A Review of the Calculation of the Concentration of Dioxin Sorbed to Bed Sediment in Gunns' Draft Integrated Impact Statement

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Abstract

A review was undertaken of the calculation of dioxin sorbed to bed sediment in Gunns's draft Integrated Impact Statement. This review found that calculation errors, failure to include background dioxin concentrations, and failure to use the permitted maximum limit of dioxin in the pulp mill effluent, results in an underestimation of dioxin concentrations by a factor of 1,390 in the *Human Health Risk Assessment* and by a factor of 90 in the *Marine Impact Assessment.*

1 Dioxin

A dioxin is any compound containing the dibenzo-p-dioxin nucleus, while a furan is any compound containing the dibenzofuran nucleus. In total, there are 75 possible polychlorinated dibenzo-p-dioxin (PCDD) congeners and 135 possible polychlorinated dibenzo-p-furan (PCDF) congeners. Each PCDD/F congener has different physical, chemical and toxicological properties. Of the 210 PCDD/F congeners, 17 have been identified as posing significant risk to human health, with 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) being identified as the most toxic compound (the "Seveso-dioxin"). The toxicity of a mixture of dioxins and furans can be expressed by converting the concentrations of each dioxin and furan to an equivalent toxicity of 2,3,7,8-TCDD. Each converted toxicity is called a dioxin and furan toxic equivalent (TEQ) [1]. In this paper, concentrations of dioxins and furans are assumed to be reported as TEQs and dioxins and furans are referred to collectively as "dioxin". For example, 10 pg TEQ/L = 10 picogram (10^{-12}g) per litre equivalent toxicity to 2,3,7,8-TCDD (referenced as pg/L or pg dioxin/L if the context is clear).

2   Introduction

The major part of the assessment of risk to marine fauna and human health relating to pollutants in the effluent outfall of Gunns Limited (Gunns) proposed pulp mill [2] is based upon work carried out by Toxicos Pty Ltd (Toxicos). A key component of this assessment is the calculation of the concentration of dioxin sorbed to bed sediment in the vicinity of the outfall (located 3 km offshore near Five Mill Bluff, northern Tasmania). The relevant reports issued by Toxicos are:

- Human Health Risk Assessment, July 2006 [3];

- Potential Impact on Nearby Seal Colonies, July 2006 [4];

- Erratum, 15th September 2006 [5];

- Marine Impact Assessment, January 2007 [6];

- Expert witness statement of Dr Roger Drew, January 2007 [7].

An erratum to the July 2006 reports was issued by Toxicos in September 2006. This *Erratum* corrected an error in dioxin concentration in the effluent which had been assumed to be 0.074 pg TEQ/L; this was changed to 3.376 pg TEQ/L based on a calculation by Jaakko Pöyry [8]. Because of this change, none of the calculated impacts of dioxin as presented in the the July 2006 reports by Toxicos should be used. The revised impacts are presented in the *Erratum*. It must be noted that the minimalist presentation of the figures in the *Erratum* makes it very difficult to relate the revised impacts to the original reports.

3   Calculation Error

Toxicos used a protocol of the US Environmental Protection Agency (US EPA) to calculate the concentration of dioxin in the sediment near the pulp mill outfall [9]. This calculation was carried out in the *Human Health Risk Assessment* (July 2006) and the *Marine Impact Assessment* (January 2007).

Dioxins are strongly hydrophobic and partition from the effluent to the sediment and the water column. Toxicos carried out a calculation to determine the concentration of dioxin in the sediment within an area they term the DV_{100} , which is the "volume of water that abstractly contains effluent at 1/100th of that discharged". The DV_{100} conceptual model "is visualised as a block of water within which the effluent constituent concentration is constant and therefore at steady state with environmental compartments it contains (e.g. stationary biota and sediment)" ([6] p.3).

