
A pilot study of air-water exchange of organochlorine compounds at three coastal estuaries in southern California

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ABSTRACT

This pilot study investigated the transport of organochlorine compounds (OCs) across the air/water interface to assess the role of the atmosphere as a source or removal mechanism in three urban estuaries of the Southern California Bight (SCB). Concentrations of chlordane, dichloro-diphenyl-trichloroethane (DDT), polychlorinated biphenyl (PCB), chlorpyrifos, and aldrin/dieldrin/endrin were measured in the atmosphere and water column at three water-quality impaired estuarine and/or embayment sites, including Ballona Creek Estuary, the Los Angeles/Long Beach Harbor, and San Diego Bay. Measured concentrations of OCs were used to calculate site-specific gas exchange and dry atmospheric particle deposition fluxes. Net air/water exchange (gas exchange + dry particle deposition) ranged from -27 to 15 ng/m²/day (*t*-chlordane), -14 to 20 ng/m²/day (*t*-DDT), 38 to 130 ng/m²/day (*t*-PCB), -5.0 to 23 ng/m²/day (chlorpyrifos), and -0.23 to 75 ng/m²/day (aldrin/dieldrin/endrin). Net volatilization out of the water column typically dominated the exchange process. These estimates suggest the atmosphere acts predominantly as a sink for OCs at these sites. This pilot study provides the first estimates of OCs air/water exchange rates reported for these waterbodies, providing insight into the role of the atmosphere in contaminated coastal waterbodies within the Southern California Bight. Additional investigation into the temporal

and spatial variability of exchange would be warranted, given the limited sample size of the present study.

INTRODUCTION

Reductions in direct discharges of OCs to coastal waters, including bans on production and use of chlordane, PCB and DDT compounds have resulted in significant decreases in point source loadings of these potentially toxic contaminants and subsequent improvements in water quality and ecosystem health in southern California (Schiff *et al.* 2000). Despite these reductions, many coastal waterbodies in southern California are listed as impaired on the State of California 303d list, and concentrations of many OCs in coastal waters of SCB remain elevated (Zeng *et al.* 2002, 2005). As current use of most OCs is limited, legacy inputs from bottom sediments and the atmosphere remain as potential contaminant sources and/or removal mechanisms for these waterbodies.

Numerous studies in other regions of the country, including Lake Michigan, New York/New Jersey harbor, Chesapeake Bay and San Francisco Bay have investigated the significance of the atmosphere as a potential source or sink of OCs to contaminated waterbodies through gas exchange at the air/water interface or dry particle deposition from the atmosphere to a waterbody surface (Franz *et al.* 1998; Totten *et al.* 2001, 2003; Bamford *et al.* 2002a; Tsai *et al.* 2002). However, the role of the atmosphere

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has not been investigated for contaminated coastal waters in the SCB. While a number of studies report concentrations of OCs in the water and sediment in the SCB, there are limited data on atmospheric concentrations of OCs near contaminated coastal waterbodies, and virtually no studies that report gas exchange and dry particle deposition fluxes for coastal waters in the SCB.

This pilot study was designed to be a range-finding investigation of air/water exchange rates, to assess the role of the atmosphere as a source or removal mechanism for OCs in coastal estuaries of southern California. To accomplish this, concentrations of OCs were measured in the atmosphere and the water column, and the magnitude and direction of gas exchange and dry particle deposition at the air/water interface were calculated for three urbanized estuaries of the SCB.

METHODS

Sample Collection

Three coastal estuaries within the SCB were sampled during the summer and fall of 2006 (Figure 1). All study sites were located near urban areas with varying degrees of local contaminant sources and historical emissions of OCs, and all sites were listed as impaired on the State of California 303(d) list (SWRCB 2002). The Ballona Creek Estuary (BCE) site, adjacent to Santa Monica Bay, is primarily urbanized, with no permitted wastewater or industrial discharges. The Los Angeles Harbor (LAH) site, adjacent to a heavily urbanized area, is the largest commercial port in the United States. 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.

