Introduction to Herders and their use in Marine Oil Spills

May 1, 2025

Presenter Bios

- Michael Hernandez
- Science Technology and Stakeholder Engagement Officer, OSRL USA
- Practical spill experience in Peru, Bahamas, Trinidad and Tobago, Gibraltar and Sri Lanka

- Kelly McFarlin, PhD
- Environmental Scientist, ExxonMobil Biomedical Sciences Inc., New Jersey
- Fate and behavior of oil in the environment, oil spill response options, environmental microbiology

- D. Abigail Renegar, PhD
- Research Scientist, National Coral Reef Institute at Nova Southeastern University, Fort Lauderdale, FL USA
- Marine Toxicology, Coral Nursery, Coral Histology

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Presentation Topics

- The Response toolbox and NEBA
- Behavior of oil on water
- What are herders?
- How have they been tested?
- Application methods and requirements
- Use in marine oil spills

The Response Toolbox

Mechanical Recovery:
Booms & Skimmers

In-Situ Burning

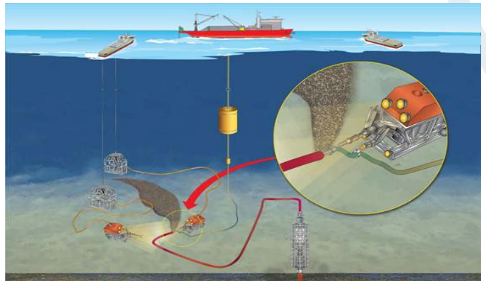
Monitor & Evaluate

Dispersants

Aerial

Vessel

Subsea



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

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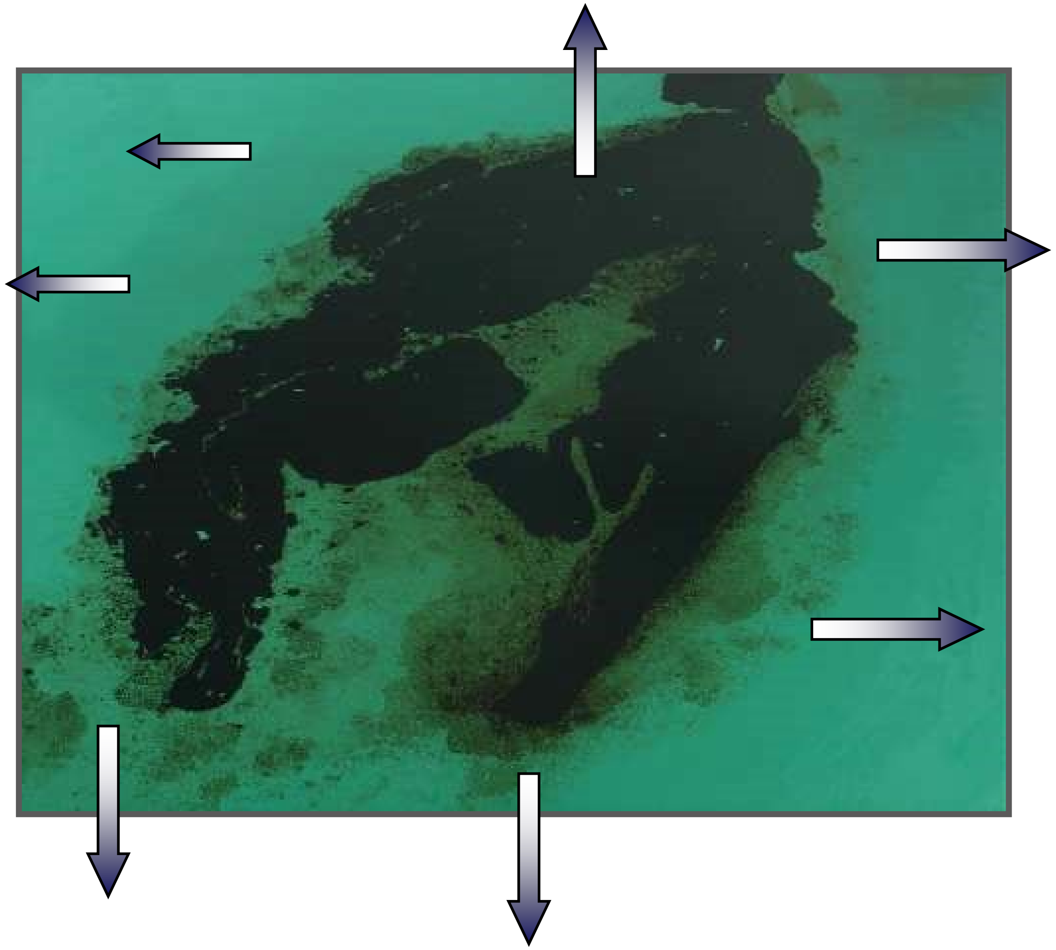
Behavior of Oil on Surface Waters

Oil slicks will continuously expand and become thinner over time

The size of the problem could increase if no response deployed

Need to prevent shoreline oiling!



