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Polycyclic aromatic hydrocarbon (PAH) contamination in San Francisco Bay: A 10-year retrospective of monitoring in an urbanized estuary

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Abstract

Polycyclic aromatic hydrocarbons (PAH) are widespread contaminants in the San Francisco Bay. Several exceedances of water quality criteria raise the possibility that PAH may be impacting aquatic biota. The Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP) has collected annual monitoring data on PAH in the Bay since 1993. Analysis of Bay water, sediment, and mussel ΣPAH concentration data showed that there were very few significant ($P<0.05$) increasing or decreasing temporal trends in ΣPAH concentrations in the Bay during the period of 1993–2001. Wet and dry season input of PAH did not show any major influence on water ΣPAH concentrations over the same period. Based on their relative contribution to the estimated total maximum PAH loading (10,700 kg/yr) into the Bay, the PAH loading pathways are ranked as storm water runoff (~51%) > tributary inflow (~28%) > wastewater treatment plant effluent (~10%) > atmospheric deposition (~8%) > dredged material disposal (~2%). The PAH sediment quality threshold of 1000 ng/g, which has been previously suggested by NOAA to protect estuarine fish such as English sole against adverse health effects, was frequently exceeded at individual monitoring stations (11 of the 26 stations exceeded the threshold over 50% of the time). Modeling results have shown that the predominant loss pathway for PAH is degradation in sediments, and unless external loading levels of PAH are controlled, the Bay is not expected to recover rapidly.

Keywords: PAH; Polycyclic aromatic hydrocarbons; Marine; Monitoring; San Francisco Bay

1. Introduction

San Francisco Bay is situated in a highly populated (6.8 million, US Census Bureau, 2000) and urbanized region and is subject to polycyclic aromatic hydrocarbon (PAH) contamination from a variety of sources and transport pathways. The Bay Area is highly industrialized and includes refineries, chemical manufacturers, and steel producers, among other industries that rely on fossil fuels for their energy needs. Commercial vessels, such as oil tankers, container ships, freighters, and cruise ships, use the Bay to transport manufactured goods, raw materials, and people. In addition, the Bay Area was recently cited as having the second highest amount of vehicular traffic congestion in the US (TTI, 2003).

The Bay receives freshwater inflow primarily from the Delta in the northeast via the Sacramento and San Joaquin Rivers, Petaluma, and Napa Rivers in the San Pablo Bay region, Alameda Creek, Coyote Creek, and Guadalupe River in the South Bay region, as well as from numerous smaller creeks and tributaries. The Delta currently discharges 37% of California's surface water runoff into the San Francisco Bay (McKee et al., 2006), while historically, Delta outflows were almost twice that amount prior to the implementation of large-scale water diversions by the State Water Project and the federal Central Valley Project. Additionally, the Bay receives storm water and

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wastewater effluents year-round from 40 wastewater treatment plants, 30 municipalities, and 30 industrial dischargers (CRWQCB, 2003). It is estimated that ~870 million cubic meters of treated wastewater effluents are discharged annually into the Bay (CRWQCB, 2004). Tributary surface waters and discharged effluents load varying amounts of PAH into the Bay.

PAH in urban areas, such as the Bay Area, can originate from a variety of sources by thermal combustion processes (e.g., cooking and heating oils, coal burning), vehicular emissions (e.g., automobiles, trucks, machinery), and biomass burning (e.g., fireplaces, controlled burning) (Simoneit, 1984). PAH generally occur as complex mixtures and not as single compounds. High-temperature combustion, as previously described for urban areas, emits the high-molecular-weight PAH (HPAH) (4 rings or more) (Neff, 1979), and some of these PAH, such as benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, chrysene, dibenz[*a,h*]anthracene, and indeno[1,2,3-*c,d*]pyrene have mutagenic and genotoxic potential (Arcos and Argus, 1975; WHO (World Health Organization), 1989). Combustion-derived PAH in the atmosphere can enter the water column directly by gaseous exchange across the air–water interface, dry deposition of airborne particulate matter, or wet deposition by rainfall, and indirectly by urban runoff (e.g., street surfaces, storm water discharge) (Hoffman et al., 1984, 1985; Dickhut and Gustafson, 1995; Dickhut et al., 2000; Tsai et al., 2002). Unburned fossil fuels (crude oil and its refined products) can also impart their PAH signature to the marine environment (Hites et al., 1980; Simcik et al., 1996; Countway et al., 2003), primarily by street surface runoff and accidental spills.

The Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP) has monitored PAH and other pollutants in San Francisco Bay water, sediments, and bivalves since 1993 (see Fig. 1 for location of RMP sampling stations). The PAH information gathered from monitoring efforts, combined with other PAH studies conducted in the San Francisco Bay, is critical for understanding PAH sources, transport pathways, loading, and fate. Given the amount of monitoring data now available, a synthesis on the current knowledge of PAH contamination and fate in the Bay is appropriate. Therefore, the aim of this paper is to evaluate the current status of PAH contamination in the San Francisco Bay based on monitoring data collected during the period 1993–2001. This effort will contribute important information needed to assist environmental decision makers with the adaptive management process by introducing relevant scientific information for making sound management decisions. Key topics discussed here include recent PAH management efforts, PAH spatial distributions and temporal trends in water, sediments, and bivalves (mussels), major sources, transport pathways, loading estimations, fate, recovery estimations, impairment assessment (aquatic biota toxicity and human health risk), and critical data gaps.

2. Methods

The 25 target PAH analyzed in RMP water, sediment, and bivalve samples over the period 1993–2001 included biphenyl, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene, 2,3,5-trimethylnaphthalene, acenaphthene, acenaphthylene, anthracene, dibenzothiophene, fluorene, phenanthrene, 1-methylphenanthrene, benz[*a*]anthracene, chrysene, fluoranthene, pyrene, benzo[*a*]pyrene, benzo[*e*]-pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, dibenz[*a,h*]anthracene, perylene, benzo[*g,h,i*]perylene, and indeno[1,2,3-*c,d*]pyrene. Total PAH (ΣPAH) was the sum of the 25 individual target PAH. Compound concentrations below detection limits were assumed to be zero for the summation of ΣPAH in each sample.

Quality assurance (QA) followed the protocol outlined in the RMP's Quality Assurance Project Plan (SFEI, 1999). Both the QA and statistical analyses details have already been described elsewhere for the RMP monitored matrices of water (Ross and Oros, 2004), sediments (Oros and Ross, 2004), and bivalves (Oros and Ross, 2005).

3. Management

At the onset of the RMP in 1993, one of the key management questions was whether ongoing discharges of PAH to the Bay, particularly from urban runoff, were causing or contributing to water quality impairment. The applicable water quality objectives at that time for PAH were the numeric objective that limited total PAH in water to a 24-h average of 15 μg/L and the two narrative water quality objectives: (1) all waters shall be maintained free of toxic substances in concentrations that are lethal to or that produce other detrimental responses in aquatic organisms, and (2) controllable water quality factors shall not cause a detrimental increase in concentrations of toxic substances found in bottom sediments or aquatic life; effects on aquatic organisms, wildlife, and human health will be considered.

Fortunately, oil spills in the Bay had become rare, infrequent events due to regulatory action in the 1970s and could be ruled out as a major source of concern. However, the State Water Resources Control Board (Water Board) began its regulatory program to require management of urban runoff in the late 1980s, and pollutants of concern in urban runoff included petroleum hydrocarbons including PAH. Hazardous waste related laws and regulations and urban runoff management programs have drawn attention to improper disposal of used oil, particularly dumping into storm drains. These efforts, in conjunction with improvements in automobiles resulting in less oil leaks, should be reflected as less oil in urban water runoff. Municipalities have also begun to implement some controls to reduce pollutants in urban runoff associated with combustion sources. However, no discharge data are available currently for either petroleum products or combustion sources in urban runoff.

In 2000, the US EPA promulgated the California Toxic Rule (CTR), which included a numerical (human health based) water quality criterion of 49 ng/L for several individual PAH compounds for the Bay. Subsequently, in 2002, RMP data from previous years were used to assess

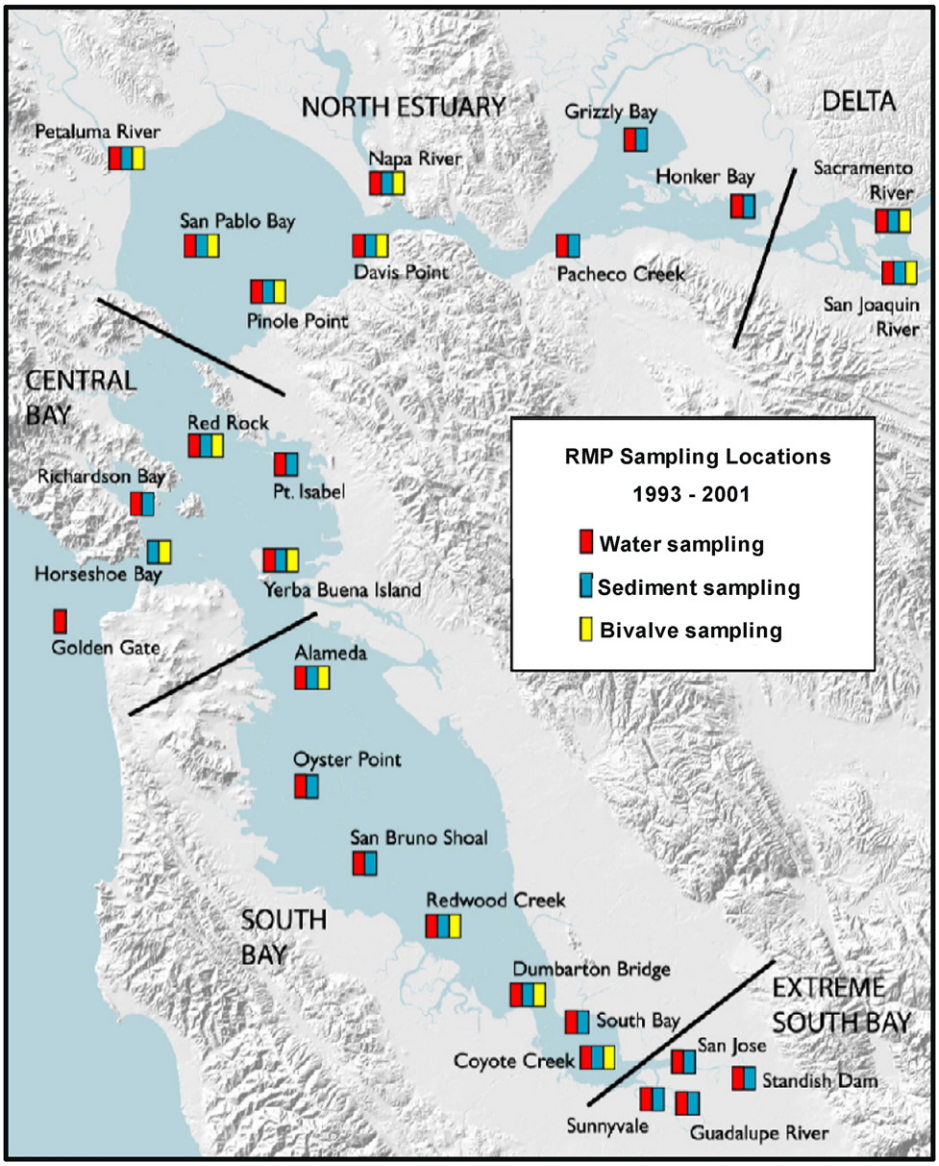

Fig. 1. Map of RMP water, surface sediments, and bivalve sampling stations in the San Francisco Bay from 1993 to 2001.

