

San Francisco Bay Atmospheric Deposition Pilot Study Part 3: Dry Deposition of PAHs and PCBs

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ACRONYMS AND ABBREVIATIONS

BAAQMD	Bay Area Air Quality Management District
CARB	California Air Resources Board
CBL	Chesapeake Biological Laboratory
CSJ	City of San Jose
DDW	Double deionized water
DL	Detection limit
FOF	Field-observation Form
HLC	Henry's law constants
IPR	Initial precision and recovery
NADP	National Atmospheric Deposition Program
ND	Non-detected
NQ	Non-quantifiable
OPR	Ongoing precision and recovery
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
POTW	Publicly Owned Treatment Works
PQL	Practical quantification level
PM ₁₀	Particulate matters with aerodynamic diameter of $\leq 10 \mu\text{m}$
PUF	Polyurethane foam
RMP	Regional Monitoring Program for Trace Substances
RRFs	Relative retention factors
SFBRWQCB	San Francisco Bay Region, California Regional Water Quality Control Board
SFEI	San Francisco Estuary Institute
SOP	Standard operating procedures
SRM	Standard reference material
TMDL	Total Maximum Daily Load
U.S. EPA	United States Environmental Protection Agency
V_d	Deposition velocity

ABSTRACT

This report is the third in a three-part series presenting and discussing the results of a Pilot Study conducted from August 1999 through November 2000 to estimate the inputs of selected trace metals and trace organic pollutants from the atmosphere to the San Francisco Estuary in California. This report covers the trace organic component of the Pilot Study that was conducted from June to November 2000.

This study evaluated dry deposition of PAHs and PCBs from the atmosphere to the San Francisco Estuary. Ambient air samples were collected at a single sampling site (Concord, CA) using a modified high-volume air-sampling device equipped with glass fiber filters and polyurethane foam (PUF). Particulate organics collected with the filters and gaseous organics collected with the PUFs were analyzed separately. Direct dry deposition flux of trace organics in the particulate phase is a function of the concentration and the deposition velocity. Estimates of deposition flux through diffusive air-water exchange require a modeling calculation that incorporates a number of critical site-specific input parameters: air concentration in the gaseous phase, water concentration in the dissolved phase, as well as wind speed and surface water temperature.

The concentrations detected in the ambient air ranged from 8.0 to 37 $\text{ng}\cdot\text{m}^{-3}$ for total PAHs and 0.21 to 0.28 $\text{ng}\cdot\text{m}^{-3}$ for total PCBs. PAHs and PCBs in the ambient air samples were predominately in the gaseous phase, ranging from 83 to 99% of these organic compounds in gaseous and particulate phases combined. Fluxes of gaseous PAHs calculated using average historical dry-season data showed high temporal variation, ranging from net volatilization of 800 $\text{ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ from the water to the atmosphere in August for the southern San Francisco Estuary, to net deposition of 1300 $\text{ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ from the atmosphere to the water in November for the northern and central regions of the Estuary. For PCBs, volatilization from the water to the atmosphere was calculated throughout the Estuary during the six-month sampling period. The volatilization flux of gaseous PCBs from different Estuary segments to the atmosphere ranged from 5.8 to 100 $\text{ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$. Organic contaminants present in the particulate phase contributed a deposition flux of 45 to 960 $\text{ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ for the PAHs and 0.39 to 2.1 $\text{ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ for the PCBs.

The monthly estimated deposition loads of total particulate organic contaminants from the atmosphere to the entire Estuary ranged from 1.5 to 33 kg for the analyzed PAHs and from 14 to 70 grams for PCBs. Fluxes of gaseous PAHs were estimated to range from net volatilization (from the Estuary to the atmosphere) of 16 $\text{kg}\cdot\text{month}^{-1}$ in July to net deposition (from the atmosphere to the Estuary) of 42 $\text{kg}\cdot\text{month}^{-1}$ in November. There was consistent net volatilization of gaseous PCBs, ranging from 650 to 2200 $\text{g}\cdot\text{month}^{-1}$, during the six-month sampling period. Combining gaseous and particulate phase fluxes, the net fluxes of PAHs ranged from net volatilization of 13 $\text{kg}\cdot\text{month}^{-1}$ to net deposition of 75 $\text{kg}\cdot\text{month}^{-1}$, while net volatilization of 580 to 2200 $\text{g}\cdot\text{month}^{-1}$ was estimated for PCBs.

This pilot study was performed under a very limited scope to obtain the first set of field data ever collected for airborne total PAHs and PCBs in the San Francisco Bay

Area. Ambient air samples were collected at only one location in Concord. Estimating fluxes of PAHs and PCBs over each Estuary segment or the entire Estuary assumed that the ambient organic concentrations measured at the station were representative of those over the entire Estuary. In addition, several additional input parameters were extrapolated from other monitoring programs conducted around the Estuary at different locations or at different times.

Given the study constraints, a semi-quantitative evaluation of the importance of atmospheric deposition in relation to other loading pathways for PAHs and PCBs is now possible. This study showed a distinct temporal variation of pollutants, especially PAHs, in ambient air and their resultant deposition flux/load estimates. Results from this study suggest that over the sampling period from June to November, there was net deposition of PAHs from the atmosphere to the Estuary, and consistent net losses of PCBs from the Estuary waters to the air. This 6-month study may not have captured the maximum net deposition fluxes of PAHs, and it is unknown whether the net volatilization of PCBs from the Estuary to the air occurs during winter season.

The net deposition of PAHs from the atmosphere to the Estuary during the six-month sampling period indicated that atmospheric transport and deposition might be a significant pathway contributing to the total loading of PAHs to the Estuary. In contrast, the Estuary is a source of PCBs being emitted to the atmosphere. Results of the sensitivity analysis confirm the importance of obtaining comprehensive time- and site-specific measurements for all input parameters in order to adequately capture the spatial and temporal variability in net fluxes of PAHs and PCBs between the atmosphere and the Estuary. Measurements of wet deposition are also needed to fill the missing component in assessing total impact of atmospheric deposition on the loadings of these pollutants to the Estuary.

1.0 INTRODUCTION

Toxic pollutants are routinely emitted into the atmosphere either naturally or by human activities such as industrial sources (stationary sources) and motor vehicles (mobile sources). Toxic pollutants can also be emitted from non-point sources such as soils, waste dumps, or agricultural fields. The distance and means by which air pollutants can be transported depend on several factors: weather conditions, type of pollutant, the phase of the pollutant (solid, liquid, condensed vapor, or gas), and the size of the particle to which the pollutant is adsorbed. These factors also affect the removal rate of a pollutant from the atmosphere. Deposition of pollutants from the atmosphere to surface water can occur through several processes, such as rain or snow scavenging of gases and particles, dry deposition of particles, deposition through cloud and fog water, and air-water diffusive exchange processes.

This Pilot Study was initiated and funded by organizations participating in the Regional Monitoring Program for Trace Substances (RMP), a long-term environmental monitoring program implemented in the San Francisco Bay region. The San Francisco Estuary Institute (SFEI), a scientific institute located in Richmond, CA, coordinated and managed the Pilot Study under the umbrella of the RMP. This report describes the methodology used in monitoring PAHs and PCBs in the ambient air, and presents the measured ambient air concentrations and the estimates of atmospheric deposition of these chemicals to the San Francisco Estuary.

2.0 OBJECTIVES OF THE STUDY

Section 303(d) of the Clean Water Act requires states to identify impaired water bodies and the pollutants causing the impairment, and to establish a Total Maximum Daily Load (TMDL) of the pollutant to the water body allowable to eliminate the impairment. PCBs have been implicated to impair beneficial uses of the San Francisco Estuary. Fish caught from the Estuary have shown PCB concentrations at levels that may pose a threat to human health if consumed. As a result of a 1994 San Francisco Bay Regional Water Quality Control Board study, the Office of Environmental Health Hazard Assessment issued an interim health advisory for people consuming fish from San Francisco Bay. This interim advisory remains in effect (Davis et al. 2000; SFBRWQCB 1999), and as a result, PCBs have been placed on the Section 303(d) list of the pollutants causing impairment of the San Francisco Estuary. Although certain PAHs at times exceed water quality criteria, they are not currently listed under 303(d). PAHs are contaminants of concern due to the toxic properties of certain PAHs, which differ in their toxic risks depending on their concentrations, chemical properties and routes of exposure (e.g. more soluble PAHs may pose greater risk to aquatic organisms). In addition, the trend of increasing PAH concentrations observed in bivalve tissues was suspected of contributing to the sediment toxicity and altered benthic communities.

In addition to identifying pollutants that impair water bodies, the state must identify pollutant sources and allocate the allowable pollutant load from those sources. The state must also establish an implementation plan, and the TMDL allocation and implementation plan must be incorporated into the state's basin plans. Estimating the relative magnitude of loading contributed from each potential source and pathway is one

of the first steps toward implementing the TMDL workplan or anti-degradation plan for a pollutant of concern.

Among the previously identified primary sources and pathways contributing pollutant loads to the water column of the Lower and Central South San Francisco Bay (TetraTech 1999), three contribute external pollutant loads to the entire San Francisco Estuary.

- a. non-point sources associated with runoff and erosion (load from tributaries and storm drains), including contribution from atmospheric deposition
- b. direct atmospheric deposition
- c. point-source wastewater effluent discharges from municipal (Publicly-Owned Treatment Works, POTWs) and industrial facilities, which may include contribution from indirect atmospheric deposition through stormwater drainage to some treatment plants.

The primary objectives of this study were to: 1) determine concentrations of PAHs and PCBs in both gaseous and particulate phases in the ambient air; and 2) estimate direct dry atmospheric deposition fluxes and loads of PAHs and PCBs across the San Francisco Estuary. Estimating fluxes and loads from wet deposition was not included in the scope of work for this study due to budget constraints.

3.0 METHODOLOGY

The San Francisco Bay Area is densely urbanized, with a mix of residential, commercial, industrial (mostly electronics/high technology and other light industries), agricultural, and undeveloped (open space) land uses. There are many congested major highways surrounding the Estuary. The Central Bay has two major airports and seaports. The South Bay is the hub for electronic industries and has an expanding major airport. Several petroleum refineries in the region are located in the North Bay where the City of Concord is situated.

In the summer, northwest winds from the Pacific coastline are drawn landward through the Golden Gate and over the lower portions of the San Francisco Peninsula (BAAQMD 1998). Wind speeds may be locally strong in regions where air is channeled through narrow openings such as the Carquinez Strait, the Golden Gate passage, or the San Bruno Gap (Figure 1). In the winter, the Bay Area experiences storm periods with moderate-to-strong winds ($>5 \text{ m}\cdot\text{sec}^{-1}$) and periods of stagnation with very light winds ($<1 \text{ m}\cdot\text{sec}^{-1}$). Winter stagnation episodes are characterized by air mass outflow from the Central Valley, nighttime drainage airflows in coastal valleys, weak onshore airflows in the afternoon, and other light and variable winds. Analogous to a Mediterranean climate, the wet season in the Bay Area between November and April, and the remaining dry season are hydrologically distinct (Trujillo et al. 1991). June 2000 through November 2000, the sample collecting period for this study, primarily covered the dry season in the Bay Area.

The California Air Resources Board (CARB) and the Bay Area Air Quality Management District (BAAQMD) are maintaining an extensive network to monitor ambient air quality in the Bay Area. Ambient air samples for the Pilot Study were collected every 12 days for six months at one of the existing air monitoring stations managed by BAAQMD in Concord, California. The sampling schedule coincided with BAAQMD's schedule established for the ambient air quality monitoring program implemented in the Bay Area.

Established methods were used for monitoring the concentrations of PAHs and PCBs in the ambient air (Bamford et al. 1999a; Nelson et al. 1998; Pirrone et al. 1995; USEPA 1999a; USEPA 1999b). Reasonable assumptions and parameters were incorporated into the model for estimating deposition fluxes and loads of PAHs and PCBs across the San Francisco Estuary. A sensitivity analysis was also conducted to evaluate the influence of the input parameters on the deposition flux estimates.

3.1 Sample Collection

Between June 5, 2000 and November 21, 2000, 24-hour integrated air samples were collected every 12 days from the BAAQMD ambient air quality monitoring station located in Concord, California (Figure 1). The 24-hour samples began and ended at 00:00 PST. Air was sampled using a modified Hi-Volume air sampler (Model GPSHV1-313; Andersen Instruments Inc., Smyrna, Georgia). The air sampler separates gas and aerosol phases of atmospheric hydrophobic organic contaminants by pulling air through a 25 cm x 20 cm, 40 μm nominal pore-size glass fiber filter and polyurethane foam (PUF;

8.5 cm by 10 cm) plug in series. Aerosols were collected on glass fiber filters, and the gas phase was collected on a PUF plug, which was held in place by a glass sleeve. Air sampler flow rates were calibrated to $\sim 0.35 \text{ m}^3 \cdot \text{minute}^{-1}$, yielding $\sim 500 \text{ m}^3$ of air for the first five samples. This was later increased to $0.5 \text{ m}^3 \cdot \text{minute}^{-1}$, yielding $\sim 800 \text{ m}^3$ of air for each subsequent sample. Table 1 lists the samples, the dates they were collected, and the total volume of air collected for each sample.

Each filter and PUF sampling assembly were prepared and pre-assembled as a single unit at the Chesapeake Biological Laboratory (CBL), and shipped to Concord, CA at least two business days prior to the next scheduled sampling date. The assemblies were shipped via a 2nd-day delivery in a cooler that was also used for the return shipment of the samples. The field operator at the monitoring station deployed and collected the sampling units. After each sampling period, the filter and PUF assemblies were removed, sealed in the cooler on blue ice, and shipped back to CBL via 2nd-day delivery. Upon sample receipt at CBL, the PUFs were removed from their glass sleeves with forceps, individually sealed in glass jars, and stored at -20°C until analysis. Filters were folded individually in aluminum foil, and stored frozen until analysis.

Prior to sampling, all glass was wrapped in aluminum foil and baked at 450°C for four hours. Glass fiber filters were also baked at 450°C sealed in aluminum foil. PUF plugs were cleaned in a bath of soap and Nanopure water, rinsed with Nanopure water, and then Soxhlet extracted with chromatographic-grade petroleum ether for 24 hours. Following extractions, PUFs were dried in a vacuum desiccator and stored in pre-baked glass containers until the sampling unit was reassembled.

3.2 Sample Analysis

3.2.1 Sample Extraction

Filter samples were extracted with dichloromethane (CH_2Cl_2) in Soxhlet flasks for 24 hours. PUF samples were extracted with petroleum ether for 24 hours in Soxhlet flasks. Extracts were reduced to $< 3 \text{ ml}$ by rotary evaporation, transferred to hexane, and further concentrated under a gentle stream of zero-grade N_2 to a final volume of $\sim 0.5 \text{ ml}$. The concentrated samples were transferred to amber auto-sample vials, which were sealed with Teflon-lined caps until quantification of PAHs.

After quantification of PAHs was completed, the remaining extracts were further purified by fractionation on an 8-gram magnesium aluminum silicate column (Florisil, 60-100 mesh, J. T. Baker Co., Phillipsburg, NJ) before PCB analyses. The Florisil was cleaned by extraction with 1:1 (v/v) acetone:hexane in Soxhlet flasks for 24 hours, activated at 550°C for 4 hours, and partially deactivated with 2.5% deionized water prior to use. The PCB congeners were eluted through the column with 35 ml petroleum ether. The PCB fraction was reduced to $< 3 \text{ ml}$ by rotary evaporation, transferred to hexane and further concentrated under a gentle stream of zero-grade N_2 to a final volume of $\sim 0.5 \text{ ml}$. The concentrated samples were then transferred to pre-cleaned amber auto-sample vials sealed with Teflon-lined caps.

3.2.2. Quantification of Analytes

Concentrations of 39 individual PAHs were quantified using a Hewlett Packard 5890 Series II Plus capillary gas chromatograph equipped with a Hewlett Packard 5972 Series Mass Selective Detector. The mass spectrometer was operated in selective ion monitoring mode (SIM) (Leister and Baker 1994). The column was a cross-linked 5% diphenyl-dimethylpolysiloxane capillary column, 30 meters in length, 0.25 mm inner diameter with a film thickness of 0.25 μm (HP - 5MS). An automated liquid sampler was used with helium as the carrier gas.

