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Modeled effects of oils - Report on expected and missing environmental effects of the selected oils based on the PETROTOX model, and derivation of the impact on the experimental design

D3.19

WP3: Determination of oil and dispersant impacts on biota using effect-based tools and ecological risk assessment

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Intermediate report I - Threshold values of Crude oil (Troll B) and dispersant (Finasol OSR52) and Regulatory Data Gap Analysis

Dr Matthieu Duchemin – 31 August 2016

Version 1.1

Matthieu Duchemin
Conseil en gestion de risques

As part of
EU Horizon 2020 project “Integrated Oil Spill Response Actions and Environmental Effects” - GRACE (679266)

Task 3.7: Modeling marine environmental hazard and risk of crude oil, dispersant and cleaning agent in oil spill response.

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Executive summary

The purpose of the work was to investigate available data for Competent Authorities to assess the environmental risk of a crude oil, Troll B and a dispersant, Finasol OSR 52 to the marine environment.

Troll B crude oil is a petroleum substances which is a complex mixtures of aliphatic, cyclic or aromatic hydrocarbons. Due to this nature, they are difficult-to-test substances but are believed to follow same mode of action. PETROTOX is model that was developed to predict acute and chronic values based on the Hydrocarbon Block Method, derived from the Target Lipid Method. Ecotoxicity data were output for the 14 available seawater species and varied from LL50 = 2.16 mg/L for a Crustaceans species to 475 mg/L for a Fish species and EL10 = 0.22 mg/L for the same Crustaceans species to 88.4 mg/L for an Algae species.

Finasol OSR 52 is a mixture of distillates of hydrocarbon, 2-aminoethanol, dipropylene glycol methyl ether, surfactants, and anti-corrosion additive. Thirty-three ecotoxicity data, some acute and some chronic, of freshwater or seawater species were collated from regulatory databases of safety data sheets for the whole mixture or individual components. All data on individual components were consistent with the only two data available on Finasol OSR 52, 48h-LC50 = 9.37 mg/L on a Crustaceans species and 96h-LC50 = 11.7 mg/L of a Fish species.

Both chemicals showed high toxicity to Crustaceans and far less to Algae and Fish. Following guidelines of various legislations to protect the marine environment, the pelagic predicted no effect concentrations for Troll B crude oil varied from 4.4 µg/L to 22.0 µg/L. For Finasol OSR 52, the pelagic predicted no-effect concentrations varied from 93.7 µg/L to 937 µg/L.

This baseline will help to design future work in this project. It will be needed to confirm that Crustaceans are most sensitive species and investigate lethal or sub-lethal toxicity on Crustaceans. Furthermore, this assessment disregards specific region, especially region with iced sea and future work should investigate in this direction as well.

1. Context of the current work

1.1. Horizon 2020 Project GRACE

In context of the EU Horizon 2020 project “Integrated Oil Spill Response Actions and Environmental Effects” - GRACE (679266) we were contracted by the Finnish Environment Institute SYKE to produce and deliver tasks as described in the project WP3 “Oil impacts on biota using biomarkers and ecological risks assessment”. This is formulated as follows:

- Task 3.7: Modeling marine environmental hazard and risk of crude oil, dispersant and cleaning agent in oil spill response.

The task has been given only one official deliverable, which is as follows:

- D3.19: Modeled effects of oils (month 6) 31.8.2016
- Report on expected and missing environmental effects of the selected oils based on the PETROTOX model, and derivation of the impact on the experimental design

However, besides of D3.19, the fulfillment of the Task 3.7. associated to the tender also requires the fulfillment of other parts of the task, as depicted in detail in the Description of Work (DoW) below.

The current document reports findings and recommendations on the existing data available to regulators to evaluate the potential hazards of a crude oil or a dispersant to the marine environment.

1.2. Description of Work

This task will assess the marine environmental hazard and risk of crude oil, dispersants and cleaning agents in oil spill response. In a wider perspective, this task will provide provisional information of secondary poisoning to humans consuming contaminated fish and shellfish. Due to public opinion and chemical management regulations (OSPAR, REACH, etc.), the oil and gas industry has run several research projects to study the ecotoxicological effects and fate of various crude oil and oil products. They thus developed the hydrocarbon method described in OECD guidance for the testing of difficult-to-test-substances (OECD, 2000). Following REACH regulation requirements, the industry built the ecotoxicological model PETROTOX, which predicts individual effects of oil products on various aquatic species (Redman et al., 2012). This model is commonly used to calculate the toxicity of petroleum products for regulatory purposes. Ecotoxicological data may also exist for chemicals that may be deployed during an oil spill event. However, the main endpoint used is lethality as it is the acute toxicity endpoint required by the regulations in place. The chronic toxicity endpoints are predicted through the use of Acute to Chronic Ratios. But this model is not meant to provide predictions on specific molecular initiating events, modes of action, other than narcosis. This task will give some input to the other tasks of this work package to increase the relevance and the use of the results obtained in this project.

First (Part 1), threshold values from crude oil and other chemicals of interest were modeled using PETROTOX and investigated from existing and available data.

Second (Part 2), a data gap analysis was performed to understand which trophic levels and tested species are missing from the available regulatory information. Those results benchmark current knowledge on the effects of the chemicals of interest. They also support the design of the investigation in the other tasks to ensure that innovation and new knowledge is produced (test substance identification, number of replicates, exposure regimes, test concentrations, etc.).

Third (Part 3), effect data from the other tasks will be collated and analyzed to investigate i) new threshold values in regards with requirements and methodologies from the Maritime Strategy Framework Directive

(The European Parliament and the Council of the European Union 2008) and ii) whether the current level of knowledge provides a sufficient level of protection to the marine environment and coastal areas.

Fourth (Part 4), exposure scenarios will be developed to reflect use of the chemicals in oil spill response (dispersant, cleaning agents, etc.). Those scenarios will be generic in order to be able to rapidly deploy site-specific ones during exercises or operations of emergency response.

