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

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Abstract

The decomposition of polycyclic aromatic hydrocarbons (PAHs) by ozone in gas and particles, under high-volume sampling, was studied by using in parallel a conventional device and a device protected with an oxidant denuder. Three different sampling regimes—short and long sampling under high-ozone concentration and long sampling under low-ozone concentration—were selected at three representative sampling sites—a boreal forest, an urban site and a background marine station. The results of our study suggest that most PAHs are susceptible to ozone degradation under high ozone atmospheric concentrations (>50 ppbv) and long sampling times (>24 h). The highest concentration ratio of total PAHs between the two sampling systems was observed under collection conditions of long sampling and high ozone concentration, especially for the gaseous PAHs (up to 2.10). Conversely, long sampling time under low ozone concentration did not affect the concentration of collected PAHs in the gas or particle phase. The most reactive PAHs collected on filters and polyurethane foam were cyclopentane[*cd*]pyrene and pyrene, respectively. The use of an oxidant denuder did not affect the PAH gas–particle distribution study. The slopes m_r and the intercepts b_r of the regression between the log K_p and log P_L^0 did not substantially deviate between the two sampling devices.
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Keywords: Polycyclic aromatic hydrocarbons degradation; High-volume sampling; Sampling artifacts; Ozone denuder; Reactivity classification

1. Introduction

For the past three decades, polycyclic aromatic hydrocarbons (PAHs) have been of environmental concern due to their toxicity and their ubiquitous presence in the environment (IARC, 1984a, 1987). High volume (hi-vol) air sampling has been used extensively in order to collect PAHs in the atmosphere and is still the technique recommended by the United States Environ-

mental Protection Agency (USEPA) for semi-volatile organic compound (SVOC) sampling in ambient air (EPA, 1999). To collect SVOCs in gas and particle phase, ambient air is drawn through a filter (glass fiber (GFF), quartz or Teflon) to retain the particles and then through a sorbing medium such as polyurethane foam (PUF) or Tenax to trap the vapor phase (Cautreels and Van Cauwenberghe, 1978; Fraser et al., 1998; Yamasaki et al., 1982). The pressure drop across the filter or the changes in ambient temperature and SVOC concentrations during sampling can result in a "blow off" of particle associated compounds from the collected particulate matter on the filter (Brorstrom et al., 1983; Eatough et al., 1993; Gundel et al., 1995; Kavouras et al.,

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1999; Peters et al., 2000). Conversely, gaseous SVOCs can be adsorbed ("blow on") onto the filter surfaces (Cotham and Bidleman, 1992; Hart and Pankow, 1994). Although these sampling techniques are suspected of suffering from the above defects they are still used extensively in the field due to their ease of application and robustness.

Another problem of hi-vol air sampling is the potential reactions occurring during the collection of SVOCs, especially PAHs, with air oxidants such as ozone, nitrogen oxides, halogens, nitric acid, hydrogen peroxide, etc. (Peters and Seifert, 1980; Pitts et al., 1980, 1986; Brorstrom et al., 1983; Grosjean et al., 1983; Nielsen, 1984; Arey et al., 1988; Alebic-Juretic et al., 1990). The heterogeneous chemical reactions of PAHs with ozone are considered an important decomposition mechanism for particle phase PAHs in the air (Grosjean et al., 1983; Alebic-Juretic et al., 1990). Grosjean et al. (1983) measured high decomposition rates for benzo [a] pyrene and perylene when these PAHs were exposed to 100 ppb of ozone for a short period of time (3 h). Pitts et al. (1986) observed, in a flow system with a 200 ppb ozone concentration, that from 50% up to 80% of selected PAHs were degraded in 3 h.

Laboratory and field studies have reported that PAHs react with O_3 on GFF filters during high volume sampling to form a large variety of nitro- (Schuetzle, 1983) and oxo- (Pitts et al., 1980) substituted polar products. These observations show that data on PAH air concentrations may suffer from substantial bias (Brorstrom et al., 1983; Peters and Seifert, 1980; Van Vaeck and Van Cauwenberghe, 1984), including underestimation of the atmospheric levels of PAHs and overestimation of the observed mutagenicity of the ambient airborne particles. According to the literature, filter material used for hi-vol sampling can also affect the degradation of PAHs by ozone (Pitts et al., 1986; Grosjean, 1983). Grosjean (1983) observed lower concentrations (by 85–90%) for PAHs collected on glass and quartz filters than those collected on Teflon filters. On the other hand, pyrogenic PAHs are generally associated with soot-rich particles, which protect them from degradation in the atmosphere (Simó et al., 1997). In a recent paper, Schauer et al. (2003) have shown that substantial degradation of 5- and 6-ring PAH can occur during filter sampling and on airborne particles. According to this study, filter reaction artifacts are shown to lead to an underestimation of the actual PAH content of urban air with a near-linear dependence on ozone volume mixing ratio.

