

Dispersants in the Arctic and Ice-prone Regions



Use of Dispersants in Cold Water & In situ Burning using Herding Agents

Alaska Oil Spill Response Symposium

Friday, March 7, 2014

Author: Dr. Tim Nedwed

ExxonMobil Upstream Research Company

Houston, Texas USA

tim.j.nedwed@exxonmobil.com

Co-author: Ian Buist

SL Ross Environmental Research

Ottawa, Canada



Discussion Topics

- Background
- Dispersants in ice / cold temperatures
- In situ burning without booms
- Summary

Spill Response Options: The Toolbox



Mechanical Recovery:
Booms & Skimmers

Monitor &
Evaluate



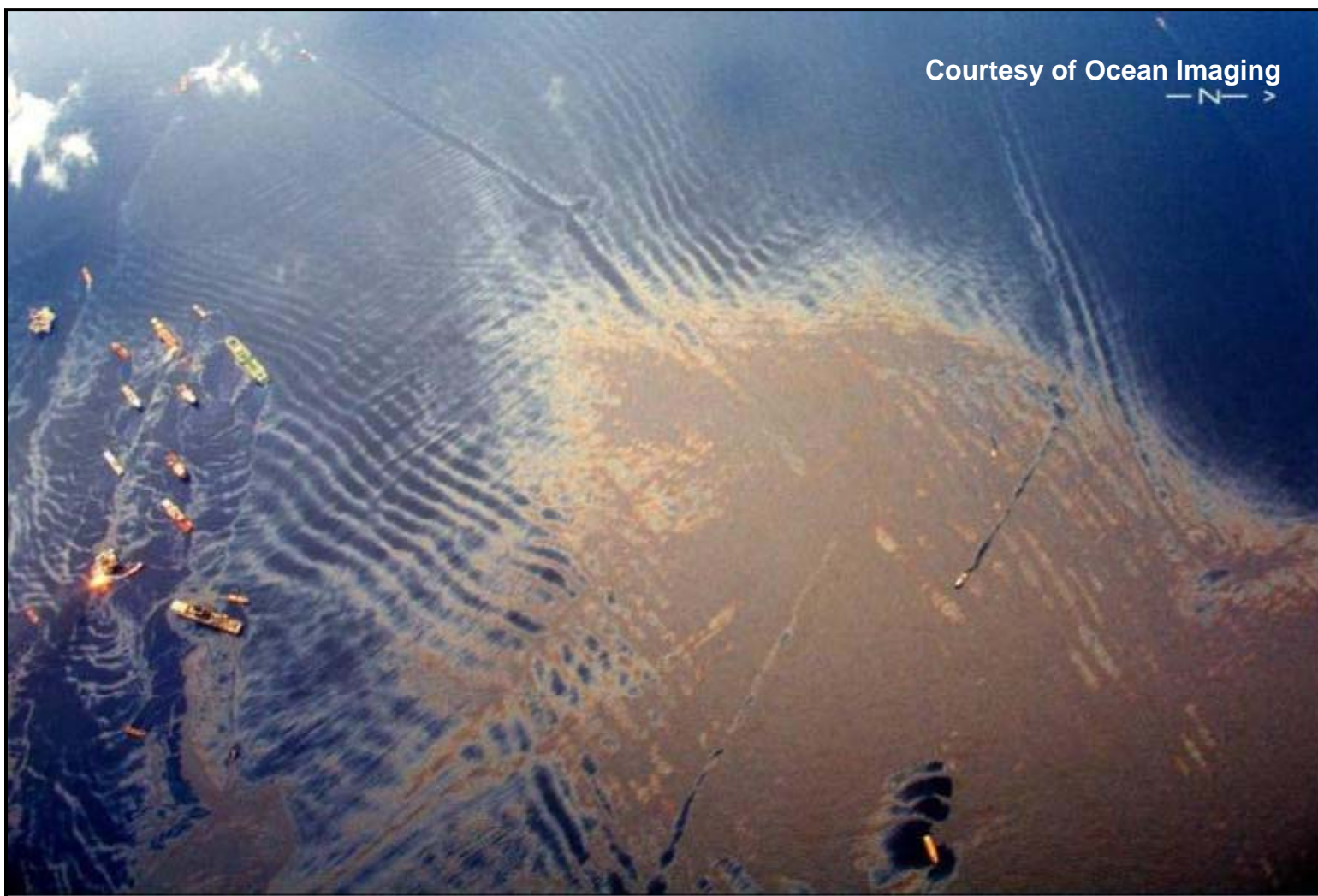
In-Situ Burning

Aerial
Dispersants

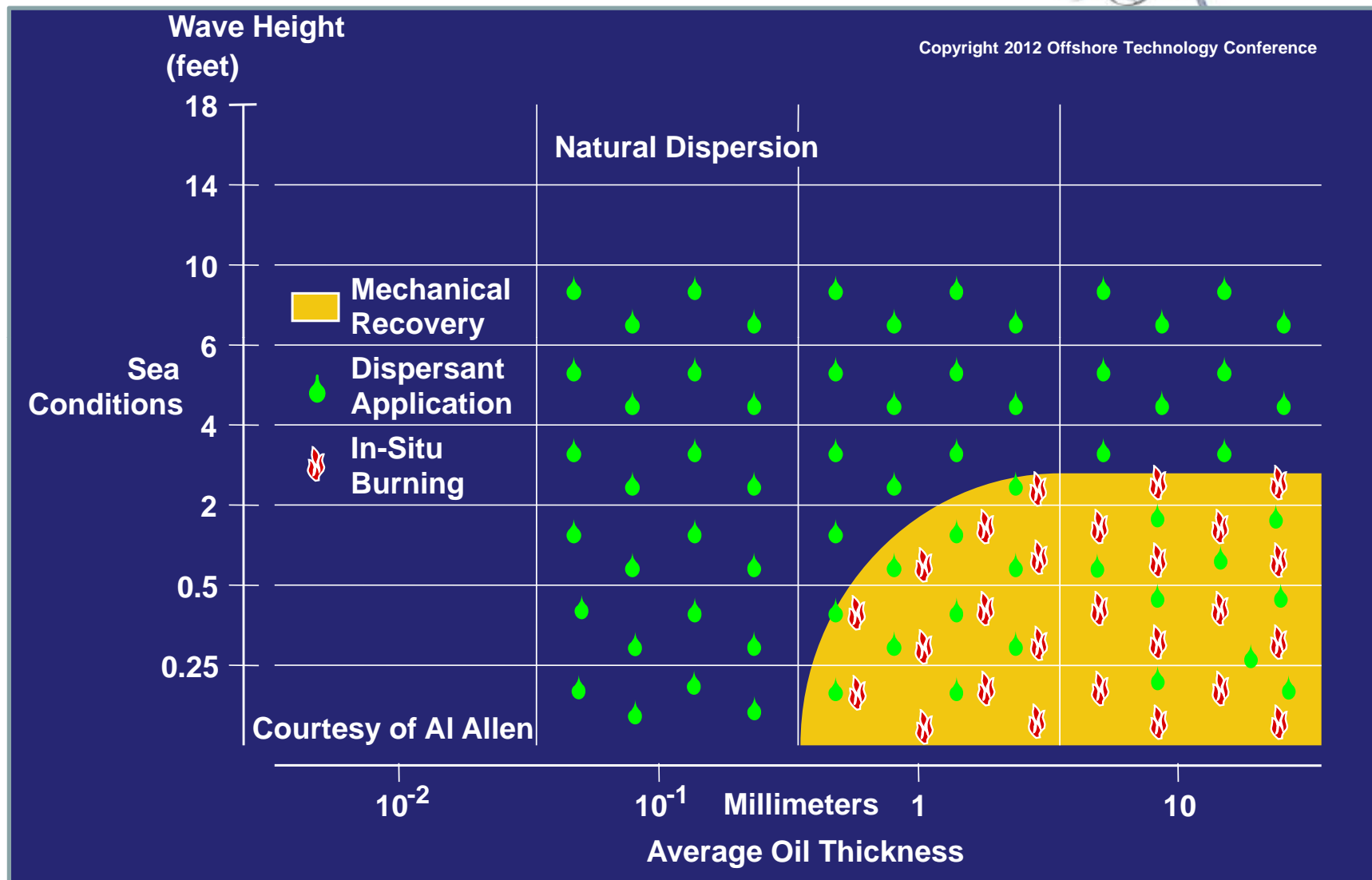


The goal is to design a response strategy
based on
Net Environmental Benefit Analysis

