



CHALLENGING THE VALIDITY OF RECENT CLAIMS THAT DISPERSANTS SUPPRESS BIODEGRADATION

Alun Lewis is an authority on oil spill dispersants and other technical aspects of oil spills such as oil 'weathering' and the fate and behaviour of spilled oil and aerial surveillance of oil spills. A graduate chemist, he worked at the BP Research Centre from 1967 until 1992, specializing in oil spill dispersants and other aspects of oil spill response from 1979 onwards. In 1993 he worked at the UK Government's Warren Spring Laboratory and then at SINTEF in Trondheim, Norway until 1997, continuing studies on oil weathering of the use of oil spill dispersants. Alun returned to the UK and worked for AEA Technology until becoming an independent oil spill consultant in 1998. Alun has worked with many organizations, both commercial and government, throughout the world,

including IPIECA and OSPRI. He has presented on numerous oil spill response / dispersant training courses over the years.

Comments on the Kleindienst et al paper;

"Chemical dispersants can suppress the activity of natural oil-degrading microorganisms" by Alun Lewis, Independent Oil Spill Consultant

a. Background

The publication on the PNAS web-site on 9th November of the above Kleindienst *et al* (there are 13 other authors) paper certainly created a good deal of media interest on the internet. The principal researcher, Dr. Samantha Joye (who is the Athletic Association Professor in Arts and Sciences in the Department of Marine Sciences in the University of Georgia's Franklin College of Arts and Sciences) was widely quoted in the press: "*The dispersants did a great job in that they got the oil off the surface,*" Joye said. "*What you see is the dispersants didn't ramp up biodegradation.*" In fact, she said she found the oil with no dispersant "*degraded a heckuva lot faster than the oil with dispersants.*"

The publication of the paper was picked up by numerous media outlets in the USA and further afield. In the UK, the Telegraph (and other UK newspapers) picked up the story under the headline "*Half of oil from BP's Gulf of Mexico spill 'may still be on sea floor'*" with quotes such as "*The dispersants did a great job in that they got the oil off the surface,*" Ms Joye said. "*What you see is the dispersants didn't ramp up biodegradation.*" So as the oil wasn't dissipated by the bacteria, Ms Joye said it might still be on the floor of the gulf.

The idea that a very significant proportion of the oil that was released from the Macondo well may be on the seabed has been a constant theme from Dr. Joye and her research group over the last 5 years. This is the latest paper in a series from the research group ECOGIG (Ecosystem Impacts of Oil & Gas Inputs to the Gulf), of which Dr. Joye is the Project Director, which seeks to provide evidence for such an hypothesis.

The 6 pages of dense text of the Kleindienst *et al* paper describes some sophisticated techniques, such as gene sequencing and measuring the rate of hydrocarbon oxidation and enzyme activities, to present the proposition that the evolution of microbial populations in the 'microcosms' were altered by the presence of dispersant. The paper concludes: "*Extrapolating this comprehensive dataset to real world scenarios questions whether dispersants stimulate microbial oil degradation in deep ocean waters and instead highlights that dispersants can exert a negative effect on microbial hydrocarbon degradation rates.*"

If this were the case, the rationale of using dispersants could be questioned, but is that what these results actually show?

b. The thesis of the paper

The very first sentence in the paper is: "*During the Deepwater Horizon oil well blowout in the Gulf of Mexico, the application of 7 million liters of chemical dispersants aimed to stimulate microbial crude oil degradation by increasing the bioavailability of oil compounds.*" From a microbiologist's viewpoint, this may seem to be the aim of using dispersants in oil spill response. From an oil spill responder's viewpoint, the perspective is rather different. The primary purpose of using dispersant application is to stop the oil released subsea from getting to the sea surface by dispersing it into the sea before it could do so (subsea dispersant addition), or by spraying dispersant onto spilled oil on the sea surface to transfer into the underlying water column. The primary aim of dispersant use is to prevent oil on the sea surface from subsequently drifting ashore and contaminating sensitive shoreline habitats such as salt-marshes and mangroves.

The initial consequence is that dispersed oil will be rapidly diluted to low concentrations in the water that are too low to cause significant toxic effects to marine organisms. If that dilution cannot be achieved, for example if the water is not deep enough, the rationale of using dispersant may be at question. The eventual consequence is that the subsequent biodegradation of the oil will be more rapid if it has been dispersed, than if it has not been dispersed. Some recalcitrant residue may remain.

The required chronological sequence is to (i) disperse the oil (by addition of dispersant), (ii) the dispersed oil to be diluted to low concentration of oil in water (dependent on prevailing currents and water depth) and (iii) the majority of the dispersed oil to be subsequently biodegraded by naturally-occurring microorganisms that are already present in the sea. Dispersant use facilitates the biodegradation of the oil by making it much more available to the existing microorganisms, but does not cause it. The biodegradation of oil will occur much more rapidly if it is dispersed, than if it is not dispersed.

