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Review of entrained oil thresholds

A Negri, D Brinkman, and R Jones

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Review of entrained oil thresholds, July 2024

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Australian Institute of Marine Science

PMB No 3
Townsville MC QLD 4810

PO Box 41775
Casuarina NT 0811

Indian Ocean Marine Research Centre
University of Western Australia, M096
Crawley WA 6009

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A	Prepared by:	Andrew Negri, Diane Brinkman, Ross Jones	*18-Jul-2024*	
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Abbreviation and expanded definition table

AIMS	Australian Institute of Marine Science
EMBA	Environment that May Be Affected
MAH	Monocyclic aromatic hydrocarbon
NOPSEMA	National Offshore Petroleum Safety and Environmental Management Authority
PAH	Polycyclic aromatic hydrocarbons, when dissolved the most toxic components of oil
ppb	Parts per billion, equivalent to µg/L
ppm	Parts per million, equivalent to mg/L
SIMAP	An integrated oil spill impact model system https://asascience.com/software/simap/
THC	Total hydrocarbons, which represents the true concentration of oil droplets, measured on a mass basis as some components cannot be quantified by other analytical methods.
Threshold	The term “threshold” is used by French-McCay (2024), while “exposure values” is used by NOPSEMA (2019) (Table 1). These are assumed to have a similar meaning and “Threshold” is used in this review. This review focusses on entrained oil thresholds in the context of oil spills, not other discharges (e.g., produced formation water).
TPH	Total petroleum hydrocarbons, which represent the hydrocarbon fraction that can be measured/quantified.
TRH	Total recoverable hydrocarbons; synonymous to TPH
Units of measurement for entrained oil	NOPSEMA (NOPSEMA, 2019) described the threshold for entrained oil in ppb (µg/L), but parameter (PAH, TAH, THC) was not specified. French-McCay (2024) used the parameter total hydrocarbons (THC) in ppb. THC represents the true concentration of all oil components, including those that are difficult to measure and is not usually reported in toxicity testing for the development of toxicity thresholds. Importantly, THC is the parameter for oil concentration estimated by spill models such as SIMAP. French-McCay (2024) assumes the NOPSEMA (NOPSEMA, 2019) ppb are in THC.

1 SUMMARY

This is an independent review of the technical note *Considerations for development of entrained oil thresholds for oil spill risk assessments* by French-McCay (2024). This review focusses on evaluating the basis upon which French-McCay (2024) assessed the 10 ppb entrained oil threshold example provided by the National Offshore Petroleum Safety and Environmental Management Authority (NOPSEMA, 2019).

French-McCay (2024), brings together multiple lines of evidence to derive generic thresholds for entrained oil of 1000 ppb total hydrocarbons (THC) for distillates and condensate and 3000 ppb THC for crude oil. French-McCay (2024) included the following logic to derive the thresholds:

- Entrained oil thresholds should be presented in THC to be consistent with the units of concentration used in oil spill modelling.
- The soluble toxic fraction of entrained oil droplets represents a low proportion of the THC, is largely not bioavailable and is rapidly depleted during weathering.
- Toxicity studies do not generate data for deriving thresholds in THC, because THC is difficult to quantify and typically not measured. Therefore, entrained oil thresholds in THC should be developed by converting toxicity values of the soluble toxic fraction (PAHs and TRH) based on its proportion of whole oil.
- Reliable toxicity thresholds expressed in PAHs and TRH from the literature were converted to THC HC5 values (protecting of 95% of species from entrained oil) and represent the French-McCay (2024) recommended thresholds for entrained oil.

The thresholds derived by French-McCay (2024) could be considered conservative when applied in oil spill risk assessments as:-

- Exposures in the open ocean are short (typically hours) but the thresholds were derived from longer exposure tests (typically ≥48 h). Since uptake of the toxic hydrocarbon fraction is time dependent, the proposed thresholds overestimate risk.
- Entrained oil droplets become depleted of their soluble fraction by weathering, no longer being a source of dissolved hydrocarbons. There is currently little evidence of harm from entrained droplets, especially highly weathered droplets, and they could be considered effectively non-toxic.