Encounter Rate is Key to Offshore Response



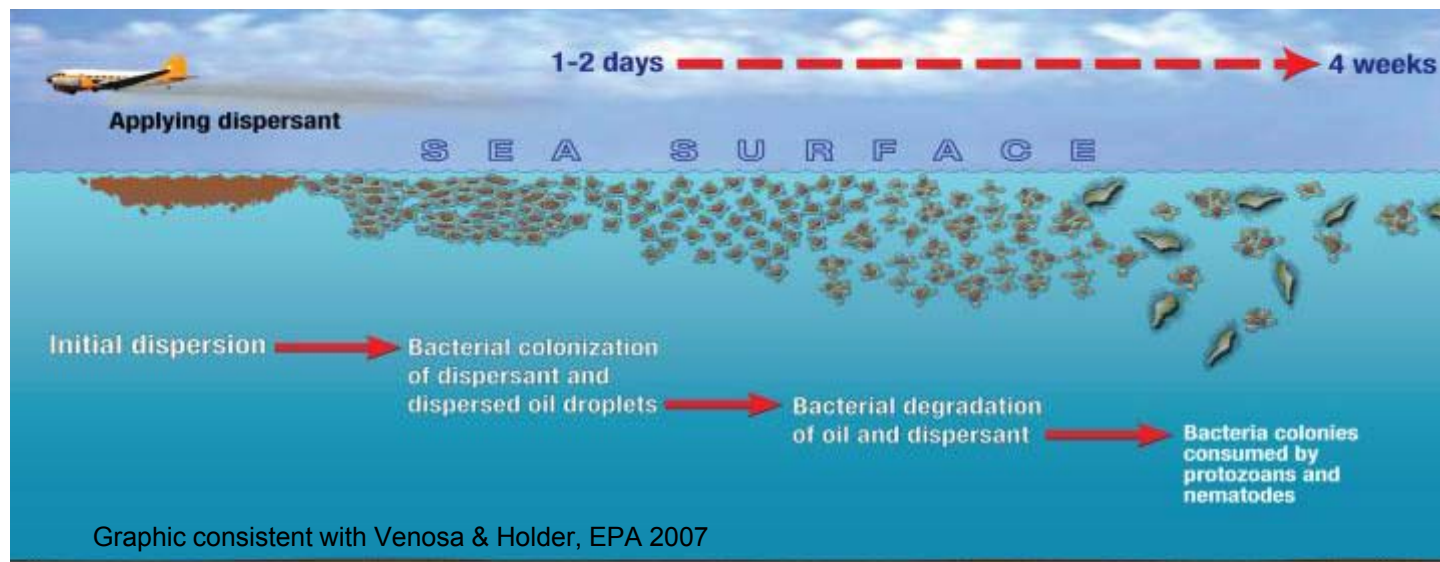
Spill Conditions Limit Response Options





Dispersants – What are they?

- Dispersants are solutions of surfactants dissolved in a solvent
- Surfactants reduce oil-water interfacial tension – allows slicks to disperse into very small droplets with minimal wave energy
- Dispersed oil rapidly dilutes to concentrations <10 ppm within minutes, <1 ppm within hours, ppb range within a day
- Each dispersed oil droplet is a concentrated food source that is rapidly colonized and degraded by marine bacteria
- Dilution allows biodegradation to occur without nutrient or oxygen limits



Dispersant Ingredients & Toxicity



Modern dispersants use ingredients found in household products

Relative Toxicity: Environment Canada Study (96 hr Rainbow Trout LC₅₀*)

<u>AGENT</u>	<u>LC₅₀ (ppm)</u>
Palmolive Dish Soap	13
Sunlight Dish Soap	13
Mr. Clean	30
Corexit® 9500 (27 times less toxic than dish soap)	350

