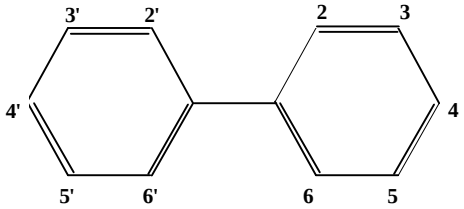
Canadian Sediment Quality Guidelines for the Protection of Aquatic Life

POLYCHLORINATED BIPHENYLS (PCBs)

Polychlorinated biphenyls (PCBs) have been identified as Track 1 substances by Environment Canada because they are persistent, bioaccumulative, released primarily as a result of human activities, and are considered "CEPA-toxic" under the Canadian Environmental Protection Act (Environment Canada 1997).

PCBs are a class of chlorinated organic compounds, represented by 209 congeners, that can be toxic to aquatic biota. PCB congeners are classified into homologous groups according to the number of chlorine atoms contained in the compound. These groups range from the monochlorobiphenyls, which have one chlorine atom, to decachlorobiphenyl, which has 10 chlorine atoms. Individual congeners within each homologous group have the same molecular formula but different properties because of dissimilar arrangements of chlorine atoms within the molecule. The identities of individual PCB compounds are determined by the number and location of chlorine atoms substituted on the biphenyl molecule (Figure 1) (Ballschmiter and Zell 1980). Individual congeners are also referred to using a numbering system established by the International Union of Pure and Applied Chemistry (Hutzinger et al. 1974). For example, 3, 4, 4', 5-tetrachlorobiphenyl is identified as PCB-81.



Ortho positions: 2, 2', 6, 6'
Meta positions: 3, 3', 5, 5'
Para positions: 4, 4'

Figure 1. Numbering system of parent biphenyl molecule for individual PCB congeners.

PCBs were produced commercially as complex mixtures of chlorobiphenyl congeners in North America and were marketed under the trade name Aroclor (Moore and Walker 1991). Although not manufactured in Canada, approximately 40 000 t of PCBs were imported and used commercially over the period 1929 to 1977 (CCREM 1986). Importation of PCBs into Canada was prohibited in 1980 (Strachan 1988).

Although the use of PCBs has been severely restricted in North America over the last two decades, the main sources to aquatic environments continue to be leaks, spills, municipal and industrial effluents, runoff from contaminated soils, leachates from unsecured landfills, and atmospheric deposition (Strachan 1988; WHO 1992). The fate and behaviour of PCBs in aquatic systems are influenced by a number of physical, chemical, and biological processes. While processes such as photooxidation, hydrolysis, and biodegradation result in the transformation of PCBs into other substances (e.g., benzoic acid, *p*-chlorobenzoic acid, and phenylpyruvic acid), other processes, such as remobilization, solubilization, volatilization, adsorption, desorption, resuspension, and bioaccumulation, are responsible for the cycling, long-range transport, and subsequent accumulation of these substances in soils, sediments, and biological tissues (Eisler 1986; Coulston and Kolbye 1994). Because of their thermal and chemical stability, the cycling of PCBs among environmental compartments represents the most important process influencing the fate of these compounds in the environment. Furthermore, the majority of PCBs that are introduced into the aquatic environment are eventually incorporated into bed sediments (Baker et al. 1985). Therefore, sediments represent an important exposure route for aquatic biota to PCBs. Canadian interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for PCBs can be used to evaluate the degree to which adverse biological effects are likely to occur as a result of exposure to PCBs in sediments.

Table 1. Interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for total PCBs and Aroclor 1254 (µg·kg^{-1} dw).

	Freshwater	Marine/estuarine
Total PCBs		
ISQG	34.1	21.5
PEL	277	189
Aroclor 1254		
ISQG	60*	63.3
PEL	340†	709

*Provisional; adoption of lowest effect level from Ontario (Persaud et al. 1993).
†Provisional; 1% TOC; adoption of severe effect level of 34 µg·g^{-1} TOC from Ontario (Persaud et al. 1993).

