
Exchange of polycyclic aromatic hydrocarbons between the atmosphere, water, and sediment in southern California coastal embayments

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ABSTRACT

This study investigated cross-media transport between both the sediment and the water column, and the water column and the atmosphere, to understand the role of each compartment as sources or sinks of polycyclic aromatic hydrocarbons (PAH) in southern California coastal waters. Concentrations of PAH were measured in the atmosphere, water column, and sediment at four water-quality impaired sites in southern California: Ballona Creek Estuary, Los Angeles Harbor, Upper Newport Bay, and San Diego Bay. These concentrations were used to calculate site-specific sediment/water and atmosphere/water exchange fluxes. The net sediment/water exchange of total PAH (*t*-PAH) was positive, indicating sediments were a source to the overlying water column. Furthermore, the net atmosphere/water flux (gas exchange + dry particle deposition) of *t*-PAH was typically positive also, indicating the water column was a net source of PAH to the surrounding atmosphere through gas exchange. However, in all cases, the magnitude of the diffusive flux of PAH out of the sediments and in to the water column far exceeds input or output of PAH through air/water exchange processes. These results demonstrate the importance of contaminated sediments as a source of PAH to the water column in coastal waters of southern California.

INTRODUCTION

PAH are directly emitted into the atmosphere and discharged into waterbodies and may accumulate in coastal estuarine and marine sediments (Zeng and

Vista 1997, Menzie *et al.* 2002, Mai *et al.* 2003). Anthropogenic sources of PAH in the atmosphere are primarily from fossil fuel combustion (e.g., gasoline and diesel vehicle exhaust, power plant and industrial emissions). Anthropogenic sources to the water and sediment include atmospheric deposition, direct discharges to the water of petroleum products from shipping activities, industrial and wastewater sources, and from urban stormwater runoff (Hoffman *et al.* 1984, Stein *et al.* 2006, Peng *et al.* 2007). Managing PAH levels in contaminated water bodies requires understanding of the transport between the atmosphere, the water column, and bottom sediments.

In other regions, a number of studies have investigated the role of the atmosphere as a potential source of PAH to polluted waterbodies, especially near urban centers (Hoff *et al.* 1996, Nelson *et al.* 1998, Franz *et al.* 1998, Bamford *et al.* 1999, Park *et al.* 2001, Tsai *et al.* 2002, Gigliotti *et al.* 2002). Significant research has been conducted on the accumulation of PAH in sediments, partitioning between the sediment and porewater, and exchange between the overlying water and contaminated bottom sediments (Gschwend and Hites 1981, McCain *et al.* 1992, McGroddy and Farrington 1995, Maruya *et al.* 1996, Simcik *et al.* 1996, Fairey *et al.* 1998, Latimer *et al.* 1999, Mitra *et al.* 1999, Anderson *et al.* 2001, Wang *et al.* 2001, Bay *et al.* 2003, Lohmann *et al.* 2005). However, few studies offer synoptic measurements in order to calculate both the air/water and sediment/water exchange fluxes for a given waterbody. Furthermore, no studies have been conducted on atmospheric deposition of PAH in the coastal waters off southern California.

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The Southern California Bight (SCB) is located adjacent to the second most populous region in the United States. This region has some of the worst air quality in the nation, including high atmospheric concentrations of PAHs. Furthermore, coastal urban embayments within the SCB are enriched in PAHs relative to nearshore coastal waters (Zeng and Vista, 1997). A recent survey of sediments in the SCB found more than 70% of the SCB area was contaminated with anthropogenic organic compounds, including PAH, and the highest concentrations were associated with bays, harbors and estuaries (Schiff *et al.* 2006). In contrast to the legacy organochlorines (e.g., DDT and PCB), which have been banned from production and use for nearly three decades, PAH continue to be introduced into the southern California environment via multiple sources.

The goal of this study was to examine the potential importance of different environmental compartments as sources or sinks of PAH in the SCB. The objectives were to characterize the distribution of PAH in the atmosphere, the water column, and the sediment, and to quantify the magnitude and direction of exchange between these compartments in selected bays, harbors and estuaries of the SCB.

METHODS

Concentrations of PAH were measured in the atmosphere (gas and particle-phase), the water column (dissolved and sorbed to suspended solids), and the surface sediment, along with measurements of total suspended solids (TSS) and total organic carbon (TOC) at four sites in the SCB. Using these measurements, fluxes between compartments were estimated, including gas exchange between the atmosphere and the water column, dry deposition of particles from the atmosphere to the water surface, sedimentation of suspended particulate matter (SPM) in the water column to the bottom sediment, and diffusive flux between the sediment porewater and the water column. Gas exchange was estimated based on a modified two-film transfer model with inputs of wind speed and Henry's Law Constants. For sediment/water exchange, porewater concentrations were estimated from measured sediment concentrations and the organic-carbon normalized partition coefficient. A simple diffusive flux model based on concentration gradients between porewater and the water column was used to calculate the exchange flux. Dry deposition and sedimentation

fluxes were estimated from measured concentrations and assumed deposition and sedimentation velocities, respectively.

