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Polycyclic aromatic hydrocarbons (PAHs) in livers of California sea otters

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Abstract

Concentrations of 16 polycyclic aromatic hydrocarbons (PAHs) were measured in livers of 81 adult female sea otters collected along the California coast in 1992–2002. Concentrations of ∑PAHs in livers of sea otters were in the range of 588–17 400 ng/g lipid wt (mean: 3880 ng/g, lipid wt). On a wet weight basis, the concentrations ranged from 17 to 1430 ng/g (mean: 146 ng/g). Overall, di- and tri-cyclic aromatic hydrocarbons, namely, naphthalene, fluorene, phenanthrene/anthracene, and acenaphthylene, were the predominant compounds found in the livers. Although petroleum-related sources appear to be the major contributors to PAH exposure in sea otters, exposure sources varied by geographical sub-regions. Dibenz[*a*,*h*]anthracene was found to comprise a significant proportion of the ∑PAH concentrations in sea otters from the northern sub-region of the study area. No significant difference existed in the concentrations of ∑PAHs among sea otters that died from infectious diseases, emaciation, and noninfectious causes. Concentrations of ∑PAHs in livers of sea otters decreased significantly from 1992 to 2002. Because of the rapid metabolism of PAHs in marine mammals such as sea otters, further studies examining the association of PAHs with health effects should determine hydroxylated metabolites in livers.

Keywords: PAHs; Marine mammal; Sea otter; California coast; Benzo[*a*]pyrene

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental contaminants found in air, water, sediment, and soil. The United States Environmental Protection Agency (USEPA) lists 16 PAHs as priority environmental pollutants. PAHs are derived from both natural (e.g., forest fires, natural petroleum seeps) and anthropogenic sources (e.g., combustion of fossil fuels, use of oil for cooking and heating, coal burning). Studies have shown that PAHs with four or more rings can induce dioxin-like activity and weak estrogenic responses (Villeneuve et al., 2002). Additionally, PAHs have been shown to be carcinogenic to humans (Menzie et al., 1992).

Although studies have reported the occurrence of PAHs in marine benthic invertebrates such as mussels and clams (Meador et al., 1995), there is a general lack of information on accumulation of PAHs in higher trophic-level predators such as marine mammals (Hellou et al., 1991). Marine mammals are exposed to PAHs through the ingestion of contaminated prey species, particularly benthic invertebrates. Because many higher trophic-level aquatic organisms can metabolize PAHs, it is generally assumed that biomagnification in foodwebs is insignificant (Nakata et al., 2003). Nevertheless, a few studies have reported the occurrence of PAHs in certain species of marine mammals (Hellou et al., 1991; Law and Whinnett, 1992). Earlier studies have analyzed muscle or blubber tissues of marine mammals for the determination of PAHs. For fish, bile samples were tested for monitoring of PAH exposures (Kammann, 2007; Johnson-Restrepo et al., 2008). Liver tissue was analyzed to monitor PAH exposures in coastal

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birds (Troisi et al., 2006). Liver tissue is expected to serve as a suitable matrix for the determination of recent exposure to PAHs. In this study, liver samples from California sea otters (*Enhydra lutris nereis*) were analyzed to determine PAH concentrations.