Finally (Part 5), refined risk assessment will be performed and compared with regulatory risk assessment, and Risk Characterization Ratios (RCR) determined. This fifth subtask, called exposure assessment phase in the risk assessment process, will be linked to the research conducted in WP4 of the GRACE project.

The present document reports the work being conducted under part 1.

1.3. Introduction to PETROTOX

The spread sheet-based model PETROTOX is designed to calculate the narcotic (base line) toxicity of petroleum products to aquatic organisms. Petroleum products are complex mixtures of aliphatic and aromatic hydrocarbons and difficult-to-test substances as defined by OECD (OECD, 2000). Due to the individual differences of each hydrocarbon in solubility, partitioning in organisms, etc. those differences will draw different toxic effects depending on the dose. The typical dose-response curve theory cannot be applied here. PETROTOX is thus based on the Target Lipid Model (TLM) and toxic unit theory of additivity of mixtures to calculate threshold for regulatory hazard assessments (Redman et al. 2012). PETROTOX is meant to give users with toxicity values based on the assumption of narcotic effects of petroleum substances, Target Lipid Method and hydrocarbon Block Method.

The spread sheet uses a three-phase (air, water, free product) oil solubility calculation (Di Toro et al. 2006) that is coupled with a database of physical and chemical properties of typical petroleum hydrocarbons to calculate the distribution of petroleum hydrocarbons among the exposure water, headspace and free product phases. The properties database was developed by CONCAWE and contains physical/chemical properties such as boiling point, solubility and octanol-water partition coefficients (K_{OW}) for 1457 hydrocarbon structures that are possibly found in petroleum products.

Based on the physical and chemical properties of each individual hydrocarbon structure of the petroleum product of interest, the computed dissolved hydrocarbon concentrations are then used by the TLM to calculate aquatic toxicity. A modification to the TLM is the use of membrane-water partition coefficients (K_{MW}) rather than K_{OW} to describe the partitioning between the water phase and the organism (Parkerton et al 2011). This modification is critical for petroleum products that have very hydrophobic compounds (log (K_{OW}) > 6.0). This version of the PETROTOX model performs the solubility and toxicity calculations with physicochemical properties derived from the database for each hydrocarbon block.

1.4. Principles of calculation

PETROTOX can be used under two modes, low or high resolution, depending on the level of information available regading the mass distribution of the petroleum product. The low resolution approach relies on the mass distribution of the two general chemical classes, aliphatic or aromatic, based on user-defined boiling point intervals following simplistic hydrocarbon block analyses. The high resolution approach relies on the known mass distribution for up to 16 chemical classes (n-paraffins, iso-paraffins, n-substituted cylcohexane, n-substituted cylcopentane, other mono-naphthenic, di-naphthenic, poly-naphthenic, n-olefin, iso-olefin, sulfur-bearing aliphatic, mono-aromatic, naphthenic mono- aromatic, di-aromatic, naphthenic di-aromatic,

poly-aromatic and sulfur-bearing aromatic). That information is usually derived from detailed GCxGC analyses.

Once the mass distribution is known, the built-in solubility model calculates the mass of the component in the product, water and air phases (3-phase model) based on K_{OW}, solubility and Henry's law constant. For the purpose of regulatory risk assessment it is accepted that petroleum products exert narcotic effects to organisms and the narcotic effects are additive (Shirazi & Linder 1991). The toxic effects are calculated based on the Target Lipid Model (Di Toro et al. 2006) and the Critical Target Lipid Body Burden (CTLBB) which is species-dependant. The TLM has been adapted to petroleum products by referring to the lethal loading concentration instead of lethal concentration due to their insoluble nature. In addition, the target lipid-water partition ratio (K_{TLW}) is used in place of K_{OW} in order to limit overestimation of calculated toxicity for super-hydrophobic hydrocarbons (Redman et al. 2014). The model calculates toxic units for each class and sums them. The model iterates the calculation by changing loading rates to reach a final sum of toxic unit of 1, meaning the LL_{50} has been populated. Bioavailability can be corrected basically by changing POC (Particulate Organic Carbon) values.

2. Predicted data on Crude oil and dispersant effects to environment

2.1. Crude Oil Troll B

PETROTOX was used to determine data on the toxic effects of Troll B crude oil. Oil is a complex mixture and is characterised by the distribution of its various components. PETROTOX requires inputting those cuts as a matter of weight. Annex 1 gives the various cuts ordered by their Initial Boiling Points (IBP) and Final Boiling Points (FBP) of Troll B.

Once the hydrocarbon blocks were defined, under the Low Resolution mode, according to their boiling points, the model inquires the phys-chem properties and uses the Target Lipid Model to output those properties of interest when designing test protocols (Table 1). Then the species need to be chosen followed by the Particulate Organic Carbon (POC) to drive the bioavailability model. POC values can be chosen manually from 0 mg/L to environmental relevant values. In the present case, the default value of 2 mg/L was chosen. This is the average POC value found in a standard Algae test. This value reflects a moderate organic matter load in the column water, thus increasing the bioavailability of the components of concern. Based on the validate TLM for each species (McGrath & Di Toro 2009), toxic units are calculated by PETROTOX and summed iteration after iteration, until it reaches 1. This will then give the loading rate which provides 50% of lethality, LL50. To populate chronic values, the same principles are followed. When needed, an Acute-to-Chronic Rate (ACR) is used to populate the loading rate providing 10% of the effect (EL10). A default value is set at 3.83 (Di Toro et al. 2006), but it can be user defined. The default value was used here. PETROTOX enables to repeat that process for every species of interest. In the current case, it was arbitrary chosen to focus only on seawater species. When the CTLBB is not known for that species, then the calculation is biased. When iteration cannot reach 1 then the calculation is also biased and shows an LL50 > 1000 (Table 2).

