TOXICITY AND BIOAVAILABILITY OF LUBRICANTS AND THEIR ADDITIVES IN THE AQUATIC ENVIRONMENT

Charles Eadsforth[1], Julia Hartmann[2], Tessa Halmans[3], Joy Worden[1], James Dawick[1], Graham Whale[1], Joris Haftka[2], Joop Hermens[2]

[1]Shell Health, Brabazon House, Concord Business Park, Threapwood Road, Manchester, M22 0RR, UK. [2]Institute for Risk Assessment Sciences, Utrecht University Yalelaan 104, 3584 CM Utrecht, The Netherlands.
[3]Shell Technology Centre-Amsterdam, Grasweg 31, 1031 HW Amsterdam, The Netherlands.

INTRODUCTION

Lubricants consist of base oil (typically accounting for 70-99%) and performance additives.
The additives (ADD) are synthetic chemicals usually supplied as "performance packages" (PACK) which contain 5 to 10 or even more individual components) which enhance or eliminate unwanted properties of the lubricant and introduce new characteristics to the formulated product.

For the purpose of communicating environmental hazard via safety data sheets and product labels, lubricants have to be classified according to their toxicity to the aquatic environment. Ideally, lubricants would be classified using aquatic toxicity data generated on the fully formulated product; however this is impractical due to the large number of combinations of base oils and additives. In the absence of test data, mixtures can be classified based on similar tested mixtures or, more frequently, on a calculation method which assesses individual hazardous ingredients (GHS, 2015). The substances which trigger environmental classification of lubricants are often the performance additives. However, it is suggested that some of the more hydrophobic additives might not be bioavailable to the aquatic ecosystem if the lubricant is exposed to the environment due to preferential partitioning to the base oil. This hypothesis is based on earlier unpublished work as well as on the partitioning behaviour of lubricant additives (OECD lubricant emissions scenario document, 2004). The aim of this project was to determine whether lubricant additive bioavailability, and thus aquatic toxicity, is altered once incorporated into the base oil of Fully Formulated Lubricant (FFL).

METHODS

1. Test media for the various substances was prepared using a Water Accommodated Fraction (WAF) approach with a stirring period of 72 hours. Highly viscous samples were added via microscopic glass slide. For the bioassays the following toxicity test kits (supplied by MicroBio Tests Inc.) were used:
   - DAPHTOXKIT F (Daphnia magna): after 24 and 48 hours acute toxicity (EL50) was calculated (performed in quadruplicate)
   - ALGALTOXKIT F (Selenastrum capricornutum): algal growth was measured at 24, 48 and 72 hours by measuring the Optical Density (OD) at 670 nm (performed in triplicate)
2. Acute and chronic toxicity of FFLs (derived using Toxkits) was compared to FFL classifications based upon the 'calculation method'.
3. Aquatic toxicity of an individual discrete additive compound (ADD 2) and a performance additive package containing ADD 2 (PACK 7) was assessed to show the relative toxicity of an additive in the presence and absence of oil.
4. LC-MS/MS analysis of the test media samples shows the concentration of ADD 2 in the water phase.

RESULTS

- Acute Daphnia immobilisation test and the algae (Selenastrum) growth inhibition test on FFLs resulted in EL50 >1000 mg/l showing no toxicity at the highest relevant loading rate for classification (Table 1); this contradicts some GHS classifications.
- PACK 7 contains 30%m/m of a single component (ADD 2), along with other undisclosed compounds, which are both very toxic to aquatic organisms (Table 2). The relative effect of ADD 2 and PACK 7 on Daphnia (Figure 1) and algae (Figure 2) decreases when tested in the presence of oil compared to the absence of oil, which indicates a mitigating influence of the base oil in the FFL on bioavailability of the toxic compound.
- This mitigating effect is further demonstrated by LC-MS/MS results which show a clear decrease in the percentage of ADD 2 entering the water phase in the presence of oil (Figure 3).

