

# Canadian Sediment Quality Guidelines for the Protection of Aquatic Life

# POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

olycyclic aromatic hydrocarbons (PAHs) are a diverse class of organic compounds that contain two or more fused aromatic (benzene) rings that can be toxic to aquatic biota at elevated concentrations. Some PAHs may contain ring structures with fewer than six carbon atoms (e.g., acenaphthylene, acenaphthene, and fluorene). In others, substitution of a carbon atom in the benzene ring by nitrogen, sulphur, or oxygen atoms results in the formation of heterocyclic aromatic compounds (McElroy et al. 1989; Wilson and Jones 1993). In addition, hydrogen atoms on the parent PAH compound be substituted for by alkyl groups may (e.g., 2-methylnaphthalene). The position of alkyl substituents is extremely important in determining the carcinogenicity of a PAH (Neff 1979; Falk-Petersen et al. 1982), and alkylation may slow the rates of microbial mineralization (degradation) of PAHs (Heitkamp and Cerniglia 1987).

Polycyclic aromatic hydrocarbons are commonly classified into one of two groups based on their molecular structure. Low molecular weight (LMW) PAHs have three or fewer aromatic rings, while high molecular weight (HMW) PAHs have four or more rings. Differences in the structure and size of individual PAHs result in substantial variability in the physical and chemical properties of these substances.

Because PAHs have widespread distribution and significant potential for causing adverse biological effects, the Ministers of the Environment and of Health from the federal government of Canada conducted an assessment of PAHs under the Canadian Environmental Protection Act. They concluded that these substances are entering the environment in quantities or concentrations, or under conditions, that are having, or may have, a harmful effect on the environment (CEPA 1985). Significant quantities of PAHs are released into the environment each year from a variety of natural (e.g., forest fires and volcanic explosions) and anthropogenic (e.g., industrial activities, fossil fuel combustion, and waste incineration) sources (Environment Canada 1998). Emissions of PAHs in Canada are almost exclusively atmospheric, and atmospheric deposition is considered to be the main source of PAHs to Canadian aquatic environments (Ringuette et al. 1993).

The fate and behavior of PAHs in aquatic systems is influenced by a number of physical, chemical, and biological processes. While some of these processes, such

as photooxidation, hydrolysis, biotransformation, biodegradation, and mineralization, result in the transformation of PAHs into other substances, other physical processes, such as adsorption, desorption, solubilization, volatilzation, resuspension, and bioaccumulation, are responsible for the cycling of these substances throughout the aquatic environment. The relative importance of each of these processes is dependent on the characteristics of the sediments and on the properties of the individual PAH under consideration. However, considering that within aquatic systems most PAHs tend to be relatively nonvolatile and poorly soluble, PAHs will become incorporated into bottom sediments, primarily by removal from the water column through their association with particulate matter (Government of Canada 1994). Because a variety of aquatic organisms live in contact with bed sediments, sediments are an important exposure route for these organisms to PAHs. Canadian interim sediment quality guidelines (ISQGs) and probable effects levels (PELs) for PAHs can be used to evaluate the degree to which adverse biological effects are likely to occur as a result of exposure to PAHs in sediments.

Canadian ISQGs and PELs for PAHs in freshwater and marine sediments were developed using a modification of the National Status and Trends Program (NSTP) approach as described in CCME (1995) (Table 1). The ISQGs and PELs refer to total concentrations of PAHs in the surficial sediment (i.e., top 5 cm), as quantified by extraction and determination by recognized analytical procedures for PAHs. Currently, there is sufficient scientific information to develop ISOGs for 13 PAHs in marine sediments and 6 PAHs in freshwater sediments. These include 7 LMW-PAHs (naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene) and 6 HMW-PAHs (fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, and dibenz(a,h)anthracene). Insufficient information was available to derive freshwater ISQGs according to the formal protocol for 6 of the LMW-PAHs and 1 HMW-PAH. For these PAHs, the corresponding marine ISQGs and PELs, derived using a modification of the NSTP approach, were provisionally adopted for freshwater, as they were the lowest biological effects-based guidelines available.

The majority of the data used to derive ISQGs and PELs for PAHs are from studies on field-collected sediments that measured concentrations of PAHs, along with concentrations of other chemicals, and associated biological effects that are compiled in the Biological

### POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

Canadian Sediment Quality Guidelines
for the Protection of Aquatic Life

Table	1.	Interim	sediment	quality	guidelines	(ISQGs)	and
		probable	e effect leve	els (PELs	) for PAHs	(µg∙kg¹ dv	w).

