Nitro-PAH Mean Air Concentrations (in pg m⁻³) Worldwide

Area	Characteristic	2-NF	2-NP	Reference
Finokalia	summer, coastal background	29	21	This study
Los Angeles, CA	summer, urban	63	2	10
Los Angeles, CA	winter, urban	74	8	10
Madrid, Spain	urban	70	20	15
Rome, Italy	urban	470	70	15
Copenhagen, Denmark	urban	91	20	25
Athens, Greece	urban	90	40	40
Baltimore, MD	winter, urban	60	7	41
Baltimore, MD	summer, urban	99	2	41
Fort Meade, FL	winter, suburban	49	4	41
Fort Meade, FL	summer, suburban	28	0.8	41

in the study area (21). However, the observed correlation does not imply that these two gaseous PAHs are transported to the area.

The reaction of volatile PAHs with OH radicals is considered as the most important reaction contributing to their removal from the atmosphere (11). Many field- and laboratory-based studies have attributed the reduction of gas-phase PAH concentrations to their reaction with OH radicals (14, 33, 39). However, in our study, only the LMW gaseous PAH (from Fl to Py; Table 3) concentration was positively correlated with the OH radical concentration. In the area studied, temperature and OH radical concentration follow the same pattern (Figure 1). No correlation was observed for the corresponding HMW PAH (from Cy[cd]Py to BaP; Table 3) concentration. A similar variation, to that observed for gaseous PAH concentrations at Finokalia, has also been observed in other background regions (28, 33). An opposite trend has been observed in the urban region of Baltimore (33): the reaction of PAHs with OH radicals (a decrease of concentration due to destruction at midday) was proposed as an important parameter influencing the gaseous PAH diurnal variation. On the contrary, in the Gulf of Chesapeake, the diurnal variation of temperature determined the volatile PAH concentration pattern to a large extent (33). We thus propose that the strong temperature dependence of PAH concentration in Finokalia dominates the counter-effect of the destruction of PAHs by OH radicals.

Nitro-PAHs. 2-NF and the 2-NP were the two nitro-PAHs determined to be in the particulate phase in Finokalia. The concentrations of 1-NP and 3-NF were below the method detection limits for all of the samples. This is consistent with a background area where anthropogenic activities and primary sources are absent. The concentrations of 2-NF and 2-NP varied from 3.4 to 70.9 pg m⁻³ (average value 28.9 pg m⁻³) and from 2.2 to 21.9 pg m⁻³ (average value 10.4 pg m⁻³), respectively (Table 4). Higher concentrations have been measured in urban regions worldwide (10, 15, 25, 40, 41) (Table 4). The average values of 2-NF and 2-NP in Athens, Greece, were 90 and 40 pg m⁻³, respectively (40). Considerably higher values were measured in Rome, Italy (470 pg m⁻³ for 2-NF and 70 pg m⁻³ for 2-NP; Table 4). Ambient measurements of nitro-PAHs in the Los Angeles basin (10) have shown that nitro-PAH levels were highest in Riverside during the summer due to the enhanced photochemistry. In the same study (10), it was observed that the gas-phase radical-initiated PAH reactions were the dominant processes, producing 2-NF as the major particle-associated nitro-PAH.

The diurnal variation of the concentration of 2-NF, 2-NP, and OH radicals for each one of the three intensive sampling days is presented in Figure 2. The maxima of concentration of 2-NF and 2-NP in Finokalia occurred at midday (11:00–15:00 EEST) for all sampling days (Figure 2). After the midday

