OIL DISPERSANTS: "*TO USE OR NOT USE*"

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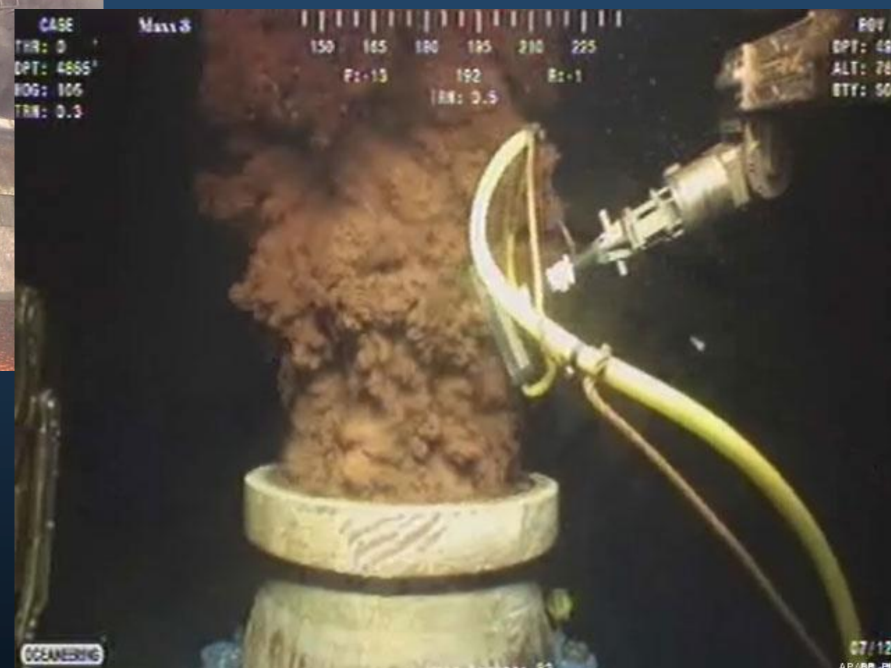
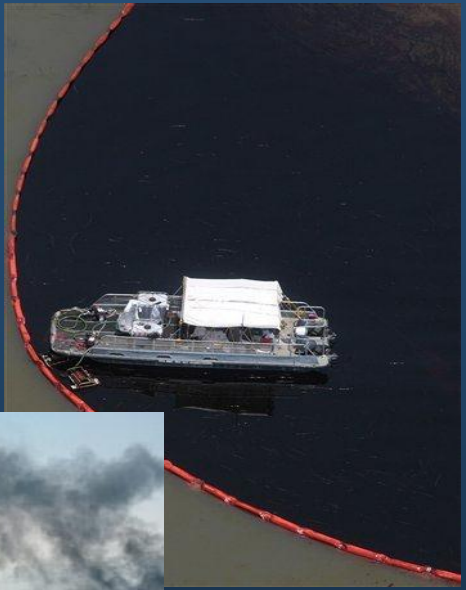
Discussion Topics

- Dispersants in the Responder's Toolbox
- Environmental Fate of Surfactants
- Bioassays – WAF versus CEWAF
- Metabolic actions – WAF versus CEWAF
- Summary and Conclusions

I. Dispersants in the Responder's Toolbox



Dispersants – One of Several Tools

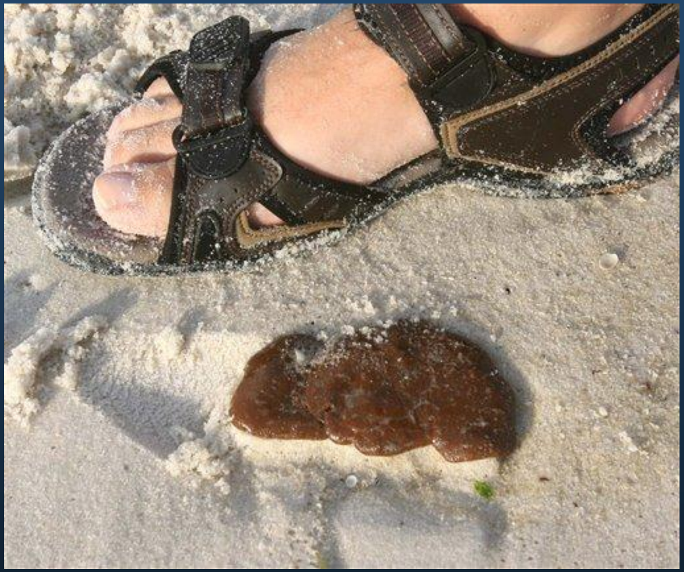


- Collection
- Burning
- Sinking
- Bioremediation

Resources and Impacts

- Dispersants might prevent slicks from forming
- Dispersed oil might remain offshore, continually break into smaller droplets and degrade