The California sea otter population, a geographically isolated subspecies, inhabits a ~250 mile stretch of the central California coast, from just south of Point Conception to Half Moon Bay in the north (Fig. 1). The coast inhabited by California sea otter has been contaminated by both natural and anthropogenic sources of PAHs (Pereira et al., 1999; Seruto et al., 2005; Oros et al., 2007). The major benthic prey species of sea otters such as mussels, clams, and crabs have been reported to contain notable levels of PAHs (Lauenstein, 1995; Pereira et al., 1996; Oros and Ross, 2005). Furthermore, because sea otters lack blubber, they consume 20–37% of their body weight daily, in order to maintain the high metabolic rate needed to keep the internal body temperature at 100 °F (Rotterman and Simon-Jackson, 1988). The combination of the notable contamination by PAHs in prey items and the high food consumption rates renders sea otters particularly vulnerable to high PAH exposures. PAHs have been shown to adversely affect the health of marine animals along the California coast (Roy et al., 2003; Brown and Steinert, 2004; Seruto et al., 2005). In an effort to understand the role of contaminants on the health of sea otters, our earlier studies determined concentrations of trace metals, perfluorinated compounds, polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and organochlorine pesticides in sea otters from the central California coast (Nakata et al., 1998; Kannan et al., 1998, 2004, 2006a,b, 2007; Perrotta, 2005). In this study, concentrations of 16 USEPA priority PAHs were measured in the livers of California sea otters, to compare exposure levels among animals that died from infectious diseases, emaciation, and noninfectious causes.

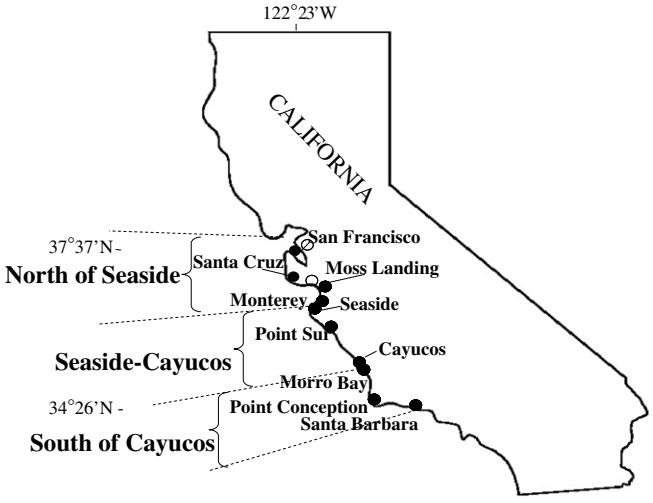

Fig. 1. Map of California showing locations of sea otter sampling, grouped by sub-regions.

2. Materials and methods

2.1. Samples

Livers from 81 adult female sea otters found freshly dead along the central California coast between 1992 and 2002 were analyzed. Samples were chosen based on sex and age to eliminate these as confounding factors. Additionally, female sea otters were chosen, because their more localized travel patterns make them better indicators of local sources of pollution. Postmortem examinations were performed at the National Wildlife Health Center in Madison, Wisconsin, for the determination of cause of death.

Cause of death was classified into one of three categories: emaciation ($n = 27$), infectious ($n = 27$), or noninfectious ($n = 27$). We grouped animals that died from infectious diseases into the infectious group, and those that died from trauma into the noninfectious group. On the basis of body/nutritional condition at the time of necropsy, emaciated otters were grouped into a separate category. The animals were emaciated probably due to inadequate food intake. The subclasses in this category were conditions that could have contributed to starvation, such as mating trauma, but these conditions alone were not expected to produce fatal debility.

2.2. Chemical analysis

Liver tissue (~10 g) was homogenized with anhydrous sodium sulfate, spiked with internal standards, chlorobiphenyl congeners #30 and #204 (25 ng), and extracted with mixed solvents of dichloromethane (300 ml) and hexane (100 ml), using a Soxhlet apparatus for 20 h (Kannan et al., 2004). The solvent was reduced (11 ml), and an aliquot (1 ml) was taken for gravimetric determination of fat content. Another aliquot was spiked with 50 ng of naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} and subjected to gel permeation chromatography (GPC) for removal of lipids. The GPC column was packed (380 mm × 22 mm i.d.) with Bio-beads S-X3 (Bio-Rad Laboratories, Hercules, CA, USA). A mixture of 50% hexane in dichloromethane was used as the mobile phase at a flow rate of 3 ml/min. The first 100 ml of the eluate were discarded, and the following 150 ml fraction, which contained the PAHs, was collected. The extract was then passed through a cartridge packed with 0.5 g of silica gel (100–200 mesh; Aldrich, Milwaukee, WI, USA) for cleanup. The sample was concentrated to 500 μl, and then injected into a gas chromatograph–mass spectrometer (GC/MS).