attainment of the PAH CTR criterion, and levels of PAH in Bay waters were found to be near and occasionally above the CTR criterion throughout the Bay. The Bay was not included on the Clean Water Act Section 303(d) list of impaired waters, on account of PAH, but the Water Board did increase its assessment activities including focusing monitoring efforts on near-shore areas that may be impacted more than far-shore areas by PAH in discharges of urban storm water runoff and other sources.

4. PAH spatial distributions

4.1. Water

Bay water samples collected from 18 individual RMP sampling stations (Fig. 1) during the period 1993–2001 were previously examined for their PAH concentration distributions. Ross and Oros (2004) reported median ΣPAH concentrations in Bay samples ranging from 5 to 147 ng/L. The highest median ΣPAH concentrations were found at Guadalupe River (147 ng/L), San Jose (138 ng/L), and Coyote Creek (84 ng/L) stations, while the lowest were found at the Sacramento River (9 ng/L), San Joaquin River (6 ng/L), and Golden Gate (5 ng/L) stations. The same PAH data set used by Ross and Oros (2004) were further examined in this study to determine if differences in ΣPAH concentrations between the individual sampling stations were significant. ΣPAH concentrations in Guadalupe River, San Jose, and Coyote Creek stations were significantly higher than Golden Gate, San Joaquin River, Sacramento River, Red Rock, Yerba Buena Island, Pinole Point, Grizzly Bay, and Alameda stations (Kruskal–Wallis, $H = 200.6$, $df = 17$, $P < 0.0005$).

By using the same water PAH data set presented in Ross and Oros (2004), the seasonal input of PAH to the Bay as an important factor influencing water column ΣPAH concentrations between individual sampling stations over the same sampling period were further examined. During the wet season (January-March), the water ΣPAH concentrations at Guadalupe River, San Jose, Coyote Creek, Petaluma River, Dumbarton Bridge, Standish Dam, and Redwood Creek stations were significantly higher than those at the Golden Gate, San Joaquin River, and Sacramento River stations (Kruskal–Wallis, $H = 118.0$, $df = 17$, $P < 0.0005$). During the dry season (July–September), the Guadalupe River and San Jose stations were significantly higher than Golden Gate, San Joaquin River, Sacramento River, and Red Rock stations (Kruskal–Wallis, $H = 90.0$, $df = 17$, $P < 0.0005$). No other significant differences were found.

Water data collected by the RMP during the period 1993–2001 were previously examined for PAH spatial distributions by Bay segments. Segments were selected based on hydrographical information with boundaries defined by embayments and straits. Ross and Oros (2004) reported the distribution of median ΣPAH concentration in the water column by various Bay segments as the following: Extreme (Lower) South Bay 120 ng/L, South Bay 49 ng/L, North Estuary 29 ng/L, Central Bay 12 ng/L, and Delta 7 ng/L. Ross and Oros (2004) found that the ΣPAH concentrations in the Extreme South Bay were significantly higher than all other Bay segments, while the Central Bay and Delta segments were significantly lower than all segments (Kruskal–Wallis, $H = 157.3$, $df = 4$, $P < 0.0005$). They suggested that the higher ΣPAH concentrations in the Extreme South Bay were possibly due to its location in a more heavily populated, urbanized, and industrialized region of the Bay, hence the greater potential for PAH input from storm water discharge and atmospheric deposition. The water column in the southern reach of the Bay is also known to have a long residence time (20 days) for conservative solutes (Gross, 1997), especially during periods of low freshwater inflow (flushing), which suggests that hydrodynamic processes are also a critical factor controlling PAH concentration and distribution in that area of the Bay. The Delta segment showed lower ΣPAH concentrations, possibly due to less urbanization and the increased dilution of PAH resulting from the higher levels of freshwater inflow entering that reach of the Bay.

The variation in spatial distribution of ΣPAH found in Bay water samples may also be influenced by water quality characteristics. For instance, water containing more particulate organic matter generally has higher contaminant concentrations since PAH sorb strongly to the surface of particles (Chin and Gschwend, 1992). PAH spatial distributions could also be influenced by water residence time, hydrodynamic processes, and proximity to sources, such as tributaries, storm water drains, and wastewater treatment plant effluent outfalls.

4.2. Sediment

Bay sediment samples collected from 26 RMP individual sampling stations (Fig. 1) during the period 1993–2001 were previously examined for their ΣPAH concentration distributions. Oros and Ross (2004) reported mean ΣPAH concentrations in Bay sediment samples, which were collected from the upper 5 cm layer, ranging from 31 to 316 mg/kg of total organic carbon (TOC). The highest mean ΣPAH concentrations were found at Horseshoe Bay (347 mg/kg TOC) and Richardson Bay (316 mg/kg TOC) stations, while the lowest were found at the Sacramento River and San Joaquin River (31 mg/kg TOC each) stations. The same PAH data set used by Oros and Ross (2004) was further examined in this study to determine if there were any significant differences in ΣPAH concentrations between the individual sampling stations. We found that the ΣPAH concentrations in Horseshoe Bay and Richardson Bay stations were significantly higher than those in San Joaquin River, Sacramento River, Red Rock, Honker Bay, Davis Point, Grizzly Bay, Pacheco Creek, Guadalupe River, Pinole Point, Napa River, and Standish Dam stations (Kruskal–Wallis, $H = 267$, $df = 25$, $P < 0.0005$).

Sediment data collected by the RMP during the period 1993–2001 were previously examined for PAH spatial distribution by Bay segments. Oros and Ross (2004) previously reported that the mean ΣPAH concentrations in sediments were spatially distributed as Central Bay 230 mg/kg TOC, South Bay 217 mg/kg TOC, North Estuary 96 mg/kg TOC, Extreme South Bay 87 mg/kg TOC, and Delta 31 mg/kg TOC. The mean ΣPAH concentrations in the Central Bay and South Bay segments were significantly higher than those in the North Estuary, Extreme South Bay, and Delta segments, and the Delta was significantly lower than all other segments (Kruskal–Wallis, $H = 156.94$, $df = 4$, $P < 0.0005$).

The variation in spatial distribution of ΣPAH found in Bay sediment samples may be influenced by sediment quality characteristics, such as grain size and organic matter content. PAH are hydrophobic compounds that partition readily into organic matter and with the fine grain (size < 0.063 mm) particles in sediments, thus sediments with high TOC and more fines (silt and clay) generally have higher contaminant concentrations than low TOC containing and sandy sediments (Luoma, 1990; Horowitz, 1991). Sediments that contain soot particles, which are formed from combustion of coal, refined fossil fuels (e.g., diesel and fuel oils), and vegetation (biomass burning), can bind or occlude PAH, thus making them less available to partition with TOC in sediments (Gustafsson and Gschwend, 1997). Spatial distributions can also be influenced by sedimentation rates and by the complex sediment transport dynamics that occur within the Bay (Krone, 1979).

4.3. Mussels

Bivalves have been widely used in long-term monitoring programs such as the RMP, NOAA's Mussel Watch

Program, and the California State Mussel Watch Program (Risebrough et al., 1980; Farrington et al., 1983; Phillips, 1988; O'Connor, 1991; Rasmussen, 1994; Lauenstein and Daskalakis, 1998; O'Connor, 2002; Oros and Ross, 2005). Various studies have shown that bivalves are excellent sentinels for monitoring of bioavailable contaminants, such as PAH for marine trends analyses (Farrington et al., 1983; Mix and Schaffer, 1983; Risebrough et al., 1983; Pereira et al., 1992; Nalepa et al., 1993; Kilikidis et al., 1994; Marvin et al., 1994; Grandy and Spliid, 1995; Shchekaturina et al., 1995; Peven et al., 1996; Sericano et al., 1996; Maruya et al., 1997; Baumard et al., 1998; Williams and McMahon, 1989; Gunther et al., 1999; Noreña-Barroso et al., 1999; Baumard et al., 1999; Kim et al., 2001; Sericano et al., 2001; Beliaeff et al., 2002; O'Connor, 2002; Yim et al., 2002; Peachey, 2003; Palma-Fleming et al., 2004; Toro et al., 2004). In addition, resident bivalves accumulate PAH and may act as surrogates to some extent for fish, birds, and mammals when it is not possible to estimate their exposures. Bivalves were transplanted at various stations in the San Francisco Bay by the RMP during the period 1993–2001 (Fig. 1) (RMP, 2001). The bivalves included mussels (*Mytilus californianus*), clams (*Corbicula fluminea*), and oysters (*Crassostrea gigas*). Mussel ΣPAH results are examined here in this study for making comparisons to other long-term mussel monitoring programs, while details on the clam and oyster results are reported elsewhere (Oros and Ross, 2005).

