Canadian Sediment Quality Guidelines for the Protection of Aquatic Life

POLYCHLORINATED DIBENZO-*p*-DIOXINS AND POLYCHLORINATED DIBENZOFURANS (PCDD/Fs)

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), commonly known as dioxins and furans, respectively, have been identified as Track 1 substances by Environment Canada because they are persistent, bioaccumulative, released primarily as a result of human activities, and considered "CEPA-toxic" under the Canadian Environmental Protection Act (Environment Canada 1997). PCDD/Fs are a class of planar tricyclic aromatic compounds with similar chemical properties (WHO 1989) containing varying amounts of chlorine (Figure 1). There are a total of 75 PCDD and 135 PCDF congeners. The 17 PCDD/F congeners that have chlorine atoms attached in at least the 2,3,7, and 8 lateral positions were selected for guideline derivation because they are the most toxic and the best-studied, and have a common mode of toxic action.

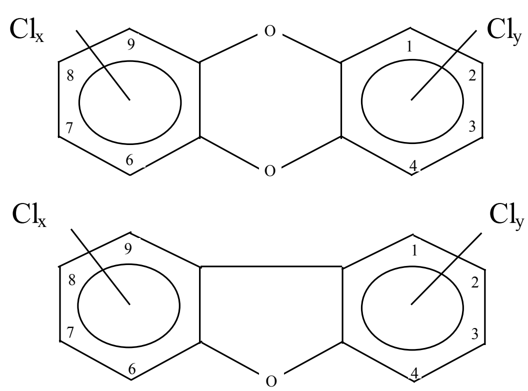

Figure 1. Chemical structure of PCDDs and PCDFs. 2,3,7,8-Substituted congeners have chlorine atoms in at least the four lateral positons, numbered 2,3,7, and 8.

PCDD/Fs are omnipresent in the air, soil, bed sediments, and biota even though they have never been intentionally produced and have no known use. They are by-products formed as a result of anthropogenic activities, including waste incineration, chemical manufacturing, petroleum refining, wood burning, metallurgical processes, fuel combustion (automobiles), residential oil combustion, and electric power generation, among others. Atmospheric releases from combustion sources contributed nearly half of the PCDD/F loading to the Canadian environment in 1997 (Environment Canada 1999a). Atmospheric transport can occur over large distances, and deposition to surface water can be quite variable, at times becoming the dominant source (Pearson et al. 1998). Historically, pulp and paper mill effluents released significant amounts of PCDD/Fs, but great improvements have occurred since the Pulp and Paper Regulations of 1992. Natural sources include forest fires and volcanic activity.

Because of their hydrophobic nature, the majority of PCDD/Fs released into aquatic systems ultimately become associated with the organic fraction of suspended and/or bed sediments and the lipid-rich tissues of aquatic organisms. PCDD/Fs that accumulate in sediments are chemically stable and, therefore, may persist for long periods of time. Limited information is available on photolysis, hydrolysis, or microbial degradation of PCDD/Fs in aquatic sediments, but the results of laboratory incubation studies suggest that these fate processes are minor (Muir et al. 1985; Ward and Matsumura 1978). Thus, bed sediments may represent long-term sources of PCDD/Fs to the aquatic food web.

Aquatic organisms may take up PCDD/Fs from water or sediment, or through the consumption of contaminated prey. Benthic organisms are exposed to particulate and dissolved PCDD/Fs in interstitial and overlying waters and to sediment-bound PCDD/Fs through surface contact and sediment ingestion. All 2,3,7,8-substituted PCDD/Fs readily accumulate in the tissues of aquatic organisms, though higher chlorinated PCDD/Fs generally accumulate to a lesser degree than lower chlorinated congeners.

Table 1. Interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for PCDD/Fs ($ng \cdot kg^{-1}$ dw).

	Freshwater	Marine/estuarine
ISQG	0.85*	0.85*†
PEL	21.5*	21.5*†

*Expressed on a TEQ basis using TEFs for fish. A safety factor of 10 was applied. See text for details.
†Provisional; adoption of the freshwater value.

Biota–sediment accumulation factors (BSAFs) are used to estimate the degree to which chemicals accumulate in biota relative to sediment. BSAFs for 2,3,7,8-tetrachloro-*p*-dibenzodioxin (2,3,7,8-TCDD) range from 0.03 to 0.85 and from 0.03 to 0.93 for freshwater and marine/estuarine systems, respectively (Environment Canada 2000). PCDD/Fs seem unusual in that they do not appear to biomagnify like other halogenated aromatics with comparable hydrophobicities (e.g., PCBs).

Canadian interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for PCDD/Fs can be used to evaluate the degree to which adverse biological effects are likely to occur as a result of exposure to PCDD/Fs in sediments.