Response options become less efficient with time

Balancing Response Options

Mechanical Recovery

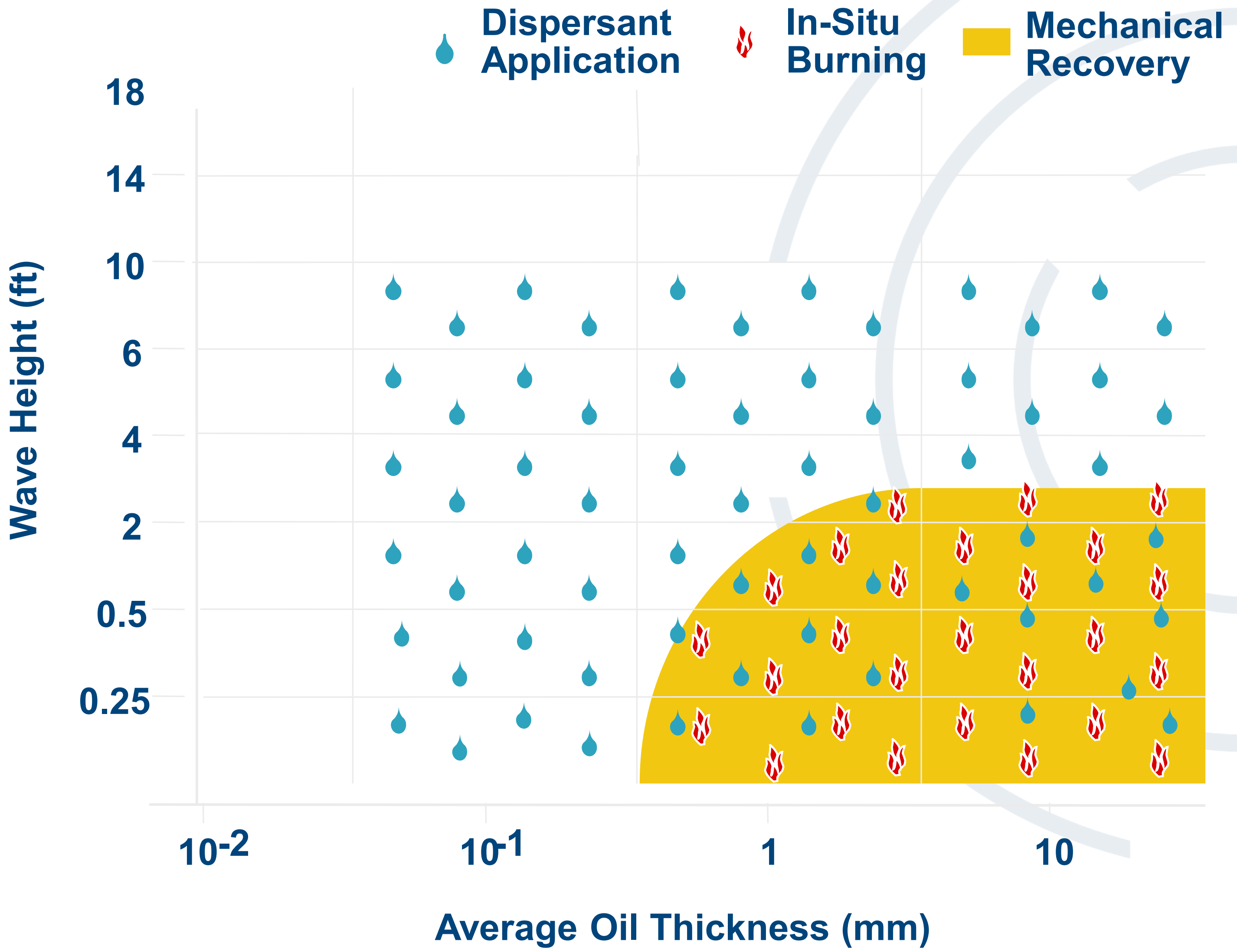
- Max Current 0.75 Knot
- Max Wind 20 Knots
- 1-2 M Max Waves
- Viscous Product Can Be a Problem
- Debris Can Cause Problems

Dispersants

- High Viscosity Can Reduce Effectiveness
- Emulsification Can Affect Effectiveness
- Short Window For Some Products

Burning

- Max Current 0.75 Knot
- Ignition Difficult Over 20 Knots
- 1 M Wave Limit
- Weathered Oil Difficult to Ignite
- High Water Content (25%+) a Problem
- Requires Fire Boom



Courtesy of Al Allen

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What are Herders?

A chemical product mainly consisting of one type of surfactant that acts on the water surrounding an oil slick and causing the oil to thicken

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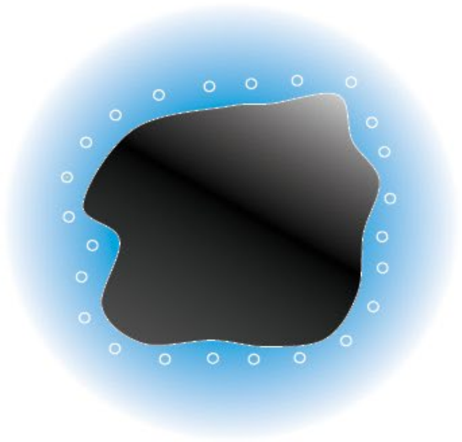
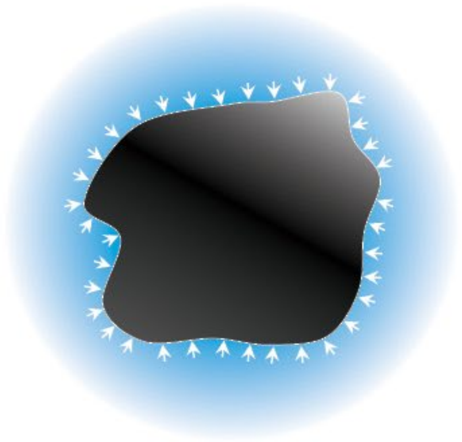
Technology of Herders



