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Abstract

A review was undertaken of the calculation of dioxin in sediment and fish as presented in Gunns’ draft Integrated Impact Statement. This review found that calculation errors and an incorrect interpretation of the results of hydrodynamic modelling has lead to an underestimation of the area of likely contamination by a factor of 785. It is highly likely there will a significant impact on sensitive aquatic organisms and marine mammals, and the eating of Australian salmon taken from the area between Five Mile Bluff and the mouth of the Tamar Estuary would constitute a significant health risk.

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

A key component in 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 review of their calculation of the concentration of dioxin sorbed to bed sediment was carried out by the author [3]. The 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, resulted in an underestimation of dioxin concentrations in sediment by a factor of 1,390 in the Human Health Risk Assessment [4] and by a factor of 90 in the Marine Impact Assessment [5].

Dioxins are strongly hydrophobic and partition from the effluent to the sediment and the water column. Toxicos determined the concentration of dioxin in the sediment within a zone they term the DV_{100}, which is the “volume of water that abstractly contains effluent at 1/100th of that discharged”. Toxicos relied on hydrodynamic modelling to estimate the volume and area of the DV_{100}, but no hydrodynamic modelling of dioxins and the partitioning of dioxin to suspended solids in the water column or to the bed sediment has been carried out.

Lane and Associates, on page 12 of their report on Marine and Migratory Avifauna [6], incorrectly assert that dioxins were, in fact, modelled: “The effluent plume will cover an area of offshore marine waters of up to 500 metres from the outfall diffuser (Vol 18, Draft IIS, sections 6.6.3, 6.6.4 and 6.7). Beyond the effluent plume levels of dioxin have been modelled at levels not exceeding water quality objectives.” The last statement is false. The hydrodynamic modelling reported in Volume 18 Appendix 63 of the draft Integrated Impact Statement (IIS) by GHD did not carry out any modelling of dioxin pollution [7]. Page 6 of the Appendix states that the assessment of “the potential for the deposition of suspended solids and the accumulation of pollutants on the sea floor (deposition zones) within the proposed mixing zone ...” was NOT part of the modelling scope.

3 Plume Dispersion Modelling

The hydrodynamic plume modelling used a Lagrangian model incorporating the projected-area entrainment (PAE) hypothesis ([7] p.47). The plume is assumed to be steady state: in the Lagrangian formulation this implies that successive elements follow the same trajectory. The plume envelope remains invariant while elements moving through it change their shape and position with time.

The trajectory is viewed as a series of non-interfering “plume-elements” which increase in mass as a result of shear-induced entrainment (due to the jet discharge) and vortex-entrainment (due to the crossflow) while rising by buoyant acceleration (Figure 3.1). The model tracks the evolution of the average properties of a plume element at each step by
conservation of horizontal and vertical momentum, conservation of mass accounting for entrainment, and conservation of tracer mass.

The dilution of the tracer is due to entrainment of background water. In the case of dioxins, the concentration of the background water is in equilibrium with, and arises from, the concentration of dioxin sorbed to bed sediment. As the concentration of dioxin builds up in the sediment over time, the concentration in the background water will increase, leading to lower effective dilution of the plume. The actual achieved dilution will depend upon the difference in concentrations between the plume and background water. Within the zone of initial dilution (ZID) the dioxin concentration will build up to a level which asymptotes towards that of the raw effluent concentration. The final concentration will depend upon the rate of flushing within the tidal-current dominated coastal environment.

![Figure 3.1: Buoyant Plume (after [10])](image)

This effect, of asymptotically increasing background dioxin concentrations, was not simulated in the hydrodynamic model, leading to significant overestimation of dioxin dilution. In the hydrodynamic model dioxin concentrations were either low (possibly arising from plume reversal) or zero. The areal extent of the DV$_{100}$, which has an average dilution of 1/100, will be significantly larger than the area of the ZID (approximately 500m x 250m) assumed by Toxicos.
4 Dioxin Load to Coastal Environment

4.1 Dioxin Concentration in Water Column

US EPA Equation 5-35 can be used to calculate total dioxin loading; the equation is reproduced here in Figure 4.1.

\[
C_{\text{wtot}} = \frac{L_T}{V_f \cdot f_{wc} + k_{wt} \cdot A_w \cdot (d_{wc} + d_{bs})}
\]