	ISQG	PEL
Marine and estuarine		
sediments		
LMW-PAHs		
Naphthalene	34.6	391
2-Methylnaphthalene	20.2	201
Acenaphthylene	5.87	128
Acenaphthene	6.71	88.9
Fluorene	21.2	144
Phenanthrene	86.7	544
Anthracene	46.9	245
HMW-PAHs		
Fluoranthene	113	1494
Pyrene	153	1398
Benz(a)anthracene	74.8	693
Chrysene	108	846
Benzo(a)pyrene	88.8	763
Dibenz(a,h)anthracene	6.22	135
Freshwater sediments		
LMW-PAHs		
Naphthalene	34.6*	391 <sup>†</sup>
2-Methylnaphthalene	$20.2^{*}$	$201^{\dagger}$
Acenaphthylene	5.87*	$128^{\dagger}$
Acenaphthene	6.71*	88.9 <sup>†</sup>
Fluorene	21.2*	$144^{\dagger}$
Phenanthrene	41.9	515
Anthracene	$46.9^{*}$	$245^{\dagger}$
HMW-PAHs		
Fluoranthene	111	2355
Pvrene	53.0	875
Benz( <i>a</i> )anthracene	31.7	385
Chrysene	57.1	862
Benzo( <i>a</i> )pyrene	31.9	782
Dibenz $(a,h)$ anthracene	6.22*	135 <sup>†</sup>

\*Provisional; adoption of marine ISQG developed using the modified NSTP approach.

<sup>†</sup>Provisional; adoption of marine PEL developed using the modified NSTP approach.

Effects Database for Sediments (BEDS) (Environment Canada 1998). Both the marine (including estuarine) and freshwater data sets represent a wide range of concentrations of PAHs, types of sediment, and mixtures of chemicals. Evaluation of the percentage of effect entries for PAHs that are below the ISQGs, between the ISQGs and the PELs, and above the PELs (Figures 1 to 19) indicates that these values define three ranges of chemical concentrations: those that are rarely, occasionally, and frequently associated with adverse biological effects, respectively (Environment Canada 1998).

### Toxicity

Adverse biological effects associated with PAHs in sediments are represented in the BEDS and include decreased benthic invertebrate abundance, diversity, and growth, and physiological and behavioural changes, among others (Environment Canada 1998, Appendixes I–XIX). Mortality is the most common acute toxicological endpoint for sediment bioassays on field-collected sediments and laboratory-spiked sediments.

The toxicity of PAHs depends on a number of factors, including the species, route of exposure, and molecular structure of the PAH. In general, LMW-PAHs are considered to be acutely toxic and noncarcinogenic to aquatic organisms, whereas, HMW-PAHs are generally not acutely toxic to aquatic organisms, but a number of them are carcinogenic (Neff 1979; Moore and Ramamoorthy 1984; Goyette and Boyd 1989). The higher acute toxicity of LMW-PAHs is enhanced by their high water solubility, whereas the lower acute toxicity of HMW-PAHs reflects their low water solubility (Duffus 1980; Uthe 1991).

Field studies on LMW-PAHs in freshwater and marine environments demonstrate that toxicity, including mortality and sublethal effects, occurs at concentrations higher than the ISQGs. For example, Ingersoll et al. (1992) observed that concentrations of phenanthrene of  $50 \ \mu g \cdot kg^4$  and  $82 \ \mu g \cdot kg^4$ , which are above the freshwater ISQG of 41.9  $\mu$ g·kg<sup>4</sup>, were significantly toxic to *Hyalella* azteca, an amphipod. However, concentrations of phenanthrene of  $7.75 \,\mu g \cdot kg^4$  and  $9.8 \,\mu g \cdot kg^4$ , which are lower than the freshwater ISOG, were not significantly toxic to H. azteca. Carr (1993) examined concentrations of various LMW-PAHs in sediments from Galveston Bay, Texas, and the associated effects on the benthic community in shallow waters of the bay. Benthic invertebrates were found in high abundance (154 organisms per square metre) in sediments where concentrations of acenaphthylene  $(0.235 \ \mu g \cdot kg^4)$ , acenaphthene  $(2.71 \ \mu g \cdot kg^4)$ , and fluorene  $(3.87 \ \mu g \cdot kg^4)$  were lower than their individual ISQGs of  $5.87 \ \mu g \cdot kg^4$ ,  $6.71 \ \mu g \cdot kg^4$ , and  $21.2 \ \mu g \cdot kg^4$ , respectively. These invertebrates were in low abundance (53 organisms per m<sup>2</sup>) at concentrations of  $6.89 \,\mu g \cdot kg^{-1}$ ,  $35.8 \,\mu g \cdot kg^{-1}$ , and  $28 \mu g \cdot kg^4$ , respectively, concentrations that exceed their respective ISQGs.