Sample Collection

Four coastal estuaries within the SCB were sampled for PAH during the summer and fall of 2006 (Table 1). All study sites were located near urban areas with varying degrees of local contaminant sources and historical sources of PAHs, and all sites are listed as impaired on the State of California 303(d) list due to elevated levels of PAH in fish tissue, sediment and /or the water column (SWRCB 2003). The Ballona Creek Estuary (BCE) site, adjacent to Santa Monica Bay, is primarily urbanized, with no permitted wastewater or industrial discharges. Air samples were collected on a rooftop ~4 km south of the estuary, adjacent to the coast. Water/sediment samples were collected at a pedestrian bridge within the estuary. The Los Angeles Harbor (LAH) site, adjacent to a heavily urbanized area, is the largest commercial port in the United States. Air samples were measured ~3 km downwind of the harbor at an existing South Coast Air Quality Management District (SCAQMD) site in the city of Wilmington. Water/sediment samples were collected from a shipping basin (the Consolidated Slip) in the inner Harbor near the mouth of Dominguez Channel. The Upper Newport Bay (UNB) site is the largest coastal wetland in southern California, and drains a watershed that is primarily residential/commercial (Peng *et al.* 2007). Air samples were collected at the University of California, Irvine, Marsh Reserve, ~2 km from the bay. Water/sediment samples were collected inside the bay near the mouth of San Diego creek. The San Diego Bay (SDB) site is home to one of the largest naval facilities in the U.S, and is also adjacent to a large urban area. Air samples were collected from the roof of the San Diego Naval Station, next to the bay at the mouth of Chollas Creek. Water/sediment samples were collected from the bay near the mouth of Chollas Creek.

Each site was sampled at least once in each compartment (air, water, and sediment; Table 1). Daily meteorological data (temperature and wind speed) were obtained from nearby National Weather Service stations (Los Angeles International Airport, Long Beach Airport, John Wayne Airport, and San Diego Lindbergh Field for BCE, LAH, UNB and SDB, respectively; NCDC 2006).

Table 1. Site specific sampling information^a.

Site	Matrix	Location (Lat, Long) ^b	# Samples Collected	Collection Date(s)	Air Temperature (°C)	Wind Speed (m/sec)	Total Suspended Solids (mg/L)	Sediment Organic Carbon (%)
Ballona Creek Estuary (BCE)	Air	33 55.658 N, 118 25.949 W	1	31-Oct to 2-Nov-06	20 ± 4	3.4 ± 0.8		
	Water	33 57.785 N, 118 27.203 W	1	06-Aug-06			4.9	
	Sediment		3	13-Jul-06 25-Jul-06 25-Sep-06				1.1
Los Angeles Harbor (LAH)	Air	33 47.580 N, 118 13.126 W	3	19-Sept to 21-Sept-06 18-Oct to 20-Oct-06 24-Oct to 26-Oct-06	20 ± 2	2.0 ± 0.5		
	Water	33 46.590 N, 118 14.640 W	3	11-Sept to 18-Sept-06 22-Sept to 25-Sept-06 13-Nov to 17-Nov-06			5.1 ± 1.7	
	Sediment		4	18-Sep-06 14-Sep-06 22-Sep-06 22-Oct-06				5.6 ± 3.1
Upper Newport Bay (UNB)	Air	33 39.797 N, 117 51.125 W	1	16-Aug to 18-Aug-06	24 ± 4	2.2 ± 0.3		
	Water	33 39.036 N, 117 52.131 W	1	22-Jul-06			18.0	
	Sediment		4	22-Jul-06				1.3
San Diego Bay (SDB)	Air	32 41.225 N, 117 07.847 W	1	27-Sept to 29-Sept-06	21 ± 1	2.8 ± 0.6		
	Water	32 41.267 N, 117 07.824 W	2	15-Sept to 18-Sept-06 27-Sept to 01-Oct-06			1.1 ± 0.7	
	Sediment		2	15-Sep-06				2.9

^aMean ±sd for temperature, wind speed, total suspended solids and sediment organic carbon.

^bWater and sediment samples were collected at the same location.

Air samples were collected using a high volume sampler (Anderson Instruments, Inc., Smyrna, GA) equipped with a glass fiber filter (GFF; Whatman, 0.7- μ m pore size) to collect particle phase compounds, followed by a polyurethane foam (PUF) plug (7 cm long and 6 cm in diameter) held in a glass sleeve to collect gas phase compounds. The gas phase was operationally defined as the concentration retained on the PUF. A sample flow rate of 0.25 m³/minute was used over a period of 24 to 48 hours. Prior to sampling, GFFs were wrapped in aluminum foil and baked at 425°C for 6 hours, then stored in hexane-rinsed aluminum foil lined Petri dishes. PUFs were cleaned by extraction with pesticide grade acetone for 24 hours, followed by extraction using 10% diethyl ether/90% n-hexane mixture for four hours, then stored in pre-cleaned glass jars with hexane rinsed, aluminum foil lined lids. After sampling, the GFFs and PUFs were returned to their original jars, wrapped in aluminum foil, transported to the laboratory in an ice chest, and stored at 4°C.