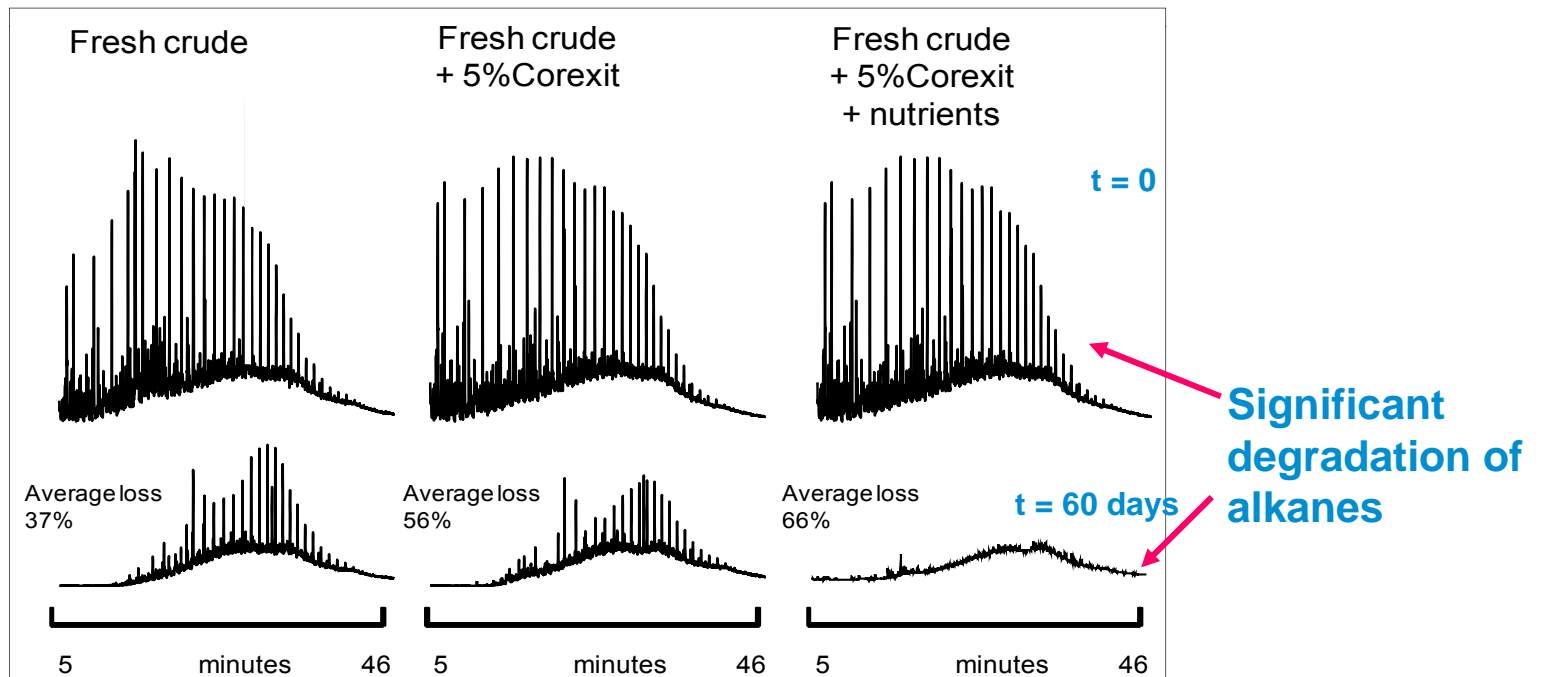
*Lethal concentration to 50% of the test organisms

Dispersed oil biodegradation study



- Joint industry dispersed-oil biodegradation study using Arctic microbes and conditions
- Seawater samples collected in the Alaskan Beaufort Sea
- Tests performed between -1 and 2°C

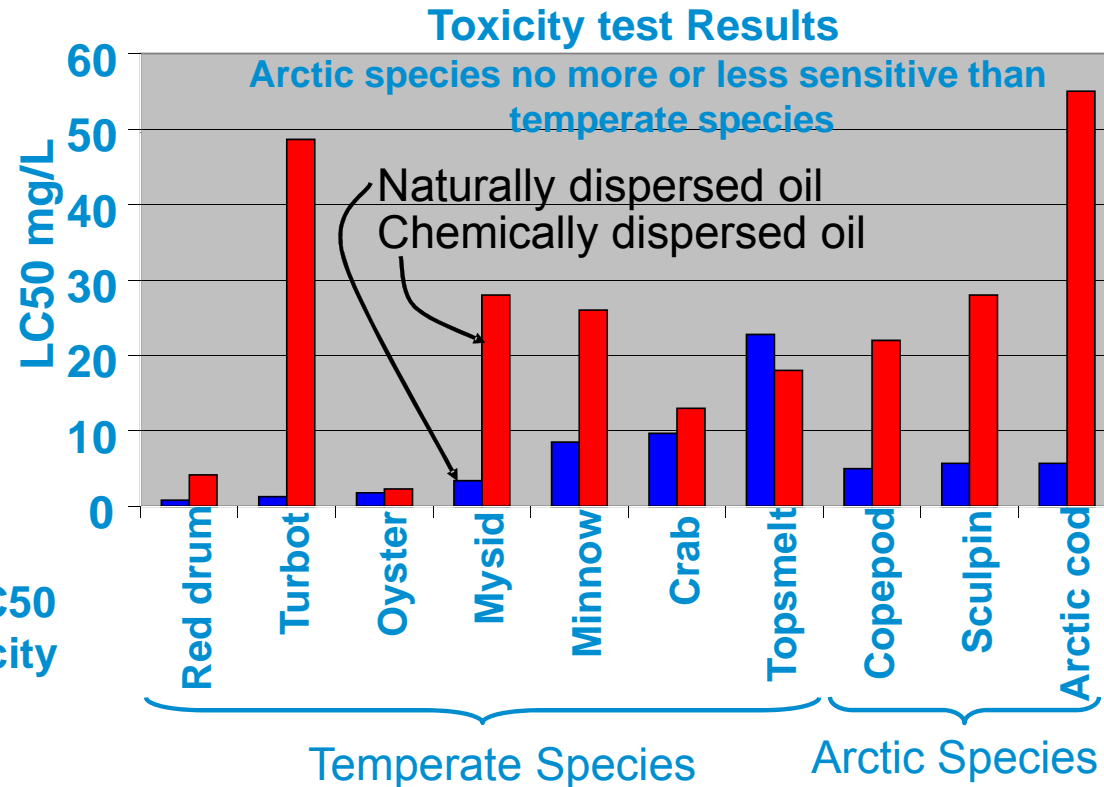
Biodegradation of Alaska North Slope crude dispersed with Corexit® 9500 (10 ppm fresh oil, 9500 (1:20), 2°C and 1% of recommended nutrient)