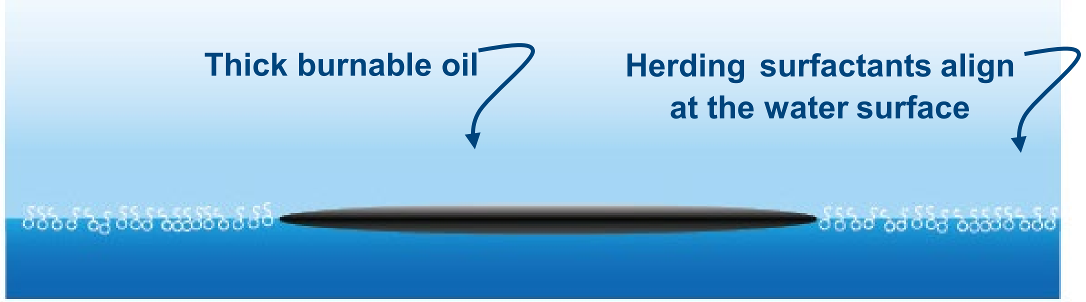
Herders sprayed on water around perimeter of slick via aircraft, boat, USV – Unmanned surface vehicle



Herders rapidly spread to form monolayer of surfactant on water surface

Herders change surface tension of water forcing slick into smaller area

Biodegradable surfactants applied to water around slick perimeter re-thicken slicks to support combustion



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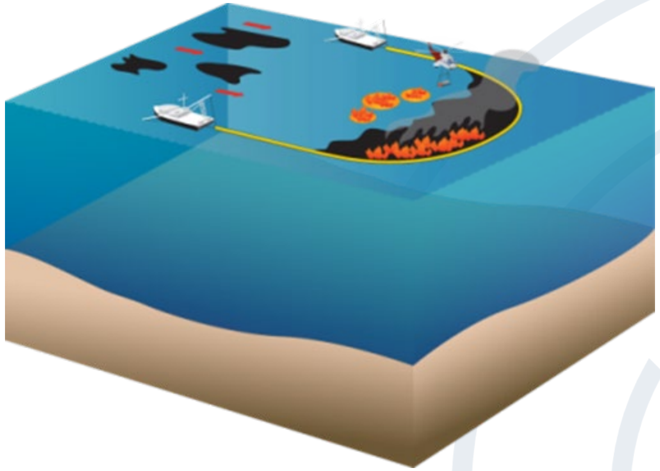
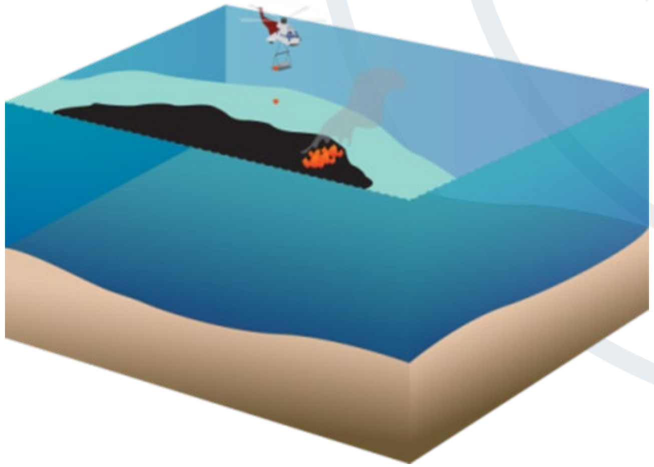
Technology of Herders

- Herders consist of a "***Surfactant boom or Chemical Boom***" to thicken slicks – no boundary required.
- Herders typically require less product than slicks treated with Dispersants.
- Herder technology was originally developed for open water.
- In 2000's research focused on marine applications with ice; but more recent research has again concentrated on open water.
- The goal is to have another tool that can be used as a response option.





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Test Tank Demo

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Application Requirements

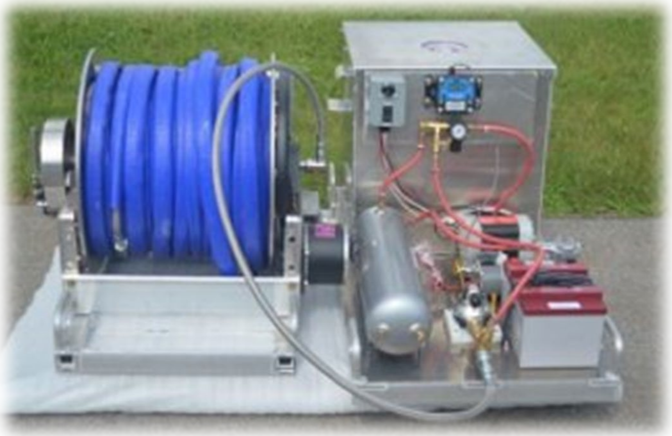
- Calm sea conditions, no breaking waves.
- Minimal wind (4-6 knots) & no rain.
- Suitable for low to medium viscosity oils.
- Only suitable on fresh or weathered crude oil (not emulsified).
- Oil must have lower spreading pressure than the herding agent.
- Low toxicity and used in extremely small quantities + more than 30 times less than the design application rate for dispersants.