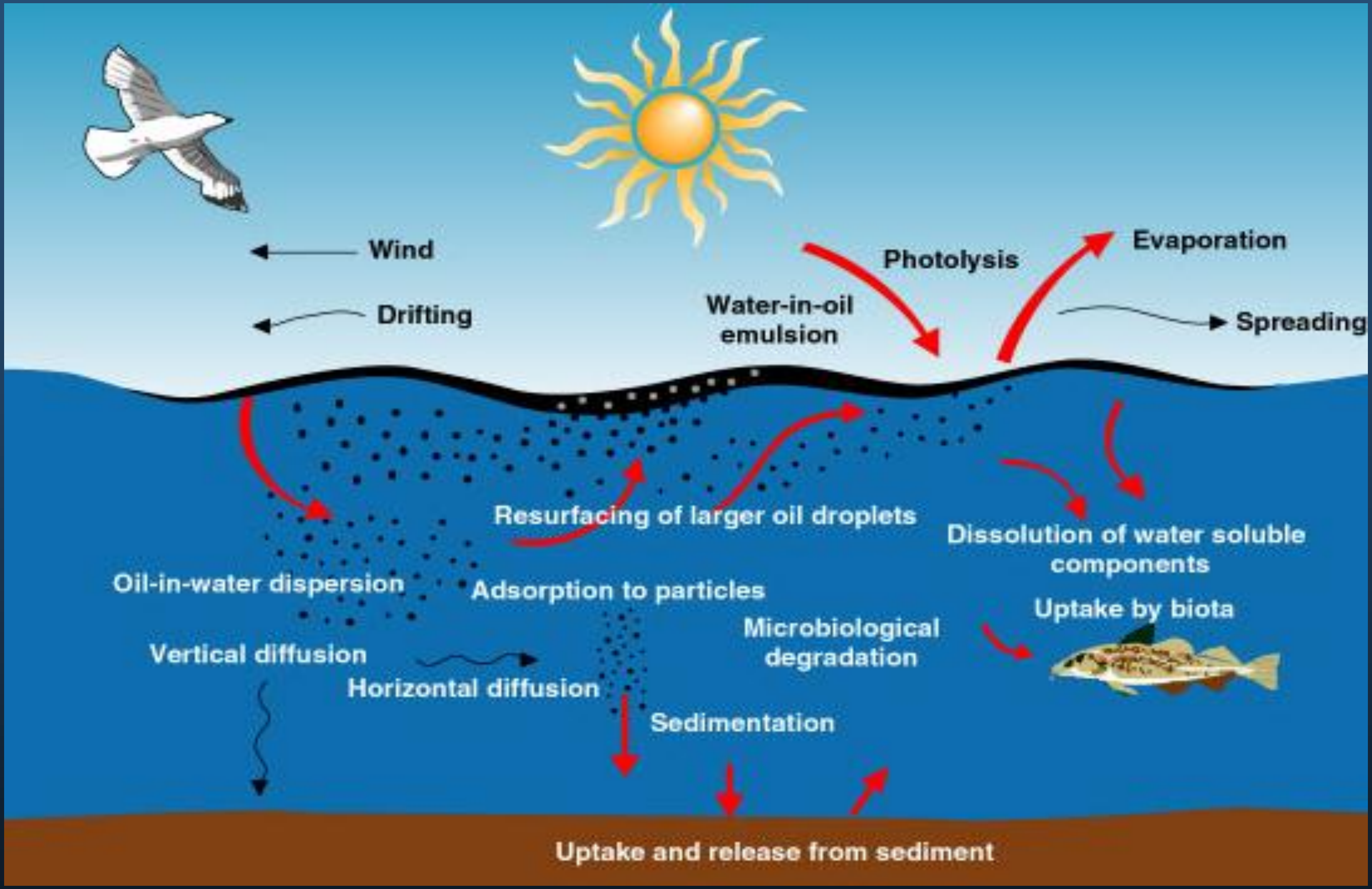
or



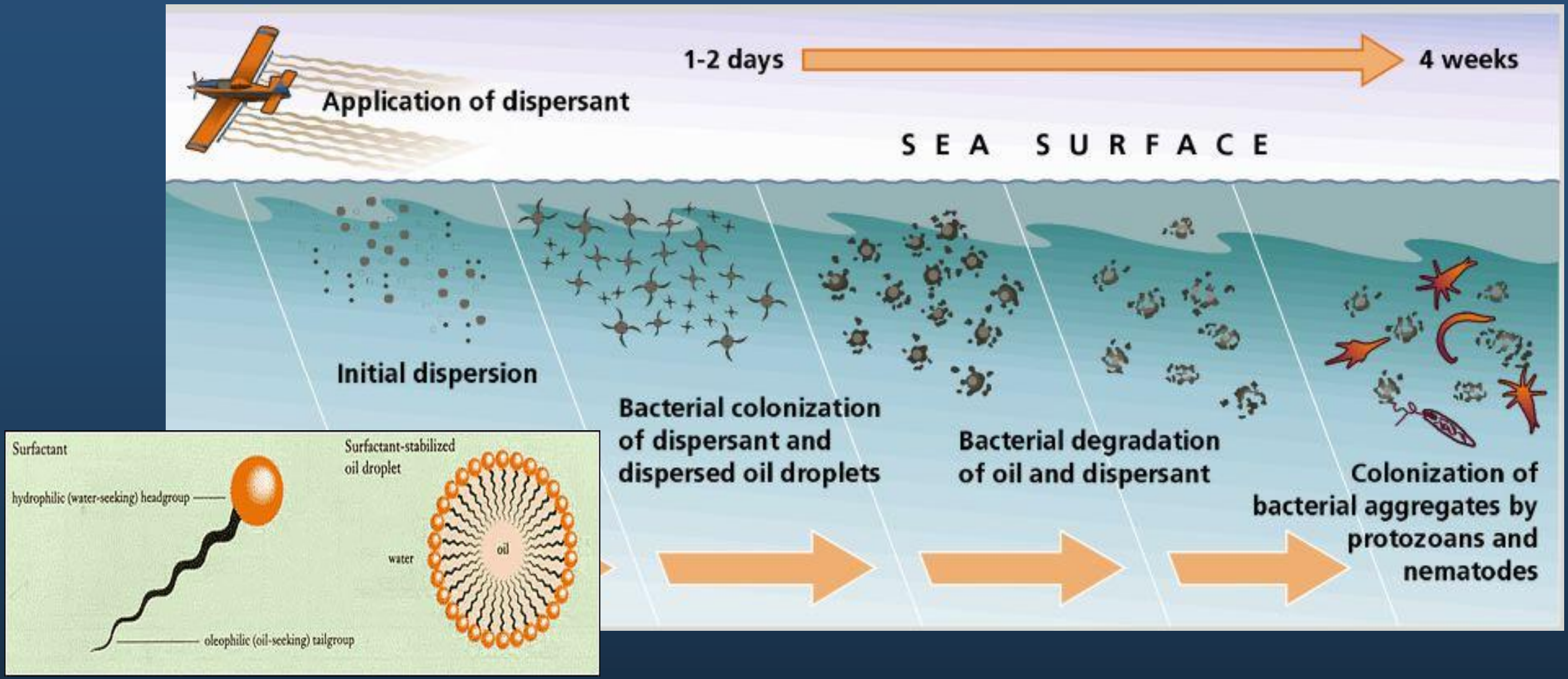
"An Audacious Decision in Crisis Gets Cautious Praise"

***Science*, August 18, 2010**

II. Environmental Fate of Surfactants

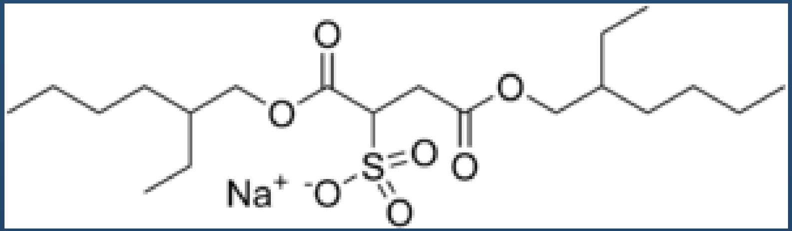


Dispersants Enhance Weathering

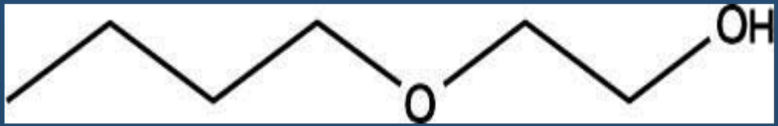


- Dispersants are similar to domestic detergents
- They break up oil and remove it from the surface
- The droplets formed are more readily digested by bacteria

