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ATMOSPHERIC CONCENTRATIONS and
DRY DEPOSITION RATES of POLYCYCLIC
AROMATIC HYDROCARBONS (PAHs) for
TAMPA BAY, FLORIDA, USA

FINAL REPORT

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Atmospheric concentrations and dry deposition rates of polycyclic aromatic hydrocarbons (PAHs) for Tampa Bay, Florida, USA

Noreen Poor^{a,*}, Raphael Tremblay^b, Heidi Kay^a, Venkat Bhethanabotla^c,
Erick Swartz^d, Mark Luther^e, Scott Campbell^c

^aCollege of Public Health, University of South Florida, 13201 Bruce B. Downs Blvd., Tampa, FL 33612, USA

^bRosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway Miami, FL 33149, USA

^cCollege of Engineering, University of South Florida, 4202 E. Fowler Ave., Tampa, FL 33620, USA

^dCBIRF (Battelle), 101 Strauss Ave, Bldg 109, Indian Head, MD 20640, USA

^eOcean Modeling and Prediction Laboratory, College of Marine Science, University of South Florida, 140 7th Avenue S., St. Petersburg, FL 33701, USA

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Abstract

Sampling of 16 USEPA priority polycyclic aromatic hydrocarbons (PAHs) at the Gandy Bridge monitoring site between May and August 2002 provided preliminary ambient air concentrations and dry deposition rates for Tampa Bay. The HiC-IOGAPS dramatically improved the recovery of lower molecular weight gas and particle PAHs, as evidenced by the recoveries of PAHs in back-up denuders and filter packs. Total PAH (gas + particle) concentrations ranged from 80 to 190 ng m⁻³. Concentrations of naphthalene, acenaphthene, fluorene, phenanthrene, fluoranthene, and pyrene were consistently higher than concentrations of the remaining 10 PAHs. Assuming an unidirectional flux of these compounds from air to water, the estimated total (gas + particle) dry deposition flux was 11.5 μg m⁻² d⁻¹, or 6.7 μg m⁻² d⁻¹ if naphthalene is excluded.

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1. Introduction

PAHs distributed in the environment are of pyrolytic, petrogenic and diagenic origin (Soclo et al., 2000) related to the cycling of organic matter by natural and human-assisted processes. Anthropogenic pyrolysis of fossil fuels, for example, occurs in virtually every human

endeavor: transportation, power production, manufacturing, agriculture and recreation.

For some watersheds, atmospheric deposition represents a significant input to the total surface water PAH burden, and may be independent of adjacent land use (Buehler et al., 2001; Fernandez et al., 2000; Rose and Rippey, 2002). Atmospherically derived PAHs in marine sediments have been linked to industrial sources (Simpson et al., 1998; Soclo et al., 2000), but Van Metre et al. (2000) showed that surface water sediment PAH concentrations tracked increases in “vehicle miles

*Corresponding author. Fax: +1-813-974-4986.

E-mail address: npoor@hsc.usf.edu (N. Poor).

traveled". Recently, Dickhut et al. (2000) and Golomb et al. (2001) identified gasoline and diesel vehicles as major contributors to atmospheric deposition of PAHs to the Chesapeake Bay, Massachusetts Bay, and Casco Bay, respectively. O'Malley et al. (1996) postulated that surface runoff of vehicular emissions and crankcase oil represented most of the PAH input to St. John's Harbor in Newfoundland. Sediment concentrations of polycyclic aromatic hydrocarbons (PAHs) are high enough in some segments of Tampa Bay to pose an environmental health threat (McConnell et al., 1996), but PAH loading rates from point sources, urban runoff, and agricultural runoff to Tampa Bay have yet to be determined.

Our study has as its goals to better characterize the PAH exchange between the atmosphere and estuary, and to identify atmospheric sources of PAHs that contribute to this exchange. We present the PAH concentrations from bayside ambient air monitoring with an integrated organic sampler that effectively segregates gas and aerosol phase PAHs (Gundel et al., 1995; Gundel and Lane, 1998), and from these concentrations estimate the PAH dry deposition rates, assuming an unidirectional flux from air to water. Deposition velocities for each PAH were estimated with an Internet-accessible NOAA buoy model, modified to include the surface transfer of a gas of limited water solubility (Bhethanabotla, 2003).

2. Materials and methods

2.1. Field sampling

A high capacity integrated organic gas and particle sampler (HiC-IOGAPS; Model 3000DB, URG Corp., Chapel Hill, NC), described by Swartz et al. (2003a, b), was installed on the seawall at an atmospheric deposition monitoring site near the eastern end of the Gandy Bridge, Tampa, and adjacent to Tampa Bay, FL (27.89°N, 82.54°W). The inlet height was 2 m above the sea wall.

Although the HiC-IOGAPS was located 180 m north of a major roadway, it is unlikely that the measurements were affected by the nearby traffic. In a separate study, Kenty et al. (in preparation) measured NO and NO₂ concentrations near the Gandy Bridge. One NO_x monitor was located 45 m south of the road while the other was 150 m north of the road and 30 m south of the HiC-IOGAPS. When winds were from the south there was no significant difference between the concentrations measured by the two NO_x monitors, suggesting that dispersion of NO and NO₂ to background levels occurred within a distance of 150 m.