Sample	CLP Classification	GHS Classification	EL50 (48h Daphnia)	ErL50 (72h Selenastrum)	Acute classification based on experimental data	GHS Classification	ErL10 (72h Selenastrum)	Chronic classification based on experimental data
FFL 1	None	Acute 2	>1000 mg/L	>1000 mg/L	None	Chronic 2	>1000 mg/L	None
FFL 2	None	None	>1000 mg/L	>1000 mg/L	None	None	>1000 mg/L	None
FFL 3	None	Acute 2	>1000 mg/L	>1000 mg/L	None	Chronic 2	>1000 mg/L	None
FFL 4	None	Acute 2	>1000 mg/L	>1000 mg/L	None	Chronic 2	>1000 mg/L	None
FFL 5	None	Acute 2	>1000 mg/L	>1000 mg/L	None	Chronic 2	>1000 mg/L	None
FFL 6	None	Acute 2	>1000 mg/L	>1000 mg/L	None	Chronic 2	305 mg/L	None
FFL 7	None	Acute 3	>1000 mg/L	798 mg/L	None	Chronic 3	90 mg/L	None
FFL 10	None	Acute 3	989 mg/L	662 mg/L	None	Chronic 3	159 mg/L	None
FFL 11	None	Acute 3	>1000 mg/L	>1000 mg/L	None	Chronic 3	>1000 mg/L	None
FFL 12	None	Acute 3	>1000 mg/L	535 mg/L	None	Chronic 3	10 mg/L	None
FFL 13	None	Acute 3	>1000 mg/L	242 mg/L	None	Chronic 3	17 mg/L	None
FFL 15	None	None	>1000 mg/L	>1000 mg/L	None	None	>1000 mg/L	None

Table 1 – Acute and chronic classifications vs. classifications based on experimental data

Sample	EL50 (48h Daphnia)	ErL50 (72h Selenastrum)	ErL10 (72h Selenastrum)
PACK 7	0.02 mg/L	0.70 mg/L	0.41 mg/L
ADD 2	0.58 mg/L	2.39 mg/L	1.92 mg/L

Table 2 – Acute and chronic classifications vs. classifications based on experimental data