Most of the above reports are derived from laboratory experiments, while a few originate from studies under atmospheric conditions. Furthermore, to the best of our knowledge, the potential degradation of gaseous PAHs on PUF has not been studied. The main objective of this study was to investigate the degradation of particulate (on GFF) and gaseous (on PUF) PAHs by ozone, during hi-vol air sampling under real atmospheric conditions. The effect of PAH degradation on their gas/particle partitioning was also studied. For this purpose, sampling was performed by using, simultaneously a high-volume sampler and a second high-volume sampler in front of which an ozone denuder system was added (Geyh et al., 1994; Kavouras et al., 1998). Samples were collected both in urban and rural areas in order to include different regimes of environmental oxidant conditions and aerosol types.

2. Experimental section

2.1. Instrumentation

Sampling was performed by using a high-volume sampler (flow rate $0.5\,m^3\,min^{-1}$) and in parallel a second high-volume sampler in front of which a denuder system was added. This denuder system contained 841 tubes (each tube had a section of $4 \times 4\,mm^2$ and a height of 20 cm) coated with a water/glycerol KNO_2 solution in order to remove ozone and other oxidants (Geyh et al., 1994; Kavouras et al., 1998). The concentration of ozone was measured at the inlet and the outlet of the denuder, so as to estimate its removal efficiency, using an ozone analyzer Dasibi 1080 AH. The efficiency of this device to remove ozone was measured for flow rates ranging from 0.1 up to $1.4\,m^3\,min^{-1}$.

2.2. Sample collection

Sampling of particle and gas PAHs was carried out at three locations: (A) Five samples were collected at a high oxidant capacity remote atmosphere at a background marine station in the Eastern Mediterranean, Finokalia (N35°24′, E25°60′) (Kouvarakis et al., 2000). The duration of the sampling was 24 h and all samples were collected between 15–17 July and 4–5 August 2000. (B) Three 2 h samples were collected at the urban centre of Heraklion (Island of Crete; N35°20′, E25°11′) on the roof of a two-story building, on 23 October 2001. (C) Four 24 h samples were collected between 5 and 9 August 2001 in a boreal forest in Finland, Hyytiälä. Hyytiälä is situated in central Finland (N61°51′, E24°17′), 50 km northeast from the city of Tampere.

2.3. Measurement of the ozone concentration and of meteorological parameters

The ozone concentration and meteorological parameters at Hyytiälä were measured by the Department of Physics of the University of Helsinki (for data see http://www.atm.helsinki.fi/~ppaalto/browse/OSOA/precampaign/database/). At Finokalia and

Heraklion, the ambient ozone concentration was measured using a Dasibi 1080 AH ozone analyzer. For details, see Kouvarakis et al. (2000). Meteorological parameters at Finokalia were measured in situ, while at Heraklion data were kindly provided by the Hellenic Ministry of Environment, Planning and Public Works.

2.4. Sample preparation and analysis

Sample preparation and analysis have been described thoroughly in a previous paper (Gogou et al., 1998). Before sampling, GFFs were heated to 500°C for 12 h. PUF plugs were boiled in water, rinsed with acetone and then Soxhlet extracted twice for 24 h with *n*-hexane (Merck, Suprasolve). PUF plugs were dried in a vacuum desiccator, placed in glass cylinders and sealed in glass jars. The GFFs were wrapped in aluminum foil.

For PAH analysis: GFFs and PUFs were spiked with a mixture of 3 perdeuterated PAHs (d_{10}-phenanthrene, d_{10}-pyrene and d_{12}-perylene) and then extracted into a Soxhlet apparatus for 24 h with *n*-hexane (Merck, Suprasolve). The sample extracts were concentrated by rotary evaporator to 1 ml. The extracts were loaded onto a 1.5 g activated silica gel (100–200 mesh) and eluted with 11 ml *n*-hexane and 15 ml *n*-hexane/toluene (9.5/5.5) under nitrogen pressure (1.4 ml/min). PAHs were collected in the second fraction. Each fraction was concentrated under a gentle stream of nitrogen. Prior to injection, a solution of d_{10}-anthracene was added as a recovery standard.

GC-MS analysis of polyaromatic hydrocarbons was carried out on a Hewlett-Packard mass-selective detector (5891A) operating in SIM mode. The mass spectrometer was directly coupled with a GC equipped with a $30\,m \times 0.25\,mm$, $0.25\,\mu m$ thick film, HP-5MS fused silica column. Field and laboratory blank samples were routinely analyzed in order to evaluate analytical bias and precision. Blank samples (including two pre-cleaned PUF plugs and two GFF filters) were prepared, treated and analyzed in the same manner as the real samples. Blank levels of individual compounds were normally very low and in most cases not detectable. Thus, method detection limits (MDL) were normally based on the instrumental detection limits. The MDL that has been determined for the analysis of PAHs was $0.001\,ng\,m^{-3}$.