Canadian ISQGs and PELs for total PCBs and Aroclor 1254 were developed using a modification of the National Status and Trends Program (NSTP) approach as described in CCME (1995) (Table 1). A paucity of toxicity data for Aroclor 1254 in freshwater sediments precluded the development of an ISQG using either the NSTP approach or the spiked-sediment toxicity test (SSTT) approach. Therefore, upon evaluation of available guidelines from other jurisdictions, the lowest effect level recommended by Ontario (60 $\mu g \cdot kg^{-1}$) was adopted provisionally as the freshwater ISQG (Persaud et al. 1993). In addition, Ontario's tentative severe effect level of 34 $\mu g \cdot g^{-1}$ TOC (or 340 $\mu g \cdot kg^{-1}$, assuming a 1% TOC) was provisionally recommended as the PEL for Aroclor 1254 in freshwater sediments. The ISQGs and PELs (Table 1) refer to total concentrations of PCBs or Aroclor 1254 in surficial sediments (i.e., top 5 cm) on a dry weight basis as quantified by standard analytical procedures.

The majority of the data used to derive the ISQGs and PELs for total PCBs and Aroclor 1254 (marine sediments only) are from studies on field-collected sediments that measured concentrations of total PCBs or Aroclor 1254, along with concentrations of other chemicals and associated biological effects. Data were compiled in the Biological Effects Database for Sediments (BEDS) (Environment Canada 1998). Both the freshwater and marine BEDS data sets for total PCBs are large, with the freshwater data set containing 67 effect entries and 197 no-effect entries and the marine data set containing 65 effect entries and 134 no-effect entries (Figures 2 and 3). Similarly, the minimum data requirements for the modified NSTP approach were met for Aroclor 1254 in marine sediments, with this data set containing 30 effect entries and 97 no-effect entries (Figure 4). These data sets represent a wide range of concentrations of total PCBs and Aroclor 1254, types of sediments, and mixtures of chemicals. Evaluation of the percentage of effect entries below the ISQGs, between the ISQGs and the PELs, and above the PELs for total PCBs and Aroclor 1254 (marine sediments only) (Figures 2, 3, and 4) 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 concentrations of total PCBs or Aroclor 1254 in sediments are represented in the BEDS. In both BEDS data sets, changes in benthic invertebrate species richness and abundance are the most common indicators of adverse biological effects (Environment Canada 1998, Appendixes I–IV). Less frequently represented endpoints include density, diversity, and biotic integrity.

The freshwater BEDS for total PCBs reveals that midges, mayflies, stoneflies, caddisflies, and bivalves were less abundant in sediments from the Detroit River, with mean concentrations of total PCBs from 1304 to 3760 $\mu g \cdot kg^{-1}$, which are above the freshwater PEL. In comparison, abundance of these organisms was higher at sites where total concentrations of PCBs were approximately 10 $\mu g \cdot kg^{-1}$, which is below the ISQG (Jaagumagi 1988). Furthermore, Ingersoll et al. (1992) reported an increase in the incidence of deformations in *Chironomus riparius*, a midge, exposed to a mean concentration of total PCBs of 342 $\mu g \cdot kg^{-1}$ (i.e., 10 times the freshwater ISQG), in sediments from the Saginaw River, Michigan.

In the marine BEDS data set, Carr (1993) observed a high abundance of oligochaetes in Galveston Bay, Texas, where the mean concentration of total PCBs was 15 $\mu g \cdot kg^{-1}$, which is below the marine ISQG. Mean concentrations of total PCBs of 20 $\mu g \cdot kg^{-1}$, below the marine ISQG, were measured in sediments from the Seybold Canal (Miami River, Florida), with no associated toxicity observed on the brown shrimp, *Penaeus aztecus*; however, significant toxicity was observed at concentrations (200 $\mu g \cdot kg^{-1}$) above the marine PEL. Increased mortality of an amphipod *(Rhepoxynius abronius)*, increased mortality and abnormal development of mussel larvae *(Mytilus edulis)*, and impaired reproduction of a copepod *(Tigriopus californicus)* were observed in San Francisco Bay sediments, where mean concentrations of total PCBs ranged from 110 to 218 $\mu g \cdot kg^{-1}$, which exceed the marine ISQG and PEL (Chapman et al. 1987).