Oros and Ross (2005) reported ΣPAH concentrations in mussels ranging from 21 to 1093 ng/g dry wt (mean 175 ng/g dry wt). The highest ΣPAH concentration was found at the Petaluma River station. The results showed no significant differences in mussel ΣPAH concentrations between the individual deployment stations (Kruskal–Wallis, $H = 8.8$, df = 6, $P = 0.185$). By using the mussel PAH data set presented in Oros and Ross (2005), the seasonal input of PAH to the Bay as an important factor influencing mussel ΣPAH concentrations between individual sampling stations over the same sampling period were further examined. The results showed that during the wet season (January–April) mussel ΣPAH concentrations were not significantly different between any of the deployment stations (Kruskal–Wallis, $H = 3.89$, df = 6, P = 0.692). On the other hand, during the dry season (July–September) mussel ΣPAH concentrations at Yerba Buena Island station (mean ΣPAH 239 ng/g dry wt) were significantly higher than those at the Pinole Point station (mean ΣPAH 186 ng/g dry wt) (Kruskal–Wallis, $H = 13.4$, df = 6, $P = 0.037$). No other significant differences were found.

The RMP's mussel data previously reported in Oros and Ross (2005) were further examined to determine if there were any significant differences in ΣPAH concentration spatial distribution by Bay segments. The results showed that there were no significant differences in mussel ΣPAH concentrations between the South Bay, Central Bay, and North Estuary segments (Kruskal–Wallis, $H = 4.4$, df = 2, $P = 0.109$). Comparisons of RMP mussel monitoring results (temporal trends) to other program data can be found in Section 5.3.

5. PAH temporal trends

5.1. Water

Water data collected by the RMP during the period 1993–2001 were previously examined for PAH temporal trends by individual sampling stations. By using linear regression analysis, Ross and Oros (2004) showed a statistically significant temporal trend for ΣPAH water concentrations at only 1 of the 18 PAH water sampling stations throughout the Bay. Water samples from the San Jose station showed a statistically significant (linear regression, $r^2 = 0.386$, $P = 0.031$) decrease in ΣPAH concentration over the 9-yr sampling period.

By using the water PAH data set presented by Ross and Oros (2004), we further determined whether the seasonal input of PAH to the Bay was an important factor that influenced water ΣPAH concentrations between individual sampling stations over the same sampling period. For the dry season (July–September), only one station, Alameda, showed a significant increasing seasonal temporal trend (linear regression, $r^2 = 0.716$, $P = 0.034$), while during the wet season (January–March), there were no significant ($P > 0.05$) seasonal temporal trends at any of the individual sampling stations. In addition, results showed there were no significant ($P > 0.05$) seasonal temporal trends in water ΣPAH concentrations in any of the Bay segments.

5.2. Sediment

Sediment data collected by the RMP during the period 1993–2001 were previously examined for PAH temporal trends by individual sampling stations. By using linear regression analysis, Oros and Ross (2004) showed a statistically significant trend for TOC normalized ΣPAH concentrations at only 1 of the 26 sampling stations throughout the Bay. The San Pablo Bay station sediments showed a significant decreasing trend in ΣPAH concentrations over the sampling period (linear regression, $r^2 = 0.314$, $P = 0.024$). This decrease in ΣPAH concentration is possibly due to erosion of surface sediments by current and wave action. Jaffe et al. (1998) previously reported that San Pablo Bay lost 7 million cubic meters of sediment from 1951 to 1983 due to water projects decreasing peak flows, which in turn decreased suspended sediment input into the Bay. Another possibility is that local long-term management actions designed to control PAH input (e.g., via storm water runoff and industrial effluent discharge) to San Pablo Bay might be working. The lack of any significant temporal trends in ΣPAH concentration at the individual sediment sampling stations, except San Pablo Bay, suggests that the ΣPAH concentrations in Bay sediments remained generally constant during the sampling period 1993–2001.

Using the sediment PAH data set presented by Oros and Ross (2004), the data were grouped into Bay segments (Delta, North Estuary, Central Bay, South Bay, and Extreme South Bay) and examined for temporal trends. The results showed that the sediment ΣPAH concentrations did not significantly ($P>0.05$) increase or decrease, but rather remained constant in all Bay segments during the period 1993–2001.

5.3. Mussels

In order to determine if long-term temporal trends in ΣPAH concentrations had occurred at any of the mussel deployment stations in the Bay, the RMP's mussel (*M. californianus*) data (1993–2001) were combined with California State Mussel Watch Program data. This expanded the entire San Francisco Bay mussel data set to include the years 1991–2001.

The ΣPAH and percent lipid concentrations were first log-transformed in an attempt to normalize the data and equalize the variances. Linear regression analysis showed a highly significant positive relationship (linear regression, $r^2 = 0.091$, $P = 0.003$) between percent lipids and ΣPAH for mussels, therefore, lipid normalization was considered appropriate (Hebert and Keenleyside, 1995). Next, mussel ΣPAH concentrations at each station were normalized for lipid content using linear regression analysis. Residuals from this analysis represent the variation in contaminant concentrations that remains after the effect of lipid content has been removed. Values falling above or below the regression line have positive or negative residuals, respectively. Therefore, adding the grand mean of the log-transformed ΣPAH rescaled the residuals. Because uptake and depuration of PAH by bivalves generally follow first-order kinetic processes (Sericano et al., 1996), which are natural log (ln)-linear with respect to time, temporal trends for the mussels were examined for each deployment station by performing a linear regression analysis using the ln(rescaled residual) as the dependent variable and sampling date as the independent variable. The presence of first-order autocorrelation in the time series data was examined using the Durbin–Watson test.

Analysis of the long-term data set showed that there was a statistically significant ($P<0.05$) temporal trend in mussel ΣPAH concentrations at only 1 of 6 mussel deployment stations over the 11-yr period (Table 1). Mussels from Redwood Creek in the South Bay showed a significant (linear regression, $r^2 = 0.282$, $P = 0.034$) decreasing temporal trend in tissue PAH concentrations. Since the use of stations as replicates within Bay segments provides greater statistical power for detecting possible temporal trends, the data were analyzed again by Bay segment (North Estuary, Central Bay, and South Bay). A statistically significant (linear regression, $r^2 = 0.118$, $P = 0.018$) decreasing temporal trend in mussel ΣPAH concentration was found in the South Bay segment. There were no trends in the North Estuary and Central Bay segments.

Table 1
Temporal trends in total PAH (ΣPAH) concentrations in mussels, *Mytilus californianus*[a], 1991–2001

	Station	ln(%lipid normalized ΣPAH)			
		P	*n*	r^2	Trend
Overall					
NE	Pinole Point	0.745	14	0.009	None
CB	Horseshoe Bay	0.270	18	0.076	None
CB	Yerba Buena Island	0.351	16	0.062	None
SB	Alameda	0.187	17	0.113	None
SB	Redwood Creek	**0.034**	16	0.282	**Decrease**
SB	Dumbarton Bridge	0.633	14	0.020	None
	Segment				
	North Estuary	0.745	14	0.009	None
	Central Bay	0.166	34	0.059	None
	South Bay	**0.018**	47	0.118	**Decrease**
Wet Season					
NE	Pinole Point	0.465	6	0.140	None
CB	Horseshoe Bay	0.158	10	0.233	None
CB	Yerba Buena Island	**0.027**	8	0.583	**Decrease**
SB	Alameda	**0.011**	9	0.627	**Decrease**
SB	Redwood Creek	0.051	8	0.497	None
SB	Dumbarton Bridge	0.341	7	0.181	None
	Segment				
	North Estuary	0.465	6	0.140	None
	Central Bay	**0.014**	18	0.320	**Decrease**
	South Bay	**<0.0005**	24	0.433	**Decrease**
Dry Season					
NE	Pinole Point	0.735	8	0.021	None
CB	Horseshoe Bay	0.563	8	0.059	None
CB	Yerba Buena Island	**0.001**	8	0.868	**Increase**
SB	Alameda	0.475	8	0.088	None
SB	Redwood Creek	0.332	8	0.156	None
SB	Dumbarton Bridge	0.257	7	0.246	None
	Segment				
	North Estuary	0.735	8	0.021	None
	Central Bay	**0.026**	16	0.305	**Increase**
	South Bay	0.598	23	0.013	None

Abbreviations: CB—Central Bay; NE—North Estuary; SB—South Bay.
[a] *M. californianus* data were normalized for lipid content since there was a statistically significant relationship between percentage lipid and ΣPAH concentration (linear regression, $P = 0.003$, $r^2 = 0.091$, $n = 95$).

The long-term mussel data set was further examined by season to determine if temporal trends in mussel ΣPAH concentrations had occurred at individual deployment stations and in Bay segments as a response to seasonal (wet and dry seasons) input (Table 1). During the wet season (January–March), decreasing temporal trends in mussel ΣPAH concentrations were found at the Yerba Buena Island (linear regression, $r^2 = 0.583$, $P = 0.027$) and Alameda (linear regression, $r^2 = 0.627$, $P = 0.011$) stations, but at no other stations. When the wet season data were analyzed by Bay segment, a significant decreasing trend was found in the Central Bay (linear regression,

$r^2 = 0.320$, $P = 0.014$) and a highly significant decrease in the South Bay (linear regression, $r^2 = 0.433$, $P < 0.0005$) segments. Analysis of the dry season (July–September) data showed a highly significant increasing trend in mussel ΣPAH concentrations at the Yerba Buena Island station (linear regression, $r^2 = 0.868$, $P = 0.001$), but at no other stations. When the dry season data were further examined by Bay segment, a significant increasing trend was found only in the Central Bay (linear regression, $r^2 = 0.305$, $P = 0.026$) segment.

The results of monitoring mussel ΣPAH concentrations in the Bay show that there are temporal trends. When the long-term mussel data were treated as a combined data set and not as separate wet and dry season data sets, only 1 of 6 individual deployment stations showed a temporal trend (Redwood Creek), which suggests that the mussel ΣPAH concentrations were relatively constant throughout the Bay over the 11-yr period. This observation is generally in agreement with the earlier long-term 1965–1993 data collected by the four US large-scale Mussel Watch Programs (US EPA 1 and US EPA 2 Mussel Watch Programs, California Mussel Watch Program, and NOAA Mussel Watch Project), which concluded that there were generally no statistically significant increasing or decreasing temporal trends for ΣPAH concentrations in US coastal waters (Lauenstein and Daskalakis, 1998). Based on the seasonal data analysis, mussel ΣPAH concentrations showed two (2 of 6 stations) decreasing temporal trends during the wet season (Yerba Buena Island and Alameda stations) and one (1 of 6 stations) increasing temporal trend during the dry season (Yerba Buena Island). This shows that conducting mussel PAH monitoring during the dry season alone could overlook the existence of temporal trends that might occur during the wet season.