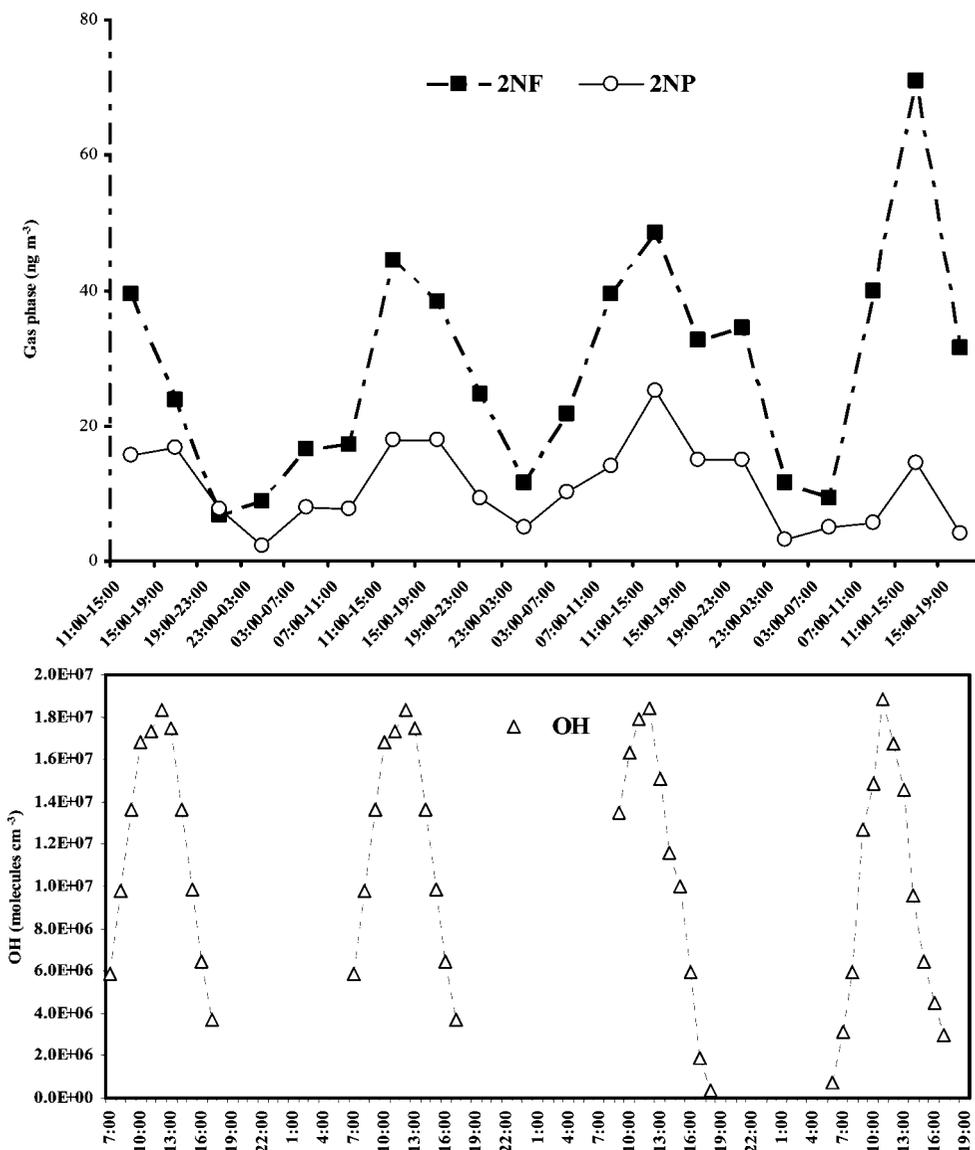


FIGURE 2. (A) Diurnal variation of 2-nitrofluoranthene (2-NF) and 2-nitropyrene (2-NP) and (B) variation of hydroxyl radical (OH) concentration (46) in Finokalia. The OH data are reproduced here from a previously reported paper (20).

concentration maximum (11:00–15:00 EEST), a sharp decrease was then observed for both nitro-PAHs and OH radicals (Figure 2). The concentrations of 2-NF measured during the day were 13, 5.7 and 6.2 times higher than those measured during the night (23:00–03:00 EEST) (Figure 2). In all cases, the variation of the concentration of 2-NF, 2-NP and OH radicals showed the same diurnal pattern. The observation of these diurnal concentration patterns implies that OH-radical-initiated formation of nitro-PAHs is the dominant process for their production (10). The absence of local anthropogenic sources and the constant origin of air masses reaching the sampling point (Figure S1, Supporting Information) exclude other possible sources for the observed diurnal variation. Photolysis and dry deposition are the most important loss processes for nitro-PAH (11). Photodecomposition rates of nitro-PAHs are strongly influenced by the physical and chemical nature of their substrate (42, 43). Fan et al. (42) measured the photostability of nitro-PAHs on combustion soot particles in the sunlight and determined that at noon the half-lives for both 1-nitropyrene and 2-nitropyrene were 0.8 h and for 2-nitrofluoranthene it was 1.2 h. The above finding might help to interpret the sharp decrease of nitro-PAH concentration that we observed after the midday maximum.