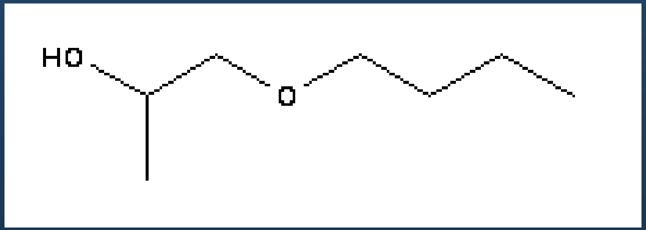
What Makes a Dispersant? Corexit 9527



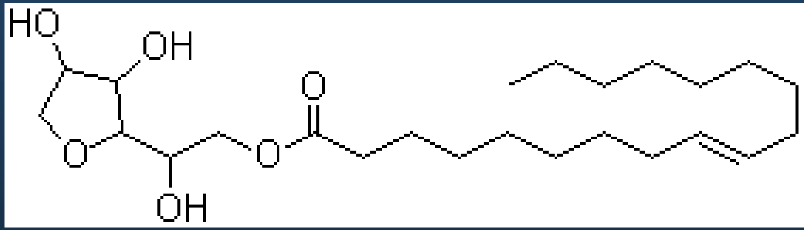
Dioctyl Sodium Sulfosuccinate



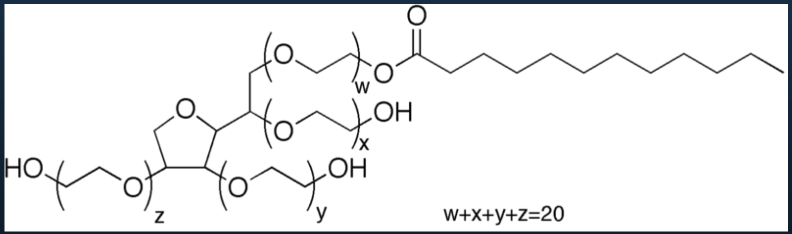
2-Butoxyethanol



Propylene Glycol Butyl Ether

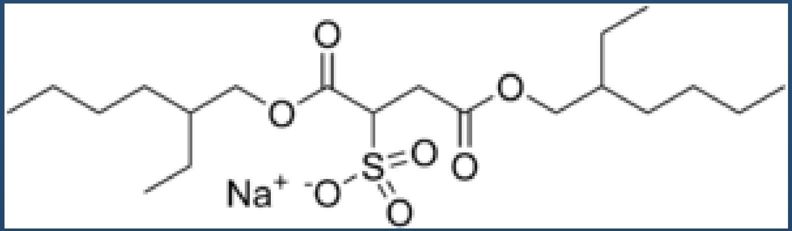


Sorbitan Monooleate



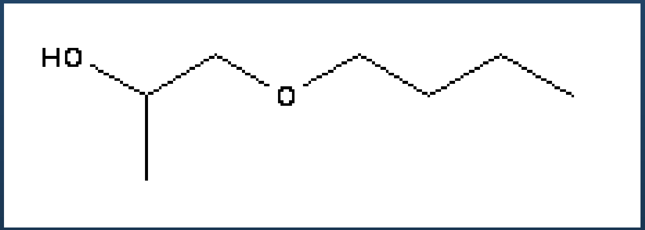
Ethoxylated Sorbitan Monooleate

What Makes a Dispersant? Corexit 9500

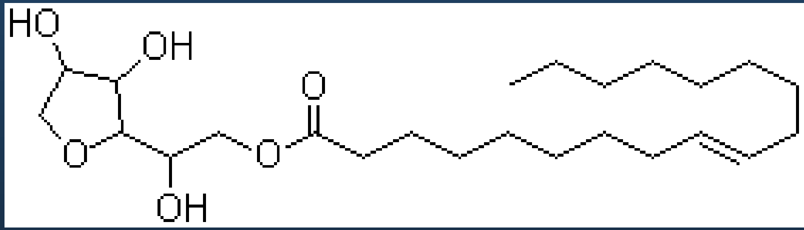


Dioctyl Sodium Sulfosuccinate

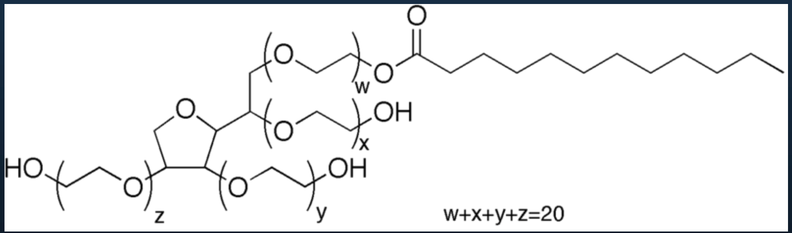
Petroleum Distillates?



Propylene Glycol Butyl Ether

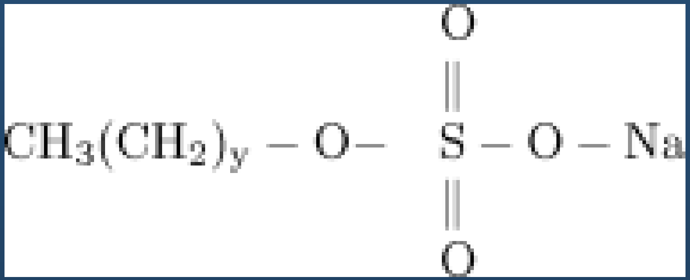


Sorbitan Monooleate

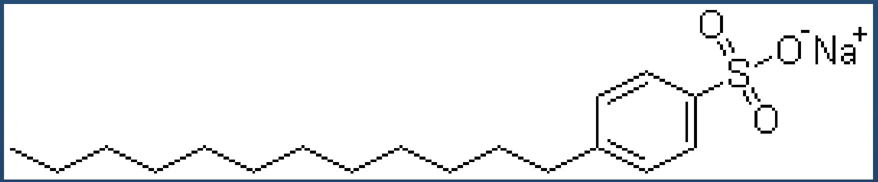


Ethoxylated Sorbitan Monooleate

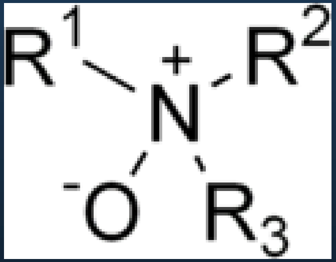
Comparison – Dawn Dishwashing Detergent



Sodium Alkyl Sulfonate



Sodium Lauryl Benzene Sulfonate

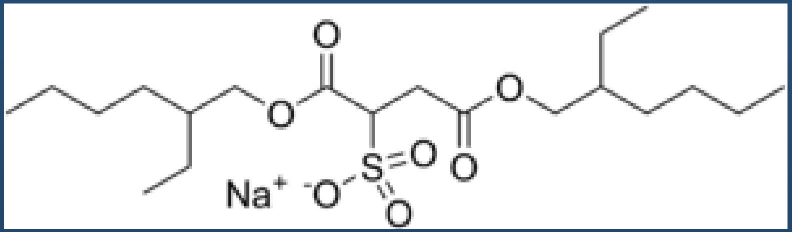


Amine Oxide

Also:

Sodium Alkyl Ethoxylate Sulfonate
Ethanol
Perfumes and Colorants

Fate of a Dispersant? DOSS



Dioctyl Sodium Sulfosuccinate

- In water and soils, degrades by 90% within 12-17 days
- Reactions include hydrolysis, oxidation (microbial, abiotic)
- Vapors photodegrade via oxidation ($t_{1/2}$ < 18 h)
- DWH – present at depth in ppb range months after the event

III. Bioassays – WAF Versus CEWAF

Early Life Stage Actions

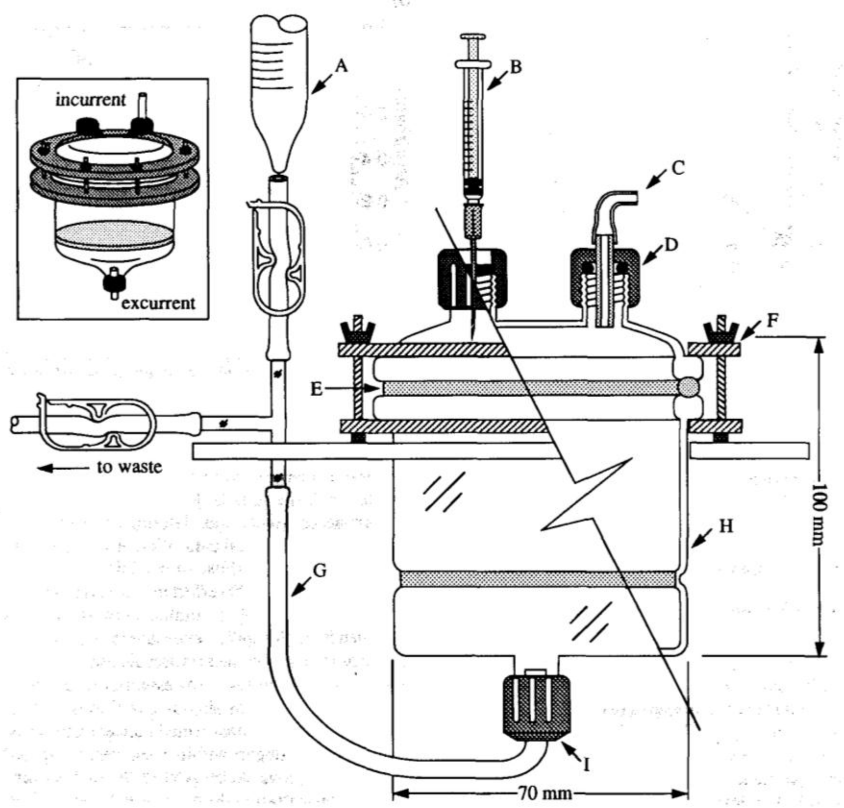


Fig. 1. Schematic diagram of toxicity test exposure chamber: A, pipette for chemistry sampling; B, syringe for food introduction through septum; C, seawater inlet; D, threaded glass fitting with phenolic cap; E, silicone O-ring-sealed glass flange; F, full-circumference aluminum flange clamp; G, silicone tubing; H, chamber body; I, chamber outlet.