Although the minimum data set for Aroclor 1254 in the freshwater sediments was not met, studies compiled in the BEDS report minimal adverse effects below the ISQG. At concentrations more than twice the freshwater ISQG, sediments were significantly toxic to midges *(C. riparius)* and amphipods *(Hyalella azteca)* (Ingersoll et al. 1992).

In the BEDS for Aroclor 1254 in marine sediments, growth of *Lytechinus pictus*, a sea urchin, was not adversely affected at concentrations slightly above the marine ISQG (i.e., 74 $\mu g \cdot kg^{-1}$) (Anderson et al. 1988). However, at concentrations ranging from 484 to 817 $\mu g \cdot kg^{-1}$, which are above the marine PEL, mortality and sediment avoidance, as well as reduced somatic and gonadal growth, were observed for *L. pictus* (Anderson et al. 1988). In addition, mean concentrations of Aroclor 1254 in the southern California bight ranging from 3310 to 10 609 $\mu g \cdot kg^{-1}$, which are above the marine PEL,

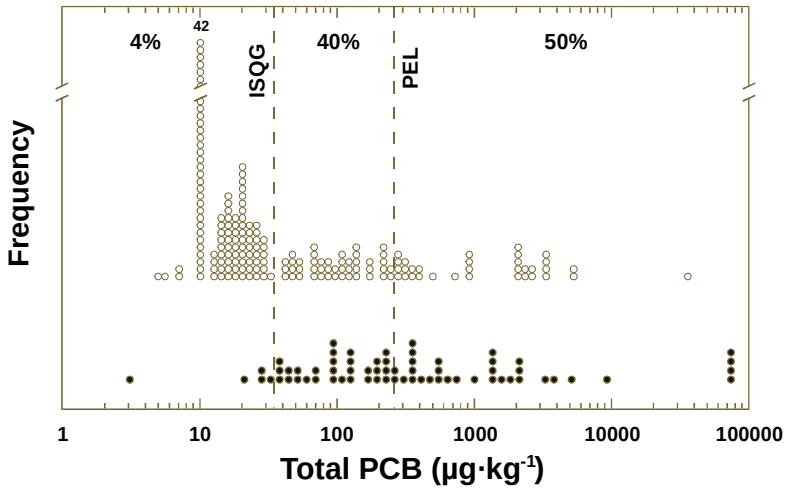


Figure 2. Distribution of total PCB concentrations in freshwater sediments that are associated with adverse biological effects (!) and no adverse biological effects (''). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.

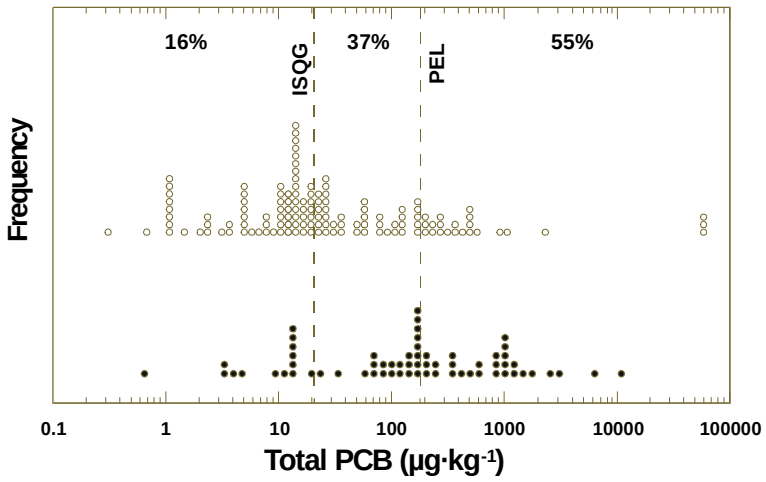


Figure 3. Distribution of total PCB concentrations in marine and estuarine sediments that are associated with adverse biological effects (!) and no adverse biological effects (''). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.