Herders were successfully used in a field test in 2008 offshore Svalbard.

Herders enabled in situ burning during a 2016 field test offshore Norway. Left photo shows herded slick and right photo show unherded slick.

Application Techniques

- Near shore with simple garden sprayers, hand pump sprayers or squirt cans.
- Commercial backpack sprayer (small boat application system)
- Boat spray systems
- Manned helicopter and remote-controlled helicopter with the DESMI-AFTI aerial application system
- The “ Jet-Ski” ROSV project … More later!


Use of Herders in an Oil Spill

- In Situ Burning = “Herd & Burn”
- Recovery = “Herd & Skim”
- Chemical Boom = “Herd & Deflect”
- Example: Kazakhstan Test of Herder and Controlled Burning
  - Northern Caspian shallow water areas, reed beds
  - 2018 trial in Damda basin
  - Herders approved for use by Kazakhstan regulator
  - NEBA-driven use:
    - Too shallow for dispersants and speed of application

686904 2020 INTERNATIONAL OIL SPILL CONFERENCE

TEST OF HERDER AND CONTROLLED BURNING OF SPILLED OIL IN KAZAKHSTAN

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ABSTRACT

Recent years have seen renewed interest in the viability of using herding chemicals in conjunction with in-situ burning. NCOC, an operator in the shallow north Caspian Sea, undertook herder research as an extension to studies performed under the Arctic Response Technology Joint Industry Programme (JIP). The purpose was to investigate the feasibility of using herders as part of their response toolkit.

Laboratory tests were performed in Kazakhstan on weathered Kashagan export crude oil, using two herders listed on the US NCP Product Schedule. Results were positive and it was considered that a reasonable size test spill under realistic conditions was required to verify laboratory work.

In November 2018 a field trial was undertaken in the boat basin at Damba in western Kazakhstan. A volume of 400 litres of artificially weathered Kashagan crude was pumped onto the water surface and allowed to spread. Air and water temperatures were just above freezing and a small amount of ice was present due to overnight low temperatures. The test was recorded by an unmanned aerial vehicle, using thermal IR and 4K video.

After the oil had been allowed to spread out to be <1 mm, i.e. too thin to sustain combustion, a small boat was used to spray Siltech OP-40 herder around the periphery of the

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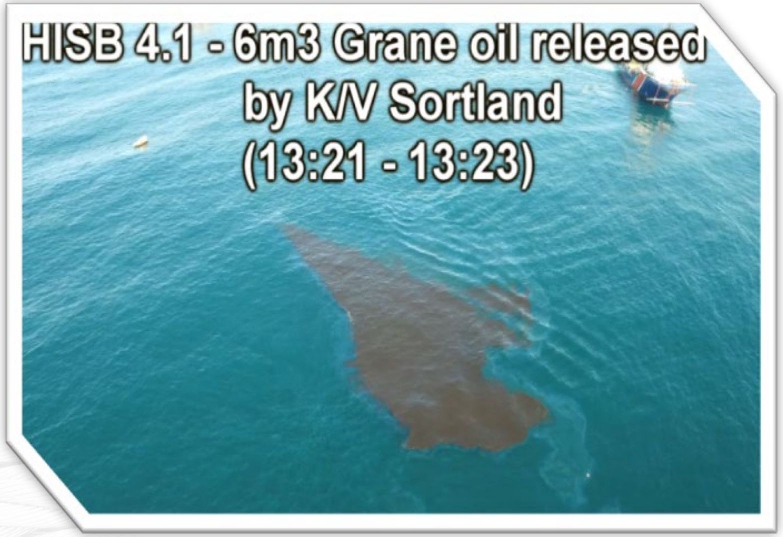
Field Testing – Norway 2016



Control slick, no herder application, 50 minutes after release

- Field test conducted June 14, 2016
- First known study to successfully burn free-floating marine oil slicks in open water.
- Herded slick burned for a total of ~30 min.
- Control slick (no herder) burned for ~12 min

Test slick after herder application, pre-burn

Slick with herder applied burning

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Chemical Herders & In Situ Burning

Chemical Properties and Field Application with ROSV

Kelly M. McFarlin, Ph.D.
Environmental Scientist, ExxonMobil

Composition of Oil Spill Response Herders

Herder	Ingredient	CAS#	Formula	Mol Wt. (g/mol)
Siltech OP-40	ethoxylated heptamethyltrisiloxane (100%)	67674-67-3	$C_{20}H_{50}O_8Si_4$	540
Thickslick 6535	sorbitan monolaurate (Span 20) (65%)	1338-39-2	$C_{18}H_{34}O_6$	347
	2-ethyl-1-butanol (35%)	97-95-0	$C_6H_{14}O$	102