Canadian ISQGs and PELs for PCDD/Fs (Table 1) 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 PCDD/Fs in marine sediment 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 Canadian ISQG for freshwater sediments was adopted provisionally as the Canadian ISQG for marine sediments. The ISQGs and PELs (Table 1) refer to the concentrations of 2,3,7,8-substituted PCDD/Fs in surficial sediments (i.e., top 5 cm) on a dry weight basis as quantified by standard analytical procedures and converted to 2,3,7,8-TCDD toxic equivalencies (TEQs) using toxic equivalency factors (TEFs) for fish (see toxicity section, Table 2) (van den Berg et al. 1998). A safety factor of 10 was applied to the ISQG and PEL (CCME 1995).

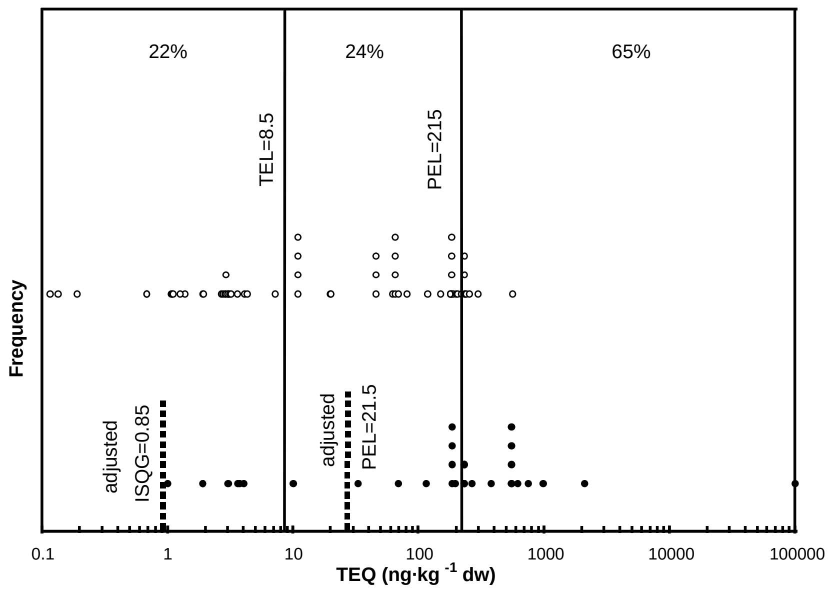

Figure 2. Distribution of PCDD/F TEQ concentrations in freshwater sediments that are associated with adverse biological effects (solid circles) and no adverse biological effects (open circles). Percentages indicate proportions of concentrations associated with effects in ranges below the TEL, between the TEL and PEL, and above the PEL. A safety factor of 10 is applied, resulting in an adjusted TEL of 0.85 ng·kg^{-1} dw and an adjusted PEL of 21.5 ng·kg^{-1} dw. Because of the use of a safety factor, caution should be used in interpreting the guideline.

In general, the threshold effect level (TEL) is recommended as the ISQG and the PEL as an additional assessment tool. For PCDD/Fs, however, a safety factor of 10 was applied to both the TEL and PEL for several reasons. First, the TEL may not adequately meet its narrative objective, that is, a chemical concentration below which adverse effects rarely occur. The TEL is considered to meet its narrative objective when the incidence of adverse biological effects below the TEL is 25% or less; a greater degree of reliability is achieved at 10% or less. In the case of PCDD/Fs, the incidence of effects below the TEL is 22% (Figure 2). This observation is due to the relatively large number of data entries belonging to the effect data set at low concentrations of PCDD/Fs (expressed as TEQ_{fish}), resulting in moderately indistinct effect and no-effect data distributions. Second, a high proportion (79%) of measured concentrations of PCDD/Fs in Canadian sediments (see section on concentrations) falls below the TEL; therefore, the data available in the Biological Effects Data Base for Sediments (BEDS) to calculate the TEL for PCDD/Fs may not fully reflect the range of PCDD/F concentrations in Canadian sediments. Third, although the sediment quality guideline (SQG) process is not intended to address bioaccumulation, sediments serve as an important source of some PCDD/F congeners in higher trophic levels. At such time that sufficient data become available to address these concerns, the application of the safety factor may be re-evaluated.

The majority of the data used to derive the ISQGs and PELs for PCDD/Fs are from studies on field-collected sediments that measured concentrations of 2,3,7,8-substitued PCDD/Fs along with concentrations of other chemicals and associated biological effects. Concentrations of 2,3,7,8-substituted congeners were converted to a TEQ basis using TEFs for fish (van den Berg et al. 1998). Data were compiled in the BEDS (Environment Canada 2000). Minimum data requirements are met for freshwater, but not for marine sediments. The freshwater data set contains 34 effect entries and 62 no-effect entries, whereas the marine data set contains 2 effect entries and 18 no-effect entries.