The sampler consisted of an inverted open-pipe Teflon-coated inlet, a Teflon-coated cyclone with a 2.5 μm cut-point at 91 L min⁻¹, two 8-channel denuders

and a filter pack in series. The filter pack included a 90-mm quartz (Pallflex) filter to collect organic aerosol, followed by three subsequent 90-mm XAD-4 impregnated quartz (Pallflex) filters to trap semi-volatile organic compounds that degassed from filters and PAHs not trapped in the denuders. The XAD-4 coated denuders and XAD-4 impregnated filters were prepared in the USEPA Office of Research and Development National Exposure Research Laboratory, Research Triangle Park, NC, by the procedure of Gundel et al. (1995) in March 2002, and delivered to Tampa, FL, with the HiC-IOGAPS in April 2002.

Typical collection times were 24 h, beginning at 0700 Eastern Standard Time. Flow rates were computer controlled and calibrated with an NIST-traceable laminar flow element prior to deployment. Samples were collected between May and August 2002.

Denuders and filters were removed and replaced in the field. Upon retrieval, the denuders were sealed on both ends with Teflon-lined caps and stored at 4 °C until extracted. Internal filter parts were cleaned with ethanol and dried with a Kimwipe[®] prior to re-loading with fresh filters. Unloaded filters were returned within 2 h to the laboratory in pre-cleaned amber storage bottles with Teflon caps and stored at 4 °C until extracted.

2.2. Laboratory analyses

All glassware was pre-cleaned with dichloromethane (MeCl₂). Glass storage vials were heated in a muffle furnace to 500 °C for 2 h, and sealed after cooling. Storage bottles were 125-mL brown borosilicate wide mouth bottles with Teflon-lined caps. Between each processing step, samples and sample extracts were equilibrated to room temperature (~20 °C). Each denuder was extracted three times (2 × 3 = 6) and each filter once (4 × 1 = 4), and these 10 extracts were analyzed separately. Repeated denuder extracts assured complete analyte recovery from the wash-roll method as compared to established methods of Soxhlet extraction for the filters. On the average 91% (65–100%) of a PAH trapped in a denuder was recovered in the first two extractions.

Extraction and concentration of PAHs from the denuders and filters followed that of Swartz et al. (2003a, b), except that we used a single solvent, MeCl₂, instead of a mixture. The denuder lower (exit) cap was replaced with a Teflon-lined cap containing a Swagelok[®] fitting, and the upper (inlet) cap was removed. The inlet side of the denuder below the epoxy beads was spiked with 0.100 mL of NIST SRM 2270 perdeuterated recovery standards (51.2 μg mL⁻¹ naphthalene-*d*₈; 5.06 μg mL⁻¹ acenaphthene-*d*₁₀, 49.5 μg mL⁻¹ pyrene-*d*₁₀, 24.80 μg mL⁻¹ benzo(*a*)pyrene-*d*₁₂, 23.49 μg mL⁻¹ benzo(*g,h,i*)perylene-*d*₁₂ and 19.86 μg mL⁻¹ perylene-*d*₁₂ in hexane/toluene). The inlet was covered with a clean

Kimwipe[®] and the spiked sample was allowed to dry. Once dry, 120 mL of MeCl₂ was poured into the denuder. The inlet cap was replaced and the denuder was slowly inverted twice, with intermittent pressure released through the Swagelok[®] fitting. The denuder was then rolled across the lab bench a pre-defined length to obtain 60 complete revolutions. This technique was repeated twice more, each time with 120 mL of MeCl₂.

The denuder extract was filtered through a 0.45 µm pore size Teflon filter (unlaminated Fluoropore, FHUP04700, Millipore Corp.) to remove any sloughed XAD-4 particles, then transferred to a 500-mL round-bottom flask and spiked with 1.00 mL of 15 µg mL⁻¹ *n*C₂₄D₅₀ in MeCl₂. Loss of the non-volatile *n*C₂₄D₅₀ was to serve as an estimate of the volume reduction losses. Extracts were immediately concentrated.

Quartz or XAD-4 coated quartz filters were individually placed into a cellulose thimble after spiking with 0.100 mL of NIST SRM 2270 perdeuterated recovery standards described above. Filter storage bottles were rinsed twice with 25 mL of MeCl₂ and these washes were added to the solvent compartment of each Soxhlet extraction system. Another 100 mL of MeCl₂ was added to each 250-mL solvent extraction flask. The Soxhlet extraction system was operated for 8 h at 4 cycles h⁻¹. After cooling, the extract was decanted into a labeled 250-mL rotary evaporation (Rotovap) flask, spiked with 1.00 mL of 15 µg mL⁻¹ *n*C₂₄D₅₀ in MeCl₂, partially rotary-evaporated, sealed and stored at 4 °C. Another 150 mL of MeCl₂ was added to the Soxhlet solvent extraction flask and the process was repeated. After cooling, the second extract was combined with the first. The Soxhlet extraction flask was rinsed with two 10-mL aliquots of MeCl₂, which were added to the Rotovap flask.