Water column samples for the dissolved phase, operationally defined as filtrates passing through a 0.7- μ m GFF, and the particle phase were collected with an Infiltrax 100 *in situ* water pumping system (Axys Environmental Systems Ltd., Sidney, BC, Canada), described in detail previously (Zeng *et al.* 1999). Briefly, water is continuously pumped through a stack of eight GFFs (Whatman 0.7- μ m pore size), to retain particles, and a PTFE column packed with XAD-II resin, to extract dissolved organics. The pump was positioned in the water column 1 m above the sediment/water interface. The unit was anchored on the seafloor by two iron chain links and suspended in the water column with a sub-surface float. The pump flow rate was set at 200 to 400 ml/minute. After sampling, the PTFE column was processed within 24 hours and GFFs were stored at -20°C.

Discrete water samples were collected with 5-L Niskin bottles for determination of TSS. Discrete samples were immediately sealed in containers with

Teflon-lined lids and transported to the laboratory on ice, then stored at 4°C.

Surface sediment (top 5 cm) was collected with either a stainless steel modified Van Veen or petite Ponar grab and transferred into pre-cleaned 500-mL glass jars. One grab per site was collected on each day of sampling. The sediment samples were placed on ice for transport, then stored in the laboratory at -20°C.

Analytical Procedures

A total of 28 individual PAH compounds with two to six rings were targeted in this study (Table 2). *t*-PAH was defined as the sum of these 28 compounds. All laboratory glassware were washed with soap and water, rinsed with de-ionized (DI) water, and kilned at ~500°C for at least 4 hours. Sediment samples were freeze-dried before extraction. PTFE columns with XAD-II resin were eluted with dichloromethane (DCM). Water column GFFs were extracted with DCM using an ASE300 Accelerated Solvent Extraction System (Dionex Corporation,

Sunnyvale, CA). Extraction conditions were as follows: 100°C; 1500 psi; stationary time 5 minutes; flushing volume 60%. Three extraction cycles were carried out for each sample. GFF and PUF samples were Soxhlet extracted with n-Hexane/ethyl ether (9:1, v/v) for 18 hours. Freeze-dried sediments were Soxhlet extracted with DCM for 18 hours. Sample extracts were concentrated and the solvent was exchanged to hexane. The extract was kept in the dark overnight at room temperature after a small amount of activated copper was added to remove sulfur.

Cleanup of all sample extracts was performed using silica gel/alumina column chromatography. Both sorbents were pre-extracted three times with DCM using the ASE300 system, dried, and activated overnight at 180 and 250°C, respectively. Silica gel and alumina were subsequently deactivated using 3% (w/w) double DI water. After the sample extract was loaded, the first 20 ml of hexane eluent and the subsequent 70 ml of 30:70% DCM/hexane mixture was collected. Sample extracts were concentrated to <5 ml using a vacuum rotary evaporator and further reduced to 500 µl using a gentle stream of ultra high purity (>99.999%) nitrogen.

Water column TSS was measured by filtering a 25- to 3000-ml aliquot of sample through a tared GFF (Whatman 25 mm diameter, 0.45-µm pore size). After drying in an oven at 60°C for 24 hours, the loaded filter was weighed to the nearest 0.001 g. The mass of inorganic salt residues was subtracted from all TSS mass determinations. For TOC in sediment, an aliquot of each dried sample was acidified with HCl vapors to remove inorganic carbon. The acidified sample was then dried, packed in a tin boat, and analyzed using a Carlo Erba 1108 CHN Elemental Analyzer (Thermo Fisher Scientific, Italy) equipped with an AS/23 autosampler.

Sample extracts containing target PAHs were analyzed using Varian 3800 gas chromatography (GC)/Saturn 2000 ion trap mass spectrometry (MS) systems (Varian, Walnut Creek, CA). A splitless volume of 1 µl was injected at 100°C. After holding for 0.05 minutes, the injector temperature was increased to 280°C at ~200°C/minute and held for 20 minutes. Carrier gas was helium (>99.999%) at a flow rate of 1.0 ml/minute. Chromatographic separations were made with a 60 m x 0.25 µm id (0.25 mm film thickness) DB-5MS column (J&W Scientific/Agilent Inc., Folsom, CA) programmed from 80°C (1 minute hold) to 176°C at 8°C/minute, followed by a ramp to 230°C at 1.5°C/minute, and a final increase to 290°C

Table 2. Target PAH compounds.

Name	Abbreviation
Naphthalene	N
1-Methylnaphthalene	1MeN
2-Methylnaphthalene	2MeN
Acenaphthylene	Acey
Acenaphthene	Ace
Biphenyl	BP
2,6-Dimethylnaphthalene	DMN
Fluorene	Flu
2,3,5-Trimethylnaphthalene	TMN
Anthracene	An
Phenanthrene	Ph
1-Methylphenanthrene	1MePh
2-Methylphenanthrene	2MePh
Fluoranthene	Fla
Pyrene	Py
3,6-Dimethylphenanthrene	DMPPh
1H-Benzo[b]fluorene	BbFlu
Benz[a]anthracene	BaA
Chrysene+triphenylene	Chry
Benzo[a]pyrene	BaP
Benzo[b+j]fluoranthene	BbF
Benzo[e]pyrene	BeP
Benzo[k]fluoranthene	BkF
Perylene	Peryl
Benzo[g,h,i]perylene	BghiP
Indeno[1,2,3-cd]pyrene	I123cdP
Dibenzo[a,h/a,c]anthracene	DBahA
9,10-Diphenylanthracene	DPhA