Table 1. Hydrocarbon blocks for Troll B crude oil based under Low resolution mode of PETROTOX 3.06 and calculated related phys-chem properties

Hydrocarbon Block	% wt	Average log Kow	Average Sub-Cooled Solubility (mg/L)	Average Molecular Weight (g/mol)	Average Henry's Law Constant (Log)	Product Phase (mg/L product)	Air Phase (mg/L headspace)	Water Phase (mg/L water)
1	1.2	2.84	1.57E+02	74.81	0.82	3.3E+00	1.0E-02	1.5E+00
2	2.5	3.72	1.72E+01	94.58	1.41	3.5E+01	3.3E-02	1.7E+00
3	5.3	4.64	1.79E+00	119.56	1.65	6.7E+02	7.1E-02	2.5E+00
4	10.7	5.90	7.55E-02	152.80	1.93	2.5E+04	6.9E-02	3.0E+00
5	9.5	7.45	1.51E-03	191.94	2.41	1.1E+05	5.1E-03	6.4E-01
6	9.4	9.04	2.58E-05	232.52	2.65	1.7E+05	2.1E-05	3.2E-02

7	12.2 (Ar)	6.77	1.72E-02	232.43	-1.22	1.6E+05	7.0E-05	8.4E+00
8	11.5	13.94	7.99E-11	364.87	3.49	2.2E+05	4.6E-13	2.0E-06
9	3.8	15.10	3.39E-12	400.15	3.32	7.1E+04	3.5E-15	1.6E-08
10	13.5	16.70	6.59E-14	425.02	4.14	2.5E+05	1.1E-17	1.3E-09
11	6.7	18.13	2.01E-15	447.37	4.85	1.3E+05	1.4E-22	6.1E-13
12	5.1	20.43	5.06E-18	506.98	5.13	0.0E+00	0.0E+00	0.0E+00
13	8.6 (Ar)	8.67	1.17E-04	323.75	-4.23	1.6E+05	3.9E-10	1.5E-01

(Ar = aromatic, rest in aliphatic)

Table 2. Predicted LL50 and EL10 values for available seawater species as calculated by PETROTOX 3.06 with POC = 2 mg/L and ACR = 3.83 (default values)

Species	Trophic level	Predicted LL50 (mg/L)	Predicted EL10 (mg/L)
Eohaustorius estuarius	Crustaceans	4.33	0.33
Rhepoxyinus abronius	Crustaceans	2.16	0.22
Mysidopsis bahia	Crustaceans	2.68	0.25
Chlamydomonas reinhardtii	Algae	2.7	0.25
Leptocheirus plumulosus	Crustaceans	4.74	0.35
Portunus pelagicus	Crustaceans	9.28	0.49
Ampelisca abdita	Crustaceans	9.63	0.49
Paleomonetes pugio	Crustaceans	12.1	0.55
Cyprinodon vareigatus	Fish	475	1.94
Oithona davisae	Crustaceans	228	3.25
Nitocra spinipes	Crustaceans	> 1000*	6.13
Neeanthes arenaceodentata	Polychete	> 1000*	6.37
Artemia salina	Crustaceans	> 1000*	7.80
Chlamydomonas angulosa	Algae	> 1000*	88.4

* Iteration could not reach 1

2.2. Dispersant Finasol OSR 52

Finasol OSR52 is an oil dispersant manufactured by Total Special Fluids. Little regulatory information was found for this compound. According to the safety datasheet (SDS) issued by Total Specialties USA, Inc, version 2.02 from 2014, Finasol OSR 52 is a mixture of proprietary surfactants, distillates from petroleum, dipropylene glycol methyl ether, 2-aminoethanol and a proprietary anti-corrosion additive (table 3). Some compounds are not disclosed (surfactants and anti-corrosion additive) but 3 have a CAS Registry number which provides the mechanism to know more about those substances. However, the exact weight composition cannot be known from the SDS, and hence information on the substances will not enable extrapolation of behaviour and effects of the dispersant to the marine environment. Champion Technologies was also selling the chemical in 2001. Thus they also had to issue an SDS to their customers. However, no further information related to composition was found.

Table 3. Composition and information on ingredients of Finasol OSR 52 (Section 3 of MSDS for USA, 2014)

Substance name	CAS registry Number	% by weight
Surfactant	Proprietary	< 25
Distillates (petroleum), hydrotreated light	64742-47-8	< 25
Dipropylene glycol methyl ether	34590-94-8	< 20
Surfactant	Proprietary	< 20
Surfactant	Proprietary	< 15
Surfactant	Proprietary	< 10
2-aminoethanol	141-43-5	< 5
Anti-corrosion additive	Proprietary	< 5

Safety data sheets are mandatory documents to communicate the hazards of a compound. It is a global regulatory requirement for selling companies to inform about the physical, human health and environmental hazards. Precautionary measures are described herein to prevent contamination and harm from accidents. SDSs are always comprised of 16 sections and section 12 always deals with environmental hazards of the chemical or the hazardous individual compounds. The information described in the MSDS suggests that the dipropylene glycol methyl ether (CAS RN 3590-94-8), the surfactants and the anti-corrosion additive do not draw individual hazardous effects to the environment. In Champion Technologies' SDS much less information on environmental hazards was available. Yet new data is described in section 12, 68% of the chemical was biodegraded within 28 d. Regulatory bodies and pollution emergency response agencies maintain databases of the dispersants available in their jurisdiction. Additional ecotoxicological data were found in the US EPA emergency response database, last updated in March 2016. Finally, the commercial brochure currently available on Finasol OSR 52 issued by Total mentions a little more information on biodegradation studies conducted by the CEDRE in France.