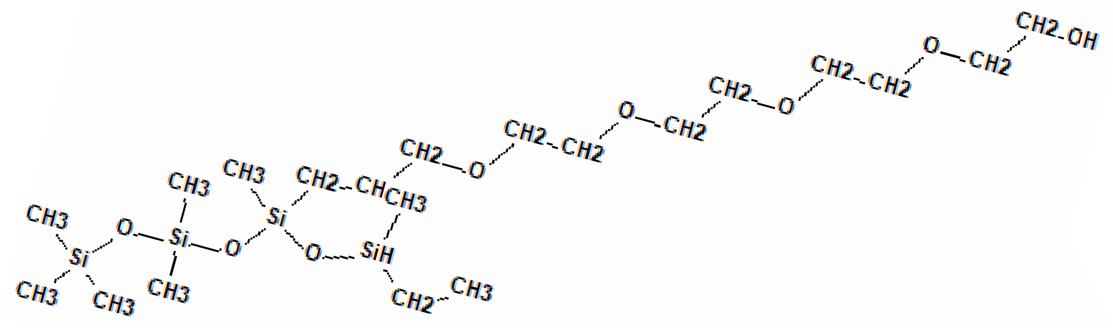
- Slitech OP-40: higher molecular weight organosilicone surfactant
- Thickslick 6535: nonionic surfactant consists of two components
  - fatty ester surfactant (65%) and aliphatic alcohol solvent (35%)

ExxonMobil

Structures of Herders

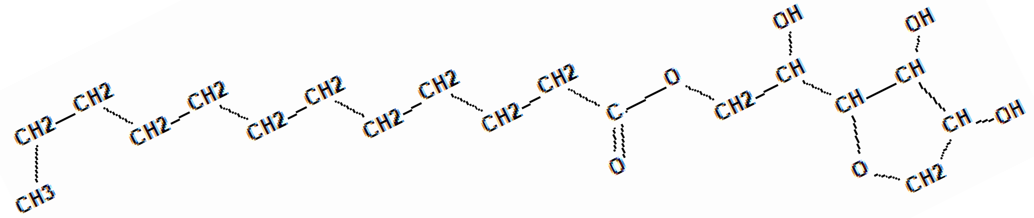
Siltech OP-40 (aka Silsurf A004-UP)

100%: ethoxylated heptamethyltrisiloxane

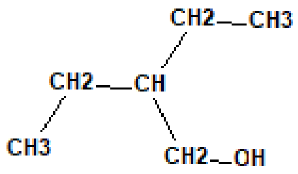


Thickslick 6535 (aka USN)

65% sorbitan monolaurate (SPAN 20)



35% 2-ethy-1-butanol



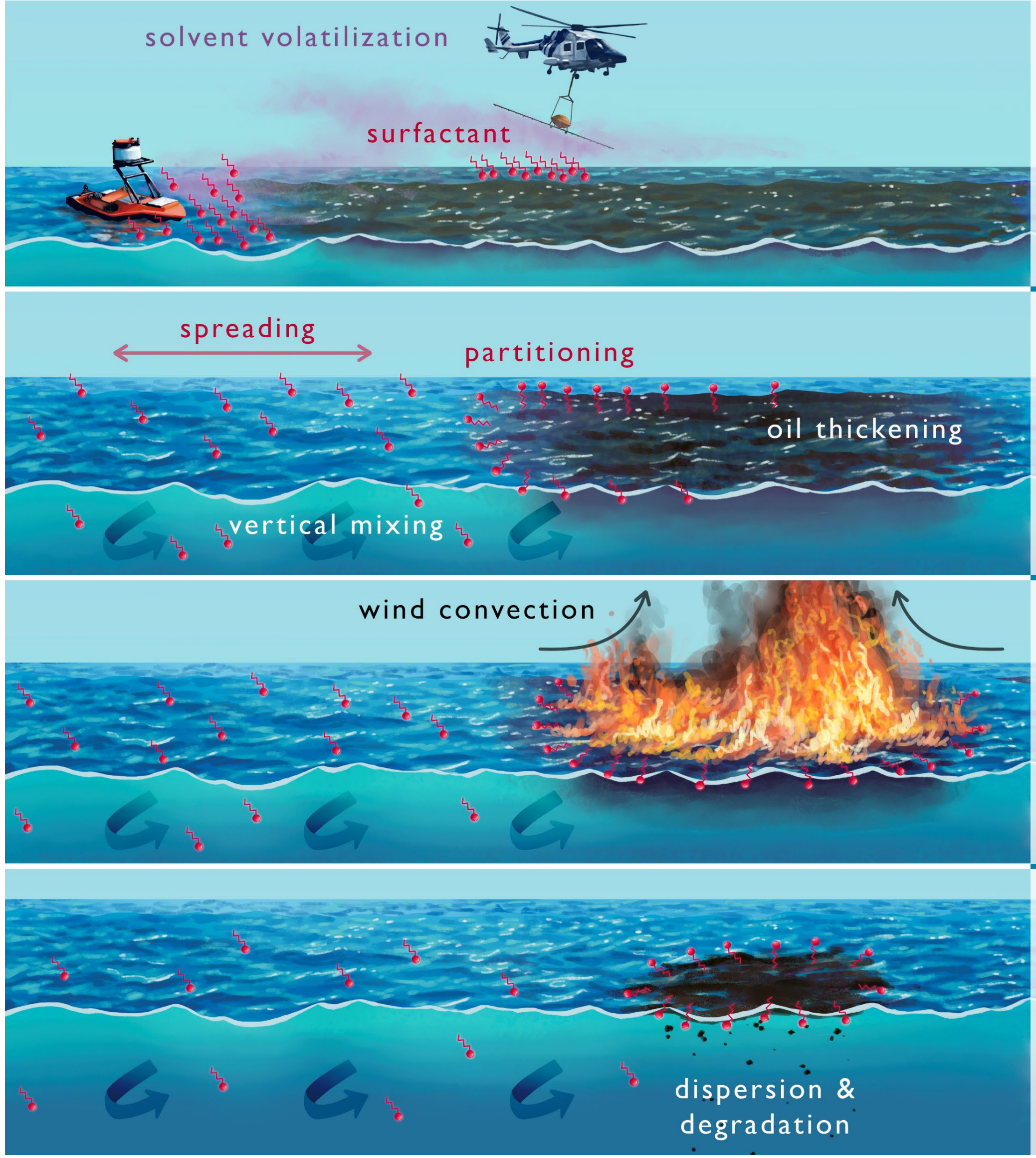
Physical Properties and Environmental Fate of Herder Ingredients

