Characterizing Dispersant/Dispersed Oil Effects

Ronald S. Tjeerdema
Department of Environme
University of California, Da

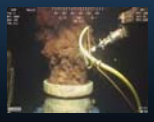
- The Responder's Tooll
- Bioassays – WAF vs C
- Metabolomics – WAF
- Chemistry and Bioavailability
- Conclusions

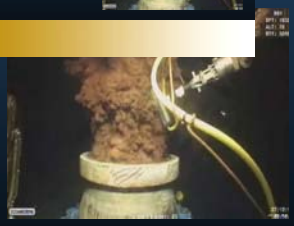
Characterizing Dispersant/Dispersed Oil Effects

Ronald S. Tjeerdema
Department of Environmental Toxicology
University of California, Davis

Topics

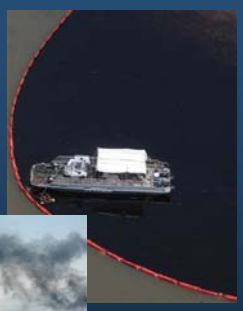
- The Responder's Toolbox
- Bioassays – WAF vs CEWAF
- Metabolomics – WAF vs CEWAF
- Chemistry and Bioavailability
- Conclusions





UCDAVIS COLLEGE OF AGRICULTURAL & ENVIRONMENTAL SCIENCES *where knowledge meets need...*

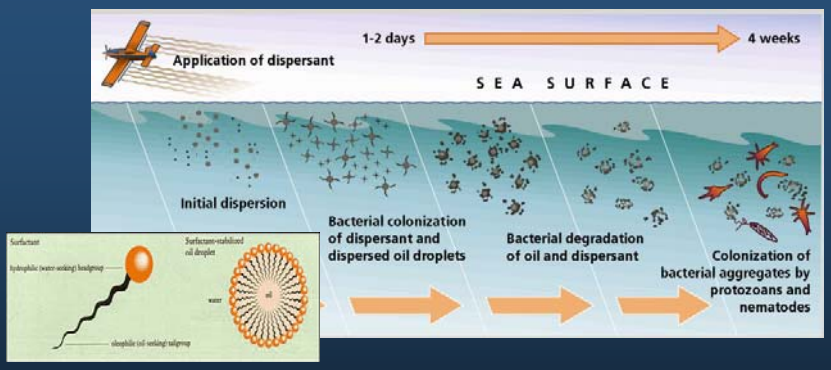
I. The Responder's Toolbox



- Collection
- Burning
- Bioremediation
- *Dispersants*

UCDAVIS COLLEGE OF AGRICULTURAL & ENVIRONMENTAL SCIENCES *where knowledge meets need...*

Dispersants Enhance Weathering



- Dispersants are similar to domestic detergents
- They break up oil and remove it from the surface
- Droplets may be more readily digested by bacteria

UCDAVIS COLLEGE OF AGRICULTURAL & ENVIRONMENTAL SCIENCES *where knowledge meets need...*

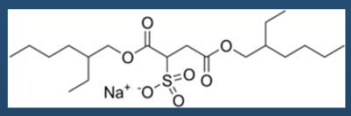
Resources and Impacts

- Dispersants may reduce slicks and shoreline impacts
- Tool selection may depend on resources at risk and in most in need of protection

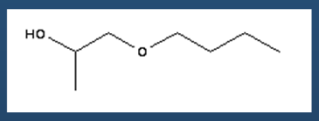
or

UCDAVIS COLLEGE OF AGRICULTURAL & ENVIRONMENTAL SCIENCES *where knowledge meets need...*

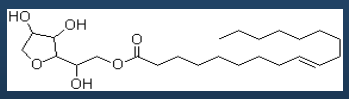
What Makes a Dispersant? Corexit 9500



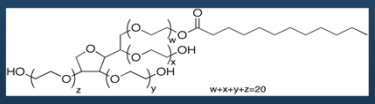
Dioctyl Sodium Sulfosuccinate



Propylene Glycol Butyl Ether



Sorbitan Monooleate

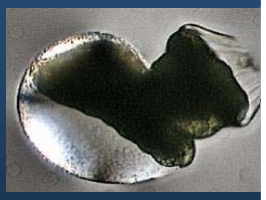


Ethoxylated Sorbitan Monooleate

Petroleum Distillates?

- In water and soils, DOSS degrades by 90% within 12-17 days
- DWH – present at depth in ppb range months after the event

II. Bioassays – WAF vs CEWAF



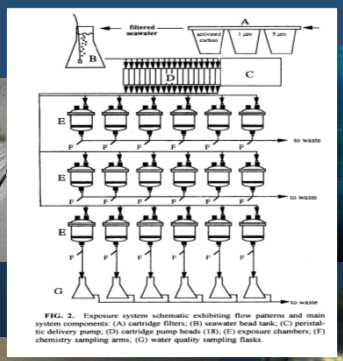


FIG. 2. Exposure system schematic exhibiting flow patterns and main system components: (A) cartridge filters; (B) seawater head tank; (C) peristaltic delivery pump; (D) cartridge pump heads (18); (E) exposure chambers; (F) chemistry sampling arms; (G) water quality sampling flasks.