Many toxicological effects have been associated with elevated concentrations of HMW-PAHs in field studies. For example, Malins et al. (1985a, 1985b) found that benzo(a)pyrene was not significantly toxic to a benthic-



Figure 1. Distribution of naphthalene concentrations in marine and estuarine sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 2. Distribution of 2-methylnapthalene concentrations in marine and estuarine sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 3. Distribution of acenaphthylene concentrations in marine and estuarine sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 4. Distribution of acenaphthene concentrations in marine and estuarine sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 5. Distribution of fluorene concentrations in marine and estuarine sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 6. Distribution of phenanthrene concentrations in marine and estuarine sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 7. Distribution of anthracene concentrations in marine and estuarine sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 8. Distribution of fluoranthene concentrations in marine and estuarine sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 9. Distribution of pyrene concentrations in marine and estuarine sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 10. Distribution of benz(a) anthracene concentrations in marine and estuarine sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 11. Distribution of chrysene concentrations in marine and estuarine sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 12. Distribution of benzo(a) pyrene concentrations in marine and estuarine sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 13. Distribution of dibenz(a,h) anthracene concentrations in marine and estuarine sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 14. Distribution of phenanthrene concentrations in freshwater sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 15. Distribution of fluoranthene concentrations in freshwater sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 16. Distribution of pyrene concentrations in freshwater sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 17. Distribution of benz(a) anthracene concentrations in freshwater sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 18. Distribution of chrysene concentrations in freshwater sediments that are associated with adverse biological effects ( $\bullet$ ) and no adverse biological effects ( $\circ$ ). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.



Figure 19. Distribution of benzo(a) pyrene concentrations in freshwater sediments that are associated with adverse biological effects (•) and no adverse biological effects (•). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.

feeding flatfish, Parophrys vetulus, in Puget Sound at a concentration of  $41 \,\mu g \cdot k g^4$ , which is lower than the marine ISQG, but was toxic at a concentration of  $1579 \,\mu g \cdot kg^4$ , which is twice the PEL. Lotufo (1997) examined the sublethal effects of fluoranthene and phenanthrene separately on reproduction and behaviour in an estuarine copepod, Schizopera knabeni Lang. After 14-d exposure, neither of the two PAHs had affected reproductive clutch size at concentrations ranging from 0 to 261 mg·kg<sup>+</sup> and 0 to 249 mg·kg<sup>+</sup> for phenanthrene and fluoranthene, respectively; production, however, was lower (Lotufo 1997). During separate 6-h exposures, S. knabeni also actively avoided sediments that had been spiked with several concentrations of phenanthrene (0-514 mg·kg<sup>4</sup>) and fluoranthene  $(0-990 \text{ mg·kg}^4)$  by burrowing into noncontaminated sediment in the same container (Lotufo 1997). All of the above sublethal effects occurred at concentrations much higher than the PELs of 1494 µg·kg<sup>-</sup> for fluoranthene and 544  $\mu$ g·kg<sup>-1</sup> for phenanthrene. In a freshwater environment, Stewart and Thompson (1995) investigated the sublethal effects of fluoranthene on the emergence (development of newly hatched larvae to adult stage) of Chironomus riparius. After a 28-d exposure to fluoranthene at concentrations of  $80 \text{ mg} \cdot \text{kg}^{4}$  and  $170 \text{ mg} \cdot \text{kg}^{4}$ , 30--70 times greater than the PEL of 2 354.9  $\mu$ g·kg<sup>-1</sup>, the median emergence time and the onset of emergence increased significantly, while the percent of total emergence decreased significantly (Stewart and Thompson 1995).