Herder	Ingredient(s)	Log K_{ow}	Water Solubility (mg/L)	Vapor Pressure @25C° (Pa)	Readily Biodegradable?	Primary Biodegradation	Ultimate Biodegradation
Siltech OP-40	Ethoxylated heptamethyltrisiloxane	6.52	0.011-0.036	1.43E-08	No	weeks	months*
Thickslick 6535	Span 20 (Sorbitan Monolaurate)	3.15	< 3 mg/L*	1.25E-09	Yes	days	days-weeks
	2-ethyl-1-butanol	1.75	4000*	204*	Yes	days	weeks

*measured values

- Thickslick components:
  - higher water solubility and lower octanol water partition coefficients predicted
  - higher biodegradation potential predicted
- Thickslick expected to exhibit lower aquatic toxicity than Siltech based on Log Kow
- Surfactant components in both herders predicted to exhibit low volatility

In-situ Burning Using Herders: 4 Main Steps



SPRAYING
- solvent lost to air
- surfactants deposited on water surface

HERDING
- surfactants spread on surface to oil slick
- slick contracts causing thickening
- waves disperse surfactant into water
- surfactants partition to oil

BURNING
- wind convection draws oil & herder into burning slick
- air emissions of herder not observed

POST-BURNING
- surfactants present in water & burn residue
- concentration in burn residue 10-1000 X water
- mass in water dominates overall fate
- surfactants naturally disperse and degrade

ExxonMobil

Parkerton & McFarlin (2024)

Remotely Operated Surface Vessel (ROSV) for Oil Spill Response

The 'Flame Throwing Jet Ski'

Joint Industry Project: OSRI, BSEE, NCOC, CCA, Shell and ExxonMobil

Built by Tactical Electronics

Purpose and Benefit of ROSV / NOMAD

Rapid-response capability for remote offshore locations

- Flexible deployment: shore, boat, or helicopter
  - Minimizes risks to health and safety
  - Faster than response boats
  - More accurate than airplanes

Herder application combined with ignition source

- FIRST OF ITS KIND!

Remote sensing capabilities

Easily shipped

- Fits in small cargo aircraft

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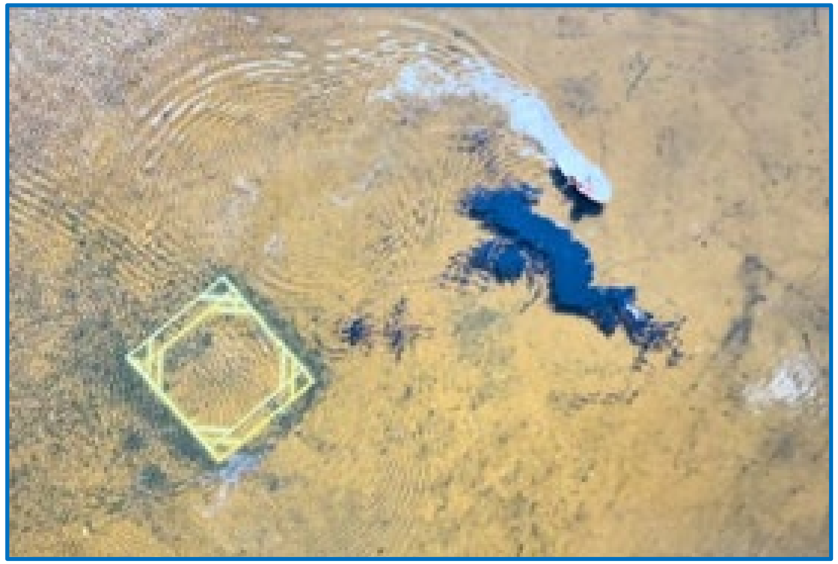
Testing Demonstration: Poker Flats, Fairbanks, AK

