REVIEW OF APPROACHES USED TO ESTABLISH SEDIMENT BENCHMARKS FOR PCDD/Fs

Richard J Wenning[1], Linda Martello[1], Timothy Iannuzzi[2]

[1]ENVIRON International, Emeryville, CA USA
[2]BBL Sciences, Annapolis, MD USA

Introduction

At present, regulatory limits for polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in sediments have not been promulgated in the United States, although various sediment quality guidelines (SQG) and benchmark values have been proposed by several state and federal agencies for specific sediment management purposes. The impetus for developing SQGs or sediment benchmarks for PCDD/Fs is largely driven by concerns regarding the potential for bioaccumulation in fish and benthic invertebrates, uptake by fish-eating birds and wildlife through aquatic food webs, and consumption by recreational and subsistence fishermen [i, ii, iii]. While sediment-based benchmarks cannot be used to assess population-level risks in aquatic systems, there is a need for such benchmarks to enable regulators to screen sites to determine if the levels of PCDD/Fs that are present warrant a risk-based investigation.

Building on earlier published work [iv], this review summarizes the different approaches that have been used to identify sediment benchmarks for PCDD/Fs in the U.S. and elsewhere. The approaches most often used are discussed, as well as the data gaps relevant to understanding the fate of PCDD/Fs in aquatic environments and the direction necessary for establishing a scientifically defensible protocol to assess PCDD/Fs in sediment.

Available PCDD/F Sediment Benchmarks

At present, 44 numeric values have been proposed as benchmarks for evaluating total PCDD/Fs, 2,3,7,8-TCDD, or other PCDD/F congeners in sediments in the U.S., Canada, and elsewhere (Table 1). Seven benchmarks have been derived exclusively for the protection of human health, ranging over several orders of magnitude from 0.9 pg/g to 60 pg/g. Ten benchmarks have been derived to

Table 1. Summary of proposed sediment quality guidelines (SQG) and benchmark values used to evaluate PCDD/Fs in sediments and aquatic environments.

