Canadian Sediment Quality Guidelines for the Protection of Aquatic Life

TOXAPHENE

Toxaphene is the common name for a complex mixture of largely uncharacterized derivatives of chlorinated camphenes and bornanes (CCREM 1987). The term "polychlorinated camphenes" (PCCs) refers to a mixture of structurally similar compounds and isomers, more than two-thirds of which contain seven to nine chlorine atoms (CCREM 1987). At least 202 isomers are known to exist (Saleh 1991), although as many as 670 configurations are possible (Jansson and Wideqvist 1983). The mixture of PCCs that make up technical grade toxaphene is discussed because of a lack of information on individual isomers.

Toxaphene, developed in 1946, is a broad-spectrum insecticide (ATSDR 1994). In 1982, evidence that PCCs were detrimental to environmental and human health led to de-registration of most registered uses of toxaphene under the Pest Control Products Act, with use restricted to ectoparasite control in livestock. The United States banned all uses in 1990 (Saleh 1991). Toxaphene has been identified as a Track 1 substance by Environment Canada because it is persistent, bioaccumulative, released primarily as a result of human activities, and is considered "CEPA-toxic" under the Canadian Environmental Protection Act (Environment Canada 1997a). While regulatory actions have eliminated many of the historic sources, PCCs still represent a significant environmental concern for several reasons. First, as a result of the extensive use of highly persistent PCCs (with half-lives of up to 14 years reported in soils [ATSDR 1994]) in North America for more than three decades, present levels of toxaphene may be linked to historic uses in Canada and the United States. Second, long-range atmospheric transport of PCCs from Asia, Africa, and Eastern Europe, where they are still produced and extensively used, may result in significant, ongoing deposition in Canadian ecosystems. In addition, there is some evidence that certain PCCs are produced unintentionally during manufacturing processes that use chlorination (ATSDR 1994). Therefore, although the use of toxaphene has been severely restricted in North America, its physicochemical properties have resulted in long-range transport and subsequent accumulation in soils, sediments, and biological tissues.

Canadian interim sediment quality guidelines (ISQGs) for toxaphene in freshwater and marine sediments were developed according to the protocol described in CCME (1995) (Table 1). The ISQGs refer to total concentrations of toxaphene in surficial sediments (i.e., top 5 cm) on a dry weight basis, as quantified by extraction and determination by standard analytical procedures. Freshwater and marine ISQGs could not be developed for toxaphene using either a modification of the National Status and Trends Program approach or the spiked-sediment toxicity test approach because of insufficient data. Therefore, guidelines from other jurisdictions were considered for adoption in the short term. The chronic freshwater sediment quality criterion for toxaphene of 0.01 $\mu g \cdot g^{-1}$ organic carbon and the chronic marine sediment quality criterion of 0.01 $\mu g \cdot g^{-1}$ organic carbon have been established by the New York State Department of Environmental Conservation using the equilibrium partitioning approach (NYSDEC 1994). These values are the lowest of the guidelines available from other jurisdictions. They have been adjusted in order to express the guidelines as dry weight of sediment so that they are consistent with other Canadian ISQGs. Therefore, the provisional freshwater ISQG is 0.1 $\mu g \cdot kg^{-1}$, and the provisional marine ISQG is 0.1 $\mu g \cdot kg^{-1}$ (assuming 1% TOC) (Table 1). The ISQGs represent numerical concentrations recommended to support and maintain aquatic life associated with bed sediments.

Toxicity

Spiked-sediment toxicity tests that evaluated the effects of sediment-associated toxaphene on freshwater and marine organisms were limited. However, a number of field studies have been conducted to evaluate the effects of sediment-associated toxaphene in freshwater and marine ecosystems (Environment Canada 1998, Appendixes Ia and Ib). Studies on field-collected sediments that

Table 1. Interim sediment quality guidelines (ISQGs) for toxaphene (PCCs) ($\mu g \cdot kg^{-1}$ dw).

	Freshwater	Marine/estuarine
ISQG	0.1*	0.1*

* Provisional 1% TOC; adoption of the chronic sediment quality criterion of 0.01 $\mu g \cdot g^{-1}$ TOC of the New York State Department of Environmental Conservation (NYSDEC 1994).

measured concentrations of toxaphene, along with concentrations of other chemicals, and associated biological effects are compiled in the Biological Effects Database for Sediments (BEDS) (Environment Canada 1998). Adverse biological effects for toxaphene in the BEDS include decreased benthic invertebrate diversity and abundance and increased mortality. Measurements of chronic toxicological endpoints such as growth or reproductive effort were rare in the BEDS. Concentrations of toxaphene in the freshwater BEDS ranged from 0.12 to 5 $\mu g \cdot kg^{-1}$. In the marine BEDS, concentrations ranged from 0.051 to 109 $\mu g \cdot kg^{-1}$.

Results of both marine and freshwater field studies indicate that toxaphene is not highly acutely toxic; however, the results of longer-term studies not included in the BEDS have demonstrated that toxaphene causes a range of chronic effects. In addition to reducing longevity, exposure to toxaphene is known to induce adverse effects on cardiovascular, hepatic, renal, endocrine, immunological, and neurological systems (ATSDR 1994). Toxaphene has also been shown to exhibit genotoxicity and carcinogenicity in laboratory studies (Saleh 1991).

