# A Guideline Value for Dioxin-Like Compounds in Marine Sediments

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Abstract: Sediments to be dredged as part of the installation of a harbor crossing in Sydney, Australia, contained measurable concentrations of dioxin-like compounds. To assess the suitability of these sediments for ocean disposal, a defensible sediment quality guideline value (SQGV) for dioxin-like compounds, expressed as pg toxic equivalent (TEQ)<sub>fish</sub>/g dry weight, was required. There were deemed to be too many uncertainties associated with a value derived using effects data from field studies. A similar issue was associated with values based on equilibrium partitioning from sediment to pore water, largely associated with the wide range of reported sediment:water partition coefficients. Greater certainty was associated with the use of a tissue residue approach based on equilibrium partitioning between sediment and organisms determined using tissue concentrations in fish, the most sensitive aquatic biota, and biota:sediment accumulation factors. The calculation of an appropriate SQGV used data for dioxin-like compounds in both fish and sediments from Sydney Harbor. A conservative SQGV for dioxin-like compounds of 70 pg TEQ/g dry weight was deemed to be adequately protective of biota that might be exposed to these contaminants in sediments at the ocean spoil ground. The approach is transferable to similar situations internationally. *Environ Toxicol Chem* 2023;42:257–271. © 2022 The Authors. *Environmental Toxicology and Chemistry* published by Wiley Periodicals LLC on behalf of SETAC.

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# INTRODUCTION

Sediment from Sydney Harbor is proposed to be dredged as part of the construction of a second harbor road tunnel crossing. The project development works have demonstrated the presence of dioxin-like compounds in sediments from the project footprint for the proposed road tunnels and it was necessary to determine whether the concentrations of these compounds will limit their suitability for offshore disposal.

Sydney Harbor sediments have been a historical source of dioxin-like compounds, largely derived from a chemical

This article includes online-only Supporting Information.

manufacturing plant operated by Timbrol Pty from 1928 and by Union Carbide from 1957. Products included 2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid, dichlorodiphenyltrichloroethane, agent orange, and bisphenol A. These products were produced largely in the period 1943–1976. The plant was located at Homebush Bay, some 12 km upstream of the proposed harbor crossing relevant for this infrastructure project. Sediments in Homebush Bay have been analyzed to a depth of 1 m and contained elevated concentrations of polychlorinated dibenzo-p-dioxins (dioxins), polychlorinated dibenzofurans (furans), and polychlorinated biphenyls (PCBs) as byproducts of the manufacturing processes prior to the commencement of the remediation works (Parsons Brinckerhoff, 2002). These sediments were remediated from 2006 to 2011 by removing 0.5 m of sediments in the most affected locations (Parsons Brinckerhoff, 2002). These compounds were distributed from Homebush Bay to areas further afield in the harbor over the decades, resulting in surface sediments at the proposed dredging site having concentrations of compounds such as

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Concentrations of dioxin-like compounds in sediments in Homebush Bay, the most contaminated area of Sydney Harbor, were as high as 5200 pg/g dry weight, but mainly in the range 400–900 pg/g (Parsons Brinckerhoff, 2002), whereas in the harbor further to the east, concentrations ranged from 32 to 370 pg toxic equivalent (TEQ)people/g dry weight (based on TEQ factors for human health impacts; Van den Berg et al., 2006), largely in depositional zones. In the area proposed for dredging during this infrastructure project, concentrations were reported ranging from 3 to 90 pg TEQfish/g dry weight (based on TEQ factors for on impacts for fish; Van den Berg et al., 1998). Surface sediments in this area were dominated by TCDD whereas deeper sediments (predominantly clay), which predate European settlement, were dominated by the far less toxic octachlorodibenzo-p-dioxin, largely derived from naturally occurring sources like bushfires, volcanos, and microbial degradation.

Concentrations of dioxin-like compounds are typically reported as toxic equivalent concentrations. Toxicity equivalency factors (TEFs) are used to convert the concentrations of each of the dioxin congeners into an equivalent total amount of 2,3,7,8-TCDD for use in risk assessment. There are TEFs for people, birds, and fish with those for fish being used for ecological risk assessment (Van den Berg et al., 1998) and they will be the basis for the calculations in the present study.

The evaluation of dredge material in Australia is undertaken in accordance with the National Assessment Guidelines for Dredging (NAGD, 2009). These guidelines outline the evaluation process and provide screening values against which to assess a range of contaminants. Although there are established sediment quality guideline values (SQGVs) for a range of metal contaminants, there are very few for organic contaminants.

In addition, there have been very few SQGVs for dioxinlike compounds published in other jurisdictions, limited largely by a lack of reliable toxicity data. lannuzzi et al. (1995) specifically reviewed the status of SQGVs for TCDD at that time. The values listed used either 1) a consideration of equilibrium partitioning between sediments and water or 2) a tissue residue partitioning approach where acceptable tissue concentrations and biota:sediment accumulation factors (BSAFs) were used to calculate sediment concentrations. They concluded that the tissue residue approach was likely to be better suited for developing appropriate SQGVs for this group of chemicals in the future.

In 2001, Canadian guidelines for dioxin-like compounds were published based on the use of sediment effects data from field studies (Canadian Council of Ministers of the Environment [CCME], 2001), following the approach pioneered by Long, MacDonald and coworkers (Long et al., 1995, 1998) as reviewed by Batley et al. (2005).

The present study critically reviews the approaches to deriving SQGVs for dioxin-like chemicals to date and uses current chemical and ecotoxicological data to derive a defensible value that can be used to evaluate the ecological

impacts of sediments to be dredged and potentially disposed of at sea.

# **METHODS**

The first step in the derivation of a defensible SQGV for dioxin-like compounds that could be applied to sediments from Sydney Harbor involved the identification of published SQGVs for these compounds that are being applied internationally, in particular, in the United States, Canada, and Europe. For the identified SQGVs, an evaluation of the basis for their derivation was undertaken. This involved obtaining the source publications explaining the derivation as well as each document referenced in the derivation document where publicly accessible. The range of SQGV derivation methods was critically evaluated. Overall, three basic approaches were identified: 1) effects-based guideline derivation, 2) equilibrium partitioning-based guideline derivation, and 3) tissue residue-based guideline derivation. These approaches require information about the ecotoxicity of this group of chemicals, their potential for bioaccumulation, and consideration of the relevant chemical characteristics such as the octanol:water partitioning coefficient (log  $K_{ow}$ ).

Identification of toxicity data that could be used in a species sensitivity distribution (SSD) to determine concentrations that would be protective of the ecosystem was an important next step. This required a literature review to identify such data and to evaluate the type of data that would be most relevant for such a distribution (organism type and exposure pathway). The literature review was undertaken by considering data from the derivation documents for existing guidelines, summary documents from the US Environmental Protection Agency (USEPA), a key recent SSD in the paper by Steevens et al. (2005), and consideration of relevant ecotoxicity data in publications (up to early 2021). The latter were identified using standard literature search techniques. The data were then used to generate an SSD to calculate the 95% and 99% species protection values in accordance with Australian guidance (NAGD, 2009; Simpson et al., 2013; Warne et al., 2018). As part of the process for generating the SSD, consideration was given to the most appropriate organism type and exposure pathway to use.