6. PAH sources, pathways, and loadings

PAH isomer pairs have similar physical-chemical properties and similar dilution and distribution with particulate matter and other environmental phases (Dickhut et al., 2000), thus ratios of PAH isomer pairs can be applied as distinct chemical tracers to infer possible PAH sources in environmental samples. For instance, PAH isomer pair ratios were used to identify automobile emissions as the major source of PAH in the Chesapeake Bay (Dickhut et al., 2000). Also, Yunker et al. (2002) applied PAH isomer pair ratios to show that PAH in the Fraser River Basin and Estuary (British Columbia, Canada) were derived from biomass, coal, and petroleum combustion.

Four PAH isomer pair ratios were applied as diagnostic tracers to identify possible sources contributing PAH to San Francisco Bay waters, sediments, and bivalves: anthracene/anthracene + phenanthrene (An/178); benz[*a*]anthracene/benz[*a*]anthracene + chrysene (BaA/228); fluoranthene/fluoranthene + pyrene (Fl/Fl + Py); and indeno[1,2,3-*c,d*]pyrene/indeno[1,2,3-*c,d*]pyrene + benzo[*g,h,i*]-perylene (IP/IP + BghiP). PAH isomer pair ratios determined from Bay water samples were compared to PAH isomer pair ratios determined from several major PAH sources (environmental samples, petroleum, and single-source combustion) compiled previously by Yunker et al. (2002). Based on the PAH isomer measurements compiled by Yunker et al. (2002): an An/178 ratio <0.10 indicates dominance of petroleum and >0.10 indicates dominance of combustion; a Fl/Fl + Py ratio <0.40 petroleum, 0.40–0.50 petroleum combustion, and >0.50 combustion of biomass and coal; a BaA/228 ratio <0.20 petroleum, 0.20–0.35 petroleum and combustion, and >0.35 combustion; and an IP/IP + BghiP ratio <0.20 petroleum, 0.20–0.50 petroleum combustion, and >0.50 combustion of biomass and coal. The results of the PAH isomer pair ratio analysis showed that the major source of PAH to San Francisco Bay water, sediments, and bivalves was combustion of petroleum, while minor amounts of PAH were derived from combustion of biomass (wood and grasses) and coal, and from uncombusted petroleum (Figs. 2–4) (Oros and Ross, 2004; Ross and Oros, 2004; Oros and Ross, 2005). Because coal is no longer used as a major fuel or mined in the Bay Area (as it was previously in the Mount Diablo Coal Mining District), its chemical signature in the Bay was attributed to soil erosion and/or tidal resuspension of historically deposited coal or coal soot in bedded sediments. Oros and Ross (2004) further identified several discrete sources of PAH found in Bay sediments that included used engine oil from gasoline passenger cars, combustion engine emissions from vehicular traffic, and creosote from treated wood pilings.

PAH loading into the Bay occurs through various transport pathways including storm water runoff, tributary inflow, wastewater treatment plant and industrial effluent discharge, atmospheric deposition, and dredged material disposal. The maximum total PAH loading contribution to the Bay from these known pathways is estimated at 10,700 kg/yr (Table 2). Although PAH input from other transport pathways could occur (e.g., oil spills which are acute events), these are generally infrequent and rarely visible in monitoring data. Based on their relative contribution to the estimated total maximum PAH loading (10,700 kg/yr) into the Bay, the PAH loading pathways are ranked as storm water runoff (~51%) > tributary inflow (~28%) > wastewater treatment plant effluent (~10%) > atmospheric deposition (~8%) > dredged material disposal (~2%) (Table 2). PAH loading from the various transport pathways are described in more detail below.

Storm water runoff is a major transport pathway for PAH into the Bay, especially during the rainy season when storm water flows are highest (Maruya et al., 1996). Gunther et al. (1991) previously estimated the total PAH contribution to the Bay from storm water runoff as 130–5500 kg/yr, which constitutes ~51% of the maximum total PAH load (10,700 kg/yr). Storm water runoff, which is the most critical transport pathway for PAH loading into

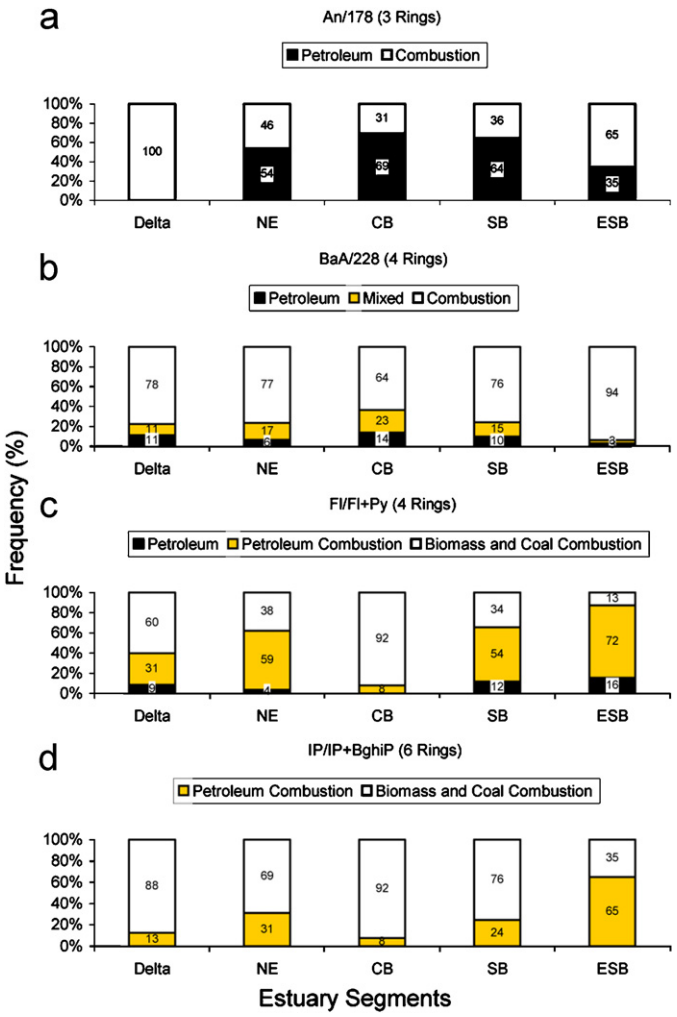

Fig. 2. Bar plots of PAH isomer pair ratios showing the estimated frequency (%) of PAH derived from various sources in water samples from different San Francisco Bay segments: (A) An/178 ratio showing percentage of PAH from petroleum and combustion sources; (B) BaA/228 showing percentage of PAH from mixed and combustion sources, (C) Fl/Fl+Py ratio showing percentage of PAH from petroleum, petroleum combustion, and biomass and coal combustion, and (D) IP/IP+BghiP ratio showing percentage of PAH from petroleum, petroleum combustion, and biomass and coal combustion sources. Abbreviations: NE = North Estuary; CB = Central Bay; SB = South Bay; and ESB = Extreme South Bay. Bar plots were generated for all individual stations within each segment where possible by determining frequency (%) of samples between source boundary lines based on Yunker et al. (2002) and previously shown for San Francisco Bay water in Ross and Oros (2004).

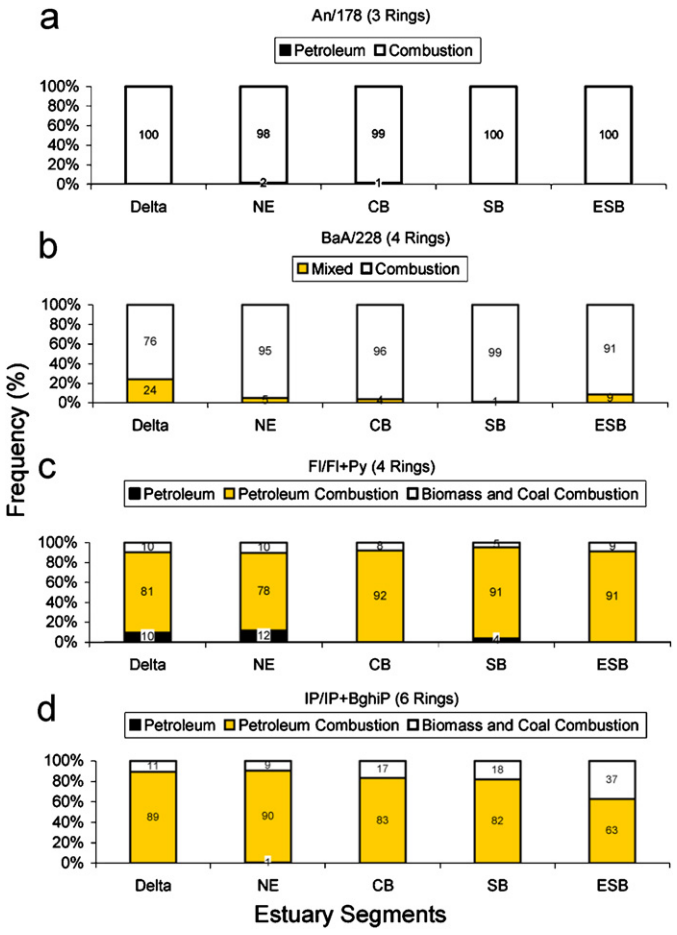

Fig. 3. Bar plots of PAH isomer ratios showing the estimated frequency (%) of PAH derived from various sources in sediment samples from different San Francisco Bay segments: (A) An/178 ratio showing percentage of PAH from petroleum and combustion sources, (B) BaA/228 showing percentage of PAH from petroleum, mixed, and combustion sources, (C) Fl/Fl+Py ratio showing percentage of PAH from petroleum, petroleum combustion, and biomass and coal combustion sources, and (D) IP/IP+BghiP ratio showing percentage of PAH from petroleum, petroleum combustion, and biomass and coal combustion sources. Abbreviations: NE = North Estuary; CB = Central Bay; SB = South Bay; and ESB = Extreme South Bay. Bar plots were generated for all individual stations within each segment where possible by determining frequency (%) of samples between source boundary lines based on Yunker et al. (2002) and previously shown for San Francisco Bay sediments in Oros and Ross (2004).

the Bay, is likely to contain used engine oil spilled from vehicles and soot from vehicular tail pipe emissions that are deposited to street surfaces.