Identification of individual PAHs was based on the retention times of the largest abundance mass ion of each PAH relative to the retention time of a calibration standard containing a mixture of all 39 PAHs (Ultra Scientific). Five internal standards consisting of deuterated PAHs (d_{10} -acenaphthene, d_{10} -phenanthrene and d_{12} -benz[*a*]anthracene, d_{12} -benzo[*a*]pyrene, d_{12} -benzo[*g,h,i*]perylene) were added to the calibration standard and samples prior to GC/MS analysis. Internal standards were used to calculate relative response factors (RRFs) for each analyte by comparing a known mass of analyte in the calibration standard to the known mass of a particular internal standard. The equation used to calculate the RRF was as follows:

$$RRF = \frac{M_{IS}}{M_{CS}} * \frac{A_{CS}}{A_{IS}}$$

Where, M_{IS} = Mass of deuterated internal standard in the calibration standard (ng)
 M_{CS} = Mass of analyte in the calibration standard (ng)
 A_{CS} = Area of analyte chromatographic peak from calibration standard
 A_{IS} = Area of deuterated internal standard chromatographic peak from calibration standard

The mass of each individual analyte (M_{PAH}) in the samples was then calculated, applying the RRF derived for the internal standard with the nearest retention time to the following equation. Total PAH concentrations were the sum of all 30 PAH compounds.

$$M_{PAH} = \frac{M_{IS}}{RRF} * \frac{A_{PAH}}{A_{IS}}$$

Where, M_{PAH} = Mass of analyte in the sample (ng)
 A_{PAH} = Area of analyte chromatographic peak from the sample

Concentrations of 119 polychlorinated biphenyl (PCB) congeners¹ were determined by capillary gas chromatography and electron capture detection using a

¹ Polychlorinated biphenyls (PCBs) are a class of chemical compounds in which 1-10 chlorine atoms are attached to the biphenyl molecule. The 209 possible chlorinated biphenyls are called “congeners.” PCBs can also be categorized by their degree of chlorination. PCBs with the same number of chlorines are called “homologs.” PCBs of a given homolog with different pattern of chlorine substitution are referred to as “isomers.”

Hewlett-Packard 5890 gas chromatography equipped with a ^{63}Ni electron capture detector, and a 60 m DB-5 capillary column (0.32 mm inner diameter and 0.25 μm film thickness, J&W Scientific). Procedures used to identify and quantify PCB congeners have been described elsewhere (Mullin et al. 1984). A calibration standard with mixed Aroclors of $610\text{ ng}\cdot\text{ml}^{-1}$ was made, and congeners were identified based on relative retention times. Similar to PAH quantification, a PCB calibration standard was used to generate RRFs for each congener relative to two non-industrially synthesized PCB internal standards (IUPAC no. 30 and IUPAC no. 204). In instances where congeners were not chromatographically resolved, their combined concentrations were reported. Total PCB concentrations in each phase were calculated as the sum of 49 resolved congeners and 31 unresolved co-eluting groups.

3.3 Quality Assurance and Quality Control

3.3.1 Field Spike and Collection Efficiencies

To evaluate the efficiency of the sampling collection procedure and transport to acquire and retain the desired organic contaminants, a PAH and PCB solution with known quantities of analytes were spiked into PUF in the field and shipped back to the laboratory for analysis. The collection efficiency of PUF has been previously investigated (Leister 1993; Simon and Bidleman 1997). Recoveries from this study indicate that the PUF efficiently traps the targeted organics, and the losses of analytes during transport are small relative to losses during subsequent laboratory procedures.

For some samples, break-through of analytes was monitored by placing a second PUF inside the glass column (two samples) or a back-up filter (six samples) in the sampling assembly. Table 1 lists the samples that had either a back-up PUF or filter. Only five of the 39 PAH measured were detected in the second PUF, and only two had concentrations greater than 15% of PAH concentrations collected in the first PUF². No significant quantities of PAHs were found in the back-up filters. PAH gas and particle concentrations reported here were calculated from only the first PUF and filter for each sample. Most PCBs were not found above detection limits in either the back-up PUFs or filters. Therefore, all PCB concentrations were only calculated from the first PUF and filter for each sample. Tables 2 and 3 list the limits of detection for PAHs and PCBs.

3.3.2 Procedural Recoveries

Four deuterated PAHs (d_8 -naphthalene, d_{10} -fluorene, d_{10} -fluoranthene and d_{12} -perylene) and two non-commercially produced PCBs (IUPAC no. 65, and IUPAC no. 166) were added to both PUF and filter samples prior to extraction in order to assess procedural recoveries. Average surrogate recoveries for PUF samples were $68\pm 8\%$ (mean \pm standard deviation) for d_8 -naphthalene, $79\pm 10\%$ for d_{10} -fluorene, $72\pm 8\%$ for d_{10} -fluoranthene, $81\pm 7\%$ for d_{12} -perylene, $73\pm 13\%$ for congener 65, and $85\pm 13\%$ for congener 166. Average surrogate recoveries for filter samples were $63\pm 19\%$ for d_8 -naphthalene, $82\pm 7\%$ for d_{10} -fluorene, $75\pm 15\%$ for d_{10} -fluoranthene, $81\pm 6\%$ for d_{12} -perylene, $72\pm 9\%$ for congener 65, and $83\pm 11\%$ for congener 166. There were no

² Five PAHs detected in the second PUF (in % of the measurement in the first PUF) were fluorene (47%), phenanthrene (14%), anthracene (12%), 1-methylfluorene (50%), and 2-methylanthracene (2%).

considerable differences in surrogate recoveries between matrices, and the overall analytical procedure had an average precision of $\pm 14\%$. To prevent overestimating mass of analytes, these data were not surrogate-corrected.

3.3.3 Trip Blanks

Trip blanks were analyzed to quantify contamination from sampling materials, collection methods, transport, and extraction. A trip blank was a second PUF and filter assembly shipped with the sample assembly. All blanks were extracted and analyzed in the same manner as the samples. The masses of most PAHs and PCBs in the blanks were insignificant compared to those in the samples. PCB and PAH concentrations in the samples were not adjusted for the contribution of the blanks.

3.3.4 Limits of Detection

The instrumental limits of detection were estimated by comparing operational signal to noise ratios of the chromatograph baseline to the expected analyte peaks. The instrumental limits of detection for PAH analytes ranged between 0.01 ng to 0.51 ng/sample (Table 2), and those for PCB congeners ranged from 0.001 ng to 0.04 ng/sample (Table 3).

The operational detection limits were set at three times the mean blank concentration for each PAH and PCB. Even though the chromatographic peaks generated by the blanks were larger than the instrumental operational signal to noise ratio peaks, the use of mean blank concentration is a more conservative method in quantifying analytes than using the signal to noise ratio from the instrumental detection limits (Leister and Baker 1994; Nelson et al. 1998). For both vapor and particulate samples, most of the heavier weight PAHs (molecular weight >166) were above their detection limits, and nearly all PCB congeners were above their detection limits. Analyte masses below the operational detection limits were reported as non-quantifiable (NQ), and analyte masses below the instrumental limits of detection were reported as non-detected (ND). The operational (blank) detection limits for all PAH and PCB analytes are shown in Tables 2 and 3, respectively.

4.0 RESULTS AND DISCUSSION

This section presents results of the ambient air sampling and estimates of fluxes and loads of PAHs and PCBs in the San Francisco Estuary. A sensitivity analysis was also performed to evaluate the influence of the input parameters on the resulting estimated fluxes and loadings.

4.1 Ambient Air Concentration

Atmospheric PAHs and PCBs in gaseous phase (PUF samples) and particulate phase (filter samples) were sampled, extracted, and analyzed separately. The concentration of total PAHs detected in the ambient air ranged from 5.7 (June 17) to 56 $\text{ng}\cdot\text{m}^{-3}$ (November 21), and the monthly average concentration ranged from 8.0 to 37 $\text{ng}\cdot\text{m}^{-3}$ (Figure 2). Particulate PAHs made up 1 to 17% of the total PAHs (gaseous and particulate fractions combined) (Table 4). The monthly average concentration of total PAHs found in November was about five times that observed during the other five months (June through October). Concentrations of total PCBs detected in the ambient air ranged from 0.17 to 0.32 $\text{ng}\cdot\text{m}^{-3}$, and the monthly average concentration showed only a minor variation, ranging from 0.22 to 0.28 $\text{ng}\cdot\text{m}^{-3}$ (Figure 3). Between 1 to 9% of the total PCBs were present in the particulate phase during the sampling period.

The CARB has collected ambient air samples at some stations around the Bay Area, using high-volume PM_{10} samplers, and they analyzed for six selected high molecular weight PAHs³ in the particulate phase (CARB 1999). An evaluation of the CARB data from 1995 through 1998 indicated that there was some spatial and seasonal variation in the concentration of particulate phase PAHs. In general, concentrations measured at the stations located in the North Bay (Concord) and South Bay (Fremont and San Jose) were similar, and they were higher than those found in the Central Bay (San Francisco) (Figure 4). This is probably due to the influence of the prevailing wind carrying cleaner air from the Pacific Ocean. An example of seasonal variation in the 1995-1998 data from the CARB Concord station is shown in Figure 5. During the months of March through September, monthly average concentrations of particulate PAHs ranged from 0.2 to 0.5 $\text{ng}\cdot\text{m}^{-3}$. Concentrations of 3 to 4 $\text{ng}\cdot\text{m}^{-3}$ were observed in December and January, about ten times the concentration detected in March through September. The increase in PAH concentration in the winter was at least partially attributable to the increase in residential wood-burning activities. Concentrations of PAHs found in the samples collected for this pilot study from June through November 2000 most likely were lower than the highest concentrations that might be found during the winter season.

Samples collected by CARB included particulate matter of $\leq 10\ \mu\text{m}$ and were analyzed only for six PAHs of higher molecular weight, which constitute a small fraction of the total PAHs in the ambient air. Nevertheless, CARB's data demonstrated that the PAH composition of ambient samples collected at the Concord Site might be representative of most of the sites around the Estuary, except locations where there is a greater influence of the prevailing wind from the Pacific Ocean.

³ The six high molecular weight PAHs analyzed include benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, and indeno(1,2,3-cd)pyrene.

Factors that influence partitioning behavior between vapor and particulate phases include the compound's vapor pressure, the ambient air temperature, and the concentration of particulate matter in the atmosphere. Effects of weather conditions on the concentrations of PAHs and PCBs in the environment have been studied (Franz and Eisenreich 1998), and the results showed that concentrations of trace organics detected in the atmosphere increased during rain events and decreased after rain events. Snow appeared to be a much more effective mechanism than rain in scavenging PAHs and PCBs in the particulate phase from the atmosphere (Table 5).

In the Bay Area, ambient air temperature and the concentration of PM₁₀ in the atmosphere may show some correlation with the partitioning of trace organics between the gaseous and particulate phases in the atmosphere. The percentage of trace organics present in the gaseous phase decreased substantially (corresponding to an increase of trace organics in the particulate phase) with the decrease in air temperature (Figure 6). The decrease in gaseous PAHs was greater than that of gaseous PCBs. During the period of October to November, the ambient air temperature decreased by 5 to 10 °C, and there was some increase in the concentration of PM₁₀ in the atmosphere⁴ (Figure 7). This observation was consistent with results reported by other investigators suggesting that the PAHs are reversibly adsorbed to atmospheric aerosols, and that the dominating factor controlling the gas-to-aerosol distribution coefficient was air temperature (McVeety and Hites 1988). Rain events during the sampling period may contribute to an increase in atmospheric concentration of trace organics. However, during this pilot study, rain events occurring on or around the sampling dates, listed in Table 6, did not show any relationship with changes in atmospheric concentrations or partitioning of trace organics. The sampling period for this study was limited, and therefore, it is unknown whether the increase in the total PAH concentration in November or the decrease of trace organics in the gaseous fraction at that time could be a consistent phenomenon occurring during the cooler season, as the PM₁₀ data from CARB seem to suggest.

4.2 Sources of PAHs and PCBs

4.2.1 PAHs

Most PAHs are not intentionally synthesized and primarily exist in the atmosphere as byproducts of the incomplete combustion of almost any fuel. PAHs enter the environment predominantly through human activities such as the combustion of fossil fuels for transportation and electricity generation, various industrial processes, biomass burning, waste incineration, and oil spills. Vehicle traffic, coke manufacturing, aluminum production, and forest fires/wood burning are the major sources of PAH emissions in the U. S. (Dickhut et al. 2000). Based on isomer ratios, sources of various particle-associated PAHs could be identified. Dickhut et al. (2000) performed an analysis of particulates collected from different environmental media throughout the Chesapeake Bay and concluded that combustion of coal was the predominant source of carcinogenic PAHs found in the surface sediments. On the other hand, most of the carcinogenic PAHs detected in the particles of air, rain, sea surface microlayer, and surface water samples

⁴ PM₁₀ signifies particulate matter with aerodynamic diameter of $\leq 10 \mu\text{m}$. These data were obtained from the samples collected by CARB from January 1995 through September 1998 at the San Jose station, which is located about 40 miles south-west of the Pilot Study sampling site in Concord (CARB 1999).

from the Chesapeake Bay region were derived from automotive sources. Dickhut et al. (2000) postulated that PAHs input to the Chesapeake Bay from motor vehicles were either degraded prior to deposition to the sediments or were diluted by previously deposited coal-derived PAHs in the seabed.

Ratios of nonalkylated to alkylated PAHs have been identified as sensitive indicators of petrogenic and pyrogenic inputs (Colombo et al. 1989). Nonalkylated/alkylated ratios are high for pyrogenic PAH mixtures (formed at higher temperature) and low for petrogenic PAHs (formed at lower temperature). In the ambient air samples collected in this study, alkylated PAHs constituted from 22 to 27% of the total PAHs, with the higher percentage of alkylated PAHs being observed in July and August at 26 and 27%, respectively. The remaining four months had 22-23% alkylated PAHs. The nonalkylated/alkylated ratios ranged between 2.7 to 3.5, typical for samples with automobile exhaust as the main source of PAHs. This is consistent with the findings in the RMP water and sediment samples.

There are a number of sources of PAHs in motor vehicle exhaust, including unburned fuel, lubricating oil, and pyrosynthesis from lower molecular weight aromatics. In a study analyzing gasoline and diesel fuel samples collected in northern California, light duty vehicles were found to be a significant source of heavier (four and five-ring) PAHs (HPAH), whereas heavy-duty diesel engines were the dominant source of three-ring lighter molecular weight PAHs (LPAH) (Marr et al. 1999). Results from a study investigating relative sources of inhalable fine particulate matter to the atmosphere showed that automobiles without catalytic converters produced total PAHs in exhaust at a rate that was more than 25-fold higher than automobiles equipped with catalytic exhaust emission control devices (Rogge et al. 1993). New heavy-duty diesel trucks tested showed an average total PAH emission rate that was only one-seventh as large as seen for the noncatalyst automobiles. The consistent dominance of the lower molecular weight PAHs, consisting of 73 to 80% of the total PAHs detected in this study (Table 8), suggests that heavy-duty diesel engines and the noncatalyst automobiles might be the major contributors of the PAHs detected in the ambient air. In RMP water and sediment samples, PAHs are predominant in the particulate phase with HPAHs as the dominant species. The discrepancy of LPAHs/HPAHs distribution in the ambient air vs. that in the water and sediment samples may represent the collective effects of environmental fate and transport processes, in addition to differences in their contributing sources and pathways.

The drastic increase of total PAHs in November was accompanied by an increase in retene concentration. It has been suggested that retene can be used as a molecular marker of wood combustion byproducts detected in the ambient air (Oros and Simoneit 1999; Ramdahl 1983). Ramdahl (1983) identified several alkylated PAH compounds which may be related to combustion of coniferous wood, with the main compound retene being formed by thermal degradation of diterpenoid resin compounds in the wood. Therefore, the drastic increase in PAHs observed in the Bay Area during cooler months was at least partially attributable to the increase in residential wood-burning activities.

4.2.2 PCBs

PCBs are a group of synthetic organic chemicals that contain 209 individual chlorinated biphenyl compounds known as congeners. PCBs do not burn easily and are good insulating materials. They were used widely as coolants and lubricants in transformers, capacitors, and other electrical equipment. Manufacturing of PCBs was banned in the U.S. in October 1977 because of the evidence that PCBs were persistent, accumulating in the environment, and causing harmful effects (ATSDR 1993). Consumer products that may contain PCBs are old fluorescent lighting fixtures, electrical devices or appliances containing capacitors made before PCB use was banned, old microscope oil, and hydraulic fluids. In addition, PCBs were also widely used in transformers, and a substantial amount of PCBs may still be in use in closed systems. As a result of their widespread use, PCBs releases into the environment were common for several decades, and still have the potential to be released today.