Oil toxicity is highly dependent on oil composition (which changes with weathering) and exposure duration. Ideally thresholds, focussed primarily on dissolved hydrocarbons, would address both issues (French-McCay et al., 2023; Parkerton et al., 2023b). More broadly, French-McCay (2024) recommended that risk assessments should primarily address dissolved hydrocarbon exposures (as well as floating and shoreline oil) rather than entrained oil, referring to the most recent guidance published in a review series in Aquatic Toxicology in 2023. In the meantime, generic thresholds for entrained oil are deemed necessary for oil spill risk assessments and defining the EMBA. We found the French-McCay (2024) technical note to be logical, factual and support the suggested approach to generate generic conservative effect thresholds for entrained oil. The French-McCay (2024) threshold for entrained oil of 1000 ppb THC is 100-fold higher than the NOPSEMA (2019) threshold of 10 ppb for defining the EMBA (assuming the same units). We agree that the entrained oil threshold should be expressed in THC. We consider 1000 ppb THC to be a conservative threshold for defining an area that may be affected by entrained oil, particularly given short open ocean exposure durations and the reduction in oil droplet toxicity through weathering.

2 REVIEW

The purpose of the technical note French-McCay (2024) was to ‘identify appropriate thresholds for use in oil spill risk assessments. The focus is on developing a THC threshold appropriate for modelled entrained oil droplets.’

French-McCay (2024) drew upon extensive relevant experience including the early development of oil toxicity and spill modelling (DFM 2002), which underpins SIMAP, widely applied in oil spill risk assessments in Australian waters and internationally. She also developed and adapted generic toxicity thresholds for oil spill risk assessments (French-McCay, 2016; French-McCay et al., 2018). French-MaCay was one of several global experts invited to participate in an AIMS initiated workshop on oil toxicity modelling in 2020 (AIMS, 2020). More recently French-McCay was a primary contributor to updating the CROSERF recommended methods for application oil spill risk assessments, published in a special issue of *Aquatic Toxicology* (Dettman et al., 2023; French-McCay et al., 2023; Parkerton et al., 2023b; Stubblefield et al., 2023).

The following section outlines the background and approach taken by French-McCay (2024), along with our assessments of each part where applicable.

2.1 Introduction of the technical note

The Introduction of the technical note, French-McCay (2024) provided a brief background to oil spill risk assessments and introduced potential issues with the entrained oil threshold examples provided by NOPSEMA (2019) (Table 1). The objectives of oil spill risk assessment were stated: ‘to evaluate whether aquatic habitats and organisms could be exposed to oil or its constituents at concentrations above levels of concern at some time after a spill’. The Environment that May Be Affected (EMBA) as applied by NOPSEMA was described: ‘all areas exceeding conservative threshold concentrations at any instant in time after a spill’. The most conservative threshold examples provided by NOPSEMA (2019) for different pathways were listed, including for dissolved oil (10 ppb) and entrained oil (10 ppb), however the parameter(s) was not explicitly specified. The NOPSEMA (2019) dissolved hydrocarbon threshold of 10 ppb was assessed by French-McCay (2024) as being consistent with previous publications. The NOPSEMA (2019) entrained oil threshold of 10 ppb was assessed as being inconsistent with the research cited (Bridges et al., 2018; French-McCay, 2016; French-McCay et al., 2018). For example, French-McCay (2016) recommended that entrained oil thresholds should be 100× greater than dissolved oil thresholds since the toxic fraction (primarily soluble aromatics) make up only a small fraction (~1%) of oil in droplets. This assessment was further supported by a statement that PAHs only make up between 1% and 7% of the composition of crude oils (these values were not referenced, but are consistent with those published in Neff et al. (2005)). Finally, it was recommended that thresholds for risk evaluations and establishing the EMBA should apply entrained oil thresholds that address ’the complexities of oil composition, weathering, partitioning in the environment, and organisms’ behaviours’.