With chemical management regulations like REACH, portals and database have been built to centralise hazard information on chemicals. Today several of them are available, driven by the authorities or academics research projects. But the reliability of the data is not always available and thus the use of such data in an environmental risk assessment is disputable. The portal maintained by the European Chemical Agency (ECHA) is probably the most up to date database because REACH required all existing data to be reported, meaning private companies had to share data they owned and data available in the scientific literature, in order to register their substances. In addition, all data had to be evaluated prior to registration. All those information are gathered below (table 4).

Table 4. Environmental information and data retrieved on Finasol OSR 52 and its compounds

Species (size)	Environmental effect	Trophic level	References
Finasol OSR 52			
Mysidopsis bahia	48h-LC50 = 9.37 mg/L	Crustaceans	US EPA[1]
Menidia beryllina	96h-LC50 = 11.7 mg/L	Fish	US EPA[1]
Following standard NF T 90-346	Biodegradation over 28d > 60%	biodegradation	Commercial brochure[2]
Not known	Biodegradation over 28d > 60%	Biodegradation	MSDS (2001)[3]
Crangon crangon	3.3% of mortality after 6 hours at 960 mg/L	Crustaceans	MSDS (2014)[4]
Distillates (petroleum), hydrotreated light			
Lepomis macrochirus (35-75 mm)	96h-LC50 = 5.9 mg/L	Fish	MSDS (2014)[4]
Oncorhynchus mykiss (35-75 mm)	96h-LC50 = 2.9 mg/L	Fish	MSDS (2014)[4]
Oncorhynchus mykiss (35-75 mm)	96h-LC50 = 2.6 mg/L	Fish	MSDS (2014)[4]
Oncorhynchus mykiss (35-75 mm)	96h-LC50 = 2.4 mg/L	Fish	MSDS (2014)[4]
Oncorhynchus mykiss (35-75 mm)	96h-LC50 = 2.2 mg/L	Fish	MSDS (2014)[4]
O.mykiss	96h-LL50 = 18 mg/L	Fish	ECHA
O.mykiss	28d-NOEC = 0.098 mg/L	Fish	ECHA
Daphnia magna	48h-EL50 = 21 mg/L 48h-NOEL = 4.5 mg/L	Crustaceans	ECHA
Daphnia magna (offspring)	21d-EL50 (repro) = 0.89 mg/L 21d-EL50 (immobilisation) = 0.81 mg/L 21d-NOEL (repro) = 0.48 mg/L 21d-NOEL (adult length) = 1.2 mg/L	Crustaceans	ECHA

Pseudokirchneriella subcapitata	96h- EL50 = 5 mg/L mg/L 72h-EL50 = 6.7 mg/L mg/L	Algae	ECHA
Tetrahymena pyriformis	estimated 72h-LL50 = 678 mg/L (QSAR)	Bacteria	ECHA
2-aminoethanol			
Lepomis macrochirus (0.3 g)	300 mg/L < 96h-LC50 < 1000 mg/L	Fish	MSDS (2014)[4]
Oncorhynchus mykiss (fingerling)	96h-LC50 > 200 mg/L	Fish	MSDS (2014)[4]
Oncorhynchus mykiss (yolk)	150 < 96h-EC50 < 196 mg/L	Fish	MSDS (2014)[4]
Pimephales promelas	96h-LC50 = 206 mg/L	Fish	ECHA
Oryzias latipes	14d-NOEC ≥ 100 mg/L 14d-LC50 ≥100 mg/L	Fish	ECHA
Daphnia magna	22h-LC50[a] = 100 mg/L	Crustaceans	ECHA
Daphnia magna (offspring)	21d-NOEC (repro) = 0.85 mg/L 21d-EC50 (repro) = 2.5 mg/L 21d-EC50 (mortality) = 15.8 mg/L	Crustaceans	ECHA
Isochrysis galbana	48h-EC50[b] = 80 mg/L	Algae	ECHA
Pseudomonas putida	30 min EC50 = 75 mg/L	Bacteria	ECHA
Daphnia magna	48h-EC0 (mobility) = 50 mg/L 48h-EC50 = 65 mg/L	Crustaceans	ECHA
Pseudokirchnerella subcapitata	72h-EC50 = 2.5 mg/L 72h-NOEC = 1 mg/L	Algae	ECHA
Dipropylene glycol methyl ether			
Poecilia reticulata	96h-LC50 ≥1000 mg/L	Fish	ECHA
Crangon crangon	96h-LC50 ≥1000 mg/L	Crustaceans	ECHA
Daphnia magna (offspring)	NOEC (21d) = 0.5 mg/L 72h-LOEC ≥ 0.5 mg/L	Crustaceans	ECHA
Pseudokirchneriella subcapitata	72h-EC50 ≥ 1000 mg/L	Algae	ECHA
Pseudomonas putida	Value for bacteria toxicity (inhibition of cell growth) = 2.4 mg/L	Bacteria	ECHA

[1] www.epa.gov/emergency-response/finasolr-osr-52
[2] Commercial brochure available at Total Specialties – Annexe
[3] Champion Technologies SDS (2001) – Annexe
[4] Total Specialties USA MSDS (2014) – Annexe

3. Data gap analysis and threshold values calculation

3.1. Regulatory Data gap analysis

3.1.1. Data gap analysis for the crude oil Troll B

The PETROTOX model has been trained and validated thoroughly with genuine experimental data (Redman et al. 2012) and it is under constant improvement (Redman et al. 2014). The highly diverse nature and the importance of petroleum products do not allow testing each individual mixture as a matter of time, either to put on the market by the manufacturers or to evaluate potential hazard by regulators. PETROTOX is now under version 3.06 and is used to drive regulatory Environmental Risk Assessment. The fact that petroleum substances are complex mixtures has regulatory implications. Those mixtures have various components for

which fate and behaviour change depending on the environmental conditions. However, similar components will act similarly and will share similar properties. Thus hydrocarbons can be grouped into blocks. Based on the generally accepted assumption that toxicity of a mixture of chemicals with same mode of actions is driven by the sum of the toxicity of individual components (additivity law), the toxicity of new mixtures can be predicted from toxicity values of its components. This approach is called the hydrocarbon block method (HBM). Because of their poor solubility and volatility which varies with concentration, it is difficult to test those substances. The Water Accommodated Fraction needs to be prepared prior to testing. This is why the phrase of loading rate instead of concentration is preferred. Toxicity can thus be assessed through Lethal Loading rate drawing 50% or 10%, LL50 or LL10, the No Observed Effect Loading rate (NOEL) or the Effect loading rate are EL values.