A Rotovap system was employed to concentrate the PAH extracts. To minimize the concentration time, the water bath was pre-heated to 60 °C (at 1 atm, bp of MeCl₂ is 40 °C while that of naphthalene is 218 °C) and the antifreeze coolant was chilled to 10 °C. Combined extract volumes were concentrated to less than 1.0 mL with the Rotovap, and then allowed to cool to room temperature. The Rotovap was operated without a vacuum at 1 rev s⁻¹ for an average of 10 min.

Concentrated extract was transferred to a GC/MS sample vial using a disposable glass pipette. Flask walls were rinsed twice with 0.5 mL of MeCl₂ and the rinses added to the sample vial. The concentrated extract was further evaporated to 0.5 mL with ultra high purity N₂ and spiked with 0.500 mL of 1.84 µg mL⁻¹ perdeuterated *p*-terphenyl in MeCl₂, intended as an internal injection standard to correct for variations in the GC/MS injection volume. The vial was stored at -15 °C until GC/MS analysis.

Shortly after sampling began, the University of South Florida (USF) College of Public Health GC/MS

developed a pump problem that took 6 months to repair. As a consequence, PAH concentrations in the extracts were determined by GC/MS in the laboratories of the University of Miami Rosenstiel School of Marine and Atmospheric Sciences (RSMAS, Miami, FL). Of the analytical spikes added to the denuders and filters by USF, three overlapped the spikes used by the RSMAS: naphthalene-*d*8, acenaphthene-*d*10 and perylene-*d*12.

The extracts were delivered to the University of Miami packed on dry ice. The XAD-4 filter samples were passed through a 0.2-µm Teflon syringe filter (Acrodisc CR PTFE) to remove suspended particles. No additional denuder or filter extract clean-up was done prior to injection on the GC/MS. This represented a trade-off between higher detection levels and potential loss of sample during purification.

Extracts were analyzed using a Hewlett-Packard (HP) 6890 Plus series GC coupled to an HP 7973 MS. Analytes were separated using a 60-m × 0.25-mm id RTX-5MS column with a 10-m guard column (Restek Corporation, # 12626-127). One-µL volumes were injected into an HP Programmable Temperature Vaporizing inlet (PTV) in pulsed splitless mode. The inlet temperature was held at 45 °C for 0.10 min and then ramped to 300 °C at 700 °C/min. The oven temperature was held at 45 °C for 1.50 min and then ramped to 300 °C at 12 °C/min. After a 7.00 min hold, the oven was ramped to a final temperature of 330 °C at the same rate and held for 8.00 min. The total run time per analysis was 43 min.

The MS was operated in selected ion mode. Peak identification was based on comparison with retention time and mass spectra of authentic standards: one ion and retention time were used to identify the perdeuterated compounds, while two ions and retention time were used to identify the non-perdeuterated compounds. Quantification was done using the most abundant ion.

External calibration curves were built using perdeuterated and non-perdeuterated PAH standards (Absolute Standards Inc., #70001 and #10009). All calibration curve standards were prepared in HR-GC grade MeCl₂ (EMD Chemicals Inc., # DX0837-1). Calibration curves for the perdeuterated PAHs were built using at least four different concentrations ranging from 100 to 5000 ng mL⁻¹. Calibration curves for the PAHs were also built with at least four different concentrations from 1 to 2000 ng mL⁻¹. All sample concentrations were within calibration ranges. Standards were analyzed following 7–9 samples to insure system integrity.

Lower detection levels were below 0.002 ng m⁻³, based on GC/MS limits of 0.1–1 µg L⁻¹ of extract (e.g., 0.002–0.02 µg m⁻³) for each analyte. Lower detection levels were calculated as 3 times the standard deviation of the sample concentrations, based on sample replicates and sample concentrations near the expected detection limit of the GC/MS. One denuder, quartz

filter, and XAD-4 coated filter were processed as lab blanks after preparation for deployment. For a field blank, we used a set of denuders and filters that were deployed in the HiC-IOGAPS for 24 h during a period in which the pump did not run. We present in Table 1 the equivalent ambient air concentrations of the USEPA priority PAHs seen on the laboratory and field blanks, which serves as a method detection level. PAH blank concentrations were not subtracted from the sample concentrations.

Recoveries of perdeuterated standards from denuders and filter packs are summarized in Table 2, and were used in calculating the ambient air PAH concentration from extract concentrations: naphthalene- d_8 for naphthalene, perylene- d_{12} for benzo(*k*)fluoranthene and benzo(*a*)pyrene, and acenaphthene- d_{10} for the remaining 13 PAHs. The recoveries increased with increasing molecular weight, and were lowest for the filter extracts—likely a consequence of the additional filtration step.

After a review of the GC/MS chromatograms, calibration curves, check standards and recoveries of perdeuterated compounds on the laboratory blanks, our best explanations for the high % recovery of perylene- d_{12} are twofold: one, imprecision in delivering the 0.100 mL spike; and two, partial evaporation of the solvent and lower molecular weight PAHs from the NIST SRM 2270 during storage, which concentrated the perylene- d_{12} .

The Environmental Protection Commission of Hillsborough County (EPCHC) provided the PM_{2.5} concentration data from a collocated sequential dichotomous

PM sampler. Poor et al. (2002) details the protocols for PM monitoring. The daily integrated PM_{2.5} concentrations were used to calculate the PAH mass per μg of particles (C_p).