The concentration of NO₃ radicals presents a recurring daily pattern in the eastern Mediterranean atmosphere (44). The highest concentration levels of NO₃ radicals were measured during the nighttime, while they were found to be negligible during the day. The average NO₃ radical concentration in Finokalia during the present study varied from 4.5 to 37 ppt_v (44). The extent of gas-phase OH- and NO₃-initiated radical reactions with pyrene and fluoranthene can be assessed through the 2-NF/2-NP concentration ratio. 2-NF is the most important nitrated product of fluoranthene reacting with OH radicals (12). It is also the exclusive product of reaction with NO₃ radicals (45). In addition, 2-NP is the exclusive nitro product of pyrene reacting with OH radicals, while it is not produced through the reaction with NO₃ radicals (12, 13, 45). Therefore, the 2-NF/2-NP ratio can be used to estimate the relative importance of nitro-PAH gas-phase production from OH- and NO₃-initiated formation pathways. Measurements of the ratio 2-NF/2-NP performed in gas-phase reaction chambers (13) have shown that for the OH-initiated pathway this ratio was ca. 6, while for the NO₃ pathway, it was substantially higher (ca 100). In our study, the 2-NF/2-NP ratio varied from 1 to 8 (average 3.5). Even in samples collected during the nighttime, the 2-NF/2-NP ratio was close to 6. Our results in relation to the observation

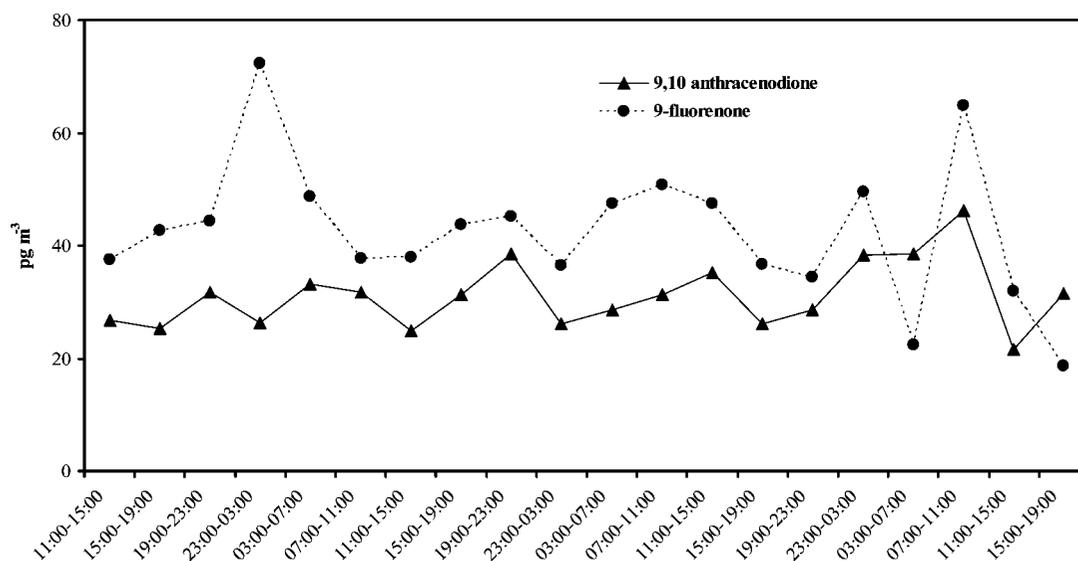


FIGURE 3. Diurnal variation of particulate oxy-PAH concentration.

of NO₃ radical diurnal patterns support the dominance of OH-radical-initiated chemistry as the main mechanism for the formation of nitro-PAHs in the study area. Values of the 2-NF/2-NP ratio <10 were observed more often (10, 15, 40, 41), whereas values >10 occur rarely (10). During the same field campaign, the study of the diurnal cycle of atmospheric PCBs and OH pointed out the dominance of OH radical chemistry in depleting the concentration of PCBs during the daytime (45).