Singer *et al.*, *Ecotoxicol. Environ. Saf.* 35:183 (1996)

Corexit 9527 – Constant versus Spiked

Table 1. Results of flow-through toxicity tests using Corexit 9527[a] on early life stages of four marine species

Species	Test	NOEC (ppm)	LC50 (ppm)	95% C.I. LC50	Slope	95% C.I. slope
Haliotis	1	1.19	1.96[a]	1.89–2.02	7.38	6.35–8.40
	2	1.50	2.20[a]	2.04–2.36	2.63	2.32–2.94
	3	0.63	1.60[a]	1.50–1.69	3.98	3.52–4.43
Holmesimysis	1	4.20	7.06	5.97–8.77	4.34	1.99–6.69
	2	4.14	7.26	6.13–8.53	5.51	2.47–8.54
	3	1.66	4.26	3.28–5.37	3.62	1.21–6.02
Atherinops	1	12.3	25.5	19.8–47.7	4.78	−0.52–10.1
	2	14.2	27.9	22.5–34.8	6.14	2.09–10.2
	3	13.9	40.6	32.3–51.0	5.53	2.20–8.86
Macrocystis	1	<2.35	NC	NC	NC	NC
	2	1.32	NC	NC	NC	NC
	3	2.07	NC	NC	NC	NC

LC50 and slope values derived from probit analysis
NC = not calculated; data inappropriate for calculation.
[a]Sublethal EC50 values.
[b]Signifies that lowest test concentration was significantly different from control.

Singer *et al., Environ. Toxicol. Chem.* 9:1387 (1990)

Table 2. Results of spiked-exposure toxicity tests using Corexit 9527 on early life stages of four marine species

Species	Test	NOEC (ppm)	MEC (ppm)	95% C.I. MEC
Haliotis	1	5.3	13.6	12.9–14.3
	2	8.4	18.1	16.8–19.5
	3	6.4	15.9	15.1–16.4
Holmesimysis	1	14.9	163.4	140.8–189.5
	2	20.5	136.4	109.5–169.8
	3	8.4	120.4	89.3–162.5
Atherinops	1	31.0	59.2	41.4–84.6
	2	50.3	86.2	68.6–108.3
	3	89.8	103.5	85.5–125.2
Macrocystis	1	16.4	89.1	80.9–93.3
	2	<13.6	86.6	72.4–96.5
	3	12.2	102.0[a]	NC

Median-effect concentrations (MEC) are IC50 for *Macrocystis*, EC50 for *Haliotis*, and LC50 for *Holmesimysis* and *Atherinops*.
NC = not calculated.
[a]Extrapolated beyond actual data set by linear regression.

Singer *et al., Environ. Toxicol. Chem.* 10:1367 (1991)

- Dispersants alone under spiked conditions generally toxic in the range of 20-150 ppm
- Spiked-exposure usually less toxic

Corexit 9527: PBCO WAF versus CEWAF

Table 2. Results of spiked-exposure toxicity tests using Prudhoe Bay crude oil alone and combined with Corexit 9527 (O:D ratio = 10:1)[a]

	EC/LC50 (mg/L $THC_{(C7\ C30)}$)					
	WAF			CEWAF		
Species/Endpoint	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3
Haliotis						
Larval abnormality	>34.03[b]	>46.99	>33.58	19.09 (18.90, 19.28)	32.70 (32.11, 33.30)	17.81 (17.65, 17.96)
Holmesimysis						
96-h mortality	>34.68	>25.45	>28.55	10.54 (9.08, 12.25)	10.75 (9.45, 12.22)	10.83 (NA)[c]
Initial narcosis	11.31 (9.14, 13.99)	11.58 (10.51, 12.77)	15.90 (14.71, 17.18)	11.07 (10.16, 12.05)	>38.33	48.03 (40.57, 56.85)
Atherinops						
96-h mortality	16.34 (14.57, 18.55)	40.20 (38.68, 41.45)	35.73 (9.37, 46.85)	28.60 (17.49, 46.76)	74.73 (62.30, 89.60)	34.06 (30.24, 38.37)
Initial narcosis	26.63 (24.82, 27.59)	>48.22	31.76 (14.65, 46.59)	>101.82	>140.97	>62.22

[a] Data are median-effect concentration and 95% confidence limits
[b] EC/LC50 estimated to be above highest test concentration
[c] Confidence limits not reliably calculable

Singer *et al., Archiv. Environ. Contam. Toxicol.* 34:177 (1998)