Many data were put out for Crustaceans species but only few for Algae and Fish. More species were available to PETROTOX, of various trophic level or phylum, like Amphibians or Chironomids, but were found irrelevant here as it was decided to focus only on seawater or brackish species.

3.1.2. Data gap analysis for the dispersant Finasol OSR 52

The data collated in table 4 are the only records available at this stage for Finasol OSR 52. The manufacturer has informed us that additional data are currently under publication.

Regulatory data have to follow regulatory requirements to be valid. They usually need to follow internationally recognised guidelines, standards or protocols. The OECD bureau for chemical management or the Office of Chemical Safety and pollution prevention (OCSPP) are issuing such guidelines which are commonly recommended by regulations on chemical management. Those guidelines are usually very close to each other and regarding the endpoint are described, it is likely the following protocols have been followed. In addition to test guidelines, regulatory data need to comply with a specific quality scheme to laboratory-generated data, such as the internationally recognised OECD's Good Laboratory Practices (GLP). GLP are a set of principles established in the late 70s by OECD's member states in order to ensure the results reported are aligned with the data acquired and respond to the objective of the study. In order to start a regulatory environmental risk assessment, regulations require to have at least data showing concentration drawing 50% of lethal effect on algae, crustaceans and fish, the base three trophic levels (OECD, 2006).

OECD 203 is the acute fish toxicity test (1992) which monitors mortality of fish and behaviour or survival over a period of 96 h. The crustacean studies have likely followed OECD 202 or OSCPP 850.1035 guidelines and monitor immobility over a period of 48 h and 96 h, respectively. The available data show that no data are available on algal toxicity, two on crustaceans and the vast majority of data on freshwater fish species. Biodegradation data are usually obtained from screening studies evaluating the ready biodegradability of a substance over 28 days, guidelines OECD 301 A to 301 F and OECD 310. There is too little information in Champion Technologies' SDS to know which one has been followed. Yet in the commercial brochure, it is mentioned the French standard NF T 90-346 and that it has been conducted by CEDRE. Finally it is interesting to note that biodegradation studies are not usually recommended on mixtures because the endpoints measured, usually bacteria respiration or Total Organic Carbon, can hardly be related to the even biodegradation of all components.

The available data suggest interestingly that algal toxicity data are missing. Yet algae are primary producers in a marine ecosystem and the underlying layer of such ecosystem to work properly. The only available data on crustaceans that can be used in a regulatory environmental risk assessment is the 48h-EC50 on *Mysidopsis bahia*. The other data have been obtained over 6h and do not reflect an effect on 50% of the population. Finally there is a good wealth of fish study data drawing some variable toxic effects depending on species. But, in the view of assessing the risk to the marine environment, it should finally be noted that only one study, the one on Crustaceans, has been performed on seawater species, all fish being freshwater species.

3.2. Data consistency calculation for Finasol OSR 52

Two types of available data exist. The data generated on the individual components and the data generated on the preparation itself. From the composition data (table 3), 3 out of 8 components are identified: distillates (petroleum), hydrotreated light; dipropylene glycol methyl ether; and 2-aminoethanol at a maximum

concentration of 25% and 5%, respectively. The additives and surfactants remain defined as “proprietary” to protect intellectual property. Based on section 12 of the MSDS suggested that dipropylene glycol methyl ether does not draw ecotoxic effects. Some ecotoxicological data are available for those components. For the distillates component, when several data exist, the toxicity of the most sensitive species is used to derive the threshold value (here the fish), following general accepted guidance for environmental hazard assessment like the one for the REACH regulation (ECHA, 2012),. That guidance also stipulates that when several data exist for the same species at similar development and under same protocol, then the geometrical mean of those data can be populated to draw on single value. In the present case, the most sensitive species are the Rainbow trout and the geometrical mean of all EC50 values is 2.51 mg/L.

Back calculation rules, as indicated in the guidance for Global Harmonised System (rev 5), (UN 2013), suggest that a theoretical preparation of water, 25% distillates (petroleum), hydrotreated light and 5% of 2-aminotethanol would populate a toxicity to fish as EC50 of 10.0 mg/L.

3.3. Threshold values calculation

The predicted no effect concentration (PNEC) is the threshold value for the environmental compartments. In the marine environment, regulations require to calculate a PNEC in the column water, $PNEC_{pelagic}$ and for the sediment compartment, $PNEC_{benthos}$, this latter is commonly called $PNEC_{sediment}$.

There are several regulations requiring assessing the risk in the marine environment, the IMO Globallast convention for the approval of ballast water treatment systems, REACH or BPR for chemicals or biocides whose application or lifecycle steps occur in the marine environment, or the OSPAR commission for the protection of North Atlantic waters from discharges and uses of chemicals deployed to support exploration and production of oil and gas platforms. Unfortunately, all regulations, covering different but overlapping jurisdictions, apply different guidance to derive PNEC values (table 5). This basically means that for the same set of data different threshold values will be populated to protect the marine environment, depending on the jurisdiction of it (Duchemin, 2012).

Furthermore, it is usually accepted that ecotoxicological data performed on freshwater species or seawater species are of same significance in the risk assessment, while no evidence supports this point as a general trend.