All air samples were collected at land-based sites selected to be generally representative of atmospheric sources near the target waterbodies, and not influenced by other sources not present at the waterbodies themselves. Air samples for BCE were collected on a rooftop approximately 4 km directly south of the estuary where the water samples were collected. Similar to the estuary, this location was upwind of urban atmospheric sources and predominantly influenced by onshore flow of marine air. Air samples for the LAH site were collected at an existing South Coast Air Quality Management District (SCAQMD) site located 3 km directly downwind of the inner harbor. The atmospheric sources near



Figure 1. Map of sampling sites in the Southern California Bight. BCE = Ballona Creek Estuary; LAH = Los Angeles Harbor; SDB = San Diego Bay.

this site were predominantly the same as those at the inner Harbor where the water samples were collected, which was located in the Consolidated Slip shipping basin, near the mouth of Dominguez Channel. Air samples for the SDB site were collected from the roof of the San Diego Naval Station, adjacent to the bay, approximately 30 m from where the water samples were collected inside the bay at the mouth of Chollas Creek.

Air and water samples were collected at least once at each site (Table 1). Daily meteorological data (temperature and wind speed) were obtained from nearby National Weather Service stations (Los Angeles International Airport, Long Beach Airport, and San Diego Lindbergh Field for BCE, LAH, and SDB, respectively; NCDC 2006).

Air samples were collected using a high volume sampler (Anderson Instruments, Inc., Smyrna, GA) equipped with a glass fiber filter (GFF; Whatman, 0.7 mm 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,

Table 1. Site specific sampling information. Mean \pm standard deviation for temperature and wind speed.

Site	Matrix	Sample ID	Collection Date(s)	Air Temperature (Deg C)	Wind Speed (m/sec)
Ballona Creek Estuary (BCE)	Air	1	31-Oct to 2-Nov-06	20 \pm 4	3.4 \pm 0.8
	Water	1	06-Aug-06		
Los Angeles Harbor (LAH)	Air	1	19-Sept to 21-Sept-06	20 \pm 2	2.0 \pm 0.5
		2	18-Oct to 20-Oct-06		
		3	24-Oct to 26-Oct-06		
	Water	1	11-Sept to 18-Sept-06		
		2	22-Sept to 25-Sept-06		
		3	13-Nov to 17-Nov-06		
San Diego Bay (SDB)	Air	1	27-Sept to 29-Sept-06	21 \pm 1	2.8 \pm 0.6
	Water	1	27-Sept to 01-Oct-06		

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 mm GFF, 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 mm 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 subsurface 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.

Analytical Procedures

A total of 58 individual OCs were targeted in this study. These included DDTs (*t*-DDT, defined as the sum of *p,p'* and *o,p'* isomers of DDT, DDE, and DDD), chlordanes (*t*-chlordane, defined as the sum of *cis* and *trans* isomers of chlordane and nonachlor, chlordene heptachlor epoxide B, and oxychlordane),

PCBs (*t*-PCB; defined as the sum of 41 PCB congeners representing tri-through nonachloro homologs), and other pesticides including aldrin/dieldrin/endrin and chlorpyrifos.

All laboratory glassware were washed with soap and water, rinsed with DI water, and kilned at ~500°C for at least 4 hours. Chemicals adsorbed on XAD-II resin were eluted out with dichloromethane (DCM). GFF and PUF samples were Soxhlet extracted with *n*-Hexane/ethyl ether (9:1, v/v) 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 μ l using a gentle stream of ultra high purity (>99.999%) nitrogen.

Sample extracts were analyzed for tri- and some tetrachlorinated PCB homologs (PCB18, 28, 37,

44, 49, 52) using a Varian 3800 gas chromatograph/Saturn 2000 ion trap mass spectrometer (GC-ITMS; Varian, Walnut Creek, CA). A splitless volume of 1 μ l was injected at 100°C (0.05-minute hold), and the injector temperature was increased to 280°C at ~200°C/minute (20-minute hold). The carrier gas was helium (>99.999%) at a flow rate of 1.0 ml/minute. Chromatographic separation was made with a 60 m \times 0.25 mm i.d. (0.25 μ m 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 at 5°C/minute (39-minute hold). The MS was operated in the electron ionization and selected ion storage mode. Quantification of individual analyte concentrations was by the internal standard method (PCB 30 as the internal standard) 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.