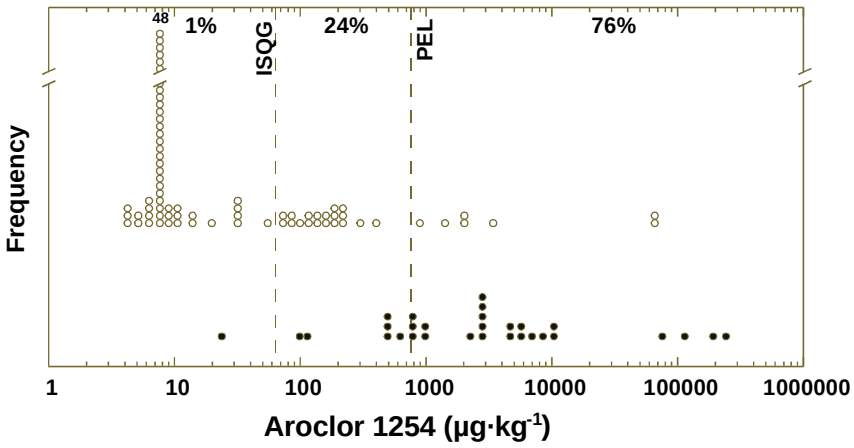


Figure 4. Distribution of Aroclor 1254 concentrations in marine and estuarine sediments that are associated with adverse biological effects (!) and no adverse biological effects (''). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.

were associated with decreased densities of arthropods, degraded benthic invertebrate communities, and mortality to *R. abronius*, an amphipod (Word and Mearns 1979; Swartz et al. 1991).

Very few spiked-sediment toxicity tests were available that investigated the toxicity of either total PCBs or Aroclor 1254 to benthic organisms. Available spiked-sediment toxicity tests reported the onset of toxicity at greater concentrations than those observed in field studies. This is likely a result of the shorter term exposure of these laboratory studies and exposure to commercial Aroclor mixtures only, as opposed to chemical mixtures containing other compounds. For example, a marine sand shrimp, *Crangon septemspinosa*, appeared to be relatively insensitive to mixtures of PCBs, with a 96-h LC_{50} of >3400 µg·kg^{-1} reported for Aroclor 1254 in marine sediments (McLeese and Metcalfe 1980). In addition, Polikarpov et al. (1983) exposed marine sandworms, *Nereis diversicolor*, to concentrations of DP5 (a formulated PCB mixture similar to Aroclor 1254) ranging from 18 700 to 89 600 µg·kg^{-1} for up to 128 d. The concentration of DP5 in reference sediments was more than twice the marine ISQG. High mortality was observed in all of the test groups, with 50% mortality occurring over 31.5–48.5 d at the various treatment concentrations, whereas 50% mortality occurred in reference sediments after 62.5 d.

In another study, Plesha et al. (1988) examined the toxicity of a mixture of Aroclor 1254 and three chlorinated hydrocarbons (i.e., *p,p'*-DDT, hexachloro-butadiene, and hexachlorobenzene) to *R. abronius*. The results indicated that marine sediments containing the mixture, including 1000 µg·kg^{-1} Aroclor 1254 (at 0.9% TOC), were significantly toxic. Even higher mortality was observed when the amphipods were exposed to sediments that had higher nominal concentrations of chlorinated hydrocarbons, including 5000 µg·kg^{-1} of Aroclor 1254. The results of this study suggest that Aroclor 1254 is toxic in the 1000 µg·kg^{-1} range, over an order of magnitude higher than the ISQG, when it is present in mixtures of chlorinated hydrocarbons.