Table 1. *NOPSEMAs '…examples of exposure values used in the past along with a basic description of their use'. Copied from NOPSEMA (2019)*

HC type	Exposure type	Exposure value* (ppb)	Description	Appearance
Entrained	Low	10	Establishes planning area for scientific monitoring based on potential for exceedance of water quality triggers	No visible oil
	High	100	As appropriate given oil characteristics for informing risk evaluation	
Dissolved	Low	10	Establishes planning area for scientific monitoring based on potential for exceedance of water quality triggers	
	Medium	50	Approximates potential toxic effects, particularly sublethal effects to sensitive species	
	High	400	Approximates toxic effects including lethal effects to sensitive species	
References: Bridges et al. (2018); French-McCay (2016); French-McCay et al. (2018)				

** These refer to instantaneous concentrations, where instantaneous would generally be determined by the model time step. Contemporary models used to inform risk assessments generally utilise a 1 hr time-step.*

2.2 Considerations for developing thresholds for entrained oil

The second section of the Technical Note, French-McCay (2024) briefly outlined multiple considerations for developing thresholds for entrained oil for risk assessments and defining the EMBA, including:

- **Bioavailability:** Dissolved hydrocarbons are the most toxic component of oils to aquatic organisms and there is little evidence to date that demonstrates direct impacts of entrained droplets (citing Parkerton et al. (2023a)). Only a fraction of the hydrocarbons in oil droplets are soluble and bioavailable. Of the components which are soluble, a substantial fraction of the lightest hydrocarbons (i.e. MAHs and soluble alkanes) are rapidly lost to volatilisation, further limiting exposure (except for light oils discharged at depth).
- **Oil composition affects toxicity:** Oil composition is complex and changes over the duration of a spill (i.e., with weathering). The toxicity of individual components of soluble hydrocarbons is inversely related to water solubility and typical ranges of lethal concentrations affecting 50% of exposed organisms (LC50s) for PAHs were provided and vary by orders of magnitude (10 ppb–100 ppm). It was suggested the evaluation of toxicity of complex oil mixtures should ideally be modelled by applying Toxicity Units (TUs), where 1 TU = LC50 (French-McCay et al., 2023; Parkerton et al., 2023b).
- **Weathering:** Weathering (a complex process of volatilization and dissolution losses, and biodegradation) changes oil composition and therefore its bioavailability and toxicity. Entrained oil droplets are an important source of dissolved hydrocarbons, but as the oil weathers, it becomes less toxic ('effectively non-toxic') for highly weathered residual oil. This highlights a key reason to avoid applying toxicity thresholds for dissolved oils to entrained (and particularly weathered) oil.
- **Duration of exposure (uptake):** The LC50 values used to derive toxicity thresholds are generally derived from relative long exposures of 48 to 96 hours. LC50 values for shorter exposures are

higher as it takes time for dissolved hydrocarbons to accumulate in organisms. This means LC50s from laboratory studies (48 to 96 h) overestimate effects if used to assess risk over shorter duration field exposures.

- **Duration of exposure (oil dynamics):** Modelling and monitoring show that oil exposures at concentrations which may be harmful to aquatic species are generally short ("minutes to hours"), even for long-lasting spills ("weeks or months"), due to varying oil movements in the water, dilution and weathering processes.
- **Duration of exposure (organism behaviour):** Exposure depends on factors such as organism habitat (e.g., location, depth) and movement (mobile, stationary).
- **Problems with measuring oil concentrations as total hydrocarbons:** Not all hydrocarbons are or can be measured. There are recent recommendations for oil analysis (Bejarano et al., 2023; Dettman et al., 2023). Total recoverable hydrocarbons (TRH) refer to hydrocarbons which can be measured, while total hydrocarbons (THC) refer to the 'true concentration of all hydrocarbons'. TRH may comprise <30% of THC in heavier oils. Oil dispersal models such as SIMAP express entrained oil as THC. There are few or no LC50s (thresholds) expressed as THC in the literature as this is difficult to measure/estimate in experimental systems.
- **Problems with applying toxicity parameters from laboratory experiments in field applications:** Toxicity studies generate effect thresholds for relatively constant exposures/oil compositions. However, oil exposures are difficult to characterise due to unknown contribution of components that cannot be quantified, volatilisation, degradation, and other experimental artefacts. Toxicity modelling provides a more reliable method to generate toxicity thresholds for complex mixtures in the field (French-McCay et al., 2023; Parkerton et al., 2023b). The toxicity thresholds (i.e. LC50s) developed in tests are numerically lower when expressed as ppb PAHs or ppb TRH as they do not account for all components in entrained oil (THC). Risk to aquatic biota would be overestimated if ppb PAHs or ppb TRH were applied directly in oil spill modelling that applies THC as a concentration metric (i.e., SIMAP).