Dispersed oil toxicity study



- Joint industry dispersed-oil toxicity study using Arctic cod, sculpin, and copepod
- Test oil was Alaska North Slope crude
- Organisms collected in the Alaskan Beaufort Sea
- Tests performed between -1 and 2°C



Dispersant efficacy in ice



Commonly expressed concerns

- Ice limits mixing energy needed for dispersion
- Cold temperatures limit activity of surfactants
- Oil becomes too viscous

Research dispelling concerns

- Brown and Goodman, 1988: Dispersant can be effective at $<5^{\circ}\text{C}$
- Brown and Goodman, 1996: Oil in broken ice effectively dispersed even in 95% ice
- EM Research 2002: Fresh ANS, Hibernia and Chayvo crudes were $> 95\%$ dispersed
- Belore, 2004: Hibernia and ANS on cold water (-0.5 to 2.4°C) were 82 to 99% dispersed



Chemical dispersion of oil in ice at OHMSETT—ice motion enhanced dispersion

New Dispersant Gel



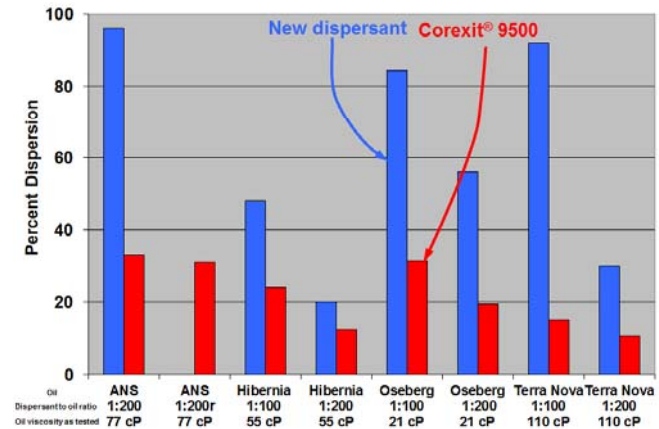
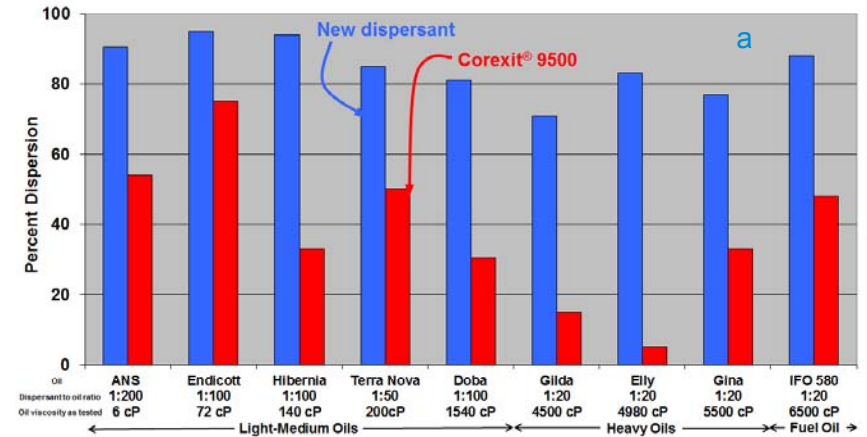
New dispersant developed for cold viscous oils – also more effective on low-viscosity oils



Gel dispersant effectively sprayed from an airplane



California OCS crude oil after application of a) COREXIT 9500 and b) dispersant gel.