4.3 Estimated Deposition Fluxes and Loads

4.3.1 Modeling Equations

In order to estimate deposition load of chemicals from the ambient air to the Estuary, a series of calculations was performed. The methodology defined in the Quality Assurance Project Plan established for the Integrated Atmospheric Deposition Network was applied to estimate the atmospheric deposition of toxic chemicals to the Great Lakes (Hoff et al. 1996). That methodology was used here to derive estimates of dry deposition of PAHs and PCBs from the atmosphere to the Estuary surface. The five equations used in the calculation are shown below. Appropriate conversion factors have been applied to all calculations to standardize parameters expressed in different units (e.g., day vs. year, ng vs. µg, m³ vs. L, etc.).

$$L_d = AK_{0L}C_{a,g}(RT/H) \text{ (gas absorption)} \\ + AC_{a,p}V_d \text{ (particulate deposition)} \quad (1)$$

$$V = AK_{0L}C_{w,d} \text{ (volatilization/evasion)} \quad (2)$$

$$1/K_{0L} = (1/k_w) + (RT/Hk_a) \quad (3)$$

$$k_{w,x} = k_{w,CO_2} (Sc_x/Sc_{CO_2})^{-0.5} \quad k_{w,CO_2} = 0.45(u_{10})^{1.64} \quad (4)$$

$$k_{a,x} = k_{a,H_2O} (D_{a,x}/D_{a,H_2O})^{0.61} \quad k_{a,H_2O} = 0.2 u_{10} + 0.3 \quad (5)$$

Where: A = area of the Estuary, m²
C_{a,g} = concentration of gaseous trace organics in air, ng·m⁻³
C_{a,p} = concentration of particulate trace organics in air, ng·m⁻³
C_{w,d} = dissolved trace organic concentration in water, µg·L⁻¹
D_{a,x} = diffusivity, cm²·sec⁻¹
H = Henry's law constant, Pa m³·mol⁻¹
K_{0L} = air-water mass transfer coefficient, m·yr⁻¹ in equations (1) and (2), m·day⁻¹ in equation (3)

$k_{w,x}$	=	water-side mass transfer coefficient, $\text{m}\cdot\text{day}^{-1}$, of the gas x
$k_{a,x}$	=	air-side mass transfer coefficient, $\text{m}\cdot\text{day}^{-1}$, of the gas x
L_d	=	total dry atmospheric deposition to the Estuary, $\text{g}\cdot\text{yr}^{-1}$
R	=	gas constant, $\text{Pa}\cdot\text{m}^3\cdot(\text{mol}\cdot^\circ\text{K})^{-1}$
Sc	=	Schmidt number
T	=	temperature, degrees Kelvin ($^\circ\text{K}$)
u_{10}	=	wind speed at 10 m height, $\text{m}\cdot\text{sec}^{-1}$
V	=	loss from volatilization/evasion ($\mu\text{g}\cdot\text{yr}^{-1}$)
V_d	=	particulate deposition velocity, $\text{m}\cdot\text{yr}^{-1}$

4.3.2 Evaluation of Modeling Input Parameters

Deposition of dry particles from the atmosphere to the Estuary surface depends on their deposition velocity (V_d), whereas deposition of chemicals in vapor phase depends primarily on an air-water exchange mechanism. Dry deposition velocity is determined from various parameters such as particle size, meteorological conditions, and characteristics of the deposition surface (Caffrey et al. 1998). Fluxes of trace organics between the atmosphere and the Estuary surface through air-water exchange is based on several chemical and physical parameters of the pollutants, wind speed, surface water temperature, the gaseous pollutant concentration in the air, and the dissolved pollutant concentration in the surface water. The selection of these modeling input parameters is described below.

4.3.2.1 Selected PAHs and PCBs

Because this pilot study did not include collection and analysis of surface water samples at the same times as the air sample collection, concentrations of dissolved PAHs and PCBs in the Estuary were obtained from the accumulated RMP database for water samples collected 1 m below the surface from 1995 through 1999. Therefore, fluxes could be calculated only for compounds previously measured in water by the RMP. To ensure the water data were most comparable with the ambient air samples collected primarily during the dry season from June to November, only results from dry-season water samples collected during July/August cruises were used. In addition, the 1998 PAH data were excluded due to some QA/QC concerns. Phenanthrene (42%) was the predominant gaseous PAH detected in the ambient air (Figure 8), and it was one of the two compounds that dominated the total of dissolved PAHs found in surface water: 21% phenanthrene and 26% fluoranthene (Figure 9)⁵. Although their fluxes were calculated individually, for graphical presentations, PAHs were grouped as LPAHs or HPAHs. LPAHs are designated as PAHs having two to three rings, and HPAHs are PAHs having four or more rings. Similarly, PCB fluxes were calculated only for congeners measured both in ambient air and surface water (Figures 10 and 11), but for graphical reporting of fluxes and loads, PCB congeners were grouped according to their degree of chlorination (homologs).

4.3.2.2 Chemical Concentrations and Meteorological Parameters

Concentrations of trace organics in the air were derived from the results obtained by this pilot study from June to November 2000, predominantly during dry weather.

⁵ The 1998 data were excluded from this evaluation due to data quality concern.

Average concentrations from RMP sampling during dry season from 1995 through 1999 were used as surrogates for dry-season water concentrations. Water samples taken close to tributaries, at the oceanic reference station outside the Golden Gate, and at Sacramento and San Joaquin River stations were excluded because they are not as representative of the overall water concentrations in the Estuary. Due to data quality issues, all of the 1998 PAH data from the RMP monitoring were excluded. Although the 1998 PCB data were included in calculating average concentrations, it should be noted that unusually heavy and persistent rainfall occurred in spring 1998, possibly skewing the averages upwards. Concentrations of PCB44 and PCB52 detected in the 1998 samples collected at two locations in the northern Estuary were 10 to 20 times the concentrations normally detected at the same locations collected in other years and similarly higher than samples collected at other locations during the same sampling cruise. The detection of high concentrations of PCB44 and PCB52 may have resulted from heavy flooding that mobilized contaminants from upstream sources in some watersheds.

In calculating air-water exchange fluxes, the monthly average gaseous concentrations in the air were used with the annual average dry season dissolved organic concentrations in the water, the monthly surface water temperature measurements, and the monthly average wind speed (Table 7). The air temperature at the water surface was assumed to be equal to the water temperature. Wind speeds were calculated from the hourly data obtained at BAAQMD's meteorological station in Concord from June to November 2000. Surface water temperature data were obtained from U.S. Geological Survey's monthly cruises around the Estuary during the same period (USGS 2001).

4.3.2.3 Deposition Velocity

Employing mathematical models, it was predicted that a minimum average deposition velocity was $0.006 \text{ cm}\cdot\text{sec}^{-1}$ for particles composed of various elements with equivalent spherical diameters between 0.09 to $0.53 \text{ }\mu\text{m}$ under a mean wind speed of $4.0 \text{ m}\cdot\text{sec}^{-1}$ and stable meteorological conditions (Caffrey et al. 1998). The V_d was $0.02 \text{ cm}\cdot\text{sec}^{-1}$ for a particle size of $2.5 \text{ }\mu\text{m}$, and the V_d increased to $11 \text{ cm}\cdot\text{sec}^{-1}$ for a particle size of $60 \text{ }\mu\text{m}$.

Actual V_d is likely to vary, depending on particle size and micrometeorological conditions. Deposition velocities ranging from 0.05 to $6.7 \text{ cm}\cdot\text{sec}^{-1}$ have been reported or used in estimating deposition fluxes of trace organics (Hillery et al. 1998; Hoff et al. 1996; Holsen et al. 1991; Kaupp and McLachlan 1999; Odabasi et al. 1999; Pirrone et al. 1995). Using greased surrogate surface plates in a study in the urban Chicago areas, Holsen et al. (1991) estimated an overall average V_d of $0.5 \text{ cm}\cdot\text{sec}^{-1}$ for PCB. Hoff et al. (1996) and Hillery et al. (1998) assumed a V_d of $0.2 \text{ cm}\cdot\text{sec}^{-1}$ in calculating deposition flux of toxic pollutants in particulate phase, including PAHs and PCBs, to the Great Lakes. By dividing the particulate fluxes measured with greased dry deposition plates by ambient particulate concentrations, Odabasi et al. (1999) estimated a particulate phase overall dry deposition V_d of $6.7\pm 2.8 \text{ cm}\cdot\text{sec}^{-1}$ for PAHs. Some estimates of V_d may represent an overestimate due to sampling artifacts of absorbing gaseous phase PAHs by the grease. The reported V_d values, ranging from 0.20 to $6.7 \text{ cm}\cdot\text{sec}^{-1}$, for particulate semi-volatile organics as summarized by Odabasi et al. (1999) showed that V_d estimated

by studies employing greased dry deposition plates were consistently higher than those estimated by other methods.

In addition, V_d is positively correlated to wind speed. In the absence of a V_d specifically derived for the Bay Area environment, this report assumed a V_d of $0.2 \text{ cm}\cdot\text{sec}^{-1}$. This assumed V_d value was believed to be the best estimate for the Bay Area, considering the average wind speed of $2 \text{ m}\cdot\text{sec}^{-1}$, the distribution of approximately 50% of the PM_{10} (particulate matter in the 0 to $10 \text{ }\mu\text{m}$ size range) in the fine particle size of $2.5 \text{ }\mu\text{m}$ or smaller (CARB 1999), and the range of V_d values predicted by Caffrey et al. (1998).

4.3.2.4 Henry's Law Constants

It is well recognized that Henry's law constants (HLC) of semi-volatile organic contaminants are very sensitive to temperature. These constants decrease 2-3 times for every 10°C decrease in temperature (Hornbuckle et al. 1994). In addition to temperature dependence, methods used in deriving the values and the purge vessels used in conducting the experiments may also affect the measurement of the HLCs (Dunnivant et al. 1988). A range of HLCs have been reported in the literature, based on estimated or measured vapor pressures (indirect method), or based on the experimental measurement of air- and water-phase concentrations (direct method) for PAHs (Bamford et al. 1999a; Hoff et al. 1996; McVeety and Hites 1988; Pirrone et al. 1995) and for PCBs (Achman et al. 1993; Bamford et al. 2000; Bamford et al. 2002; Brunner et al. 1990; Dunnivant et al. 1988; Hornbuckle et al. 1994; Murphy et al. 1987). This report used the experimentally measured HLCs for PAHs (Bamford et al. 1999b) and measured and calculated HLC values for PCBs (Bamford et al. 2000; Bamford et al. 2002) (Tables 10 & 11 respectively). Where there was a lack of data on HLC temperature dependence in the literature, equation (6) below was used to derive the HLC at the temperature of interest (tenHulscher et al. 1992).

$$\text{Log } H_T = \text{log } H_{298} - 2611/T + 8.76 \quad (6)$$

where: H_T = Henry's law constant at temperature T
 H_{298} = Henry's law constant at 298°K
T = Temperature at air-water interface in $^\circ\text{K}$

4.3.2.5 Diffusivity

Diffusivity in of the various PAH and PCB compounds in air and water were derived using the estimation method of Fuller, Schettler, and Giddings in air, and the method of Hayduk and Laudie for water (Lyman et al. 1990).

4.4 Fluxes and Loads of PAHs and PCBs Across the Estuary

Dry particle deposition, gaseous air-water exchange, and wet deposition via rain and snow are the three major atmospheric pathways for semi-volatile organic chemical input to aquatic systems (Zhang et al. 1999). Air-water exchanges of PAHs and PCBs have been thought to be especially important in the whole-system cycling of these compounds in lake-wide mass balance, and as a potential mode of direct entry to the aquatic food chain. Results from several studies have shown that the gaseous flux is

strongly seasonally dependent and individual chemicals may show volatilization (from the Estuary to the atmosphere) behavior in one season and deposition (from the atmosphere to the Estuary) in another season (Hoff et al. 1996). PCBs exhibited net volatilization on a whole-lake annual basis from Lake Superior and Lake Michigan in the early 1990s, while PAHs yielded net air-to-water transfer in Chesapeake Bay, Green Bay, and Lake Michigan (Zhang et al. 1999).

Equations (1) through (5) presented in Section 4.2 were used to calculate dry deposition of PAHs and PCBs in both gaseous and particulate phases. Organic contaminant concentrations, meteorological parameters, and HLCs used in the calculation are presented in Tables 7-13. Results of the flux calculations demonstrate that if concentrations of gaseous organic contaminants in the atmosphere, water temperature, and wind speed are the same, Estuary segments with lower concentrations of dissolved organic contaminants in the water would have greater tendency to exhibit net deposition (absorption) of organic contaminants from the air to the water. Conversely, Estuary segments with higher dissolved organic contaminants in the water will have greater tendency to exhibit net volatilization of these contaminants from the water to the air.

A comparison of the estimated deposition flux of gaseous PAHs and PCBs to different segments of the San Francisco Estuary is presented in Table 14 and Figures 12 and 14, respectively. Among the four site-specific input parameters used in calculating fluxes, only water concentration and water temperature were based on segment-specific data. Air concentrations were measured only at one station close to the northern Estuary, and wind speed was obtained from a meteorological station also situated in the northern Estuary. Therefore, fluxes calculated for the Central Bay and South Bay were estimates based on assumption of air concentrations equivalent to those in the North Bay. Segment-specific data on air concentrations along with wind speeds are needed to further refine the fluxes estimated for the other segments of the Estuary.

Throughout the Estuary, net fluxes of gaseous PAHs exhibited high month-to-month variation, ranging from net volatilization (positive fluxes) of $800 \text{ ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ from water to the atmosphere in July in the South Bay to net deposition (negative fluxes) of $1,300 \text{ ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ from the atmosphere to the North and Central Bay waters in November (Figure 12). In the North Bay, there was generally less volatilization or more deposition of gaseous PAHs from the atmosphere to the water than in other segments. Differences in flux estimated among different Estuary segments were entirely due to differences in water concentrations of dissolved PAH concentrations measured in different segments of the Estuary (Table 12), because all other input parameters used in calculating fluxes were assumed to remain the same among Estuary segments. Monthly variation in the flux estimates within each Estuary segment was due to changes in PAH concentrations in the atmosphere, ambient temperature, and wind speeds.

Loads of total gaseous PAHs to the Estuary were estimated to range from $+15 \text{ kg}\cdot\text{month}^{-1}$ in July and August (net volatilization from the Estuary to the atmosphere) to $-42 \text{ kg}\cdot\text{month}^{-1}$ in November (net deposition from the atmosphere to the Estuary). LPAH

gaseous flux was larger than that of HPAH for most months in the study, regardless of the net direction of gaseous PAH flux (Figure 12).

Consistent volatilization of gaseous PCBs from the water to the atmosphere was estimated throughout the Estuary during the six-month sampling period (Table 14, Figure 14). Volatilization flux of PCBs from various segments of the Estuary ranged 12 to 43 $\text{ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ in North Bay, 5.8 to 21 $\text{ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ in Central Bay, and 31 to 100 $\text{ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ in South Bay. Similar the PAHs, the differences in magnitude of volatilization were related to the differences in the water concentrations of dissolved PCBs in different Estuary segments (Table 13) and monthly variation in ambient temperature (Table 7). Gaseous flux of PCBs was about evenly distributed between lighter (di- to tetra-) and heavier (penta- to octa-) homologs (Figure 14).

Although there were monthly differences in atmospheric PCB concentrations that would affect calculated fluxes, the variations were not as large as seen for PAHs. The greatest flux of PCBs from the water to the atmosphere is in the South Bay. This estimated net loss of gaseous PCBs from the Estuary to the atmosphere is consistent with the results reported by other investigators from studies conducted in estuaries located in areas of the eastern U.S. (Achman et al. 1993; Hoff et al. 1996; Hornbuckle et al. 1994; Hornbuckle et al. 1995; Nelson et al. 1998; Zhang et al. 1999) and in Lake Tahoe (Datta et al. 1998).

Unlike air-water diffusive exchange that can result in a net loss due to volatilization, direct deposition of particulates exclusively adds to the net loading of trace organic contaminants from the atmosphere to the Estuary. Based on the particulate contaminant concentrations detected in the atmosphere (for compounds measured in both air and water) and an assumed V_d of $0.2\text{ cm}\cdot\text{sec}^{-1}$, the deposition flux of particulate contaminants ranged from 45 to 960 $\text{ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ for total PAHs and 0.39 to 2.1 $\text{ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ for total PCBs (Table 14, Figures 13, 15). The monthly deposition load of total particulate was approximately -1.5 to -33 kg (net deposition from the atmosphere to the Estuary) for PAHs and -14 to -70 grams for PCBs over the whole estuary (Table 15).

In contrast to the gaseous flux dominated by lighter PAHs, HPAHs constituted most of the particulate flux in all months (Figure 13). Combining loads of gaseous phase and particulate phase flux, the net loads of PAHs ranged from net volatilization of 13 $\text{kg}\cdot\text{month}^{-1}$ to net deposition of 75 $\text{kg}\cdot\text{month}^{-1}$. Similarly, the particulate flux of PCBs is dominated by deposition of the heavier homologs. Combining the particulate load with gaseous exchange, a net volatilization of 580 to 2200 $\text{g}\cdot\text{month}^{-1}$ was estimated for PCBs over the entire estuary.

This study did not measure deposition fluxes and loads of PAHs and PCBs that were attributable to wet deposition via rainfall. In the mercury component of this pilot study, wet deposition constituted approximately 20% of the total atmospheric deposition (wet and dry deposition combined) (Tsai and Hoenicke 2001). PAHs and PCBs in rainfall contribute only additional deposition to the Estuary, which either increases any estimated net deposition (from the atmosphere to the Estuary) or decreases the estimated

net volatilization (from the Estuary to the atmosphere). The actual magnitude of the contributing offset from wet deposition is unknown without empirical measurements.