Tributary inflow to the Bay is primarily from the Delta via the Sacramento and San Joaquin Rivers, from the Petaluma and Napa Rivers in the North Estuary, and from the Guadalupe River and Coyote Creek in the South Bay. There are also numerous smaller tributaries and creeks that release surface waters into the Bay. Tributary inflow is especially high during the rainy season. The Delta alone is estimated to currently discharge ~37% of California's surface water runoff into the Bay (McKee et al., 2006). Gunther et al. (1991) previously estimated the total PAH contribution to the Bay from tributary inflow as 3000 kg/yr, which constitutes ~28% of the maximum total PAH load.

Wastewater treatment plants discharge ~870 million cubic meters of treated effluent annually into the Bay (CRWQCB, 2004), which could represent a significant PAH contribution from a point source. Davis et al. (2000) estimated the total PAH contribution to the Bay from treatment plant and industrial effluent discharges as 200–1100 kg/yr, which represents ~10% of the maximum total PAH load.

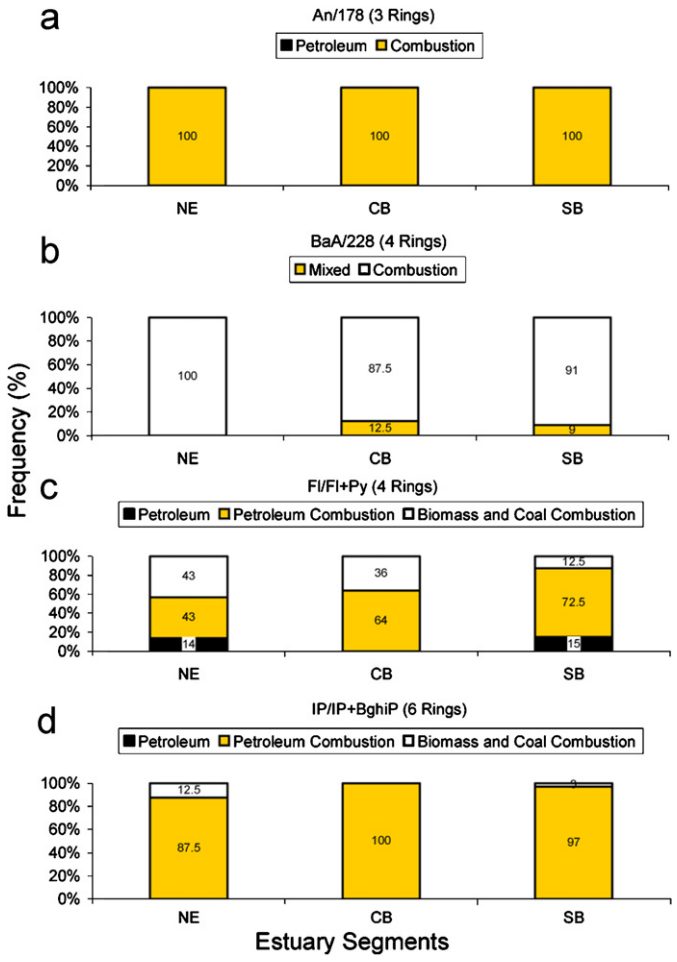

Fig. 4. Bar plots of PAH isomer ratios showing the estimated frequency (%) of PAH derived from various sources in mussels from different San Francisco Bay segments: (A) An/178 ratio showing percentage of PAH from petroleum and combustion sources, (B) BaA/228 showing percentage of PAH from petroleum, mixed and combustion sources, (C) Fl/Fl + Py ratio showing percentage of PAH from petroleum, petroleum combustion, and biomass and coal combustion sources, and (D) IP/IP + BghiP ratio showing percentage of PAH from petroleum, petroleum combustion, and biomass and coal combustion sources. Abbreviations: NE = North Estuary; CB = Central Bay; SB = South Bay. Bar plots were generated for all individual stations within each segment where possible by determining frequency (%) of samples between source boundary lines based on Yunker et al. (2002) and previously shown for San Francisco Bay bivalves in Oros and Ross (2005).

PAH emitted to the atmosphere from both point (e.g., industrial emissions) and non-point sources (e.g., vehicular and machinery emissions) occurs year around. PAH enter the water column by gas exchange across the air–water interface, dry deposition of airborne particulate matter (e.g., soot), or wet deposition by rainfall sequestration. Atmospheric deposition of PAH from conifer wood combustion has been previously identified as a loading pathway into the Bay (Tsai et al., 2002), especially during winter months when fireplace and woodstove use and burning of wood is increased in the Bay Area (Gullett et al., 2003). Wildfires (non-controlled biomass burning) also contribute combustion emissions to the atmosphere, especially during the summer and fall seasons when the regional climate conditions are hot and dry, and the abundance of biomass fuel available for burning is highest. Tsai et al. (2002) estimated that the total PAH contribution to the Bay from atmospheric deposition is 890 kg/yr, which constitutes ~8% of the maximum total PAH load.

An estimated 3–6 million cubic yards of sediment are dredged annually from shipping channels and related navigation facilities in the Bay (US ACE, 1998). Approximately 80% of this dredged material is disposed at designated sites located in the Bay. Total PAH loading from dredging previously buried PAH and disposing them to surface sediments is estimated to be 210 kg/yr, which represents ~2% of the maximum total PAH load into the Bay. Dredging and dredged material disposal sites and activities in the Bay are conducted within site-specific work windows that are detailed in the Long-Term Management Strategy (LTMS) Management Plan (US ACE, 1998).

Acute input events such as oil spills could also contribute PAH to the Bay, but loading levels are generally unknown and/or variable. Oil tankers transport millions of gallons of crude oil and refined petroleum products in and out of the Bay each year. Petroleum refineries, which are concentrated in the Central and Northern reaches of the Bay, require the use of storage tanks and miles of transport pipelines for operation, which increases the risk of major oil spills within the Bay boundaries. Several major spills occurred during the period 1993–2001. For instance, on October 28, 1996, a ship in the San Francisco dry docks

Table 2
Estimated total PAH loads (kg/yr) from various sources

Source	Estimated minimum load	Estimated maximum load	% of ΣPAH load[a]	Reference
Stormwater runoff	130	5500	51	Gunther et al. (1991)
Tributary inflow		3000	28	Gunther et al. (1991)
Effluent discharge	200	1100	10	Davis et al. (2000)
Atmospheric deposition		890	8	Tsai et al. (2002)
Dredged material disposal		210	2	Davis et al. (2000)
Total PAH load[b]	330	10700	100	

[a]Based on the estimated maximum load.
[b]This table is cited from Greenfield and Davis (2005).

spilled over 8000 gallons (30,283 liters) of bunker C oil; on April 27, 2004, a transport pipeline ruptured spilling over 70,000 gallons (264,979 L) of diesel oil into Suisun Marsh; and on February 7, 2005, a transport pipeline ruptured spilling 500 gallons (1893 L) of jet fuel into the Oakland Estuary. Oil and petroleum product spills contribute unknown quantities of PAH into the water column and it is not known how much residual PAH from spilled oil and petroleum products remain in the Bay after completion of recovery and cleanup activities. PAH derived from petroleum, however, are preferentially biodegraded compared to combustion-derived PAH (Jones et al., 1986).

7. Impairment assessment

7.1. Aquatic biota toxicity

PAH are toxic, and some PAH are mutagenic and genotoxic (Arcos and Argus, 1975; WHO, 1989), thus chronic exposure to PAH can be threatening to marine biota and wildlife (Peterson et al., 2003). PAH contamination in San Francisco Bay sediments has been previously correlated with adverse impacts on fish and invertebrates (Spies and Rice, 1988; Spies et al., 1988; Thompson et al., 1999). To further substantiate these observations, two important screening tools for sediment contaminant concentrations, the marine sediment quality threshold and the marine sediment quality guideline (SQG), may be used to assess the potential for sediment total PAH concentrations to affect sediment toxicity. The marine sediment quality threshold suggested by Johnson et al. (2002) was developed as a screening tool to protect estuarine fish against health effects, while the Effects Range marine SQGs were developed by Long et al. (1995) to identify concentrations of contaminants that are associated with adverse biological effects on marine amphipods.

Johnson et al. (2002) suggested a sediment quality threshold of 1000 ng/g dry wt for sediment ΣPAH (sum of 22 individual PAH) concentrations to protect estuarine fish against health effects that included selected degenerative liver lesions, spawning inhibition, and reduced egg viability. This threshold is based on effects evident in English sole (*Pleuronectes vetulus*) in Puget Sound. English sole occur in the San Francisco Bay, mainly as juveniles rather than as adults, but they are not a common species. The 1000 ng/g threshold as proposed by Johnson et al. (2002) is the lowest concentration where effects in English sole begin to be observed. At concentrations >1000 ng/g, there appears to be a substantial increase in the risk of liver disease and reproductive impairment, and potential effects on growth. Johnson et al. (2002), based on their English sole data and model, further pointed out that at ΣPAH concentrations of 5000 ng/g the levels of hepatic DNA adducts would be approximately 10-fold the levels found in English sole from uncontaminated reference sites, about 30% of the fish population was predicted to have some form of liver disease, and the number of fish failing to spawn was predicted to increase from about 12% to over 35%. At 10000 ng/g, DNA adducts levels in English sole would have increased 12–13-fold, 50% of the fish would be expected to have liver disease, nearly 30% of the females would show inhibition of gonadal growth, and over 40% would show inhibition of spawning. The ΣPAH threshold concentrations for observed DNA damage, liver lesions, and reproductive abnormalities are shown in Table 3.