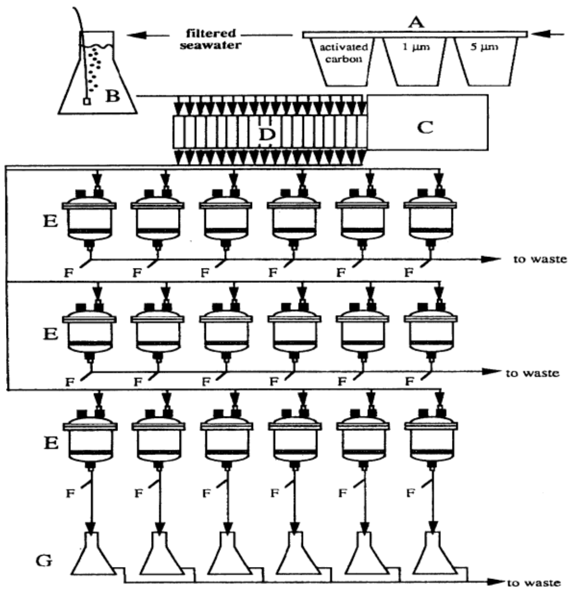


FIG. 2. Exposure system schematic exhibiting flow patterns and main system components: (A) cartridge filters; (B) seawater head tank; (C) peristaltic delivery pump; (D) cartridge pump heads (18); (E) exposure chambers; (F) chemistry sampling arms; (G) water quality sampling flasks.

Corexit 9527 – Constant versus Spiked

Table 1. Results of flow-through toxicity tests using Corexit 9527® 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.

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.

- Compared actions of dispersants under constant versus spiked exposure conditions
- Spiked-exposure usually less toxic

Spiked Exposure MEC Range

- Dispersants alone under spiked conditions generally toxic in the range of 20-150 ppm

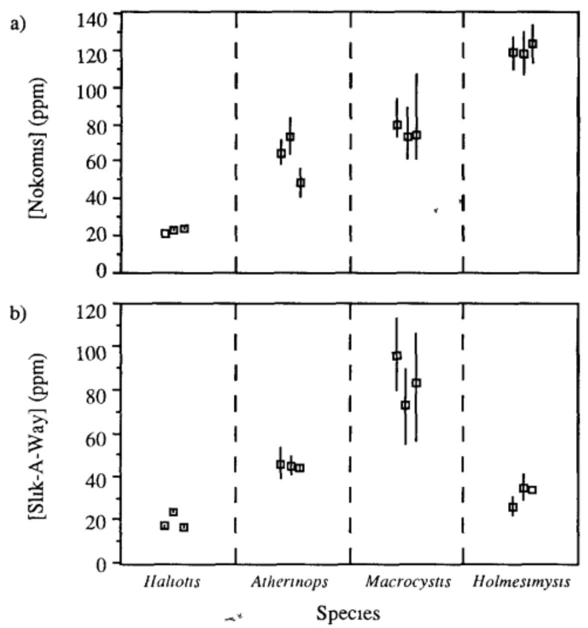


Fig 3 Comparison of median effect concentration estimates for four marine species (a) Nokomis® 3, (b) Slik A-Way Data symbols represent median effect concentration ± 95% confidence limits *Haliotis* and *Holmesimysis* data are from Singer et al [14]

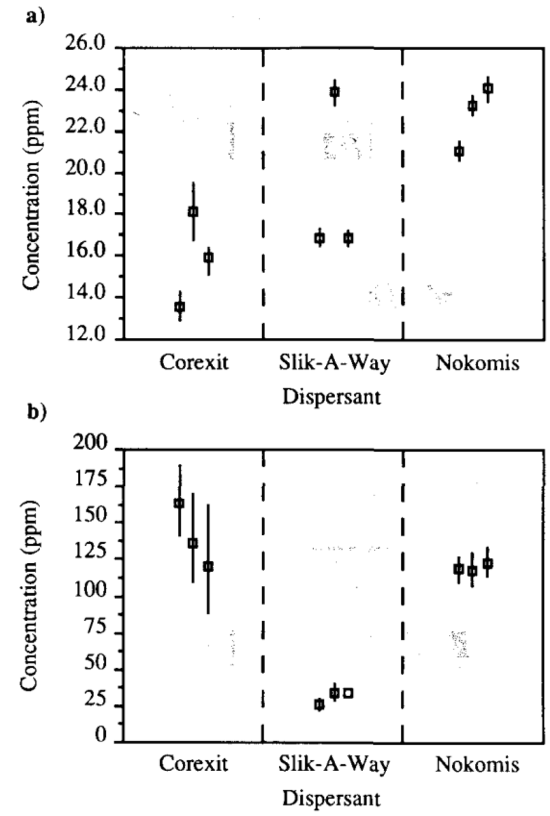


Fig. 6. Comparison of median-effect concentration estimates from triplicate toxicity tests using Corexit® 9527, Slik-A-Way, and Nokomis® 3 for **(a)** *Haliotis* and **(b)** *Holmesimysis*. Data points represent EC50/LC50 ± 95% confidence limits. Corexit data are from Singer et al. [8].

Corexit 9500

- Toxicity of Corexits 9527 and 9500 is similar for abalone, but not for mysids

TABLE 2
Results of Triplicate Corexit 9500 Toxicity Tests Using *Haliotis* and *Holmesimysis*

Test		NOEC	EC_{50} (95% CL)
Haliotis	1	7.6	19.7 (19.5, 20.0)
	2	5.7	12.8 (12.4, 13.1)
	3	9.7	13.6 (13.4, 13.7)
Holmesimysis	1	41.4	158.0 (103.1, 242.0)
	2	142.3	245.4 (207.5, 290.1)
	3	124.4	223.7 (188.3, 265.7)

Note. All data expressed in initial ppm (v/v).

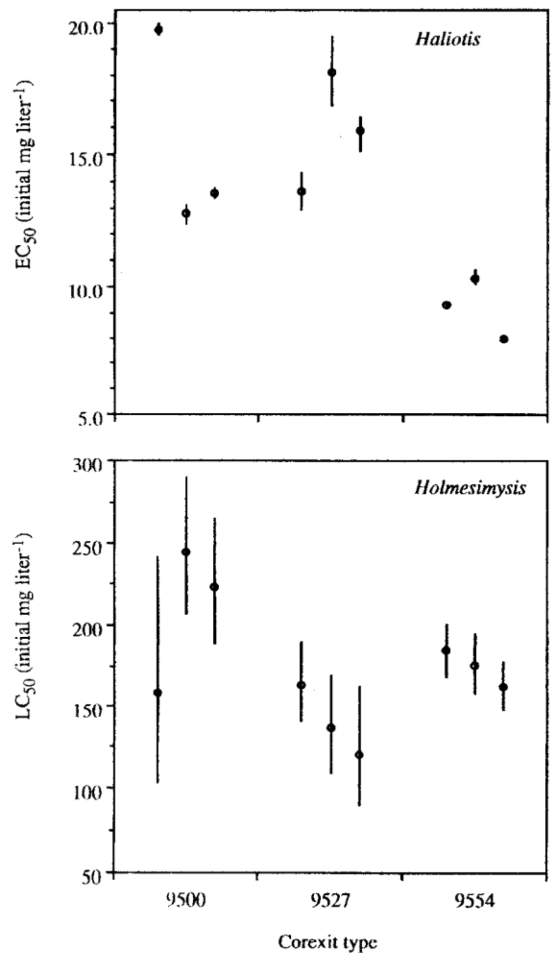


FIG. 5. Comparison of median-effect concentrations of triplicate *Haliotis* (top) and *Holmesimysis* (bottom) toxicity tests using Corexit 9500, 9527, and 9554. Data symbols represent EC/LC_{50} with 95% confidence intervals.