This second section provided valuable background and context for the development of thresholds for entrained oil.

2.3 Recommendations for thresholds

The French-McCay (2024) Technical Note recommended alternative generic thresholds for entrained oil for application in risk assessments or to define the EMBA. The recommended thresholds were developed from a logic that tied together information on: (1) toxicity of soluble hydrocarbons; (2) the units appropriate for assessing risk of oil droplets (THC); (3) the identification of reliable toxicity test results and converting those results into THC units; and (4) comparison with other thresholds. These lines of evidence were supported by multiple peer-reviewed research articles.

2.3.1 PAH-based thresholds for dissolved hydrocarbons

- French-McCay (2024) summarised experimental evidence that acute lethal concentrations of total PAHs (LC50s) generally range from 10 to 300 ppb. For open-water oil spills, where short-term exposures are expected, an **acute threshold of 10 ppb total PAH was recommended.** This is consistent with NOPSEMA (2019).
- An acute-to-chronic ratio of 10 was recommended as being conservatively appropriate to convert an acute toxicity threshold to a chronic sub-lethal effects threshold. **The potential no**

effect concentration (PNEC) would be 1 ppb total PAH ("where exposure durations are sufficiently long for such effects to occur").

- The effects of UV radiation on oil toxicity was addressed, including the phototoxicity where UV increases toxicity. **An acute toxicity threshold that accounts for phototoxicity was proposed as 1 ppb total PAH**.

We previously assessed the generic PAH-based thresholds for dissolved hydrocarbons of 10 ppb against experimental and modelled toxicity values for two fresh and weathered condensates and concluded this threshold was protective of >95% of species in both our experiments and target lipid model database (Negri et al., 2021). The additional factors applied to account for chronic and UV radiation ratios are also appropriate, based on the referenced literature and other laboratory studies.

2.3.2 THC-based threshold for entrained oil

- **Units should be expressed in THC:** French-McCay (2024) points out that for a valid risk assessment, the threshold units for entrained droplet thresholds need to match the units for oil concentrations predicted in spill modelling SIMAP – namely THC.
- **THC can be inferred from TRH:** Toxicity data informs the development of thresholds; however, there is virtually no toxicity data expressed in THC. Instead, toxicity expressed as THC can be inferred from toxicity expressed as either total PAHs or TRH (the fraction of total oil that can be measured).
- **TRH thresholds for entrained oil:** French-McCay (2024) primarily drew upon the data presented in a publication by Bejarano et al. (2017), in which thresholds for multiple oil types were developed based on total PAH and TRH (termed TPH in their study). This dataset is appropriate for assessing thresholds for entrained oil as it includes toxicity data derived using methods that generate entrained droplets from multiple oils.
- Bejarano et al. (2017) found that the lowest HC5 threshold (concentrations below which 95% of species are protected) among entrained oil types was ~500 ppb TRH (measurable hydrocarbons) for a light fuel oil. HC5 values were greater for medium oils (3000 ppb) compared to other light oils (1000 ppb). *Note: there is a typo on page 13 in French-McCay (2024) where 560 ppm should read 5.6 ppm, but that does not change the argument being made.*
- **Converting TRH to THC thresholds:** PAHs represent only a small fraction of TPH (Bejarano et al., 2017). This was expressed in Table 1 (French-McCay, 2024) as ratios of TPH/PAH, which ranged from 14 to 39.
- PAHs represent an even lower proportion of THC, for example, the ratios of THC/PAH have been reported as typically 100 (Forth et al., 2017; French-McCay, 2002). It is possible that these ratios could be as low as 14 if PAHs constitute up to 7% in some fresh oils (Neff et al., 2005; Negri et al., 2021). However, in medium and heavy oils, a large proportion of these PAHs would be poorly soluble or insoluble and not bioavailable. Or in condensates and light oils, most PAHs would be more soluble and rapidly lost, resulting in an increase in THC/PAH ratios on droplet weathering. Hence the 100 ratio is deemed reasonable.
- French-McCay (2024) converted the Bejarano et al. (2017) HC5 thresholds from TPH to THC based on the above two datasets/assumptions. The lowest HC5 was ~3000 ppb THC for light crude oils. We replicated these calculations and found them reasonable and correct.
- **Other data:** French-McCay (2024) then considered thresholds developed in other publications such as Smit et al. (2009), which expressed HC5 values in THC; however, the results were not

comparable as the THC metric in that study was difficult to define (unclear what fraction it represented), and the toxicity metrics applied were based on more sensitive no observed effect concentrations with exposures > 7 days.