Sample extracts (2 μl) were injected into a Hewlett-Packard 6890 gas chromatograph interfaced with a Hewlett-Packard 5973 mass spectrometer. Injections were made in splitless mode, and PAHs were separated on a 30-m ZB-5 (5% diphenyl/dimethylpolysiloxane) capillary column (250 μm i.d. × 0.25 μm film thickness). The oven temperature program was set to 100° C for 1 min, 3 °C/min to 200 °C, hold 3 min, 2 °C/min to 290 °C, hold for 5 min.

The inlet and interface temperatures were set to 250 °C and 300 °C, respectively. Quantification ions were monitored for each compound at $m/z = 128$ for naphthalene, 136 for naphthalene-d_8, 152 for acenaphthylene, 153 for acenaphthene, 162 for acenaphthene-d_{10}, 166 for fluorene, 178 for phenanthrene and anthracene, 188 for phenanthrene-d_{10}, 202 for fluoranthene and pyrene, 228 for benzo[*a*]anthracene and chrysene, 240 for chrysene-d_{12}, 252 for benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, and benzo[*a*]pyrene, 262 for perylene-d_{12}, 276 for benzo[*g*,*h*,*i*]-perylene and indeno[1,2,3-*cd*]pyrene, and 278 for dibenz[*a*,*h*]anthracene.

Deuterated PAHs spiked into the samples showed acceptable recoveries ranging from 72% to 125%. Reported concentrations were not corrected for the recoveries of the internal standards. The detection limit for individual PAHs in samples ranged from 0.5 to 1 ng/g, on a wet weight basis. Concentrations below the detection limit were assigned a value of zero for the calculation of mean and for statistical analysis. Phenanthrene and anthracene co-eluted in our analysis as did benzo[*b*]fluoranthene and benzo[*k*]fluoranthene; therefore, the concentrations for each pair are reported as the sum of the two compounds. Quantification of individual PAHs was based on external calibration standards containing known concentrations of 16 priority PAHs. The term ∑PAHs refers to the sum of 16 priority PAHs.

3. Results and discussion

3.1. Concentrations and profiles

PAHs were found in all of the 81 liver samples analyzed. Overall mean concentration of ∑PAHs ranged from 17 to 1430 ng/g, wet wt (mean: 146; median: 94.3). On a lipid weight basis, ∑PAH concentrations ranged from 588 to 17400 ng/g, lipid wt (mean: 3880; median: 2960). Concentrations of ∑PAHs were significantly correlated with lipid content in the livers (Fig. 2). The highest ∑PAH concentration, on a wet weight basis, was found in an emaciated otter collected south of Cayucos in 1993. This value was seven times the standard deviation of the mean and is therefore considered to be an outlier (Grubb's test; $p < 0.05$). This value was removed from further analysis, unless specified otherwise.

Reports of the occurrence of PAHs in marine mammals are meager thus far. A few earlier studies that measured PAHs in marine mammals reported the values as chrysene equivalents in blubber tissues (Hellou et al., 1991; Law and Whinnett, 1992); therefore, direct comparison of our data with the data from those earlier studies is not possible. A study of PAHs in beluga whales from the St. Lawrence Estuary in Canada reported concentrations of 16 priority PAHs in livers to range from 111 to 303 ng/g, wet wt (Beland et al., 1991); the concentrations in the beluga whale livers were similar to the concentrations that we have found in the sea otter livers. Some of the highest concentrations of PAHs (sum of 14 PAHs), ranging from 1600 to 36200 ng/g, wet wt, were reported in blubber of fin whales and striped dolphins from the Mediterranean Sea, collected during 1993–1996 (Marsili et al., 2001).