Spiked-sediment toxicity tests for PAHs report toxicity to benthic organisms at higher concentrations than those observed in field studies. This is likely a result of the shorter-term exposure of these laboratory studies and exposure to only one PAH, as opposed to a mixture of several PAHs and chemicals (Environment Canada 1998). For example, Lotufo (1997) examined the separate toxicities of phenanthrene and fluoranthene on the survival of S. knabeni, an estuarine copepod. The 4-d LC<sub>50</sub>s of 473 mg·kg<sup>4</sup> for phenanthrene and  $>2100 \text{ mg} \cdot \text{kg}^4$  for fluoranthene were much higher than their respective PELs of 544  $\mu$ g·kg<sup>4</sup> and 1494  $\mu$ g·kg<sup>4</sup> (Lotufo 1997). Similarly, in a freshwater environment, the 32-d LC<sub>50</sub>s for Diporeia spp. ranged between 147 and 223 mg·kg<sup>+</sup> in sediments spiked with pyrene (Landrum et al. 1994). These LC<sub>50</sub>s are 160–250 times greater than the PEL of 875  $\mu$ g·kg<sup>-1</sup>.

Mixtures of PAHs have also been spiked into freshwater sediments. Landrum et al. (1991) spiked sediment with a mixture of fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)pyrene, and four other HMW-PAHs. The endpoints examined were sediment avoidance and mortality. At the highest

mixture concentration of  $327 \text{ nmol} \cdot \text{g}^{4}$  (approximately 73.2 mg·kg<sup>4</sup> for all PAHs in the sediment), 38% mortality was observed in *Diporeia* spp. after 19 d, while 28% mortality was observed after 26 d. In sublethal tests, at the highest concentration of  $327 \text{ nmol} \cdot \text{g}^{4}$  (73.2 mg·kg<sup>4</sup>), 17% avoidance of sediment was reported for *Diporeia* spp. after 72 and 144 h (Landrum et al. 1991).

In spiked-sediment toxicity tests with marine sediments, higher levels of organic carbon in the sediment have been shown to reduce the toxicity of PAHs to benthic organisms. For example, Swartz et al. (1990) examined the acute toxicity of bulk concentrations of fluoranthene to *Rhepoxynius abronius*, a marine benthic amphipod, in sediments containing 0.18%, 0.31%, and 0.48% TOC. The 10-d LC<sub>50</sub>s, based on measured concentrations of fluoranthene, were  $3.4 \text{ mg}\cdot\text{kg}^4$ ,  $6.5 \text{ mg}\cdot\text{kg}^4$ , and  $10.7 \text{ mg}\cdot\text{kg}^4$ , respectively. These results suggest that organic matter can modify the toxicity of PAHs to marine benthic organisms.

Results of both marine and freshwater spiked-sediment toxicity tests indicate that toxic levels of PAHs are consistently above the ISQGs, confirming that the guidelines are concentrations below which adverse biological effects will rarely occur. Further, these studies provide additional evidence that toxic levels of PAHs in sediments are greater than or similar to the PELs, confirming that effects are more likely to be observed when concentrations of PAHs exceed the PELs. The ISQGs and PELs for PAHs are therefore expected to be valuable tools for assessing the ecotoxicological relevance of PAHs in sediments.

# Concentrations

It was beyond the scope and intent of the original document (Environment Canada 1998) to present an extensive review of concentrations of PAHs in Canadian sediments. Instead, several case studies were presented to illustrate the measured concentrations of PAHs at locations in various proximities to anthropogenic sources. Sediment chemistry data from three marine and three freshwater areas were reviewed to provide examples of the concentrations of PAHs reported in Canadian sediments (Environment Canada 1998). These areas were chosen because data were available from recent studies and because the areas reflect a variety of sources of PAHs and degrees of contamination. The marine areas included Sydney Harbour, Nova Scotia; Vancouver Harbour, British Columbia; and the Mackenzie River delta, Northwest Territories. The freshwater areas included northern rivers and lakes from the Northern Rivers Basin Study in Alberta; Hamilton Harbour, Ontario; and the watersheds of 13 rivers in Quebec, including a freshwater section of the St. Lawrence River.