Chemical	Media	Value	Approach	Reference
Proposed to Protect Human Health				
2,3,7,8-TCDD	FW & SW	10,000 pg/g OC	equilibrium partition (EqP)	NYDEC (1999) [21]
2,3,7,8-TCDD	FW & SW	10-100 pg/g	tissue residue (TR)	NYDEC (1989) [22]
2,3,7,8-TCDD	FW	1 pg/g	detection limit (DL)	WDNR (1988) [23]
PCDD/Fs	--	9.0 pg/g	cleanup screening level	WADE (1997) [24]
PCDD/Fs	--	0.90 pg/g	Sediment. quality standard	WADE (1997) [24]
PCDDs	--	60 pg/g	case-specific sediment standard	WADE (1997) [24]
2,3,7,8-TCDF	--	5-10 pg/g	detection limit	Germany (pc) [25]
Proposed to Protect Wildlife				
2,3,7,8-TCDD	FW	20 pg/g	sediment quality guideline (SQG)	USEPA (1993) [1]
2,3,7,8-TCDD	FW	33 pg/g	SQG	USEPA (1993) [1]
2,3,7,8-TCDD	--	60-100 pg/g	TR - fish	USEPA (1993) [1]
2,3,7,8-TCDD	--	21-210 pg/g	TR - birds	USEPA (1993) [1]
2,3,7,8-TCDD	--	2.5 - 25 pg/g	TR - mammals	USEPA (1993) [1]
2,3,7,8-TCDD	FW & SW	3-30 pg/g	TR - wildlife	NYDEC (1989) [22]
2,3,7,8-TCDD	FW & SW	<1E+07 pg/g OC	EqP - aquatic biota	NYDEC (1999) [21]
2,3,7,8-TCDD	FW & SW	200 pg/g OC	EqP - wildlife	NYDEC (1999) [21]
2,3,7,8-TCDD	fish tissue	0.059	BSAF	USEPA (1995) [26]
2,3,7,8-TCDD	amphipod	25,000 pg/g	NOAEL	Barber et al. (1998) [27]
Proposed to Protect Human Health and Wildlife				
2,3,7,8-TCDD	FW	10 pg/g	sediment quality objective	Boddington (1990) [28]
2,3,7,8-TCDD	FW	100,000 pg/g	EqP	Newell (1989) [29]
2,3,7,8-TCDD	FW & SW	10 pg/g	DL	NYDEC (1999) [21]
2,3,7,8-TCDD	FW & SW	0.014-0.14 pg/g	TR	NYDEC (1989) [22]
2,3,7,8-TCDD	--	7,400 pg/g OC	TR	Parkerton (1991) [30]
2,3,7,8-TCDD	--	3,300 pg/g OC	TR - whole crab	Parkerton (1991) [30]
2,3,7,8-TCDD	--	20,400 pg/g OC	TR - crab muscle	Parkerton (1991) [30]
PCDDs	FW	3.3 pg/g	ecological data quality level	USEPA (1998) [31]
PCDFs	FW	0.013 pg/g	ecological data quality level	USEPA (1998) [31]
2,3,7,8-TCDD	SW	5 pg/g	SQG – Gray's Harbor, WA	WADMMP (pc) [32]
PCDDs	SW	15 pg/g	SQG – Gray's Harbor, WA	WADMMP (pc) [32]
PCDDs	residential soil	1000 pg/g	Preliminary remediation goal (PRG)	USEPA (1998) [33]
PCDDs	industrial soil	5,000 to 20,000 pg/g	PRG	USEPA (1998) [33]
2,3,7,8-TCDF	FW	1 pg/g dw	disposal of dredged sediments	Fitchko (1989) [34]
2,3,7,8-TCDD	FW	1 pg/g	disposal of dredged sediments	Sullivan (1985) [35]
2,3,7,8-TCDF	FW	1 pg/g	disposal of dredged sediments	Sullivan (1985) [35]
2,3,7,8-TCDD	marine	>1,000 pg/g	DL	USACE (1983) [5]
2,3,7,8-TCDD	fish tissue	0.69 pg/g	National Sediment Quality Survey	USEPA (1998) [36]
2,3,7,8-TCDD	--	4 pg/g	dredged material disposal	WADE (1991) [37]
2,3,7,8-TCDD	FW CMC	<10 pg/g	screening tables (SQuiRTs)	NOAA (1999) [38]
2,3,7,8-TCDD	FW CCC	< 0.01 pg/g	SQuiRTs	NOAA (1999) [38]
2,3,7,8-TCDD	FW sed.	8.8 pg/g dw	SQuiRTs - upper threshold	NOAA (1999) [38]
2,3,7,8-TCDD	SW	3.6 pg/g dw	SQuiRTs - apparent effects	NOAA (1999) [38]
PCDD/Fs	FW	0.85 pg TEQ/g dw	environmental quality guidance	CCME (1999) [39]
PCDD/Fs	FW	21.5 pg TEQ/g dw	environmental quality guidance	CCME (1999) [39]
PCDD/Fs	SW	0.85 pg TEQ/g dw	environmental quality guidance	CCME (1999) [39]
PCDD/Fs	SW	21.5 pg TEQ/g dw	environmental quality guidance	CCME (1999) [39]

Notes:

--: not indicated; CCME: Canadian Council of Ministers of the Environment; dw: dry weight; Env. Can.: Environment Canada EqP: equilibrium partitioning; FW: fresh water; NOAEL: No observable adverse effect level; NYDEC: New York State Dept. of Environmental Conservation; sed: sediment; SW: salt water; TEQ: toxicity equivalent; TR: tissue residue; USACE: U.S. Army Corps of Engineers; NOAA: U.S. National Oceanic and Atmospheric Administration; WADE: Washington Dept. of Ecology; WADMMP: Washington Dredged Material Management Plan; WDNR: WI Department of Natural Resources.

protect a range of aquatic organisms (i.e., benthic invertebrates, fish, shellfish) and wildlife that may be exposed through the food web. These values also range widely, from 2.5 to 25,000 pg/g (dry weight) and 200 to <10,000,000 pg/g organic carbon (OC). Twenty-eight benchmarks are intended to protect both human and ecological receptors, with values ranging from 0.01 pg/g to 100,000 pg/g and 3,300 to 24,000 pg/g OC.