Toxicity

In mammals, birds, and fish, PCDD/Fs are thought to elicit most, if not all, of their toxicity via the aryl hydrocarbon (*Ah*) receptor, causing a multitude of biological and toxic responses (Environment Canada 2000). This mode of action of PCDD/Fs in aquatic invertebrates and plants has not yet been confirmed.

TEFs allow comparison of toxicity of environmental samples or experimental doses that have different congener profiles. They are order-of-magnitude estimates of the toxicity of 2,3,7,8-substituted PCCD/Fs relative to 2,3,7,8-TCDD. TEFs are derived only for those congeners with *Ah* receptor-mediated responses and are based on all available scientific data. Additivity of *Ah*-active congeners within a chemical mixture is assumed, but non-additive interactions among *Ah*-active congeners, non-*Ah*-active congeners, or other xenobiotics are not considered. The estimate of the toxic potency of a sample, relative to 2,3,7,8-TCDD, is termed the toxic equivalency unit (TEQ) and is the sum of the individual congener concentrations multiplied by their respective TEFs. When TEFs for fish are used in this document, the result is termed "TEQ_{fish}". Toxic equivalents based on fish responses used for evaluation of toxicity should be re-evaluated when mechanisms and relative toxicity of the various PCDD/Fs to invertebrates are better known.

Table 2. Chlorine substitution and toxic equivalency factors (TEFs) for selected PCDD and PCDF congeners (Environment Canada 2000).

Structure	TEFs for fish
PCDDs	
2,3,7,8-TCDD	1
1,2,3,7,8-PCDD	1
1,2,3,4,7,8-HCDD	0.5
1,2,3,6,7,8-HCDD	0.01
1,2,3,7,8,9-HCDD	0.01
1,2,3,4,6,7,8-HCDD	0.001
OCDD	0.0001
PCDFs	
2,3,7,8-TCDF	0.05
1,2,3,7,8-PCDF	0.05
2,3,4,7,8-PCDF	0.5
1,2,3,4,7,8-HCDF	0.1
1,2,3,6,7,8-HCDD	0.1
1,2,3,7,8,9-HCDF	0.1
2,3,4,6,7,8-HCDF	0.1
1,2,3,4,6,7,8-HCDF	0.01
1,2,3,4,7,8,9-HCDF	0.01
OCDF	0.0001

*1998 WHO TEF values (van den Berg et al. 1998); see text for details.

Adverse biological effects associated with concentrations of 2,3,7,8-substituted PCDD/Fs in sediment are represented in the BEDS. In the BEDS, changes in benthic invertebrate abundance, and weight and length are the most common indicators of adverse biological effects (Environment Canada 2000). Less frequently observed endpoints include deformities and proportion of sexually mature individuals. Ingersoll et al. (1992) summarized information collected from benthic field surveys of several areas in the Great Lakes basin, including the Buffalo and

Saginaw Rivers and Indiana Harbour. Mean TEQ_{fish} concentrations in the collected sediments ranged from 0.12 to 2 100 ng·kg^{-1} dw. Relative densities of those species present were used to assess the health of benthic communities. For example, sediments collected from Canagagigue Creek, Ontario, were assessed for their potential toxicity to an ephemeropteran (*Hexagenia limbata*), larvae of a midge (*Chironomus tentans*), and fathead minnows (Jaagumagi and Bedard 1997). Mean TEQ_{fish} concentrations in groups of samples ranged from 10.86 to 184.79 ng·kg^{-1} dw. Endpoints measured in bioassays of collected sediments included survival and growth. Field-collected sediments that significantly reduced these endpoints were deemed toxic. For example, sediments containing a mean TEQ_{fish} concentration of 184.79 ng·kg^{-1} dw were significantly toxic (i.e., 50% mortality) to *H. limbata* after 21 d of exposure (Jaagumagi and Bedard 1997). In comparison, sediments with a mean TEQ_{fish} concentration of 10.86 ng·kg^{-1} dw were not significantly toxic (i.e., 0% mortality) to *H. limbata* in the same bioassay (Jaagumagi and Bedard 1997).

The marine BEDS data set is too small to draw generalizations regarding the indicators and incidence of adverse biological effects.

Concentrations

Environmental monitoring of PCDD/Fs in sediment has focused on contaminated sites, particularly in the vicinity of pulp and paper mills. The Canadian pulp and paper industry has made significant reductions in PCDD/F effluent emissions since the Pulp and Paper Effluent Regulations of 1992 (Halliburton and Simpson 1999). Improvements to industry technology have translated into significant improvements in the health of wildlife (Environment Canada 2000). Comprehensive monitoring of Canadian sediments occurred from 1986 to 1993; recent data are not readily available. As such, the environmental concentrations of PCDD/Fs in sediments reported below on a geographically comparative basis may not reflect current levels.