2.3. Atmospheric deposition meteorology and modeling

The dry deposition rate (F) of each PAH was calculated as the product of the ambient air concentration (C) and deposition velocity (v_d), with units of $\text{ng m}^{-2} \text{s}^{-1}$, ng m^{-3} , and m s^{-1} , respectively (Eq. (1)):

$$F = C v_d. \quad (1)$$

For deposition velocity calculations, we used 6-min averaged measurements of air temperature, water temperature, 5-m wind speed, and 5-m relative humidity from the USF College of Marine Science (COMS) monitoring station located in Tampa Bay, which is 27 km south southwest of the Gandy Bridge air monitoring site (27.66°N, 82.59°W). This station collects, over water, atmospheric turbulence data and is part of the Bay Regional Atmospheric Chemistry Experiment (BRACE) sponsored by the Florida Department of Environmental Protection (FDEP). Data were downloaded from the USF COMS website (Luther, 2003).

Dry deposition velocities for gas-phase PAHs were calculated with the USF College of Engineering website version of the NOAA buoy model/Gas model (Bhethanabotla, 2003). This model extends the iterative bulk exchange model of Valigura (1995) developed for water-soluble gases (e.g., sulfur dioxide and nitric acid) to

Table 1
Laboratory and field blank PAH concentrations, expressed as ng m^{-3}

	Denuder	Lab blanks		Field blanks	
		Quartz filter	XAD-4 filter	Total denuders	Total filters
Naphthalene	0.270	0.199	1.250	1.493	3.235
Acenaphthylene	BD	0.016	BD	0.008	0.055
Acenaphthene	0.292	0.064	0.235	0.039	0.020
Fluorene	0.104	0.069	0.114	0.054	0.135
Phenanthrene	0.705	0.487	0.886	0.297	2.226
Anthracene	0.050	0.027	0.939	0.032	0.071
Fluoranthene	0.271	0.203	0.282	0.209	0.650
Pyrene	0.188	0.120	0.221	0.120	0.685
Benzo(<i>a</i>)anthracene	BD	BD	BD	BD	0.003
Chrysene	BD	0.017	0.020	BD	BD
Benzo(<i>b</i>)fluoranthene	BD	BD	BD	0.003	0.064
Benzo(<i>k</i>)fluoranthene	BD	BD	BD	0.001	0.002
Benzo(<i>a</i>)pyrene	BD	BD	BD	BD	0.004
Indeno(1,2,3- <i>cd</i>)pyrene	BD	0.019	BD	BD	BD
Dibenz(<i>a,h</i>)anthracene	BD	BD	BD	BD	BD
Benzo(<i>g,h,i</i>)perylene	BD	BD	BD	0.006	0.046

BD = below lower detection level.

Table 2
Average perdeuterated PAH recoveries (%) in HiC-IOGAPS denuder and filter samples

Standard	Upper denuder	Lower denuder	Quartz and XAD-4-coated filters
Naphthalene- d_8	73 ± 10	63 ± 18	38 ± 17
Acenaphthene- d_{10}	96 ± 10	86 ± 10	52 ± 18
Perylene- d_{12}	160 ± 60	136 ± 13	93 ± 37

include the exchange of gases with limited water solubility. The revised model includes an aerodynamic resistance (Valigura, 1995) and an over-water surface resistance (Seinfeld and Pandis, 1998) to mass transfer. The revised model requires as inputs air temperature, water temperature, wind speed and relative humidity. For each gas modeled, the model requires as inputs the Henry's Law constants and temperature dependence of Henry's Law constants. Table 3 lists the Henry's Law constants (H_L) and temperature dependence of Henry's Law constants used as model inputs, where H_L ($M \text{ atm}^{-1}$) is defined by Eq. (1), C_w^{sat} (M) is the saturation of PAH in pure water, and p is the PAH partial pressure (atm):

$$H_L = \frac{C_w^{\text{sat}}}{p}. \quad (2)$$

The aqueous solubility of a PAH decreases with increasing ionic strength, favoring the evasion of PAH from water to air (Alaee et al., 1996). For a rough approximation of this effect, the Henry's Law constants (H_L) input into the NOAA buoy model were first corrected for the PAH water solubility in sea water using Eq. (3), where the Setschenow or salting out coefficient $K^s = 0.3$, the total molar salt concentration [salt] = 0.5 M, and $C_{w,\text{salt}}^{\text{sat}}$ (M) is the water saturation of the PAH in salt water (Schwarzenbach et al., 1993):

$$C_{w,\text{salt}}^{\text{sat}} = \frac{C_w^{\text{sat}}}{10^{K[\text{salt}]}}. \quad (3)$$

The exchange of organic gases at the air–water interface depends upon the gas solubility and temperature, and both the air and water concentrations of the gas. For the Chesapeake Bay (Dickhut and Gustafson, 1995; Bamford et al., 1999) and the Corpus Christi Bay (Park et al., 2002), researchers give convincing argument that the net exchange of PAHs at the air–water interface could be in either direction. In the absence of bay water PAH concentrations, however, we have assumed that the PAH water concentrations are ≈ 0 and that our estimates for the gaseous PAH fluxes represent an upper limit.