Concentrations

Total PCBs and Aroclor 1254 have been detected in sediment samples from a variety of locations across Canada (Environment Canada 1998). While PCB levels

are generally low, elevated concentrations may occur in the vicinity of existing or historical sources of PCBs, such as landfills and contaminated sites.

The levels of total PCBs in freshwater sediments of the Fraser River, British Columbia, ranged from <10 to 34 $\mu g \cdot kg^{-1}$ (Environment Canada 1994a), while in the Great Lakes region a higher mean concentration of total PCBs (i.e., 3927 $\mu g \cdot kg^{-1}$) reflects industrial activity along the industrial shoreline of Hamilton Harbour (Lake Ontario) (Mudroch et al. 1989). Concentrations of total PCBs in freshwater sediments in Atlantic and Arctic Canada range from 1 to 350 $\mu g \cdot kg^{-1}$ (Environment Canada 1998).

Levels of total PCBs in marine sediments tend to reflect activities that have impacted on harbours, such as industrial and municipal emissions and shipping traffic. On the Pacific mainland coast, concentrations of total PCBs as high as 8400 $\mu g \cdot kg^{-1}$ were reported in sediments of Burrard Inlet, British Columbia (Environment Canada 1994a). In Atlantic Canada, a mean concentration of total PCBs of 5162 $\mu g \cdot kg^{-1}$ was reported for a site in Halifax Harbour, Nova Scotia, whereas concentrations of total PCBs in sediments from coastal areas of New Brunswick ranged from 1 to 389 $\mu g \cdot kg^{-1}$ (Environment Canada 1994b). Bright et al. (1995a) measured concentrations of total PCBs in sediments from Queen Maud Gulf and Wellington Bay in the Arctic Ocean that ranged from 0.052 to 0.44 $\mu g \cdot kg^{-1}$.

Concentrations of Aroclor 1254 in freshwater sediments also vary substantially across the country. In the Fraser River, British Columbia, a maximum concentration of 60 $\mu g \cdot kg^{-1}$ was measured in samples collected between 1983 and 1990 (Environment Canada 1994a). Sediment quality surveys of Hamilton Harbour, Lake Ontario, reported concentrations of Aroclor 1254 as high as 3321 $\mu g \cdot kg^{-1}$ (Mudroch et al. 1989), however, concentrations generally range from 0.7 to 474 $\mu g \cdot kg^{-1}$ in the Great Lakes region (Environment Canada 1998).

As for total PCBs, levels of Aroclor 1254 in marine sediments tend to be elevated in harbours and along shipping routes. For example, levels of Aroclor 1254 in sediments of Burrard Inlet, British Columbia, ranged from 0.45 to 9640 $\mu g \cdot kg^{-1}$, with the highest concentrations observed in the vicinity of several shipyards (Environment Canada 1994a). In Comox Harbour, British Columbia, concentrations of Aroclor 1254 ranged from <10 to 690 $\mu g \cdot kg^{-1}$ (Environment Canada 1994a). In addition, Aroclor 1254 in sediment samples from various locations in Quebec and Newfoundland ranged from 1 to 90 $\mu g \cdot kg^{-1}$ (Matheson and Bradshaw 1985; Environment Canada 1994b), whereas concentrations of <45 $\mu g \cdot kg^{-1}$ were measured in sediments from the Arctic Ocean (Hargrave et al. 1989; Bright et al. 1995b).