Because this project deals with offshore pollution combat it is decided to consider only estuarine or seawater species and to calculate PNECs with available data. For Troll B a number of acute and chronic data are available on Algae, Crustaceans and Fish. Acute and chronic data are also available on an additional phylum, Polychetes. The most sensitive species is *Rhepoxyinus abronius*, and PNEC can be derived from its EL10 value. According to REACH guidance (ECHA, 2012), on sewater species not enough data are available to claim to use an assessment factor of 10, because a second additional phylum data is missing. Yet there is data available from the PETROTOX model if freshwater species would be considered. According to OSPAR and CHARM guidance (CHARM, 2005), with such data an assessment factor of 10 can be used. Finally, according to GESAMP and the BWM/Circ13/Rev3 (2015), an assessment factor of 10 can also be used with such data (table 5).

Table 5. PNEC derivation calculated per jurisdiction for Crude Oil Troll B

Jurisdiction and applied regulation	Ecotoxicity data used	Assessment factor and justification	PNEC pelagic
IMO	EL10 = 0.22 mg/L	10	22.0 µg/L
OSPAR		10	22.0 µg/L
REACH		50	4.4 µg/L

For Finasol OSR 52, only data for Fish and Crustaceans are available for this mixture. However, there are additional data available for the individual hazardous components on Algae, Crustaceans and ish. Toxicity data on individual components are consistent with data on the full mixture. Thus the level of certainty is quite high if we consider all available data. Acute data is available for Algae, Crustaceans and Fish, but chronic data are only available for Crustaceans. In the regulation, algae test results cannot be considered as chronic data as stand-alone, despite the guidelines test the toxicity of a chemical over several generations of individuals. According to REACH, an assessment factor of 100 can thus be used. But OSPAR guidelines recommend with such data an assessment factor of 10, just like GESAMP (table 6).

Table 6. PNEC derivation calculated per jurisdiction for Finasol OSR 52

Jurisdiction and applied regulation	Ecotoxicity data used	Assessment factor and justification	PNEC pelagic
IMO		10	937 µg/L
OSPAR	48h-EC50 = 9.37 mg/L	10	937 µg/L
EU		100	93.7 µg/L

4. Conclusions and recommendations

The objective of this work was to retrieve regulatory available data to perform environmental risk assessment of Troll B crude oil and the dispersant Finasol OSR 52. Data were output from PETROTOX 3.06 to estimate acute and chronic toxicity of the crude oil. Data available of regulatory database or safety data sheet were retrieved and analysed for Finasol OSR 52.

From a regulatory perspective, data are available to draw predicted no effect concentration for the marine environment, with a high level of confidence, following current guidance proposed with regulations. However, data are unbalanced in terms of the represented phylum. PETROTOX includes a high number of seawater Crustaceans but only 1 fish species and 1 algae species. Available data for the dispersant are mainly focused on its hazardous components, only 2 data available on the preparation, one for Fish and one for Crustaceans. All data available also provides enough information on the protocols used for repeatability or to fill in the gaps of phylum tested.

It was important to stick to the substance sameness of the crude oil and Finasol OSR 52, because it is not known what the basis of the manufacturer to build a category is. A component may change from two products of the same category with dramatic different impact on toxicity.

However, it is important to mention that the assumption made for PETROTOX represents Best Available Technique and state of knowledge for a sound regulation of petroleum substances. In addition, no data are specific to regions where sea can get iced. Those results and limitations give opportunity for the GRACE project to produce new data of interest for regulators if comparable endpoints and test conditions are reproduced.

Finally, both for the crude oil and the dispersant, toxicity data were available for bacteria communities. They are not playing a role in the hazard assessment phase. Yet, bacteria communities are critical for potential degradation routes and those data will then play a role I predicting fate and exposure.

5. References

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Annex 1

Crude: **TROLL BLEND 2011 01**
Reference: **TROLLBLEND201101**

Crude Summary Report

General Information		Molecules (% wt on crude)		Whole Crude Properties	
Name:	TROLL BLEND 2011 01	methane + ethane	0.04	Density @ 15°C (g/cc)	0.845
Reference:	TROLLBLEND201101	propane	0.30	API Gravity	35.9
Traded Crude:	Troll	isobutane	0.25	Total Sulphur (% wt)	0.14
Origin:	Norway	n-butane	0.74	Pour Point (°C)	-15
Sample Date:	08 januar 2011	isopentane	0.63	Viscosity @ 20°C (cSt)	6
Assay Date:	02 mars 2011	n-pentane	0.86	Viscosity @ 40°C (cSt)	3
Issue Date:	03 mars 2011	cyclopentane	0.14	Nickel (ppm)	0.5
Comments:		C_6 paraffins	1.72	Vanadium (ppm)	0.3
		C_6 naphthenes	1.90	Total Nitrogen (ppm)	540
		benzene	0.35	Total Acid Number (mgKOH/g	0.70
		C_7 paraffins	1.63	Mercaptan Sulphur (ppm)	0
		C_7 naphthenes	2.88	Hydrogen Sulphide (ppm)	-
		toluene	0.96	Reid Vapour Pressure (psi)	6.3