None of these benchmarks have been adopted for widespread regulatory application in the U.S. or abroad. The most often cited benchmark values include the U.S. EPA Region 10 and the U.S. ACE dredge spoils disposal guidelines (4 and 1000 pg/g, respectively) [v, vi], the U.S. EPA's fish and wildlife (bird and mammal) guidelines developed specifically for Lake Ontario (2.5 – 210 pg/g)[1] and the benchmark for sediments in the Great Lakes (10 ppt) proposed by the Great Lakes Science Advisory Board of the International Joint Commission [vii].

Approaches Used to Establish Different Benchmarks

In general, three approaches have been favored by scientists and regulators as the most appropriate for use in deriving benchmark concentrations of PCDD/Fs in sediment: the background approach, equilibrium partitioning (EqP), and the tissue residue-based (TRB) method. The EqP method is currently supported by the USEPA for the development of sediment quality criteria for non-ionic organic chemicals [viii]. The EqP approach assumes that partitioning of sediment-bound chemicals between pore water and sediment organic carbon is governed by the organic carbon partition coefficient (K_{oc}) under steady-state conditions.

The TRB approach calculates the concentration in sediment predicted to result in a tissue residue in biota that poses no harm to an organism or to predators that consume the organism [1]. The TRB method is based on biota-sediment accumulation factors (BSAF). BSAFs are calculated based on the assumption that non-polar organic chemicals readily partition from sediment OC to lipid in aquatic organisms [ix]. The TRB method addresses several sources of uncertainty typically associated with estimating the partitioning of PCDD/Fs between sediments, water and biota, particularly the determination of octanol-water partition coefficients (K_{ow}), K_{oc} values, and bioconcentration factors (BCFs). It is widely recognized that bioconcentration of PCDD/Fs by aquatic organisms from water is limited and generally insignificant as an exposure pathway, and that body burdens are primarily attributable to ingestion of food and sediment [x, xi].

Limitations in the Current Approaches

The application of chemical-specific SQGs or benchmarks is generally limited because proposed or promulgated guidelines do not address the additive, synergistic, or antagonistic effects of co-occurring contaminants, or the bioaccumulative effects to aquatic biota, wildlife, and humans [xii]. In addition, such generic benchmarks do not take into account the various site-specific factors that regulate exposure to, and the effects of, chemical contaminants in aquatic ecosystems.

Methods that incorporate direct measures of biological effects, such as spiked sediment bioassays (SSB), sediment quality Triads (SQT), and toxicity identification evaluations (TIE) are to some degree able to account for additive, synergistic and antagonistic effects to benthic organisms (or appropriate laboratory test organisms), but do not address bioaccumulative effects in wildlife or humans.

Furthermore, the limited information available regarding congener-specific PCDD/F toxicity in aquatic organisms and sediment-water partitioning is primarily responsible for the considerable uncertainties associated with the application of different sediment assessment methods and sediment screening models. Three important data gaps in current approaches to PCDD/F ecological risk assessment have been identified that affect all sediment assessment methods: (a) the absence of dose-response relationships in a wide variety of aquatic, avian and mammalian species from a wide variety of habitat types; (b) identification of indicator species representative of a variety of habitat types; and (c) methodological and statistical guidance for the determination of site-specific BSAF values [1, xiii].