For the tissue-residue approach, derivation of an appropriate BSAFs (USEPA, 1993) using data from Sydney Harbor was a key consideration. In doing this, the chemical characteristics of this group of chemicals needed to be reviewed to ensure that choices made in regard to BSAFs were appropriately conservative, given the wide range of individual dioxinlike chemicals.

Once all relevant inputs for the SQGV calculations had been determined and the guideline values calculated, these were then compared and discussed, and a value applicable to Sydney Harbor selected.

# RESULTS AND DISCUSSION Effects-based guidelines

The sediment quality guidelines developed by Canada in 2001 (CCME, 2001) were the first to use the effects-based

approach for dioxin-like compounds. Toxicity data from the National Status and Trends Program in the United States (the BEDS database) were used to derive both a threshold effects level (TEL) and a probable effects level (PEL), following MacDonald et al. (1996). A TEL of 8.5 pg TEQ<sub>fish</sub>/g dry weight and a PEL of 215 pg TEQ<sub>fish</sub> /g dry weight were derived. A safety factor of 10 was used to account for bioaccumulation and the lack of clear separation between the effect and no effect datasets, resulting in a TEL of 0.85 pg TEQ<sub>fish</sub>/g and a PEL of 215 pg TEQ<sub>fish</sub>/g dry weight.

The Canadian data were largely sourced for freshwater sediments (CCME, 2001; for which there were sufficient data to generate a guideline using this approach). These were from field studies of contaminated sediments with multiple chemicals present. Data were limited for marine sediments (there were not sufficient data to generate a guideline using this approach for marine sediments alone). One data point was available for a spiked-sediment toxicity test for marine sediments. Their guidelines were used to evaluate both marine and freshwater sediments.

Our review of the data underpinning the Canadian guideline values (Environment Canada, 2001a,b) indicated that there were uncertainties in these data which limited the usefulness of the values for this group of contaminants (Batley et al., 2005). One concern is that the data used are likely to be conservative for effects due to dioxin-like compounds because most of the sediments were also contaminated with metals and polycylic aromatic hydrocarbons (PAHs), and the concentrations of PAHs particularly were more likely to be the cause of the effects seen in the sediment bioassays. This effect is known as cooccurrence and is a well-known limitation of this approach (Jones-Lee & Lee, 2005; Simpson et al., 2013).

The toxicity data used in the derivation were largely from studies using benthic invertebrates (midges, amphipods, oyster larvae, mayflies, chironomids), for example Barber et al. (1998), Bedard and Petro (1997), USEPA (1997), Ingersoll et al. (1996), and Ward et al. (1993), and in one instance (Call et al., 1991) for a fish, a fathead minnow. The toxic effects of these contaminants that are mediated by the aryl hydrocarbon receptor are known to occur at much lower concentrations than effects due to other mechanisms. Invertebrates and plants do not contain this receptor. This significantly limits the potential for impacts on them from dioxin-like compounds. It has been demonstrated that fish are the most sensitive aquatic organisms to effects from exposure to dioxin-like compounds (Barber et al., 1998).

As a consequence of the above, the effects-based approach was not pursued for Sydney Harbor sediments.

#### Equilibrium partitioning-based guidelines

The USEPA developed an approach to determine benchmarks for screening sediments for nonionic organic chemicals (USEPA, 2003a, 2008, 2012) based on equilibrium partitioning theory. This holds that a nonionic chemical in sediment partitions between sediment organic carbon, pore water, and benthic organisms and, when at equilibrium, if the concentration in one phase is known, then the others can be predicted. It assumes that effects from such a chemical are primarily driven by how much of the chemical dissolves into the pore water to which an organism is exposed and that benthic organisms have similar sensitivity to organisms that live in the water column. It also assumes that the concentration in the pore water (i.e., the dissolved concentration) is driven only (or at least primarily) by partitioning between water and organic carbon present in the sediment (and dissolved and particulate organic carbon within the water; USEPA, 2003a, 2008, 2012).

For chemicals such as the dioxin family, these are relevant assumptions. The characteristics of these chemicals fit with the assumptions because they are highly lipophilic and prefer to move between organic carbon in soil or sediment or into lipid in organisms rather than stay in water.

Estimating concentrations that might be present in pore water based on bulk sediment concentrations can be undertaken using a partition coefficient, the organic carbon:water partition coefficient ( $K_{oc}$ ) or  $K_{ow}$ .

**Sediment–water partitioning.** A summary of the partitioning characteristics for TCDD was prepared by the USEPA in 1993 (USEPA, 1993). Although this was quite some time ago, it remains a useful resource for data on this aspect.

The partitioning of other dioxin-like compounds may be different to that for TCDD but using a value for TCDD to represent all chemicals in the family is likely to overestimate how the larger molecules could partition into water, so it is an appropriately conservative approach. Measuring partition coefficients for chemicals like these is quite difficult due to their very low water solubility. The difficulty in such measurements has been discussed in relation to PCBs by Linkov et al. (2005).

A range of studies were undertaken to estimate/measure  $K_{\rm ow}$  (or  $K_{\rm oc}$ ) for TCDD as reviewed by the USEPA (1993). Depending on the measurement technique, log10  $K_{\rm ow}$  values for TCDD were found to range from 6.4 to 7 in one study reported in their review (and to be above 6.4 to 8.0 in another). These values are all in the expected range given the characteristics of these chemicals. The USEPA recommended using a value of 7 for both log10  $K_{\rm ow}$  and log10  $K_{\rm oc}$ . This was considered as a conservative and appropriate approach (USEPA, 1993).

A comprehensive assessment of dioxin-like compounds was undertaken by the USEPA over approximately a decade from the mid-1990s to mid-2000s. Updated recommendations were made for  $K_{\rm oc}$  values in the most recent update from 2003 for use in modelling the fate and transport of dioxin-like compounds (USEPA, 2003b). All of the data were taken from studies undertaken in the 1990s or earlier.

Studies have also been undertaken considering the partitioning of these chemicals to different forms of organic carbon. The organic carbon present in sediments can be normal amorphous organic carbon. It can also be present as black carbon, the fraction of organic carbon arising from combustion sources (both natural and arising from human activities; Accardi-Dey & Gschwend, 2001; Forbes et al., 2006; Ghosh et al., 2003; Gustafsson et al., 1996; Swedish Environmental Protection Agency, 2009). Dioxin-like chemicals (and other chemicals with similar characteristics) tend to partition more strongly to black carbon, so if there is a significant proportion of black carbon within the total organic carbon content of a sediment sample then this would reduce the amount that can partition to water and be taken up by aquatic organisms (Accardi-Dey & Gschwend, 2001; Forbes et al., 2006; Ghosh et al., 2003; Gustafsson et al., 1996; Swedish Environmental Protection Agency, 2009). It was noted that when black carbon was present, the log  $K_{oc}$  values increased (i.e., less partitioned into water), ranging from 7.5 to just over 9.