Of the three marine areas, sediments from the Mackenzie River delta had the lowest concentrations of PAHs, sediments from Vancouver Harbour were intermediate in concentration, and the highest concentrations were measured in Sydney Harbour. For example, the mean concentration of acenaphthene was  $8.1 > 5.2 \ \mu g \cdot kg^4$  in the Mackenzie River delta and ranged from 10 to  $480 \ \mu g \cdot kg^4$  in Vancouver Harbour and  $14 \times 10^3$  to  $490 \times 10^3 \ \mu g \cdot kg^4$  in Sydney Harbour. For naphthalene, the mean concentration in sediments from the Mackenzie River delta was  $76 > 39 \ \mu g \cdot kg^4$ ; whereas concentrations in Vancouver Harbour ranged from <10 to  $1170 \ \mu g \cdot kg^4$  and from  $208 \times 10^3$  to  $17 \times 10^6 \ \mu g \cdot kg^4$  in Sydney Harbour.

The concentrations of PAHs in the freshwater sediments reviewed were generally lower than those reported for the marine sediments. Of the three freshwater areas, concentrations were lowest in the Northern River Basins Study area, concentrations in Quebec rivers were intermediate, whereas concentrations in Hamilton Harbour were typically an order of magnitude higher. For example, concentrations of benzo(*a*)pyrene ranged from 6.0 to  $21.3 \,\mu g \cdot kg^4$  in the Northern River Basins Study area, <20 to  $345 \,\mu g \cdot kg^4$  for freshwater rivers in Quebec, and 120 to  $69 \,000 \,\mu g \cdot kg^4$  in Hamilton Harbour. For phenanthrene, concentrations ranged from 15 to  $142.2 \,\mu g \cdot kg^4$  in sediments from the Northern River Basins Study area, <20 to  $752 \,\mu g \cdot kg^4$  in Quebec, and 260 to  $189 \,000 \,\mu g \cdot kg^4$  in Hamilton Harbour.

# Additional Considerations

Regardless of the origin of PAHs in sediments, aquatic organisms may be adversely affected by exposure to elevated levels. As is evident in Figures 1 to 19, the occurrence of adverse biological effects cannot be precisely predicted from concentration data alone, particularly in the concentration ranges between the ISQGs and PELs. The likelihood of adverse biological effects occurring in response to exposure to PAHs at a particular site depends on the sensitivity of individual species and the endpoints examined. In addition, the bioavailability of PAHs is influenced by several factors, including physicochemical properties of the PAH (e.g., molecular weight and Kow), geochemical factors (e.g., total organic matter content and particle size), and biological factors (e.g., feeding behaviour and life stage) (Environment Canada 1998). For example, in bivalve mollusks, higher rates of bioaccumulation of PAHs have been observed in deposit feeders than in suspension feeders (Roesijadi et al. 1978; Foster et al. 1987).

The bioavailability of sediment-associated PAHs is also influenced by their source. For example, Paine et al. (1996) reported that PAHs associated with coal, coke, or

### POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

pitch from an aluminium smelter had limited bioavailability and, hence, low toxicity. However, PAHs from petroleum and related sources are likely to be more bioavailable to sediment-dwelling organisms than other sources of PAHs because they can more readily desorb from sediment particulates.

Benthic organisms are exposed to PAHs through various routes of exposure, including exposure to particulate or dissolved PAHs in interstitial or overlying waters, as well as to sediment-bound PAHs through surface contact and sediment ingestion. The relative importance of each of these exposure routes is likely to differ among various species and life history stages. Nevertheless, sediments represent the most important exposure route for many benthic invertebrates (Environment Canada 1998). Data on the concentrations of PAHs in bulk sediments provide important information for evaluating sediment contamination, however, such measurements do not necessarily reflect the bioavailable fraction of these substances. Differences in bioavailability will be observed for individual PAHs and different types of sediment (DeWitt et al. 1992; Wood et al. 1997).

Collectively, the available data on the physical and chemical properties of PAHs indicate that these substances are generally hydrophobic and have a high potential for adsorption to suspended particles in air and water (NRCC 1983; Sloof et al. 1989). The log Kow values of the 13 PAHs considered ranged from 5.32 to 6.04 for HMW-PAHs and 3.37 to 4.46 for LMW-PAHs (Environment Canada 1998). Studies investigating bioaccumulation by various aquatic organisms illustrate that the bioaccumulation of PAHs from the water is greatest for substances with a log Kow value between 5.0 and 5.6, with relatively less bioaccumulation occurring for substances having higher or lower log Kow values (Trucco et al. 1983; Neff 1985; de Voogt et al. 1991). For sediments, the bioaccumulation of several sedimentassociated PAHs (e.g., anthracene, phenanthrene, pyrene, benz(a)anthracene, and benzo(a)pyrene) by Diporeia hoyi, an amphipod, was highest at a log Kow of approximately 5 (Landrum 1989). Bioaccumulation is thought to be highest for these PAHs because substances with lower log  $K_{ow}$  values (i.e., <5) are more rapidly eliminated, while substances with higher log Kow values (i.e., >6) are taken up more slowly because they are more strongly sorbed to sediments (Landrum 1989). Uptake of the higher molecular weight substances, which have higher Kow values, may also be reduced due to slower transport across biological membranes.

