KOEBERG NUCLEAR POWER STATION CWDP

Addendum Report:

Evaluation of Toxicity Risks associated with the discharge of film forming amine (FFA) to the marine environment

PREPARED FOR:

PRDW

Consulting Port and Coastal Engineers

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1 INTRODUCTION

The Koeberg Nuclear Power Station (KNPS) currently employs hydrazine to control dissolved oxygen concentrations, pH levels and associated corrosion in boilers, amongst other purposes. Excess/residual hydrazine is discharged into the sea where it may generate toxicity effects, specifically in kelp sporophytes. To avoid such risks KNPS is evaluating the use of film forming amine (FFA) products instead of hydrazine. These are water repellent (hydrophobic) chemicals that form a mono-molecular film on metal surfaces thereby protecting them from corrosion. The Material Safety Data Sheet for a commercially available FFA, ODACON® F, identifies the product as being very toxic to aquatic organisms even though it is rated as being slightly soluble to insoluble with a rapid degradation rate (Reicon 2018). Reported LC_{50} values are variable which appears to be linked to uncertainty on whether observed toxicity was due to physical or chemical effects.

As part of their product evaluation KNPS requires an evaluation of toxicity risks associated with episodic discharges of representative FFAs to the receiving marine environment.

2 FFA CHEMICAL AND PHYSICAL PROPERTIES

The candidate FFAs assessed are hydrogenated alkyl amine (CAS # 61788-45-2) and octadecylamine (CAS # 124-30-1 (EU 2008). These compounds are defined as oligo alkylamine fatty amines. The chemical formula of octadecylamine is $C_{18}H_{39}N$, alternatively written as CH_3-$(CH_2)_{17}$-NH_2 (Santa Cruz Biotechnology 2010, Odar and Rudling 2017). Hydrogenated alkyl amine is also a C_{18} compound but includes C_{12}-C_{16} compounds such as non-hydrogenated tallow alkyl amine, (Z)-Octadec-9-enylamine and coco alkyl amine (EU 2008). Typically, in their native form the physical state of FFAs are colourless or white solids and are rated as being insoluble. Note, however, that the commercially available FFA product, ODACON® F, is sold in liquid form implying that it contains a solubilising agent (Reicon, 2018). Melting points are in the range of 48-56 °C and decomposition occurs at 450 °C. Breakdown products include ammonia (NH_3), hydrogen, carbon dioxide and methane (CH_4) (EU 2008).

As stated above FFAs are strongly hydrophobic as reflected in octanol/water coefficients (K_{ow}) of Log 7 with an estimated soil water coefficient (K_{oc}) of log 5.5 as calculated from the Log K_{oc}/Log K_{ow} relationship for non-polar organic compounds (Di Toro 1985). Strong adsorption to particulate matter is therefore expected [1] (OECD 2018). Given the high K_{ow} FFAs in general should bioconcentrate in aquatic organisms. Due to strong particle affinity this is most likely through ingestion, with candidate organisms being filter and deposit feeders. Contrary to this, FFAs are not

[1] http://www.ncbi.nlm.nih.gov/compound/15793#-section:environment-Fate-Exposure-summary

regarded as being persistent in aquatic environments as biodegradation rates are below the 60-day half-life threshold for marine water and 180 days for marine sediments[2].

3 FFA TOXICITY TO MARINE ORGANISMS

The measurement of FFA toxicity effects on aquatic organisms is complicated by the affinity of the chemicals for surfaces, thereby reducing the dissolved fraction in chemical exposures (OECD 2018), and uncertainty on the actual toxicity effect; i.e. is the observed response due to film forming or chemical toxicity? These uncertainties have led to most of the reported toxicity assessments as being subject to caveats (e.g. EU 2008). These mostly relate to what the actual toxicity agent exposure concentration was and how this declined, or not, over the period of exposure. EU (2008) provide summary toxicity data (EC_{50}, NOEC and, for aquatic plants EBC_{50}) for freshwater fish, invertebrates and algae. No information on FFA toxicity effects in marine organisms could be sourced in this assessment.

Toxicity test data listed in EU (2008) show an increasing gradient with carbon chain length; C_{12}-C_{16} FFA compounds exhibiting lower toxicities than C_{18} compounds. As stated above, hydrogenated tallow amine and octadecylamine are C_{18} compounds, recorded toxicity levels for such are summarised in Table 3-1.

Table 3-1: Summary of fresh water mean LC_{50} and NOEC levels in fish and invertebrates and mean EBC_{50} concentrations for algae for C_{18} FFA compounds (from EU 2008).

Test Organism	**LC_{50} (mg/L)**	**n**	**NOEC (mg/L)**	**n**
Fish	0.37	4	0.24	4
Invertebrates	0.16	6	0.04	5
	EBC_{50} (mg/L)	**n**	**NOEC** (mg/L)	**n**
Algae	0.12	7	0.05	7

The summary data indicate that fish are the least sensitive of the tested organisms but show LC_{50} values below 1 mg/L which classifies the FFA compounds as being toxic to aquatic organisms (e.g. Leung et al 2001).

The toxicity test results summarised above were derived from exposures in low to zero carbon load conditions. Additions of humic acid to a concentration of 5 mg/L in test chambers showed an order of magnitude decrease in FFA toxicity levels across all groups tested (EU 2008). Consequently, under expected natural conditions with normal organic carbon loads toxicities would be above 1 mg/L.