3. Results and discussion

3.1. Environmental atmospheric parameters

Table 1 contains the sampling information for the three sampling sites, including the ozone mean concentration, the relative humidity (RH) and the mean temperature for each site. A characteristic seasonal trend of the O_3 concentration was reported for the station of Finokalia, with minimum values recorded during the winter (around 35 ppbv) and a maximum of up to 70 ppbv during the summer (Kouvarakis et al., 2000). Ozone levels measured at Finokalia during the summer are among the highest reported for rural areas in Europe (EMEP, 1998). For the sampling period, ozone concentrations ranged between 55 and 63 ppbv (mean concentration for the sampling period 58.3 ppbv; Table 1). The corresponding variation for the mean daily temperature was between 23.9°C and 26.2°C (mean temperature for the sampling period 25.2°C; Table 1) and the mean RH was 67.1% (Table 1). The corresponding parameters measured at the urban center of Heraklion were very similar to those of Finokalia: ozone concentrations varied from 54 up to 58 ppbv (mean concentration for the sampling period 56.1 ppbv; Table 1), temperature from 20.4°C to 30.1°C (mean temperature for the sampling period 26.4°C; Table 1) and the mean RH was 63.7% (Table 1). Conversely, the Hyytiälä forest was characterized by lower levels of O_3. During the sampling period, the mean daily average ozone concentration varied from 23 up to 32 ppbv (mean concentration for the sampling period 26.9 ppbv; Table 1). The mean temperature at Hyytiälä varied from 14.6°C to 16.4°C (mean temperature for the sampling period 15.5°C; Table 1) and the mean RH was 75.5%.

Table 1
Sampling information and meteorological parameters

Sampling sites	No. of samples	Sampling time (h)	Mean O_3 (ppbv)	Mean RH (%)	Mean T (°C)
Finokalia Background marine station (N35°24′, E25°60′)	5	24	58.3	67.1	25.2
Heraklion Urban area (N35°20′, E25°11′)	3	2	56.1	63.7	26.4
Hyytiälä Boreal forest (N61°51′, E24°17′)	4	24	26.9	75.5	15.5

Table 2

Atmospheric (min–max) concentrations (ng m^{-3}) of PAHs collected in the gas and particle phases at the three sampling sites by the conventional sampler

	Hyytiälä		Finokalia		Heraklion	
	Particulate	Gas	Particulate	Gas	Particulate	Gas
Fluorene	(0.022–0.045)	(0.477–2.13)	(0.017–0.075)	(0.435–3.076)	(0.006–0.029)	(4.487–9.500)
Phenanthrene	(0.030–0.090)	(3.39–6.900)	(0.040–0.107)	(1.370–10.153)	(0.139–0.149)	(15.727–20.264)
Anthracene	(0.003–0.014)	(0.265–2.480)	(0.012–0.029)	(0.257–2.329)	(0.010–0.013)	(1.987–2.791)
Methyl-phenanthrenes	(<0.001[a]–0.040)	(0.919–2.052)	(0.008–0.083)	(0.906–5.278)	(0.077–0.125)	(6.574–7.843)
Fluoranthene	(0.019–0.030)	(0.518–0.821)	(0.018–0.111)	(0.750–3.000)	(0.104–0.908)	(2.479–3.335)
Dimethyl-phenanthrenes	(<0.001–0.025)	(0.324–0.407)	(0.016–0.06)	(0.281–1.188)	(0.050–0.425)	(2.559–3.249)
Pyrene	(0.022–0.067)	(0.485–0.650)	(0.020–0.114)	(0.350–3.857)	(0.093–0.140)	(2.351–3.598)
Methyl-pyrenes	(<0.001–0.025)	(0.057–0.229)	(0.021–0.050)	(0.016–0.582)	(0.036–0.093)	(0.423–0.587)
Retene	(<0.001–0.002)	(0.013–0.034)	(<0.001–0.030)	(0.034–0.115)	(0.008–0.045)	(0.051–0.085)
Cyclopentane[*cd*]pyrene	(<0.001–0.03)	(0.011–0.050)	(0.013–0.070)	(0.050–0.138)	(0.133–0.185)	(0.239–0.360)
Benzo[*a*]anthracene	(0.002–0.007)	(0.013–0.037)	(0.005–0.030)	(0.037–0.267)	(0.116–0.530)	(0.173–0.464)
Chrysene/triphenylene	(0.008–0.037)	(0.025–0.119)	(0.028–0.112)	(0.119–0.916)	(0.343–1.695)	(0.346–1.128)
methylchrysene	<0.001	(<0.001–0.010)	(<0.001–0.010)	(<0.001–0.039)	(0.039–0.109)	(0.022–0.102)
Benzo[*b*]fluoranthene	(0.016–0.035)	(0.003–0.015)	(0.023–0.110)	(0.003–0.014)	(0.263–3.093)	(0.049–0.280)
Benzo[*k*]fluoranthene	(0.008–0.046)	(0.006–0.029)	(0.014–0.123)	(0.002–0.051)	(0.507–3.938)	(0.043–0.192)
Benzo[*e*]pyrene	(0.003–0.013)	(0.003–0.034)	(0.008–0.075)	(<0.001–0.018)	(0.441–2.564)	(0.020–0.296)
Benzo[*a*]pyrene	(0.001–0.007)	(0.003–0.058)	(0.003–0.040)	(<0.001–0.012)	(0.177–1.434)	(0.008–0.129)
Perylene	(<0.001–0.004)	<0.001	(0.004–0.019)	<0.001	(0.034–0.407)	(0.006–0.037)
Anthranthrene	(0.005–0.025)	(0.003–0.014)	(0.015–0.075)	(<0.001–0.027)	(0.298–2.418)	(<0.001–0.003)
Indeno[*1,2,3-cd*]pyrene	(0.019–0.133)	(<0.001–0.035)	(0.017–0.208)	(<0.001–0.083)	(0.877–7.930)	(0.018–0.138)
Benzo[*ghi*]perylene	(0.007–0.040)	(0.004–0.034)	(0.020–0.099)	(<0.001–0.108)	(1.620–10.291)	(0.018–0.213)
Coronene	(<0.001–0.025)	<0.001	(0.009–0.050)	<0.001	(0.093–0.644)	<0.001
Total PAH concentration	(0.236–0.831)	(11.475–15.203)	(0.590–1.749)	(5.316–38.334)	(5.768–37.055)	(44.724–49.596)

[a] MDL.