Oxy-PAHs. Low concentrations of oxy-PAHs were measured during the present field work, and most of the studied compounds exhibited levels below our method detection limits. 9,10-Anthracenedione and 9-fluorenone were the most abundant compounds, and their average concentrations were 34.2 and 46.3 pg m⁻³, respectively. A clear diurnal pattern was not observed during our study (Figure 3), concurrently with the absence of a diurnal pattern for the corresponding concentration of ozone (21). However, a recent study on the formation of 9,10-phenanthrenequinone through the reaction of phenanthrene with OH and NO₃ radicals and ozone (46) indicated that the nighttime NO₃-radical-initiated reaction of gas-phase phenanthrene may be a significant source of oxy-PAHs in the ambient atmosphere. Significant concentrations of oxy-PAHs have been observed in urban areas worldwide: the average concentrations of 9, 10 anthracenedione and 9-fluorenone in the urban area of Temuco in Chile were 237.7 and 1550.5 pg m⁻³ and in Santiago, Chile, were 223.5 and 597 pg m⁻³, respectively (18). The low concentrations detected in Finokalia are characteristic of the absence of local emission sources.

Acknowledgments

This study was financially supported by the European Commission Environment and Climate Program - ADIOS project (Contract EVK3-CT-2000-00035), the Research Committee of the University of Crete (ELKE), and the Max Plank Institute (MINOS project).

Supporting Information Available

The Quality Assurance Procedure: Table S1 containing the average PAH concentration in the particulate and gas phase and Figure S1 showing backward trajectories of air masses reaching the sampling station of Finokalia (Island of Crete) during the field campaign. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Douben, P. E. T. *Introduction in PAHs: An Ecotoxicological Perspective*; John Wiley & Sons: West Sussex, England, 2003.
- (2) Cotham, W. E.; Bidleman, T. Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in air at an urban and a rural site near Lake Michigan. *Environ. Sci. Technol.* **1995**, *29*, 2782–2789.
- (3) Gigliotti, C. L.; Dachs, J.; Nelson, E. D.; Brunciak, P. A.; Eisenreich, S. J. Polycyclic aromatic hydrocarbons in the New Jersey coastal atmosphere. *Environ. Sci. Technol.* **2000**, *34*, 3547–3554.
- (4) Sofuoglu, A.; Odabasi, M.; Tasdemir, Y.; Khalili, N. R.; Holsen, T. M. Temperature dependence of gas-phase polycyclic aromatic hydrocarbons and organochlorine pesticide concentrations in Chicago air. *Atmos. Environ.* **2001**, *35*, 6503–6510.
- (5) Tsapakis, M.; Stephanou, E. G. Occurrence of gaseous and particulate polycyclic aromatic hydrocarbons in the urban atmosphere: study of sources and ambient temperature effect on the gas/particle concentration and distribution. *Environ. Pollut.* **2005**, *133*, 147–156.
- (6) Gundel, L. A.; Lee, V. C.; Mahanama, K. R. R.; Stevens, R. K.; Daisey, J. M. Direct determination of the phase distributions of semi-volatile polycyclic aromatic hydrocarbons using annular denuders. *Atmos. Environ.* **1995**, *29*, 1719–1733.
- (7) Kavouras, I. G.; Lawrence, J.; Koutrakis, P.; Stephanou, E. G.; Oyola, P. Measurement of particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago de Chile: source reconciliation and evaluation of sampling artifacts. *Atmos. Environ.* **1999**, *33*, 4977–4986.
- (8) Cotham, W. E.; Bidleman, T. F. Laboratory investigations of the partitioning of organochlorine compounds between the gas phase and atmospheric aerosols on glass fiber filters. *Environ. Sci. Technol.* **1992**, *26*, 469–478.
- (9) Tsapakis, M.; Stephanou, E. G. Collection of gas and particle semi-volatile organic compounds: use of an oxidant denuder to minimize polycyclic aromatic hydrocarbons degradation during high-volume air sampling. *Atmos. Environ.* **2003**, *37*, 4935–4944.
- (10) Reisen, F.; Arey, J. Atmospheric reactions influence seasonal PAH and nitro-PAH concentrations in the Los Angeles basin. *Environ. Sci. Technol.* **2005**, *39*, 64–73.
- (11) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Chemistry of the Upper and Lower Atmosphere*; Academic Press: San Diego, 2000.
- (12) Arey, J.; Zielinska, B.; Atkinson, R.; Winer, A. M.; Ramdahl, T.; Pitts, J. N., Jr. The formation of nitro-PAH from the gas-phase reactions of fluoranthene and pyrene with the OH radical in the presence of NO_x. *Atmos. Environ.* **1986**, *20*, 2339–2345.
- (13) Atkinson, R.; Arey, J.; Zielinska, B.; Aschmann, S. M. Kinetics and nitro-products of the gas-phase OH and NO₃ radical initiated reactions of naphthalene-d8, fluoranthene-d10 and pyrene. *Int. J. Chem. Kinet.* **1990**, *22*, 999–1014.
- (14) Atkinson, R.; Arey, J. *Lifetimes and fates of toxic air contaminants in California's atmosphere*, Final report to California Air Resources Board: Sacramento, CA, 1997; Contact No. 93-307.