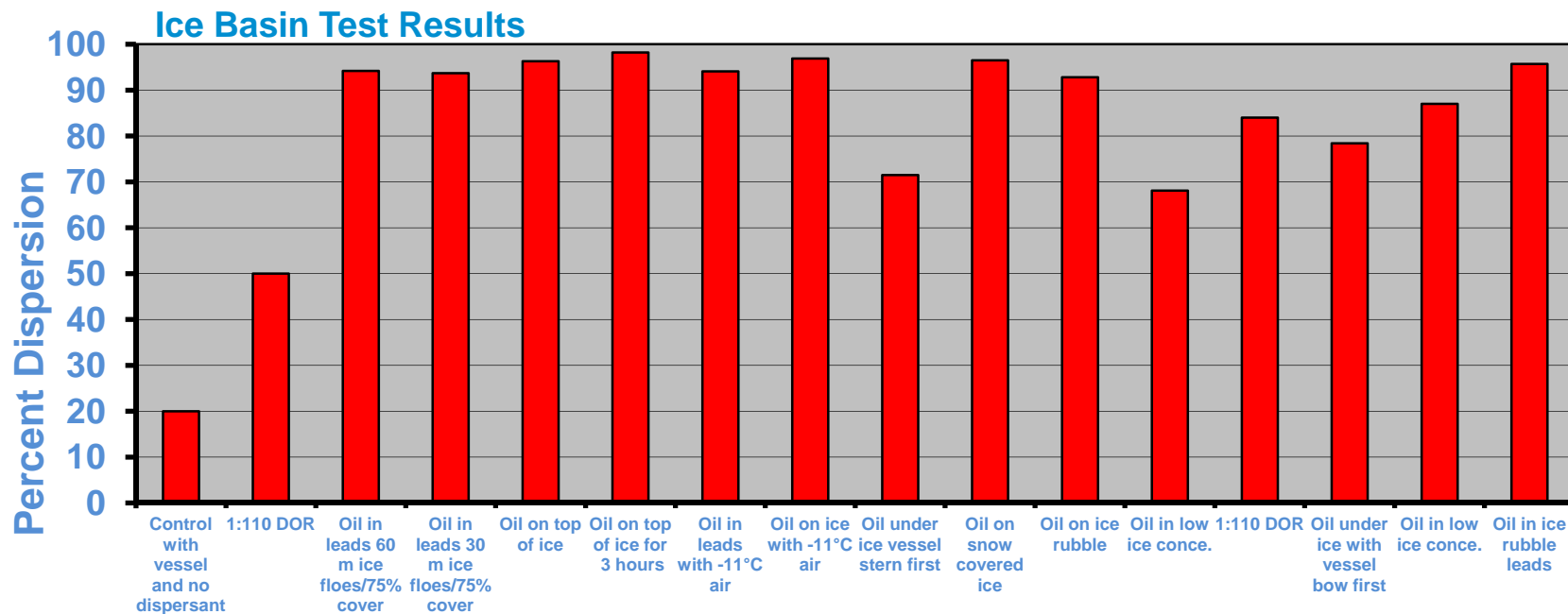
Dispersant-effectiveness results comparing the new dispersant to a commercial dispersant (a: water temperatures between 10 and 15°C, b: near 0°C).

Icebreaker Enhanced Dispersion

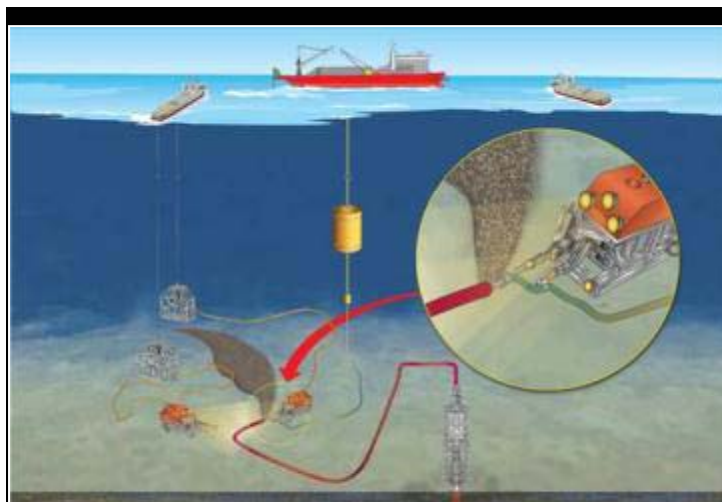
Chemical Dispersion Enhanced by Icebreaker Prop Wash



Completed basin tests using a 1:25 scale Azimuthal Stern Drive Icebreaker



Subsea Dispersant Injection



Oil Mineral Aggregates (OMA)



- In the early 1990's EM researchers found that clay-sized particles interacted with oil to create a fine dispersion
- Canadian researchers have been evaluating this phenomenon for OSR
- DFO Canada and Canadian Coast Guard completed field testing that proved the process was effective in concentrated ice