Toxicos summarise the equations used to calculate the concentration of dioxin in the sediment within this DV_{100} in their Figure 13.7 ([6] p.159), presented here in **Figure** 3.1.
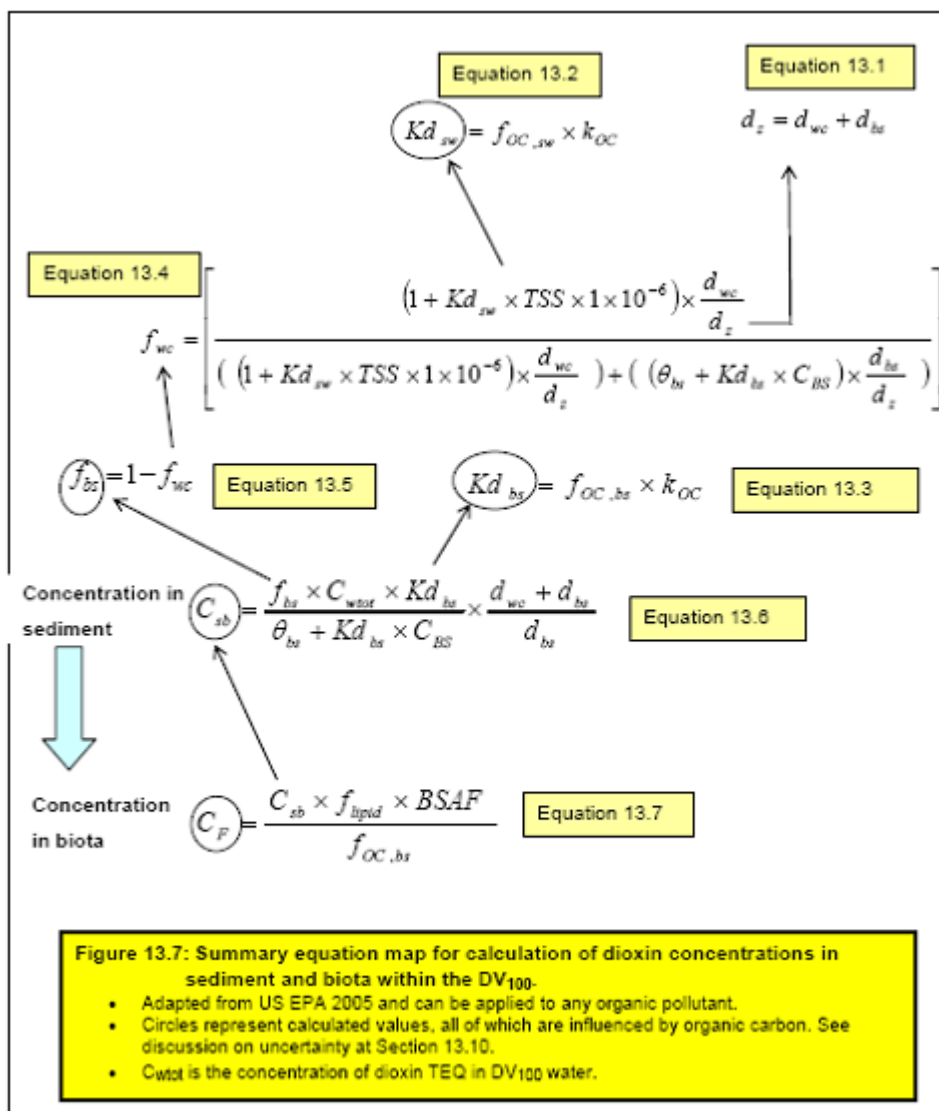
Figure 3.1: Summary of Toxicos Equations

Their Equation 13.6 is the same as Equation 5-47 cited in the US EPA protocol given here in **Figure** 3.2. COPC is an acronym for *Compound of Particular Interest*, in this case *dioxin*.

Figure 3.2: US EPA Equation 5-47 *(emphasis added)*

In US EPA Equation 5-47 Toxicos incorrectly set the parameter C_{wtot} equal to the dioxin concentration in the water: C_{wtot} is actually the concentration of dioxin in the water column <u>and sediment</u>. The definitions of the variables they use are given in their Table 13.9 ([6] p.160), an extract of which is shown here in **Figure** 3.3. Toxicos define the variable C_{wtot} (as used in their equation 13.6) as the "total dioxin concentration in DV_{100} <u>water</u>".

Figure 3.3: Toxicos Dioxin Concentration Assumption *(emphasis added)*

This is incorrect: the dioxin concentration in water is C_{wctot} as defined in Equation 5-45 of the US EPA protocol, reproduced here in **Figure** 3.4.