Table 3
Relationship of sediment PAH concentration (ppb or ng/g dry wt) with hepatic and reproductive abnormalities (cited from Johnson et al. (2002))

Effect[a]	Threshold[b] (ppb dry wt)	Threshold confidence limits (ppb dry wt)
DNA damage	288	6–1318
Liver lesions		
Neoplasms	2800	11–5500
Foci of cellular alteration	54 (ns)	na–870
Specific degeneration/necrosis	940	600–1400
Proliferative lesions	230	1.4–830
Any lesion	620	300–1000
Reproductive abnormalities		
Inhibited gonadal growth	4000	nd
Inhibited spawning	630	nd
Infertile eggs	630	nd
Abnormal larvae	630 (ns)	nd

na = not available.
nd = not determined due to lack of sufficient data.
ns = not significant.
[a]From Johnson et al. (2002): Based on experiments with English sole. For all liver lesions, inhibited gonadal growth, and inhibited spawning, effect endpoints are sampling site prevalences. For DNA damage, endpoint is mean concentration of PAHDNA adducts.
[b]From Johnson et al. (2002): For liver lesions, thresholds are estimated from hockeystick regression; For reproductive abnormalities, threshold equals the geometric mean of the highest sediment PAH concentrations where the effect level was at background and the lowest sediment PAH concentration where an increase in effect level was observed.

Applying the findings of Johnson et al. (2002) to San Francisco Bay sediment stations, the percent of observations that exceeded the 1000 ng/g sediment quality threshold over the period 1991–2001 are shown in Table 4. San Pablo Bay, Point Isabel, and Richardson Bay stations exceeded the threshold 100% of the time. On a segment scale, the Central Bay and South Bay segments, which are also the most highly urbanized regions of the Bay, had the highest number of threshold exceedances (10 of the 14 stations in the Central and South Bay segments exceeded the threshold over 50% of the time). The 1000 ng/g sediment quality threshold may be applicable to other bottom-dwelling fish that are comparable in habits to English sole, such as the starry flounder (*Platichthys stellatus*). For instance, Stehr et al. (1997) previously reported that low-molecular-weight PAH (LPAH, 2–3 rings) and HPAH (4–5 rings) in San Francisco Bay sediments were associated with an increased risk in Starry flounder for developing liver lesions, such as specific

Table 4
Total PAH concentrations (ppb or ng/g dry wt) in San Francisco Bay sediment sampling stations for comparison to PAH sediment quality threshold suggested by Johnson et al. (2002)

	Station	1993–03	1993–09	1994–02	1994–08	1995–02	1995–08	1996–02	1996–07	1997–01	1997–08	1998–02	1998–07	1999–02	1999–07	2000–02	2000–07	2001–02	2001–08	% Exceedances[a] of 1000 ppb threshold	% Exceedances[b] of 4022 ppb ERL
Delta	Sacramento River	62	34	151	222	74	40	171	18	241	2	171	27	30	55		34	18	18	0	0
Delta	San Joaquin River	153	42	118	52	52	65	340	82	873	46	114	397	227	89		210		71	0	0
NE	Honker Bay			*1259*	338	554	354	278	421	393	383	375	599	701	392		572		451	7	0
NE	Grizzly Bay	216	208	*2041*	561	414	388	636	364	446	38	360	566	785	591		432		482	6	0
NE	Pacheco Creek	32	56	483	181	69	265	155	134	90	163	168	603	282	258		153		151	0	0
NE	Napa River	405	320	*1521*	526	776	596	448	603	987	579	*1907*	*1185*	*2477*	807	753	935	503	630	22	0
NE	Davis Point	67	171	138	65	166	82	80	37	7	99	120	125	88	60	54	156	56	137	0	0
NE	Pinole Point	478	294	982	678	322	329	434	413	374	583	423	697	837	816		682		552	0	0
NE	San Pablo Bay	*2976*	*1910*	***4845***	*2937*	*1386*	*1643*	*2054*	*3818*	***4681***	*2136*	*2591*	***4204***	*3471*	*1135*	*2185*	*1090*	*1247*	*1344*	100	***17***
NE	Petaluma River					*1038*	927	*1040*	626	398	503	420	842	637	515	*1590*	771	*3563*	469	22	0
CB	Red Rock			93	3	46	11	163	56	18	163	246	50	248	38		30		21	0	0
CB	Point Isabel	*1440*	*1336*	*3865*	*1180*	*2181*	*1579*	*1286*	*1675*	*1063*	*1531*	*1069*	*1506*	*1868*	*1007*		*1682*		*2144*	100	0
CB	Richardson Bay	*2245*	*2130*	*3473*	*1542*	*1691*	*1596*	*1850*	*2859*	*1133*	*1415*	*1278*	*1738*	*1833*	*1677*		*2115*		*2231*	100	0
CB	Horseshoe Bay	*1513*	*1138*	*3864*	*2032*	*1597*	872	851	*1867*	*3118*	585	*1816*	*1772*	*2722*	*2351*		*2433*		*1706*	81	0
CB	Yerba Buena Island	740	*1510*	*1603*	*1456*	881	778	*1166*	889	572	829	*1199*	*3576*	*1664*	997		991		*1775*	50	0
SB	Alameda			***4594***	*1666*	*2867*	*1701*	986	*1549*	856	*2351*	*1857*	*2609*	*2911*	*2222*		*3511*		*2218*	86	***7***
SB	Oyster Point	*1077*	*1552*	*2923*	972	*1932*	901	*2324*	*1565*	*1938*	521	*1938*	999	*1670*	*1187*		947		*1206*	69	0
SB	San Bruno Shoal			*2156*	*1592*	*1655*	*1159*	*1367*	*1297*	*1071*	*1129*	*1104*	*1376*	*2058*	993		*1437*		*1991*	93	0
SB	Redwood Creek	*1494*	909	*3507*	*1046*	*1691*	*1149*	*1763*	*2088*	*1090*	*1286*	*1128*	*1842*	*2228*	*1053*		*1502*		*1370*	94	0
SB	Dumbarton Bridge	*1758*	*1419*	*3002*	*1557*	*2057*	*1697*	*2624*	*1669*	*1419*	*1796*	953	*1776*	*2646*	*1449*		*1784*		*1914*	94	0
SB	South Bay	*1772*	860	***5238***	*1674*	*1620*	*1315*	*2535*	*1945*	*1003*	*1254*	999	*1126*	*1682*	*1383*		*1262*		*1349*	88	***6***
SB	Coyote Creek					*1001*	*1074*	*1309*	901	647	992	465	*1050*	749	478		*1186*		696	42	0
SB	San Jose							508	817	336	*1148*	786	*2642*	917	840		416		*1116*	30	0
SB	Sunnyvale							477		368		667	856	936	332		*1032*			14	0
EI	Standish Dam							454	668	384	657	142	534	824	697		708		810	0	0
EI	Guadalupe River									*1120*	*1135*	866	697	*1507*	854		849		914	38	0

Abbreviations: CB—Central Bay; EI—Estuary Interface; NE—North Estuary; SB—South Bay.

[a]The percentage of observations that exceeded the PAH sediment quality threshold of 1000 ppb (ng/g dry wt) for total PAH as suggested by Johnson et al. (2002). Johnson et al. (2002) suggested the 1000 ppb total PAH threshold to protect estuarine fish against health effects including selected degenerative liver lesions, spawning inhibition, and reduced egg viability. Thresholds were based on Puget Sound sediments and effects evident in English sole (*Pleuronectes vetulus*). At >1000 ppb there appears to be a substantial increase in the risk of liver disease and reproductive impairment, and potential effects on growth. Threshold exceedances are in Italic.

[b]The percentage of observations that exceeded the total PAH Effects Range Low (ERL, 4022 ppb) sediment quality guideline as suggested by Long et al. (1995). ERL exceedances are in bold–italic numbers. The ERL was established primarily to protect the health of benthic invertebrates. Total PAH are the sum of 25 PAH: biphenyl, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene, 2,3,5-trimethylnaphthalene, acenaphthene acenaphthylene, anthracene, dibenzothiophene, fluorene, phenanthrene, 1-methylphenanthrene, benz[*a*]anthracene, chrysene, fluoranthene, pyrene, benzo[*a*]pyrene, benzo[*e*]pyrene, benzo[*b*] fluoranthene, benzo[*k*]fluoranthene, dibenzo[*a,h*]anthracene, perylene, benzo[*g,h,i*]perylene, and indeno[1,2,3-*c,d*]pyrene.

degeneration/necrosis and hydropic vacuolation. Hydropic vacuolation of biliary epithelial cells and hepatocytes was the most prevalent liver lesion found in starry flounder. Stehr et al. (1997) also reported that LPAH and HPAH in sediment were associated with an increased risk in white croaker (*Genyonemus lineatus*) for developing liver necrosis, while LPAH in sediments were associated with an increased risk of developing specific degeneration/necrosis. In addition, Spies et al. (1988) previously reported low prevalence of liver lesions including hepatic neoplasms and foci of cellular alterations in starry flounder from the San Francisco Bay. Based on the relatively small dataset, histological biological indicators of toxicant exposure appear to be present in two San Francisco Bay bottom-dwelling fish species, starry flounder, and white croaker. The data suggest that PAH contamination in San Francisco Bay sediments could be a principal factor causing fish liver disease and reproductive impairment, and potential effects on growth.

For the Effects Range marine SQGs developed by Long et al. (1995), which are based primarily on benthic invertebrates, total PAH concentrations (dry weight basis) below the effects range low (ERL) (4022 ng/g) are interpreted as being rarely associated with adverse effects. The ERL is the concentration equivalent to the lower 10^{th} percentile of the data compiled by Long et al. (1995) to which adverse effects in benthic invertebrates were linked. The total PAH concentrations between the ERL and effects range median or (ERM) (44792 ng/g) are interpreted as being occasionally associated with adverse affects, and total PAH concentrations above the ERM are interpreted as being frequently associated with adverse effects. Based on the RMP's monitoring data ΣPAH concentrations (sum of 25 individual PAH) shown in Table 4, the ERL SQG of 4022 ng/g was exceeded at only 3 of the 26 RMP sediment sampling stations, which include the San Pablo Bay (3 incidences: 1994, 1997, 1998), Alameda (1 incidence: 1994), and South Bay (1 incidence: 1994) stations. Based on the ΣPAH dataset, the ERL guideline has not been exceeded at any of the RMP's sediment sampling stations since 1998. Four of the five incidences of ERL exceedances occurred during the wet season months of January and February, which is also the period of peak storm water inflow to the Bay. Based on the very few exceedances of the ERL guideline, PAH sediment contamination might not be a critical factor influencing benthic invertebrate health.