For OC pesticides and higher chlorinated PCB congeners (PCB66, 70, 74, 77, 81, 87, 99, 101, 105, 110, 114, 118, 119, 123, 126, 128, 138, 149, 151, 153/168, 156, 157, 158, 167, 169, 170, 177, 180, 183, 187, 189, 194, 200, 201, 206), sample extracts were analyzed using an Agilent 7890 GC/5975C quadrupole mass selective detector (GC-MSD; Wilmington, DE, USA). The analytical column was a DB-XLB (30 m \times 0.25 mm \times 0.25 μ m; Agilent J&W Scientific). The GC oven temperature program was as follows: 90°C (1-minute hold); ramp to 150°C at 5°C/minute, ramp to 260°C at 3°C/minute, and ramp to 320°C at 20°C/minute (5-minute hold). A 10-minute post run segment at 330 °C with carrier gas (helium) backflush was programmed after each injection. The splitless injection volume was 1 μ l with a He flow rate of 1.9 ml/minute. The MSD was operated in negative chemical ionization (NCI) mode with methane as the reagent gas at 40% flow rate. The temperatures of the MSD transfer line, ion source and quadrupole were 320, 150, 150°C, respectively. Selected ion monitoring (SIM) mode was used and target analytes were quantified using the internal standard method (with PCB205 as the internal standard) using a 6-point (2 to 250 ppb) calibration curve.

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. Mean field blanks ranged from 0 to 7% (chlordanes), 3 to 17% (DDTs), 25 to 49% (PCBs), 9 to 54% (chlorpyrifos), and 0 to 22% (aldrin/dieldrin/endrin) of their respective mean sample mass, and all concentrations in the corresponding air samples were field blank corrected. Procedural blanks for all media, which were analyzed using the same protocols followed for sample analysis, did not contain target analytes.

Because sample volumes were variable, compound specific detection limits were also variable (Table 2). Samples were spiked with a mixture of surrogates prior to extraction to estimate recovery efficiency. Mean recoveries of surrogates in all media were 78 \pm 9% and 87% \pm 10% for PCB65 and PCB209, respectively. Because mean recoveries were considered quantitative (i.e., >70% and <130%), sample concentrations were not corrected for surrogate recovery.

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. Colloidal interactions in the water column were not accounted for in the gas exchange calculation. For each exchange process, a flux was calculated for individual compounds and summed to give a total for PCB, DDT and chlordane compounds. For concentration sums and flux calculations, $\frac{1}{2}$ MDL was substituted for concentrations below detection. If a compound was below detection in both air and water, no gas exchange 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 by:

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

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, and H' is the dimensionless Henry's Law constant.

Table 2. Nominal detection limits by sample matrix for organochlorine compounds. STD = standard deviation for the mean.

	Atmosphere (pg/m ³)		Dissolved Water Column (ng/L)	
	Range of Individual Compounds/Congeners	Mean±STD	Range of Individual Compounds/Congeners	Mean±STD
Chlordanes	0.87 - 6.9	3.1 ± 2.1	0.00044 - 0.0064	0.0021 ± 0.0015
DDTs	13 - 49	28 ± 12	0.0066 - 0.046	0.018 ± 0.0095
PCBs	0.15 - 9.2	2.2 ± 2.5	0.00008 - 0.0087	0.0014 ± 0.0017
Chlorpyrifos	4.4 - 4.9	4.7 ± 0.20	0.0022 - 0.0046	0.0031 ± 0.00089
Aldrin/Dieldrin/Endrin	2.7 - 30	13 ± 12	0.0014 - 0.028	0.0085 ± 0.0081

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

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

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):

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

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):

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

where $k_{w(CO_2)}$ is the mass transfer coefficient in water for CO₂.