It should also be noted that estimates for deposition flux of dry particles assumed a V_d of $0.2 \text{ cm}\cdot\text{sec}^{-1}$. Although this assumption is our current best estimate for the Bay Area environment (see Section 4.3.3), it may represent an underestimate. Assuming a higher V_d value would further increase any net deposition seen (e.g., PAHs in the colder months) but decrease the loss for compounds showing net loss from the Estuary (e.g., PAHs in the summer, and PCBs). In order to achieve a net zero flux of PCBs from the Estuary to the air, one would have to assume a V_d of around $4 \text{ cm}\cdot\text{sec}^{-1}$, an unlikely value given conditions in the region.

Numerous investigators have studied ambient air concentrations and deposition fluxes of PAHs and PCBs. A comparison of some results reported in the literature with those from this study is presented in Tables 16 and 17. Ambient air concentrations of total PAHs detected at 8.0 to $37 \text{ ng}\cdot\text{m}^{-3}$ in the Bay Area were three to 13 times greater than the concentrations detected at a rural site around Chesapeake Bay (Offenberg and Baker 1999) or greater than 30 times the regional background concentrations detected around the Great Lakes (Cortes et al. 2000) (Table 16). Compared to the measurements reported in urbanized areas, air concentrations of PAHs detected in the Bay Area were ten times lower than those measured in the urban Chicago area (Odabasi et al. 1999), but comparable to those found around the urbanized areas in Baltimore (Offenberg and Baker 1999) and New Jersey (Gigliotti et al. 2000). Estimated fluxes in other studies ranged from net absorption (negative values) to net volatilization (positive values). Differences in the magnitude and direction of fluxes were highly dependent on the input parameters incorporated into the equations that were used to calculate the fluxes (see Sections 4.3 described earlier and Section 4.6 below). It should also be noted that using different methods for monitoring ambient air concentrations or using different approaches for estimating deposition fluxes in different studies also affects the reported results. For example, using a water surface sampler in the sample collection (Odabasi et al. 1999) or assuming a dry deposition velocity (Leister and Baker 1994) do not account for the potential loss from the Estuary to the atmosphere via air-water diffusive exchange process. In addition, the total number and specific PAHs measured may differ from one study to another.

A comparison of the air concentrations and deposition fluxes of total PCBs reported by some investigators is presented in Table 17. Concentrations of total PCB (analyzed for a total of 209 congeners) of 0.22 to $0.28 \text{ ng}\cdot\text{m}^{-3}$ detected in this study were two to five times the concentrations measured in the Lake Tahoe basin or the regional background concentrations found in the more pristine areas around the Great Lakes. These concentrations, however, were in the lower end of the concentrations measured in the air samples collected from more impacted areas over the Great Lakes (Table 17). Studies conducted in the Lake Michigan area in 1989 and 1991 showed that Green Bay and Lake Michigan were major sinks of PCBs and volatilization of these compounds from the Bay and the Lake were major sources to the regional atmosphere (Achman et al. 1993; Hornbuckle et al. 1995; Pirrone et al. 1995). Higher volatilization fluxes occurred

at higher water temperatures, higher wind speeds and when there were large differences between the vapor and dissolved-phase concentrations (Hornbuckle et al. 1994). Hornbuckle et al. (1994) reported in their studies conducted from 1988 to 1992 in Lake Superior that the largest depositional flux of PCBs from the atmosphere to the water occurred in May due to higher gaseous PCB concentrations. The highest volatilization flux (from the water to the atmosphere) happened in August when water temperatures and the seasonal wind speed were the highest. The estimated fluxes of PCBs presented earlier in this section suggest that volatilization from the Estuary is a source of the compounds to the atmosphere in the Bay Area.

4.5 Sensitivity Analysis of Deposition Flux Estimates

A sensitivity analysis was performed to evaluate how uncertainty in each input parameter in the air-water diffusive flux-calculation model would affect the magnitude and direction of the estimated fluxes of trace organics in gaseous phase. The sensitivity analysis was run with a range of values for an input parameter to determine how the estimated fluxes responded to the changes in that parameter, and to identify the input parameters that require more accurate measurement in order to obtain better flux estimates.

Phenanthrene and tetrachlorobiphenyls were used for illustration in this analysis. Phenanthrene was the predominant PAH measured in the air samples collected in this study and one of the two predominant dissolved PAHs measured in the water samples collected by the RMP. Tetrachlorobiphenyls are the PCB homologs with an intermediate degree of chlorination among the congeners detected in the air and water samples. The sensitivity analysis focused on the four site-specific input parameters that affect the flux estimates: gaseous air concentration, dissolved water concentration, ambient temperature, and wind speed. Input parameters such as diffusivity, deposition velocity, and Henry's law constants are chemical-specific values derived from the literature, and were not included in this analysis.

In the sensitivity analysis, each input parameter was varied individually with all other parameters set to their default values (Tables 18 and 19). The range of values used for gaseous air concentrations were the range of measurements obtained in this study. The upper end of the PAH air concentration used in this analysis was set at approximately twice the highest concentration measured in this study to account for the possibility that the actual maximum PAH concentration might be two times higher. Dissolved water concentrations were the range of the Estuary-wide seasonal average derived from the 1995-1999 RMP water data. Water temperature data represent the range of the Estuary-wide monthly average measurements obtained by USGS in 2000. The range of wind speed data represents the range of the annual average measurements at 24 cities around the Bay Area in 2000. Defaults were set at values comparable to the data used in this study for calculating fluxes. Positive correlation means that an increase in the value of the input parameter enhances net volatilization from the Estuary to the atmosphere. Conversely, a parameter with a negative correlation increases net deposition from the air to the Estuary with an increase in that parameter.

Fluxes of gaseous phenanthrene are very sensitive to the input parameters included in the flux-calculation model. Under most scenarios evaluated in this analysis, a net deposition of PAHs from the atmosphere to the Estuary occurred (i.e. negative fluxes shown in Table 18). Net volatilization of phenanthrene from the Estuary to the atmosphere (i.e. positive deposition fluxes) occurred only under two scenarios: a low gaseous concentration in the air ($5.5 \text{ ng}\cdot\text{m}^{-3}$) or a high dissolved concentration in water ($17 \text{ ng}\cdot\text{L}^{-1}$). Increasing PAH air concentration from $5.5 \text{ ng}\cdot\text{m}^{-3}$ to $100 \text{ ng}\cdot\text{m}^{-3}$, while keeping the other three input parameters at default values, resulted in flux changing from a net volatilization (from the Estuary) of $580 \text{ ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ to a net deposition (to the Estuary) of $16,000 \text{ ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ (Table 18). Conversely, increasing water concentration from $2.0 \text{ ng}\cdot\text{L}^{-1}$ to $17 \text{ ng}\cdot\text{L}^{-1}$ resulted in flux shifting from net deposition of $1,400 \text{ ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ to net volatilization of $1,500 \text{ ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$. Wind speed and ambient temperature also have similar but smaller influences on the resulting fluxes. Increasing wind speed enhances net deposition, while warmer ambient temperature enhances volatilization. The wind speeds used in this analysis were relatively low, ranging from 2.5 to $5.4 \text{ m}\cdot\text{sec}^{-1}$, and did not take into account the high variation of wind speeds that might occur on a day-to-day basis. Higher wind speed at any given day will result in a large increase in the magnitude of the estimated fluxes.

Chemicals having different properties will exhibit differing sensitivities in the response of their fluxes to the changes in the input parameters. Chemicals with lower volatility have greater tendency to be deposited from the atmosphere to the Estuary. Fluxes of gaseous tetrachlorobiphenyls, much less volatile chemicals than phenanthrene, consistently exhibited net volatilization in all the scenarios assessed in the sensitivity analysis (Table 19). Increases in gaseous concentration in the air enhance deposition from the atmosphere to the Estuary (negative correlation) while the increases of dissolved concentration in the water, ambient temperature, and wind speed enhance volatilization from the Estuary to the atmosphere (positive correlation).

In addition to the input parameters evaluated in this analysis, it should be noted that the HLC values used in modeling the air-water diffusive exchanges have significant impact on the resulting flux estimates. Results from more recent measurements (Bamford et al. 2000; Bamford et al. 2002) indicated that the reported or measured HLCs for some PCB congeners could differ by up to one order of magnitude. For example, using HLC values for PCBs reported by Achman et al. (1993), rather than those based on the data obtained by Bamford et al. used here, resulted in net volatilization fluxes of PCBs roughly half the estimates presented in this report.

This pilot study covered a very limited scope. Ambient air samples were collected at only one location over a six-month period. Estimating fluxes for each Estuary segment or the entire Estuary assumed that the atmospheric organic contaminant concentrations measured at the Concord Station were representative of the entire Estuary. In addition, several other input parameters were extrapolated from other monitoring data collected around the Estuary at different locations or at different times. This study showed a distinct temporal variation, especially for PAHs, of ambient air concentrations and subsequent flux and load estimates. This 6-month study provides the essential

groundwork for further studies in the San Francisco Bay Area. Obtaining comprehensive measurements of the site-specific parameters is critical to the accurate estimate of the magnitude as well as the direction of the fluxes for PAHs and PCBs over the Estuary. Accurate site-specific data are most needed for the measurements of ambient air and water concentrations. Furthermore, studies are needed to obtain estimates of loading from wet deposition, another component contributing to atmospheric deposition.

5.0 CONCLUSIONS

Concentrations of organic contaminants detected in the ambient air ranged from 8.0 to 37 ng·m⁻³ and 0.21 to 0.28 ng·m⁻³ for total PAHs and total PCBs, respectively. PAHs and PCBs in the ambient air were predominantly in the gaseous phase, ranging from 83 to 99% of the total concentrations in the atmosphere. While concentrations of PCBs in the ambient air were rather consistent from month to month, concentrations of PAHs exhibited high seasonal variation, with the highest concentrations detected in November being almost five times higher than the concentrations detected in August. This increase in PAH concentrations in the air also shifted the flux from net volatilization in August to net deposition in November.

Estimated monthly deposition load of total particulate from the atmosphere to the Estuary was 1.5 to 33 kg and 14 to 70 grams for PAHs and PCBs, respectively. Fluxes of total gaseous PAHs to the Estuary were estimated to range from net volatilization of 15 kg·month⁻¹ to net deposition of 42 kg·month⁻¹. There was consistent net volatilization of gaseous PCBs, ranging from 650 to 2200 g·month⁻¹, throughout the six-month sampling period. Combining fluxes of gaseous phase and particulate phase, the net fluxes of PAHs ranged from net volatilization of 13 kg·month⁻¹ to net deposition of 75 kg·month⁻¹, while a net volatilization of 580 to 2200 g·month⁻¹ was estimated for PCBs.

Results of this study show that atmospheric deposition was a pathway contributing a net loading of PAHs to the San Francisco Estuary in the study period. On the other hand, the Estuary appears to be a source of PCBs being emitted to the atmosphere. This pilot study, although performed with limited spatial and temporal scope, provides the essential groundwork for further studies in the San Francisco Bay Area. Results of the sensitivity analysis indicated that obtaining more comprehensive and longer-term data for the site-specific input parameters is critical to the accurate estimate of spatial and temporal distribution, as well as net fluxes of PAHs and PCBs over the Estuary. Among the four site-specific parameters being assessed in the sensitivity analysis, relative concentrations of the contaminants in the air and in the water exert the most influence in the direction and magnitude of the resulting flux. Studies are also needed to obtain estimates of wet deposition, a component missing in this study needed to determine total flux estimates of PAHs and PCBs from the atmosphere to the San Francisco Estuary.

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Table 1 Sampling Parameters - Atmospheric Deposition of Trace Organics to the San Francisco Estuary

Sampling Date	Sample Duration (min)	Average Flowrate (liter/min)	Total Volume (m ³)	PUF Back-up Y = yes	Filter Back-Up Y = yes	Trip Blank Y = yes
05/22/00	Field Spike					
06/05/00	1414	341	481		Y	Y
06/17/00	1406	351	493		Y	Y
06/29/00	1412	343	485		Y	Y
07/11/00	1442	349	503			Y
07/23/00	1406	387	544		Y	Y
08/04/00	1406	563	792			
08/22/00	1408	563	793			Y
08/28/00	1408	568	800		Y	Y
09/09/00	1412	566	799		Y	Y
09/21/00	1408	568	800			Y
10/03/00	1411	568	802			Y
10/15/00	1415	568	804			Y
10/27/00	1409	566	797	Y		Y
11/08/00	1407	568	799	Y		
11/21/00	1408	554	781			

Table 2 Detection Limits for PAHs in both PUF and Filter

Compound	PUF		Filter	
	Instrument DL (ng/sample)	Blank DL (ng/sample)	Instrument DL (ng/sample)	Blank DL (ng/sample)
Naphthalene	0.028	477.35	0.028	5.178
Azulene	0.040	0.00	0.040	0.000
2-Methylnaphthalene	0.105	607.13	0.105	3.685
1-Methylnaphthalene	0.012	187.88	0.012	0.256
Acenaphthylene	0.033	294.10	0.033	0.000
Biphenyl	0.010	158.65	0.010	0.000
Acenaphthene	0.055	115.93	0.055	0.000
Fluorene	0.058	176.13	0.058	2.132
Phenanthrene	0.050	289.71	0.050	0.000
Anthracene	0.052	0.00	0.052	0.000
1-Methylfluorene	0.101	100.55	0.101	2.303
4,5-Methylenepheneanthrene	0.050	3.15	0.050	0.000
2-Methylphenanthrene	0.072	35.20	0.072	2.736
2-Methylanthracene	0.074	0.00	0.074	0.000
1-Methylanthracene	0.084	27.50	0.084	3.287
1-Methylphenanthrene	0.057	12.43	0.057	0.474
9-Methylanthracene	0.087	0.00	0.087	0.000
Fluoranthene	0.064	25.04	0.064	1.064
Pyrene	0.069	40.27	0.069	5.216
3,6-Dimethylphenanthrene	0.084	0.00	0.084	0.000
9,10-Dimethylanthracene	0.150	0.00	0.150	0.000
Benzo[a]fluorene	0.093	9.43	0.093	0.365
Benzo[b]fluorene	0.142	0.00	0.142	1.758
Benzo[a]anthracene	0.144	0.00	0.144	0.000
Chrysene + Triphenylene	0.097	0.00	0.097	3.217
Naphthacene	0.179	0.00	0.179	0.000
Retene	0.273	5.85	0.273	17.314
Benzo[b]fluoranthene	0.296	0.00	0.296	0.000
Benzo[k]fluoranthene	0.213	0.00	0.213	0.000
Benzo[e] pyrene	0.224	0.00	0.224	0.000
Benzo[a] pyrene	0.298	0.00	0.298	0.000
Perylene	0.218	0.00	0.218	0.000
Dimethylbenz[a]anthracene	0.512	0.29	0.512	2.067
3-Methylcholanthrene	0.504	0.00	0.504	13.229
Indeno[1,2,3-c,d]pyrene	0.147	0.00	0.147	0.000
Benzo[g,h,i]perylene	0.207	0.00	0.207	0.000
Anthanthrene	0.226	0.00	0.226	0.000
Dibenz[a,h+ac]anthracene	0.174	0.00	0.174	0.000
Coronene	0.321	0.00	0.321	0.027

DL – Detection Limit; Blank DL is the operational detection limit.