The marine sediment quality threshold and SQG are both important screening tools for determining the potential for sediment PAH concentrations to affect the health of estuarine fish and benthic invertebrates, respectively. San Francisco Bay sediment ΣPAH concentrations are well above pre-industrial sediment concentrations (36–931 ng/g dry wt, Pereira et al., 1999) and are occasionally high enough to cause adverse biological effects. The total PAH concentration ERL SQG of 4022 ng/g was exceeded on five occasions during the period 1993–2001. Although they are not shown here, it is important to mention that individual PAH with established ERLs may also be used to evaluate the potential for biological effects. The PAH sediment quality threshold of 1000 ng/g, which is suggested to protect estuarine fish, such as English sole, against adverse health effects, was frequently exceeded in the Bay with 11 of the 26 sediment sampling stations exceeding the threshold over 50% of the time during the period 1993–2001. Exceedances of the threshold suggest that English sole and perhaps other bottom feeding fish are prone to or could be currently experiencing adverse biological effects from PAH in sediments.

Several studies have shown that San Francisco Bay fish and other aquatic biota populations are being impacted by PAH contamination; however, these were conducted using sediments from heavily contaminated sites. For instance, in fish exposure experiments, Gunther et al. (1997) reported that hepatic ethoxyresorufin-O-deethylase (EROD) induction/activity in speckled sanddabs (*Citharichthys stigmaeus*), a flat fish, was highly correlated with total PAH ($r^2 = 0.70$, $P < 0.05$) or total polychlorinated biphenyl concentrations in Castro Cove sediments. EROD induction/activity is an excellent biomarker of chemical exposure in fish (Whyte et al. 2000). In another study, sediment contamination and toxicity were monitored at 14 sites in the San Francisco Bay from 1991 to 1996 (Thompson et al., 1999). These authors applied bulk sediment bioassays using *Eohaustorius estuarius* and sediment elutriate bioassays using larval bivalves (*Mytilus* spp., and *Crassostrea gigas*). Amphipod tests provide information about acute effects of contaminants that are sorbed onto bulk sediments, while bivalve tests provide information about the effects of contaminants in the water-soluble fraction of sediments on developing embryos. Thompson et al. (1999) reported that statistically significant relationships between amphipod toxicity and sediment contaminant concentrations, which were normalized to sediment TOC content, were found at several stations. For instance, at Alameda station LPAH (Pearson's correlation, $r^2 = -0.953$, $P < 0.05$) and HPAH (Pearson's correlation, $r^2 = -0.855$, $P < 0.05$) were each significantly and inversely correlated with percent survival, and LPAH and HPAH were usually above their ERLs (552 and 1700 ng/g dry wt, respectively). At San Bruno Shoal station, LPAH were correlated with amphipod toxicity, but the LPAH concentration was always below its ERL, while the HPAH concentration was always above its ERL when amphipod toxicity was found. In Castro Cove, PAH, among other contaminants measured, were inversely and significantly correlated with amphipod survival (LPAH, Pearson's correlation, $r^2 = -0.468$, $P < 0.05$; HPAH, Pearson's correlation, $r^2 = -0.557$, $P < 0.05$). Furthermore, when Thompson et al. (1999) combined Alameda and Castro Cove PAH data, they found that LPAH concentrations above 474 ng/g and HPAH concentrations above 1983 ng/g were always associated with amphipod toxicity (Fig. 5). These concentrations were near the LPAH and HPAH ERLs. The PAH found in Castro Cove were

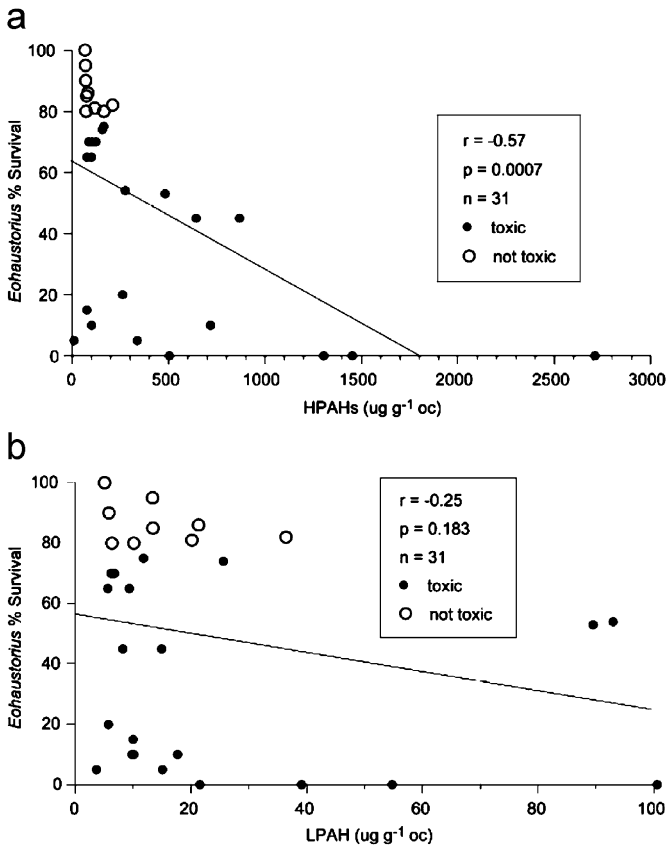

Fig. 5. Plot of *Eohaustorius* percent survival and low-molecular-weight PAH (LPAH) and high-molecular-weight PAH (HPAH) in sediments from Alameda and Castro Cove sites where PAH were statistically associated with amphipod toxicity. Figure courtesy of Bruce Thompson (San Francisco Estuary Institute).

determined to be derived from past oil refinery discharge of effluent in that area.

7.2. Human health risk

The total PAH concentration limit that is considered by the US EPA to present risks to human consumers of fish and shellfish is 6000 ng/g wet weight, which is based on human health risk assessment and is considered to be protective of recreational, tribal, ethnic, and subsistence fishers who are likely to consume more fish and shellfish than the general population (US EPA, 2000). In 1994, the Bay Protection and Toxic Cleanup Program conducted the first pilot study to measure contaminant concentrations in eight species of San Francisco Bay fish (CRWQCB, 1995). The study results showed that of the 24 individual PAH measured, their concentrations in fish tissues (flesh and skin) were near or below their method detection limits (range 2–3 ng/g) in all samples measured. If each of the 24 individual PAH was assigned a concentration equivalent to the method detection limit, which is within the range of 2–3 ng/g, then the ΣPAH concentration (sum of 24 individual PAH) would range from 48 to 72 ng/g, which is at least 83–125 times lower that the US EPA criteria of 6000 ng/g. Additional fish studies were conducted later by the RMP in 1997, 2000, and 2003 but fish PAH concentrations were not measured because these compounds were not deemed an issue from a consumptive standpoint. The below method detection limit results for PAH in San Francisco Bay fish are to be expected since almost all fish have an inducible enzyme that metabolizes PAH.

Shellfish such as oysters, mussels, and clams have been regularly monitored in the Bay since 1991. Bay shellfish data are generally not used to determine human consumption and risk assessment, since these monitored shellfish are generally transplanted into the Bay (except oysters, which are resident species), maintained in cages for a limited period (90–100 days), and are not consumed by humans (at least not that we are aware of). Bay shellfish ΣPAH concentrations on a wet weight basis (when available) were compared to the US EPA criterion of 6000 ng/g. RMP bivalve samples collected from 1995 to 2001 showed the following ΣPAH concentration ranges: oysters 14–352 ng/g, mussels 4–110 ng/g, and clams 5–84 ng/g. For all shellfish as a group, their ΣPAH concentrations were 17 to 1500 times lower that the US EPA criterion of 6000 ng/g. Therefore, based on the RMP's fish and shellfish data, it appears that humans that consume PAH contaminated Bay fish and shellfish are at low risk for adverse health effects.

RMP data from 1993–2001 were previously used to assess attainment of the CTR numerical (human health based) PAH water quality criteria (Greenfield and Davis, 2005). Of the 25 individual PAH, which are routinely monitored in the Bay by the RMP, only 12 have established CTR water quality criteria. Of those 12 individual PAH, only five of them occasionally exceeded criteria during the period of 1993–2001 including benzo[*b*]-fluoranthene (5 exceedances), indeno[1,2,3-*c,d*]pyrene (4 exceedances), benz[*a*]anthracene (3 exceedances), benzo[*a*]-pyrene (2 exceedances), and benzo[*k*]fluoranthene (1 exceedance). These PAH, which are HPAH that contain 4–6 aromatic rings in their structure, are derived primarily from high-temperature combustion processes (Neff, 1979).

8. Modeling PAH fate and bay recovery

Models are useful tools for evaluating the loading and long-term fate of chemical contaminants such as PAH. Greenfield and Davis (2005) developed a PAH mass budget model to simulate PAH cycling in the Bay. The model treated the Bay as a single box with interacting Bay water and sediment compartments, and it explicitly incorporated PAH loading from various sources, volatilization losses to the atmosphere, losses due to outflow to the open ocean, degradation losses in water and sediments, and losses due to burial in bedded sediments. Greenfield and Davis (2005) found that for all PAH, the predominant loss pathway was degradation in sediment, which equaled ~80–90% of the total loss (Fig. 6). For naphthalene, phenanthrene, and

fluoranthene, which are 2–4 ring LPAH, volatilization equaled about 10% of total loss. For benzo[*b*]fluoranthene, dibenz[*a,h*]anthracene, and benzo[*g,h,i*]perylene, which are 5–6 ring HPAH, there was almost no loss through volatilization and ~10% of total loss from outflow. Uncertainty analysis showed that there was a high degree of influence and uncertainty for PAH degradation rates used in the model. Greenfield and Davis (2005) suggested that improved estimates for degradation would significantly improve the predictive ability of their PAH model.