3.2. PAH in atmospheric gas and particle phase

Twenty two parent and substituted PAHs with a molecular mass from 166 (fluorene) to 300 (coronene) were determined in the particulate phase, while 20 PAHs with a molecular mass 166 (fluorene) to 276 (benzo-[*ghi*]perylene) were analyzed in the gas phase of samples of the three sampling sites (Table 2). All the above samples were collected using the conventional sampling device (see Section 2). Total PAH concentration (Table 2) for all three sites was higher in the gas phase (Hyytiälä: 11.48–15.20 ng m^{-3}; Finokalia: 5.32–38.33 ng m^{-3}; Heraklion: 44.72–49.60 ng m^{-3}) than in the corresponding particle phase (Hyytiälä: 0.24–0.83 ng m^{-3}; Finokalia: 0.59–1.75 ng m^{-3}; Heraklion: 5.77–37.10 ng m^{-3}). The most abundant PAHs in the gas phase at the three sites were fluorene (mean concentration 1.32, 1.46 and 7.22 ng m^{-3} in Hyytiälä, Finokalia and Heraklion, respectively), phenanthrene (mean concentration 5.21, 4.21 and 18.50 ng m^{-3} in Hyytiälä, Finokalia and Heraklion, respectively) and the methyl-phenanthrenes (mean concentration 1.39, 1.83 and 7.37 ng m^{-3} in Hyytiälä, Finokalia and Heraklion, respectively). There are few studies in the literature reporting on the gas phase concentration of PAHs. The concentration ranges of phenanthrene and fluoranthene

(Table 2) in Hyytiälä (3.39–6.90 and 0.52–0.82 ng m^{-3}, respectively) were lower, and in Finokalia (1.37–10.15 and 0.75–3.00 ng m^{-3}, respectively) in the same order of magnitude as those determined by Nelson et al. (1998) in Chesapeake Bay: 0.36–10.8 and 0.10–1.90 ng m^{-3}, for phenanthrene and fluoranthene, respectively. The pyrogenic PAHs benzofluoranthenes (mean concentration 0.06, 0.12 and 3.06 ng m^{-3} in Hyytiälä, Finokalia and Heraklion, respectively), indeno[1,2,3-*c,d*]pyrene (mean concentration 0.07, 0.10 and 3.50 ng m^{-3} in Hyytiälä, Finokalia and Heraklion, respectively) and benzo[*ghi*]-perylene (mean concentration 0.02, 0.06 and 4.57 ng m^{-3} in Hyytiälä, Finokalia and Heraklion, respectively) were the most abundant compounds collected in the particle phase at the three sites. The analysis of PAHs in both gas and particle aerosol phases has shown that the concentration of PAHs may be underestimated if the particulate phase of the ambient aerosol is only measured.

3.3. Evaluation of the ozone removal by the oxidant denuder

The concentration of ozone was measured at the inlet and the outlet of the denuder in order to calculate its removal efficiency. The efficiency of the denuder was
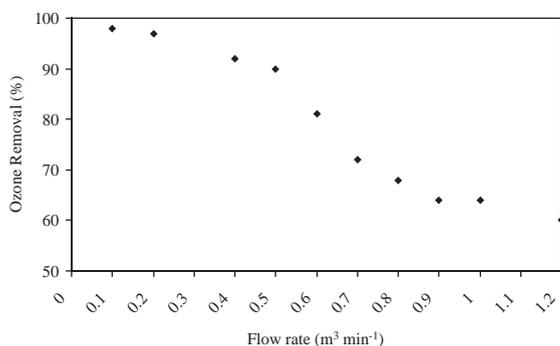
Fig. 1. Denuder efficiency related to different sampling flow rates.

tested for a wide range of flow rates ($0.1–1.4\,m^3\,min^{-1}$). Fig. 1 shows the result of this experiment. It is noticeable that the removal efficiency of the denuder decreases from ca. 98% for a flow rate of $0.1\,m^3\,min^{-1}$, to 60% for a flow rate of $1.2\,m^3\,min^{-1}$. The flow rate we used was $0.5\,m^3\,min^{-1}$, allowing an ozone removal efficiency of ca. 90% (Fig. 1).