The results of numerous studies have shown that organic carbon content is one of the most important factors affecting the bioavailability of PAHs (Environment

Canada 1998). In addition, differences in bioavailability have been observed in sediments having similar levels of organic carbon, suggesting that the type of organic carbon present in the sediment is also important (Suedel and Rodgers 1991: Harkey et al. 1995). The presence of clavs and other fine materials, which directly affect particle size distribution, may contribute significantly to the sorption of nonpolar organic chemicals to bed sediments, thereby reducing their bioavailability (Neff 1984; Rodgers et al. 1987). The presence of dissolved organic carbon and dissolved humic material in interstitial water can also reduce the bioavailability of PAHs to sediment-dwelling organisms. The roles of the various factors that modify the bioavailability of PAHs should be considered, along with the recommended ISQGs and PELs, in site-specific assessments of PAHs in sediments.

Currently, the degree to which PAHs will be bioavailable at particular sites cannot be predicted conclusively from physicochemical sediment characteristics or attributes of endemic organisms. Nonetheless, the incidence of adverse biological effects associated with exposure to PAHs increases as concentrations of PAHs increase in a range of sediment types (Figures 1 to 19). Therefore, the recommended Canadian ISQGs and PELs for PAHs will be useful in assessing the ecotoxicological significance of PAHs in sediments.

#### References

- Carr, R.S. 1993. Sediment quality assessment survey of the Galveston Bay System. Galveston Bay National Estuary Program Report, GBNEP-30.
- CCME (Canadian Council of Ministers of the Environment). 1995. Protocol for the derivation of Canadian sediment quality guidelines for the protection of aquatic life. CCME EPC-98E. Prepared by Environment Canada, Guidelines Division, Technical Secretariat of the CCME Task Group on Water Quality Guidelines, Ottawa. [Reprinted in Canadian environmental quality guidelines, Chapter 6, Canadian Council of Ministers of the Environment, 1999, Winnipeg.] CEPA (Canadian Environmental Protection Act), R.S., 1985. c. 16 (4th
- CEPA (Canadian Environmental Protection Act), R.S., 1985. c. 16 (4th Supp.).
- de Voogt, P., B. van Hattum, P. Leonards, J.C. Klamer, and H. Govers. 1991. Bioconcentration of polycyclic heteroaromatic hydrocarbons in the guppy (*Poecilia reticulata*). Aquat. Toxicol. 20:169–194.
- DeWitt, T.H., R.J. Ozretich, R.C. Swartz, J.O. Lamberson, D.W. Schultz, G.R. Ditsworth, J.K.P. Jones, L. Hoselton, and L.M. Smith. 1992. The influence of organic matter quality on the toxicity and partitioning of sediment-associated fluoranthene. Environ. Toxicol. Chem. 11:197–208.
- Duffus, J.H. 1980. Environmental toxicology. A. Cottrell and T.R.E. Southwood, eds. Edward Arnold, Ltd., London.
- Environment Canada. 1998. Canadian sediment quality guidelines for polycyclic aromatic hydrocarbons (PAHs): Supporting document. Environmental Conservation Service, Ecosystem Science Directorate, Science Policy and Environmental Quality Branch, Guidelines and Standards Division, Ottawa. Draft.
- Falk-Petersen, I.-G., L.J. Saethre, and S. Lönning. 1982. Toxic effects of naphthalene and methylnaphthalenes on marine plankton organisms. Sarsia 67(3):171–178.