Figure 3.4: US EPA Equation 5-45 *(emphasis added)*

4 Impact of Error

Toxicos carried out a calculation of dioxin concentration in sediment in the *Human Health Risk Assessment* (July 2006) and the *Marine Impact Assessment* (January 2007). The calculations used in each of these reports used different assumptions with respect to the values of key parameters. Toxicos give no explanation for their use of these different parameters. Gunns have not withdrawn either of these reports from the draft IIS or from the referral under the Commonwealth EPBC Act. The *Marine Impact Assessment* used parameter values measured in Australian marine sediment; these may be more appropriate than the US EPA default values, but it is not clear that they are representative of conditions in the vicinity of the effluent outfall. The only Tasmanian marine sediment sample was taken at Cape Grim, far to the West; an estuarine sediment sample was taken in the lower Tamar River but this was not used in the Toxicos analysis.

4.1 Human Risk Assessment

In the Toxicos DV_{100}, we are given the concentration of dioxin in the water column; namely,

$$C_{\text{wctot}} = 0.034 \, \text{pg/L}. \tag{4.1}$$

US EPA equation 5-45 can be rearranged to solve for C_{wtot}, the concentration of dioxin in the water column and sediment:

$$C_{\text{wtot}} = \frac{C_{\text{wctot}}}{f_{\text{wc}}} \frac{d_{\text{wc}}}{d_{\text{wc}} + d_{\text{bs}}}, \tag{4.2}$$

where f_{wc} is the fraction of total water body dioxin in the water column given by Equation 36-A of the US EPA protocol (Toxicos equation 13.4) given here in **Figure** 4.1.

Recommended Equation for Calculating:
Fraction of Total Water Body COPC Concentration in
the Water Column (f_{wc}) and Benthic Sediment (f_{bs})

$$f_{wc} = \frac{(1 + Kd_{sw} \cdot TSS \cdot 1 \times 10^{-6}) \cdot d_{wc}/d_z}{(1 + Kd_{sw} \cdot TSS \cdot 1 \times 10^{-6}) \cdot d_{wc}/d_z + (\theta_{bs} + Kd_{bs} \cdot C_{BS}) \cdot d_{bs}/d_z} \qquad \text{Equation 5-36A}$$

$$f_{bs} = 1 - f_{wc} \qquad \text{Equation 5-36B}$$

where

f_{wc}	=	Fraction of total water body COPC concentration in the water column (unitless)
f_{bs}	=	Fraction of total water body COPC concentration in benthic sediment (unitless)
Kd_{sw}	=	Suspended sediments/surface water partition coefficient (L water/kg suspended sediment)
TSS	=	Total suspended solids concentration (mg/L)
1×10^{-6}	=	Units conversion factor (kg/mg)
d_z	=	Total water body depth (m)
θ_{bs}	=	Bed sediment porosity ($L_{water}/L_{sediment}$)
Kd_{bs}	=	Bed sediment/sediment pore water partition coefficient (L water/kg bottom sediment)
C_{BS}	=	Bed sediment concentration (g/cm³ [equivalent to kg/L])
d_{wc}	=	Depth of water column (m)
d_{bs}	=	Depth of upper benthic sediment layer (m)

Figure 4.1: US EPA Equation 5-36

The *Human Health Risk Assessment* used a value of Kd_{bs} = 292000 L/kg (the sediment/sediment pore water partition coefficient, which is a compound specific value and obtained from the US EPA database [10]). Total suspended solids (*TSS*, mg/L) were assumed to be zero. The water column depth (d_{wc}) is 26m based on the average depth near the proposed outfall; for the depth of upper benthic sediment layer (d_{bs}) a default value of 0.03m was adopted based on the median of values cited by US EPA [10]; for bed sediment porosity (θ_{bs}), a default value of 0.6 was adopted [10]; for bed sediment bulk density (C_{bs}), a default value of 1.0 g/cc was used [10].

Substituting these values into US EPA Equation 5-36A gives

$$f_{wc} = 0.002959 \qquad (4.3)$$

Putting this into equation (4.2) we obtain

$$C_{\text{wtot}} = 338 \times C_{\text{wctot}}. \tag{4.4}$$

Because Toxicos incorrectly used C_{wctot} in US EPA Equation 5-47 instead of C_{wtot}, it follows immediately that the correct estimate of dioxin concentration sorbed to bed sediment is given by $C_{\text{sb}}^{\text{correct}} = 338 \times C_{\text{sb}}^{\text{Toxicos}}$. That is, Toxicos underestimated the dioxin concentration in the sediment by a factor of 338.