PAHs – Polycyclic aromatic hydrocarbons

PUF – Polyurethane foam

Table 3 Detection Limits for PCBs in both PUF and Filter

Compound	PUF		Filter	
	Instrument DL (ng/sample)	Blank DL (ng/sample)	Instrument DL (ng/sample)	Blank DL (ng/sample)
1	0.016	2.315	0.016	0.000
3	0.042	0.468	0.042	0.000
4+10	0.000	0.082	0.000	0.152
7+9	0.001	0.000	0.001	0.062
6	0.002	0.000	0.002	0.015
5+8	0.004	2.589	0.004	1.037
19	0.001	0.000	0.001	0.000
12+13	0.013	0.081	0.013	0.000
18	0.015	0.705	0.015	0.000
15+17	0.015	0.654	0.015	0.262
24+27	0.001	0.018	0.001	0.005
16+32	0.016	0.611	0.016	0.218
29	0.001	0.000	0.001	0.000
26	0.020	0.298	0.020	0.000
25	0.013	0.080	0.013	0.086
31+28	0.029	0.530	0.029	0.000
33+21+53	0.017	0.411	0.017	0.057
51	0.010	7.439	0.010	0.082
22	0.033	0.000	0.033	0.214
45	0.001	0.006	0.001	0.023
46	0.007	0.000	0.007	0.168
52	0.014	0.000	0.014	0.000
49	0.012	0.000	0.012	0.000
48+47	0.011	0.000	0.011	0.000
44	0.016	0.000	0.016	0.000
37+42	0.018	0.000	0.018	0.000
41+64+71	0.013	0.499	0.013	0.102
40	0.013	0.040	0.013	0.000
100	0.008	0.000	0.008	0.000
63	0.015	0.000	0.015	0.000
74	0.017	0.593	0.017	0.000
70+76	0.026	0.544	0.026	0.000
66+95	0.019	0.000	0.019	0.000
91	0.009	0.000	0.009	0.114
56+60	0.027	0.060	0.027	0.000
92+84	0.043	0.000	0.043	0.000
89	0.019	0.177	0.019	0.000
101	0.008	0.163	0.008	0.022
99	0.010	0.094	0.010	0.000
119	0.001	0.015	0.001	0.023
83	0.005	0.027	0.005	0.000
97	0.005	0.000	0.005	0.000
81+87	0.003	0.112	0.003	0.046
85	0.013	0.000	0.013	0.000

Table 3 (Continued) Limits of Detection for PCBs in both PUF and Filter

Compound	PUF		Filter	
	Instrument DL (ng/sample)	Blank DL(ng/sample)	Instrument DL (ng/sample)	Blank DL(ng/sample)
136	0.007	0.000	0.007	0.000
110+77	0.014	0.064	0.014	0.000
82	0.009	0.000	0.009	0.000
151	0.011	0.000	0.011	0.000
135+144+147+124	0.005	0.000	0.005	0.000
107	0.004	0.009	0.004	0.000
123+149	0.011	0.000	0.011	0.000
118	0.011	0.025	0.011	0.000
134+114+131	0.005	0.072	0.005	0.000
146	0.005	0.201	0.005	0.125
132+153+105	0.019	0.734	0.019	0.628
141	0.021	0.000	0.021	0.000
137+130+176	0.011	0.000	0.011	0.000
163+138	0.017	0.226	0.017	0.000
158	0.003	0.121	0.003	0.113
129+178	0.014	0.000	0.014	0.000
187+182	0.013	0.063	0.013	0.000
183	0.019	0.000	0.019	0.000
128	0.010	0.000	0.010	0.000
185+167	0.016	0.000	0.016	0.000
174	0.013	0.000	0.013	0.000
177	0.016	0.128	0.016	0.000
202+171+156	0.013	0.315	0.013	0.000
157+200	0.022	0.000	0.022	0.000
172	0.010	0.000	0.010	0.000
197	0.033	0.000	0.033	0.000
180	0.018	0.000	0.018	0.000
193	0.030	0.000	0.030	0.000
191	0.015	0.000	0.015	0.000
199	0.007	0.000	0.007	0.000
170+190	0.030	0.000	0.030	0.000
198	0.021	0.000	0.021	0.000
201	0.024	0.000	0.024	0.000
203+196	0.028	0.000	0.028	0.000
189	0.006	0.000	0.006	0.000
208+195	0.035	0.000	0.035	0.000
207	0.009	0.000	0.009	0.000
194	0.013	0.000	0.013	0.000
205	0.009	0.000	0.009	0.000
206	0.021	0.000	0.021	0.000
209	0.002	0.000	0.002	0.000

DL – Detection Limit

PUF – Polyurethane foam

PCBs – Polychlorinated biphenyls

Table 4 Distribution of Total PAHs and PCBs in Gaseous and Particulate Phases

Sampling Date	Distribution of PAHs (%)		Distribution of PCBs (%)	
	Gaseous Phase	Particulate Phase	Gaseous Phase	Particulate Phase
6/5/00	99	1	98	2
6/17/00	96	4	98	2
6/29/00	95	5	95	5
7/11/00	96	5	99	1
7/23/00	94	6	98	2
8/4/00	95	5	98	2
8/22/00	93	7	98	2
8/28/00	92	8	95	5
9/9/00	95	5	98	2
9/21/00	93	7	97	3
10/3/00	91	9	97	3
10/15/00	89	11	96	4
10/27/00	94	6	98	2
11/8/00	85	15	95	5
11/21/00	83	17	91	9

Table 5 Effects of Weather Conditions on the Concentration of PAHs and PCBs Detected in Various Environmental Media¹

Weather Conditions	Ambient Air Samples	
	Total Concentration (ng·m ⁻³)	Particulate Phase (%)
	PAHs	
Before Rain	14.6	17
During Rain	23.9	11
After Rain	9.6	0
Before/During Snow	7.2 to 11.0	18 to 26
During/After Snow	3.1 to 5.0	0
	PCBs	
Before Rain	0.347	9.5
During Rain	0.548	8.5
After Rain	0.124	0
Before Snow	0.082	8.9
Sample Types	Total Concentration (ng·L ⁻¹)	Particulate Phase (%)
	PAHs	
Rain Sample	81	40
Snow Sample	477 to 17580	93 to 96
	PCBs	
Rain Sample	2.78	66
Snow Sample	1.91 to 7.91	79 to 88

¹ Data was obtained from Franz and Einsenreich (1998). Samples were collected in the winter of 1991-1992 at a suburban site in Minnesota.

Table 6 Rain Events that Occurred On or Near Sampling Dates

Sampling Date	Rain Before Sampling Date	Rain On Sampling Date	Rain After Sampling Date
June 5, 2000	No	No	No
June 17, 2000	No	No	No
June 29, 2000	No	No	No
July 11, 2000	No	No	No
July 23, 2000	No	No	No
August 4, 2000	No	No	No
August 22, 2000	No	No	No
August 28, 2000	No	No	No
September 9, 2000	No	No	No
September 21, 2000	No	No	0.04 inch (9/22)
October 3, 2000	No	No	No
October 15, 2000	0.12 inch (10/10 to 10/11)	No	No
October 27, 2000	10/26 (0.4 inch)	0.1 inch	0.33 inch (10/28)
November 8, 2000	No	No	No
November 21, 2000	No	0.03 inch	No

Table 7 Monthly Average Meteorological Parameters

Meteorology	Jun	Jul	Aug	Sep	Oct	Nov
Water Temperature (°C)a	19	19	20	19	18	15
Wind Speed (m·sec ⁻¹)b	2.6	3.0	2.5	1.9	2.1	1.4

Table 8 Monthly Average Gaseous PAH Concentrations in Ambient Air (pg·m⁻³)^c

PAHs	Jun	Jul	Aug	Sep	Oct	Nov
1-Methylnaphthalene	<	<	<	<	<	310
2-Methylnaphthalene	<	<	<	<	<	730
Azulene	<	<	<	<	<	<
Biphenyl	<	<	<	<	<	330
Naphthalene	<	<	<	<	<	<
1-Methylfluorene	470	390	200	280	330	970
Acenaphthene	200	160	<	80	120	190
Acenaphthylene	<	<	<	<	200	1400
Fluorene	540	590	290	540	670	1700
1-Methylanthracene	380	530	510	430	430	1100
1-Methylphenanthrene	220	290	290	230	250	750
2-Methylanthracene	34	36	53	47	82	360
2-Methylphenanthrene	490	650	640	560	600	1500
3,6-Dimethylphenanthrene	110	150	140	96	120	260
9,10-Dimethylanthracene	<	<	<	<	<	<
9-Methylanthracene	<	<	<	<	<	<
Anthracene	180	160	190	190	270	1700
Phenanthrene	3700	3600	3100	3600	3700	12000
Retene	100	130	97	85	150	1100
4,5-Methylenephenanthrene	140	140	190	190	220	770
Benzo[a]fluorene	56	76	63	89	65	250
Benzo[b]fluorene	20	21	26	29	43	140
Fluoranthene	610	700	830	670	770	2500
Benz[a]anthracene	12	21	15	22	25	150
Chrysene	44	60	55	58	49	170
Dimethylbenz[a]anthracene	2	3	1	<	1	4
Naphthacene	<	<	<	<	<	<
Pyrene	620	740	760	670	840	2500
3-Methylcholanthrene	<	<	<	<	<	<
Benzo[a]pyrene	4	5	3	4	2	3
Benzo[b]fluoranthene	5	6	5	4	8	22
Benzo[e]pyrene	5	4	3	1	2	9
Benzo[k]fluoranthene	<	<	<	<	<	<
Dibenz[a,h]anthracene	<	<	<	<	<	<
Perylene	<	<	<	<	<	<
Anthanthrene	<	<	<	<	<	<
Benzo[g,h,i]perylene	25	20	12	<	1	1
Indeno[1,2,3-c,d]pyrene	1	<	<	<	<	<
Coronene	24	16	17	<	<	<

Table 9 Average Gaseous PCB Concentrations in Ambient Air (pg·m⁻³)^c

PCBs (IUPAC)	Jun	Jul	Aug	Sep	Oct	Nov
1	3	4	1	2	1	1
3	1	<	<	<	2	3
4 + 10	0.6	<	0.6	<	<	<
7 + 9	0.8	0.2	0.3	0.4	0.3	0.5
6	3	1	1	2	1	2
5 + 8	43	35	29	44	35	47
19	<	<	0.1	<	<	<
12 + 13	1	1	1	1	1	2
18	10	7.0	8	9	6	9
15 + 17	7	5	6	7	5	7
24 + 27	0.1	0.1	0.1	0.1	0.1	0.1
16 + 32	9	7	9	9	6	8
29	0.02	0.02	0.03	0.02	0.02	0.1
26	1	1	2	2	1	1
25	0.7	0.6	0.8	0.9	0.6	0.8
31+28	12	11	14	14	10	12
33 + 21 + 53	9	8	11	11	7	7
51	5	21	<	6	7	16
22	8	6	10	11	7	6
45	<	<	<	<	<	<
46	0.6	0.2	1	1	0.9	1
52	9	8	10	10	7	8
49	<	<	6	6	2	<
48 + 47	2	1	2	2	1	1
44	7	6	9	9	6	7
37 + 42	4	3	5	6	4	4
41 + 64 + 71	5	4	6	6	4	4
40	1	0.7	1	1	0.8	0.8
100	<	15	18	21	8	17
63	0.7	0.6	1	1	0.9	0.8
74	2	2	3	3	2	2
70 + 76	9	9	12	12	9	7
66 + 95	<	8	<	<	10	<
91	2	2	2	2	2	2
56 + 60	4	3	5	4	3	3
92 + 84	<	<	<	<	<	2
89	7	9	10	6	10	9
101	5	5	6	6	4	4
99	<	<	<	<	<	<
119	0.4	0.9	1	1	1	1
83	0.2	0.4	0.4	0.4	0.4	0.4
97	1	1	1	1	1	0.8
81 + 87	0.4	0.7	2	2	1	1
85	1	2	2	1	1	0.5
136	0.6	0.7	0.8	0.7	0.6	0.5
77 + 110	8	9	11	11	8	7
82	0.9	1	0.7	0.8	0.7	<
151	1	2	1	1	1	1
135 + 144 + 147 + 124	0.7	0.7	0.6	0.6	0.3	0.4
107	0.1	0.3	0.3	0.3	0.2	0.1
123 + 149	4	4	5	4	4	3

118	3	4	5	2	4	3
134 + 114 + 131	<	<	<	<	<	<
146	<	<	0.1	<	<	<
132 + 153 + 105	5	6	7	6	5	4
141	1	2	2	2	1	1
137 + 130 + 176	<	<	<	<	<	<
163 + 138	4	6	6	6	5	3
158	<	<	0.1	0.1	0.1	<
129 + 178	<	0.8	0.8	0.1	0.1	0.2
187 + 182	1	2	2	2	1	1
183	0.9	1	1	1	1	0.6
128	0.5	0.9	0.8	0.7	0.6	0.4
185 + 167	<	<	0.3	<	0.2	0.2
174	0.7	1	1	1	0.8	0.6
177	0.7	0.8	1	1	0.7	0.4
202 + 171 + 156	0.8	1	2	1	1	0.9
157 + 200	<	<	0.3	<	<	<
172	<	0.1	0.1	0.04	0.1	0.03
197	<	<	<	<	0.5	<
180	0.3	<	1	1	0.7	0.4
193	<	<	<	<	<	<
191	<	<	<	<	<	<
199	<	<	<	0.1	<	<
170 + 190	0.3	0.8	1	0.7	0.5	0.3
198	<	<	<	<	<	<
201	0.6	1	1	0.9	0.7	0.5
203 + 196	0.7	1	1	1	0.8	0.5
189	<	<	0.01	0.02	0.01	<
208 + 195	<	<	<	<	<	<
207	<	<	0.1	0.03	0.02	<
194	<	<	0.1	<	<	<
205	0.1	<	0.03	<	0.02	<
206	<	<	0.6	0.9	0.7	0.1
209	<	<	0.04	0.02	0.00	<

^a Water temperature data from the USGS monthly cruises in 2000 (USGS 2001).

^b Year 2000 monthly average wind speed data from BAAQMD's meteorological station in Concord.

^c Gaseous organic concentrations in the ambient air measured by this pilot study in 2000.

^d Average dissolved organic concentrations in the water obtained by the Regional Monitoring Program July/August cruises from 1995 to 1999 throughout the Estuary. The 1998 PAH data were excluded due to data quality issues.

LPAH PAHs with two or three rings.

HPAH PAHs with four or more rings.

Table 10 Henry's Law Constants of PAHs (Pa m³/mol)^a

Compound	15°C	18°C	19°C	20°C
1-Methylnaphthalene	24.62	30.64	32.93	35.37
2-Methylnaphthalene	27.22	33.01	35.17	37.46
Biphenyl	15.86	19.03	20.21	21.45
Naphthalene	23.78	28.55	30.32	32.18
1-Methylfluorene	4.92	6.13	6.59	7.09
Acenaphthene	8.19	10.35	11.17	12.06
Acenaphthylene	5.68	7.18	7.76	8.38
Fluorene	4.92	6.13	6.59	7.09
1-Methylanthracene	2.68	3.31	3.55	3.80
1-Methylphenanthrene	2.87	3.38	3.57	3.76
2-Methylanthracene	2.68	3.31	3.55	3.80
2-Methylphenanthrene	2.87	3.38	3.57	3.76
3,6-Dimethylphenanthrene	2.87	3.38	3.57	3.76
9,10-dimethylanthracene	2.68	3.31	3.55	3.80
Anthracene	2.68	3.31	3.55	3.80
Phenanthrene	2.17	2.69	2.89	3.10
Retene	2.87	3.38	3.57	3.76
4,5-Methylenepheneanthrene	2.87	3.38	3.57	3.76
Benzo[a]fluorene	1.61	1.88	1.98	2.09
Benzo[b]fluorene	1.61	1.88	1.98	2.09
Fluoranthene	1.04	1.24	1.31	1.39
Benz[a]anthracene	0.44	0.59	0.65	0.72
Chrysene	0.12	0.19	0.22	0.25
Dimethylbenz[a]anthracene	0.44	0.59	0.65	0.72
Pyrene	0.97	1.18	1.25	1.34
Benzo[a]pyrene	0.03	0.03	0.03	0.03
Benzo[b]fluoranthene	0.01	0.01	0.01	0.01
Benzo[e]pyrene	0.01	0.01	0.01	0.01
Benzo[k]fluoranthene	0.01	0.01	0.01	0.01
Dibenz[a,h]anthracene	3.23	3.88	4.12	4.37
Perylene	1.7E-03	2.0E-03	2.1E-03	2.2E-03
Anthanthrene	0.04	0.05	0.05	0.06
Benzo[g,h,i]perylene	0.04	0.05	0.05	0.06
Indeno[1,2,3-c,d]pyrene	0.01	0.01	0.01	0.01
Coronene	2.4E-04	2.8E-04	3.0E-04	3.2E-04

^a Henry's law constants of PAHs derived from Bamford et al. (1999) when reported there, otherwise from compiled chemical properties (Mackay et al. 1999).

Table 11 Henry's Law Constants of PCBs (Pa m³/mol)^a

PCB (IUPAC)	15°C	18°C	19°C	20°C
5	12.12	15.04	16.15	17.33
8	13.38	16.35	17.46	18.64
18	14.99	17.60	18.56	19.56
28	22.39	26.02	27.33	28.71
31	16.75	20.18	21.45	22.80
44	18.17	20.51	21.35	22.21
49	26.97	30.41	31.63	32.89
52	19.72	22.72	23.80	24.93
60	22.99	26.18	27.33	28.52
66	22.80	26.10	27.29	28.52
70	20.83	23.83	24.91	26.04
74	27.30	30.75	31.98	33.25
87	22.39	26.02	27.33	28.71
95	35.65	39.44	40.77	42.14
97	28.68	33.01	34.57	36.19
99	39.83	43.19	44.35	45.54
101	27.54	31.62	33.09	34.62
105	11.34	15.87	17.72	19.78
110	23.75	28.28	29.96	31.72
118	17.45	21.85	23.53	25.32
128	6.05	10.16	12.05	14.28
132	24.41	32.07	35.08	38.35
138	12.90	18.96	21.52	24.41
141	19.63	26.86	29.77	32.98
149	34.87	42.88	45.90	49.11
151	42.38	50.27	53.17	56.22
153	20.66	27.75	30.57	33.67
156	7.40	12.14	14.28	16.78
158	15.74	22.43	25.21	28.30
170	1.88	3.85	4.87	6.15
174	9.80	16.13	19.00	22.35
177	10.15	16.62	19.55	22.97
180	4.82	9.04	11.12	13.65
183	14.73	22.84	26.39	30.46
187	16.52	25.26	29.05	33.38
194	1.00	2.08	2.65	3.37
195	1.41	2.91	3.70	4.70
196	1.41	2.91	3.70	4.70
200	12.43	23.40	28.81	35.42
203	1.41	2.91	3.70	4.70

^a Henry's law constants of PCB homologs were the average values calculated from the data presented by Achman et al. (1993).