Values for log  $K_{oc}$  of 6.5 and 7.5 have been used in the present study and will be appropriate and conservative for Sydney Harbor, especially if there is a significant proportion of black carbon in the sediments, as might be expected for a historical working harbor in a heavily urbanized area.

The equation to calculate a sediment quality benchmark using equilibrium partitioning theory from the USEPA guidance (USEPA, 2003a, 2008, 2012) is as follows:

$$ESB_{WQCOC} = K_{oc} \times CF \times FCV$$
(1)

where ESB<sub>WQCOC</sub> is the equilibrium partitioning sediment benchmark normalized for organic carbon (pg/g<sub>oc</sub>) and K<sub>OC</sub> is organic carbon partitioning coefficient (L/kg organic carbon), that is,  $3 \times 10^{6}$  (equivalent to log K<sub>oc</sub> of 6.5) for TCDD. This is one of the lowest K<sub>oc</sub> values measured for TCDD specifically. The more chlorinated compounds have K<sub>oc</sub> values that are even higher, so using this is conservative for the whole group of dioxin-like compounds (USEPA, 1993). The conversion factor from kilograms to grams of organic carbon (=0.001) is CF and FCV is the final chronic value (the relevant ecotoxicity-based value derived from water exposures, pg/L; USEPA, 2003a, 2008, 2012).

This calculation can be undertaken using a number of values for both  $K_{oc}$  and the FCV. For the latter, there are a number of options, namely the value from the USEPA review (USEPA, 1993) or another jurisdiction's water quality guideline value.

Using the lowest no-effect concentration reported in the USEPA (1993) review (40 pg TCDD/L) provided the following guideline:

$$ESB_{WQCOC} = 3 \times 10^6 \times 0.001 \times 40 ESB_{WQCOC}$$
  
= 120000 pg TEQ /g organic carbon (2)

ESB<sub>WQCOC</sub> = 1200 pg TEQ/g dry weight (normalized to 1% organic carbon)

(3)

Rather than using the above FCV, a derivation was undertaken for a water quality guideline for TCDD using available chronic toxicity data in an SSD, following the procedures recommended for Australia and New Zealand by Warne et al. (2018). Sufficient data were only available for freshwater species. The distribution was found to be bimodal, with fish being the most sensitive species compared with plants and invertebrates, so the data for fish only were used to derive concentrations that are protective of 95% and 99% of fish species (see Supporting Information, Table S1, and Supporting Information, Figure S1). Given that plants and invertebrates are less sensitive to the effects of TCDD, these guideline values based on fish data will be protective of these species.

Given that TCDD bioaccumulates, a 99% species protection value of 0.6 pg TCDD/L was used in the calculation as recommended for bioaccumulating compounds (Warne et al., 2018):

$$ESB_{WQCOC} = 3 \times 10^6 \times 0.001 \times 0.6$$
(4)

 $ESB_{WQCOC} = 1800 \text{ pg TEQ/g organic carbon}$  (5)

 $ESB_{WQCOC} = 18 \text{ pg TEQ/g dry weight}$ (normalized to 1% organic carbon) (6)

The above calculation used a value of 6.5 for log  $K_{oc}$ . Using this value adds conservatism to the calculation. Using a value of 7.5 for log  $K_{oc}$  gives an ESB<sub>WQCOC</sub> of 180 pg TEQ/g dry weight. A value for log  $K_{oc}$  of 7.5 is more relevant, given that the dioxin-like compounds in the sediments in the Parramatta River at the western end of Sydney Harbor are a mix of the dioxin-like compounds, not just TCDD. All of the dioxin-like compounds with more than four chlorine atoms will be more strongly attached to the sediments than those like TCDD and 2,3,7, 8-tetrachlorodibenzofuran. This means they will have higher values for log  $K_{oc}$ .

Assuming each congener is present at the limit of reporting when not detected, the proportions for each congener contributing to sediment concentrations in the Parramatta River ranged as shown in Table 1.

TABLE 1: Dioxin congener proportions, Parramatta River

Congener	Range (%)
TCDF	0.25–0.47
TCDD	34–46
1,2,3,7,8-PeCDF	0.04–0.06
2,3,4,7,8-PeCDF	2.2–2.5
1,2,3,7,8-PeCDD	3.4–8.1
1,2,3,4,7,8-HxCDF	1.3–2
1,2,3,6,7,8-HxCDF	0.4–0.5
2,3,4,6,7,8-HxCDF	0.3–0.4
1,2,3,7,8,9-HxCDF	0.01–0.08
1,2,3,4,7,8-HxCDD	0.8–1.2
1,2,3,6,7,8-HxCDD	7–8
1,2,3,7,8,9-HxCDD	2–3
1,2,3,4,6,7,8-HpCDF	1.3–1.6
1,2,3,4,7,8,9-HpCDF	0.12–0.17
1,2,3,4,6,7,8-HpCDD	22–27
OCDF	0.1–0.2
OCDD	10.7–14.2

It can be seen from this information that the individual congener TCDD contributes at most 50% of the total TEQs for the sediments in the Parramatta River.

Using the 6.5–7.5 range for log  $K_{\rm oc}$  gives a range of 18–180 pg TEQ/g dry weight for sediment guideline values based on equilibrium partitioning into pore water using the characteristics of TCDD. The actual mix of dioxin-like compounds present in Sydney Harbor will partition somewhat less than for TCDD alone. This would result in a higher SQGV if it was possible to calculate it accurately.

The SQGV calculation relies on a value for 99% species protection of 0.6 pg/L for TCDD, which is again based on freshwater species and because of the bimodality of the organism response to TCDD is based on fish data only.

Given the characteristics of these compounds (i.e., nonionic), the assumption that the value would be similar in marine waters is not unreasonable (Warne et al., 2018).

This method of SQGV derivation is not robust for a number of reasons, including: 1) the difficulty in measuring  $K_{oc}$  for these types of chemicals; 2) the use of a parameter value for a single individual congener (TCDD) to estimate the behavior of a mixture of these chemicals given that these chemicals are always present as a mixture; 3) the difficulty in accessing sufficient (preferably chronic) data from ecotoxicity tests where the water concentration was used in determining the relevant endpoint; 4) the large errors associated with determination of a species protection value at the extreme tail of the SSD; and 5) the relationship between the effects of these chemicals in fish and the tissue residues of these chemicals is stronger/more robust than the relationship with water concentrations.

Guidelines have been developed using equilibrium partitioning by other organizations. lannuzzi et al. (1995) listed SQGVs based on equilibrium partitioning which include: 1) 10 000 pg/g organic carbon (100 pg/g dry wt for 1% organic carbon) based on  $K_{oc}$  of  $10^7$  and a final chronic value of 1 pg/L; 2) 200 pg/g organic carbon (2 pg/g dry wt for 1% organic carbon) based on  $K_{oc}$  of  $10^7$  and a final chronic value of 0.02 pg/L; 3) 10 000 000 pg/g organic carbon (100 000 pg/g dry wt for 1% organic carbon) based on  $K_{oc}$  of  $10^7$  and a final chronic value of 1000 pg/L; and 4) 330 pg/g organic carbon (3.3 pg/g dry wt for 1% organic carbon) based on  $K_{oc}$  of  $3.3 \times 10^6$  and a final chronic value of 0.1 pg/L (lannuzzi et al., 1995).