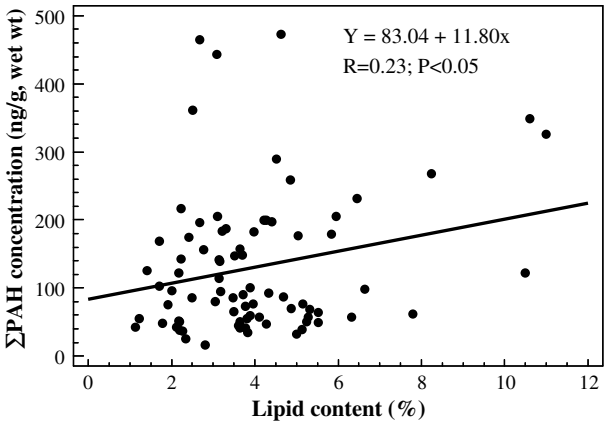

Fig. 2. Relationship between ∑PAH concentration and lipid content in the livers of California sea otters. The outlier with the highest ∑PAH concentration has been removed.

Several studies have reported the occurrence of PAHs in water, sediment, and benthic invertebrates from the California coast (Table 1). Occurrence of PAHs in the livers of sea otters is supported by the presence of these contaminants in major prey species. The range of ∑PAH concentrations found in the livers of sea otters was similar to that reported for several species of benthic invertebrates collected from the California coast during 1992–2001 (Table 1).

Naphthalene was the major PAH in the sea otter livers accounting for, on average, 21% of the ∑PAH concentrations (Fig. 3A). Naphthalene was followed by (ordered by decreasing concentration) dibenz[*a*,*h*]anthracene (18%), fluorene (17%), phenanthrene + anthracene (14%), acenaphthylene (12%), acenaphthene (7.8%), fluoranthene (7.3%), and pyrene (2%). Benzo[*a*]pyrene, benzo[*g*,*h*,*i*]perylene, and indeno[1,2,3-*cd*]pyrene were not detected in any of the samples. Overall, di- and tri-cyclic PAHs accounted for 72% of the ∑PAH concentrations in sea otters. The predominance of di- and tri-cyclic PAHs over tetra- and penta-cyclic PAHs suggests petrogenic sources. A natural oil seep is reported to have been occurring off the coast of Santa Barbara (Coal Oil Point) for thousands of years (Seruto et al., 2005). In contrast to urban sources of PAHs, low-molecular-weight-PAHs are the primary constituents of natural petroleum seeps (Seruto et al., 2005). Sediments collected near a natural oil seep from Coal Oil Point contained predominantly acenaphthene, acenaphthylene, fluorene, fluoranthene, and phenanthrene (Seruto et al., 2005). However, the proportions of naphthalene and dibenz[*a*,*h*]anthracene in the natural oil seep near Coal Oil Point were considerably lower than the proportions that we found in sea otter livers. This discrepancy suggests the presence of additional sources of PAH contamination along the central California coast. Overall, PAH profiles in sea otter tissues suggest sources arising from petroleum sources. The composition of ∑PAHs did not differ

Table 1
Concentrations of PAHs in sea otter livers compared with those reported for water, sediment, mussels, oysters, clams, and crabs from the California coast