- The ANZECC 2000 guidelines (ANZECC and ARMCANZ, 2000) include a TPH-based sublethal acute threshold of 168 ppb TPH and a sublethal chronic threshold 7 ppb TPH for dissolved hydrocarbons based on an analyses by Tsvetnenko (1998). The suitability of these thresholds for application to entrained droplets was questioned in French-McCay (2024) due to: (1) the soluble fractions assessed were not relatable to field exposures of entrained oil; (2) lowering of the threshold for volatilisation loss rather than increasing the threshold to account for unmeasurable oil component in THC; and (3) an outdated acute-to-chronic ratio of 25 was applied (10 is now recommended). This critique is valid and the Tsvetnenko (1998) thresholds are less reliable than the Bejarano et al. (2017) data for developing entrained oil thresholds.
- An acute exposure concentration of 1000 ppb TPH was reported in three other cited publications as being of low concern for sensitive life stages or for sublethal impacts. For consistency with oil spill modelling units French-McCay (2024) suggested converting these TPH thresholds to 3000 ppb THC (as previously explained).

We have previously independently recommended that the NOPSEMA (2019) example thresholds for entrained oil are conservative and should be greater than for dissolved hydrocarbons (Negri, 2023). French-McCay (2024) recommended THC thresholds of 1000 ppb for entrained distillates and condensates, and 3000 ppb for crude oil are supported by the above evidence.

2.3.3 Consideration of duration of exposure for developing thresholds

In this section French-McCay (2024) contends that the toxicity values for exposures ≥48 h is 'highly conservative' since oil exposures at effect concentrations are typically short (hours, not days) and therefore an acute to chronic ratio correction is not needed for exposures in open waters. French-McCay (2024) suggests compensating by three possible methods: (1) increasing thresholds further for short duration exposure; (2) averaging modelled THC values over several hours; or (3) applying a dose metric in ppb-hours.

This consideration is valid, as the effect concentrations for short field durations (hours) are far higher than those recorded following in typical 48 h+ experimental exposures. It is likely that the thresholds developed from 48 and 96 hour exposure data would be at least an order of magnitude lower than acute thresholds for hour-long exposures expected in the field. The NOPSEMA (2019) example threshold and the French-McCay (2024) recommended thresholds for entrained-oil (both based on acute toxicity data from relatively long exposures) are therefore conservative if applied to assess the risks posed by exposures as short as an hour.

2.4 Conclusion

2.4.1 Thresholds

Here, French-McCay (2024) concludes that a 10 ppb PAH threshold for dissolved hydrocarbons is suitable for protecting sensitive aquatic biota in the open ocean. For entrained oil droplets, 1000 ppb THC was recommended for all oil and weathering states, while 3000 ppb THC was recommended for crude oil. It was also noted that risk assessments should focus more on dissolved hydrocarbon exposure (floating and shoreline oil) rather than entrained oil, referring to the most recent guidance published in a review series in Aquatic Toxicology in 2023.

These conclusions are well founded in the reasoning and literature outlined in the previous sections.

2.4.2 Consideration regarding EMBAs

In this final section French-McCay (2024) contends that an entrained oil threshold applied to define the EMBA of 10 ppb THC (Table 1) is too conservative as it identifies an unnecessarily wide geographical area, where 'near the outer bounds' exposures reaching this low threshold would be infrequent and for very short durations. The consequences of this include wasted effort in monitoring and less effective monitoring within an area that might be impacted. Applying a more 'realistic' threshold to define the EMBA was therefore proposed.

We agree that the entrained oil threshold should be expressed in THC. We consider 1000 ppb THC to be a conservative threshold for defining an area that may be affected by entrained oil, particularly given short open ocean exposure durations and the reduction in oil droplet toxicity through weathering.

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