Table 12 Average Concentrations of Dissolved PAHs in Water of Different San Francisco Estuary Segments (pg·L⁻¹)¹

PAHs	North	Central	South
1-Methylnaphthalene	190	290	350
2,3,5-Trimethylnaphthalene	45	50	100
2,6-Dimethylnaphthalene	63	110	110
2-Methylnaphthalene	150	380	300
Biphenyl	120	190	210
Naphthalene	370	520	460
Acenaphthene	230	500	500
Acenaphthylene	32	43	53
Fluorene	550	620	1000
1-Methylphenanthrene	210	210	280
Anthracene	5	37	120
Dibenzothiophene	62	86	200
Phenanthrene	1200	1200	2000
Fluoranthene	1600	1800	2400
Benz[a]anthracene	110	77	210
Chrysene	200	130	240
Pyrene	1200	550	1700
Benzo[a]pyrene	3	35	23
Benzo[b]fluoranthene	110	66	200
Benzo[e]pyrene	96	70	200
Benzo[k]fluoranthene	26	54	71
Dibenz[a,h]anthracene	27	76	48
Perylene	<	<	<
Benzo[g,h,i]perylene	<	<	3
Indeno[1,2,3-c,d]pyrene	34	110	73
Coronene	<	<	8

¹ Average dissolved organic concentrations in the water obtained by the Regional Monitoring Program July/August cruises from 1995 to 1999 throughout the Estuary. The 1998 PAH data were excluded due to data quality issues.

Table 13 Average Concentrations of Dissolved PCBs in Water of Different San Francisco Estuary Segments (pg·L⁻¹)¹

PCB (IUPAC)	North	Central	South
5 + 8	21	8.5	18
18	6	4	22
31 + 28	15	10	48
44	9.1	3	16
49	5.3	3.4	14
52	18	7.7	22
56 + 60	2.2	0.7	5.5
70 + 76	6.9	3.5	12
74	1.7	1.3	5.7
81 + 87	3.8	1.4	6.2
66 + 95	14	8.8	38
97	2.9	1.3	6
99	4.1	2.1	9.2
101	5.1	3.8	19
77 + 110	9.1	5	18
118	4.8	3.4	13
128	0.65	0.25	1.6
163 + 138	4.8	3.1	14
141	0.24	0.1	1.8
123 + 149	6.8	3.9	18
151	2.6	1.5	6.9
132 + 153 + 105	10	5.2	27
202 + 171 + 156	0.24	0.09	0.79
158	0.16	0.17	1
170 + 190	0.28	0.09	2
174	0.38	0.14	2.5
177	0.36	0.21	1.9
180	1.5	0.72	5.3
183	0.45	0.19	1.9
187 + 182	2	0.87	5.7
194	0.03	0.07	0.47
208 + 195	<	<	0.03
203 + 196	<	<	0.93
157 + 200	<	0.2	0.4
203	<	0.01	0.37

¹ Average dissolved organic concentrations in the water obtained by the Regional Monitoring Program July/August cruises from 1995 to 1999 throughout the Estuary. The 1998 PAH data were excluded due to data quality issues.

Table 14 Fluxes of Particulate and Gaseous Trace Organics Over the San Francisco Estuary (June to November 2000)¹

Flux ($\text{ng}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$)				
	Particulate ²	North	Gaseous Central	South
PAHs				
June	-45	83	290	670
July	-69	92	350	800
August	-83	150	350	730
September	-70	41	160	440
October	-130	-59	86	380
November	-960	-1300	-1300	-1100
PCBs				
June	-0.85	34	17	83
July	-0.39	43	21	100
August	-0.67	32	16	79
September	-0.87	21	9.7	50
October	-0.67	24	12	59
November	-2.1	12	5.8	31

¹ All values represent monthly averages. Values >0 indicate net volatilization from the Estuary to the Atmosphere. Values <0 indicate net deposition from the atmosphere to the Estuary.

² Assumes a deposition velocity of $0.2\text{ cm}\cdot\text{sec}^{-1}$.

Table 15 Monthly Loads of Trace Organics Over the San Francisco Estuary from June through November 2000¹

PAHs (kg-month ⁻¹)			
North Bay	Particulate ²	Gaseous	Net Deposition
June	-0.59	1.1	0.51
July	-0.91	1.2	0.30
August	-1.1	2.0	0.94
September	-0.93	0.54	-0.39
October	-1.7	-0.77	-2.5
November	-13	-18	-30
Central Bay			
June	-0.29	1.9	1.6
July	-0.45	2.3	1.8
August	-0.54	2.3	1.7
September	-0.46	1.1	0.61
October	-0.86	0.56	-0.3
November	-6.3	-8.3	-15
South Bay			
June	-0.66	9.9	9.3
July	-1.0	12	11
August	-1.2	11	9.5
September	-1.0	6.4	5.4
October	-1.9	5.6	3.7
November	-14	-16	-30

PCBs (g-month ⁻¹)			
North Bay	Particulate ²	Gaseous	Net Deposition
June	-11	450	440
July	-5	570	560
August	-9	430	420
September	-11	270	260
October	-9	320	310
November	-27	160	140
Central Bay			
June	-6	110	100
July	-3	130	130
August	-4	100	97
September	-6	63	57
October	-4	76	72
November	-13	38	24
South Bay			
June	-13	1200	1200
July	-6	1500	1500
August	-10	1200	1200
September	-13	740	730
October	-10	870	860
November	-30	450	420

¹ All values represent monthly averages. Values >0 indicate net volatilization from the Estuary to the Atmosphere. Values <0 indicate net deposition from the atmosphere to the Estuary.

² Assumes a deposition velocity of 0.2 cm·sec⁻¹.

Table 16 Comparison of Ambient Air Concentration and Estimated Net Dry Deposition Flux of PAHs Reported in the Literature

Sampling	Site Characteristics	Concentration (ng·m ⁻³) ^a	Deposition Flux (ng·m ⁻² ·day ⁻¹) ^b	Citation
Eagle Harbor, Lake Superior (1991-1997)	Regional background	0.85 (g) 0.19 (p) (average)	NA	Cortes et al. 2000
Sleeping Bear Dunes, Lake Michigan (1991-1997)	Regional background	1.2 (g) 0.31 (p) (average)	NA	Cortes et al. 2000
Sturgeon Pt, Lake Erie (1991-1997)	Influence from Buffalo, NY	4.8 (g) 1.2 (p) (average)	NA	Cortes et al. 2000
Sandy Hook, NJ (Feb. 98 to Oct. 98)	Coastal site at the tip of a peninsula extending into the Atlantic Ocean	2.8 to 42 (g) 0.15 to 4.0 (p)	NA	Gigliotti et al. 2000
New Brunswick, NJ (Oct 97 to Oct 98)	Suburban site in close proximity to major traffic arteries	3.5 to 84 (g) 0.38 to 12 (p)	NA	Gigliotti et al. 2000
Chicago, IL (June to Oct. 1995)	Urban site	144 to 853 (g) 10 to 48 (p)	-172,000 to -626,000 ^c (gas+particles)	Odabasi et al., 1999
Ft. McHenry, Baltimore (June 1996)	Urban site	17 to 113 (g) 0.88 to 9.72 (p)	NA	Offenberg and Baker 1999
Hart-Miller Island, Northern Chesapeake Bay (June 1996)	Over-water	2.9 to 14 (g) 0.23 to 2.4 (p)	NA	Offenberg and Baker 1999
Stillpond, Northern Chesapeake Bay (June 1996)	Rural site	NQ to 5.7 (g) 0.15 to 0.70 (p)	NA	Offenberg and Baker 1999
Elms Environmental Education Center, Chesapeake Bay (June 90 to Dec. 91)	Rural site	2.7 (g+p) (geometric mean)	-337 ^d (gas+particles)	Leister and Baker 1994
San Francisco Estuary (June to Nov. 2000)	Urban site in close proximity to major highways	7.5 to 31 (g) 0.3 to 6.1 (p) (monthly average)	-2,300 to +730 (gas+particles)	This Study

NA -- Not available

^a (g) denotes gaseous phase; (p) denotes particulate phase

^b Positive numbers indicate net flux from water to air; negative numbers indicate net flux from air to water.

^c Collected with a water surface sampler.

^d Calculated by using a dry deposition velocity of 0.49 cm·sec⁻¹.

Table 17 Comparison of Ambient Air Concentration and Estimated Net Dry Deposition Flux of PCBs Reported in the Literature

Sampling	Site Characteristics	Concentration (ng·m ⁻³)	Deposition Flux (ng·m ⁻² ·day ⁻¹) ^a	Citation
Ft. McHenry, Baltimore (June 1996)	Urban site	0.38 to 3.4 (g)	NA	Offenberg and Baker 1999
Hart-Miller Island, Northern Chesapeake Bay (June 1996)	Over-water	0.21 to 0.74 (g)	NA	Offenberg and Baker 1999
Stillpond, Northern Chesapeake Bay (June 1996)	Rural site	NQ to 0.34 (g)	NA	Offenberg and Baker 1999
Site 5, Southern Lake Michigan (May 94)	15 km NE Chicago (receives urban influence)	0.14 to 0.25 (g)	-20 to +31 (g)	Zhang et al. 1999
Southern Lake Michigan (July 94)	Site 0: 5 km from shore Site 1: 12 km SE Chicago Site 5: 15 km NE Chicago	Site 0: 0.13 to 0.20 Site 1: 0.21 to 1.1 Site 5: 0.31 to 0.95 (gaseous only)	-13 to +30 (g) (all sites)	Zhang et al. 1999
Site 5, Southern Lake Michigan (Jan. 95)	15 km NE Chicago (receives urban influence)	0.13 to 0.28 (g)	+15 to +59 (g)	Zhang et al. 1999
Lake Tahoe Basin, CA-NV (July 1997)	Rural site	0.062 to 0.083 (g) (average)	Positive value (net volatilization)	Datta et al. 1998
Chesapeake Bay (Mar. Apr. June 93)	Northern Bay	0.20 to 0.92 (g)	-63 to +800 (g) (Entire Bay)	Nelson et al. 1998
Chesapeake Bay (March, April, June 1993)	Southern Bay	0.33 to 1.4 (g)	-63 to +800 (g) (Entire Bay)	Nelson et al. 1998
Eagle Harbor, Lake Superior (90-93)	Regional background	0.090 (g) 0.006 (p)	Positive value (net volatilization)	Hoff et al. 1996
Sleeping Bear Dunes, Lake Michigan (90-93)	Regional background	0.16 (g) 0.005 (p)	Positive value (net volatilization)	Hoff et al. 1996
Sturgeon Pt, Lake Erie (90-93)	Influence from Buffalo, NY	0.36 (g) 0.009 (p)	Positive value (net volatilization)	Hoff et al. 1996
Pt. Petre, Lake Ontario (90-93)	Regional background	0.17 (g) 0.005 (p)	Positive value (net volatilization)	Hoff et al. 1996
Lake Michigan (Sept. 91)	Over-water	0.12 to 1.5 (g)	+24 to +220 (g)	Hornbuckle et al. 1995
Green Bay, Lake Michigan (May 92)	Over-water	0.33 to 0.41 (g)	NA	Hornbuckle et al. 1995
Northern Lake Michigan (Aug. 92)	Over-water	0.33 to 0.38 (g)	NA	Hornbuckle et al. 1995
San Francisco Estuary (June to Nov. 2000)	Urban site	0.21 to 0.27 (g) 0.004 to 0.017 (p) (monthly average)	+3.7 to +100	This Study

NA- Not available

(g) denotes gaseous phase; (p) denotes particulate phase

^a Positive numbers indicate net flux from water to air; negative numbers indicate net flux from air to water.

Table 17 (continued) Comparison of Ambient Air Concentration and Estimated Net Dry Deposition Flux of PCBs Reported in the Literature

Sampling	Site Characteristics	Concentration (ng·m⁻³)	Deposition Flux (ng·m⁻²·day⁻¹)^a	Citation
Chicago, IL (July to Aug. 91)	Urban site	2.1 (g+p) (mean)	NA	Pirrone et al. 1995
South Haven, MI (July to Aug. 91)	Rural site	0.67 (g+p) (mean)	NA	Pirrone et al. 1995
Lake Michigan (July to Aug. 91)	Over-water	0.81 (g+p) (mean)	+520 (g) -2.4 (p)	Pirrone et al. 1995
Lake Superior (July 88)	Over-water	0.27 to 0.45 (g)	+55 to +80 (g)	Hornbuckle et al. 1994
Lake Superior (Aug. 90)	Over-water	0.11 to 0.80 (g)	+35 to +110 (g)	Hornbuckle et al. 1994
Lake Superior (May 92)	Over-water	0.22 to 0.41 (g)	-16 to -29 (g)	Hornbuckle et al. 1994
Elms Environmental Education Center, Chesapeake Bay (June 90 to Dec. 91)	Rural site	0.21 (g+p) (geometric mean)	-3.8	Leister and Baker 1994
Green Bay, Lake Michigan (June, July, and Oct. 1989)	Over-water	0.31 to 2.3 (g)	+13 to +1300	Achman et al. 1993
Southern Green Bay, Lake Michigan (1989 to 1991)	Over-water	1.2 (g)	NA	Hornbuckle et al. 1993
Central Green Bay, Lake Michigan (1989 to 1991)	Over-water	0.40 (g)	NA	Hornbuckle et al. 1993
Northern Green Bay, Lake Michigan (1989 to 1991)	Over-water	0.33	NA	Hornbuckle et al. 1993
Green Bay, Lake Michigan	Over-land within 2 km of the shore	0.27 to 0.42 (g)	NA	Hornbuckle et al. 1993
San Francisco Estuary (June to Nov. 2000)	Urban site	0.17 to 0.31 (g) 0.003 to 0.023 (p)	+5.6 to +26	This Study

NA -- Not available

(g) denotes gaseous phase; (p) denotes particulate phase

^a Positive numbers indicate net flux from water to air; negative numbers indicate net flux from air to water.

Table 18 Sensitivity Analysis of Input Parameters Used in Calculating Diffusive Fluxes of Gaseous PAH*

Parameter	Range of Values	Deposition Flux ^a (ng·m ⁻² ·day ⁻¹)	Correlation ^b
Gaseous PAH Concentration in Air (ng·m ⁻³)	5.5	+580	Negative
	10 (default)	-220	
	20	-2,000	
	46	-6,608	
	100	-16,000	
Wind Speed (m·sec ⁻¹)	2.5 (default)	-220	Negative
	3.0	-270	
	4.0	-380	
	5.4	-530	
Dissolved PAH Concentration in Water (ng·L ⁻¹)	2.0	-1,400	Positive
	4.0	-1,000	
	8.0 (default)	-220	
	17	+1,500	
Ambient Water Temperature (°C)	11	-1,100	Positive
	15	-580	
	18 (default)	-220	
	20	-8	

* Phenanthrene was used as the representative PAH for this analysis.

^a Positive flux indicates net volatilization from the Estuary to the atmosphere; Negative flux indicates net deposition from the atmosphere to the Estuary.

^b Positive correlation means that an increase in the value of the input parameter enhances net volatilization from the Estuary to the atmosphere; Negative correlation means that an increase in the input parameter value enhances net deposition from the atmosphere to the Estuary.

Table 19 Sensitivity Analysis of Input Parameters Used in Calculating Diffusive Fluxes of Gaseous PCB*

Parameter	Range of Values	Deposition Flux ^a (ng·m ⁻² ·day ⁻¹)	Correlation ^b
Gaseous PCB Concentration in Air (ng·m ⁻³)	0.17	+27	Negative
	0.2 (default)	+25	
	0.25	+22	
	0.31	+19	
Wind Speed (m·sec ⁻¹)	2.5 (default)	+25	Positive
	3.0	+33	
	4.0	+49	
	5.4	+74	
Dissolved PCB Concentration in Water (ng·L ⁻¹)	0.096	+6	Positive
	0.1	+16	
	0.2 (default)	+25	
	0.26	+37	
Ambient Temperature (°C)	11	+16	Positive
	15	+22	
	18 (default)	+25	
	20	+28	

* Tetrachlorobiphenyl was used as the representative PCBs for this analysis.

^a Positive flux indicates net volatilization from the Estuary to the atmosphere; Negative flux indicates net deposition from the atmosphere to the Estuary.