Table 3
Henry's Law constant (H_L) at 298.15 K and temperature dependence of the Henry's Law constant ($\Delta h/R$) for 16 USEPA priority PAHs, based on $-\ln(H_L)/d(1/T) = \Delta h/R$, where h is the solution enthalpy and R is the ideal gas constant (ECERG, 2003; MacKay and Callcott, 1998; Sander, 1999; TenHulscher et al., 1992; USEPA, 1982)

PAH	H_L (M/atm)	$d\ln(H_L)/d(1/T)$ (K)
Naphthalene	2.1	3600
Acenaphthylene	9.1	5500
Acenaphthene	4.1	2800
Fluorene	8.5	3000
Phenanthrene	9.5	4700
Anthracene	35	4000
Fluoranthene	110	6900
Pyrene	59	5200
Benzo(a)anthracene	78	8600
Chrysene	140	14,000
Benzo(b)fluoranthene	1500	5500
Benzo(k)fluoranthene	1700	5900
Benzo(a)pyrene	2200	4700
Indeno(1,2,3-c,d)pyrene	2900	3600
Dibenz(a,h)anthracene	6×10^5	^a
Benzo(g,h,i)perylene	3000	3200

^aNot found in literature.

Dry deposition velocities for particle-phase PAHs were calculated with the USF College of Engineering website version of the integrated NOAA buoy model/Williams model (Bhethanabotla, 2003). This model combines the micrometeorological parameters produced by the NOAA buoy model (Valigura, 1995) to compute the aerodynamic resistance, with a surface resistance that accounts for mass transfer across either a smooth or broken water surface (Williams, 1982).

BRACE-related measurements of size-specified PAHs were made with a micro-orifice impactor (MOI) sampler at a peri-urban site on the eastern side of Tampa (27.97°N, 82.23°W) in May 2002. These measurements revealed that for benzo(b+k)fluoranthene, benzo(a)pyrene and benzo(e)pyrene the particle diameter mode was 1 μm , but for the higher molecular weight indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene, and dibenzo(a,h)anthracene the particle diameter mode was 0.5 μm (Tremblay and Zika, 2003). Distributions of these particles extended from 0.01 to 20 μm . In a measurement campaign at the University of Bayreuth, Kaupp and McLachlan (1999) found PAH aerosols predominantly in the 0.15–1.35 μm particle diameter size range; Allen et al. (1996), however, discovered that lower molecular PAHs in urban areas and most PAHs in rural areas had a significant mass fraction in the coarse mode. With no local information on the size distribution of the lower molecular weight PAH particles, we assumed that all of the particles were 2.5 μm in diameter. This biases high

our estimate of the deposition rate for particles collected by the HiC-IOGAPS, but does not account for coarse particle PAH deposition.

3. Results and discussion

The HiC-IOGAPS dramatically improved the recovery of lower molecular weight gas and particle PAHs, as evidenced by the recoveries of PAHs in back-up denuders and filter packs (Tables 4 and 5). For example, naphthalene and anthracene have a significant amount of total mass on the second denuder (Table 4); and more naphthalene was trapped in the last two XAD-4 filters than in the first quartz filter or second XAD-4 filter (Table 5). According to Swartz et al. (2003a) and Gundel et al. (1995), the short residence time of the ambient air in the denuders minimizes the artifacts due to particle losses or particle evaporation within the denuder. If breakthrough is defined by 10% or more of the PAH mass on the second denuder (Gundel et al., 1995), then breakthrough routinely occurred. Gundel et al. (1995) characterized the denuder capacity at flow rates up to 20 L min⁻¹ and for up to 22 h for a similar annular denuder construction; breakthrough of naphthalene was seen at 20 L min⁻¹ after 3 h of sampling. With design improvements, Gundel and Lane (1998) predicted a 0.0098% penetration of phenanthrene in a multi-channel IOGAPS at

Table 4

Average distribution of PAH mass (%) in first (upper) and second (lower) denuder of the HiC-IOGAPS: upper denuder/total denuder; lower denuder/total denuder, and average capture efficiency (%)

PAH	Upper denuder	Lower denuder	η
Naphthalene	65	35	Negative
Acenaphthylene	79	21	89
Acenaphthene	80	20	80
Fluorene	86	14	88
Phenanthrene	82	18	84
Anthracene	53	47	Negative
Fluoranthene	79	21	80
Pyrene	80	20	80
Benzo(a)anthracene	86	14	Negative
Chrysene	81	19	77
Benzo(b)fluoranthene	66	34	Negative
Benzo(k)fluoranthene	57	43	Negative
Benzo(a)pyrene	BD	BD	BD
Indeno(1,2,3-c,d)pyrene	BD	BD	BD
Dibenzo(b)anthracene	BD	BD	BD
Benzo(g,h,i)perylene	43	57	Negative

BD = below the lower detection level; Negative = one or more values of η were negative.