- (15) Ciccio, P.; Ceninato, A.; Brancaleoni, E.; Frattoni, M.; Zacchei, P.; Miguel, A. H.; Vasconcellos, P. Formation and transport of 2-nitrofluoranthene and 2-nitropyrene of photochemical origin in the troposphere. *J. Geophys. Res.* **1996**, *101*, 19567–19581.
- (16) Ramdahl, T. Polycyclic aromatic ketones in environmental samples. *Environ. Sci. Technol.* **1983**, *17*, 666–670.
- (17) Wilson, N. K.; McCurdy, T. R.; Chuang, J. C. Concentrations and phase distributions of nitrated and oxygenated polycyclic aromatic hydrocarbons in ambient air. *Atmos. Environ.* **1995**, *29*, 2575–2584.
- (18) Tsapakis, M.; Lagoudaki, E.; Stephanou, E. G.; Kavouras, I. G.; Koutrakis, P.; Oyola, P.; von Baer, D. The composition and sources of PM_{2.5} organic aerosol in two urban areas of Chile. *Atmos. Environ.* **2002**, *36*, 3851–3863.
- (19) IPCS Environmental Health Criteria 229. *Selected Nitro- and Nitro-Oxy-Polycyclic Aromatic Hydrocarbons*; International Programme on Chemical Safety, World Health Organization: Geneva, Switzerland, 2003.
- (20) Berresheim, H.; Plass-Dülmer, C.; Elste, T.; Mihalopoulos, N.; Rohrer, F. OH in the coastal boundary layer of Crete during MINOS: Measurements and relationship with ozone photolysis. *Atmos. Chem. Phys.* **2003**, *3*, 639–649.
- (21) Kouvarakis, G.; Tsigaridis, K.; Kanakidou, M.; Mihalopoulos, N. Temporal variations of surface regional background ozone over Crete Island in the southeast Mediterranean. *J. Geophys. Res.* **2000**, *105*, 4399–4407.
- (22) Mihalopoulos, N.; Stephanou, E.; Kanakidou, M.; Pilitsidis, S.; Bousquet, P. Tropospheric aerosol ionic composition in the Eastern Mediterranean region. *Tellus, Ser. B* **1997**, *49*, 314–326.
- (23) Draxler, R. R.; Hess, G. D. *Description of the HYSPLIT_4 modeling system, Tech. Mem. ERL ARL-224*; National Oceanic & Atmospheric Administration: Silver Spring, MD, 1997.
- (24) Tsapakis, M.; Stephanou, E. G. Polycyclic aromatic hydrocarbons in the atmosphere of the Eastern Mediterranean. *Environ. Sci. Technol.* **2005**, *39*, 6584–6590.
- (25) Feilberg, A.; Poulsen, M. W.; Nielsen, T.; Henrik, S. Occurrence and sources of particulate nitro-polycyclic aromatic hydrocarbons in ambient air in Denmark. *Atmos. Environ.* **2001**, *35*, 353–366.
- (26) Mandalakis, M.; Tsapakis, M.; Stephanou, E. G. Optimization and application of high-resolution gas chromatography with ion trap tandem mass spectrometry to the determination of polychlorinated biphenyls in atmospheric aerosols. *J. Chromatogr., A* **2001**, *925*, 183–196.
- (27) Gogou, A. I.; Apostolaki, M.; Stephanou, E. G. Determination of organic molecular markers in marine aerosols and sediments: one step flash chromatography compound class fractionation and capillary gas chromatographic analysis. *J. Chromatogr., A* **1998**, *799*, 215–231.
- (28) Lee, R. G. M.; Hung, H.; Mackay, D.; Jones, K. C. Measurement and modeling of the diurnal cycling of atmospheric PCBs and PAHs. *Environ. Sci. Technol.* **1998**, *32*, 2172–2179.
- (29) Behymer, T. D.; Hites, R. A. Photolysis of polycyclic aromatic hydrocarbons adsorbed on fly ash. *Environ. Sci. Technol.* **1988**, *22*, 1311–1319.
- (30) Kamens, R. M.; Guo, Z.; Fulcher, J. N.; Bell, D. A. Influence of Humidity, Sunlight and temperature on the daytime decay of polyaromatic hydrocarbons on atmospheric soot particles. *Environ. Sci. Technol.* **1988**, *22*, 1228–1234.