Equation 5-35

where

- \( C_{\text{wtot}} \): Total water body COPC concentration (including water column and bed sediment) (g COPC/m\(^3\) water body)
- \( L_T \): Total COPC load to the water body (including deposition, runoff, and erosion) (g/yr)
- \( V_f \): Average volumetric flow rate through water body (m\(^3\)/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 (m\(^2\))
- \( d_{wc} \): Depth of water column (m)
- \( d_{bs} \): Depth of upper benthic sediment layer (m)

Figure 4.1: US EPA Equation 5-35

The average volumetric dissipation, \( k_{wt} \), is zero due to the very low volatilisation of dioxins from the surface of the water; thus the equation simplifies to

\[
C_{\text{wtot}} = \frac{L_T}{V_f \cdot f_{wc}}.
\]

(4.1)

The average volumetric flow rate through the water body, \( V_f \), can be calculated from the flushing time of Bass Strait coastal waters \[9\] and the influx of effluent to the water body. At the flushing time, 63\% of the original water has been displaced by water outside of the area. The rate of dilution of original water due to flushing declines exponentially; thus the actual volume of external water influx is equal to the volume of the water body itself. That is, if \( V_{wb} \) is the volume of the water body, and \( \tau \) is the flushing time in years, then the average volumetric flux due to flushing alone, \( Q_{wb} \), is

\[
Q_{wb} = \frac{V_{wb}}{\tau}.
\]

(4.2)
The total average volumetric flow rate through the water body is given by \( V_f = Q_{wb} + Q_e \), where \( Q_e \) is the average annual effluent rate. From equation (4.1) we obtain

\[
C_{w,tot} = \frac{L_T}{(Q_{wb} + Q_e) \cdot f_{wc}.} \tag{4.3}
\]

Using US EPA Equation 5-45 ([3], Figure 3.4) and substituting \( L_T = C_e Q_e \), the concentration of dioxin in the water column, \( C_{w,tot} \), becomes

\[
C_{w,tot} = \frac{C_e Q_e}{Q_{wb} + Q_e} \cdot \frac{d_{wc} + d_{bs}}{d_{wc}}, \tag{4.4}
\]

where \( C_e \) is the concentration of dioxin in the effluent, \( d_{wc} \) is depth of water column, and \( d_{bs} \) is depth of sediment layer (thickness). The water column depth \( (d_{wc}) \) is the average coastal depth near the proposed outfall and is approximately 20m; 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 [8]. The ratio \( \frac{d_{wc} + d_{bs}}{d_{wc}} = 1.0015 \approx 1 \). On making this approximation and substituting equation (4.2), equation (4.4) becomes

\[
C_{w,tot} = \frac{C_e V_e}{V_{wb} + V_e}. \tag{4.5}
\]

where \( V_e = Q_e \tau \) is the volume of effluent discharged over one flushing period. Defining \( N_{wb} = \frac{V_{wb}}{V_e} \), the ratio of the water-body volume to the volume of effluent discharged in the flushing period, equation (4.5) becomes

\[
C_{w,tot} = \frac{C_e}{1 + N_{wb}}. \tag{4.6}
\]

1/100 Dilution Zone

The total volume of effluent released during the flushing period \( \tau = 0.5 \) yr is \( V_e = 738 \) L/s \( \times \) \( 86400 \) s \( \times \) 182.5 days = 11.64 GL. Setting the dilution to 1/100, gives \( N_{100} = 99 \) with \( V_{100} = 1152 \) GL. This volume is 370 times greater than that of the DV_{100} zone used by Toxicos.

4.2 Area of Contamination

Toxicos presented maps showing the dilution of a conservative tracer emitted at the effluent outfall ([5] Appendix 7). These maps were based on the hydrodynamic modelling
carried out by GHD. A minimum dilution/maximum concentration map is reproduced here in Figure 4.2 for the bottom layer of the (near field) hydrodynamic model.

The preparation of the dilution map was made by running the hydrodynamic model for a period of two months (using oceanographic conditions for April 2005) and storing at three-hour intervals (simulation time) tracer concentration distributions. These distributions were treated as raw data and were statistically processed to generate median, 95th percentile and maximum tracer concentration maps (Section 4). The dilution maps are the reciprocal of tracer concentration, scaled to initial tracer concentration in the effluent.