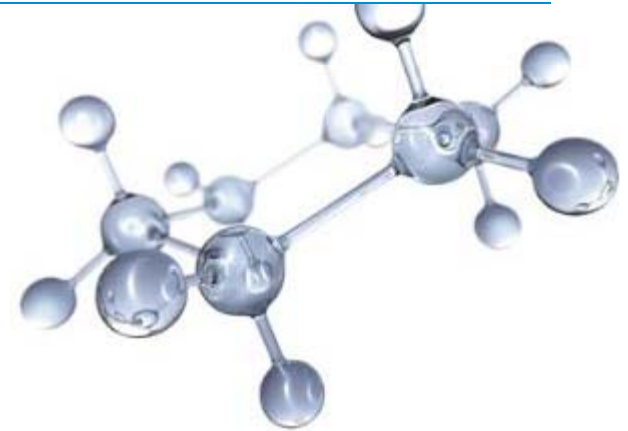
Photos taken during field tests of OMA-treated oil in ice after enhancing the dispersion with propeller wash of an icebreaker

Current Research on Dispersants in the Arctic



- **Oil and Gas Producers (OGP) Arctic Spill Response Technology Joint Industry Project**
 - Project 1: resurfacing potential of **dispersed oil** under ice
 - Primary need is under ice turbulence
 - Project 2: dispersant testing in ice / cold conditions
 - Goal is to define the boundaries for dispersant use in ice / cold
 - Includes evaluation of surface / subsurface use of dispersants and surface use of OMA

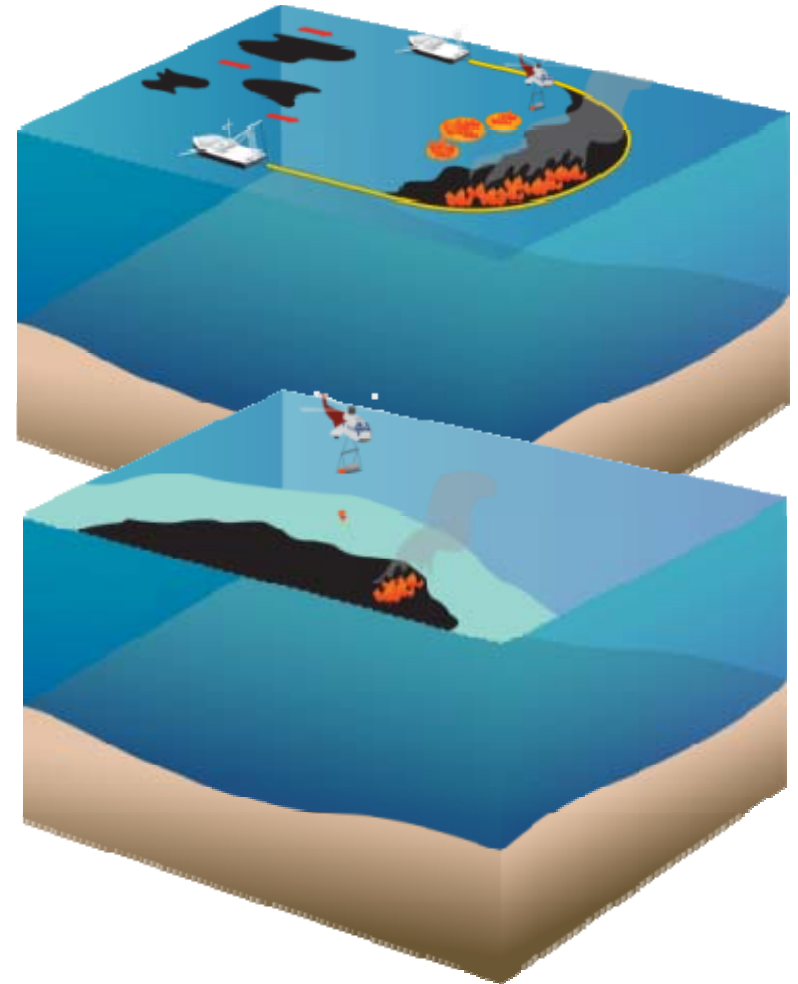
The use of herders to
enable in situ burning
without boom



Technology Description



- Herders use surfactants as a 'chemical boom' to thicken slicks, no boundary required
- Herders require at least an order of magnitude less product than treating slicks with dispersants
- Herder technology has been evaluated for marine applications with ice and is now being studied for open water conditions
- The goal is to develop another tool that can be applied using aircraft to make ISB a routinely used response option



Research Needs



- Research has proven that the concept works
- Herders have been formulated to be low toxicity and rapidly biodegradable
- Additional research is needed to determine the operating limits
 - Need to determine working range oil types and oil weathering for herders
 - Herders may work in sea states greater than boom as the surfactants reduce wave cresting

Results of EPA Required Toxicity Testing for NCP Listing

Herder	Menidia beryllina (minnow) 96 hr LC ₅₀	Mysidopsis bahia (shrimp) 48 hr LC ₅₀
Thickslick™	138 ppm (practically non-toxic ^a)	286 ppm (practically non-toxic ^a)