The paper states. *“In response to oil spills, chemical dispersants are applied to the oil-contaminated seawater to disperse surface slicks into smaller droplets that are presumed to be more bioavailable to microorganisms. We provide evidence that chemical dispersants applied to either deep water or surface water from the Gulf of Mexico did not stimulate oil biodegradation.”*

c. Key questions about the paper

The paper states in the introduction: *“In laboratory experiments, we **simulated** environmental conditions comparable to the hydrocarbon-rich, 1,100 m deep plume that formed during the Deepwater Horizon discharge.”* On page 2 it is stated *“Experimental conditions (SI Appendix, Table S1) **mimicked** those prevailing in the DWH deep-water hydrocarbon plume (6–13, 18), the chemistry of which varied substantially over space and time (18).”*

The key questions to be asked are:

- Precisely what was done in these experiments?
- How closely did these experiments resemble the actual conditions that prevailed in the plume of dispersed oil that was presents at a water depth of 1,100 metres at the Deepwater Horizon incident?

An accurate simulation of the subsea release of a very large volumes of gas and crude oil into the sea at a depth of 1,520 metres (where the pressure is 150 atmospheres) would be exceedingly difficult to simulate in a laboratory experiment.

The description given in the **Materials and Methods, Microcosm Setup and Sampling** section (on page 5 of 6) is brief:

“Setup and sampling of microcosms are described in detail in [SI Appendix, SI Materials and Methods](#). In brief, 72 2-L glass bottles (1.8-L sample per bottle) were incubated on a roller table ([SI Appendix, Fig. S2](#)). Treatments (WAF, dispersant-only, and CEWAF ± nutrients) and controls (abiotic and biotic) were run in triplicate for each time point. Sampling (except for the CEWAF + nutrients treatment) was performed after 0 d (T0), 1 wk (T1), 2.5 wk (16 d; T2), 4 wk (T3), and 6 wk (T4); CEWAF + nutrients treatments were sampled at T0, T1, and T4. CEWAFs were prepared by mixing pasteurized seawater with oil and/or dispersants for 48 h at room temperature and subsequently subsampling CEWAFs, excluding contamination by oil or dispersants phases ([SI Appendix](#)).”

At the bottom of page 1 it says: This article contains supporting information online at: www.pnas.org/lookup/suppl/doi:10.1073/pnas.1507380112/-/DCSupplemental.

This is a 13.6 Mb download of 58 pages, but for ISCO readers interested in this topic it is well worth the slight effort of obtaining this document. The first paragraph of the SI Appendix unequivocally states:

*“Our laboratory experiments simulated the conditions of the Deepwater Horizon (DWH) deepwater plume **very realistically.**”*

And then continues:

“The dispersant dilutions were 1:60,000 (v/v) in Corexit 9500 (‘dispersant-only’) treatments and 1:30,000 (v/v) in the chemically enhanced water-accommodated fraction (CEWAF) treatments ([SI Appendix Fig. S1 and S2](#)). These dilutions resulted in dispersant concentrations (~19 µg/L) that were comparable to concentrations observed in the DWH plume in situ (below detection to 12 µg/L) (1).”

For readers unfamiliar with the terminology being used, ‘water-accommodated fraction’, or WAF, is the water obtained after stirring oil into water and then letting the oil float out. The idea is to leave the partially water-soluble, and potentially toxic, chemical compounds from the oil in the water. CEWAF is the same thing, but using oil and dispersant.

d. Units of concentration of dispersant in seawater - that is the question

Sharp-eyed ISCO readers may have noticed something odd about the mixture of units used to express the concentration of the dispersant diluted into the seawater. The dispersant volume to seawater volume (v/v) ratios of 1:60,000 and 1:30,000 are said to produce dispersant concentrations of ~19µg/L in seawater. (L is used in the USA to represent litre.) It is not clear where the ~19 µg/L dispersant concentration in water comes from; it is only mentioned once in the paper and without a supporting reference. The maximum concentration of Corexit 9500 actually measured in the seawater of the deep plume at the DWH incident was somewhat lower at 6µg/L (Gray et al, 2014).

The units used are very important. A µg is a microgram, a millionth of a gram. 19 µg of dispersant (which has a density of about 0.95 gm/ml) in one litre, that is 1,000 mls, of seawater (seawater a density of 1.025 gm/ml), is about 18 parts per billion of dispersant in seawater. The actually measured maximum dispersant concentration in the water of the plume at DWH, based on measurement of the DOSS in water concentrations, was 6 parts per billion of dispersant in seawater

But - and this is an important point - v/v ratios of dispersant to water of 1:60,000 and 1:30,000 are much, much higher than concentrations expressed as µg/L or parts per billion. 1:60,000 v/v is one volume of dispersant in 60,000 volumes water and that is 16.7 volume of dispersant in 1,000,000 seawater equals 16.7 parts per million (ppm). 1:30,000 v/v dispersant to seawater is 33.3 parts per million (ppm).

e. What were the concentrations of dispersant in the seawater used in the microcosms?