Table 5

Average distribution of PAH mass (%) in quartz filter and XAD filters of the HiC-IOGAPS: quartz filter/total filter, XAD filter/total filter

PAH	Quartz filter	1st XAD-4 filter	2nd XAD-4 filter	3rd XAD-4 filter
Naphthalene	8	19	36	36
Acenaphthylene ^a	3	30	0	0
Acenaphthene	19	48	21	12
Fluorene	22	47	17	14
Phenanthrene	25	33	23	19
Anthracene	29	44	15	11
Fluoranthene	26	31	22	22
Pyrene	28	27	23	22
Benzo(a)anthracene	52	18	16	15
Chrysene	46	30	14	11
Benzo(b)fluoranthene ^a	45	15	4	2
Benzo(k)fluoranthene ^a	45	14	8	0
Benzo(a)pyrene ^a	50	17	0	0
Indeno(1,2,3-c,d)pyrene ^a	50	17	0	0
Dibenzo(b)anthracene	BD	BD	BD	BD
Benzo(g,h,i)perylene	80	18	1	1

BD = below the lower detection level.

^aInfluenced by one or more days of total particle PAH mass below detection.

50 L min⁻¹, more optimistic than the results shown in Table 4.

Swartz et al. (2003b) obtained PAH extraction efficiencies of >95% from XAD-4 coated denuders and filters after normalizing the results for the losses associated with volume reduction. Two significant differences in their procedures included an 11.5 h versus a 24-h sampling period, and extraction of the PAHs with a 1:1:1 by volume hexane, dichloromethane and methanol solvent mixture versus a dichloromethane (MeCl₂) mixture for this study.

The influent PAH concentration (C_{in}) can be calculated from Eq. (4), where C_1 is the PAH concentration found on the first denuder. If we assume that the capture efficiency (η) is the same for both the first and second denuders for a given PAH, we can solve for η by Eq. (5), where C_2 is the PAH concentration found on the second denuder. This approach, however, yields average negative efficiencies when the PAH mass on the second denuder is greater than on the first denuder for one or more sampling days (Table 4). As an alternative approach we have approximated η as the percent of the total recovered on the first denuder. The PAH concentration after the second denuder (C_{out}) is computed from Eq. (6). We further assumed that the PAH that exits the denuder is quantitatively captured across the four filters, and C_{out} was debited from the

particle concentration and added to the gas concentration:

$$C_{\text{in}} = \frac{C_1}{\eta}, \quad (4)$$

$$\eta = 1 - \left(\frac{C_2}{C_1} \right), \quad (5)$$

$$C_{\text{out}} = C_{\text{in}}(n^2 - 2\eta + 1). \quad (6)$$

Swartz et al. (2003b) reported average capture efficiencies for the denuders and filters, excluding naphthalene, of 89% and >90%, respectively. In this study, the average denuder capture efficiency was 83%, but only if naphthalene, anthracene, and 5-ring PAHs are excluded (Table 4).

The average daily ambient air concentrations of PAH gases and particles for 7 summertime days are presented in Tables 6 and 7. The reported concentrations have been corrected as described above to account for gas-phase PAH not trapped by the denuders. Naphthalene, acenaphthene, fluorene, phenanthrene, fluoranthene and pyrene are the PAHs with the highest atmospheric concentrations in both phases. The concentrations for the three- and four-ring PAHs fall between the corresponding average values for PAHs measured by Dachs et al. (2002) in July 1997 at a Chesapeake Bay and Baltimore inner harbor site, respectively. We are reporting concentrations that are also similar to those

Table 6

Average daily ambient air concentrations of gas-phase PAHs measured with the HiC-IOGAPS at the Gandy Bridge site in Tampa, Florida. Values below the lower detection level are given as zero

PAH	Minimum (ng m ⁻³)	Maximum (ng m ⁻³)	Mean (ng m ⁻³)
Naphthalene	39.32	115.37	71.70
Acenaphthylene	0.00	0.53	0.21
Acenaphthene	2.29	6.81	4.07
Fluorene	3.76	8.90	6.15
Phenanthrene	10.05	21.15	13.34
Anthracene	0.03	0.94	0.50
Fluoranthene	3.31	6.13	4.91
Pyrene	1.21	2.29	1.74
Benzo(a)anthracene	0.00	0.13	0.04
Chrysene	0.12	1.20	0.46
Benzo(b)fluoranthene	0.02	0.10	0.06
Benzo(k)fluoranthene	0.00	0.02	0.01
Benzo(a)pyrene	0.00	0.05	0.01
Indeno(1,2,3-c,d)pyrene	0.00	0.08	0.02
Dibenzo(b)anthracene	0.00	0.06	0.01
Benzo(g,h,i)perylene	0.01	0.08	0.04

Table 7

Average daily ambient air concentrations of particle-phase PAHs measured with the HiC-IOGAPS at the Gandy Bridge site in Tampa, FL

PAH	Minimum (ng m ⁻³)	Maximum (ng m ⁻³)	Mean (ng m ⁻³)
Naphthalene	0.00	86.41	24.32
Acenaphthylene	0.00	0.04	0.00
Acenaphthene	0.07	0.45	0.20
Fluorene	0.14	0.36	0.27
Phenanthrene	1.45	3.74	2.37
Anthracene	0.00	0.05	0.00
Fluoranthene	0.43	2.27	0.99
Pyrene	0.26	1.58	0.61
Benzo(a)anthracene	0.01	0.03	0.01
Chrysene	0.03	0.05	0.04
Benzo(b)fluoranthene	0.00	0.07	0.02
Benzo(k)fluoranthene	0.00	0.02	0.01
Benzo(a)pyrene	0.00	0.01	0.00
Indeno(1,2,3-c,d)pyrene	0.00	0.05	0.02
Dibenzo(b)anthracene	0.00	0.00	0.00
Benzo(g,h,i)perylene	0.01	0.17	0.04

Values below the lower detection level are given as zero.

seen in Athens, Greece, at both an urban and a coastal site (Mandalakis et al., 2002).