Corexit 9527: PBCO WAF versus CEWAF

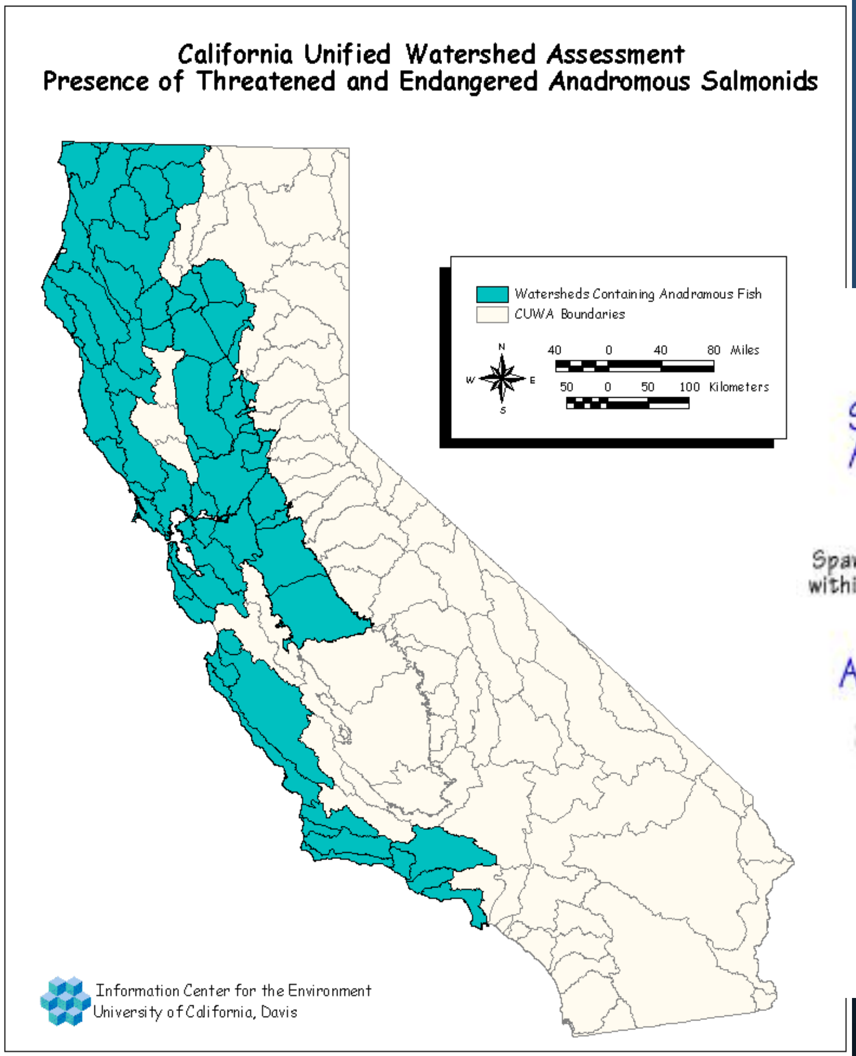
Table 2. Results of spiked-exposure toxicity tests using Prudhoe Bay crude oil alone and combined with Corexit 9527 (O:D ratio = 10:1)[a]

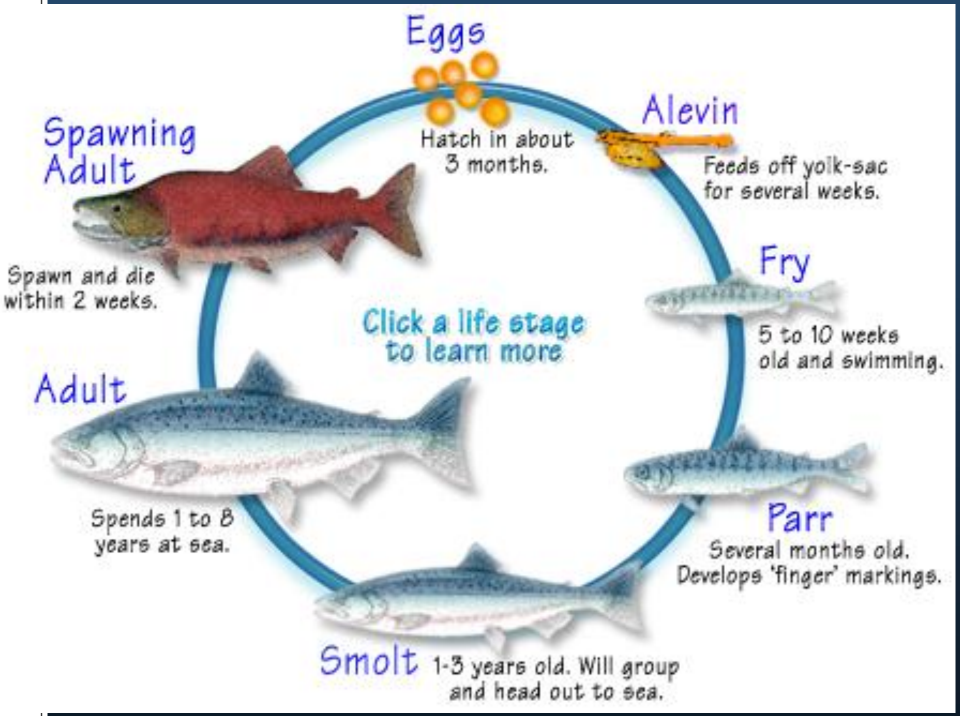
Species/Endpoint	EC/LC50 (mg/L $THC_{(C7-C30)}$) WAF Test 1	WAF Test 2	WAF Test 3	CEWAF Test 1	CEWAF Test 2	CEWAF Test 3
Haliotis						
Larval abnormality	>34.03[b]	>46.99	>33.58	19.09 (18.90, 19.28)	32.70 (32.11, 33.30)	17.81 (17.65, 17.96)
Holmesimysis						
96-h mortality	>34.68	>25.45	>28.55	10.54 (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

- In general, WAF is less toxic than CEWAF
- However, trend is reversed for narcosis...
- Which is more important?
- What about the chemistry?

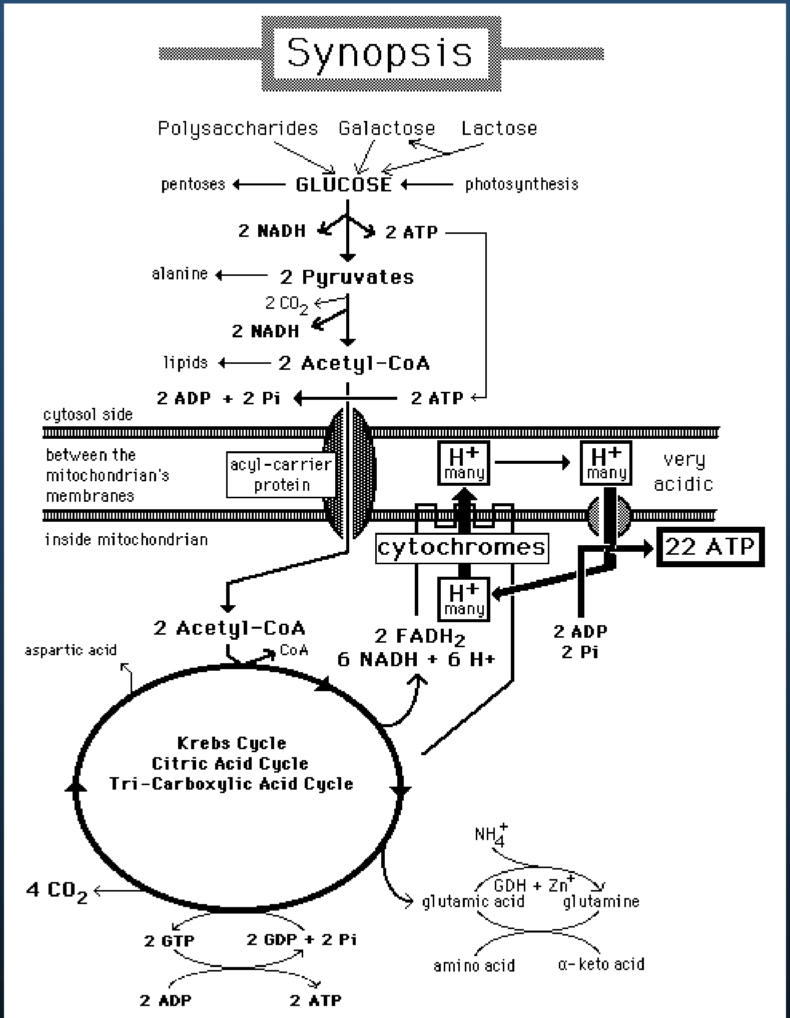
IV. Metabolic Actions – WAF Versus CEWAF