Additional Considerations

The occurrence of adverse biological effects resulting from exposure to PCBs in sediments cannot be precisely predicted from concentration data alone, particularly in the concentration ranges between the ISQGs and the PELs (Figures 2, 3, and 4). The likelihood of adverse biological effects occurring in response to exposure to PCBs at a particular site depends on the sensitivity of individual species and the endpoints examined. In addition, a variety of physicochemical (e.g., lipophilicity and size of individual congeners, weathering, and changes in PCB profiles), geochemical (e.g., organic matter content, clay content, and sediment particle size), and biological (e.g., feeding behaviour and uptake rates) factors affect the bioavailability of PCBs (Landrum and Robbins 1990; Environment Canada 1998). For example, Boese et al. (1995) demonstrated that the bioaccumulation of PCBs in a clam, *Macoma nasuta*, was inversely related to the TOC content in the sediment. In addition, a study on amphipods suggested that higher levels of PCBs were accumulated when these organisms resided in coarse versus fine-grained sediments (Lynch and Johnson 1982). The larger surface areas and higher clay contents associated with fine-grained sediments may provide more binding sites for PCBs, rendering them less available for uptake.

Many authors have reported that PCBs with high K_{ow}s (i.e., highly chlorinated PCB congeners) bioaccumulate to a greater degree in benthic organisms than PCBs with lower K_{ow}s (Environment Canada 1998). However, bioavailability appears to be maximal for mid-K_{ow} congeners. For example, a controlled study on a clam *(M. nasuta)* determined that pentachlorobiphenyls (where log K_{ow} = 6.2 to 6.5) were most readily accumulated (Boese et al. 1995). Modeling studies suggest that highly chlorinated PCBs are too large to pass through biological membranes (Gobas et al. 1986) rendering them unavailable for uptake. Moreover, these PCBs may be too hydrophobic to be released from the surfaces of particles when ingested by benthic organisms (D. Haffner 1997, University of Windsor, Windsor, Ontario, pers. com.). Once taken up by an organism, PCBs tend to partition into tissues with high lipid contents (Rowan and Rasmussen 1992; Leblanc 1995). The relationship between lipid content and PCB concentration is evident across trophic levels in the food web (Hawker and Connell 1989).

Benthic organisms may be exposed to PCBs through various routes, including exposure to dissolved or particulate-associated PCBs in interstitial or overlying waters, sediment-bound PCBs through surface contact,

and sediment ingestion during feeding. Contact with contaminated water and sediments represents the primary route of exposure to PCBs for benthos (Evans and Landrum 1989; Landrum et al. 1989).

It should be noted that although the ISQGs and PELs recommended for total PCBs and Aroclor 1254 are developed to be protective of benthic invertebrates, they do not specifically account for the potential for adverse biological effects on higher trophic levels that may result from dietary exposure. Bioaccumulation to high levels in biota as well as biomagnification in food chains are critical aspects of the environmental fate and behaviour of PCBs (WHO 1992). Therefore, Canadian tissue residue guidelines for the protection of wildlife consumers of aquatic organisms should be used in conjunction with the ISQGs and PELs to evaluate the potential for adverse biological effects on other components of aquatic ecosystems.

In addition, it is recommended that congener-specific analyses of total PCBs, as opposed to analyses of Aroclor mixtures, be used for sediment samples that are environmentally weathered or have been historically contaminated. Diagenesis of sediments and dechlorination of PCBs may alter the original Aroclor profile, making it difficult or impossible to match Aroclor patterns, and may lead to a high degree of error in estimating the concentration of PCBs as Aroclor mixtures in sediment samples (Duinker et al. 1991). Thus, measurements of mixtures of Aroclor (including 1254) may be more appropriate for sediments in which recent contamination is suspected.

Currently, the degree to which PCBs will be bioavailable at particular sites cannot be predicted accurately from the physicochemical characteristics of sediments or the attributes of endemic organisms (Environment Canada 1998). Nonetheless, the incidence of adverse biological effects associated with exposure to PCBs increases as concentrations of PCBs increase in a range of sediment types (Figures 2, 3, and 4). Therefore, the recommended Canadian ISQGs and PELs for PCBs will be useful in assessing the ecotoxicological significance of PCBs in sediments.

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