In general, 2,3,7,8-substituted PCDD/Fs in freshwater samples were not detected (<1–200 ng·kg^{-1} dw depending on congener and laboratory) in samples collected upstream from pulp mills. Sediment samples collected from downstream sites in British Columbia and Ontario had the highest TEQ_{fish} levels, 158 and 126 ng·kg^{-1} dw, respectively (Dwernychuk et al. 1991a, 1991b; Mah et al. 1989; Trudel 1991). PCDD/F levels at downstream sites in Alberta and Quebec were lower, with TEQ_{fish} levels of 3.7 and 47 ng·kg^{-1} dw, respectively (Crosley 1996; Trudel 1991). In the Maritimes, the highest TEQ_{fish} level at a downstream site was 15 ng·kg^{-1} dw (Trudel 1991). In Alberta, British Columbia, and Quebec, 2,3,7,8-TCDF was the congener most often detected at high levels, while in Ontario, OCDD and OCDF were more prevalent.

Fewer data are available for marine and estuarine sediments compared to freshwater sediments, although PCDD/Fs have been measured in both the Pacific and Atlantic regions of Canada (Environment Canada 2000).

The most contaminated coastal marine areas of British Columbia appear to be Howe Sound at Squamish and Hecate Strait, with TEQ_{fish} levels up to 127 and 101 ng·kg^{-1} dw, respectively (Trudel 1991). Sediment samples collected from the Atlantic coast were much less contaminated than those from the Pacific coast. The most contaminated coastal site in Nova Scotia was Port Hawksbury, with a TEQ_{fish} level of 10.5 ng·kg^{-1} dw (Trudel 1991).

Additional Considerations

The likelihood of adverse biological effects occurring in response to exposure to PCDD/Fs at a particular site depends on the sensitivity of individual species and the endpoints examined. In addition, a variety of physicochemical factors (e.g., lipophilicity and size and spatial configuration of individual congeners, and changes in PCDD/F profiles), geochemical factors (e.g., organic matter content, clay content, and sediment particle size), and biological factors (e.g., feeding behaviour and uptake rates) affect the bioavailability of PCDD/Fs (see BSAFs above and Environment Canada 2000).

Currently, the degree to which dioxins and furans will be bioavailable at particular sites cannot be predicted accurately from the physicochemical characteristics of sediments or the attributes of endemic organisms (Environment Canada 2000). Nonetheless, the incidence of adverse biological effects associated with exposure to dioxins and furans increases as their concentrations increase in a range of sediment types (Figure 2). Therefore, the recommended Canadian ISQGs and PELs for dioxins and furans will be useful in assessing the ecotoxicological significance of dioxins and furans in sediments.

The CCME decided recently not to recommend Canadian water quality guidelines for highly hydrophobic substances because of higher scientific uncertainty in the assessments of these chemicals and vanishingly small concentrations found in surface waters. Instead, guideline development has focused on SQGs and tissue residue guidelines (TRGs) to protect wildlife that consume aquatic biota. The ISQGs and PELs recommended for dioxins and furans do not specifically account for the potential for adverse biological effects on higher trophic levels that may result from dietary exposure. Therefore, TRGs 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.

Implementation of the Canadian ISQGs and the TRGs for PCDD/Fs requires special consideration of polychlorinated biphenyls (PCBs). PCBs are a class of 209 synthetic organic compounds; 12 PCB congeners have a coplanar structure. Like 2,3,7,8-substituted PCDD/Fs, coplanar PCBs elicit toxic effects through the *Ah* receptor and thereby contribute to TEQ. Thus, the environmental quality guidelines (EQGs) for PCDD/Fs and PCBs are intimately related and should be considered concurrently. For sediment, the TEQ_{fish}-based ISQGs presented here should apply to concentrations of 2,3,7,8-substituted PCDD/Fs and coplanar PCBs to protect aquatic life from additive effects mediated by the *Ah* receptor. To protect aquatic life from non-coplanar PCBs, the total concentration of all PCB congeners should meet the recommended ISQGs for total PCBs (34.1 and 21.5 $\mu g \cdot kg^{-1}$ dw for freshwater and marine sediments, respectively). Where it can be demonstrated that the PCB congener profile is consistent with that of Aroclor 1254, then the ISQGs for Aroclor 1254 (60 and 63.3 $\mu g \cdot kg^{-1}$ dw for freshwater and marine sediments, respectively) apply. (For background information on and derivation details of Canadian EQGs for PCBs, see Environment Canada 1998 and 1999b.)

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Excerpt from Publication No. 1299; ISBN1-896997-34-1

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