at 5°C/minute (39 minute hold). Selected ion storage mode was used to analyze the samples. Quantification of individual analyte concentrations was by the internal standard method (2-fluorobiphenyl, p-terphenyl-d₁₄, dibenzo[a,h]anthracene-d₁₄ as the internal standards) using a 6-point (50 to 2000 ppb) calibration curve. Extracts were diluted and/or concentrated accordingly to bring analyte concentrations into the calibration range.

Quality Assurance

Field blanks consisting of pre-cleaned GFFs and PUFs, transported to and from the field for each sampling event, were handled and processed in the same manner as air samples. On average, field blanks were 8 and 22% of samples for GFFs and PUFs, respectively, and concentrations in the corresponding air samples were field blank corrected. Procedural blanks for all media were analyzed using the same protocols followed for analysis of samples.

Because sample volumes, particularly for the water column, were variable, detection limits were sample and compound specific (Table 3). Samples were spiked with a mixture of surrogates (naphthalene-d₈, acenaphthylene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, perylene-d₁₂, benzo[g,h,i]perylene-d₁₂) prior to extraction to estimate recovery efficiency (Table 3). Because mean recoveries were considered quantitative (>70%), sample concentrations were not corrected for surrogate recovery. Standard Reference Materials (e.g., SRM1941b: a marine sediment) were extracted and analyzed following the same procedures as the samples (Table 3).

Data Analysis

Air/water exchange calculations focused on gas exchange at the air/water interface, and dry particle deposition from the atmosphere to the water. Sediment/water exchange calculations included diffusive transport between the sediment porewater and the overlying water column, and sedimentation of SPM from the water column. For each exchange process, a flux was calculated for individual PAH compounds and summed to give a total.

For concentration sums and flux calculations, 1/2 MDL was substituted for concentrations below the detection limit. If a compound was below detection in both air and water for gas exchange, or both water and sediment for diffusive sediment/water exchange, no flux calculation was made.

Gas exchange model

Calculations of gas exchange between the atmosphere and water were based on a modified two-film resistance model (Whitman 1923, Liss and Slater 1974). In this model, the rate of transfer is controlled by diffusion across the air/water interface. The net flux is defined as:

$$F = k_{ol} (C_w - C_a/H') \quad (1)$$

where F is the net flux (ng/m²/day), k_{ol} is the overall mass transfer coefficient (m/day), C_w and C_a are the dissolved and gaseous phase concentrations (ng/m³) in water and air, respectively. H' is the dimensionless Henry's Law constant.

Table 3. Nominal detection limits for PAH and mean recovery of spiked matrix and SRM 1941b by sample matrix ± standard deviation (sd).

Sample Matrix	Detection Limit		Matrix Spike Recovery
	Range	Mean ±sd	Mean ±sd (%)
Atmosphere			
Gaseous (pg/m ³)	1.5 - 86	12 ±19	86 ±20
Particulate (ng/g)	0.15 - 8.8	1.2 ±1.9	77 ±15
Water Column			
Dissolved (ng/L)	0.010 - 0.60	0.085 ±0.130	85 ±6
Particulate (ng/g dry weight)	0.15 - 8.8	1.2 ±1.9	93 ±24
Sediment (ng/g dry weight)	0.4 - 24	3.4 ±4.2	94 ±13 ^a

^a SRM 1941b

The reciprocal of k_{ol} is the sum of the resistance to mass transfer in the air and water as:

$$1/k_{ol} = 1/k_w + 1/(k_a * H') \quad (2)$$

where k_w and k_a are the water side and air side mass transfer coefficients, respectively.

The following correlation was used to calculate k_a for H₂O vapor (Schwarzenbach *et al.* 1993):

$$k_{a(H_2O)} \sim 0.2 * u_{10} + 0.3 \quad (3)$$

where $k_{a(H_2O)}$ is the mass transfer coefficient in air for H₂O (cm/s), and u_{10} is the wind speed (m/s) above the water surface at 10 m.

The following equation was used to calculate k_w for CO₂ (Wanninkhoff 1992):

$$k_{w(CO_2)} = 0.45 * u_{10}^{1.64} \quad (4)$$

where $k_w(CO_2)$ is the mass transfer coefficient in water for CO₂.

The relationships in (a) and (b) have been used previously by a number of researchers to calculate gas exchange of organic compounds over water (Achman *et al.* 1993, Eisenreich *et al.* 1997, Totten *et al.* 2001).