NOMAD: OSRC Stage 2 - YouTube



Purpose: to evaluate ability to herd and ignite a floating oil slick

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In-situ Burning

Basic Requirements

- Oil layer thickness must be at least 2 to 3 mm (0.08–0.12 in) to sustain combustion
- Oil must have some volatiles and not contain too much water

Efficiency of in-situ burning

- Efficiency of a burn depends on the oil thickness
  - “Chimney effect” (convective wind herding) thickens oil during burn
- Thick oil layers can burn at a rate of 2.5 mm/minute (1 inch in 10 minutes)
- Burn times range from 10 – 30 minutes for free-floating oil slicks
- Combustion normally continues until the final thickness is approximately 1 mm
  - Burn efficiencies ≥ 90% can be achieved

ExxonMobil

IPIECA / IOGP, 2016, Controlled In-situ Burning of Spilled Oil, International Association of Oil & Gas Producers, IOGP Report 523.

Summary

- Herder application results in very low and short duration water column exposures
- Herders not persistent and are subject to degradation
- The ROSV / NOMAD is a rapid-response vehicle that can be used for OSR by providing remote sensing and in-situ burn response capabilities
  - Can be rapidly transported to remote locations and in conditions that are not safe for aircraft
  - Can reach oil slicks faster than traditional boats
  - Can operate in a wide range of conditions
    - Reduce risk to personnel