The “**Water-accommodated fractions**” section of the SI give the details of the dilutions used to produce the seawater that was used in the microcosms:

Preparation	Volumes used			
	Oil (mls)	Dispt (mls)	Water (mls)	Total (mls)
WAF	150	0	850	1,000
Dispersant only	0	15	850	865
CEWAF	150	15	850	1,015

The oil and water (and dispersant in the CEWAF) were mixed with a 600 rpm magnetic stirrer for two days, allowed to settle for an hour then sub-sampled. The important thing about WAF is that only a very small proportion of oil is present as partially water-soluble chemical compounds, so only a small proportion of the ‘oil’ ends up in the WAF. However, being composed of a lot of surfactants and solvents, the majority of the dispersant will end up in the “dispersant only solution” and in the CEWAF.

It is noteworthy that a dispersant to oil ratio (DOR) of 1:10 was used in these experiments when the actual subsea dispersant treatment rate at the DWH incident was at DORs of between 1:100 and 1:200. The experimenters chose to use a dispersant treatment rate that was 10 to 20 times higher than that used at the DWH incident.

The “**Setup and sampling of microcosms**” section describes how these materials were further diluted for use in the microcosms:

Next, 0.4 L of sterile WAF, dispersant-only, or CEWAF (±nutrients) was added to 1.4 L seawater. To achieve comparable addition of dissolved organic carbon across treatments, the prepared solutions were diluted with an appropriate volume of sterile seawater (0.2 µm filtered and pasteurized for 2 h at 65°C).

Dispersant was much more soluble in water than oil; to generate 0.4 L of diluted solutions, only 1.56 ml of original dispersant-only solution or 3.26 ml of CEWAF (±nutrients) was added. For WAF, 0.4 L of undiluted WAF was added.

Microcosm	Aliquot taken		Seawater in microcosm		Dispersant concentration in microcosm		
	Aliquot Taken (mls)	Contains Dispt (mls)	Made up to (mls)	Add 1,400 (mls)	mls Dispersant / ml seawater	ppm	v/v ratio
WAF	400	0	400	1,800	0	0	0
Dispersant only	1.56	0.02705 ($\frac{1.56}{865} \times 15$)	400	1,800	0.00001503 ($\frac{0.02705}{1800}$)	15.0	1:66,538
CEWAF	3.26	0.04818 ($\frac{3.26}{1,015} \times 15$)	400	1,800	0.00002677 ($\frac{0.04818}{1800}$)	26.8	1:37,362

(I ask ISCO readers to use their pocket calculators to check through these very simple calculations.)

These dilutions resulted in dispersant in seawater concentrations of 1:66,538 v/v and 1:37,362 v/v which are 15 parts per million and 26.8 parts per million.

The dispersant in seawater concentrations used in the microcosms are **790** and **1,410** times higher, respectively, than the 19 µg/L (19 parts per billion) said in the paper to be "*comparable to concentrations observed in the DWH plume*". These dispersant concentrations are also **2,500** and **4,466** times higher than the maximum of 6 µg/L (6 parts per billion) of dispersant in seawater measured in the deep water plume at the DWH incident.

The dispersant in water concentrations used in the experiments are patently **not** "*very realistic*" in "*simulating the conditions of the Deepwater Horizon (DWH) deepwater plume*" and this undermines the purpose (and results) of the study.

f. Consequences and Conclusions

Because of the apparent error in calculating the dilutions of the dispersant in seawater, the 'microcosms' contained far too much dispersant, by factors of approximately **2,500** to **4,500**, compared the dispersant concentrations in the deep water plume that were actually measured at the DWH incident. This compounded the intentional decision to use a dispersant treatment rate in the experiments with a DOR of 1:10, which is 10 to 20 times higher than was actually used for subsea dispersant use at the DWH incident.

The differences in results obtained by comparing the WAF and CEWAF experiments could be due to many reasons. The Span™ and Tween™ surfactants in the dispersant, being composed of sorbitan (a hexitol (sugar) derivative), esterified with fatty acids (from vegetable oil) and with a polyoxyethylene chain are readily biodegradable (as the paper acknowledges). The microbial populations in the microcosms containing dispersant therefore rapidly developed to preferentially biodegrade the surfactants in the 'nutritious soup' of the excess of dispersant; the oil component was minor in the CEWAF.

Comparisons of the results from the WAF 'microcosm' (with no dispersant) and the CEWAF 'microcosms' (with a vast excess of dispersant), normalised on the basis of dissolved organic carbon (DOC), can therefore **not** be interpreted as indicating what may have happened at the DWH incident. The results obtained are an artefact of the methods used to obtain them and say very little about real world dispersant use.

References

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