- In general, WAF was less toxic than CEWAF
- However, trend is reversed for narcosis
- Toxicity is species, life stage and endpoint specific

Corexit 9500

- Toxicity of Corexits 9527 and 9500 was similar for abalone, but not for mysids
- Toxicity also depends on specific formulation and exposure conditions
- *What about the chemistry used to measure endpoints?*

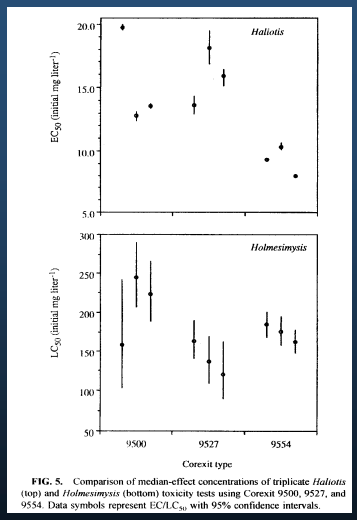
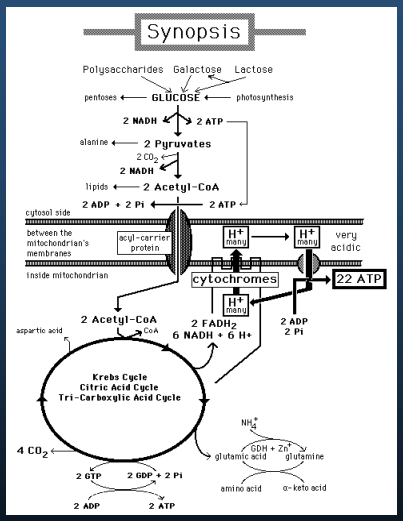


FIG. 5. Comparison of median-effect concentrations of triplicate *Haliotis* (top) and *Holmesimysis* (bottom) toxicity tests using Corexit 9500, 9527, and 9554. Data symbols represent EC/LC_{50} with 95% confidence intervals.

Singer *et al., Ecotoxicol. Environ. Saf.* 35:183 (1996)

III. Metabolomics – WAF vs CEWAF

- Assess actions of WAF vs CEWAF of PBCO in fishes under spiked- exposure conditions
- Apply ^{1}H-NMR-based metabolomics to demonstrate *very sensitive* sublethal actions on metabolism and amino acid balance



CROSERF Methods

WAF Exposures

CEWAF Exposures

Singer *et al.*, *Mar. Pollut. Bull.* 40:1007 (2000)

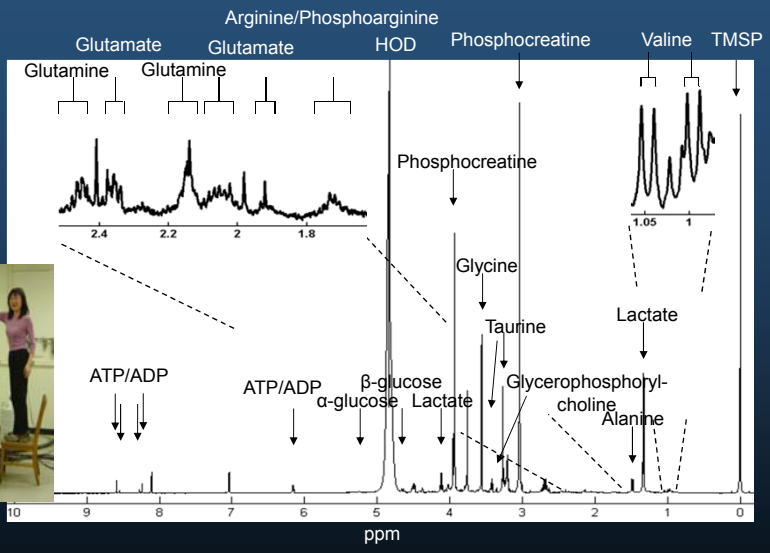
Traditional Comparative Toxicity

- Total petroleum hydrocarbons (TPH; C_{10} – C_{36}); GC-FID
- Volatiles (BTEX; C_6-C_9); purge-and-trap GC-MS
- Total hydrocarbon content (THC; C_6–C_{36}) – BTEX + TPH
- Spiked exposures confirmed via THC

Fish Species	WAF 96-h LC50	CEWAF 96-h LC50
Salmon Pre-Smolts	7.6 mg/L THC	48.6 mg/L THC
Salmon Smolts	7.5 mg/L THC	156 mg/L THC
Topsmelt Adults	> 3.4 mg/L THC	56.4 mg/L THC

Lin *et al.*, *Aquat. Toxicol.* 95:230 (2009)
Van Scoy *et al.*, *Ecotoxicol. Environ. Saf.* 73:710 (2010)
Van Scoy *et al.*, *Ecotoxicol. Environ. Saf.* 78:99 (2012)