These relationships have been used previously by a number of researchers to calculate gas exchange of organic compounds over water (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):

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

where D_a is the molecular diffusivity in air, and

$$k_{w(unknown)} = k_{w(CO_2)} * [D_{a(unknown)}/D_{a(H_2O)}]^{0.5}$$

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. For PCBs, temperature corrected Henry's Law Constants for 20°C were obtained from Bamford *et al.* (2002b). For pesticides, Henry's Law Constants for 20°C were obtained from compiled chemical properties when available (Mackay *et al.* 1997), or calculated as described in Hilal *et al.* (2003).

Dry Particle Deposition Model

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

$$F = C_p * V_d$$

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)

RESULTS

Sampling Conditions and Multimedia Concentrations

Daily average meteorological conditions varied by site (Table 1). A total of five gas and particle phase atmospheric samples and five dissolved water column samples were collected between August and November, 2006.

Chlordane compounds were detected in the air and water-column in all samples (Table 3). Atmospheric concentrations of *t*-chlordane ranged from 81 pg/m³ to 618 pg/m³ in the gas phase, and 5.5 to 434 pg/m³ in the particle phase. Atmospheric *t*-chlordane concentrations were predominantly in the gas phase (75 - 99%) at LAH and in the particle-phase (66 - 67%) at BCE and SDB. Atmospheric concentrations in both the gas and particle phase were typically dominated by *cis*- and *trans*-chlordane and *cis*- and *trans*-nonachlor, with some exceptions. For example, heptachlor Epoxide B comprised 50% of the gas phase for a single sample at LAH. Distributions of atmospheric concentrations in both the gas and particle phase were not well correlated among samples, indicating both spatial and temporal variability in atmospheric concentrations. For three out of five samples *t*-chlordane concentrations were below MDL in the particle phase, and two of five samples in the gas phase had *t*-chlordane concentrations within a factor of two to four of the MDL. Dissolved water column concentrations of *t*-chlordane ranged from 91 to 194 pg/L. *Cis*- and *trans*-chlordane and *trans*-nonachlor comprised more than 70% of dissolved water column concentrations in all samples.

DDT compounds were detected in the water column in all samples, and were detected in the air in all but one sample (BCE; Table 3). Atmospheric concentrations for individual DDT compounds were typically below the reporting limit, ranging from ND to 63 pg/m³ and ND to 87 pg/m³ in the gas and particle phases, respectively. Distributions of individual DDT compound in the air were variable, with no single DDT compound dominating across samples. In the water column, dissolved *t*-DDT concentrations ranged from 42 ng/L to 570 pg/L. *p,p*-DDD and *p,p*-DDE comprised 73 to 83% of all dissolved water column samples.

PCBs were detected in the air and water-column in all samples (Table 3). Atmospheric *t*-PCB

concentrations ranged from 91 to 230 pg/m³ and 31 to 112 pg/m³ in the gas and particle phases, respectively. In the water column, dissolved *t*-PCB concentrations ranged from 210 to 700 pg/L. Lesser-chlorinated PCB congeners (Cl3 to Cl5) represented the bulk of *t*-PCB concentrations in all air and water samples (57 - 100%) except in the atmospheric gas phase at a single sample at LAH, which was comprised of 60% higher chlorinated PCB congeners (Cl7 to Cl9). The congeners detected varied by sample and by medium. In the air, 4 to 21 congeners were detected in the gas phase, 8 to 24 congeners were detected in the particle phase, and 17 to 27 congeners were detected in the dissolved water column in any given sample. Six PCB congeners were detected in all 5 air samples (PCB28, 52, 74, 123, 128, 180), and 15 PCB congeners were detected in all 5 water column samples (PCB49, 52, 66, 70, 74, 87, 99, 101, 105, 110, 118, 138, 149, 151, 153/168). Of these, only PCB52 was detected in both the air and water in all samples.