^b Positive correlation means that an increase in the value of the input parameter enhances net volatilization from the Estuary to the atmosphere; Negative correlation means that an increase in the input parameter value enhances net deposition from the atmosphere to the Estuary.

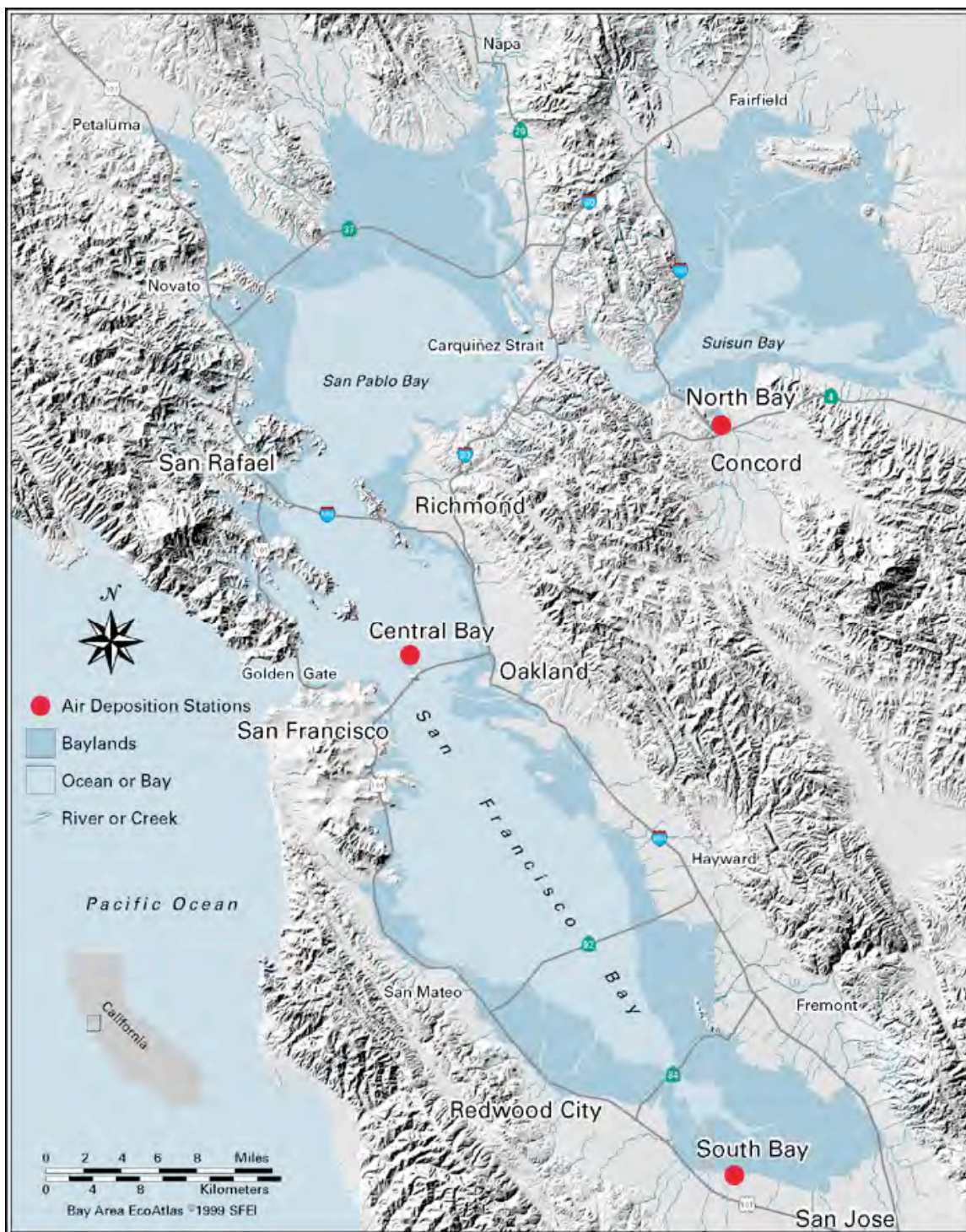


Figure 1 Monitoring Sites Included in the San Francisco Bay Atmospheric Deposition Pilot Study

Figure 2. Monthly Average Concentrations of Total PAHs in the Ambient Air (2000)

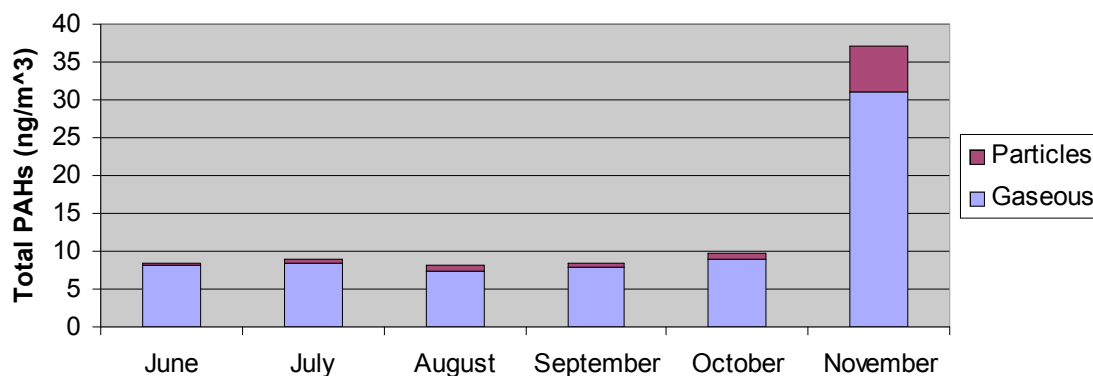


Figure 3. Monthly Average Concentrations of Total PCBs in the Ambient Air (2000)

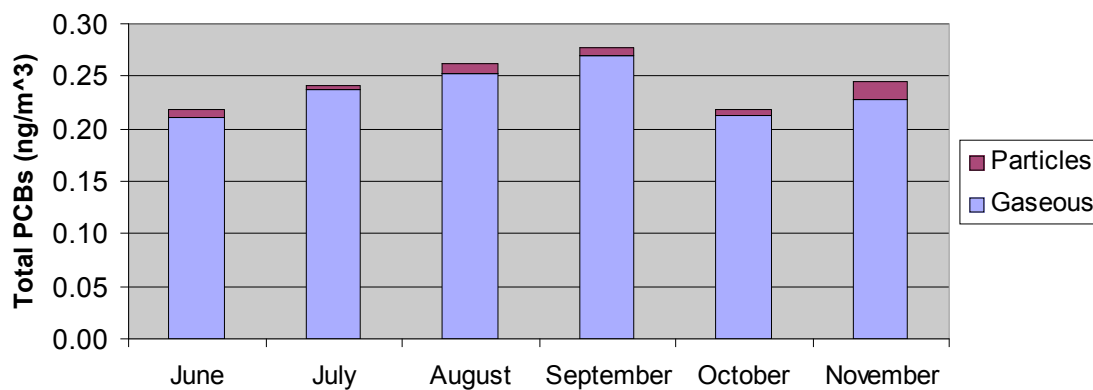
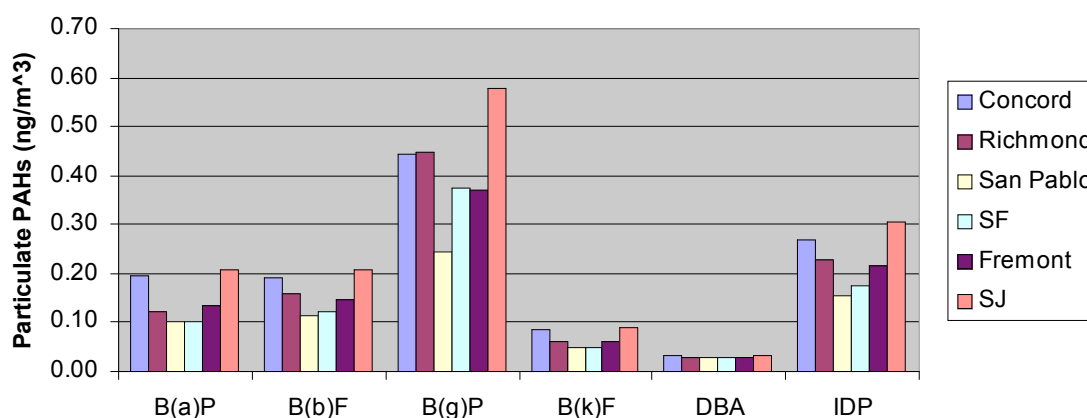


Figure 4. Average Concentrations of Particulate PAHs in the Ambient Air (1995-1998) (Data from CARB 1999)



B(a)P benzo(a) pyrene; B(b)F benzo(b)fluoranthene; B(g)P benzo(g,h,i)perylene;
 B(k)F benzo(k)fluoranthene; DBA dibenzo(a,h)anthrene; IDP indeno(1,2,3-cd)pyrene

Figure 5. Concentrations of Particulate PAHs in the Ambient Air, Concord, CA (1995-1998) (Data from CARB 1999)

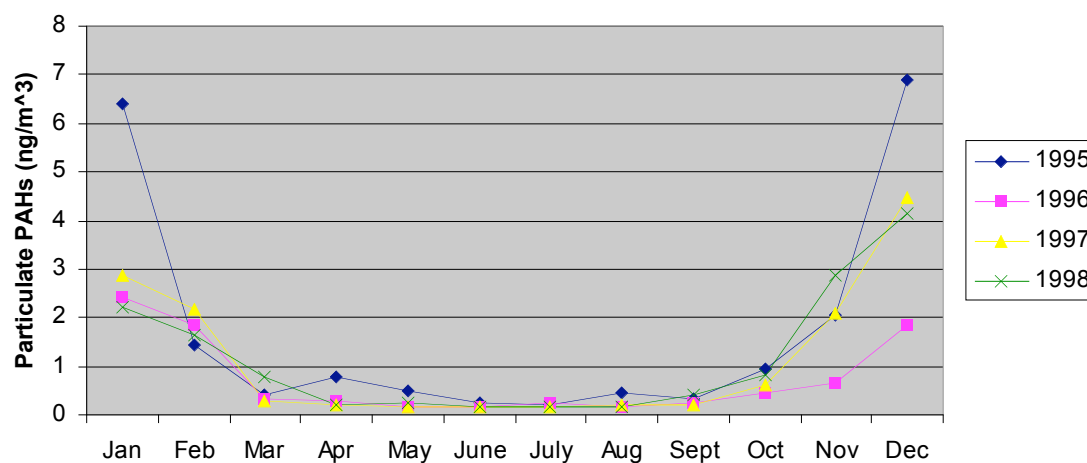


Figure 6. Influence of Air Temperature on the Distribution of Trace Organics in Gaseous Phase

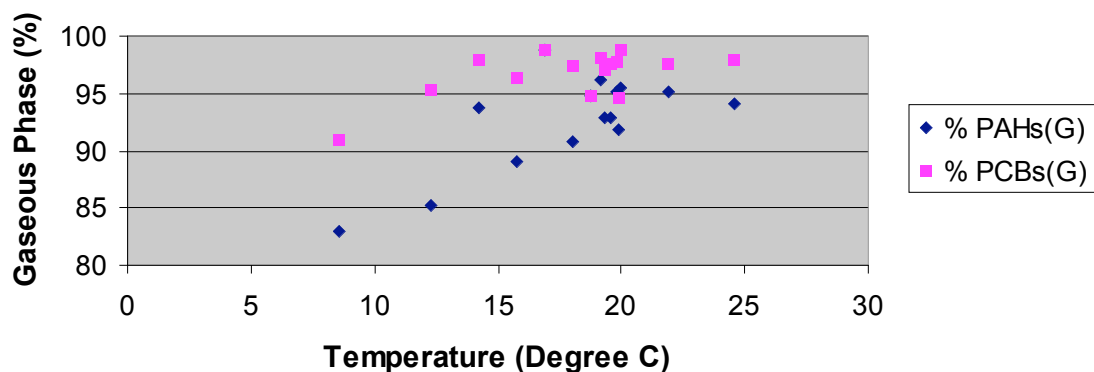


Figure 7. Average PM10 Concentration in the Ambient Air San Jose, CA (1995 to 1998) (Data from CARB 1999)

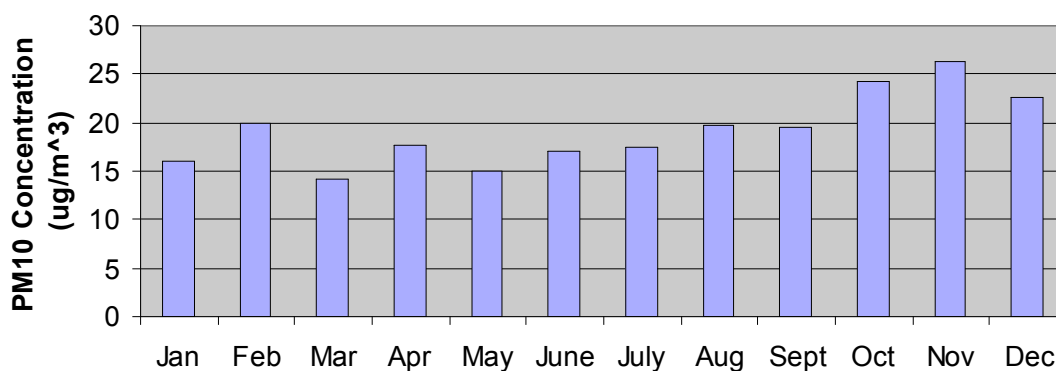


Figure 8. Average Relative Concentrations of Gaseous PAHs in the Ambient Air, Concord, CA (June to November 2000)

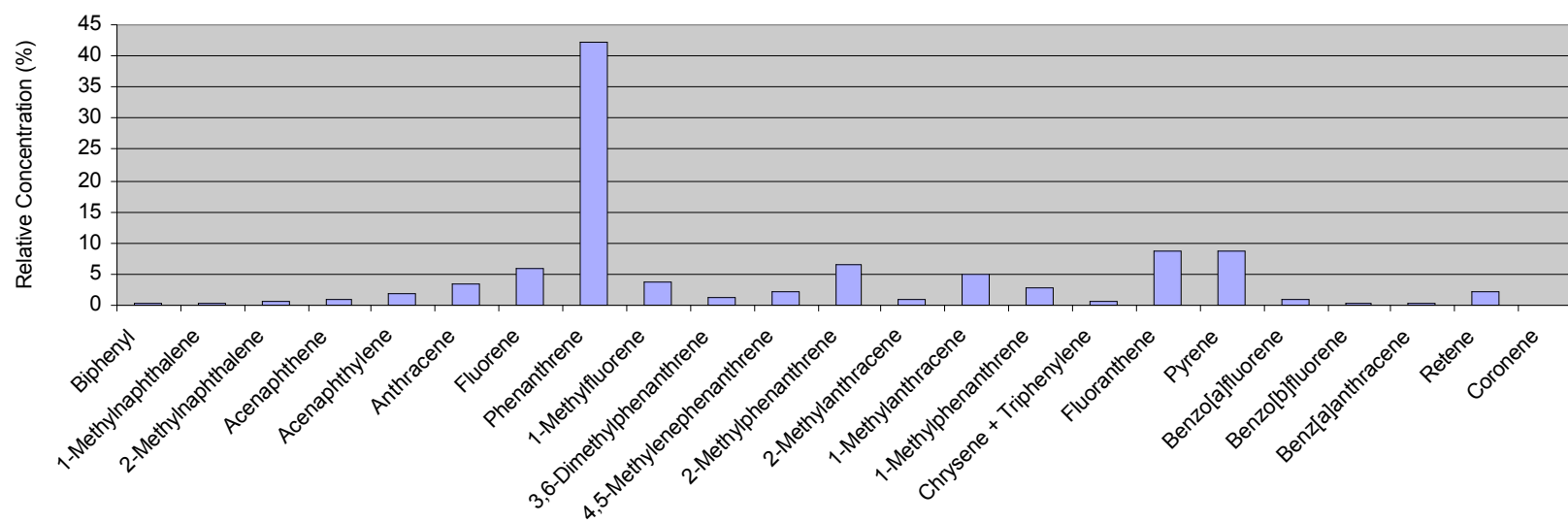


Figure 9. Average Relative Concentrations of Dissolved PAHs in Surface Water of the San Francisco Estuary (RMP Dry Season 1995 to 1999)