Because the rate of transfer is related to the molecular diffusivity, these estimates for $k_a(H_2O)$ and $k_w(CO_2)$ allow prediction of k_a and k_w for other compounds of interest with the following relationships (Schwarzenbach *et al.* 1993):

$$k_{a(unknown)} = k_{a(H_2O)} * [D_{a(unknown)}/D_{a(H_2O)}]^{0.67} \quad (5)$$

where D_a is the molecular diffusivity in air, and

$$k_{w(unknown)} = k_{w(CO_2)} * [Sc_{(unknown)}/Sc_{(CO_2)}]^{-1/2} \quad (6)$$

where Sc is the Schmidt number, calculated by dividing the kinematic viscosity of seawater at 20°C (cm²/second) by the molecular diffusivity in water.

Mean measured air and water concentrations and mean wind speeds from each site were used in the above equations to calculate the net gas exchange flux at each site. Other inputs included the molecular diffusivities of individual compounds in air (D_a) and water (D_w), and Henry's Law constants. D_a and D_w for 20°C were calculated based on the method of Fuller *et al.* (1966) and Wilke and Change (1955), respectively, employing the LeBas molar volume estimates as needed. Temperature corrected Henry's Law Constants for 20°C were obtained from Bamford *et al.* (1999), when reported, otherwise, from compiled chemical properties (Mackay *et al.* 1999).

Dry particle deposition model

Dry particle deposition was calculated from measured particle concentrations in the air and the particle deposition velocity:

$$F = C_p * V_d \quad (7)$$

where F is the dry deposition flux (ng/m²/day), C_p (ng/m³) is the particle-phase concentration of the compound in the air, and V_d (cm/s) is the dry deposition velocity of the particles in the air. A deposition velocity of 0.2 cm/s was used for this study, as recommended by the Integrated Atmospheric Deposition Network (Hoff *et al.* 1996).

Diffusive flux model

The model of diffusive exchange between the water column and the sediment was based on Fick's gradient-flux law, assuming a well mixed upper sediment layer (top 5 cm) and equilibrium between the sediment and porewater up to the boundary layer. The flux across the sediment/water interface was calculated as:

$$F = k_s (C_{pw} - C_w) \quad (8)$$

where F is the diffusive flux between the sediment and the water column (ng/m²/day), C_w and C_{pw} are the water column and porewater concentrations (ng/m³), respectively, and k_s (m/day) is the sediment/water mass transfer coefficient.

Compound specific k_s values were calculated as (Schwarzenbach *et al.* 1993):

$$k_s = D_w / h \quad (9)$$

where D_w (m^2/day) is the molecular diffusion coefficient, and height (h ; m) is the thickness of the boundary layer. A typical value for height of 5×10^{-4} m was used (Schwarzenbach *et al.* 1993).

Sediment porewater concentrations were calculated from sediment concentrations as:

$$C_{pw} = C_{sed} / (K_{oc} * f_{oc}) \quad (10)$$

where C_{pw} (ng/m^3) is the concentration in the porewater, C_{sed} (ng/g) is the concentration in the sediment, K_{oc} (ml/g) is the organic carbon normalized partition coefficient, and f_{oc} is the fraction of organic carbon in the sediment. K_{oc} values were obtained from a compilation by Delle Site (2001), or from compiled chemical properties (Mackay *et al.* 1992). The average value for sediments was used when available.

Sedimentation model

Sedimentation of organic compounds sorbed to SPM in the water column was calculated analogous to the dry particle deposition flux:

$$F = W_s * C_s \quad (11)$$

where C_s (ng/m^3) is the sorbed concentration of organic compound on SPM in the water column, and W_s (m/day) is the sedimentation velocity. A value of 1 m/day was used for W_s (Mackay 2001).

RESULTS

Sampling Conditions and Multimedia Concentrations

Daily average wind speeds during atmospheric sampling at the four sites ranged from 2.0 to 3.4 m/sec , and daily average temperatures ranged from 20 to 24°C (Table 1). Mean TSS in the water column ranged from 1.1 to 18 mg/L , and sediment organic

carbon ranged from 1.1 to 5.6% (Table 1). Detectable concentrations of PAH were found in air, water, and sediment at all sites (Table 4).

Atmospheric concentrations of *t*-PAH (gas + particle) ranged from 3.6 to 28 ng/m^3 . The gas phase comprised over 90% of the total atmospheric concentrations at all sites. The majority of the particle phase was comprised of 4 to 6 ring PAH (57 to 82%), while the gas phase was dominated by 2 to 3 ring PAH (55 to 73%) except at SDB (46%). Concentrations of individual PAH ranged from not detected (ND) to 11 ng/m^3 in the gas phase, and ND to 0.68 ng/m^3 in the particle phase. The largest contributors to *t*-PAH (gas + particle) were phenanthrenes (parent and methylated), fluoranthene, and pyrene (73 to 96%).

Water column concentrations of *t*-PAH ranged from 5.6 to 75 ng/L in the dissolved phase, and 3.3 to 71 ng/L on SPM. Concentrations of individual PAH ranged from not detected (ND) to 22 ng/L in the dissolved phase, and ND to 17 ng/L on SPM. As in the atmosphere, phenanthrene, methyl-phenanthrenes, fluoranthene and pyrene dominated water concentrations, contributing between 57 and 70% in the dissolved phase, and 48 to 78% in the sorbed phase. Most of the remaining PAH on SPM was contributed by other 4 to 6 ring PAH compounds (e.g., BbF, chrysene).