Other pesticides (Chlorpyrifos and Aldrin/dieldrin/endrin) were detected in the majority of atmosphere and water column samples (Table 3). Atmospheric concentrations of these pesticides ranged from ND to 79 pg/m³ and ND to 5.8 pg/m³ in the gas and particle phases, respectively. Dissolved water concentrations ranged from ND to 180 pg/L.

Gas Exchange at the Air/Water Interface

A positive gas exchange flux indicated net volatilization from the water column to the atmosphere, while a negative gas exchange flux indicated net absorption from the atmosphere into the water column. With few exceptions, the majority of samples had a positive gas exchange flux for all compounds, indicating volatilization from the water column into the atmosphere dominated gas exchange (Table 4). Fluxes ranged from 3.5 to 48 ng/m²/day for *t*-chlordane, -6.9 to 32 ng/m²/day for *t*-DDT, and 49 to 135 ng/m²/day for *t*-PCB and -4.9 to 30 ng/m²/day for chlorpyrifos, and aldrin/dieldrin/endrin.

Dry Particle Deposition

Dry particle deposition flux is negative, indicating movement from the atmosphere to the water column. Dry particle deposition fluxes ranged from -1.3 to -75 ng/m²/day (*t*-chlordane), -5.9 to -15 ng/m²/day (*t*-DDT), -5.3 to -19 ng/m²/day (*t*-PCB) and -0.03 to -2.6 ng/m²/day (chlorpyrifos, aldrin/dieldrin/endrin; Table 4). With few exceptions, the magnitudes

Table 3. Concentrations of organochlorine compounds measured in the atmosphere and water column at three coastal sites in southern California. BCE = Ballona Creek Estuary; LAH = Los Angeles Harbor; SDB = San Diego Bay.

Site	Sample ID	Parameter	Atmosphere (pg/m ³)		Water Column - Dissolved (pg/L)
			Gas Phase	Particle Phase	
BCE	1	<i>t</i> -Chlordane	225	434	194
LAH	1		618	7.3	136
	2		222	5.5	167
	3		52	18	124
SDB	1		81	162	91
BCE	1	<i>t</i> -DDT	ND	ND	182
LAH	1		42	34	458
	2		57	87	570
	3		63	53	416
SDB	1		56	42	41
BCE	1	<i>t</i> -PCB	119	112	210
LAH	1		230	31	490
	2		91	48	700
	3		147	61	414
SDB	1		192	34	259
BCE	1	Chlorpyrifos	6.2	1.1	90
LAH	1		79	0.20	43
	2		19	2.7	55
	3		12	0.04	69
SDB	1		64	0.69	7.0
BCE	1	Aldrin	1.8	ND	2.0
LAH	1		0.41	0.18	1.0
	2		0.09	1.2	1.0
	3		0.09	ND	1.0
SDB	1		0.07	0.24	ND
BCE	1	Dieldrin	ND	ND	180
LAH	1		46	ND	75
	2		12	5.8	85
	3		7.3	ND	71
SDB	1		5.3	ND	36
BCE	1	Endrin	ND	ND	44
LAH	1		26	ND	73
	2		35	ND	140
	3		ND	ND	60
SDB	1		4.7	0.65	11

Table 4. Calculated air/water exchange fluxes in ng/m²/day. BCE = Ballona Creek Estuary; LAH = Los Angeles Harbor; SDB = San Diego Bay. A positive air/water flux indicates movement from the water to the atmosphere (upward). Net air-water exchange = gas exchange-dry particle deposition.