3.4. Evaluation of PAH decomposition during sampling

The decomposition of PAHs by ozone (O_3) in the gas and particulate phases, under high-volume sampling conditions, was studied by using simultaneously the conventional device and the device protected with an oxidant denuder as described above (see Section 2). The mass concentration of each PAH in the particle (P) and the gas (G) phase from the conventional sampler was compared to the corresponding mass concentrations in the particle (PD) and gas (GD) phase collected with the sampler protected by the ozone denuder. The decomposition losses due to PAH degradation by ozone on the GFF and the PUF (of the conventional sampling device vs. denuder protected sampling device) was expressed as the ratio of the mass concentrations PD/P and GD/G, respectively. If PD/D and GD/G ratios are substantially higher than 1.0 (e.g. >1.50), we suggest that PAH decomposition is more intense during sampling with the conventional system than with the denuder-protected sampling device. In order to improve the reliability of our results, only those concentrations exceeding 20 times the MDL ($0.001\,ng\,m^{-3}$) were considered for the PAH members present in the particle and/or gas phase.

The PD/P and GD/G mean values for the total concentration of all measured PAHs were, at Finokalia (higher ozone concentration and long sampling time), 1.40 (±0.14) and 2.10 (±0.28), respectively. The corresponding mean values observed at Heraklion (higher ozone concentration and short sampling time)

were 1.20 (±0.90) for PD/P and 1.20 (±0.50) for GD/G and at Hyytiälä (lower ozone concentration and long sampling time) 1.00 (±0.13) for PD/P and 1.00 (±0.15) for GD/D. The results from the measurements at the three sites show that long sampling times under relatively high ambient ozone concentration may have a significant effect especially on the gas phase concentration measurement.

The total concentration of PAHs in the gas phase was seriously underestimated (up to 50%) at Finokalia by using the conventional sampling device without protection from the ambient oxidants. This effect was not observed at Hyytiälä, where relatively low ambient ozone concentrations were measured and was less pronounced (up to 17%) or at Heraklion where the sampling time was short; although the average ambient ozone concentration was as high as at Finokalia. Regarding the total concentration of PAHs in the particle phase, the sampling artifact without the denuder was less marked. The largest difference between the two sampling systems concerning the total concentration of PAHs in the particle phase was observed again at Finokalia (up to 28%) in comparison to Heraklion (up to 17%). Total concentration of PAHs measured at Hyytiälä in the particle phase apparently did not differ between the two sampling systems.

Beyond the observed differences between the three sites, a noticeable difference was also observed between the PD/P and GD/G ratios of the total PAH concentrations at Finokalia. PD/P values (mean 1.40) were lower than the corresponding GD/G values (mean 2.10). This observation shows that the reactions of PAHs with ozone on the PUF are more effective than on GFF. This is also probably due to the protection offered to PAHs by soot carbon and the other micro-constituents of the aerosol matter towards degradation by oxidants (Alebic-Juretic et al., 1990; Simó et al., 1997).

A more detailed study of the differences in concentration, when individual PAH members are considered, between the two sampling systems is presented in Fig. 2. The highest (>1.5) average PD/P values were observed at Finokalia for cyclopenta[cd]pyrene (2.04), dimethylphenanthrenes (1.86), benzo[a]pyrene (1.74), anthranthene (1.72) and pyrene (1.67) (Fig. 2). Van Vaeck and Van Cauwenberghe (1984), by exposing diesel particulate matter to ppm ozone levels, showed that benzo[a]pyrene and benzo[a]anthracene reacted faster than benzo[e]pyrene and chrysene, respectively. They assumed that under hi-vol sampling, some transformation of PAHs may occur on the filter during sample collection. This assumption is proved by our experiment at Finokalia, where PD/P ratios for benzo[a]pyrene and benzo[a]anthracene were significantly higher than the corresponding ratios for benzo[e]pyrene (1.08) and chrysene (1.22) (Fig. 2). The average PD/P ratios observed at Heraklion for benzo[a]pyrene (2.24), pyrene

(1.81), anthranthrene (1.78), and cyclopenta[cd]pyrene (1.74) also confirm their reactive character in comparison to benzo[e]pyrene (1.19) and chrysene (1.05) (Fig. 2). On the basis of this observation, it should be noted that benzo[a]pyrene, pyrene, anthranthene, and cyclopenta[cd]pyrene in the particle phase can be easily degraded on filters even with short sampling times.

Although the estimated half-lives (measured in the laboratory by using an ozone concentration of 50 ppb) for the most reactive PAHs such as benzo[a]pyrene, benzo[a]anthracene and perylene are <1 h (Alebic-Juretic et al., 1990) in Heraklion (2 h of sampling), no such drastic losses were observed. This probably occurs because the collection of PAHs on the filter is a continuous process and only a low proportion of the collected PAHs could react with the O_3 within the two sampling hours. Pitts et al. (1986) have also shown that the most reactive PAH, both on filter and ambient air particulate organic matter (exposed to 200 ppb ozone for 3 h), were benzo[a]pyrene, benzo[a]anthracene and pyrene. The same authors noticed that the degradation of the above PAHs was much lower when the RH increased from 1% to 50%.