Concentrations of *t*-PAH in the sediment ranged from 650 to 11,000 ng/g dry weight. Four to six ring compounds dominated (85 to 91%). Individual PAH concentrations in the sediment ranged from ND to 1,600 ng/g dry weight. Typically, the largest contributions were from fluoranthene (10 to 12%), pyrene (11 to 18%) and chrysene (12 to 15% at all sites except UNB).

For all media, concentrations generally followed the pattern of highest to lowest as follows: LAH > SDB > BCE > UNB. Concentrations in all media at UNB were at least one order of magnitude lower than at the other three sites.

Individual PAH compounds within the same media were similarly distributed at all four sites, indicating a similar mix of sources within each media across the region. PAH distributions in the sediment and water column (both dissolved and sorbed) at LAH and SDB were strongly correlated ($r > 0.93$, $p < 0.001$). Moderate to strong correlations were found in the atmosphere and in the water column among most sites ($0.47 < r < 0.98$, $p < 0.01$). SDB and UNB were not significantly correlated ($p > 0.15$) with any sites in the atmospheric particle

Table 4. PAH concentrations in each medium by site. Mean concentrations \pm standard deviation (sd) are given where $n > 1$.

Site ^a	Parameter	Atmosphere		Water Column		Sediment (ng/g dry wt)
		Gaseous (ng/m ³)	Particulate (ng/m ³)	Dissolved (ng/m ³)	Particulate (ng/g dry wt)	
BCE	t-PAH	15.53	1.67	10,646	3,906	2,463 \pm 3,127
	2 - 3 Ring PAH	8.61	0.41	5,137	2,848	362 \pm 419
	4 - 6 Ring PAH	6.92	1.25	5,509	1,058	2,101 \pm 2,708
LAH	t-PAH	25.86 \pm 9.41	2.01 \pm 1.69	74,538 \pm 15,150	13,960 \pm 6,047	11,076 \pm 1,252
	2 - 3 Ring PAH	18.87 \pm 5.52	0.36 \pm 0.12	36,223 \pm 7,742	5,418 \pm 2,420	1,541 \pm 181
	4 - 6 Ring PAH	6.99 \pm 3.89	1.65 \pm 1.57	38,315 \pm 7,408	8,542 \pm 3,627	9,535 \pm 1,071
UNB	t-PAH	3.36	0.27	5,591	181	654 \pm 256
	2 - 3 Ring PAH	2.21	0.05	2,850	104	77 \pm 25
	4 - 6 Ring PAH	1.15	0.21	2,741	77	576 \pm 230
SDB	t-PAH	21.67	2.50	52,436 \pm 4,771	40,335 \pm 37,744	6,767 \pm 540
	2 - 3 Ring PAH	9.89	1.08	19,856 \pm 3,473	28,328 \pm 30,371	641 \pm 76
	4 - 6 Ring PAH	11.79	1.43	32,580 \pm 1,298	12,006 \pm 7,372	6,125 \pm 464

^aBCE = Ballona Creek Estuary; LAH = Los Angeles Harbor; UNB = Upper Newport Bay; SDB = San Diego Bay.

phase and water column, respectively.

Individual PAH compounds within different compartments at a single site were also similarly distributed, again linking these compartments and suggesting a similar mix of sources across media at a site. Moderate correlations were observed between PAH distributions in the atmospheric gas phase and the dissolved water column ($r > 0.49$, $p < 0.008$) except at SDB, and the dissolved water column and the sediment porewater ($0.411 < r < 0.72$, $p < 0.03$) at all sites. Moderate correlations were also observed between PAH distributions in the sediment and the sorbed water column ($0.45 < r < 0.75$, $p < 0.02$) at all sites. In all cases, the strongest correlations between PAH distributions across media were observed at LAH ($0.58 < r < 0.75$, $p < 0.001$).

Exchange Between the Atmosphere and Water Column

The net gas exchange flux (volatilization – absorption) was positive (net volatilization) at UNB, SDB, and LAH; and negative (net absorption) at BCE (Table 5). At those sites with net volatilization, gas exchange was primarily driven by 2 to 3 ring PAH; while at BCE, which had net absorption, gas exchange was driven by 4 to 6 ring PAH. The largest gas exchange fluxes, observed at LAH and SDB, were driven by the high water concentrations

of PAH at these sites. Net absorption was observed at BCE because this site had relatively low water concentrations (five to seven times lower than SDB and LAH), but air concentrations that were within a factor of two of those sites. UNB, which had the lowest air and water concentrations, had the smallest magnitude of gas exchange.

Dry particle deposition fluxes were typically an order of magnitude lower than gas exchange (Table 5). The negative sign for dry particle deposition indicates movement was downward, from the air to the water. Dry particle deposition fluxes at SDB, LAH, and BCE were all within a factor of two, while UNB flux was six to nine times smaller. Dry particle deposition was dominated by 4 to 6 ring PAH, which constituted the bulk of the atmospheric particle phase at all sites.