Marine species in general are considered to be more sensitive to toxins than freshwater species as shown by the accepted conversion factor of 0.1 when converting toxicity levels from freshwater to marine conditions (OECD 1992). Natural marine waters characteristically contain dissolved organic

[2] https://-www.epa.gov/sites/production/files/2017-09/documents/pbt_public_webinar_-_9-5-17.pdf

compounds as well as particulate organic and inorganic particles and therefore the observed reduction in FFA toxicity is likely to apply. This being the case the toxicity concentrations summarised in Table 3-1 are considered to be applicable the marine environment.

To account for the differences between freshwater and the marine environment, the water quality threshold is adjusted by an assessment factor of 10 (AF, ANZECC 2000, OECD 1992) applied to the lowest NOEC concentration listed in Table 3-1; i.e. 0.004 mg/L C_{18} chain FFA compound.

The sole marine sediment toxicity criterion that could be sourced in this assessment is the PNEC[3] estimate of 0.376 mg/L. This is derived from a freshwater sediment estimate of 3.76 mg/L (Reicon 2018). Given that no supporting data are provided for this estimate it is treated caution.

4 PREDICTED FFA CONCENTRATION IN THE KPS DISCHARGE

The predicted FFA concentration at the end of the outfall channel following within-channel mixing of the CRF (circulating water system) effluent with the co-discharges as predicted from hydrodynamic modelling. The estimate is based on dosing with ODACON at 5 mg/L which has a 10% concentration of octadecylamine giving 0.5 mg/L in the XCA and SEK systems (D Jeannes, KNPS, *in litt*.). Assuming concurrent discharge of the XCA and SEK, the concentration of octadecylamine is reduced to 0.0012 mg/L at the end of the outfall channel (point of discharge into sea) due to dilution and mixing with the CRF discharge. The dilution factors in the outfall channel are obtained from the model results described in PRDW (2015). This will obviously dilute further in the receiving water body as the combined effluents enter the far-field mixing phase.

5 CONCLUSIONS

The predicted discharge concentration is of a similar order of magnitude as the estimated water quality threshold but a factor of 3 lower. As the water quality threshold was derived from NOEC levels through application of an AF of 10 estimated discharge concentrations are 30x lower than the NOECs. Additionally, given the propensity of FFAs to adsorb to particulate matter it is probable that the dissolved FFA fraction will rapidly diminish in the receiving environment over and above attenuation through mixing in the effluent discharge plume. A further mitigating factor is that FFA discharges would be intermittent and linked to boilers being brought back into operation following lay-ups. Dissolved phase toxicity effects are therefore considered to be unlikely. The particle adsorbed FFA will be distributed in the far-field and may accumulate in the identified depositional areas of Murray Harbour on Robben Island and/or the KNPS cooling water intake basin (PRDW 2015). Given that FFA compounds are not classified as being persistent in aquatic environments due to measured moderately rapid degradation rates (EU 2008), deleterious effects on biota in the

[3] PNEC = Probable no effect concentration

depositional areas are also unlikely. The predicted high sediment PNEC would support this conclusion but, as noted, should be considered as a ‘low confidence’ estimate.

As the predicted discharge concentration is below the defined receiving water quality threshold and discharges will be intermittent, from this toxicity evaluation, FFAs are considered to be less of a toxicity risk than hydrazine.

6 REFERENCES

ANZECC, 2000. Aquatic Ecosystems — Rationale and Background Information. In Australian and New Zealand Guidelines for Fresh and Marine Water Quality (Volume 2). pp. 8.1–1 – 8.1–32. Available at: http://link.springer.com/content/pdf/10.1007/978-94-007-5704-2_92.pdf [Accessed October 3, 2019].

Di Toro DM 1985. A particle interaction model of reversible organic chemical sorption. Chemosphere 14(10), 1503-11538.

Leung MY, et al 2001. Can saltwater toxicity be predicted from freshwater data? Marine Pollution Bulletin 42(11), 1007-1013.

Odar S and P Rudling 2017. Use of film forming amines (FFA) in nuclear power plants for lay-up and power operation. Advanced Nuclear Technology International, Tollered, Sweden. 21 pp.

OECD 1992. Report of the Organisation for Economic Co-operation and Development (OECD) workshop on the extrapolation of laboratory aquatic toxicity data to the real environment. OECD Monograph No. 60, Organisation for Economic Co-operation and Development, Paris.

OECD 2018. Guidance document on aqueous-phase aquatic tocixity testing of difficult test chemicals. OECD Environment, Health and Safety Publications Series on Testing and Assessment No 23. Environment Directorate: Organisation for Economic Co-operation and Development, Paris.

PRDW 2015. Koeberg Nuclear Power Station: Coastal processes technical information in support of the coatal waters discharge permit application. Dispersion modelling of thermal, chemical sediment and radionuclide discharges specialist study. PRDW Report reference S2015-RP-CE-001_R4. 237pp.

Reicon 2018. ODACON® F Safety Data Sheet. Reicon, Leipzig, Germany.

Santa Cruz Biotechnology 2010. Octadecylamine Material safety Data Sheet. Santa Cruz Biotechnology Inc., Santa Cruz, California, USA.