^aas defined by the US EPA aquatic toxicity ranking system (<http://www.epa.gov/espp/litstatus/effects/redleg-frog/naled/appendix-i.pdf>)

Results of Biodegradation Testing

Herder	% biodegradation Day 1	% biodegradation Day 20
Thickslick™	14.8	>99

Laboratory Testing Video



Field Results in Ice



0.4 mm thick,
excluding sheen

**Oil release &
spread
(15 minutes)**

*630 liters of fresh
crude*



**Herder applied
& contracts
slick
(9 minutes)**



4.1 mm thick
at ignition

**Ignition & ISB
(9 minutes)**

Courtesy of Ian Buist/SL Ross

Field Results in Ice - Video



Herder Commercialization

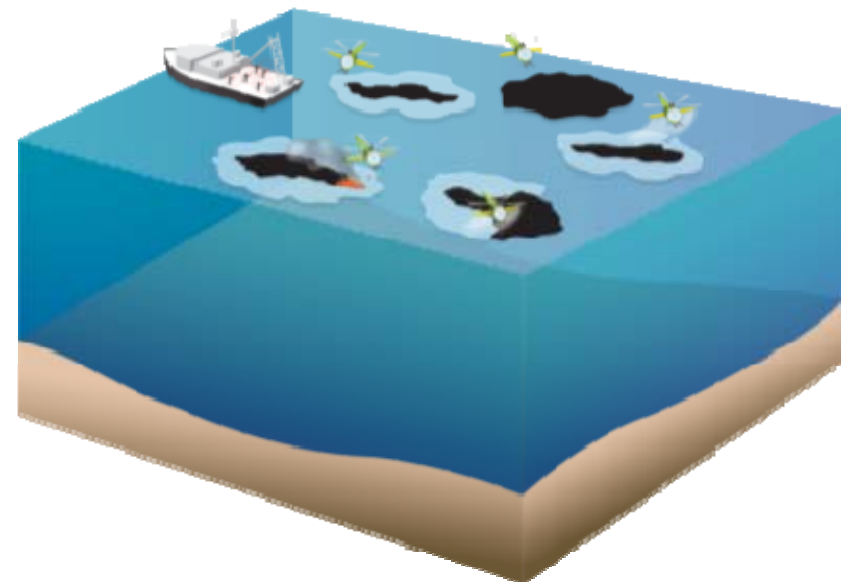
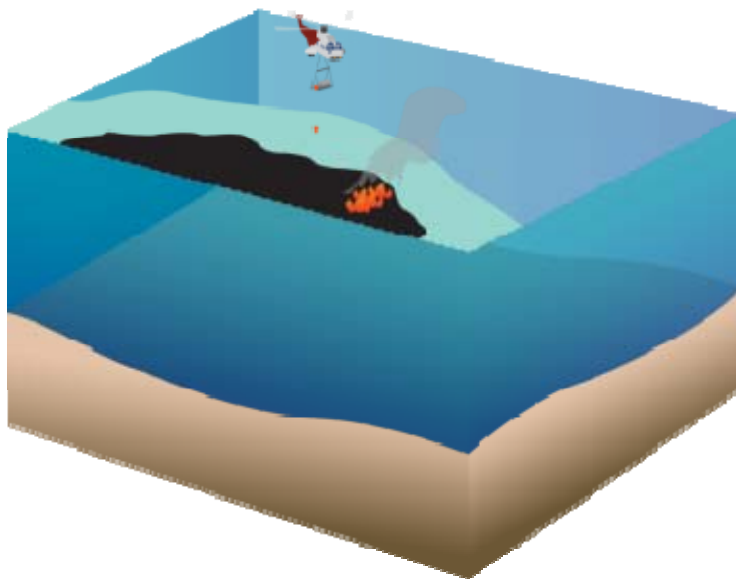


- Working with OSR Vendor
- Obtained listing of two herders on US EPA NCP Product Schedule
- Helicopter-mounted delivery system built
- Commercial quantity of herders available

Field Testing



- Planning for a field test in 2015
 - Primary goal is to use a manned helicopter to both spray herder and ignite slick
 - Secondary goal is to use a remote-controlled helicopter to perform same activities



Summary



- *Mechanical recovery can have limitations offshore – both for large spills and spills in ice*
- *Dispersants enhance the natural biodegradation process – petroleum degrading microbes exist in all marine environments*
- *Dispersant use presents a necessary tradeoff and should be a primary response option*
- *Herding agents provide another oil spill response option that can be applied solely by aircraft to demonstrate herder effectiveness*



QUESTIONS?