Site	Sample ID	Parameter	Gas Exchange	Dry Particle Deposition	Net Air-Water Exchange
BCE	1	<i>t</i> -Chlordane	48	-75	-27
LAH	1		4	-1.3	2.3
	2		16	-0.94	15
	3		9	-3.0	6.2
SDB	1		18	-28	-10
BCE	1	<i>t</i> -DDT	5.6	-14	-8.71
LAH	1		26	-5.9	20
	2		32	-15	17
	3		13	-9.1	3.8
SDB	1		-6.9	-7.2	-14
BCE	1	<i>t</i> -PCB	73	-19	54
LAH	1		85	-5.3	79
	2		135	-8.3	126
	3		49	-11	38
SDB	1		62	-5.9	56
BCE	1	Chlorpyrifos	23	-0.18	23
LAH	1		0.76	-0.04	0.73
	2		7.5	-0.46	7.0
	3		6.9	-0.0077	6.9
SDB	1		-4.9	-0.12	-5.02
BCE	1	Aldrin	0.83	-0.24	0.59
LAH	1		0.21	-0.030	0.18
	2		0.22	-0.20	0.018
	3		0.13	-0.04	0.093
SDB	1		-0.00015	-0.23	-0.23
BCE	1	Dieldrin	75	-0.63	75
LAH	1		15	-0.66	14
	2		19	-1.0	18
	3		9.4	-0.67	8.8
SDB	1		10	-0.60	9.8
BCE	1	Endrin	18	-2.4	16
LAH	1		15	-2.5	12
	2		30	-2.5	27
	3		8.0	-2.6	5.4
SDB	1		3.2	-0.11	3.1

of gas exchange fluxes were greater than dry particle deposition fluxes for all compounds.

Net Air/Water Exchange

The net air/water exchange (gas exchange + dry particle deposition) varied by compound class and site (Table 4). Typically, gas exchange (dominated by volatilization out of the water) exceeded dry particle deposition, and net air/water exchange was positive. Exceptions included *t*-chlordane and *t*-DDT at BCE and SDB, and aldrin and chlorpyrifos at SDB. In the case of *t*-chlordane at BCE and SDB and *t*-DDT at BCE, gas exchange was positive (net volatilization), however the magnitude of dry particle deposition was greater, and thus net exchange to the waterbody was negative. In all other cases where net exchange was negative, gas exchange was negative also (net absorption).

DISCUSSION

These results suggest the atmosphere acts predominantly as a removal mechanism of OCs from the water column in the coastal waterbodies in the present study, and that gas exchange is the dominant exchange process between the water and the atmosphere. This pilot study presents the first estimates of OCs air/water exchange reported for these waterbodies, providing insight into the role of the atmosphere in contaminated coastal waterbodies within the Southern California Bight. The relatively small magnitude of net air/water exchange for aldrin suggests these waterbodies may be approaching equilibrium (e.g., the amount absorbed into the water column from the atmosphere equals the amount volatilized from the water into the atmosphere).

In order to verify the direction of the flux, if not the magnitude, the fugacity ratio approach developed by Rowe *et al.* (2007) was used. In this approach, the fugacity ratio, f , is equal to one at equilibrium. Uncertainty in Henry's Law constants was accounted for by selecting the lowest reasonable Henry's Law constants available, which would produce the most conservative values of f . For the present study, the fugacity ratios were calculated using temperature corrected Henry's Law constants identified in Rowe *et al.* (2007) as the lowest reasonable available. Because the data in the present study were log-normally distributed, the calculated fugacity ratios were log transformed, and a t-test of the pooled data for each congener was used to determine if log f was

statistically different from 0 at the 95% confidence level (e.g., not at equilibrium). For the majority of the PCB congeners, the logs of the fugacity ratios were significantly different from 0 at the 95% confidence level, indicating net gas exchange was not at equilibrium, and confirming the direction of the fluxes reported in Table 4. For 10 PCB congeners (PCB 37, 87, 138, 158, 170, 177, 183, 187, 200, and 206) the fugacity ratios available were not different from 0 at the 95% CI, indicating these congeners were likely near equilibrium. However, because these congeners represented only 3 to 12% of the calculated *t*-PCB gas-exchange flux at any site, assuming a gas exchange flux of zero for these ten congeners and re-calculating the net air/water exchange for *t*-PCB would not change the sign of the net fluxes reported in Table 4 at any site. Thus, uncertainty in Henry's law constants used in the flux calculations would not change the sign of the calculated fluxes reported in the present study.