Clearly there is large uncertainty associated with this approach, specifically associated with the choice of  $K_{oc}$ .

# Sediment–biota partitioning: the tissue residue approach

This approach is relevant for dioxin-like compounds, given that the ecotoxicity of these chemicals to aquatic species has been related to the accumulation of these chemicals during exposure and concentrations in tissues (and in eggs specifically), and those tissue residues have been related to effects on survival and other relevant endpoints, that is, tissue residue benchmarks (Foekema et al., 2016; Steevens et al., 2005; USEPA, 1993). The approach requires a toxicity reference value that is based on tissue residues rather than water concentrations.

The USEPA (1993) developed SQGVs for TCDD based on tissue residues in eggs for lake trout, the most sensitive species identified for effects on survival and growth in early life stages. The tissue residue value was 50 pg TCDD/g wet weight. This value was combined with an assumed value for a BSAF to determine a concentration in sediment associated with that tissue residue value. For comparison, the USEPA-derived SQGV-low, defined as the highest concentration unlikely to cause effects for sensitive species, was 60 pg TCDD/g dry weight (USEPA, 1993). The SQGV-high was 100 pg TCDD/g dry weight and this represented the lowest exposure concentration likely to result in severe effects in sensitive species (USEPA, 1993). This SQGV-high was based on LC/EC50 values that are equivalent to a concentration of 80 pg TCDD/g lipid in fish tissue (this is also equivalent to 80 pg TEQ<sub>fish</sub>/g lipid). These values appear to be no longer in use by the USEPA.

The BSAF describes the amount of a chemical in sediment that can be accumulated by relevant biota. The USEPA (1993) review recommended a generic approach for BSAFs, choosing a value of 0.3 (USEPA, 1993). This value was based on a review of the available literature, which indicated BSAFs ranged from 0.03 to 0.3 for a range of environments and fish species. The highest value was chosen to ensure the approach being developed was conservative (USEPA, 1993).

In the case of Sydney Harbor, an alternative approach was adopted, using a large amount of existing site-specific data to calculate a more specific BSAF directly.

#### **Guideline calculation**

Once a tissue residue-based toxicity reference value and a BSAF have been determined, the following calculation can be undertaken:

$$BSAF = \frac{\text{concentration in organism}}{\text{concentration in sediment}}$$
(7)

Rearranging this equation as follows provides the calculation of the sediment concentration that will appropriately limit the tissue residues that might be present in biota to provide protection:

$$Concentration in sediment = \frac{concentration in organism}{BSAF}$$
(8)

It is noted that this calculation requires that the "concentration in organism" value be in terms of lipid and the "concentration in sediment" value be in terms of organic carbon.

An extension of the tissue-residue approach was carried out by Steevens et al. (2005). In that paper, an SSD for the concentrations of dioxin-like compounds in eggs related to no effects was developed. Values from this distribution were used to develop SQGVs using BSAFs. They argued that the use of tissue residue data (i.e., egg concentrations) for dioxin-like compounds to estimate effects concentrations was a better surrogate for dose at the site of action than water concentrations because they already include consideration of bioavailability, uptake into the organism, metabolic actions within the organisms, and all routes of exposure. This is particularly important for chemicals that bioaccumulate and where effects have been shown to be related to the amount accumulated, as is the case for these chemicals (McElroy et al., 2011; Meador et al., 2011).

Steevens et al. (2005) used data from fish exposed via water, maternal transfer, or direct injection into the eggs. These included lake trout exposed via all three pathways, brook trout exposed via water and maternal transfer, and rainbow trout exposed via injection into the eggs and via water as well as a number of other species exposed via only one pathway. Their results for the different exposure pathways were: 1) for brook trout, the lethal residue at 50% effect (LR50) values for the two exposure pathways were within a factor of 2; 2) for rainbow trout, the LR50 values for the two exposure pathways were within a factor of 2; and 3) for lake trout, the LR50 values for the three exposure pathways were within a factor of 2. For lake trout, there were seven different studies that exposed eggs via the same exposure pathway. The results for these seven studies also reported LR50 values within a factor of 2, that is, 0.53, 0.93, 1.21, 0.86, 0.81, 0.68, and 1.06 ng TCDD/g lipid.

The results of Steevens et al. (2005) showed that the different exposure pathways result in LR50 values that are no different in variability than when different laboratories measure the same endpoint via the same exposure pathway. It is important to consider the normal levels of variability in toxicity tests when evaluating such matters. Hence, the conclusion reached, that data from studies using different types of exposure could still be considered together, is supported.

Their data for 26 linked pairs were obtained from relevant databases, that is, tissue residue measurements along with effects observations, for 10 different fish species: brook trout, channel catfish, fathead minnow, Japanese medaka, lake herring, lake trout, northern pike, rainbow trout, white sucker, and zebrafish (Steevens et al., 2005). The studies targeted were well-designed and controlled laboratory studies. Exposure was to TCDD or a mixture of dioxin-like compounds determined as TEQ<sub>fish</sub>.

Two endpoints from each study were used to construct species sensitivity distributions: 1) the geometric mean of the lowest observed effect residue (LOER) and the no observed effect residue (NOER) (where residue = concentration in eggs), and 2) the LR50. Only one value was chosen for each species so the distributions were not biased/dominated by data for one or two species.

Their evaluation made use of data collected between 1991 and 1998. The values for the highest level of species protection are essentially the same as those reported by the USEPA (1993). Most of the available data for use in these SSDs were for salmonid species, which are particularly sensitive to exposure to dioxin-like compounds. The 90% species protection values derived from the SSDs for the two endpoints were 699 and 909 pg TEQ<sub>fish</sub>/g lipid (Steevens et al., 2005).

## Additional ecotoxicity studies

We located more recent studies that had assessed the ecotoxicity of TCDD (based on lethal concentrations/residues) to a number of other fish species, particularly sturgeon species (Buckler et al., 2015; Park et al., 2014; Tillitt et al., 2017; Toomey et al., 2001; Yamauchi et al., 2006).

Tillitt et al. (2017) assessed the sensitivity of early life stages of lake sturgeon to TCDD and to a single PCB congener of importance in the Great Lakes. This is a freshwater species. The chemicals were present in water that the fertilized eggs were exposed to for at least an hour shortly after fertilization. A range of doses was used to establish a dose response. Six replicates were used for each treatment and each replicate started with approximately 180 eggs. The study ran to 60 days postfertilization and a range of endpoints were observed. Nominal concentrations used to set up the experiment ranged from 1 to 50 ng/g egg wet weight (i.e., 1000-50 000 pg TCDD/g wet wt). The measured tissue residues ranged from 0.08-8.96 ng/g egg wet weight (i.e., 80-8960 pg TCDD/g wet wt). The results for the study were based on measured concentrations which ensures the relevant accumulation of the chemical was built into the calculations. The median lethal concentration (LD50) value was 610 pg TCDD/g wet weight. The lipid content of the eggs was 7.7%.