Objectives

- Assess actions of WAF versus CEWAF of PBCO in fishes under spiked-exposure conditions
- Apply ^{1}H-NMR-based metabolomic analysis to denonstrate sublethal actions



Methods – WAF Exposures

- Methods of CROSERF (Singer *et al.* 2000)
- Polycarbonate 20-L carboys and 18-L aquaria
- WAFs spun at low rate with minimal vortex (~150 rpm, 24 h)
- Aquaria sampled for TPH and THC, 8 fish introduced, and clean water flushing initiated

Methods – CEWAF Exposures

- Add oil, create vortex of 20 to 25%

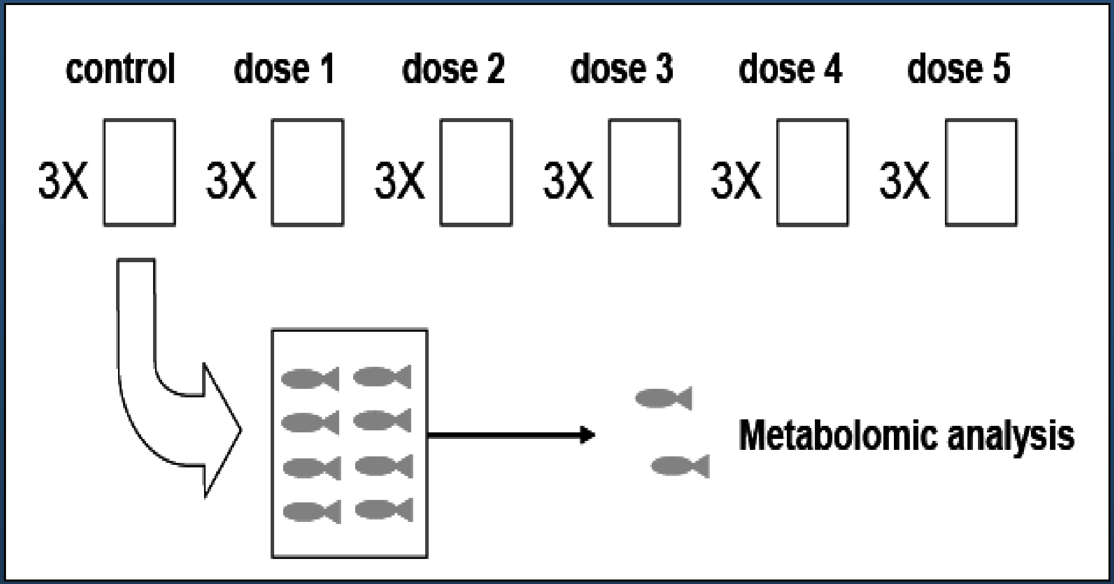
- Pipet 10% (by oil weight) Corexit 9500

- Spin for 18 h, settle for 6 h

Methods – Analytical Chemistry

- Total petroleum hydrocarbons (TPH; $C_{10} – C_{36}$) – via GC-FID
- Volatile hydrocarbons (BTEX; C_6-C_9) – benzene, toluene, ethyl benzene and xylenes analyzed via GC/MS with purge-and-trap extraction
- Total hydrocarbon content (THC; C_6–C_{36}) – calculated as BTEX + TPH
- Spiked exposures confirmed via THC

Experimental Design and Comparative Toxicity



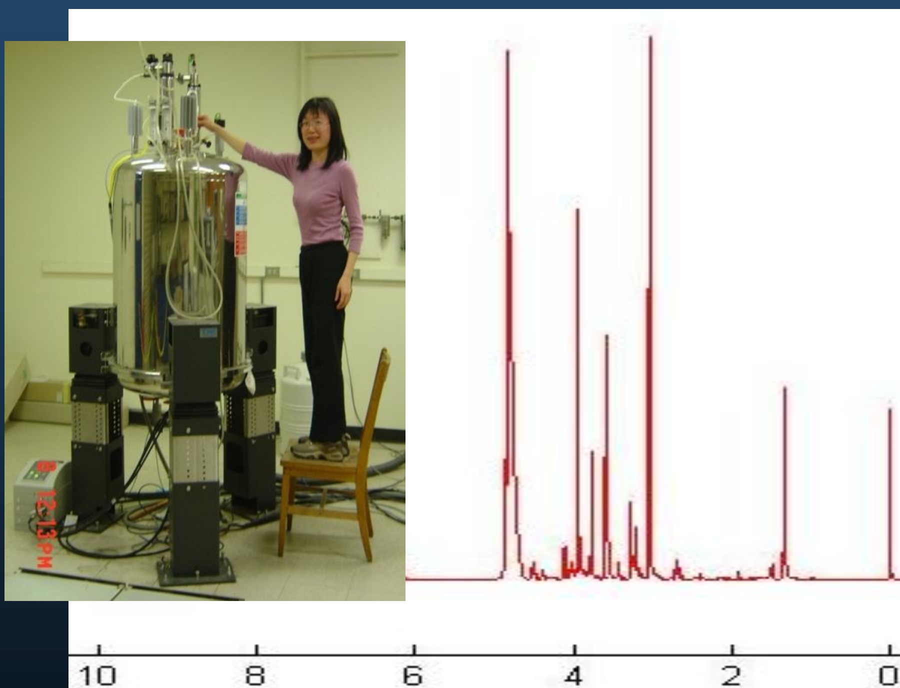
Three total tests for each (WAF and CEWAF)

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

NMR-Based Metabolomics Approach

Sample prep (tissue or biofluid)

1-D NMR analysis



ppm

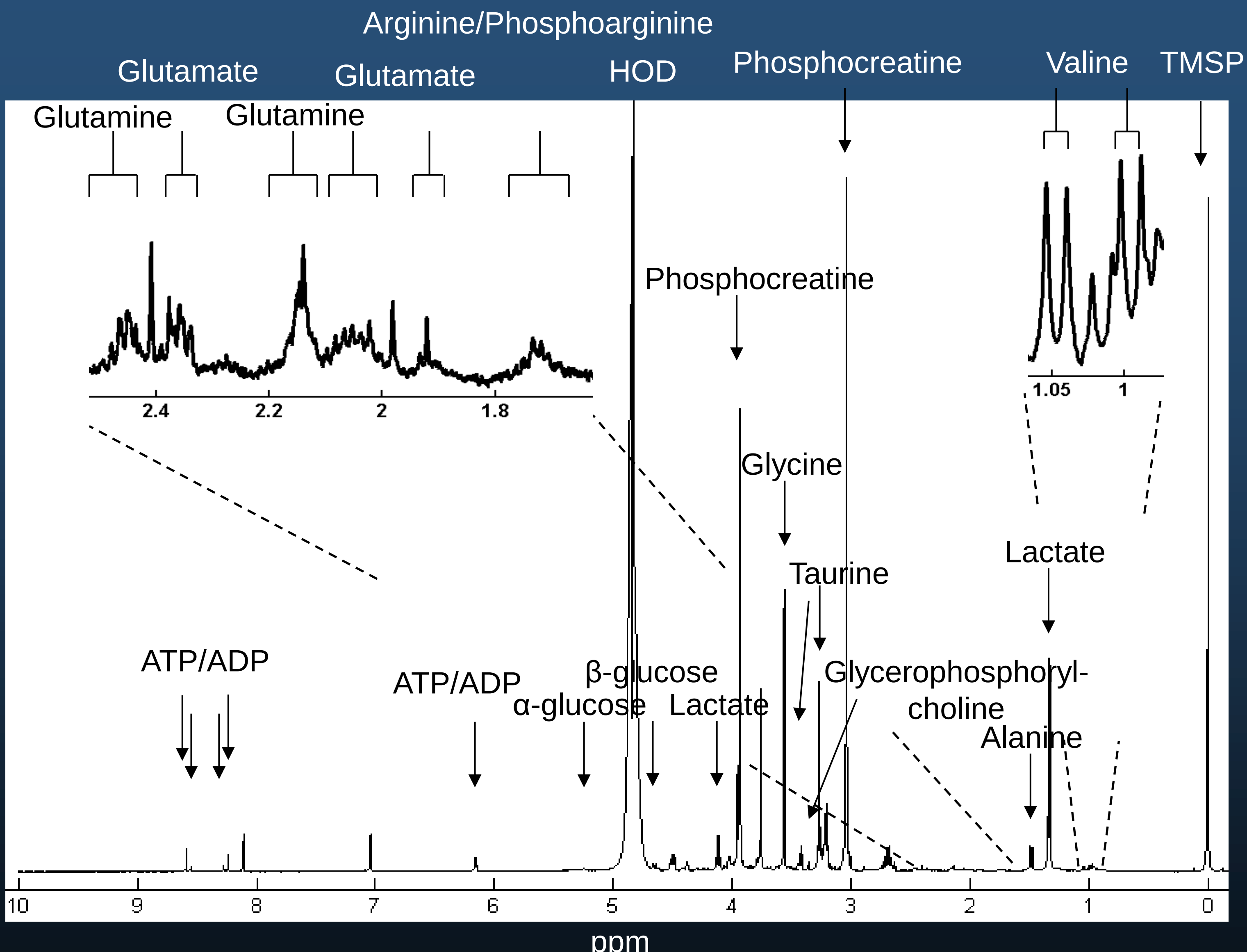
Peak assignment
1-D (^1H NMR)
2-D (^1H-^1H COSY & ^1H-^{13}C HSQC)