- (31) Odum, R. J.; McDow, S. R.; Kamens, R. M. Mechanistic and kinetic studies of the photodegradation of Benzo[a]anthracene in the presence of methoxyphenols. *Environ. Sci. Technol.* **1994**, *28*, 1285–1290.
- (32) Simo, R.; Grimalt, J. O.; Albaiges, J. Loss of unburned-fuel hydrocarbons from combustion aerosols during atmospheric transport. *Environ. Sci. Technol.* **1997**, *31*, 2697–2700.
- (33) Dachs, J.; Glenn, T. R.; Gigliotti, C. L.; Brunciak, P.; Totten, L.; Nelson, E. D.; Franz, T. P.; Eisenreich, S. J. Processes driving the short-term variability of polycyclic aromatic hydrocarbons in the Baltimore and northern Chesapeake Bay atmosphere, USA. *Atmos. Environ.* **2002**, *36*, 2281–2295.
- (34) Kavouras, I. G.; Stephanou, E. G. Organic primary and secondary aerosol constituents in urban, background marine and forest atmosphere: Comparative study of their particle size distribution. *J. Geophys. Res.* **2002**, *107*, D8; DOI: 10.1029/2000JD000278.
- (35) Seinfeld, J. H.; Pandis, S. N. *Atmospheric chemistry and physics: Air pollution to climate*; John Wiley & Sons: New York, 1998.
- (36) Hornbuckle, K. C.; Eisenreich, S. J. Dynamics of gaseous semivolatiles organic compounds in a terrestrial ecosystem - Effects of diurnal and seasonal climate variations. *Atmos. Environ.* **1996**, *30*, 3935–3945.
- (37) Mandalakis, M.; Stephanou, E. G. Study of atmospheric PCB concentrations over the eastern Mediterranean Sea. *J. Geophys. Res.* **2002**, *107*, 4716.
- (38) Simcik, M. F.; Eisenreich, S. J.; Lioy, P. J. Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmos. Environ.* **1999**, *33*, 5071–5079.
- (39) Simcik, M. F.; Zhang, H.; Eisenreich, S. J.; Franz, T. P. Urban Contamination of the Chicago/Coastal Lake Michigan Atmosphere by PCBs and PAHs during AEOLOS. *Environ. Sci. Technol.* **1997**, *31*, 2141–2147.
- (40) Marino, F.; Cecinato, A.; Siskos, P. A. Nitro-PAH in ambient particulate matter in the atmosphere of Athens. *Chemosphere* **2000**, *40*, 533–537.
- (41) Bamford, H. A.; Baker, J. E. Nitro-polycyclic aromatic hydrocarbon concentrations and sources in urban and suburban atmospheres of the Mid-Atlantic region. *Atmos. Environ.* **2003**, *37*, 2077–2091.
- (42) Fan, Z.; Kamens, M. R.; Hu, J.; Zhang, J.; McDow, S. Photostability of Nitro-polycyclic aromatic hydrocarbons on combustion soot particles in sunlight. *Environ. Sci. Technol.* **1996**, *30*, 1358–1364.
- (43) Feilberg, A.; Nielsen, T. Effect of aerosol chemical composition on the photodegradation of nitro-polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* **2000**, *34*, 789–797.
- (44) Vrekoussis, M.; Kanakidou, M.; Mihalopoulos, N.; Crutzen, P. J.; Lelieveld, J.; Perner, D.; Berresheim, H.; Baboukas, E. Role of NO₃ radicals in oxidation processes in the eastern Mediterranean troposphere during the MINOS campaign. *Atmos. Chem. Phys.* **2004**, *4*, 169–182.
- (45) Mandalakis, M.; Berresheim, H.; Stephanou, E. G. Direct evidence for PCB destruction in the subtropical troposphere by OH radicals. *Environ. Sci. Technol.* **2003**, *37*, 542–547.
- (46) Wang, L.; Atkinson, R.; Arey, J. Formation of 9,10-phenanthrenequinone by atmospheric gas-phase reaction of phenanthrene. *Atmos. Environ.* **2007**, *41*, 2025–2035.

ES071160E