The two month simulation period used to generate these maps is only a third of the flushing time for the near coastal region. Moreover, as dioxins are persistent and accumulate in the sediment, equilibrium between dioxin concentration in the effluent and that in the sediment near the outfall may take years to achieve. The dilution maps are misleading (for dioxin) and the dilution contours should not be used for quantitative analysis of the distribution of dioxins in the coastal marine area.

Although the spatial extent of the pollutant area has been underestimated, the bound-
ary of the dilution zone was used to define an *area of likely contamination* (ALC). This boundary is shown in Figure 4.2 and extends approximately 3 km to the east from the outfall and approximately 12 km westwards along the coast. The area covered by the plume is approximately 110 km$^2$. Between Low Head and Five Mile Bluff, the plume intrudes into the Commonwealth marine environment over an area of approximately 12 km$^2$. Average water depth between the shoreline and the Commonwealth marine area is approximately 20 m; thus the total volume of water in the ALC is $V_{wb} = 110 \text{ km}^2 \times 20 \text{ km} = 2200 \text{ GL}$. The ratio between the volume of water in the contamination zone and the effluent flushing volume is $N_{wb} = 189$; giving an average dilution in the ALC of 1/190.

5 Dioxin Concentration in Area of Likely Contamination

The calculation of dioxin concentration in sediment and fish in the *area of likely contamination* is carried out using a protocol of the US EPA ([8], [5] Figure 13.7). The concentration of dioxin in sediment is calculated using US EPA Equation 5-36 ([3] Figure 4.1) which returns $f_{wc}$, the fraction of total water body dioxin concentration in the water column. Significant inputs to the calculation include: suspended sediments/surface water partition coefficient, bed sediment/sediment pore water partition coefficient, suspended solids organic fraction, sediment organic fraction, and background dioxin concentrations. A Monte Carlo approach [12] to the estimation of dioxin concentrations was used with the inputs to the Monte Carlo analysis defined below. In the Monte Carlo analysis, measured data were discretely sampled (equivalent to bootstrap sampling [16]).

$f_{OC,bs}$ *Organic carbon fraction in bed sediment.* The fraction of organic carbon in marine and estuarine sediments at sites around Australia was report by Müller et al. [13]. They measured the total organic carbon (TOC) of 12 marine sediments and 12 estuarine sediments. Aquenol Pty Ltd (Aquentol) surveyed the proposed outfall site and observed bare sand covered an average of 43.6% of the seabed, whilst bare reef of various types covered an average of 24.1%. The remaining areas of seabed comprised 28.3% flora cover (algae, in addition to the seagrass *Zostera tasmanica*) and 4.1% faunal cover. The ALC extends from east of Five Mile Bluff to the Tamar Estuary, a distance of 15 km: because Aquentol surveyed only the area in the immediate vicinity of the effluent outfall, the sediment bed types surveyed may not be representative of the whole of the ALC.

In the analysis, the measured marine TOCs were used for 80% of the Monte Carlo sampling, and the measured estuarine TOCs were used for the remaining 20%. Use of 20% estuarine TOCs, which on average are higher than marine TOCs, is consistent with 28% of the surveyed bed area having flora cover (which will have higher TOC than the reef and sand areas of the contaminant zone), and is consistent with the ALC extending into the Tamar Estuary. The measured TOC data were discretely sampled in the Monte
Carlo analysis.

\( f_{OC,sw} \) **Organic carbon fraction in suspended solids.** The US EPA gives a default value of 7.5% for organic carbon fraction in suspended solids. The protocol, however, states that the 7.5% average for suspended material was based on a sediment carbon content of 3% to 5% \cite{15}. 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. In the Monte Carlo analysis a triangular distribution with low 1, mode 2 and high 10 was sampled and used to scale the TOC in the sediment from which the TOC in the suspended solids was calculated. Maximum TOC was truncated to 10%.

\( K_{OC} \) **Organic carbon partition coefficient.** A default value of the organic carbon partition coefficient of 3,890,000 L/kg is given by the US EPA \cite{8}. This is based on laboratory measurements. While the US EPA protocol assumes equilibrium between sediment and water column dioxin concentrations, there is significant evidence that dioxin sorption to sediment is non-linear (increases at high concentrations in the sediment \cite{17}) and is hysteretic (adsorption is significant faster than desorption, which may be irreversible \cite{18}, \cite{19}, \cite{20}). Moreover, recent field measurements have shown that actual sediment partition coefficients can be significantly larger, by 2 orders of magnitude, than laboratory measured values \cite{21}. This uncertainty was implemented in the Monte Carlo analysis by scaling the default value by a factor selected from a range of 0.1 to 100; a triangular distribution with low -1, mode 1 and high 2 was sampled, and used as the logarithm (base 10) of the scaling factor. (Logarithmic sampling was used so as to avoid biasing the scaling factor to high values.)