They also included LD50 data based on residues in eggs for additional species not included in the Steevens et al. (2005) paper. Some of these data were from studies in the 1990s but some were more recent. The data include LD50 values for the following additional species: 1) red sea bream (*Pagrus major*)— 360 pg TCDD/g egg wet weight (marine species); 2) mummichog (*Fundulus heteroclitus*)—250 pg TCDD/g egg wet weight (marine species); 3) crucian carp (*Carassius auratus*)—240 pg TCDD/g egg wet weight (freshwater species; Park et al., 2014; Tillitt et al., 2017; Toomey et al., 2001; Yamauchi et al., 2006). The effects on the marine species are within the same range as specified for the freshwater species (Park et al., 2014; Tillitt et al., 2017; Toomey et al., 2001; Yamauchi et al., 2014; Tillitt et al., 2017; Toomey et al., 2001; Yamauchi et al., 2014; Tillitt et al., 2017; Toomey et al., 2001; Yamauchi et al., 2014; Tillitt

Buckler et al. (2015) reported a study on two other sturgeon species by the same research group as that of Tillitt et al. (2017). The same approach was adopted with the shovelnose sturgeon and pallid sturgeon, both freshwater species. Newly fertilized eggs were exposed to TCDD or PCB126 in water for 1 h followed by observation while in clean water for 31 days postfertilization. This approach has been shown to be an adequate surrogate for exposure via transfer from the mother. The LD50 values for the two species were 12 000 pg TCDD/g egg wet weight for the pallid sturgeon and 13 000 pg TCDD/g egg wet weight for the shovelnose sturgeon. For the purposes of our study, it has been assumed that these eggs have a similar lipid content to the lake sturgeon discussed above (i.e., 7.7%). Steevens et al. (2005) reported lipid content in eggs for all the species used in the distribution. The lipid content ranged from 1.7% to 8%. Trout species were all in the range 7%–8%. Zebrafish, fathead minnow, and medaka all had lower levels, approximately 2%. Using a lower lipid content leads to a higher value on a lipid-normalized basis. Consequently, a value of 8% lipid has been assumed for the studies where lipid results were not included.

Given the availability of relevant additional data, the SSD data set used by Steevens et al. (2005) has been updated as shown in Table 2.

The data listed in Table 2 were then used in new SSDs to determine the 95th percentile using the ssdTools package (shiny app), which can be found at https://bcgov-env.shinyapps. io/ssdtools/.

It is noted that LOER/NOER data could not be found in the source papers for the red sea bream, mummichog, and crucian carp studies.

The SSD using the LR50/LD50 data is shown in Figure 1. This distribution contains data for 16 different species of fish.

The SSD using the geometric mean of LOER and NOER data is shown in Figure 2. This distribution contains data for 13 different species of fish.

These data are based on measured tissue concentrations in eggs, which means that bioaccumulation of these chemicals is directly assessed as part of the study. Toxicity has been shown to be well related to the amount of the chemicals accumulated within the fish and particularly within eggs. Also, it has been shown that the pathway of exposure (maternal transfer, water exposure or direct injection) makes little difference to the effects seen—it is the total amount accumulated in the early lifestage (eggs/fry) that can be related to the effects seen.

Often results in environmental investigations are for wholebody concentrations or for concentrations in fillets. A study undertaken in the late 1990s looked at tissue distributions (eggs and muscle) for a range of organochlorine compounds (including dioxin-like compounds) and fish species (Russell et al., 1999). This review allowed the development of a model to estimate egg concentrations from muscle or fillet data and vice versa. The analysis showed that there was essentially a 1:1 relationship between muscle/fillet maternal concentrations and concentrations in eggs based on lipid-normalized results. This adjustment was used in the Steevens et al. (2005) paper when considering application of their benchmarks (Russell et al., 1999).

The USEPA reported that concentrations in eggs in the laboratory studies were approximately 30%–40% of the concentrations in the parent fish on a wet weight basis. For lipid-normalized data, the results for a study in Lake Ontario indicated eggs contained approximately 65% of the concentration in the parents (USEPA, 1993).

Based on the study by Russell et al. (1999; as used by Steevens et al., 2005), the tissue residue benchmarks based on the egg concentrations can also be applied to whole-body

TABLE 2: Updated data for species sensitivity distributions based on data from Steevens et al. (2005) plus additional data for the sturgeon and other species

	Geometric mean of LOER and NOER data		LR50/LD50 data			
Fish species	pg TEQ/g wet weight	pg TEQ/g lipid	pg TEQ/g wet weight	pg TEQ/g lipid	% Lipid in eggsª	Reference
Brook trout	110	1 680	130	1 870	6.8	Johnson et al. (1998)
Channel catfish	570	12 000	640	13 400	4.8	Elonen et al. (1998)
Fathead minnow	320	13 300	540	22 500	2.4	Elonen et al. (1998)
Japanese medaka	660	22 700	1110	38 300	2.9	Elonen et al. (1998)
Lake herring	220	3300	900	13 700	6.6	Elonen et al. (1998)
Lake trout	34	420	42	530	8.0	Guiney et al. (1996); Walker et al. (1994)
Northern pike	1460	34 900	2460	58 600	4.2	Elonen et al. (1998)
Rainbow trout	200	3050	200	3100	6.5	Walker et al. (1996); Walker and Peterson (1991); Walker et al. (1992)
White sucker	1020	40 700	1900	75 600	2.5	Elonen et al. (1998)
Zebrafish	920	54 200	2500	147 000	1.7	Elonen et al. (1998); Henry et al. (1997)
Lake sturgeon	505	6560	610	7900	7.7%	Tillitt et al. (2017)
Shovelnose sturgeon	8000	104 000	13 000	170 000	8% (assumed from lake sturgeon)	Buckler et al. (2015)
Pallid sturgeon	5000	65 000	12 000	160 000	8% (assumed from lake sturgeon)	Buckler et al. (2015)
Red sea bream	NA	NA	360	6100	5.9% (Forster & Ogata, 1996)	Yamauchi et al. (2006)
Mummichog	NA	NA	250	3600	6.9% (Fortin et al., 2008)	Toomey et al. (2001)
Crucian carp	NA	NA	240	3000	8% (assumed from lake sturgeon)	Park et al. (2014)

<sup>a</sup>Lipid content is as specified in Steevens et al. (2005) unless otherwise stated.

LOER; NOER; LR50 = median lethal residue; LD50 = median lethal dose; TEQ = toxic equivalency.



FIGURE 1: Species sensitivity distribution using median lethal residue/median lethal dose data (concentration refers to the tissue residue in eggs in pg 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)/g lipid; the 95% species protection value is 671 pg TCDD/g lipid).

or fillet concentrations for lipid-normalized data without adjustment.

It is recommended that the lowest of the two values for the 95th percentile of the distribution of tissue residue responses from Figures 1 and 2 be used in the present study to develop a SQGV, that is, 671 pg TCDD/g lipid. This value is based on data for the largest number of species and on a robust endpoint (survival of young).