The total net exchange between the atmosphere and the water column (gas exchange + dry particle deposition) indicated net volatilization at LAH, UNB, and SDB; and net absorption at BCE (Table 5). Gas exchange was the dominant process of transport between the air and water at all sites. The overall magnitude of the net air-water exchange was larger at LAH and SDB than at BCE by four to six times, and larger than UNB by at least one order of magnitude.

Exchange Between the Water Column and Sediment

Diffusive fluxes of *t*-PAH between the water column and sediment were positive at all sites, indicating the sediment was a source to the water column (Table 5). LAH, SDB, and BCE diffusive fluxes were three to four times greater than at UNB. Diffusive flux out of the sediment into the water column was dominated by 2 to 3 ring PAH (84 to 90%) even though concentrations in the sediment were dominated by 4 to 6 ring PAH. The smaller K_{oc} for the lighter PAH favored rapid transport from the sediment to the water column.

Sedimentation fluxes were one order of magnitude smaller than diffusive fluxes at all sites (Table 5). Because sedimentation was small compared with diffusive flux, the direction of net exchange between the water column and the sediment (diffusive + sedimentation) was determined by the diffusive flux, and indicated net transport from sediment to water at all sites (Table 5).

DISCUSSION

Multimedia Concentrations

High PAH concentrations, especially in the water and sediment at LAH and SDB are not surprising because both water bodies are heavily used for commercial and/or military shipping activities, and historical sediment contamination at these sites has been well documented (Fahey *et al.* 1998, Anderson *et al.* 2001). In addition, both LAH and SDB are adjacent to highly urbanized areas, with numerous atmospheric sources of PAH (e.g., heavy duty truck traffic, industrial activities, congested roadways). In contrast, both UNB and BCE were also adjacent to urban areas, but neither site had the commercial/military shipping activities or heavy industrial activities that were associated with LAH and SDB. Furthermore, the least impacted site (e.g., lowest PAH concentrations in all media) was UNB, which, not surprisingly, is the watershed with the lowest degree of urbanization, and the greatest percentage of open space among the sample sites by far.

The concentration ranges of PAHs observed in this study were generally within the range of concentrations reported elsewhere for urban areas (Table 6). The highest air concentrations of PAH in southern California were ~20 to 40% lower than other highly urban coastal areas (San Francisco, Baltimore, New York/New Jersey), but dissolved water concentra-

tions were nearly twice as high at LAH compared with Baltimore Harbor, seven times higher than San Francisco Estuary, and similar to New York Harbor. Sediment concentrations in the present study were generally within the range observed in these same urban harbors.

Significance of Atmosphere-Water vs. Sediment-Water Exchange

The exchange estimates presented here demonstrate the importance of contaminated sediments as a source of PAH to the water column in coastal waters of southern California. In all cases, the magnitude of the diffusive flux of PAH out of the sediments and in to the water column far exceeds input or output of PAH through air/water exchange processes. For example, the water area of the Port of Los Angeles (POLA) is approximately 13 km². Based on the air/water and sediment/water exchange fluxes estimated for LAH, the sediments contribute approximately 2,000 kg/year of PAH to the water column of POLA, while only approximately 30 kg/year are removed from the water column into the atmosphere through volatilization. Thus, because of high sediment concentrations, input to the water column from the sediment far exceeds input/output from the water column due to air/water exchange.

There are a number of limitations to the exchange estimates calculated in this study. First, the small sample size ($n < 5$) at each site limits the applicability of the exchange estimates to larger spatial and temporal scales. Second, there are uncertainties in a number of literature-derived input parameters (e.g., K_h , K_{oc}) in the exchange models used in this paper. Third, the exchange models included in this study do not account for all exchange processes, including particle resuspension or desorption of organic compounds from resuspended sediments. Fourth, use of K_{oc} to predict partitioning between the sediment and the porewater may overestimate the porewater concentration.

A sensitivity analysis was performed to address some of the limitations on air/water gas exchange and sediment/water diffusive exchange calculations. For gas exchange, variations in temperature (and subsequent temperature-dependent changes in K_h) and wind speed were assessed, to account for the range of these parameters typical for southern California coastal areas. For diffusive exchange between the sediment and the water column, K_{oc} values, PAH sediment concentrations available for parti-

Table 5. Estimated multimedia exchange fluxes in units of ng/m²/day. A positive air/water flux indicates movement from the water to the atmosphere (upward). A positive sediment/water flux indicates movement from the sediment to the water (upward).

Site	Parameter	Air/Water Exchange			Sediment/Water Exchange		
		Net Gas Exchange	Dry Particle Deposition	Net Air/Water Exchange	Diffusive	Sedimentation	Net Sediment/Water Exchange
BCE	t-PAH	-726	-288	-1,015	411,613	-19,140	392,473
	2 - 3 Ring PAH	298	-72	226	322,628	-13,954	308,673
	4 - 6 Ring PAH	-1,024	-217	-1,241	88,985	-5,186	83,800
LAH	t-PAH	6,229	-347	5,882	407,134	-71,196	335,938
	2 - 3 Ring PAH	4,545	-61	4,484	327,249	-27,629	299,620
	4 - 6 Ring PAH	1,684	-286	1,398	79,885	-43,567	36,319
UNB	t-PAH	277	-46	231	98,595	-3,313	95,282
	2 - 3 Ring PAH	282	-9.1	273	80,421	-1,901	78,520
	4 - 6 Ring PAH	-5	-37	-42	18,174	-1,412	16,762
SDB	t-PAH	4,714	-433	4,281	323,367	-44,368	278,998
	2 - 3 Ring PAH	3,886	-186	3,700	230,537	-31,161	199,376
	4 - 6 Ring PAH	827	-246	581	92,830	-13,207	79,623

tioning into porewater, and the overall mass transfer coefficient were varied to account for uncertainties in literature derived K_{oc} values, limitations associated with the use of K_{oc} for determining PAH sediment porewater concentrations, and inclusion of turbulent transport mechanisms.