\( K_{d_{sw}}, K_{d_{hs}} \) **Sediment/water partition coefficients.** The suspended sediments/surface water partition coefficient was obtained by multiplying the organic carbon content of the suspended sediments by the organic carbon partition coefficient. The bed sediments/pore water partition coefficient was obtained by multiplying the organic carbon content of the bed sediments by the organic carbon partition coefficient.

**TSS Total suspended solids concentration.** Aquenol measured the suspended solids concentration from 17 samples taken near the outfall (\cite{13} Appendix 10). In the Monte Carlo analysis these values were discretely sampled.

**Background dioxin concentration.** As part of the National Dioxin Project, Gatehouse \cite{27} measured the level of dioxins in marine and estuarine sediments. Measured background levels of dioxin range from 29 to 4200 pg dioxin/kg for Australian marine
5 DIOXIN CONCENTRATION IN AREA OF LIKELY CONTAMINATION

sediments, with a mean of 670 pg/kg. Estuarine dioxin levels ranged from 66 to 520,000 pg/kg, the highest concentrations were found in sediments from the urban and industrial regions of the Parramatta River estuary. Background dioxin concentrations arise from airborne deposition, coastal erosion, runoff and dioxin concentrations in suspended solids and other (organic) detritus. Only measured values for marine sediments were used in the Mont Carlo analysis; these were sampled discretely.

5.1 Concentration in Sediment

Dioxin concentration in the mill effluent was set at 13 pg TEQ/L, the maximum permissible limit under proposed emission limits [22]. The Monte Carlo analysis was carried out using 100,000 trial simulations.

The calculated average concentration of dioxin in the area of likely contamination is 4,370 pg/kg including background concentrations. Figure 5.1 shows the calculated cumulative probability distribution of dioxin concentration in the sediment. The probability of exceedance gives that fraction of the ALC where dioxin concentrations are higher than the plotted value.

![Figure 5.1: Dioxin Concentration in Sediment](image)

60% of the sediments have dioxin concentrations which exceed the Environment Canada...
lower limit of 850 pg/kg for sensitive marine life [23], 55% of the sediments exceed the limit of 1,000 pg/kg of the Wisconsin Department of Natural Resources for the protection of human receptors [24], 40% of the sediments exceed the lower limit of 2500 pg/kg given by the US EPA for the protection of mammals [25] and 5% of the sediments exceed the proposed Dutch limit of 15000 for protection of fish eating predators [24]. (Dioxin limits are reviewed in References [24] and [26]).

5.2 Bioaccumulation of Dioxin in Fish

Extremely hydrophobic pollutants like dioxins, furans, and PCBs have a high tendency to bioaccumulate and are sorbed to the bed sediments more than associated with the water phase. The US EPA recommends using biota-sediment accumulation factors (BSAFs) to calculate concentrations of dioxins, furans, and PCBs in fish ([8] pp 5-84). A BSAF equal to one indicates that the dioxin concentration is the same in the soil as in the organism (on a lipid normalised basis), a BSAF less than one indicates the dioxin concentration is higher in the soil than in the organism, and a BSAF greater than one indicates the dioxin concentration is higher in the organism than in the soil.

Toxicos used an average BSAF of 0.046, within a range 0.0008 to 0.20 ([5] Table 13.3); the US EPA recommends a value of 0.09 based on organic content of 3% and whole fish lipid content of 7% (compared to 2% average lipid content for Australian fish ([13] Table E2e). A recent survey gave a mean BSAF of 0.433 for fish from the New York Bight [16].

For this study, two sentinel fish species (geographically near to the area of interest) were selected from the survey of Gatehouse [27], together with the US EPA standard fish. The lipid fraction and BSAF for the fish are given in Table 5.1.