Filter capture efficiencies were typically less than 80%, if Eq. (5) is applied to the first two filters in series (Table 5). With the exceptions of naphthalene, fluorene, and fluoranthene, however, after correction for gas-phase PAH trapped on the filter, the particulate PAH concentrations were at or below the amounts seen on laboratory and filter blanks (Table 7).

The total PAH concentration was typically dominated by gas-phase PAHs (Table 8). Our uncertainty estimate included a measurement precision of 12% (Gundel et al., 1995) and the standard errors for the perdeuterated standard recoveries. The low PAH concentrations observed on field and laboratory blanks (Table 1) argued against contamination of the XAD-4 during sample media preparation and handling.

The average ΣPAH concentration previously reported for the Gandy Bridge site from March 2001 to October 2001 ($n = 36$) was 14 ng m⁻³ with the largest contributions from phenanthrene, fluoranthene and pyrene (Poor, 2002). These samples were collected at the Gandy Bridge site but with a USEPA Compendium Method TO-4A sampler (USEPA, 1999), which featured a total suspended particulate (TSP) inlet, and a 10-cm diameter quartz filter followed by a 6-cm × 10-cm piece of polyurethane foam (PUF). The sampling configuration favored the volatilization of lower molecular PAHs from the quartz filter and PUF, and average daily naphthalene concentrations did not exceed 2.0 ng m⁻³, which is

Table 8
Gas, particle and total PAH concentrations measured with the HiC-IOGAPS at the Gandy Bridge site in Tampa, FL

Sampling date	Σ PAH gas (ng m^{-3})	Σ PAH particle (ng m^{-3})	Σ PAH total (ng m^{-3})
30 May 02	158 ± 28	4 ± 1	162 ± 28
31 May 02	138 ± 22	47 ± 9	186 ± 24
1 Jun 02	111 ± 20	11 ± 2	122 ± 21
7 Jun 02 ^a	63 ± 10	18 ± 3	81 ± 10
13 Jun 02	72 ± 11	13 ± 2	85 ± 11
25 Jun 02	106 ± 18	18 ± 3	124 ± 19
1 Jul 02	74 ± 12	95 ± 19	169 ± 22

^a48-h sample.

in striking contrast with the average daily naphthalene concentration of 99 ng m^{-3} (Tables 6 and 7) seen in this study. Swartz et al. (2003a, b) obtained a 11.5-h average daytime naphthalene concentration of 270 ng m^{-3} with a HiC-IOGAPS in La Porte, TX, on 31 August 2000, after correcting for recovery inefficiencies.

Recoveries of lower molecular weight PAHs across two XAD-4 coated denuders and four filters, three of which were impregnated with XAD-4, illustrate the apparent ease with which these compounds elute through the sampling media (Tables 4 and 5). Coupled with the disproportional loss of lower molecular weight PAHs in the extraction, filtration and concentration processes, we believe it likely that our estimates of the gas-phase concentrations of the 2–4-ring PAHs are underestimated. Particle-phase concentrations are underestimated as well, as the Hi-IOGAPS did not capture coarse particles.

The model presented in Eq. (7) explains well experimental data on the partitioning of organic compounds between gas and aerosol phases (Harner and Bildeman, 1998). $K_p = C_p/C_g$, where C_p is the PAH concentration per μg of particles ($\text{ng } \mu\text{g}^{-1}$), C_g is the gas concentration (ng m^{-3}), K_p is the particle/gas partition coefficient, p_L^0 is the subcooled liquid vapor pressure (Pa), and m and b are the slope and intercept of a best-fit straight line through a log–log transformation of the experimental data. Under equilibrium conditions, a slope m of -1 is expected (Harner and Bildeman, 1998). The fit of this model to the seven days of PAH concentration data acquired at the Gandy Bridge site is shown in Fig. 1. For individual days, the slopes of the log K_p versus $\log p_L^0$ ranged from -0.1 to -0.3 :

$$\log K_p = m \log p_L^0 + b. \quad (7)$$

The slopes of the best-fit line shown in Fig. 1 deviate significantly from -1 . Harner and Bildeman (1998) suggest that such a deviation could be explained by

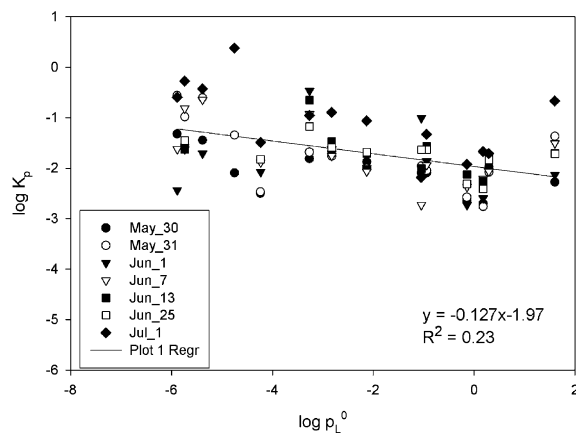


Fig. 1. Plot of $\log K_p$ versus $\log p_L^0$ for the USEPA 16 priority PAHs.

non-equilibrium behavior, or that some particulate PAHs may not be exchangeable with the atmosphere although they are recovered by solvent extraction from the aerosol. The data plotted were corrected to account for gas-phase PAH not trapped by the denuders, but as suggested by the presence of PAHs in the last two XAD-4 filters (Table 5), the method failed to capture all of the gaseous and re-volatilized particulate PAHs for the lower molecular weight compounds.

