REGIONAL MONITORING PROGRAM FOR WATER QUALITY IN THE SAN FRANCISCO ESTUARY

Toxic Potential of PAHs in San Francisco Estuary Sediments

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) derived from unburned petroleum products (petrogenic), and combustion of fossil fuels (pyrogenic) accumulate in marine sediments because of their strong association with particles. Several PAHs (e.g. benz[*a*]anthracene, benz[*b*]fluoranthene, benz[*k*]fluoranthene, benzo[*a*]pyrene, chrysene, dibenz[*a,h*]anthracene, and indeno[1,2,3-*cd*]pyrene) have mutagenic and genotoxic potential (Arcos and Argus, 1975; WHO, 1989), and the long-term toxicity and persistence of PAHs raises concerns about their potential effects on marine biota (Peterson *et al.*, 2003). This is of special interest in highly urbanized areas like the San Francisco Estuary where there can be chronic and uncontrolled PAH inputs from multiple sources. The aim of this study is to evaluate the potential for biological effects in various species due to PAH exposure.

Methods

Sediment samples (top 5 cm) collected by the Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP) between 1993 and 2003 were evaluated for potential PAH toxicity (Figure 1) using several different approaches.

Sediment Quality Guidelines (SQGs)

Concentrations for 13 PAH compounds (2-methylnaphthalene, acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, fluoranthene, fluorene, naphthalene, phenanthrene, and pyrene) were compared with the U.S. National Oceanographic and Atmospheric Administration (NOAA) marine sediment threshold effects level (TEL) guidelines for the protection of aquatic life (Buchman, 1999).

Dioxin-equivalent Toxicity Factors (TEQs)

Total PAH TEQs were calculated, where possible, for each sample. The 13 individual PAH concentrations were multiplied by their respective fish potency factors (FPFs), as compiled by Barron *et al.* (2004), and the products summed to obtain the total PAH TEQ. FPFs were derived using data on CYP1A induction and aryl hydrocarbon receptor (AhR) binding for different species and tissues.

NOAA - National Marine Fisheries Service (NMFS) Effects Threshold

Total sediment PAH concentrations, the sum of 25 individual target PAH monitored by the RMP, were compared with the effects threshold value of 1000 ng/g suggested by NOAA to protect estuarine bottom-fish (Johnson *et al.*, 2002). Johnson *et al.* (2002) found minimal risk of DNA damage, liver lesions, and impacts on growth and reproduction of English sole (*Pleuronectes vetulus*) at sediment PAH concentrations at or below 1000 ng/g, but at higher levels the risk of PAH-related injury increased substantially.

10-day Amphipod Sediment Bioassays

A subset of RMP sediment samples is used to conduct sediment bioassays. Amphipod (*Eohaustorius estuarius*) mortality in 10-day sediment toxicity tests in relationship to total PAH concentrations was evaluated by binary logistic regression. A sample being considered toxic if there was a significant difference between the laboratory control and test replicates using a separate variance t-test (alpha = 0.01), and the difference between the mean endpoint value (% survival) in the control and the mean endpoint value in the test sample was greater than the 90th percentile minimum significant difference (MSD).