Air/water flux sensitivity analysis

Temperatures at the coast in southern California do not vary greatly over the year, with an average daily low temperature in the winter of approximately 10°C, to an average daily high in the summer of 25°C (NCDC 2006). Over this temperature range, Bamford *et al.* (1999) observed an average percent change in K_h of $\pm 50\%$. Daily wind speeds in coastal areas of southern California typically average between 2 and 4 m/s, and more than 90% of the daily mean wind speeds were between 1 and 5 m/s in 2006 (NCDC 2006).

At LAH and SDB, the direction of the net gas exchange did not change with variations in temperature (between 10°C and 25°C) and subsequent variation of $\pm 50\% K_h$, or wind speed (between 1 and 5 m/s). Thus, we expect net volatilization at LAH and SDB throughout the majority of the year. In contrast, for wind speeds greater than 1 m/s, increasing the temperature resulted in a change to net volatilization at BCE. Similarly, at wind speeds less than 5 m/s, decreasing the temperature resulted in a change to net absorption at UNB.

These results demonstrate the water column acts as a net source to the atmosphere at LAH and SDB because of high water concentrations at these sites, which overwhelm any sensitivity to changing meteorological conditions. In contrast, for BCE and UNB, the atmosphere may be a source or a sink at different times of the year, depending on the meteorological conditions. Net volatilization is favored with higher temperatures and higher wind speeds, while net absorption is favored at lower temperatures and lower wind speeds. This analysis assumes the concentrations in the air and water reported here are representative of concentrations throughout the year.

Sediment/water flux sensitivity analysis

Sediment porewater concentrations were estimated from equilibrium partitioning based on literature K_{oc} values and sediment concentrations. Literature K_{oc} values for some compounds can vary by as much as 50% due to differences in methods of determining K_{oc} , as well as differences in sorbing properties of the test soil carbon (Karickhoff *et al.* 1979, ASTM 1987). Sensitivity analysis using K_{oc} values of $\pm 50\%$ produced diffusive flux estimates with the same direction of exchange, and within the same order of magnitude as the fluxes reported in Table 6.

In addition, the use of K_{oc} and equilibrium partitioning may overestimate sediment porewater concentrations because pyrogenic PAHs attached to soot particles are not described well by equilibrium parti-

Table 6. Comparison of t-PAH concentrations in the atmosphere, water column, and sediment.

	Southern California ^a	San Francisco Estuary ^b	Chesapeake Bay ^c	Baltimore Harbor ^{c,d,e}	New York/New Jersey Harbor ^{f,g}
Atmospheric Gas Phase (ng/m ³)	3.4 - 26	6.7 - 31	20	39	13 - 44
Atmospheric Particle Phase (ng/m ³)	0.27 - 2.5		0.769	2.1	0.83 - 3.0
Water Column - Dissolved (ng/m ³)	5,591 - 74,538	6,633 - 10,859		44,820	10,677 - 72,183
Sediment (ng/g dry wt)	654 - 11,076			90 - 46,200	5,887

^a range of site means.

^b Tsai *et al.* . 2005; air tPAH = 39, dissolved water tPAH = 26.

^c Dachs *et al.* . 2002; air tPAH = 24.

^d Bamford *et al.* . 1999; dissolved water tPAH = 13.

^e Ashley and Baker 1999; sediment tPAH = 32.

^f Gigliotti *et al.* . 2002; air/water tPAH = 36.

^g Lamoureux and Brownawell 1999; sediment tPAH = 26.

tioning. McGroddy and Farrington (1995) estimated 5 to 50% of sediment phenanthrene and pyrene was available for partitioning into the dissolved fraction of porewater and subsequent diffusive exchange with the water column in Boston Harbor. If only 5% of sediment PAH reported here are available for partitioning into porewater, the diffusive fluxes reported in Table 6 reduce by an order of magnitude. With this reduction, the direction of net sediment/water exchange remains the same for BCE and UNB, but reverses for LAH and SDB. This is because at the later sites, sedimentation from the water column would exceed diffusive flux out of the sediment. Thus, especially for the LAH and SDB sites, the sediment/water diffusive fluxes reported in Table 6 must be viewed with caution. The equilibrium-partitioning model used here may not be adequate for predicting porewater concentrations of PAH in these sediments, and additional study specific to these waterbodies may be required. However, even with reduced diffusive fluxes, the magnitude of the net sediment/water exchange remains one order of magnitude higher than the net air/water exchange.

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