Cut Data			Atmospheric Cuts									Vacuum Cuts			
Start (°C)	IBP	IBP	C5	65	100	150	200	250	300	350	370	370	450	500	550
End (°C)	FBP	C4	65	100	150	200	250	300	350	370	FBP	450	500	550	FBP
Yield (% wt)		1.3	2.5	5.3	10.7	9.5	9.4	12.2	11.5	3.8	33.9	13.5	6.7	5.1	8.6
Yield (% vol)		2.0	3.3	6.2	11.6	10.0	9.5	12.0	11.1	3.6	30.8	12.6	6.2	4.6	7.4
Cumulative Yield (% wt)		1.3	3.9	9.2	19.9	29.3	38.7	50.9	62.4	66.1	100.0				
Density @ 15°C (g/cc)	0.845		0.646	0.730	0.779	0.800	0.831	0.856	0.875	0.889	0.925	0.903	0.913	0.927	0.973
API Gravity	35.9		87.6	62.2	50.2	45.3	38.7	33.8	30.2	27.6	21.3	25.2	23.4	21.1	13.8
UOPK	11.9				11.5	11.6	11.6	11.6	11.7	11.7	12.0	11.9	12.1	12.2	12.1
Total Sulphur (% wt)	0.139		0.000	0.000	0.002	0.012	0.022	0.049	0.123	0.182	0.322	0.212	0.262	0.331	0.54
Mercaptan Sulphur (ppm)	0		0.1	0.4	0.6	0.6	0.6	0.4							
Total Nitrogen (ppm)	540						1	5	40	148	1563	447	827	1404	3989
Basic Nitrogen (ppm)	169						0.38	2.8	23.7	68.87	482	149	267	395.8	1226
Total Acid Number (mgKOH/g	0.70		0.00	0.00	0.01	0.02	0.05	0.16	0.61	1.05	1.49	1.29	1.61	1.85	1.49
Viscosity @ 20°C (cSt)	5.75					1.26									
Viscosity @ 40°C (cSt)	3.45					0.95	1.66	2.97	6.41	12.1					
Viscosity @ 50°C (cSt)	2.79						1.43	2.43	4.93	8.84	110	18.8	68.5	229	
Viscosity @ 60°C (cSt)											66.6	13.8	42.9	125	
Viscosity @ 100°C (cSt)											15.2	5.26	10.8	21.6	271
Viscosity @ 130°C (cSt)															64.5
RON (Clear)			78.4	63.7	67.5	41.6									
MON (Clear)			77.5	60.8	63.9	39.4									
Paraffins (% wt)	32.5		94.5	45.9	29.5	37.0									
Naphthenes (%wt)	39.0		5.5	47.5	45.0	39.8									
Aromatics (% wt)	28.6		0.0	6.6	25.5	23.2									
Pour Point (°C)	-15						-53	-30	-4	11	38	26	39	46	43
Cloud Point (°C)							-52	-29	-4						
Freeze Point (°C)						-69	-48	-24							
Smoke Point (mm)						22	19	15							
Cetane Index						34	40	47	53	58					
Naphthalenes (% vol)						0.4	4.6	9.9	14.4						
Aniline Point (°C)					43.7	48.5	58.2	64.9	71.2	78.2		87.6	94.5	96.8	
Hydrogen (% wt)			16.5	14.8	13.5	13.9	13.4	13.0	12.8	12.7		12.7	12.7	12.7	
Wax (% wt)	5.0										11.6	11.8	13.4	13.1	8.8
C_7 Asphaltenes (% wt)	0.1										0.2		0.0	0.0	0.6
Micro Carbon Residue (% wt)	0.9										2.7		0.0	0.7	10.4
Rams. Carbon Residue (% wt	0.8										2.4		0.0	0.6	9.0
Vanadium (ppm)	0.3										1.0		0.0	0.0	4.0
Nickel (ppm)	0.5										1.6		0.0	0.0	6.2
Iron (ppm)	-										-		-	-	

Annex 2
Safety data sheets and commercial brochures

TOTAL

Material Safety Data Sheet

Section 1. Chemical Product and Company Identification

Product name FINASOL OSR 52

In Case of Emergency
Chemtrec:
(800) 424-9300
On behalf of TOTAL SPECIALTIES USA, INC. contact:
Total Petrochemicals & Refining USA, Inc.:
(800) 322-3462

Supplier TOTAL SPECIALTIES USA, INC.
1201 Louisiana Street, Suite 1800
Houston,TX 77002

Technical Information **For non-emergency** product information:
email product.stewardship@total.com

Chemical Family Not available.

MSDS# SF0033

CAS Registry Number Mixture.

Section 2. Hazards Identification

Emergency Overview MAY BE HARMFUL IF SWALLOWED.
MAY BE IRRITATING TO EYES, SKIN AND RESPIRATORY SYSTEM.

Routes of Entry Dermal contact. Eye contact. Ingestion.

Potential Acute Health Effects

Eyes Irritating to eyes. Contact with eyes may cause severe irritation and possible burns.

Skin Irritating to skin. Absorbed through skin. Skin contact may produce burns.

Inhalation Material is irritating to mucous membranes and upper respiratory tract.

Ingestion Aspiration hazard if swallowed. Can enter lungs and cause damage. May cause burns to mouth, throat and stomach.

Potential Chronic Health Effects Not listed as a carcinogen by OSHA, NTP or IARC.

Repeated or prolonged contact with irritants may cause dermatitis. Repeated or prolonged contact with spray or mist may produce chronic eye irritation and severe skin irritation.

Medical Conditions Aggravated by Overexposure Pre-existing disorders involving any target organs mentioned in this MSDS as being at risk may be aggravated by over-exposure to this product.

Overexposure /Signs/ Symptoms Direct contact may cause irritation and redness. Inflammation of the eye is characterized by redness, watering, and itching.

See Toxicological Information (Section 11)

Section 3. Composition and Information on Ingredients

Occupational exposure limits, if available, are listed in Section 8.

Substance Name	CAS #	% by Weight
Surfactant	Proprietary	< 25
Distillates (petroleum), hydrotreated light	64742-47-8	< 20
Dipropylene glycol methyl ether	34590-94-8	< 20
Surfactant	Proprietary	< 20
Surfactant	Proprietary	< 15
Surfactant	Proprietary	< 10
2-aminoethanol	141-43-5	< 5
Anti-Corrosion additive	Proprietary	< 5

Section 4. First Aid Measures

Eye Contact Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention.

Skin Contact In case of contact, immediately flush skin with plenty of water. Remove contaminated clothing and shoes. Cold water may be used. Wash clothing before reuse. Clean shoes thoroughly before reuse. Get medical attention.