The method used by Toxicos to calculate the dioxin concentration in the DV_{100} zone is unconventional. Usually, the average annual dioxin load to the water-body is calculated including airborne deposition, runoff (in this case, the influx from the outfall) and dioxins resulting from erosion of soil (not applicable to the DV_{100}). This approach uses US EPA Equation 5-35 to calculate the total dioxin loading; the equation is reproduced here in Figure 4.2.

Recommended Equation for Calculating:
Total Water Body COPC Concentration (C_{wtot})

$$C_{wtot} = \frac{L_T}{Vf_x \cdot f_{wc} + k_{wt} \cdot A_W \cdot (d_{wc} + d_{bs})} \qquad \text{Equation 5-35}$$

where

C_{wtot}	=	Total water body COPC concentration (including water column and bed sediment) (g COPC/m³ water body)
L_T	=	Total COPC load to the water body (including deposition, runoff, and erosion) (g/yr)
Vf_x	=	Average volumetric flow rate through water body (m³/yr)
f_{wc}	=	Fraction of total water body COPC concentration in the water column (unitless)
k_{wt}	=	Overall total water body COPC dissipation rate constant (yr^{-1})
A_W	=	Water body surface area (m²)
d_{wc}	=	Depth of water column (m)
d_{bs}	=	Depth of upper benthic sediment layer (m)

Figure 4.2: US EPA Equation 5-35

The total dioxin load is given by

$$L_T = C_e \frac{Vf_x}{100} \tag{4.5}$$

where Vf_x is the annual average volumetric flow rate through the DV_{100} (L/yr) and C_e is the effluent concentration (pg/L). Because the dioxin is assumed to be diluted by a factor of 100 , every 100L of water entering the DV_{100} is comprised of 99L seawater and 1L of effluent which is continuously flushed through the zone. The average volumetric

dissipation, k_{wt}, is zero due to the very low volatilisation of dioxins from the surface of the water. Substitution into US EPA Equation 5-35 gives

$$C_{wtot} = \frac{1}{f_{wc}} \frac{C_e}{100}. \tag{4.6}$$

Setting $C_{wctot} = \frac{C_e}{100}$ equation (4.6) only differs from equation (4.2) by the factor $\frac{d_{wc}}{d_{wc}+d_{bs}} = 0.999$, confirming $C_{wtot} = 338 \times C_{wctot}$.

4.2   Marine Impact Assessment

In the *Marine Impact Assessment* Toxicos calculated a value of Kd_{bs} , the sediment/sediment pore water partition coefficient, based upon the mean organic fraction of Australian marine sediments taken in a recent survey ([11]Table D3d). They did not assume that the total suspended solids in the water were zero. Under these assumptions, they calculate a value of $f_{wc} = 0.19$. (Note that the value of 0.019 reported Toxicos in Table 13.9 ([6] p.159) is incorrect, the actual value is 0.19.) Thus $\frac{1}{f_{wc}} = 5.4$. Applying the same correction as above, this implies that their calculation of dioxin concentrations in the sediment has been underestimated by a factor of 5.4 as compared to a proper implementation of the US EPA protocol.

Measurements of organic carbon content of suspended solids near the vicinity of the outfall area have not been made. Toxicos used the US EPA default value of 7.5%. The US EPA protocol, however, states that the 7.5% average for suspended material was based on a sediment carbon content of 3% to 5% [12]. Given the very low carbon content of the Australian marine sediments which lie in the range 0.048% to 1.4% with a mean 0.33%, a more appropriate average for organic content of suspended material at the effluent outfall, based on the same reasoning as the US EPA, is twice that of the sediment; that is, 0.66%. If this value is used in Toxicos Equation 13.2, instead of the inconsistent US EPA value of 7.5%, then dioxin concentration in sediment is underestimated by a factor of 15, compared to the Toxicos reported value (including the factor of 5.4).

5   Background Dioxin Concentrations

Measured background levels of dioxin range from 29 to 4200 pg dioxin/kg for Australian marine sediments, with a mean of 670 pg/kg ([11]Table D3c). These background dioxin concentrations were ignored in the Toxicos analysis. Background dioxin concentrations arise from airborne deposition, coastal erosion, run-off and dioxin concentrations in suspended solids and other (organic) detritus. If the average background concentration is included in the analysis, then Toxicos have underestimated concentrations by a factor of 44 for the *Marine Impact Assessment* and 360 for the *Human Health Risk Assessment*.