- Foster, G.D., S.M. Baksi, and J.C. Means. 1987. Bioaccumulation of trace organic contaminants from sediments by Baltic clams (*Macoma balthica*) and soft-shell clams (*Mya arenaria*). Environ. Toxicol. Chem. 6:969–976.
- Government of Canada. 1994. Polycyclic aromatic hydrocarbons: Canadian Environmental Protection Act Priority Substances List Assessment Report. Environment Canada and Health Canada, Ottawa.
- Goyette, D., and J. Boyd. 1989. The relationship between polycyclic aromatic hydrocarbon (PAH) concentrations in sediment and the prevalence of liver lesions in English sole (*Parophrys vetulus*) from Vancouver Harbour 1985/86 and 1987. Environment Canada, Conservation and Protection, Environmental Protection, Pacific and Yukon Region, Marine Programs. Draft.
- Harkey, G.A., P.L. Van Hoof, and P.F. Landrum. 1995. Bioavailability of polycyclic aromatic hydrocarbons from a historically contaminated sediment core. Environ. Toxicol. Chem. 14(9):1551–1560.
- Heitkamp, M.A., and C.E. Cerniglia. 1987. Effects of chemical structure and exposure on the microbial degradation of polycyclic aromatic hydrocarbons in freshwater and estuarine ecosystems. Environ. Toxicol. Chem. 6:535–546.
- Ingersoll, C.G., W.G. Brumbaugh, A.M. Farag, T.W. La Point, and D.F. Woodward. 1992. Effects of metal-contaminated sediment, water, and diet on aquatic organisms. Second draft of the final report for the USEPA Milltown Endangerment Assessment Project. National Fisheries Contaminant Research Center, U.S. Fish and Wildlife Service, Columbia, MO. Prepared for U.S. Environmental Protection Agency, Helena, MT.
- Landrum, P.F. 1989. Bioavailability and toxicokinetics of polycyclic aromatic hydrocarbons sorbed to sediments for the amphipod *Pontoporeia hoyi*. Environ. Sci. Technol. 23(5):588–594.
- Landrum, P.F., B.J. Eadie, and W.R. Faust. 1991. Toxicokinetics and toxicity of a mixture of sediment-associated polycyclic aromatic hydrocarbons to the amphipod *Diporeia* (sp). Environ. Toxicol. Chem. 10:35–46.
- Landrum, P.F., W.S. Dupuis, and J. Kukkonen. 1994. Toxicokinetics and toxicity of sediment-associated pyrene and phenanthrene in *Diporeia* spp.: Examination of equilibrium-partitioning theory and residue-based effects for assessing hazard. Environ. Toxicol. Chem. 13(11):1769–1780.
- Lotufo, G.R. 1997. Toxicity of sediment-associated PAHs to an estuarine copepod: Effects on survival, feeding, reproduction and behavior. Mar. Environ. Res. 44(2):149–166.
- Malins, D.C., M.M. Krahn, D.W. Brown, L.D. Rhodes, M.S. Myers, B.B. McCain, and S.-L. Chan. 1985a. Toxic chemicals in marine sediment and biota from Mukilteo, Washington: Relationships with hepatic neoplasms and other hepatic lesions in English sole (*Parophrys vetulus*). J. Nat. Cancer Inst. 74:487–494.
- Malins, D.C., M.M. Krahn, M.S. Myers, L.D. Rhodes, D.W. Brown, C.A. Krone, B.B. McCain, and S.-L. Chan. 1985b. Toxic chemicals in sediments and biota from a creosote-polluted harbor: Relationships with hepatic neoplasms and other hepatic lesions in English sole (*Parophrys vetulus*). Carcinogenesis 6(10):1463–1469.
- McElroy, A.E., J.W. Farrington, and J.M. Teal. 1989. Bioavailability of PAHs in the aquatic environment. In: Metabolism of PAHs in the aquatic environment, U. Varanasi, ed. CRC Press, Inc., Boca Raton, FL.
- Moore, J.W., and S. Ramamoorthy. 1984. Aromatic hydrocarbons: Polycyclics. In: Organic chemicals in natural waters: Applied monitoring and impact assessment, R.S. DeSanto, ed. Springer– Verlag, New York.