Figure 1

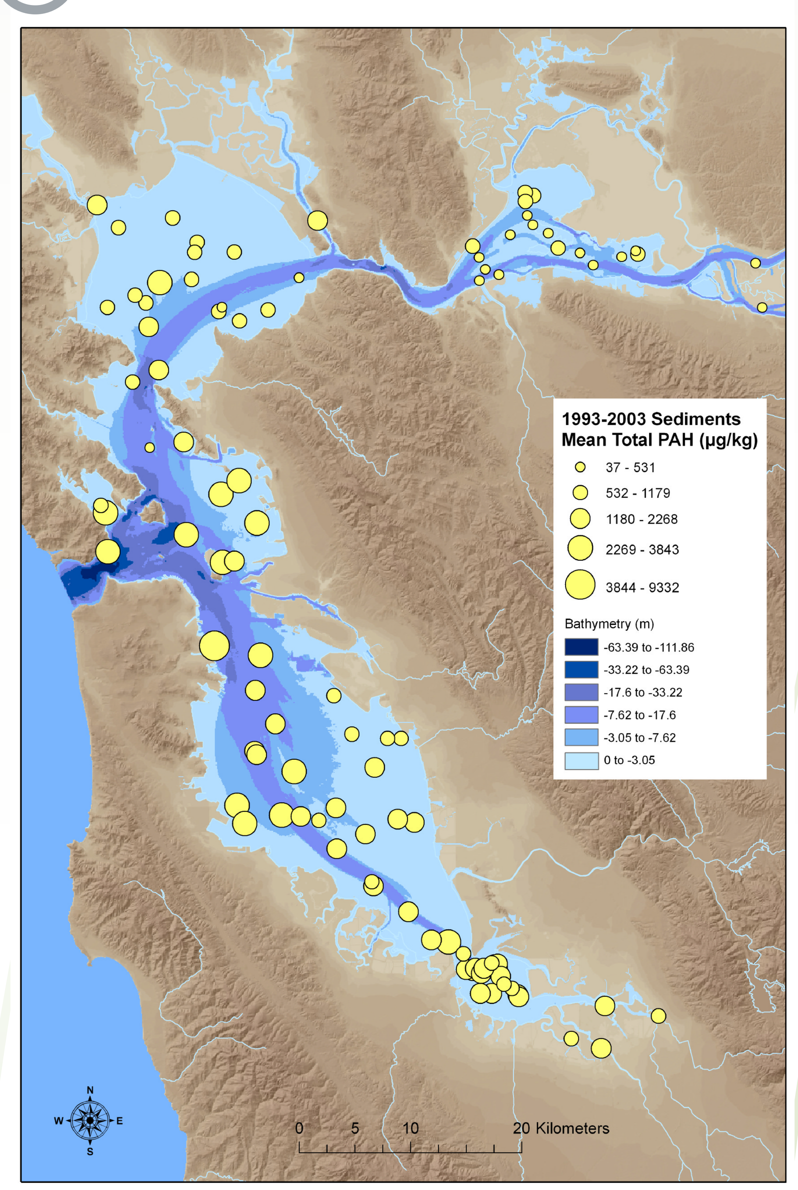

Figure 1. Mean total PAH concentrations (ug/kg dry weight) measured at RMP sediment sampling sites, 1993-2003.

Results

Mean sediment total PAH concentrations vary widely throughout the estuary (Figure 1), and have a highly significant positive relationship with the mean sediment PAH TEQ values (Pearson correlation, $r = 0.978$, $p < 0.0005$, $n = 98$).

Sediment Quality Guidelines (SQGs)

In decreasing order, the most important individual PAHs, based on NOAA marine SQGs, are dibenz[a,h]anthracene whose TEL guideline (6.22 ng/g) is exceeded in 63% (297 of 470) samples, fluoranthene (272 samples > 112.82 ng/g) and pyrene (268 samples > 152.66 ng/g) (Table 1).

Table 1

Table 1. Comparison of individual sediment PAH concentrations with the NOAA marine sediment threshold effects level (TEL) guidelines for the protection of aquatic life (Buchman, 1999).

PAH	TEL Guidelines (ng/g)	Percent of Samples Exceeding TEL Guideline
dibenz[*a,h*]anthracene	6.22	63% (297 of 470 samples)
fluoranthene	112.82	58% (272 samples)
pyrene	152.66	57% (268 samples)
benzo[*a*]pyrene	88.81	54% (255 samples)
acenaphthylene	5.87	54% (254 samples)
benz[*a*]anthracene	74.83	41% (191 samples)
acenaphthene	6.71	38% (178 samples)
phenanthrene	86.68	36% (168 samples)
chrysene	107.77	32% (149 samples)
naphthalene	34.57	22% (102 samples)
anthracene	46.85	17% (80 samples)
fluorene	21.17	7% (35 samples)
2-methylnaphthalene	20.21	7% (31 samples)

Dioxin-equivalent Toxicity Factors (TEQs)

A linear regression analysis of total PAH TEQs against the three most important PAHs yields significant results for dibenz[a,h]anthracene (Figure 2: $p < 0.0005$, $n = 470$, adj-r^2 = 0.763), fluoranthene (Figure 3: $p < 0.0005$, $n = 470$, adj-r^2 = 0.802), and pyrene (Figure 4: $p < 0.0005$, $n = 470$, adj-r^2 = 0.848). Examination reveals that 303 out of 470 sediment samples (64.5%) have TEQ values that are above the no observed effect concentration (NOEC) of 200 pg TEQ/g. Whereas, only 44 out of 470 samples (9.4%) were below the suggested safe value of 20 pg TEQ/g (Eljarrat *et al.*, 2001).

NOAA - National Marine Fisheries Service (NMFS) Effects Threshold

Evaluation indicates that 276 out of 470 sediment samples (59%) had total PAH concentrations above the proposed NOAA effects threshold of 1000 ng/g. This suggests a substantially increased risk of PAH-related damage to bottom-fish in the San Francisco Estuary.

10-day Amphipod Sediment Bioassays

The relationship between 10-day amphipod sediment bioassay results and total PAH concentration measured in RMP sediment samples is shown in Figure 5. Binary logistic regression reveals that amphipod survival was significantly and negatively related to total PAH concentrations (Figure 6; $p < 0.0005$, $n = 251$). The magnitude of the effect (reduced survival) increasing as the probability of toxicity increases. Total PAH concentrations corresponding to a 20, 50, and 80% probability of observing sediment toxicity were approximately 280 ug/kg, 2690 ug/kg, and 5100 ug/kg, respectively.