Multivariate statistical analysis

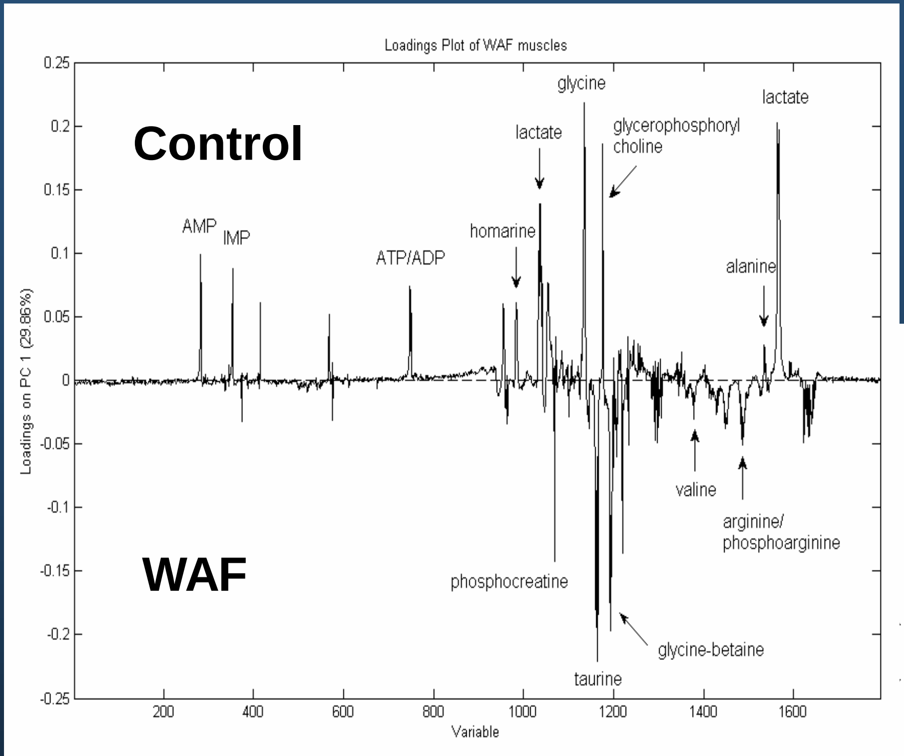
$$ab = \left\{ \begin{array}{ccccc} a_1b_1, & a_1b_2, & a_1b_3 & \cdots & a_1b_n \\ a_2b_1, & a_2b_2, & a_2b_3 & \cdots & a_2b_n \\ a_3b_1, & a_3b_2, & a_3b_3 & \cdots & a_3b_n \\ \vdots & \vdots & \vdots & & \vdots \\ a_mb_1, & a_mb_2, & a_mb_3 & \cdots & a_mb_n \end{array} \right\}$$

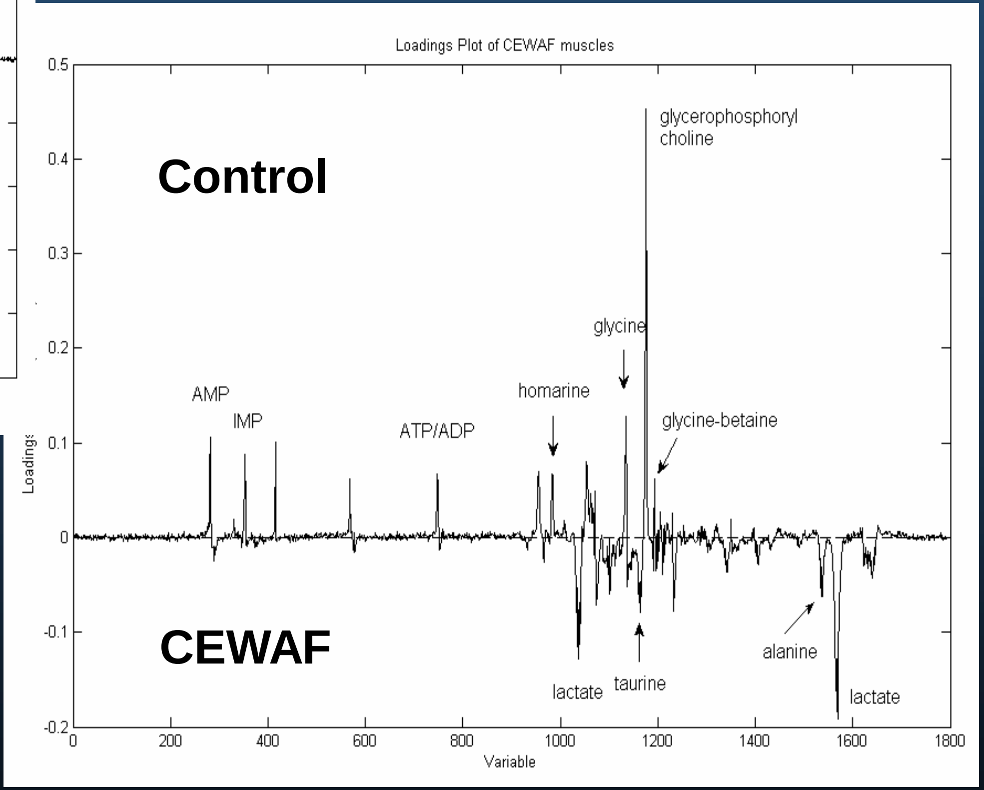
Metabolite profiling
(metabolomic classification/ biochemical mechanism)