The EqP method has been criticized as being non-representative of field sediment chemistry conditions [11]. In particular, chemical concentrations in the water column and sediments are often not in equilibrium, particularly in estuaries, rivers and streams. Several significant uncertainties are associated with the EqP model, including (a) the identification of the appropriate final chronic toxicological value (FCV), which typically are developed for water column species exposed to sediment pore water; (b) the variability of reported K_{ow} and K_{oc} values; (c) the assumption that organic carbon is the only sediment parameter that influences bioavailability; and (d) the uncertainty regarding the role of suspended solids [12, xiv, xv, xvi]. The TRB method may be more appropriate than the EqP method for developing sediment benchmarks for PCDD/F; however, there is not sufficient scientific data to develop acceptable tissue concentrations for representative organisms from a variety of aquatic ecosystems [xvii]. This is particularly true for estuarine and marine organisms, for which virtually no PCDD/F tissue residue-toxicity relationships have been established [1, 10, xviii].

A major limitation of both the EqP and TRB methods, as well as other methods of deriving sediment quality guidelines and benchmarks, is the inability to account for potential intermittent or infrequent exposure(s) of mobile or migrating organisms such as fish and crustaceans [10]. The same is true for aquatic wildlife such as fish-eating birds that may use an affected water body for foraging or nesting. The available biological models typically assume that organisms are exposed to chemicals in sediments for their entire life. Although this may be true for some benthic invertebrates, it is not true for the vast majority of aquatic organisms, particularly migratory fish and crustaceans that are consumed by humans and wildlife. This limitation would likely result in benchmarks intended to protect humans and wildlife that are overly conservative.

Data Needs

The promulgation of a national SQG or benchmark value for PCDD/Fs does not appear to be forthcoming in the U.S. anytime soon. In U.S. states and some agencies where guideline values have been promulgated or proposed and used for sediment management decision-making, the results have not been without controversy. In New York / New Jersey Harbor, for example, where sediment management is viewed as a high priority by several local, state, and federal agencies, there has been little agreement and significant scientific debate over the appropriate method for determining pass/fail criteria for PCDD/Fs in dredged material [xix]. Data collected over the past ten years have produced contrary scientific evidence on the toxicity, bioavailability and bioaccumulation potential of PCDD/F congeners in the limited number of organisms for which studies have been conducted [xx]. In addition, there is general agreement that the bioavailability and toxicity of PCDD/F, as well as many other sediment-contaminants, is dependent on several waterway-specific physical and chemical properties such as grain size and organic carbon content of sediments, sediment chemistry, rates of sediment resuspension/remobilization, and the resident biological community [12].

If the current approach to setting total maximum daily levels (TMDLs) in California and elsewhere in the U.S. is any indication, it is more likely in the future that SQGs for PCDD/Fs and many other organic and inorganic contaminants will be established for individual watersheds and/or for different sediment management purposes. Waterway-specific assessments can provide a more accurate classification of the relative degree of contamination and potential ecotoxicity. In addition, such an approach takes into account the ecological, commercial, and recreational values of a waterway to both humans and ecological receptors. By doing so, however, there must be an adequate chemistry, biological, and ecological database from which to understand conditions in both the aquatic and the surrounding terrestrial environments and to derive meaningful and relevant environmental quality benchmarks.

Among the three approaches identified to date, the TRB method, which relies on acceptable tissue concentrations and BSAFs to calculate sediment concentrations, appears to be one of the more promising approaches for developing SQGs. As part of a weight-of-evidence approach to ecological risk assessment [12], the TRB approach, together with information derived using other assessment tools, may provide the best means for establishing a scientifically defensible foundation for developing benchmarks to screen effect and no-effect concentrations in sediment on a waterway-specific basis. In the meantime, additional work is needed on several ecological and ecotoxicological issues important to understanding the fate of PCDD/Fs in sediments and aquatic environments, particularly including tissue residue-toxicity relationships for PCDD/Fs in a variety of aquatic organisms and habitats.

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