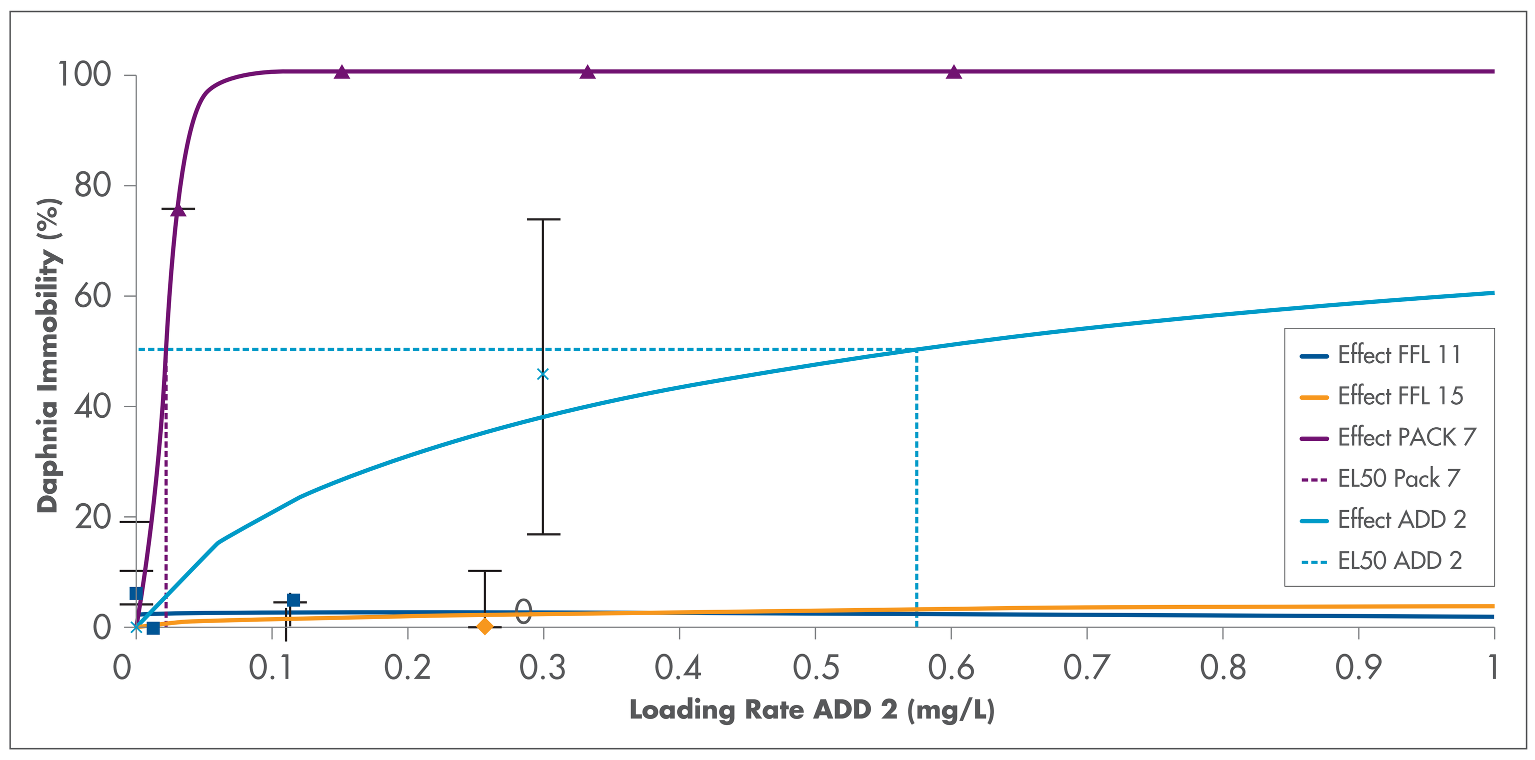

Figure 1 – Relative average effect of ADD 2 on % immobility of Daphnia magna after 48h exposure in the presence of oil (FFL) compared to the effect in the absence of oil (ADD 2 and PACK 7)

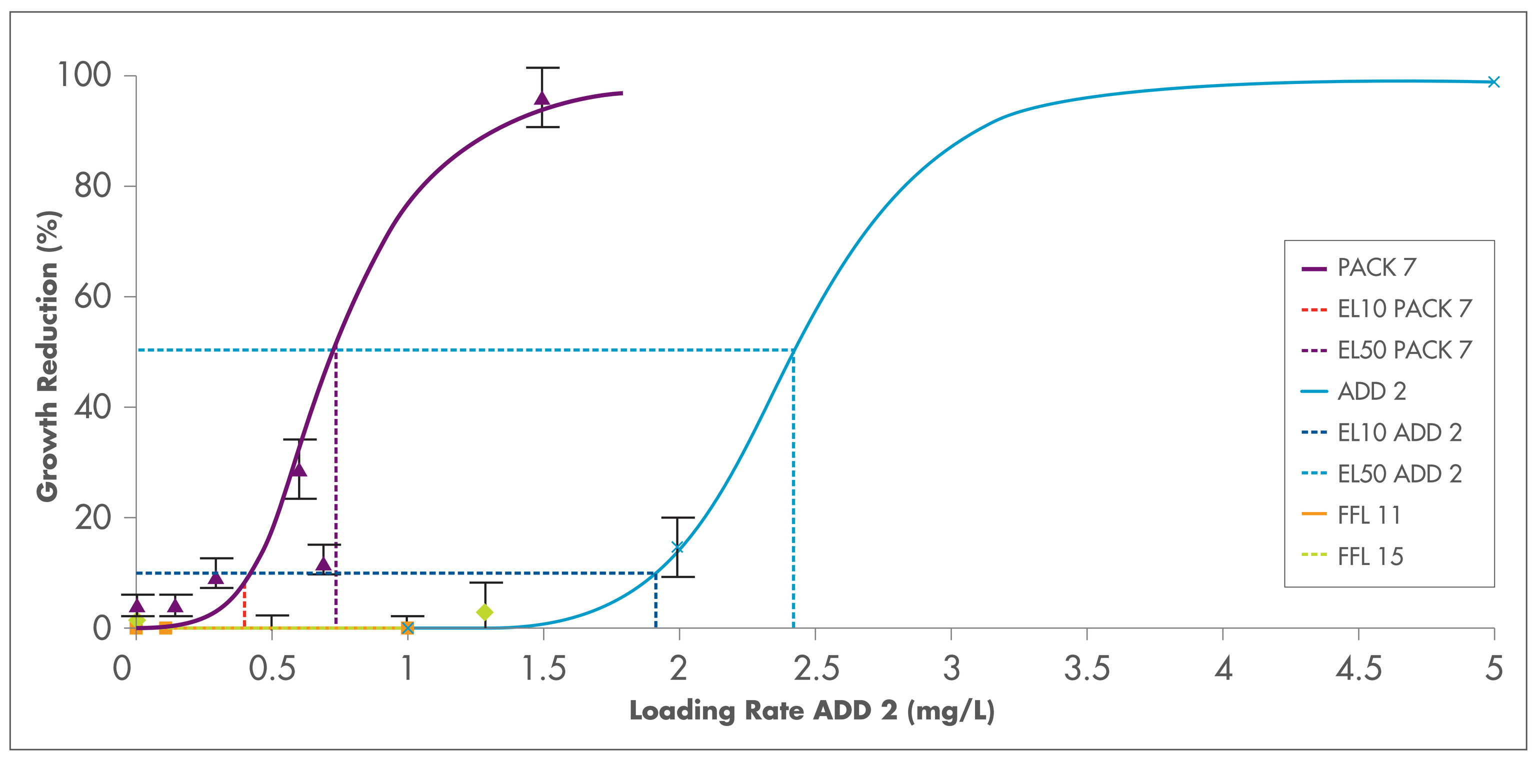

Figure 2 – Relative average effect of ADD 2 on % growth inhibition of Selenastrum Capricornutum after 48h exposure in the presence of oil (FFL) compared to the effect in the absence of oil (ADD 2 and PACK 7)