Figure 2

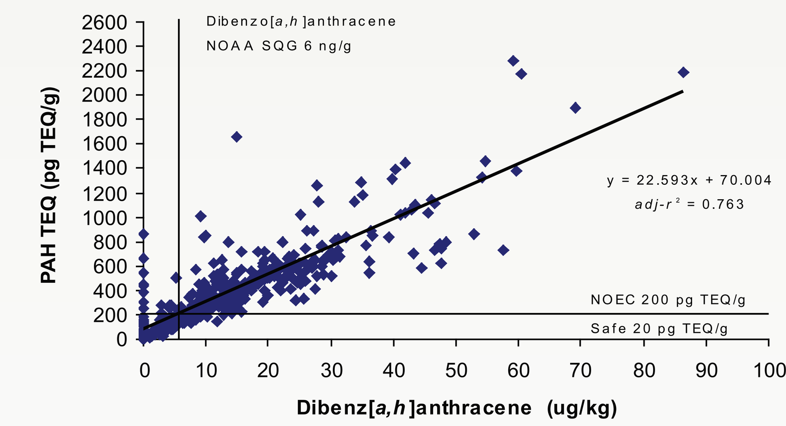

Figure 2. Dioxin-equivalent toxicity of PAHs (PAH TEQs) in RMP sediment samples compared to dibenz[*a,h*]anthracene concentrations, 1993-2003. The safe and NOEC TEQ sediment values, and the NOAA SQG for dibenz[*a,h*]anthracene are indicated.

Figure 3

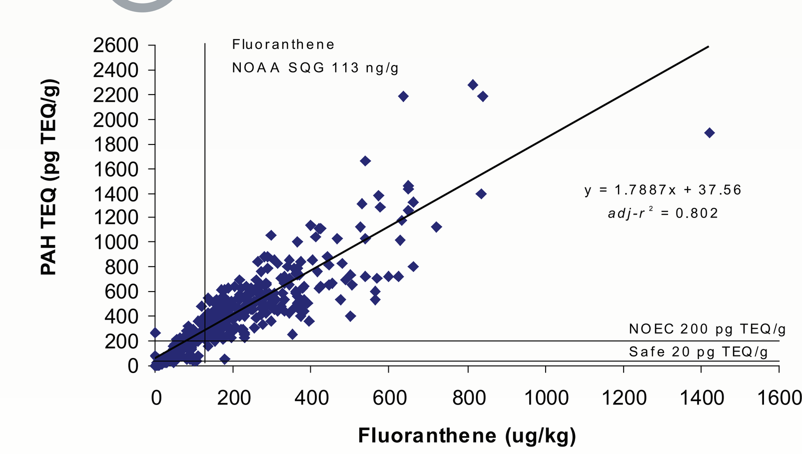

Figure 3. Dioxin-equivalent toxicity of PAHs (PAH TEQs) in RMP sediment samples compared to fluoranthene concentrations, 1993-2003. The safe and NOEC TEQ sediment values, and the NOAA SQG for fluoranthene are indicated.

Figure 4

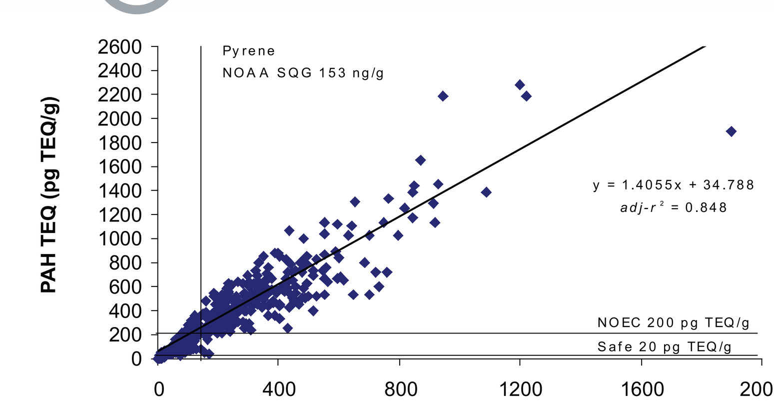

Figure 4. Dioxin-equivalent toxicity of PAHs (PAH TEQs) in RMP sediment samples compared to pyrene concentrations, 1993-2003. The safe and NOEC TEQ sediment values, and the NOAA SQG for pyrene are indicated.