PAH gas deposition velocities and total deposition rates are given in Table 9. Modeled gas deposition velocities ranged from 0.07 to 0.63 cm s^{-1} . The deposition velocity calculated for indeno(1,2,3-c,d)pyrene was used as a best guess for dibenz(a,h)anthracene. The deposition velocities for acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene were $\sim 50\%$ lower than the gas-phase overall mass transfer coefficient obtained by Odabasi et al. (2001) with a water surface sampler. For a $2.5\text{-}\mu\text{m}$ diameter particle, the average deposition velocity was 0.02 cm s^{-1} . Higher deposition rates of naphthalene, acenaphthene, fluorene, phenanthrene, fluoranthene, and pyrene were a consequence of their higher gas-phase concentrations. For phenanthrene, fluoranthene, and pyrene, the deposition rates were significantly higher than the ~ 1 , 0.7 , and $0.3 \mu\text{g m}^{-2} \text{ d}^{-1}$, respectively, reported by Poor (2002) for Tampa Bay. The average total dry flux to the bay surface, assuming a unidirectional flux, is $11.5 \mu\text{g m}^{-2} \text{ d}^{-1}$ (4.4 ty^{-1} to Tampa Bay) or $6.7 \mu\text{g m}^{-2} \text{ d}^{-1}$ if naphthalene is excluded. Golomb et al. (2001) directly measured deposition of PAHs to a surrogate water surface. The average Σ PAH (excluding naphthalene) deposition rate was $2.3 \mu\text{g m}^{-2} \text{ d}^{-1}$ for an urban-dominated site in Massachusetts, a factor of 10 higher than a rural site in Maine but $\sim 50\%$ lower than that reported in this study.

Table 9

Summary of PAH gas deposition velocities and gas and total (gas + particle) dry fluxes to Tampa Bay

PAH	Average v_d (cm s ⁻¹) ^a	Average gas flux ($\mu\text{g m}^{-2} \text{d}^{-1}$)	Average total flux ($\mu\text{g m}^{-2} \text{d}^{-1}$)
Naphthalene	0.07	4.33	4.76
Acenaphthylene	0.15	0.03	0.03
Acenaphthene	0.15	0.52	0.52
Fluorene	0.24	1.25	1.26
Phenanthrene	0.18	2.07	2.11
Anthracene	0.40	0.17	0.17
Fluoranthene	0.44	1.86	1.87
Pyrene	0.42	0.64	0.65
Benzo(a)anthracene	0.31	0.01	0.01
Chrysene	0.16	0.06	0.06
Benzo(b)fluoranthene	0.61	0.03	0.03
Benzo(k)fluoranthene	0.61	0.00	0.01
Benzo(a)pyrene	0.62	0.01	0.01
Indeno(1,2,3-c,d)pyrene	0.62	0.01	0.01
Dibenzo(b)anthracene	0.62	0.01	0.01
Benzo(g,h,i)perylene	0.63	0.02	0.02
Σ PAH		11.0	11.5 ^b

^aGas-phase deposition velocity; particle phase deposition velocity is 0.02 cm s⁻¹.^b6.7 $\mu\text{g m}^{-2} \text{d}^{-1}$ if naphthalene is excluded.

4. Conclusions

An advantage of the Hi-IOGAPS is its segregation of PAH gases and aerosols: dual denuders and multiple filters serve as diagnostics for gas and particle collection efficiency. Our results suggest, however, that the gas-phase PAHs are not quantitatively captured. The Hi-IOGAPS did not capture coarse particles, thus some fraction of the atmospheric PAHs was excluded by this sampling method.

Atmospheric deposition velocities for partially water-soluble gaseous PAHs and particles, respectively, were calculated with a NOAA buoy/Gas model and an integrated NOAA buoy/Williams model, both of which can be run from the Internet (Bhethanabotla, 2003). Further testing and development of this model is required, however, to define its performance relative to other computational approaches and to extend its application to a bi-directional flux.

Observed Σ PAH concentrations were for 5 of the 7 days $\geq 100 \text{ ng m}^{-3}$ and were dominated by naphthalene, acenaphthene, fluorene, phenanthrene, fluoranthene, and pyrene. The total (gas + particle) dry deposition flux was $11.5 \mu\text{g m}^{-2} \text{d}^{-1}$ ($6.7 \mu\text{g m}^{-2} \text{d}^{-1}$ if naphthalene is excluded), which is higher than estimates reported for Corpus Christi Bay (Park et al., 2002) and Massachusetts Bay (Golomb et al., 2001). These differences are a likely consequence of our assumption that the exchange of PAHs at the water's surface is unidirectional.

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