#### **Determination of BSAFs for Sydney Harbor**

The determination of BSAFs from paired data was outlined by Burkhard (2009) for the USEPA. Two methods were discussed—a regression approach and an averaging approach. The averaging approach has been adopted in the present study in line with the USEPA recommendations. Biota:sediment accumulation factors are often considered more useful than bioaccumulation factors (based on water concentrations) for chemicals with characteristics such as dioxin-like chemicals which are more stable over time in sediments and fish tissue than in water (Burkhard et al., 2004). The usefulness of such factors does depend on the sediment samples being reflective of the chemical concentrations to which the fish are likely to be exposed. An understanding of the home range of the fish species is an important aspect of ensuring this relationship (Burkhard et al., 2005). Burkhard (2009) noted that organisms with small foraging ranges are likely to be more representative of a study site than those with large foraging ranges.

Burkhard et al. (2005) noted that site-specific BSAFs were most desirable when evaluating bioaccumulation in a particular area of interest. They listed the major conditions incorporated into the development of BSAFs from field measured data: 1) distribution of chemicals between sediment and water column; 2) relationship of food web to water and sediment; 3) length of the food web (trophic levels); 4) bioavailability of the chemicals due to levels of organic carbon; and 5) metabolic transformation rates for the chemicals (Burkhard et al., 2005).

Most of these conditions/parameters are quite variable between ecosystems, which may impact on the applicability of BSAFs from one location being used for a completely different ecosystem. Investigations have shown that, although the values of BSAFs may change between different ecosystems when bioavailability or length of food web and so forth may change, the ranking of the values for related chemical groups remains consistent (Burkhard et al., 2005).

Between 2005 and 2010, the New South Wales Environment Protection Authority (NSW EPA) undertook an investigation of dioxin-like compounds in fish and sediments in Sydney Harbor. The results of the investigation of fish tissue residues were reported by Manning et al. (2017). These data indicated that the species with the highest tissue concentrations were those that appeared to have a larger foraging range that included the contaminated sediments within Homebush Bay. Species that



FIGURE 2: Species sensitivity distribution for geometric mean of lowest observed effect residue and no observed effect residue data (concentration refers to tissue residue in eggs in pg 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD)/g lipid; the 95% species protection value is 672 pg TCDD/g lipid; Supporting Information, Figure S1, is based on water concentrations not tissue residues).

were known to have smaller foraging ranges based on advice from fisheries experts had smaller tissue residues, especially if they were primarily herbivorous.

Sediments were collected in the same locations as the fish sampling, but these results have not been published (Tony Roach NSW DECCW, Sydney, NSW Australia, personal communication, 2007). The sediment samples collected for the NSW EPA investigation targeted the surficial sediments in particular, which are the most relevant for determining BSAFs.

Access to the fish and sediment data from the NSW EPA investigation has been provided by NSW EPA for the present study and other work being undertaken by Transport for NSW.

Additional sampling and analysis of dioxin-like compounds in sediments was undertaken for other Transport for NSW projects in the Parramatta River and these data are also relevant for this evaluation of BSAFs. These samples targeted the surficial sediments.

There are a number of additional studies for sediment concentrations in Sydney Harbor (Birch et al., 2007; Parsons Brinckerhoff, 2002). These data have not been included in our study because they focused on sediments within Homebush Bay rather than the Parramatta River.

The primary source site of dioxin-like compounds is located in the upper part of the Parramatta River, near the former Union Carbide site in Homebush Bay. Biota:sediment accumulation factors from data collected in this area (i.e., the Parramatta River) are more likely to be related to the anthropogenic sourced dioxin-like compounds from this site in Homebush Bay for which the major contributor to total TEQs is TCDD. Other parts of the harbor have sediments containing dioxin-like compounds from natural sources and from all the various combustion sources relevant for urban areas (like vehicles, wood heaters, etc.). These sources tend to include more furantype dioxin-like compounds or the more chlorinated dioxin-like compounds which make smaller contributions to the overall relevant total equivalent concentrations. The more heavily chlorinated dioxin-like compounds will be more tightly attached to particles and are less likely to partition to biota or water. Focusing on the area with the higher TCDD concentrations will be conservative for the whole harbor.

Fish tissue concentrations have been based on reported average concentrations for the various fish species collected in the western part of Sydney Harbor, that is, upstream of the Sydney Harbor Bridge in the Parramatta River (Manning et al., 2017; Table 3). Thirteen different species were sampled in this part of Sydney Harbor during the present study.

These data include a range of fish species. Some are known to be primarily herbivorous and/or with a limited foraging area such as luderick and sand whiting. Other species were found to have higher tissue concentrations regardless of where in Sydney Harbor they were caught, indicating that they had a large foraging area and were likely to have visited the contaminated sediments within Homebush Bay, which were significantly higher than the rest of Sydney Harbor until

TABLE 3:	Fish	data	from	Sydney	Harbor	for	use i	in (	calculating	bio-
ta:sedime	nt ac	cumul	ation	factors	3					

Fish	pg TEQ <sub>fish</sub> /g wet weight fillet	% Lipid	pg TEQ <sub>fish</sub> /g lipid fillet	pg TEQ <sub>fish</sub> /g lipid whole body
Bream	4.73	2.4	197	256
Dusky flathead	1.28	0.3	428	556
Leather jacket	0.28	0.3	92	120
Flounder	2.50	0.8	312	406
Luderick	2.55	3	85	111
Sand whiting	0.80	0.5	160	208
Sea mullet	23.1	8.3	278	361
Silver biddie	8.56	2.3	372	484
Silver trevally	6.20	4	155	202
Tailor	14.1	6.4	220	286
Trumpeter whiting	1.34	0.6	223	290
Yellowtail scad	10.2	2.9	352	458
Mulloway	4.62	1.9	243	316

<sup>a</sup>Data from Table 1 in Manning et al. (2017); only data for fish species caught in the western part of Sydney Harbor are used. Data were reported using World Health Organization toxic equivalency factors (TEFs) for people (Van den Berg et al., 2006), but for this exercise the raw data have been revisited using TEFs for fish (Van den Berg et al., 1998). TEQ = toxic equivalency.

remediation was completed in 2011 to 2012. Species that were in this category included bream and mullet.

The NSW EPA study was designed to allow risks for human consumption to be evaluated, so the data are for fillets not whole fish. A number of studies have been undertaken comparing whole-body and fillet concentrations for dioxin-like compounds and PCBs (Amrhein et al., 1999; Bevelhimer et al., 1997; Fair et al., 2018; Fliedner et al., 2018).

Fliedner et al. (2018) used three species of fish (chub, bream, and perch) collected in Germany. Fillets and wholebody samples were analyzed. For both dioxin-like compounds and PCBs, concentrations in the whole body were higher than those in fillets. The mean conversion factor to apply to fillet concentrations to estimate whole-body concentrations was 1.3 for dioxin-like compounds using lipid-normalized data. The ratios for fillet to whole-body concentrations for the individual samples were 1.03, 1.1, 1.21, 1.36, 1.19, and 1.85 on a lipidnormalized basis for dioxin-like compounds and 0.97, 1.07, 1, 1.06, 1.38, and 1.14 on a lipid-normalized basis for PCBs.