Figure 5

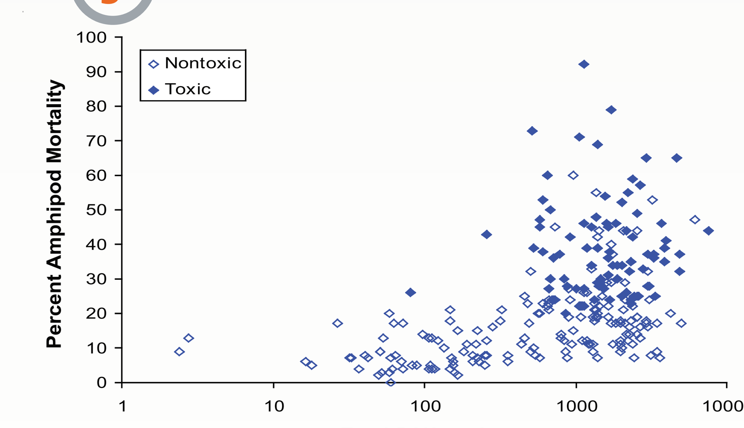

Figure 5. Scatter plot showing results of 10-day amphipod sediment bioassays in relation to total PAH concentrations measured in synoptic sediment samples collected at the same site. Note: logarithmic scale for x-axis.

Figure 6

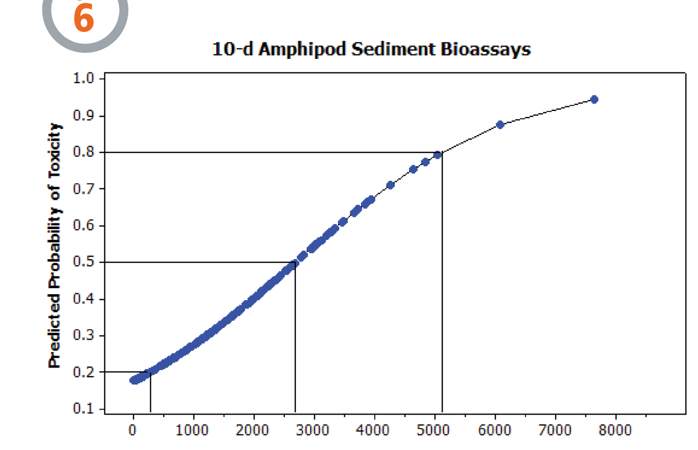

Figure 6. Binary logistic regression model and total PAH concentrations corresponding to a 20, 50, and 80% probability of observing sediment toxicity to amphipods in 10-day toxicity tests (280, 2690, and 5100 ug/kg, respectively).

Conclusions

Based on NOAA marine SQG comparisons for the protection of aquatic life, the most important individual PAHs (dibenz[*a,h*]anthracene, fluoranthene and pyrene) in San Francisco Estuary sediment samples show a potential for chronic toxicity from exposure to PAH. PAH, however, are virtually always found as complex mixtures of covarying compounds; therefore, guidelines for individual PAHs are unlikely to be as appropriate, or useful, as guidelines based on PAH mixtures.SQG comparisons where PAH are expressed as mixtures, such as total PAH TEQs and total PAH concentrations, confirm that exposure to PAH in San Francisco Estuary sediments substantially increase the potential risk of injury and mortality to estuarine species. Together these results show that despite concerns and limitations inherent in the different guidelines, their appropriate use can contribute to a weight of evidence approach when making a determination whether PAH pose relatively low or very high potential for sediment toxicity.

References

Arcos, J.C. and M.G. Argus, 1975. Chemical induction of cancer. Structural basis and biological mechanisms, IIA. Academic Press, New York.

Barron, M.G., R. Heintz, and S.D. Rice. 2004. Relative potency of PAHs and heterocycles as aryl hydrocarbon receptor agonists in fish. *Marine Environmental Research*, 58:95-100.

Buchman, M.F., 1999. NOAA Screening Quick Reference Tables, NOAA HAZMAT Report 99-1, Seattle WA, Coastal Protection and Restoration Division, National Oceanic and Atmospheric Administration, 12 pages.

Eljarrat, E, J. Caixach, J. Rivera, M. De Torres, and A. Ginebreda. 2001. Toxic potency assessment of non- and mono-ortho PCBs, PCDDs, PCDFs, and PAHs in Northwest Mediterranean sediments (Catalonia, Spain). *Environmental Science and Technology,* 35:3589-3594

Johnson, L.L, T.K. Collier, and J.E. Stein. 2002. An analysis in support of sediment quality thresholds for polycyclic aromatic hydrocarbons (PAHs) to protect estuarine fish. *Aquatic Conservation: Marine and Freshwater Ecosystems*, 12:517-538.

Peterson, C.H., S.D. Rice, J.W. Short, D. Esler, J.L. Bodkin, B.E. Ballachey, and D.B. Irons. 2003. Long-term ecosystem response to Exxon Valdez oil spill. *Science*, 302:2082-2086.

WHO, World Health Organization, 1989. IARC Monographs, 46. Lyon, France: International Agency for Research on Cancer, p.41-155.

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