Concentrations

The limited data available on concentrations of toxaphene in Canadian freshwater and marine sediments indicate that most concentrations are above the ISQGs. For example, toxaphene was not detected in freshwater sediments collected at 14 locations in the lower Fraser River, British Columbia, between 1987 and 1992 (Swain and Walton 1988, 1993). However, the detection limits achieved in these studies were relatively high (30 to 300 $\mu g \cdot kg^{-1}$). More recently, at much lower detection limits (i.e., <1.1 $\mu g \cdot kg^{-1}$), toxaphene was not detected in sediments from six lake systems in British Columbia (R.W. Macdonald 1998, Institute of Ocean Sciences, pers. com.). However, sediment concentrations in lakes in northwestern Ontario, western Canada, and the Arctic ranged from 2.6 to 5.3 $\mu g \cdot kg^{-1}$, <0.2 to 110 $\mu g \cdot kg^{-1}$, and 0.01 to 17 $\mu g \cdot kg^{-1}$, respectively (Muir et al. 1995; Donald et al. 1998).

In marine and estuarine sediments, concentrations are typically below detection limits (Environment Canada 1998). For example, in 1989, Swain and Walton (1990) sampled 12 locations in Boundary Bay, British Columbia, and observed that concentrations in the sediment were below the detection limit of <30 $\mu g \cdot kg^{-1}$. Subsequent monitoring in this area also revealed undetectable levels of toxaphene (<30 $\mu g \cdot kg^{-1}$) (Swain and Walton 1990, 1993).

Additional Considerations

Regardless of the origin of toxaphene in sediments, aquatic organisms may be adversely affected by exposure to elevated levels. However, the occurrence of adverse biological effects from exposure to toxaphene cannot be precisely predicted from concentration data alone. The likelihood of adverse biological effects occurring at a particular site depends on the sensitivity of individual species, the endpoints examined, as well as a variety of physicochemical (e.g., chlorination and K_{ow}), geochemical (e.g., TOC and particle size), and biological (e.g., feeding behaviour and life stage) factors that affect the bioavailability of toxaphene (Environment Canada 1998).

Benthic organisms are exposed to both particulate and dissolved forms of toxaphene in interstitial and overlying waters, as well as to sediment-bound toxaphene through surface contact and sediment ingestion. Toxaphene can bioaccumulate in biological tissues and biomagnify in the food chain, but not to the same extent as other more highly persistent chlorinated hydrocarbons (e.g., DDT and PCBs). This is largely attributed to the relatively lower hydrophobicity and higher water solubility of toxaphene, which enables metabolic breakdown to occur more readily than that of other chlorinated hydrocarbons.

Some physicochemical characteristics of nonpolar organic compounds have the potential to influence their bioavailability to aquatic organisms. Octanol–water partition coefficients (K_{ow}) and water solubility have been identified as important factors affecting the bioavailability of sediment-associated organic substances. Estimates of K_{ow}s for PCCs differ substantially among studies. For example, Sanborn et al. (1976) reported a log K_{ow} of 2.92 for PCCs, whereas Karickhoff and Long (1995) reported that the log K_{ow} for PCCs was much higher at 5.56.

While other organochlorine pesticides, such as DDT, tend to accumulate in the tissues with the highest lipid content (Rogers and Hall 1987; Muir et al. 1992; Larsson et al. 1993), the distribution of toxaphene in fish tissues appears to be less related to lipid content (Muir et al. 1993a, 1993b, 1994a, 1994b). This may, in part, be due to the relatively higher water solubility of toxaphene compared to that of other organochlorine pesticides.

Environmental weathering, photolysis, volatilization, and preferential degradation of certain components may

significantly modify the composition of PCCs in sediments (Bidleman et al. 1988; Fowler et al. 1993). Selective uptake, metabolization, and excretion of certain PCCs by aquatic and terrestrial organisms can further alter the mixture of PCCs in tissue samples (ATSDR 1994). Therefore, PCCs in environmental samples may be very different from the technical grade toxaphene that is used as the analytical standard (Hargrave et al. 1994). Isomer-specific analyses would ameliorate this limitation, however, only a few of the hundreds of isomers present in technical grade toxaphene have been identified.

The complexity of the chemical composition of toxaphene and the difficulties associated with the analytical measurement of its constituents may account for the limited data currently available. Some areas that require further research include composition and chemical identification of PCCs in commercially formulated technical grade toxaphene, physical and chemical properties of PCCs, and the environmental fate, bioavailability, and toxicity of sediment-associated toxaphene.

Although ISQGs 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 toxaphene (Kidd et al. 1995; Muir et al. 1990; 1994a, 1994b). Canadian tissue residue guidelines for the protection of wildlife consumers of aquatic organisms have been developed to consider the effects of bioaccumulative substances, such as toxaphene, on higher trophic levels (Environment Canada 1997b). Therefore, Canadian tissue residue guidelines should be used in conjunction with ISQGs to evaluate the potential for adverse biological effects on other components of aquatic ecosystems.

The ISQGs recommended for toxaphene reflect our current state of knowledge regarding the concentrations, environmental fate, and biological effects of sediment-associated toxaphene. These ISQGs provide reference points that can be used in conjunction with other scientific tools to evaluate the potential for adverse biological effects of toxaphene in sediments. In addition, these guidelines provide interim targets that can be used in assessing progress toward virtual elimination. In the above context, it is anticipated that the recommended ISQGs for toxaphene will be useful in assessing the ecotoxicological significance of toxaphene in sediments.

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