6   Concentration of Dioxin in Mill Effluent

The Toxicos analysis assumed that dioxin concentration in the effluent was 3.376 pg/L. This effluent dioxin concentration is an estimate by Jaakko Pöyry based on 10% of average

Canadian/Swedish mill effluent concentrations in the 1990s [8]. The proposed process for the manufacture of chlorine dioxide, however, is new to the pulp industry and has only been used previously for the manufacture of sodium chlorite [13]. It is highly likely that this process will take considerable time to be integrated into the pulp mill bleaching plant. During this period chlorine gas carryover in the chlorine dioxide bleaching gas (in solution) could significantly exceed design specifications and increase the dioxin load in the mill effluent. Moreover, because it is new technology, there is no guarantee that the process will reduce chlorine levels to those of existing pulp mills which used established technologies.

Historical emissions data from other mills which use a different chlorine dioxide manufacturing process should not have been used to estimate dioxin concentrations for the proposed mill. US EPA guidelines on emission modelling state that the correct effluent concentration for screening studies is 100% of the allowable emission limit: "As a minimum, the source should be modelled using the design capacity (100 percent load)" [14]. In this case, the dioxin concentration in the effluent should be at least the maximum concentration according to the emission limit guidelines: that is, 13 pg TEQ/L ([15], [6] p.122).

The use of the maximum limit imposed by the emission guidelines may not be conservative. During the commissioning period of the mill, the guidelines state only that: "*the proponent/operator will take all practicable steps to achieve the emission limits defined, which, for this period, may be regarded as targets*" ([15] p.38). Because the chlorine dioxide manufacturing process has not previously been integrated with a pulp mill, it is probable that the composition of the mill effluents will fall outside of the emission limits, and this may occur for a considerable period of time. The commissioning period is at least 18 months [16].

If the proper emission limit of 13 pg dioxin/L is used, rather than the Jaakko Pöyry estimate of 3.376 pg dioxin/L, together with previous corrections, the Toxicos analysis underestimates concentrations by a factor of 90 for the *Marine Impact* Assessmentt and 1,390 for the *Human Health Risk Assessment*.

7 Screening Studies

Toxicos applied the US EPA protocol to a "dilution zone" near the effluent outfall. The dilution zone was assumed to be that volume in which the pollutant had been diluted by a factor of $1/100$ from the concentration in the effluent pipeline, the so called DV_{100}. This methodology is not appropriate for the calculation of dioxin concentrations which are hydrophobic and strongly sorb to sediment. The US EPA states that their equations (as applied in the US EPA protocol): "*predict the steady-state mass of contaminants in the water column and underlying sediments, and don't address the dynamic exchange of contaminants between the water body and the sediments following changes in external loadings. While appropriate for calculating risk under long-term average conditions, evaluating complex water bodies or shorter term loading scenarios might be improved by using a dynamic modeling framework*". ([10]p.5-62)

In addition, the Toxicos analysis applied only to single point "average" values of sed-

iment properties, and did not look at the range of sediment types and seabed in the vicinity of the outfall which include sandy sediment, basalt outcrops, seagrass beds and reefs. Each of these will have a different range of appropriate parameters, particularly organic carbon content. A proper screening study would have looked at the range of possible dioxin concentration outcomes and determined the likelihood that dioxin contamination from the mill effluent could pose a risk to sensitive aquatic organism, marine mammals, birds, fish and humans. No probabilistic risk analyses were undertaken.

8   Conclusion

This review found that calculation errors, use of inappropriate parameter values, failure to include background dioxin concentrations, and failure to use the permitted maximum limit of dioxin in the pulp mill effluent, results in an underestimation of dioxin concentrations by a factor of 1,390 in the *Human Health Risk Assessment* and by a factor of 90 in the *Marine Impact Assessment*. The impacts of these errors are far reaching and invalidate all of the quantitative ecotoxicological analyses prepared for assessment under the Tasmanian Pulp Mill Assessment Act 2007 and for assessment of the pulp mill project under the Australian Environment Protection and Biodiversity Conservation Act 1999.

9   References

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