In Hyytiälä, only the anthranthrene PD/P ratio (1.59, Fig. 2) indicated that degradation may occur during sampling even with long collection times (Table 1). Under these conditions, even the reactive PAHs such as benzo[a]pyrene, benzo[a]anthracene, pyrene and cyclopenta[cd]pyrene gave PD/P ratios <1.40 (Fig. 2). The differences between the three sampling sites should be interpreted in view of their differences in ozone concentrations and sampling times and not in RH (Table 1). Peters and Seifert (1980) established a strong effect of the ozone ambient concentration (from 15 up to 50 ppbv) on the losses of benzo[a]pyrene during high volume sampling. For most PAHs, the GD/G values were substantially higher than the corresponding PD/P (Fig. 2). Pyrene (3.77), benzo[a]anthracene (3.05), fluorene (2.86), cyclopenta[cd]pyrene (2.64), anthracene (2.49) and other PAHs such as dimethyl-phenanthrenes, methyl-phenathrenes and fluoranthene gave average GD/G ratios >2 in all Finokalia samples (Fig. 2). The high reactivity of pyrene on the PUF might be explained by the presence of humidity on its surface as predicted by Butkovik et al. (1983) on the basis of the kinetic experiment of PAH ozonolysis in aqueous solutions. The lower GD/G average ratios (mostly <1.50, Fig. 2) observed at Heraklion and Hyytiälä compared with Finokalia reflect the differences in the collection time (Finokalia and Heraklion) and in the O_3 concentration (Finokalia and Hyytiälä) between the sampling sites.

By using PD/P and GD/G ratios from the samples collected at Finokalia, the relative reactivity (RR) of PAHs, with respect to degradation on GFF and PUF, was calculated as the ratio of the PD/P and GD/G value of each compound to the corresponding PD/P and GD/

G ratio of the most reactive PAH (Table 3). The RR values calculated in the present study are mostly in accordance with those proposed by Nielsen (1984) in a classification scheme for the reactivity of key PAHs in electrophilic reactions. Although Nielsen's experiments concerned the relative rates of nitration in a mixture of polar solvents (water–methanol–dioxane), they have also been used to predict the reactivity scale of particle-associated PAHs during heterogeneous reactions (Nielsen, 1984). The most reactive PAHs in the particle phase were cyclopenta[cd]pyrene (1.00), di-methyl-phenanthrenes (0.91), benzo[a]pyrene (0.86), anthranthene (0.84), and pyrene (0.82) (Table 3). In the gas phase, the most reactive PAHs were pyrene (1.00), benzo[a]anthracene (0.81) and cyclopenta[cd]pyrene (0.70) (Table 3). Fraser et al. (1998), in a field study, also confirmed the high reactivity of alkyl-substituted PAHs. A reactivity scale similar to that observed for particulate PAHs in our study has been reported for the heterogeneous PAH degradation with ozone on a silica gel carrier (Alebic-Juretic et al., 1990) and on diesel exhaust particulate matter (Van Vaeck and Van Cauwenberghe, 1984).

3.5. Influence of degradation sampling artifact on PAH gas–particle distribution

The distribution of SVOCs between the gas (A) and the particulate (F) phase is one of the most important factors controlling their removal mechanisms and residence time in the atmosphere (Pankow and Bidleman, 1992). Useful information regarding the partitioning can be derived from the regression curve between the $\log K_p$ and $\log P_L^0$ according to the equation:

$$\log K_p = m_r \log p_L^0 + b_r.$$

The slope m_r and the intercept b_r are characteristic parameters for the sorption process and can reflect the sorbents properties (Pankow and Bidleman, 1992; Goss and Schwarzenbach, 1998). It has been suggested that at equilibrium, the slope for either adsorption or absorption should be close to −1 (Pankow and Bidleman, 1992). Since slopes that deviate from −1 have been determined in field measurements, intense debate has occurred concerning the range of values that slopes can take and the reasons why slopes m_r can deviate from −1 (Pankow and Bidleman, 1992; Goss and Schwarzenbach, 1998; Simcik et al., 1998). Shallow slopes observed in studies, according to Pankow and Bidleman (1992), may be due to: (a) increasing or decreasing atmospheric concentrations or temperature over the measurement period; (b) the presence of nonexchangeable compounds on or in the particles; (c) differences in the "excess" heat of desorption (heat of desorption minus heat of volatilization) of the various compounds; (d) slow adsorption kinetic when relatively clean particles enter
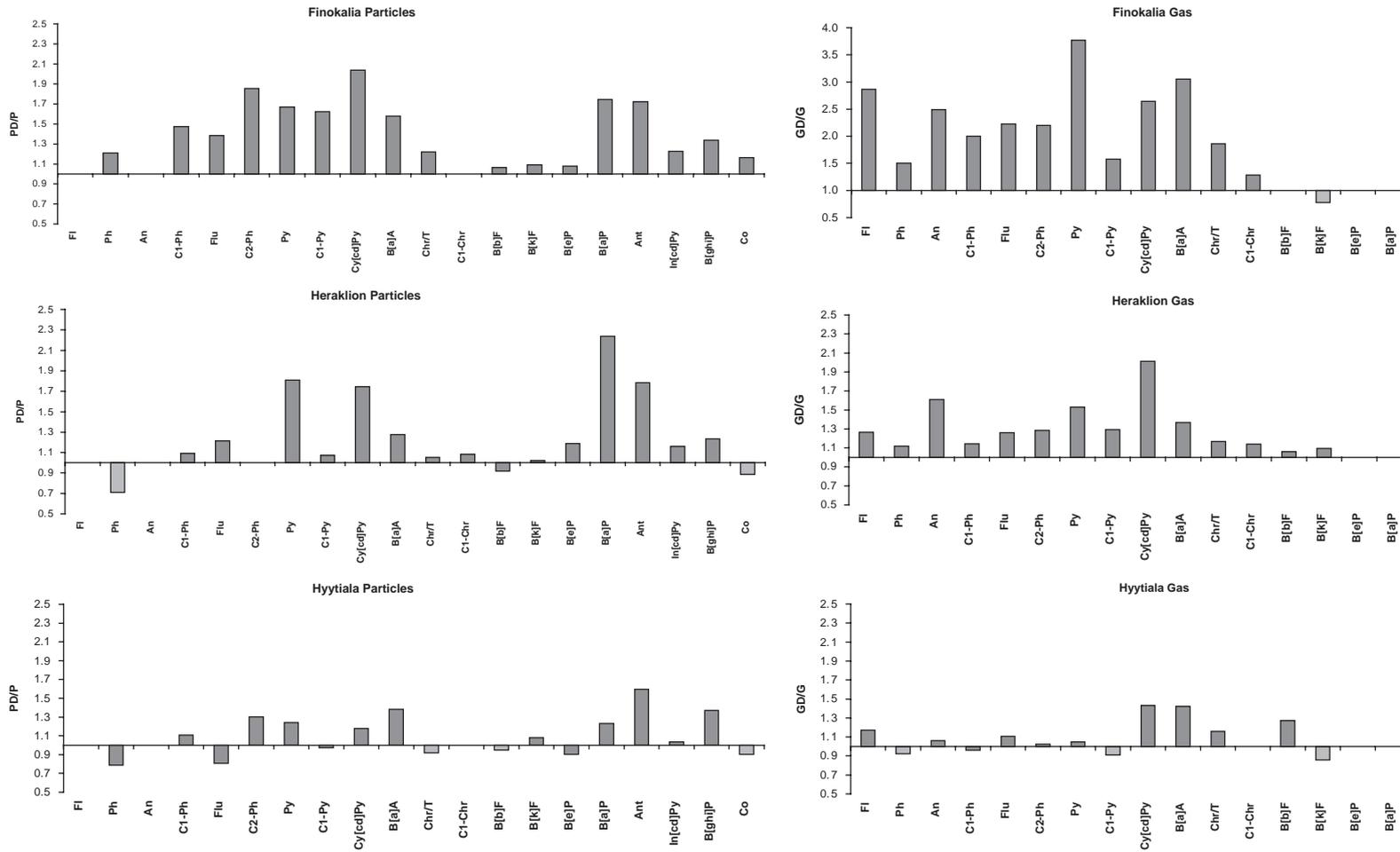
Fig. 2. Average ratios of concentrations measured by the two sampling systems for particulate (PD/P) and gaseous (GD/G) PAHs. Fluorene (Fl); Phenanthrene (Ph); Anthracene (An); Methyl-phenanthrene (C1-Ph); Fluoarenthene (Flu); Dimethyl-phenanthrene (C2-Ph); Pyrene (Py); Methyl-pyrenes (C1-Py); Cyclopentane[*cd*]pyrene (Cy[*cd*]Py); Benzo[a]antrhacene (B[*a*]A); Chrysene/triphenylene (Chr/T); Methylchrysene (C1-Chr); Benzo[*b*]fluoranthene (B[*b*]F); Benzo[k]fluoranthene (B[*k*]F); Benzo[*e*]pyrene (B[*e*]P); Benzo[*a*]pyrene (B[*a*]P); Anthanthrene (Ant); Indeno[1,2,3-*cd*]pyrene (In[*cd*]Py); Benzo[*ghi*]perylene (B[*ghi*]P); and Coronene (Co).

Table 3
RR of PAHs in relation to reactions with ozone on glass fiber filter and polyurethane foam during high-volume sampling

Compound	RR$_{Particles}$[a]	RR$_{Gas}$[b]	Reactivity scale[c]
Cyclopentane[*cd*]pyrene	1.00	0.70	II
Dimethyl-phenanthrenes	0.91	0.58	
Benzo[*a*]pyrene	0.86	NR	II
Anthranthrene	0.84	NR	II
Pyrene	0.82	1.00	III
Methyl-pyrenes	0.80	0.42	
Benzo[*a*]antrhacene	0.77	0.81	III
Methyl-phenanthrenes	0.72	0.53	
Fluorene	0.68	0.59	V
Benzo[*ghi*]perylene	0.66	NR	III
Indeno[*1,2,3-cd*]pyrene	0.60	0.49	V
Chrysene/triphenylene	0.60	0.49	IV
Phenanthrene	0.59	0.40	V
Coronene	0.57	NR	IV
Benzo[*k*]fluoranthene	0.54	0.21	V
Benzo[*e*]pyrene	0.53	NR	IV
Benzo[*b*]fluoranthene	0.52	NR	V
Fluoranthene	NR[d]	0.76	
Antrhacene	NR	0.66	II
Methyl-chrysene	NR	0.34	

[a] RR$_{particles}$ = [(PD/P)$_A$/(PD/P)$_X$].
[b] RR$_{gas}$ = [(GD/G)$_A$/(GD/G)$_X$]; A: PAHs with the highest PD/P or GD/G ratio (Refer to Fig. 2).
[c] Adapted from Nielsen (1984).
[d] NR: not reported (concentration < 20 × MDL).