Amrhein et al. (1999) did a similar investigation. They found whole-body to fillet ratios that averaged 0.92 and 0.80, for coho salmon and rainbow trout, respectively (Supporting Information, Table S3; i.e., there were higher concentrations measured in the fillets than for the whole body).

A more recent study compared concentrations of PCBs, PBDEs, and organochlorine pesticides in whole fish and fillets (Fair et al., 2018). The results for PCBs (most relevant for dioxinlike compounds) indicate that average whole-fish to fillet ratios were 1.47, 1.54, 1.11, 1.10, and 1.04 based on lipid-normalized data and depending on species. The fish were collected in a range of marine/estuarine locations (Fair et al., 2018).

Another study from the late 1990s considered the use of fish fillet data to predict whole-fish concentrations (Bevelhimer et al., 1997). The study reviewed data for a range of metals as

well as PCBs and chlordane. The PCB data are relevant in our study. The whole-body to fillet ratios ranged from 0.25 to 2.9 for the individual samples on a lipid-normalized basis. For catfish, the relationship was close to 1:1. For bass, the variation was greater but using a ratio of 2.3 was useful for most samples (Bevelhimer et al., 1997).

Using all of the data reported in these studies (given the limitations of the published information), the mean fillet to whole-body concentration ratio was 1.02 (see Supporting Information, Table S4). The study by Fliedner et al. (2018) recommended the use of a value of 1.3. This value is higher than the mean value for the dataset, so is a conservative approach for use in our study (Supporting Information, Table S4).

A whole-fish to fillet concentration ratio of 1.3 has been used to estimate whole-body concentrations (lipid normalized) to allow the calculation of BSAFs (shown in Table 3).

Sediment concentrations have been reported for samples collected within the Parramatta River as part of the NSW EPA investigation and for the additional sampling undertaken by Transport for NSW as part of investigations related to the Wentworth Point Marina development. The number of sediment samples available for our study was limited. There were 10 samples taken within the Parramatta River as part of the NSW EPA investigation in 2007. These samples were collected in two groups of five—one group was located close to and upstream of Homebush Bay where the original source of these chemicals is located whereas the other group was located downstream but still within the Parramatta River. Another five samples were collected within the Parramatta River in a similar location to the second group from 2007 during more recent work in 2015.

For the NSW EPA investigation (i.e., 2007), sediment collected in the Parramatta River reported concentrations ranging from 200 to 600 pg TEQ<sub>fish</sub>/g dry weight. Organic carbon concentrations in these sediments were 3% on average.

Additional sediment data collected in 2015, as part of the marina development investigation, reported concentrations in the Parramatta River ranging from 390 to 790 pg TEQ<sub>fish</sub> /g dry weight. Organic carbon in these sediments (the reference sites in the Parramatta River) averaged 3.2%.

Overall, there were five samples collected in the Parramatta River as part of the work in 2015 and 10 samples collected in 2007. The data are listed in Table 4. The table also shows the organic carbon normalization.

Biota sediment accumulation factors determined using the overall averages for the fish tissue concentrations (lipid normalized) and each of the sediment concentrations (organiccarbon normalized) are shown in Supporting Information, Table S4.

The 95th percentile BSAFs vary from 0.02 to 0.1 depending on the fish species. Dusky flathead had the highest BSAF (95th percentile). This is a bottom-dwelling species with a relatively low level of lipid. This combination has resulted in the highest average tissue concentration, which is why this species has the highest BSAF values. These results cover the range of data reported by the USEPA (1993). The 95th percentile for the **TABLE 4:** Sediment data from Sydney Harbor for use in calculating biota:sediment accumulation factor values

	Sediment (ave Weste				
Site	pg TEQ <sub>fish</sub> /g dry weight	pg TEQ <sub>fish</sub> /g organic carbon	Organic carbon (%)		
NSW EPA invest	igation <sup>a</sup>				
5-1	327	12 600	2.6		
5-2	351	11 000	3.2		
5-3	324	11 200	2.9		
5-4	145	4530	3.2		
5-5	211	5700	3.7		
4-1	209	7460	2.8		
4-2	264	9100	2.9		
4-3	277	9890	2.8		
4-4	302	10 800	2.8		
4-5	397	13 200	3		
Transport for NSW investigation <sup>b</sup>					
R1	253	9240	4.2		
R2	293	18 400	2.2		
R3	355	17 700	3		
R4	383	17 200	3.4		
R5	479	23 200	3.4		

<sup>a</sup>Tony Roach, NSW DECCW, Sydney, NSW Australia, personal communication, 2007.

<sup>b</sup>Manning, 2017.

 $\mathsf{TEQ}=\mathsf{toxic}$  equivalency;  $\mathsf{NSWEPA}=\mathsf{New}$  South Wales Environment Protection Authority.

whole dataset is 0.08 so using the 95th percentile for the dusky flathead is a conservative approach. A value of 0.1 has therefore been used for our study.

# Determination of a sediment quality guideline value using tissue residues

Using tissue residues, the USEPA (1993) determined a SQGV of 60 pg TEQ<sub>fish</sub>/g dry weight. It is possible to back-calculate the "concentration in organism" on which this was based assuming fish have an average lipid content of 8%. This calculation indicates that this SQGV is equivalent to a value of 625 pg TEQ<sub>fish</sub>/g lipid. The USEPA used a BSAF of 0.3 in their calculation (USEPA, 1993). More recent work was undertaken in Lake Michigan (Burkhard et al., 2004). The range of BSAFs determined in Burkhard et al., 2004 was <0.001 to 0.32 for dioxin-like compounds, which is similar to the value determined in the 1990s.

Using Equation 8, the relevant calculation using this approach is:

Concentration in sediment = 
$$\frac{\text{concentration in organism}}{\text{BSAF}}$$
(9)

Concentration in sediment = 
$$\frac{625}{0.3}$$
 (10)

Concentration in sediment

= 2000 pg TEQ<sub>fish</sub>/g organic carbon (11)

Normalizing this value to 1% organic carbon to make it comparable to the standard approach for Australian sediment guidelines for organic chemicals, this converts to 20 pg TEQ<sub>fish</sub>/g dry weight.

Using the same BSAF and adjusting the tissue residue benchmark to  $699 \text{ pg TEQ}_{\text{fish}}/\text{g}$  lipid (i.e., the value recommended by Steevens et al. [2005] [without the update including more recent data]) provides the following:

Concentration in sediment = 
$$\frac{\text{concentration in organism}}{\text{BSAF}}$$
 (12)

Concentration in sediment = 
$$\frac{699}{0.3}$$
 (13)

Normalizing this value to 1% organic carbon to make it comparable to the standard approach for Australian sediment guidelines for organic chemicals, this converts to 23 pg TEQ<sub>fish</sub>/g dry weight.