Location	Year	Type of sample	Concentration	Remarks	Reference
Central California	1992–2002	Sea otter liver	66–5700 (584)[a] ng/g dry wt	Dry wt converted[b]	This study
California coast	1992	Mussels and oysters	64–4800 ng/g dry wt	24 PAHs	Lauenstein (1995)
San Francisco Estuary	1993–2001	Mussels	21–1090 (175) ng/g dry wt	25 PAHs	Oros and Ross (2005)
	1993–2001	Oysters	184–6900 (678) ng/g dry wt	25 PAHs	Oros and Ross (2005)
	1993–2001	Clams	78–720 (323) ng/g dry wt	25 PAHs	Oros and Ross (2005)
San Joaquin Valley	1992	Clam	70–370 ng/g dry wt	21 PAHs; dry wt converted[b]	Pereira et al. (1996)
Central and South California coast	2000–2001	Sand crab	20–2060 ng/g dry wt	25 PAHs	Dugan et al. (2005)
San Joaquin Valley	1992	Water	1.2–22 ng/l	21 PAHs; dissolved phase only	Pereira et al. (1996)
San Francisco Bay	1993–2001	Water	7–120 ng/l	25 PAHs	Oros et al. (2007)
San Francisco Estuary	1993–2001	Sediment	31–230 μg/g TOC	25 PAHs	Oros and Ross (2004)
Moss Landing	1985–1987	Sediment	1400–3000 ng/g dry wt		Rice et al. (1993)
Elkhorn Slough	1985–1987	Sediment	150–375 ng/g dry wt		Rice et al. (1993)

[a] Values in parentheses are means.
[b] Dry weight conversion is based on a moisture content of 75% in liver tissues.

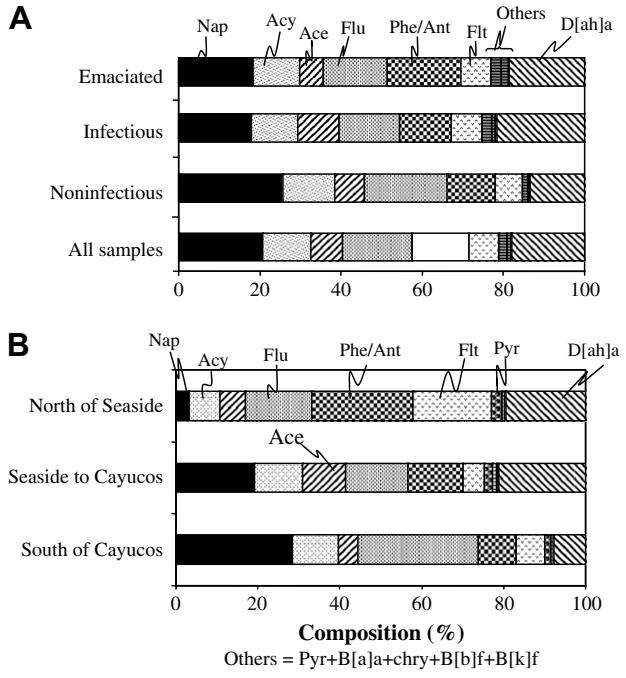

Fig. 3. Percent contributions of individual PAHs to ∑PAH concentrations in the livers of sea otters. (A) For all samples, and for each of three mortality groups. (B) For the three geographical sub-regions of the sea otter range. Values below the detection limit were assigned zero. (Nap = naphthalene; Acy = acenaphthylene; Ace = acenaphthene; Flu = fluorene; Phe/Ant = phenanthrene/anthracene; Flt = fluoranthene; Pyr = pyrene; B[*a*]a = benzo[*a*]anthracene; Chry = chrysene; B[*b*]f = benzo[*b*]fluoranthene; B[*k*]f = benzo[*k*]fluoranthene; D[*ah*]a = dibenz[*a*,*h*]-anthracene).

significantly between the otters that died from infectious diseases and those that died from noninfectious causes. However, when otters were grouped based on the stranding location into three geographical segments as north of Seaside, Seaside to Cayucos, and south of Cayucos, PAH profiles were found to differ significantly among the three segments (Fig. 3B). The three categories were chosen based on past studies, natural division of the coastline, and the availability of data for each sub-region. Sea otters collected south of Cayucos contained a significantly higher percentage (28%) of naphthalene than did the sea otters collected north of Seaside (3%). On the other hand, otters collected north of Seaside contained a significantly higher proportion (20%) of dibenz[*a*,*h*]anthracene than did the otters collected south of Cayucos (7.7%). Similarly, the proportion of phenanthrene and anthracene was threefold higher in otters collected north of Seaside than in the otters collected south of Cayucos. The differences in PAH profiles among the three sub-regions suggest the existence of multiple sources that varied by location. The northern range of the sea otter habitat, especially near Monterey Bay, is influenced by urban sources of PAHs originating primarily from combustion-related emissions. The southern range near Santa Barbara, where the Coal Oil Point natural petroleum seep is sited, is influenced by petroleum-related inputs of PAHs. The PAH distribution in otters collected between Seaside and Cayucos was intermediate between the northern and southern distributions (Fig. 3B).