<table>
<thead>
<tr>
<th>Fish Species</th>
<th>Lipid</th>
<th>BSAF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australian Salmon (Derwent River)</td>
<td>0.062</td>
<td>0.2</td>
</tr>
<tr>
<td>Flathead (Lower Yarra)</td>
<td>0.009</td>
<td>0.046</td>
</tr>
<tr>
<td>US EPA standard fish</td>
<td>0.07</td>
<td>0.09</td>
</tr>
</tbody>
</table>

While Australian salmon (*Arripus trutta*) are migratory, the eastern subspecies have their breeding and nursery area in Bass Strait and Tasmanian waters; young fish spend the first two years of their life in estuaries and inlets. The calculated average dioxin content for Australian salmon was 22,750 pg/kg. This is similar to the measured average dioxin content of 29,100 pg/kg for bream sampled from Sydney Harbour which is contaminated with dioxins [28].
The average dioxin content of the flathead was 760 pg/kg and the average dioxin content of the US EPA standard fish was 11,560 pg/kg. Figure 5.2 shows the cumulative probability distribution for each fish, giving the probability that dioxin concentration in the fish will exceed the plotted value. Also shown in the figure are the Australian and European action limits for dioxin concentration in fish ([29], [30]), which are 4,000 pg dioxin/kg fish and 6,000 pg dioxin/kg fish, respectively. The US EPA proposes a risk threshold of 700 pg dioxin/kg-fish for mammalian wildlife, a high risk threshold of 7,000 pg dioxin/kg-fish for mammalian wildlife, a risk threshold of 6,000 pg dioxin/kg-fish for avian wildlife, and a high risk threshold for avian wildlife of 60,000 pg/kg fish ([5] Table 13.5).

Both the EPA standard fish and Australian salmon exceed the lowest threshold of 700 pg/kg more than 85% of the time; flathead exceed the threshold 30% of the time; and, Australian salmon exceed the Australian action limit of 6,000 pg/kg (recommended by the Port Jackson Expert Panel [29]) more than 55% of the time: that is, more often than not.
5.3 Impact on Human Health

In 2002, the Australian National Health and Medical Research Council (NHMRC) established a tolerable monthly intake (TMI) for dioxins of 70 pg TEQ/kg of body weight from all sources (including food, air and dermal exposure). The tolerable intake was established on a monthly basis to indicate the long-term nature of any potential dioxin toxicity.

Using the same criteria as Food Standards Australia New Zealand (FSANZ), consumption of one 210g serve of Australian salmon per month would exceed the tolerable monthly intake for dioxins by 120%. It is likely that commercial and recreational fisheries in the area would need to be closed or restricted.

6 Conclusion

In the Marine Impact Assessment Toxicos state that their assessment leads to the “inevitable conclusion that the small amount of dioxin in the discharged Bell Bay effluent will not adversely affect local aquatic mammals or birds” ([5] p7). In the Human Health Risk Assessment they state that “anticipated dioxin concentrations in discharged mill effluent do not pose a health risk to people consuming fish caught in the vicinity of the outfall” ([4] p10). These statements are demonstrably wrong.

The review of the Toxicos calculation of dioxin sorbed to bed sediment showed that errors in the implementation of the US EPA protocol, 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. This review found that Toxicos underestimated the area of the 1/100 dilution zone, the DV$_{100}$, by a factor of 370; the hydrodynamic modelling carried out for the draft IIS did not model dioxins, and is incapable of quantifying the dilution and dispersion of dioxins in the vicinity of the effluent outfall.

An area of likely contamination extending from Five Mile Bluff to the Tamar Estuary was considered in the screening analysis carried out in this review. This area covers some 110 km$^2$, intrudes at least 12 km$^2$ into the Commonwealth marine area, and is 785 times larger than the 0.14 km$^2$ area used by Toxicos in their analysis. Using the US EPA protocol and Monte Carlo analysis, the average dioxin concentration in sediment in the area was calculated to be 4,370 pg/kg. This value exceeds the lower limit of 2,500 pg/kg proposed by the US EPA for the protection of marine mammals by 75%.

The analysis implies that the eating of Australian salmon taken from the area between Five Mile Bluff and the mouth of the Tamar Estuary would constitute a significant health risk. The average concentration of dioxin in Australian salmon would exceed the Australian action limit by 280%. Using the same criteria as FSANZ, consumption of one
210g serve of Australian salmon per month would exceed the tolerable monthly intake for dioxins by 120%.

This review has shown that the calculation of dioxin concentrations in sediment and fish from near the effluent outfall as presented in Gunns’ draft Integrated Impact Statement is wrong. All of the quantitative ecotoxicological analyses with respect to dioxin, 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, are invalid.

7 References