NMR Spectrum of Muscle Extract



Similar Changes in Profiles – *Topsmelt*

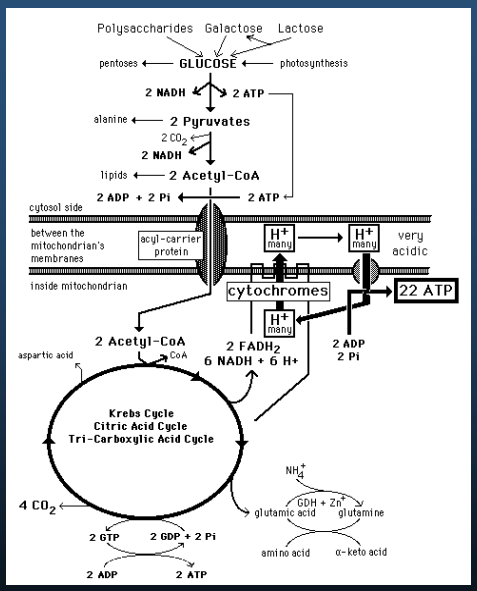
	96 h		78 d	
Metabolites	**WAF**	**CEWAF**	**WAF**	**CEWAF**
Valine	↑	↑	↓	↑
Lactate	↓	↓	↑	↑
Alanine	↑	↑	↓	↓
Arginine/Phosphoarginine	↑	↓	↓	↓
Glutamine	↑	↑	↓	↓
Succinate	↑	↑	↓	↓
Phosphocreatine	↓	↓	↑	↓
Taurine	↑	↑	↓	↓
Glycine	↑	↓	↑	↑
AMP	↓	↓	↓	↓
Histidine	↓	↓	↓	↓
ATP/ADP	↓	↓	↓	↓

Van Scoy *et al.*, *Ecotoxicol. Environ. Saf.* 78:99 (2012)

UCDAVIS COLLEGE OF AGRICULTURAL & ENVIRONMENTAL SCIENCES where knowledge meets need...

Implications

- WAF and CEWAF *both* increased free amino acids
- Ala, Arg, Gln, Glu, Val may result from proteolysis – or may be diverted from intermediary metabolism for new protein synthesis
- Diversion may reduce ATP available for development



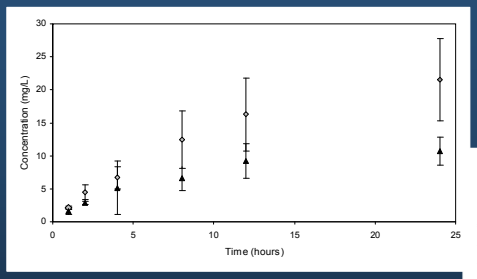
Why are WAF and CEWAF Actions Similar?

- LC50s, based on THC (*dissolved* + *particulate*) were very different: WAF, 7.5 mg/L; CEWAF, 156 mg/L (salmon)
- However, toxicity may result from "bioavailable" (dissolved) fractions – not THC
- *Hypothesis – dissolved fractions produced in WAF and CEWAF are not significantly different*
- Tested with triolein-filled semi-permeable membrane devices (SPMDs)

IV. Chemistry and Bioavailability

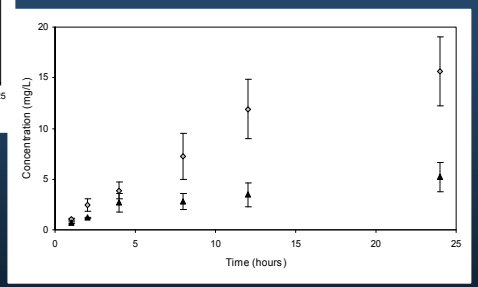
- CROSERF WAF and CEWAF
- Constant exposure – one SPMD removed at 1, 2, 4, 8, 12, 24 h
- Collect dissolved fraction via dialysis with hexane
- Analysis via GC-MS

SPMD Results



Naphthalene WAF vs CEWAF

WAF (▲) CEWAF (◆)



1-Methylnaphthalene WAF vs CEWAF

- Dissolved concentrations similar in first few hours (usual spiked period)

Van Scoy *et al.*, *Environ. Sci.: Processes Impacts* 15:2016 (2013)

Conclusions

- Dispersants are one of several tools
- WAF and CEWAF toxicity depends on species, life stage, exposure, endpoint *and chemical analysis*
- Corexit 9500 decreases oil lethality to fishes some 7 to 20-fold – *based on total hydrocarbons*
- Similar metabolic impacts are possibly due to similar bioavailable fractions – *dependent on analysis*
- *Thus, use care in comparing literature values*

UCDAVIS COLLEGE OF AGRICULTURAL & ENVIRONMENTAL SCIENCES *where knowledge meets need...*