Both dry particle deposition and gas exchange fluxes of *t*-PCB calculated for Lake Michigan were of the same order of magnitude as the present study (Totten *et al.* 2003, Franz *et al.* 1998), while those calculated for the northern San Francisco Bay Estuary were lower than in the present study by at least a factor of two, and as much as an order of magnitude (Tsai *et al.* 2002). In contrast, compared with the present study, *t*-PCB gas exchange fluxes were higher in the New York/New Jersey Harbor Estuary (Totten *et al.* 2001), Chesapeake Bay (Bamford *et al.* 2002a), and the Delaware River (Rowe *et al.* 2007) by one to two orders of magnitude. These differences are partially due to differences in historical sources, resulting in higher sediment/water concentrations in those regions, and higher wind speeds during sample collection, resulting in greater volatilization. As was the case in the present study, volatilization out of the water dominated gas exchange of PCBs in all of these waterbodies.

Significance of Air/Water Exchange

The air/water fluxes derived from the measurements are components of the mass balance for the individual constituents in the water column (in the atmosphere also, but this is beyond the scope of this study). The net (air/water) flux to/from the water can be expressed as an equivalent residence time in the water column, assuming typical values of water column (10 m). Residence times in the water column range from 14 to 564 days. These values imply

additional contaminant sources/sinks to the water column. Resuspension and desorption of contaminated sediment is a possible source that was not quantified in this study. A recent study in the San Diego Bay concluded that resuspension from sediments is a large source of PCBs to the San Diego Bay (Peng *et al.* 2002). Dry weather urban runoff from adjacent watersheds may also be a source. In addition, water movements associated with local tidal currents are also a likely mechanism acting as a source or sink for OCs at the measurement sites in the present study (Peng *et al.* 2002).

Limitations

There were a number of limitations to the exchange estimates calculated in this study. First, because this study was designed as a pilot study, the sample size was small for each site ($n < 5$) which limited characterization of spatial and temporal variability in air and water concentrations and calculated fluxes. Thus, fluxes presented in this paper provide only a snapshot of conditions at a specific location and time and may not be representative of annual rates over the entire waterbody. Additional measurements would be needed to better characterize spatial and temporal variability of air/water exchange at these sites. However, conditions during all sampling in the present study were representative of typical meteorological conditions that are dominant throughout the dry weather season in southern California (e.g., quiescent, non-storm conditions). Furthermore, water column concentrations of *t*-DDT and *t*-PCB in the present study were generally of the same order of magnitude as measurements reported for nearshore locations in the SCB (Zeng *et al.* 1999) and San Diego Bay (Zeng *et al.* 2002). No recent measurements of air concentrations of OCs have been reported for coastal areas of the SCB.

Second, air and water samples at two of the three sites (BCE and LAH) were not collected simultaneously, which limits the accuracy of the flux calculations at these sites. Air samples at BCE and LAH were collected at land-based sites downwind from their respective waterbodies. In the case of BCE, the land based site was located in an area dominated by on-shore flow of fresh marine air, upwind of urban sources, so large differences in air concentrations between the small spatial scale of the estuary and the air sampling site are expected to be minimal. However, the air samples for the

LAH site were collected downwind of the water, in an area influenced by industrial and commercial activities from the port. Thus measured air concentrations for the LAH site may be higher than air concentrations directly over the water. Lower air concentrations would favor increased volatilization out of the water, which would not change the direction of the fluxes reported in Table 4 for the majority of OCs.

Lastly, colloidal-contaminant interactions in the water column were not accounted for in this study. Thus, volatilization fluxes may be overestimated. Totten *et al.* (2001) estimated colloidal interactions decreased the volatilization flux of PCBs in the New York/New Jersey Harbor by approximately 15%. However, in the majority of cases where volatilization exceeded absorption in the present study, the difference was at least a factor of four; and more often, a factor of ten or more, thus colloidal interactions are not expected to change the direction or substantially change the magnitude of the net fluxes.

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