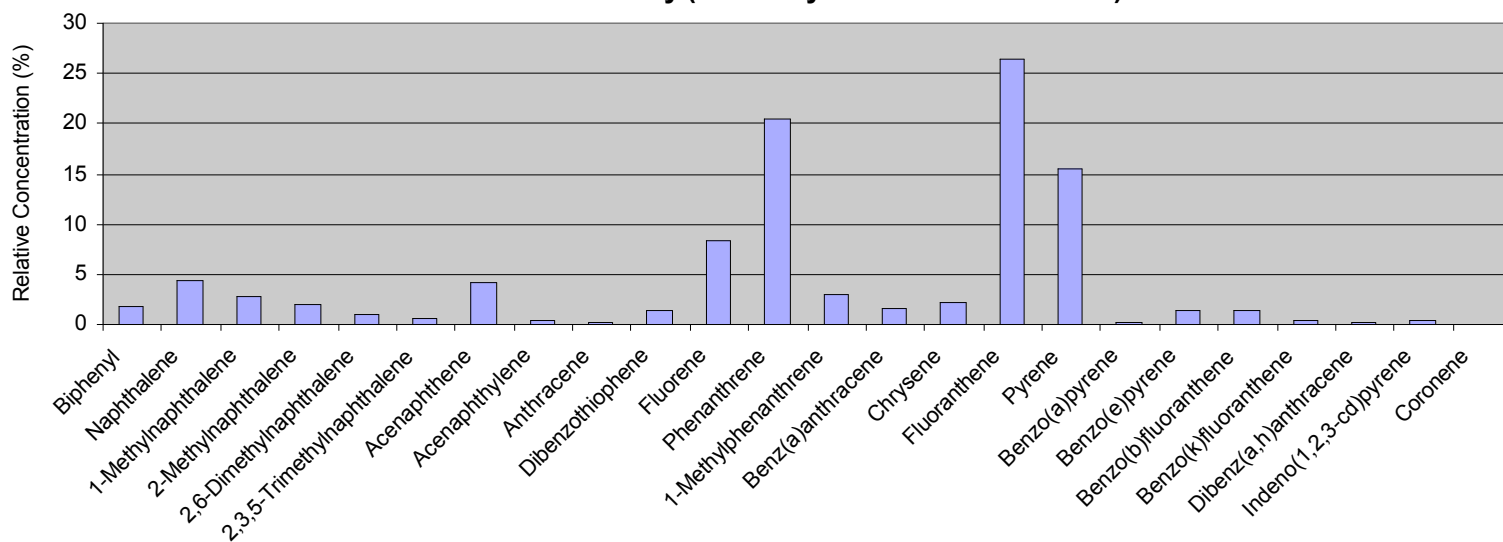


Figure 10. Average Relative Concentrations of Gaseous PCB Congeners in the Ambient Air, Concord, CA (June to November 2000)

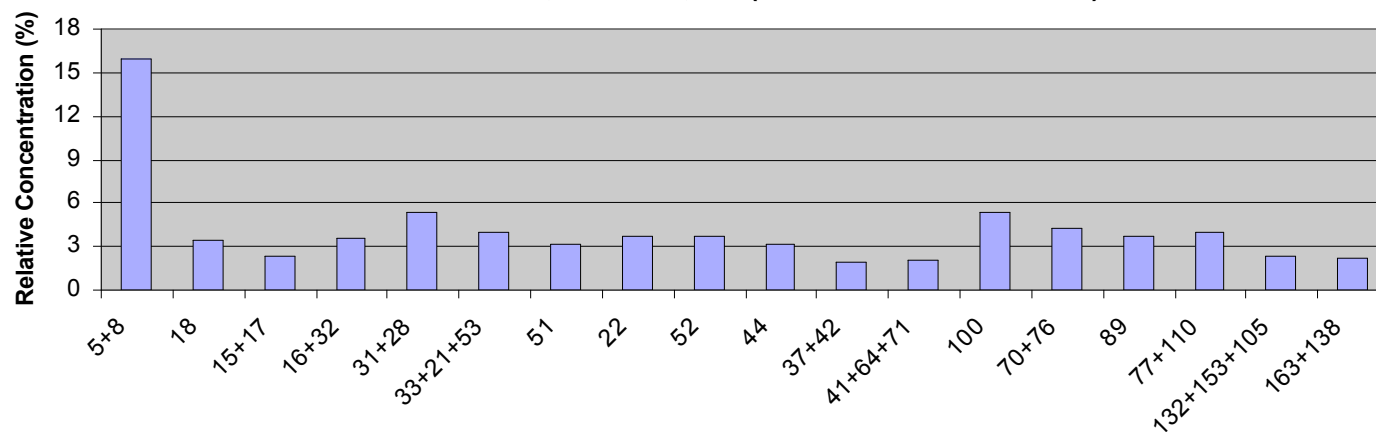


Figure 11. Average Relative Concentrations of Dissolved PCB Congeners in Surface Water of the San Francisco Estuary (RMP Dry Season 1995-1999)

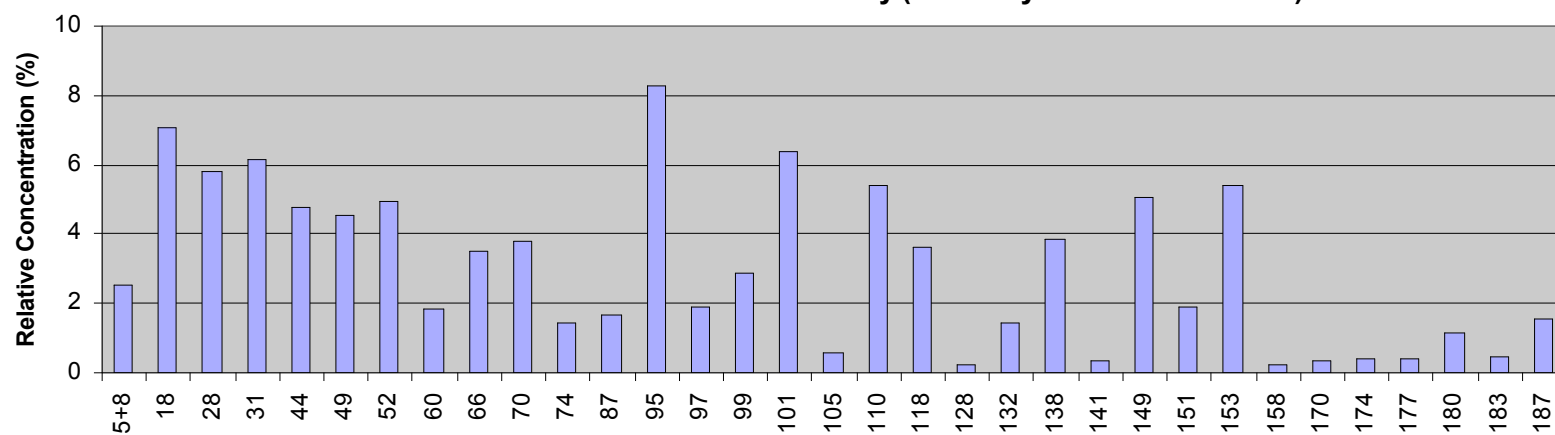


Figure 12 Flux of Gaseous PAHs in Segments of the San Francisco Estuary (2000)
 (Values >0 indicate net volatilization. Values <0 indicate net deposition.)

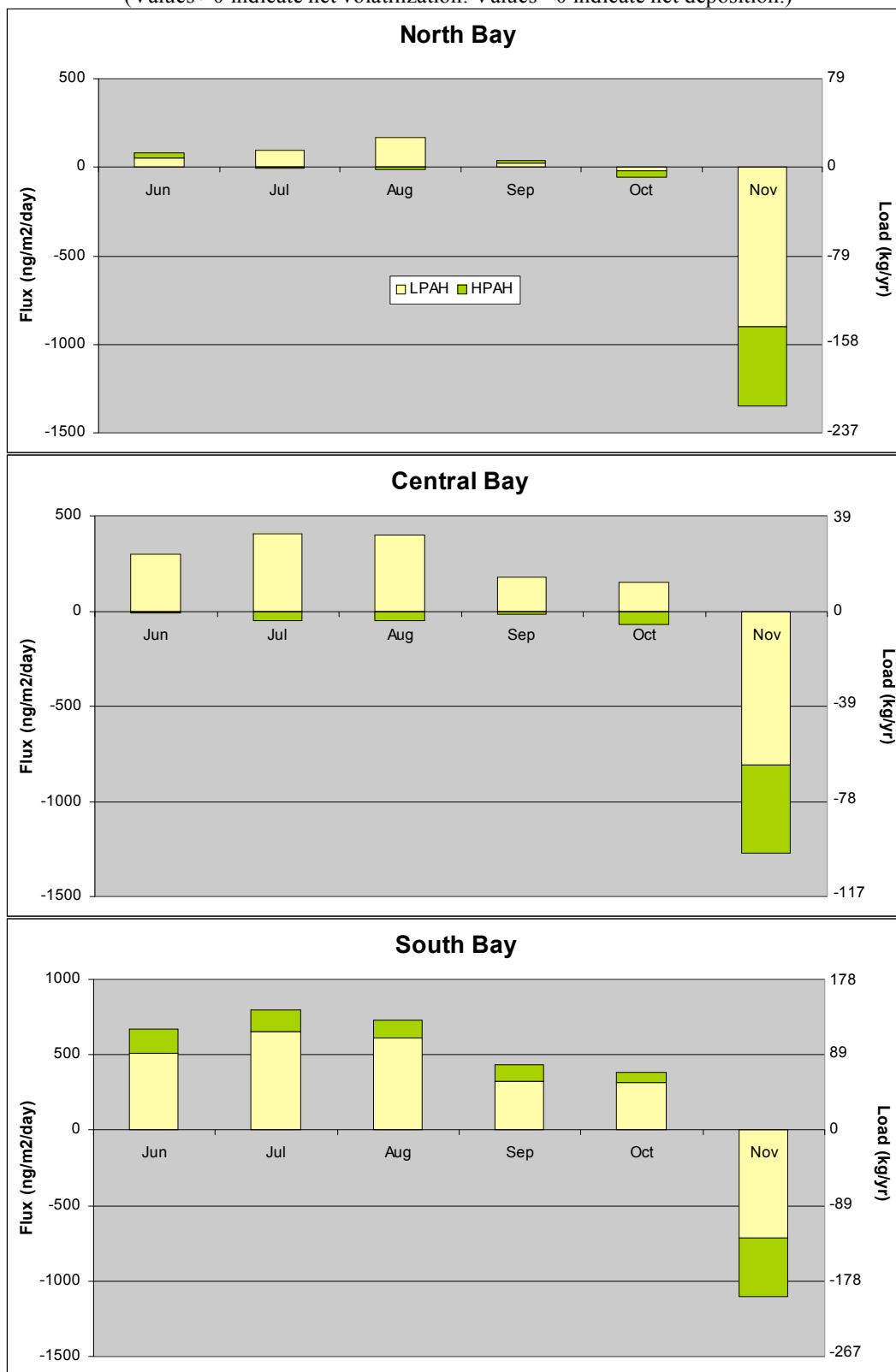


Figure 13 Flux of Particulate PAHs in the San Francisco Estuary (2000)
(Values <0 indicate net deposition.)

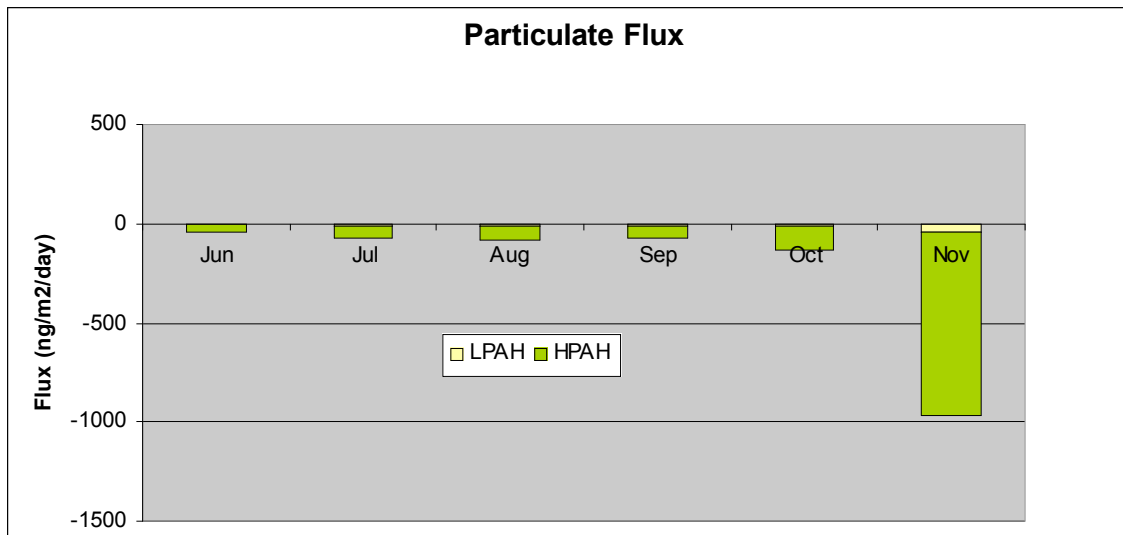


Figure 14 Flux of Gaseous PCBs in Segments of the San Francisco Estuary (2000)
 (Values >0 indicate net volatilization. Values <0 indicate net deposition.)

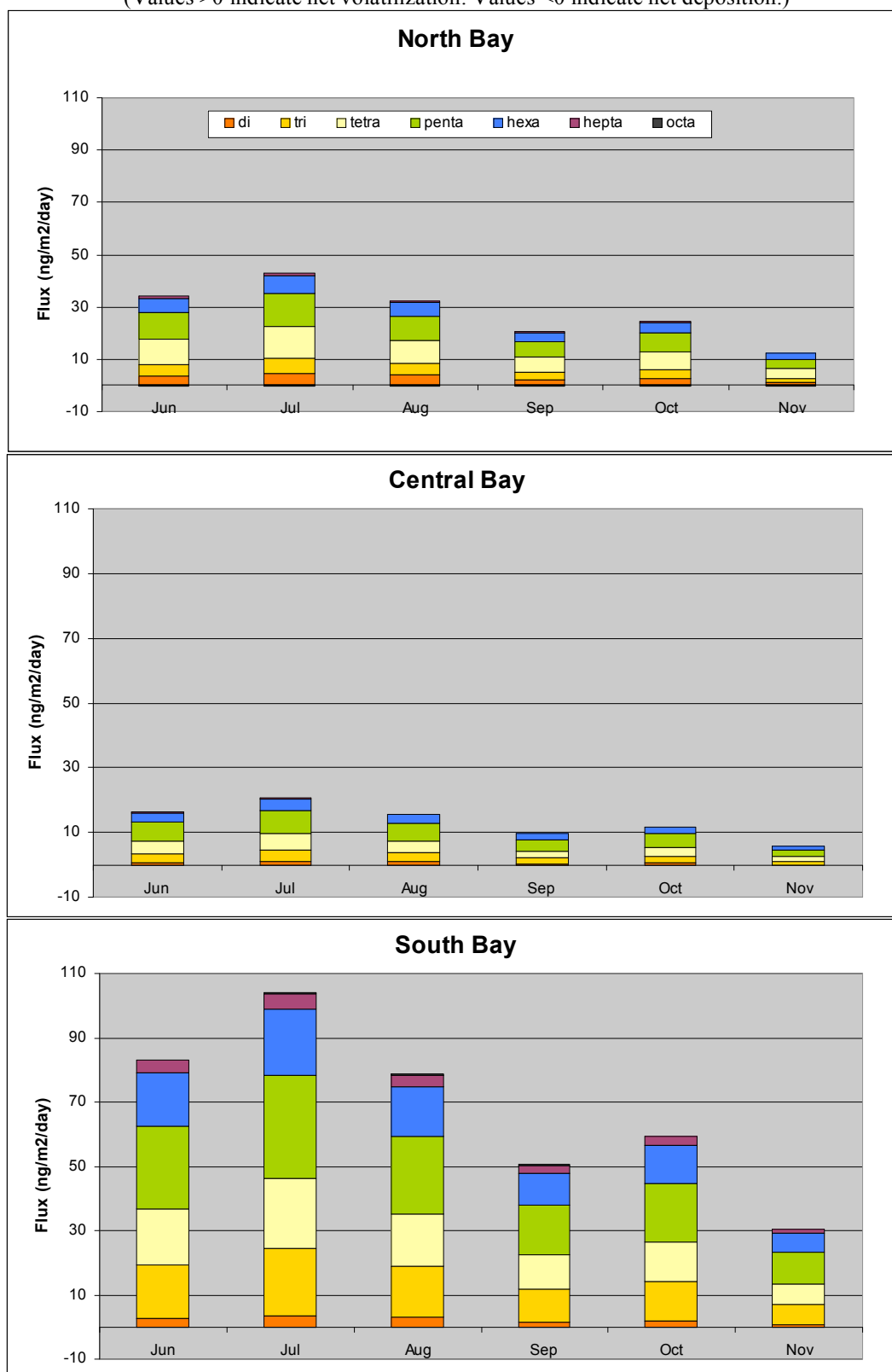


Figure 15 Flux of Particulate PCBs in the San Francisco Estuary (2000)
 (Values <0 indicate net deposition.)