NMR Spectrum of Muscle Extract



Muscle Loadings Plots





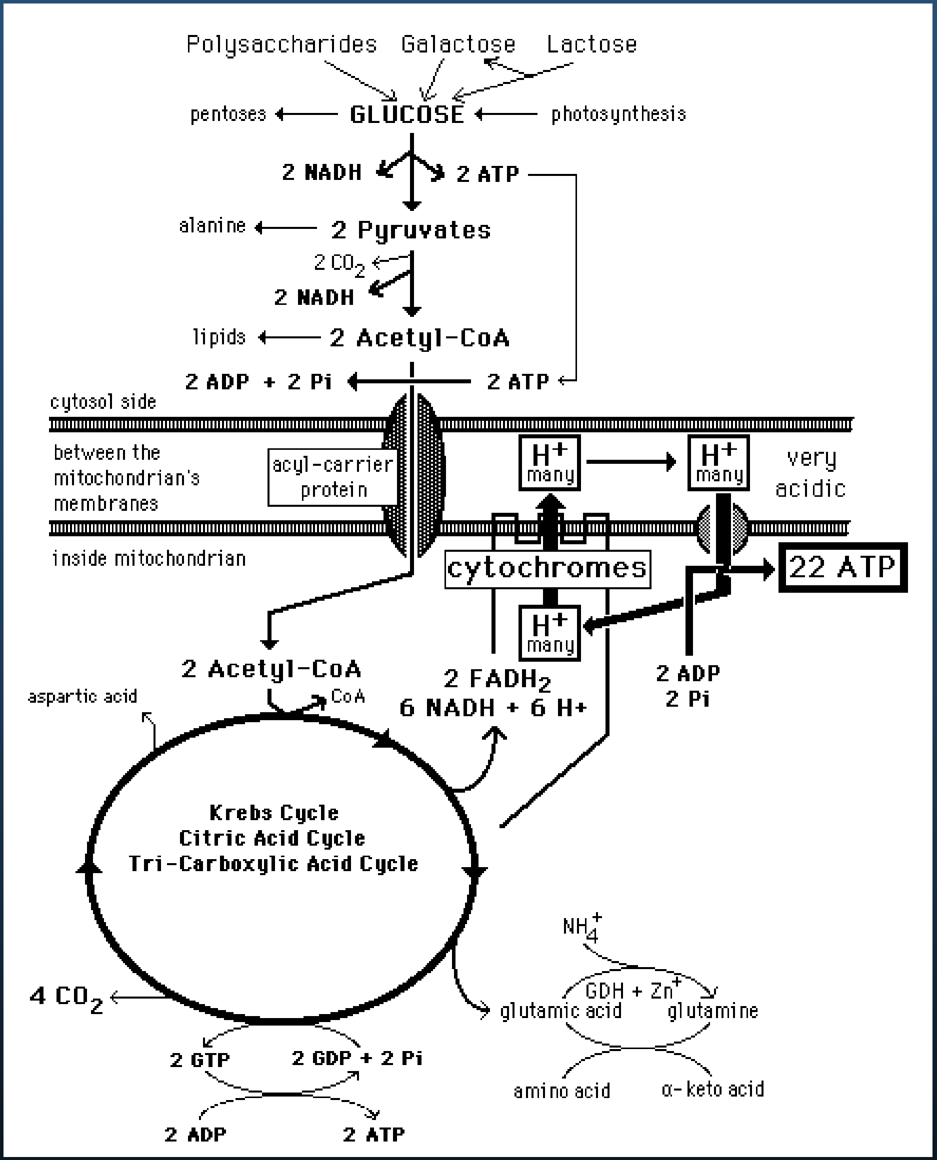
Changes in Metabolite Profiles – Topsmelt

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

*P<0.05

Implications

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



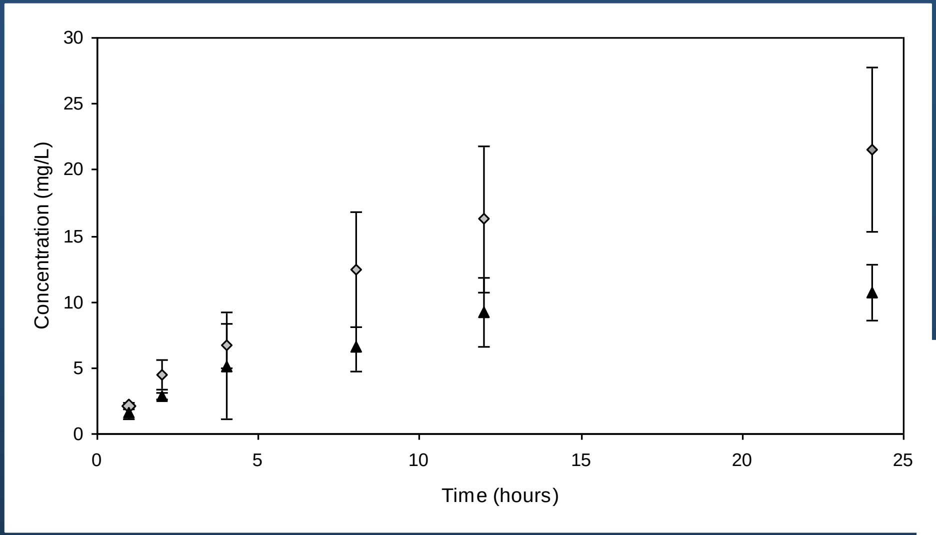
Why are WAF and CEWAF Results Similar?

- LC50s, based on THC (*dissolved* + *particulate*) were very different: WAF, 7.5 mg/L; CEWAF, 156 mg/L (up to 20x)
- Actions may result from "bioavailable" (dissolved) fractions – not total hydrocarbons (THC)
- Hypothesis – dissolved fractions produced in WAF and CEWAF are not significantly different
- Used semi-permeable membrane devices (SPMDs) to determine

Summary – SPMD Techniques

- Prepare WAF or CEWAF
- Static 24-h exposures
- One SPMD removed at time 1, 2, 4, 8, 12 and 24 h
- Collect dissolved fraction via dialysis with hexane
- Analysis via GC-MS

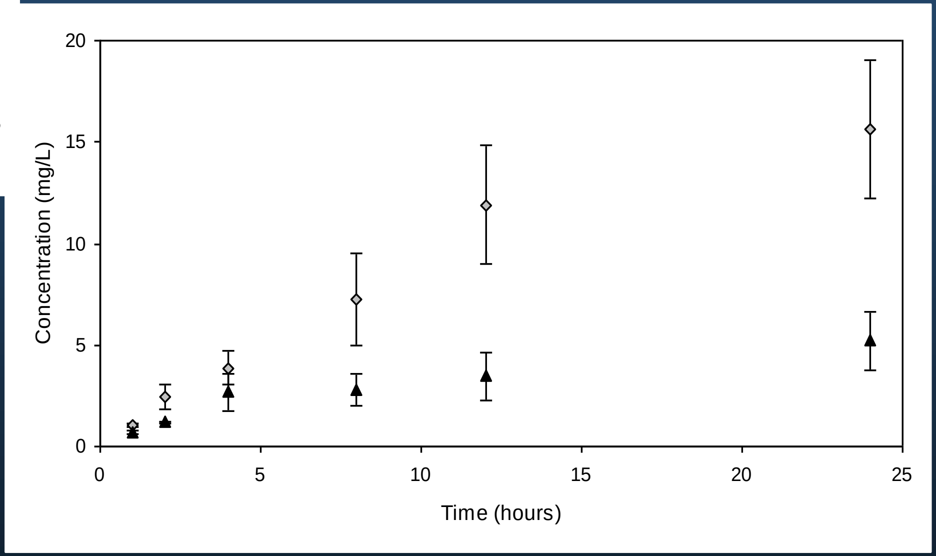
Semi-Permeable (SPMD) Membrane Results



Naphthalene WAF versus CEWAF

WAF (▲) CEWAF (◆)

- Dissolved concentrations very similar during first few hours (think spike)



1-Methylnaphthalene WAF versus CEWAF

Conclusions

- Dispersants are one of several tools – enhance weathering
- Corexits degrade rapidly under normal environmental conditions – may persist under colder conditions (DWH)
- Dispersants (and DOSS) have LC50s in the ppm range
- WAF and CEWAF toxicity may be species/stage specific
- Corexit 9500 decreases oil lethality to fishes some 7 to 20-fold – *based on total hydrocarbons*
- Metabolic impacts may be similar due to similarity in dissolved (bioavailable) fractions – *boils down to analysis*

Acknowledgements

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NOAA – via the UNH Coastal Response Research Center