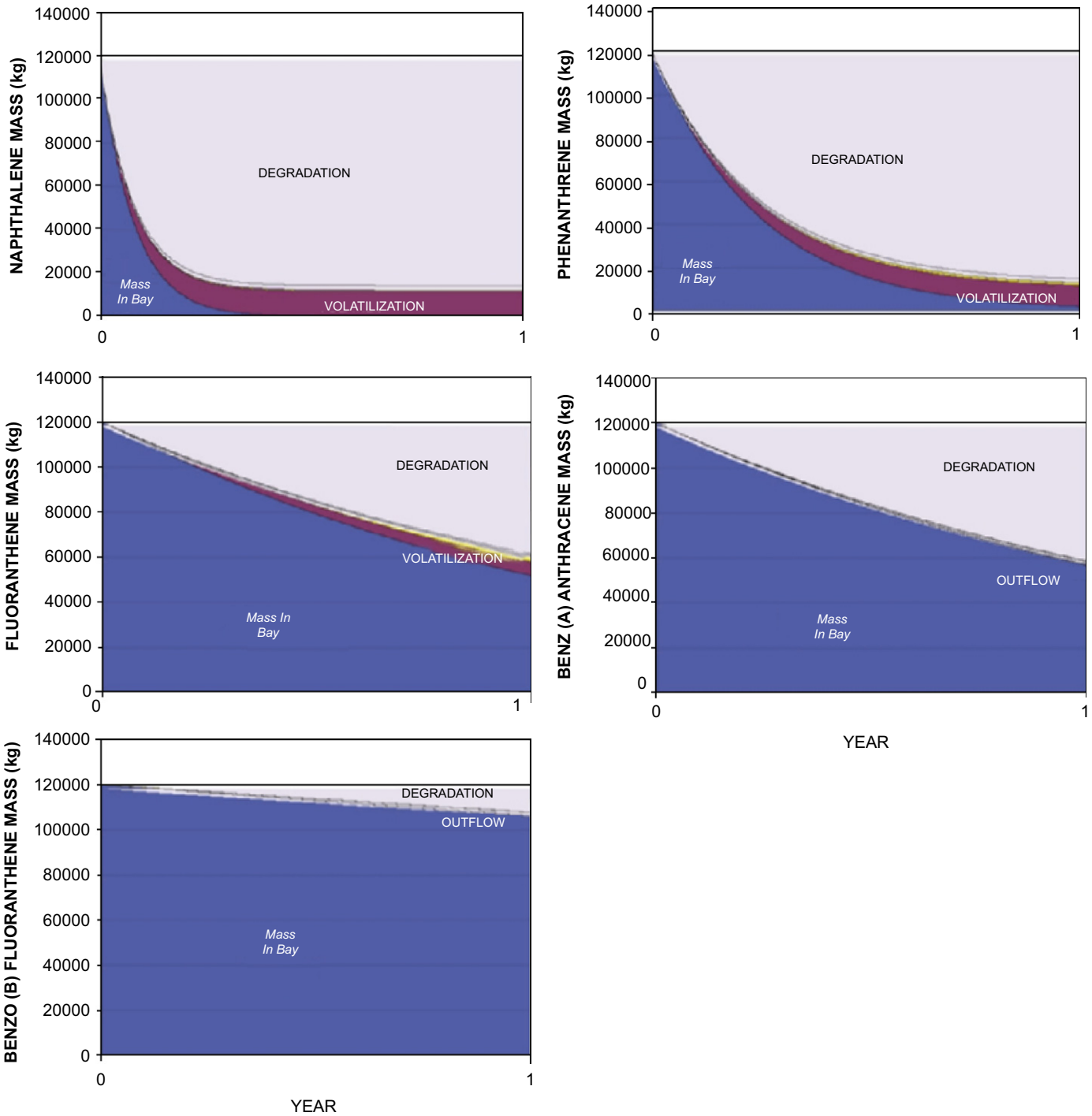

Fig. 6. Predicted losses from the Bay through different pathways for five different PAH compounds over a 1-yr period. The major loss pathways include degradation, volatilization to the atmosphere, outflow to the Pacific Ocean, and sediment burial; assumes no external PAH load and an initial PAH starting mass of 120,000 kg (Greenfield and Davis, 2005). For instance, given an initial starting mass of 120,000 kg for an individual PAH and no external loading, the estimated time required for loss of one-half of the initial starting mass in the Bay is 21 days for naphthalene (2 rings), 63 days for phenanthrene (3 rings), 302 days for fluoranthene (4 rings), and 5.6 yr for benzo[*b*]fluoranthene (5 rings). Figure courtesy of Ben Greenfield (San Francisco Estuary Institute).

Greenfield and Davis (2005) further evaluated the long-term recovery of the Bay under different PAH mass loading scenarios. For example, given an initial starting mass of 120,000 kg for an individual PAH and no external loading, they found that the estimated time required for loss of one-half of the initial starting mass in the Bay was 21 days for naphthalene (2 rings), 63 days for phenanthrene (3 rings), 302 days for fluoranthene (4 rings), and 5.6 yr for benzo[*b*]fluoranthene (5 rings). When the external loading rate was set at 10,000 kg/yr, which is the current estimated PAH loading rate, the long-term steady-state mass increased as PAH size increased. For instance, the total mass lost for naphthalene was >99% of its initial mass, but for the 5–6 ring HPAH, it was only 34% of their initial mass. Greenfield and Davis (2005) concluded that both of these loading scenarios indicated relatively rapid loss of LPAH in comparison to HPAH, which suggested that LPAH would respond more rapidly to management actions that reduce PAH loading.

The one-box model applied by Greenfield and Davis (2005) predicted the long-term fate of PAH in the Bay based on a Bay-wide parameterization of important physical and hydrographical characteristics (e.g., sediment dynamics, depth of active sediment layer, and hydraulic residence times). The RMP in cooperation with the USGS is currently developing a multi-box model to improve the spatial resolution of the PAH one-box model developed by Greenfield and Davis (2005). Overall, models such as these are a valuable tool for understanding contaminant fate processes and making recovery predictions for contaminants.

9. Critical data gaps

Bedded sediments in some areas of the Bay are eroding (Jaffe et al., 1998; Foxgrover et al., 2004). For instance, in South San Francisco Bay during the period from 1956 to 1983, sediment loss approached 3 million m^3/yr (Foxgrover et al., 2004), while in San Pablo Bay between 1951 and 1983, approximately 7 million m^3 of sediment were eroded (Jaffe et al., 1998). Therefore, it is quite possible that previously buried (historic) PAH could be remobilizing by erosion and then dispersed by tidal activity back into the water column as components of resuspended sediments. Tides are responsible for most of the mixing that occurs in the Bay, and tidal dispersion has been reported as the key mechanism for moving materials (Cheng and Smith, 1985). The extent of erosion in the Bay is not well understood, and PAH resuspension from bedded sediments has not been demonstrated.

Soot formed by combustion processes might play a major role in PAH cycling and bioavailability in the Bay. It has also been suggested that factors more complex than simple equilibrium partitioning of PAH into sediment-associated organic carbon (OC) may control PAH concentrations in sediments (McGroddy and Farrington, 1995; McGroddy et al., 1996; Maruya et al., 1997). In their Bay study, Maruya et al. (1997) reported that variations in the partitioning of PAH between sediment and their porewaters along an intertidal gradient and between wet and dry seasons were attributed to the soot content of sediment. Activity coefficients of the PAH were generally lower in soot particles, resulting in higher retention of PAH in soot particles and lower than expected PAH concentrations in porewaters. Maruya et al. (1997) further showed that the presence of soot and combustion-derived PAHs, together with substrate heterogeneity, invalidated or limited the utility of the simple sediment–water equilibrium partitioning models that are used for accurate prediction of bioavailable PAH concentrations. This observation is very important in light of recent efforts to develop sediment quality criteria based on current models of the sediment-water equilibrium partitioning of specific toxic compounds. Quantifying the magnitude of this effect will be important for further understanding the extent of PAH bioavailability in the Bay. Future modeling efforts should also take into careful consideration the role of soot carbon in PAH bioavailability and assimilation into sensitive Bay fauna.

10. Summary and conclusions

PAH are widespread contaminants in San Francisco Bay water, sediments, and biota. Analysis of Bay water, sediment, and mussel PAH concentration data showed that there were very few significantly ($P<0.05$) increasing or decreasing temporal trends in ΣPAH concentrations in the Bay during the period 1993–2001. Wet and dry season input of PAH did not show any major influence on water ΣPAH concentrations over the same period.

Storm water runoff is estimated to be the most important transport pathway for PAH into the Bay (~51% of the total maximum PAH loading level). Atmospheric deposition, which was believed to be the major PAH transport pathway into the Bay since PAH are generally derived from combustion processes, is only a minor (~8% of the total maximum PAH loading level) transport pathway for PAH entering into the Bay. Gains in PAH loading reduction to the Bay from storm water runoff could likely be achieved through the implementation of Best Management Practices at the watershed scale that are designed to cleanup and control spilled engine oil and soot deposits on street, highway, parking lot, and gas station surfaces to minimize their potential input into storm water systems. However, additional measurements of PAH loading from various transport pathways need to be made so that controllable sources can be targeted for management.

Modeling results showed that the predominant loss pathway for PAH in the Bay was degradation in sediment, which equaled ~80–90% of the total loss in the Bay. Other loss pathways included volatilization and outflow through the Golden Gate. Uncertainty analysis showed there was a high degree of influence and uncertainty for PAH degradation rates used in the one-box model and improved estimates for degradation would significantly improve the

predictive ability for PAH modeling. The one-box model was also used to predict the long-term fate of PAH in the Bay based on a Bay-wide parameterization of important physical and hydrographical characteristics. The model predicted that unless the external loading levels of PAH are controlled, the Bay is not expected to recover rapidly. LPAH are expected to respond (decrease in concentration) more quickly to changes in water quality management than the HPAH.

The PAH sediment quality threshold of 1000 ng/g suggested by Johnson et al. (2002) should be evaluated more carefully as a potential management screening tool for protecting estuarine fish against adverse health effects. For the San Francisco Bay, 11 of the 26 sediment sampling stations exceeded the threshold over 50% of the time. The sediment quality threshold was more frequently exceeded in Bay sediments than the ERL, which is used primarily to protect benthic invertebrates, through the period 1993–2001, while the CTR water quality standard for individual PAH, which is used to protect human health, was rarely exceeded. Since the sediment quality threshold was developed in Puget Sound using English sole, more investigations into effects of PAH on other fish species is warranted. Not all species of fish respond to contamination in the same manner and species-to-species differences are to be expected. Applying the best screening tool for protecting fish against adverse health effects caused by chemical pollutant exposure is extremely important, given the recent reports that fish populations in the Bay and its Delta are continuing to decline.

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