3.2. Comparison of PAHs among mortality categories, and locations, and over time

Mean concentrations of ∑PAHs in otters from the infectious, emaciated, and noninfectious categories were 4100, 3600, and 3900 ng/g, lipid wt, respectively; the corre-

sponding concentrations on a wet weight basis were 136, 108, and 194 ng/g (Fig. 4). ∑PAH concentrations did not differ significantly among the three mortality categories (Kruskall–Wallis test; $p > 0.05$). The lack of difference in ∑PAH concentrations among the three mortality categories can be explained by the rapid metabolism of PAHs by sea otters. The half-lives of PAHs in marine invertebrates are on the order of a few days to a few weeks (Meador et al., 1995), and are thought to be shorter in sea otters, at a higher trophic level. Fish and birds exposed to PAHs contained concentrations of monohydroxylated metabolites of PAHs that are higher than the concentrations of the parent compounds (Troisi et al., 2006; Johnson-Restrepo et al., 2008). Although un-metabolized PAHs can have toxic effects, the ability of reactive metabolites, such as hydroxides, epoxides, and dihydrodiols of some PAHs, to bind to cellular proteins and DNA can produce biochemical disruptions and cell damage leading to mutations, developmental malformations, tumors, and cancers (Varanasi et al., 1989). Although the concentrations of PAHs that we measured in liver tissues of sea otters suggest recent exposures to PAHs, further studies examining the association of PAHs with health effects should determine hydroxylated metabolites and protein/DNA adducts of PAHs in tissues.

Mean concentrations of ∑PAHs in sea otters in the north of Seaside, Seaside to Cayucos, and south of Cayucos categories were 3700, 3800, and 4000 ng/g, lipid wt, respectively; the corresponding values on a wet weight basis were 130, 136, and 170 ng/g. Although differences existed in the profiles of individual PAHs among the three sub-regions of the coastline, as discussed above, these differences in mean concentrations were not statistically significant (Fig. 5). This suggests that contamination by PAHs is widespread along the central California coast.

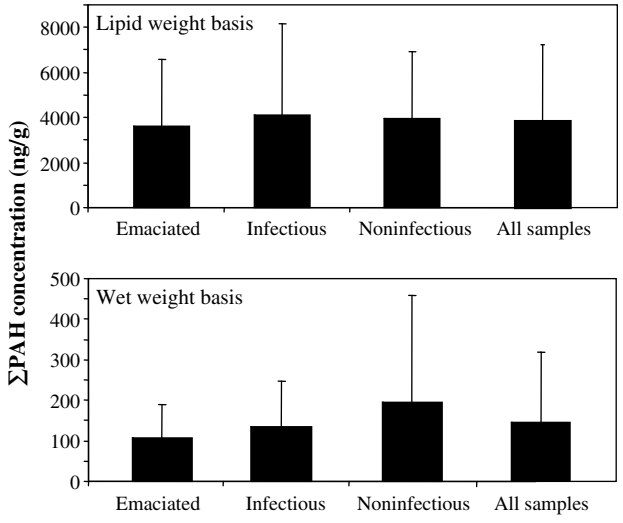

Fig. 4. Mean (±SD) concentrations of ∑PAHs in the livers of sea otters from California. Values for all of the samples and for the three mortality groups are presented. Values below the detection limit were assigned zero for calculation of mean and SD.