- Neff, J.M. 1979. Polycyclic aromatic hydrocarbons in the aquatic environment: Sources, fate and biological effects. Applied Science Publishers, Ltd., Essex, England.
- ———. 1984. Bioaccumulation of organic micropollutants from sediments and suspended particulates by aquatic animals. Fresenius J. Anal. Chem. 319:132–136.
- ———. 1985. Polycyclic aromatic hydrocarbons. In: Fundamentals of aquatic toxicology: Methods and applications, G.M. Rand and S.R. Petrocelli, eds. Hemisphere Publishing Corporation, New York.
- NRCC (National Research Council of Canada). 1983. Polycyclic aromatic hydrocarbons in the aquatic environment: Formation, sources, fate and effects on aquatic biota. NRC Associate Committee on Scientific Criteria for Environmental Quality. Publication No. NRCC 18981. Ottawa.
- Paine, M.D., P.M. Chapman, P.J. Allard, M.H. Murdoch, and D. Minifie. 1996. Limited bioavailability of sediment PAH near an aluminium smelter: Contamination does not equal effects. Environ. Toxicol. Chem. 15(11):2003–2018.
- Ringuette, S., A. Germain, C. Gonthier, and F. Perron. 1993. Presence of PAHs in the Canadian environment: An overview. Priority Substances List Supporting Document No. 2. Prepared for Environment Canada, Conservation and Protection, Quebec Region, Montreal.
- Rodgers, J.H., K.L. Dickson, F.Y. Saleh, and C.A. Staples. 1987. Bioavailaiblity of sediment-bound chemicals to aquatic organisms: Some theory, evidence and research needs. In: Fate and effects of sediment-bound chemicals in aquatic systems, SETAC Special Publication Series, K.L. Dickson, A.W. Maki, and W.A. Brungs, eds. Pergamon Press. New York.
- Roesijadi, G.J., J.W. Anderson, and J.W. Blaylock. 1978. Uptake of hydrocarbons from marine sediments contaminated with Prudhoe Bay crude oil: Influence of feeding type of test species and availability of polycyclic aromatic hydrocarbons. J. Fish. Res. Board Can. 35:608– 614.
- Sloof, W., J.A. Janus, A.J. Matthijsen, G.K. Montizaan, and J.P.M. Ros. 1989. Integrated criteria document PAHs. Report No. 758474011. National Institute of Public Health and Environmental Protection, Biltoven, The Netherlands.
- Stewart, K.M., and R.S. Thompson. 1995. Fluoranthene as a model toxicant in sediment studies with *Chironomus riparius*. J. Aquat. Ecosyst. Health 4:231–238.
- Suedel, B.C., and J.H Rodgers, Jr. 1991. Variability of bottom sediment characteristics of the continental United States. Water Res. Bull. 27:101–109.
- Swartz, R.C., D.W. Schults, T.H. DeWitt., G.R. Ditsworth, and J.O. Lamberson. 1990. Toxicity of fluoranthene in sediment to marine amphipods: A test of the equilibrium partitioning approach to sediment quality criteria. Environ. Toxicol. Chem. 9:1071–1080.
- Trucco, R.G., F.R. Engelhardt, and B. Stacey. 1983. Toxicity, accumulation, and clearance of aromatic hydrocarbons in *Daphnia pulex*. Environ. Pollut. (Ser. A) 31:191–202.
- Uthe, J.F. 1991. Polycyclic aromatic hydrocarbons in the environment. Can. Chem. News 43(7):25–27.
- Wilson, S.C., and K.C. Jones. 1993. Bioremediation of soil contaminated with polynuclear aromatic hydrocarbons (PAHs): A review. Environ. Pollut. 81(3):229–249.
- Wood, L.W., P. O'Keefe, and B. Bush. 1997. Similarity analysis of PAH and PCB bioaccumulation patterns in sediment-exposed *Chironomus tentans* larvae. Environ. Toxicol. Chem. 16(2):283–292.

## POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

### Canadian Sediment Quality Guidelines for the Protection of Aquatic Life

Reference listing:

Canadian Council of Ministers of the Environment. 1999. Canadian sediment quality guidelines for the protection of aquatic life: Polycyclic aromatic hydrocarbons (PAHs). In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

For further scientific information, contact:

Environment Canada Guidelines and Standards Division 351 St. Joseph Blvd. Hull, QC K1A 0H3 Phone: (819) 953-1550 Facsimile: (819) 953-0461 E-mail: ceqg-rcqe@ec.gc.ca Internet: http://www.ec.gc.ca

© Canadian Council of Ministers of the Environment 1999 Excerpt from Publication No. 1299; ISBN 1-896997-34-1 For additional copies, contact:

CCME Documents c/o Manitoba Statutory Publications 200 Vaughan St. Winnipeg, MB R3C 1T5 Phone: (204) 945-4664 Facsimile: (204) 945-7172 E-mail: spccme@chc.gov.mb.ca

Aussi disponible en français.