Inhalation If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

SAFETY DATA SHEET
FINASOL OSR 52

1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND THE COMPANY:

PRODUCT NAME: FINASOL OSR 52

APPLICATIONS: DISPERSION OF PETROLEUM DISTILLATES IN A MARINE ENVIRONMENT

SUPPLIER: CHAMPION TECHNOLOGIES
Minto Avenue
Altens Ind. Est.
Aberdeen AB12 3JZ

EMERGENCY TELEPHONES: [24Hr] 00 44 (0)1224 879022
OUT OF OFFICE HOURS ASK FOR HEALTH AND SAFETY

2. COMPOSITION/INFORMATION ON INGREDIENTS:

NAME	CAS No.:	CONTENT	SYMBOL:	RISK:
DISTILLATES (PETROLEUM), HYDROTREATED LIGHT; KEROSINE - UNSPECIFIED	64742-47-8	<10-30 %	Xn	

3. HAZARDS IDENTIFICATION:

Not regarded as a health hazard under current legislation.

4. FIRST AID MEASURES:

GENERAL: First Aid treatments follow the principles of UK HSE "First Aid at Work" training

INHALATION: Move the exposed person to fresh air at once. Get medical attention if any discomfort continues.

INGESTION: NEVER MAKE AN UNCONSCIOUS PERSON VOMIT OR DRINK FLUIDS! Rinse mouth thoroughly. Drink plenty of water. Get medical attention if any discomfort continues.

SKIN: Remove affected person from source of contamination. Get medical attention if irritation persists after washing.

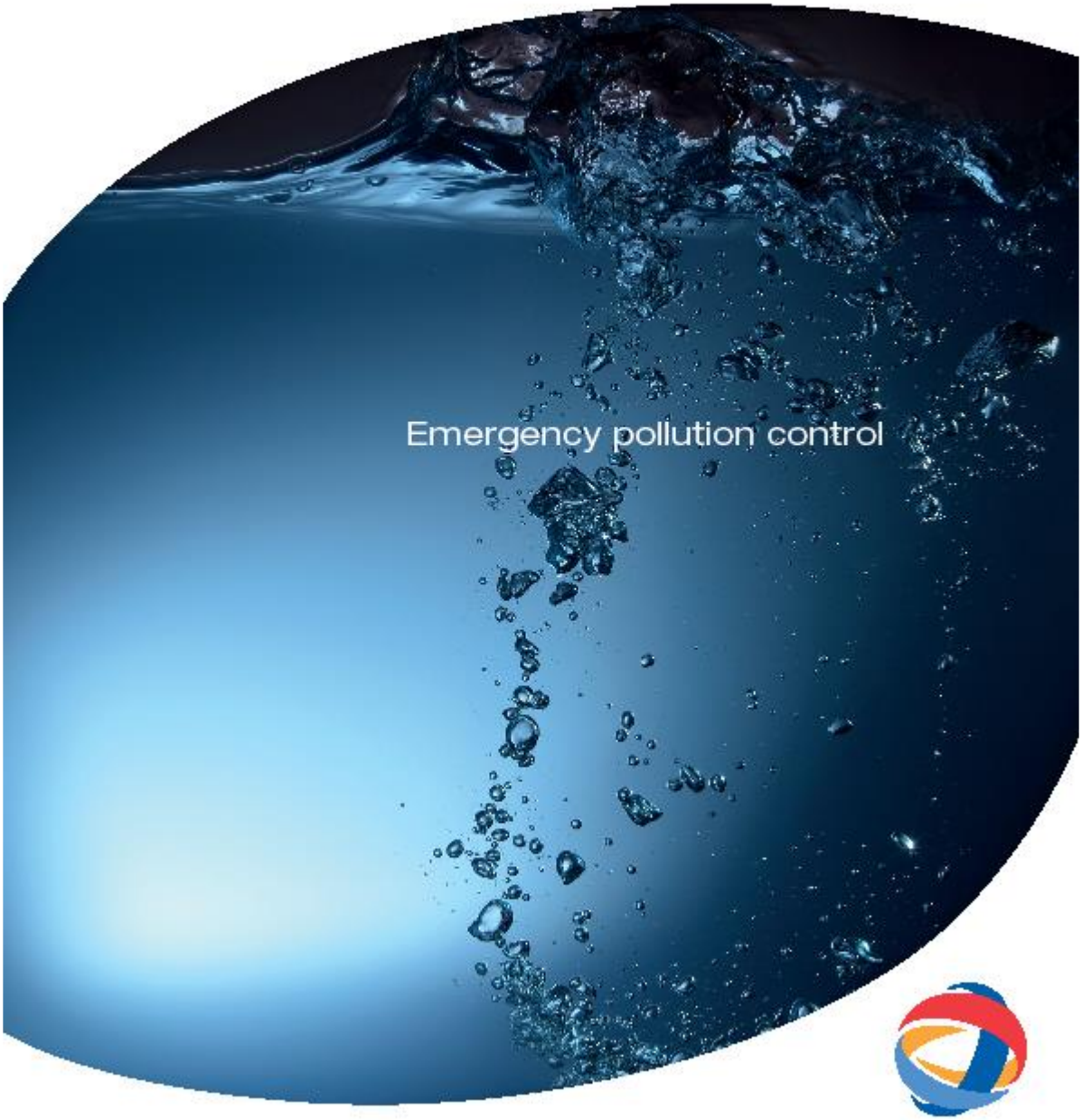
EYES: Make sure to remove any contact lenses from the eyes before rinsing. Promptly wash eyes with plenty of water while lifting the eye lids. Continue to rinse for at least 15 minutes. Get medical attention if any discomfort continues.

5. FIRE FIGHTING MEASURES:


FINASOL®
Marine Dispersants
TOTAL

FINASOL®

Marine Dispersants



TOTAL