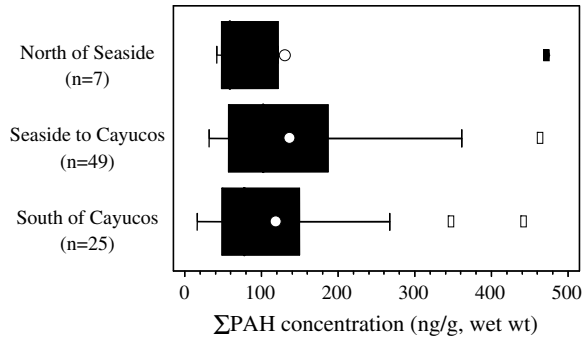

Fig. 5. Box-and-whisker plots of ∑PAH concentrations in sea otters stratified by three geographical sub-regions of the sea otter range; one outlier value for south of Cayucos (1430 ng/g) was removed. White solid line is the median and white circle is the mean; lower and upper limits of the box represent 25th and 75th percentiles; the whiskers extend to the last observation within 1.5 times the interquartile range. The squares are far outside points.

Nevertheless, the sources of PAH contamination do evidently vary, depending on the location.

Because the adult female sea otter samples analyzed in this study were collected from 1992 to 2002, temporal trends in the concentrations of PAHs could be examined for that decade. Concentrations of ∑PAHs in sea otters declined significantly ($p < 0.05$) from 1992 to 2002 (Fig. 6). In particular, concentrations of ∑PAHs were significantly lower in otters collected after 1998. This suggests a temporal decline in the emission of PAHs along the California coast. Anthropogenic sources and emissions of PAHs along the southern California coast have decreased steadily since the 1970s (Schiff et al., 2000). However, studies from urban areas, such as the San Francisco Estuary, have shown an absence of any significant decrease or increase in the concentrations of PAHs in water, bivalves, and sediment collected during 1993–2001 (Oros and Ross, 2004, 2005; Ross and Oros, 2004; Oros et al., 2007).

In summary, our study shows the presence of PAHs in livers of sea otters at concentrations on the order of several tens to few hundreds of ng/g on a wet weight basis.

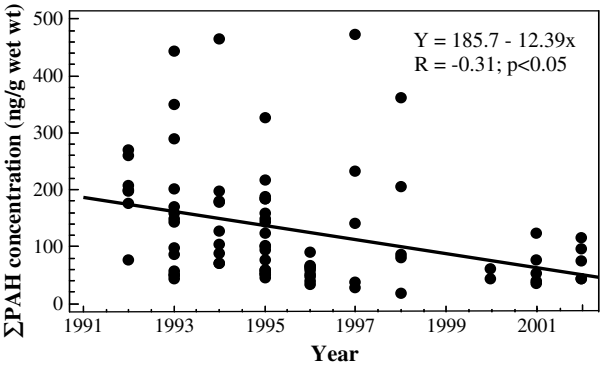

Fig. 6. Temporal trends in ∑PAH concentrations in the livers of California sea otters from 1992 to 2002. The outlier with the highest PAH concentration (sample from 1993) has been removed.

PAH concentrations are significantly correlated with lipid content in the livers of sea otters. Naphthalene, fluorene, phenanthrene/anthracene, and acenaphthylene were the predominant compounds found. In addition, dibenz[*a*,*h*]anthracene was found at a significant proportion in the ∑PAHs. Petroleum appears to be the major source of PAHs along the central California coast. Concentrations of ∑PAHs in sea otter livers declined significantly from 1992 to 2002. No significant association was found between ∑PAH concentration and affliction from infectious disease in sea otters. Although occurrence of PAHs in livers suggests ongoing exposures, it should be noted that PAHs are metabolized relatively rapidly in mammals. Therefore, future studies examining association of PAHs with health effects should measure hydroxylated metabolites and protein/DNA adducts.

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