However, the large study of tissue residues and sediment concentrations in Sydney Harbor allows a more relevant value for the BSAF to be determined. The literature review has also allowed an update to the SSD for dioxin-like compounds. This allows a final adjustment to determine a SQGV.

The concentration in organism used in this final calculation is based on the 95% point of the updated distributions as shown in Figures 1 and 2, that is, 671 pg TEQ<sub>fish</sub>/g lipid using the data for LC/LR50 values and 672 pg TEQ<sub>fish</sub>/g lipid using the data based on the no-observable-effect concentration/NOER data (smaller dataset). A value of 671 pg TEQ<sub>fish</sub>/g lipid has been assumed for our study.

Concentration in sediment = 
$$\frac{\text{concentration in organism}}{\text{BSAF}}$$
 (15)

Concentration in sediment = 
$$\frac{671}{0.1}$$
 (16)

Concentration in sediment equals

Normalizing this value to 1% organic carbon to make it comparable to the standard approach for Australian sediment guidelines for organic chemicals, this converts to  $67 \text{ pg TEQ}_{fish}/\text{g}$  dry weight, which can be rounded to  $70 \text{ pg TEQ}_{fish}/\text{g}$  dry weight, given the uncertainties.

### **SUMMARY**

Table 5 summarizes the various SQGVs whose derivations have been discussed in the present study. The study provides an opportunity to assess values developed using a variety of methods and to consider which are the most appropriate for application to a site-specific assessment of sediments contaminated with dioxin-like substances, in our case sediment from Sydney Harbor at a proposed dredging site.

We have already discussed the issues that limit the usefulness of the Canadian guideline values (CCME 2001) which include the use of invertebrate data for a group of chemicals that do not act in invertebrates via the most relevant mechanism of action and the assumption that the effects seen in field data are due to a chemical or chemical group of interest regardless of the other chemicals present in the sediments.

Our study reported a guideline based on sediment:water partitioning in the range  $18-180 \text{ pg TEQ/g} \, dry$  weight, but, given the mix of congeners present in the sediments, a value closer to  $180 \text{ pg TEQ/g} \, dry$  weight is more relevant than  $18 \text{ pg TEQ/g} \, dry$  weight. The uncertainties in this derivation have been highlighted by others (lannuzzi et al., 1995) and for that reason we too favor a guideline based on tissue residues.

The development of the guideline using tissue residues has used ecotoxicity data that have been gathered from studies including those that are recent. The SSD is based on data for 16 species, which is significantly more than the recommended minimum for determining such distributions. The data are also based on a direct measure of bioaccumulation (i.e., tissue residues) so are the most appropriate data to use for dioxin-like compounds. As a result, the ecotoxicity endpoint included in the guideline calculation is considered robust.

In addition, the BSAF used in the guideline calculation is based on data that are relevant for understanding the relationship between tissue concentrations and the levels in sediments essentially the same as that being dredged (i.e., Sydney Harbor sediments). The data are also for species relatively similar to those present at the spoil ground. These data are based on marine/estuarine species compared with BSAFs available for freshwater environments from North America.

TABLE 5: Summary of derived sediment quality guideline values

#### Applicability of guidelines at the dredging site

The guidelines developed in the present study were for use in evaluating dredge spoil for disposal. Using Sydney Harborbased BSAFs in the development of this guideline should ensure the guideline value is conservative for application at the dredging site, which is located outside of Sydney Harbor (~10 km offshore from the Sydney Harbor entrance). It should be conservative because it is expected that the accumulation of these chemicals in biota in the offshore location where these sediments may be disposed will be lower than was the case for fish living in Sydney Harbor (i.e., smaller BSAF than used in calculating the proposed guideline) for the following reasons: 1) BSAFs for Sydney Harbor were generated using data for sediments with up to 500 pg TEQ $_{fish}$ /g dry weight whereas what will be disposed at the spoil ground is expected to have concentrations approximately 20 pg TEQ<sub>fish</sub>/g dry weight based on advice from those managing the dredging works. 2) Biota:sediment accumulation factors for Sydney Harbor were generated using data for fish in much shallower waters than is expected at the spoil ground, where waters are approximately 100 m deep. Most organisms will have more limited access to sediments when they are this deep. 3) Once spoil falls through water column and settles it will not get stirred up as much as sediments in the harbor given the depth in the area and the lack of regular boat movements and so on. The area is not considered a dispersive environment, which is why this area has been designated as a long-term spoil ground. The lack of resuspension is particularly the case for clay materials, which form a large portion of the material to be dredged. Limiting resuspension must minimize uptake into organisms because it limits exposure. 4) The larger home ranges for higher organisms present in the spoil ground (i.e., large fish, aquatic mammals or seabirds, and even fish species similar in size to those analyzed in the harbor) will not obtain 100% of their diet from benthic and other organisms that will live near the

Guideline description	Sediment quality guideline pg TEQfish/g dry weight	Comments
Canadian TEL	0.85	Based on sediment data from BEDS database
Canadian PEL	21.5	
Sediment:water equilibrium partitioning		
USEPA (1993) ecotoxicity NOEC based	1200	Based on 40 pg/L in pore water and normalized to 1% organic carbon
Using 99% species protection water quality guideline value and log $K_{ow}$ of 6.5 in equilibrium partitioning calculation	18	Based on 0.6 pg/L in pore water and normalized to 1% organic carbon
As above but using $\log K_{ow}$ of 7.5 in equilibrium partitioning calculation	180	Based on 0.6 pg/L in pore water and normalized to 1% organic carbon
Partitioning—tissue residue based		5
USEPA (1993) tissue residue benchmark and USEPA (1993) BSAF of 0.3	20	Based on 625 pg/g lipid, assumed BSAF of 0.3 and normalized to 1% organic carbon
Steevens et al. (2005) 95% species protection value tissue residue and USEPA (1993) BSAF of 0.3	23	Based on 699 pg/g lipid, assumed BSAF of 0.3 and normalized to 1% organic carbon
Updated species sensitivity distribution using the Steevens et al. (2005) approach with additional data and 95th percentile Sydney Harbor BSAF	70	Based on 671 pg/g lipid, assumed BSAF of 0.1 and normalized to 1% organic carbon and rounded

TEQ = toxic equivalency; USEPA, US Environmental Protection Agency; BSAF = biota:sediment accumulation factor; TEL = threshold effects level; PEL = probable effects level; NOEC = no observable effect concentration.

sediments in the disposal location. This will limit the potential accumulation up the food chain and will result in lower BSAFs. A lower BSAF will effectively mean that a guideline value that is protective for fish and other organisms at the spoil ground (where it possible to calculate such a BSAF and guideline value) would be higher, that is, less stringent, than the derived  $70 \text{ pg TEQ}_{\text{fish}}/\text{g}$  dry weight developed using the data from Sydney Harbor.

*Supporting information*—The Supporting Information is available on the Wiley Online Library at https://doi.org/10.1002/etc.5499.

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*Conflict of Interest*—The authors declare no conflict of interest.

*Data Availability Statement*—All data are contained in the database in the Supporting Information.

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