Table 4
Comparison of m_r, b_r and R^2, for the regression $\log K_p = m_r \log P_L^0 + b_r$

	m_r	b_r	R^2
Heraklion			
Conventional sampler	(−0.84 to −0.89)	(−6.77 to −7.08)	(0.95–0.98)
Denuder sampler	(−0.88 to −0.90)	(−7.00 to −7.29)	(0.95–0.99)
Finokalia			
Conventional sampler	(−0.47 to −0.83)	(−4.44 to −6.05)	(0.74–0.84)
Denuder sampler	(−0.50 to 0.79)	(−4.85 to −6.06)	(0.74–0.88)
Hyytiälä			
Conventional sampler	(−0.41 to −0.59)	(−4.35 to −4.90)	(0.65–0.92)
Denuder sampler	(−0.43 to −0.55)	(−4.44 to −5.23)	(0.68–0.92)

See Pankow and Bidleman (1992), measured with the two samplers (conventional and denuder-protected) at the three sampling sites.

a contaminated atmosphere; (e) slow desorption kinetics when relatively contaminated particles are either emitted to a relatively clean atmosphere or diluted by less contaminated air; (f) sampling artifacts; and (g) none-quilibrium. However, Goss and Schwarzenbach (1998) and Simcik et al. (1998) suggested that slopes m_r can easily deviate from −1 even in the case when equilibrium sorption processes occur and sampling artifacts are negligible.

The constants m_r and b_r measured at the three sites are reported in Table 4. The slopes m_r of PAHs for Heraklion (−0.84 to −0.89) were closer to −1 than for Finokalia (−0.47 to −0.83) and Hyytiälä (−0.41 to −0.59) (Table 4). Heraklion slopes were closer to −1 than those calculated by Lohmann et al. (2000) in Manchester (−0.62 to −0.72).

Chemical reactions of PAHs with oxidants during high-volume sampling have been suspected as a potential source of artifacts (Pankow and Bidleman, 1992). In the present study, an agreement was observed between m_r and b_r values measured with the two sampling systems at all sites. At Hyytiälä, due to low ambient

ozone levels (Table 1) the differences in concentration between the two sampling systems were negligible. Thus, one should not expect that degradation during sampling affects the study of gas–particle partitioning of PAHs. In Heraklion, where collection of PAHs was performed under short sampling time (2 h), less artifacts due to degradation through oxidation reactions were observed, even though ozone concentrations were the highest (Table 1). Therefore, a difference between the two sampling systems in gas–particle partitioning study was not observed. At Finokalia, where a substantial degradation of some reactive PAH was observed, the differences in the slope (m_r) and intercept (b_r) were not statistically significant (Table 4). The interpretation we propose for this observation is that degradation (due to reactions with ozone) for most PAHs on the filter and the foam were comparable (Fig. 2) and consequently, the $\log K_p$ for individual PAHs did not change significantly.

4. Conclusions

The decomposition of PAHs by ozone in the gas and particle phases, under high-volume sampling, was studied by using a conventional device and a device protected with an oxidant denuder simultaneously. Three different sampling regimes—namely, short (urban site, Heraklion on the island of Crete) and long (marine background site, Finokalia on the island of Crete) sampling under relatively high-ozone concentrations and long sampling under relatively low-ozone concentrations (boreal forest, Hyytiälä in Finland)—were selected. The results from the measurements have shown that long sampling times under high ambient ozone concentration may have an obvious effect, especially on the gas-phase concentration measurement.

The total concentration of PAHs in the gas phase was seriously underestimated (up to 50%) at Finokalia by using the conventional sampling device without protection from the ambient oxidants. This effect was not observed at Hyytiälä where lower ambient ozone concentrations were measured and was less pronounced (up to 17%) at Heraklion where the sampling time was very short. Regarding the total concentration of PAHs in the particle phase, the sampling artifact when using the conventional sampling system without the denuder, was less marked. The highest difference between the two sampling systems, concerning the total concentration of PAHs in the particle phase, was observed again at Finokalia (up to 28%) in comparison to Heraklion (up to 17%). Total concentration of PAHs measured at Hyytiälä in the particle phase did not apparently differ between the two sampling systems. We also observed that the reactions of PAHs with ozone on the PUF are more effective than on GFF. The use of an oxidant denuder did not affect the PAH gas–particle distribution. The slopes m_r and the intercepts b_r of the regression between the $\log K_p$ and $\log P_L^0$ did not substantially deviate between the two sampling devices.

Our data have significant toxicological and chemical implications regarding the composition of PAHs sampled under typical high-volume conditions and high-oxidant levels: compounds such as anthanthrene, anthracene, benzo[*a*]pyrene, cyclopenta[*cd*]pyrene and benzo[*a*]anthracene, classified by IARC as probable or possible human carcinogens, may be seriously underestimated.

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