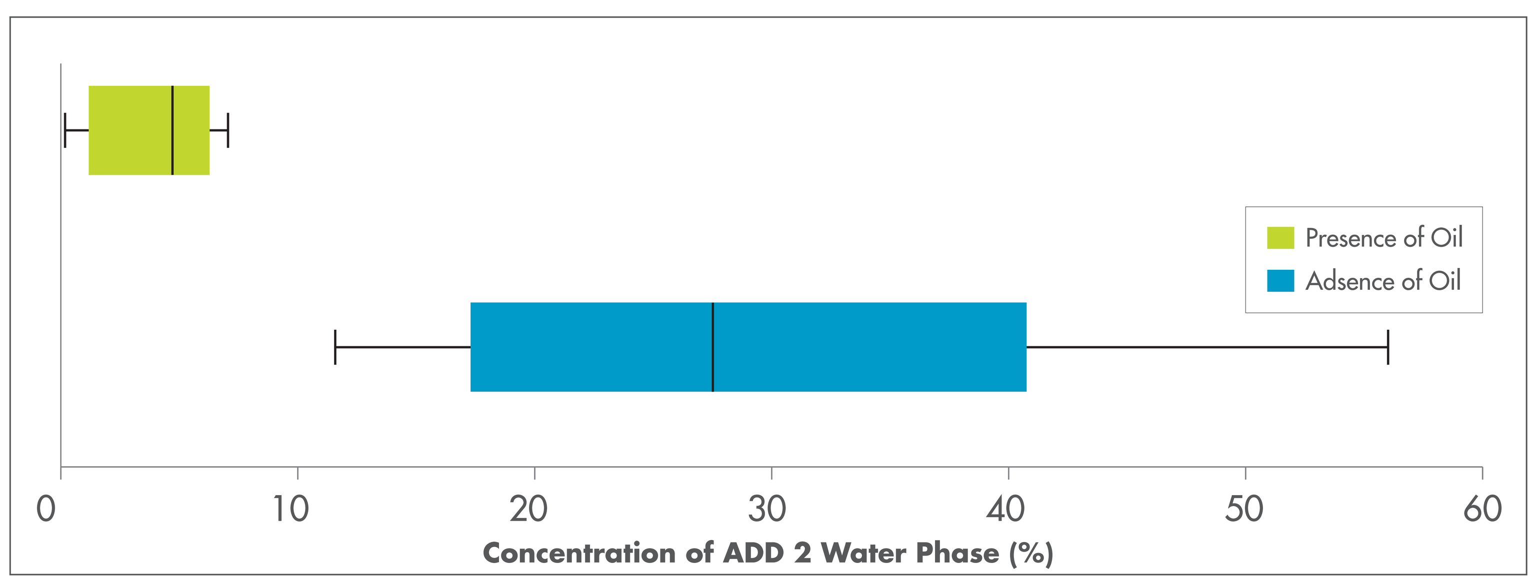

Figure 3 – Box plot showing percentage ADD 2 entering the water phase

Note: *the percentage of ADD 2 entering the water phase is calculated using the arithmetic mean aqueous concentration compared to the theoretical loading rate of ADD 2 in the specific sample. The ADD 2 WAF initial loading rate was 1.5 mg/L.*

CONCLUSIONS

- The FFLs tested do not meet criteria for classification as toxic to the aquatic environment, contradicting the current GHS and CLP classifications based on the mixture rules calculation method.
- Overall aquatic toxicity of FFLs is reduced because toxic additive bioavailability is decreased in the presence of oil; as ADD 2 is fairly hydrophobic (log Kow = 4.28) it showed a preference to reside in the oil phase.
- PACK 7 (which contains ADD 2 and approximately 9 other performance additives) was found to be more toxic than ADD 2 alone. This suggests that the other (undisclosed) hazardous components contribute to the overall toxic effect.
- This project provides an alternative approach for environmental classification and labelling for formulated lubricants under EU CLP and GHS regulations, and could lead to declassification of many FFLs. In addition, the data generated from this project will be used to help formulate a simplified approach for the hazard assessment of lubricant products used by the offshore oil and gas industry.
- Further work investigating the bioavailability of lubricant additives to aquatic organisms exposed to fully formulated lubricants is warranted.

References

OECD (2004) Emission Scenario Document on Lubricant and Lubricant Additives. OECD series on emission scenario documents ENV/JM/MONO(2004)21.

Globally Harmonized System of Classification and Labelling of Chemicals (2015).