Ecotoxicity of Herders

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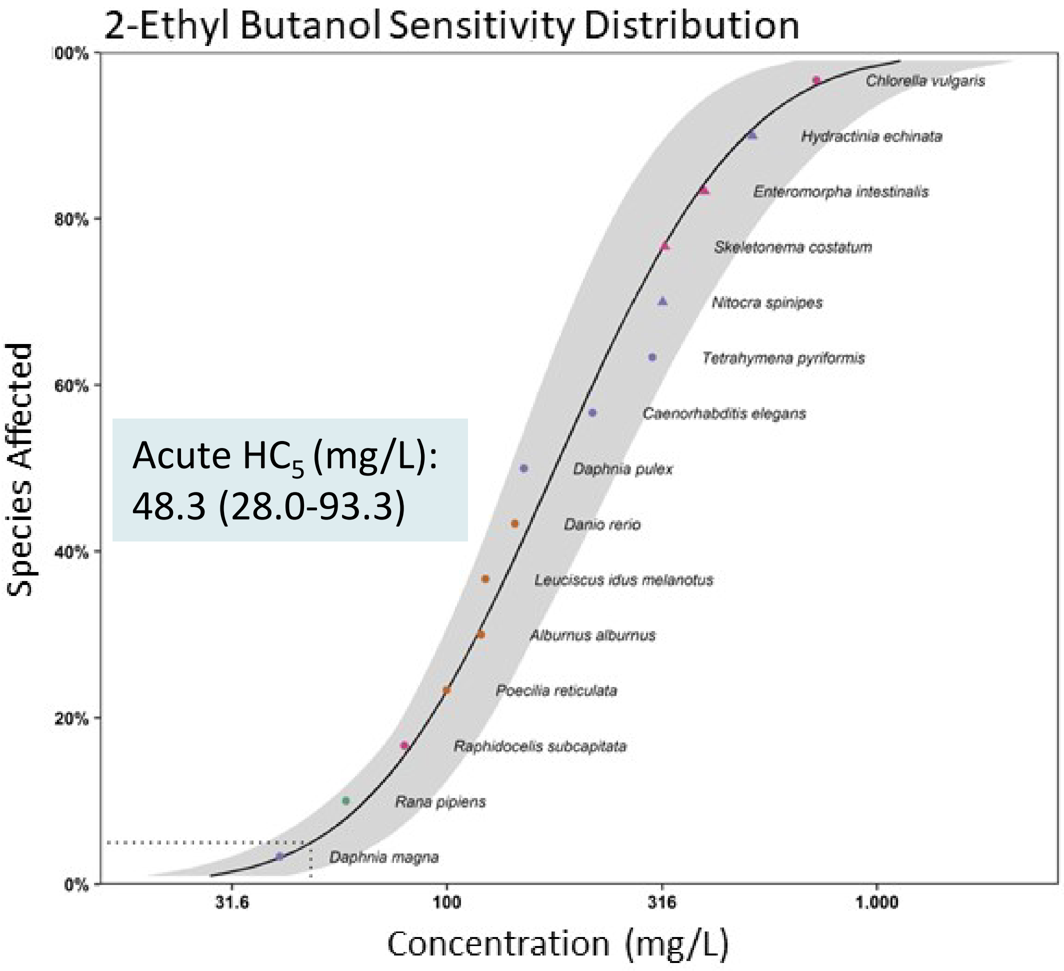
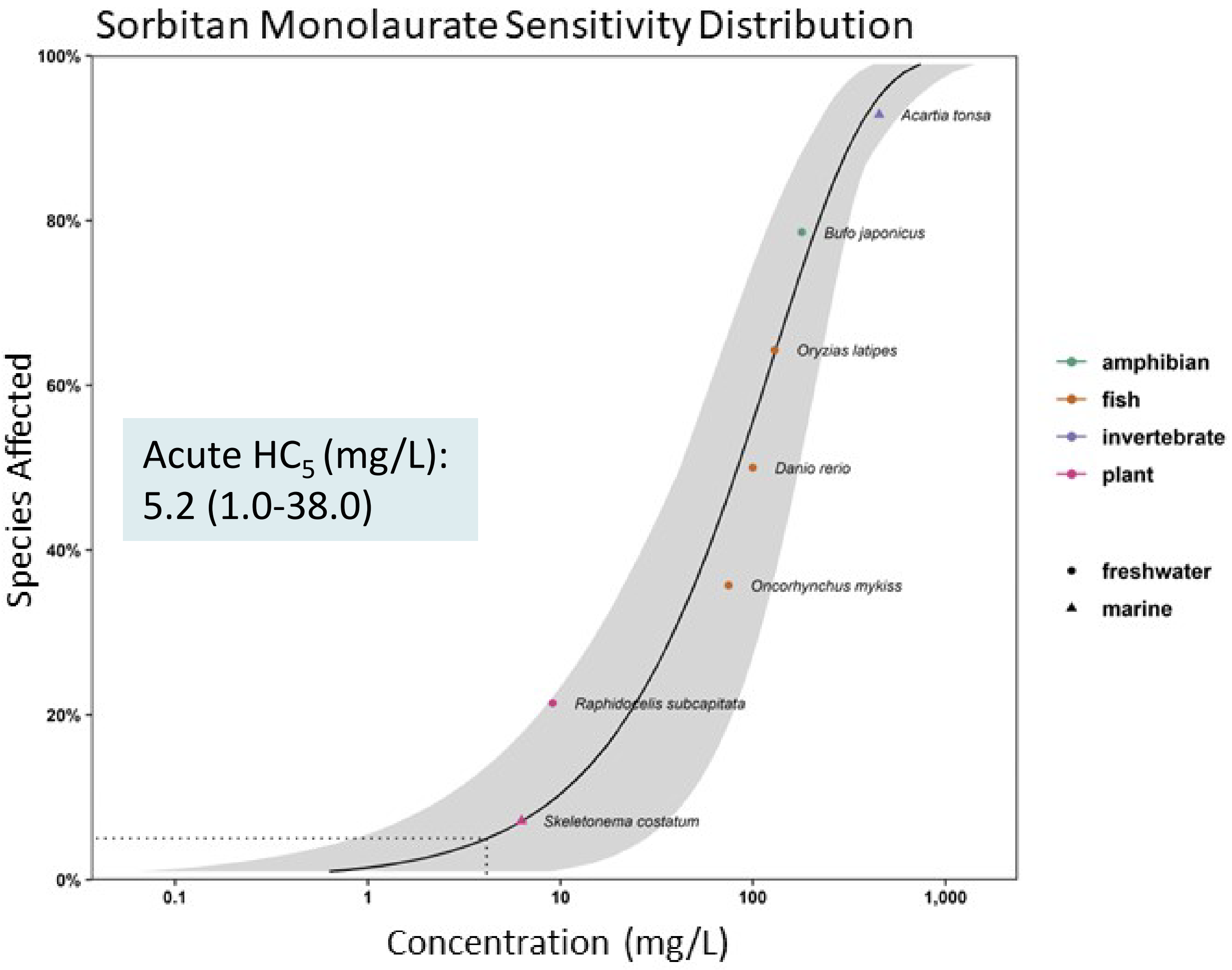
Overview

- Toxicity of herder components
- Toxicity of herders
- Toxicity of herders and oil

Aquatic toxicity of herder components





Parkerton, T. F., & McFarlin, K. (2024). Environmental hazard and preliminary risk assessment of herding agents used in next generation oil spill response. *Marine Pollution Bulletin*, *208*, 116885.

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Aquatic toxicity of herders

- Seven aquatic species were tested with both Siltech OP-40 and ThickSlick 6535 to evaluate acute herder toxicity and relative species sensitivity.
- The toxicity assessment included: acute tests with *Americamysis bahia* and *Menidia beryllina*, the freshwater crustacean *Ceriodaphina dubia*, and the freshwater fish *Pimephales promelas*; development of the echinoderm *Arbacia unctulate*; and growth of a freshwater alga *Raphidocelis subcapitata* and marine alga *Dunaliella tertiolecta*.
- Greater toxicity of Siltech OP-40 compared to ThickSlick 6535.

Table 1. Toxicity endpoint values (ppm) for seven species exposed to Siltech OP-40

Species	Endpoint	NOEC	LOEC	LC/EC50 (95% confidence interval)	
P. promelas	Survival	3	6	4.4	(1.3–7.6)
M. beryllina	Survival	3	6	3.7	(2–5.5)
A. punctulata	Development	0.5	1	1.1	(0.5–1.7)
C. dubia	Survival	3	6	6.4	(4.5–8.2)
A. bahia	Survival	7.5	15	11.5	(9.5–13.4)
R. subcapitata	Growth	–	1.25	32.8[a]	(21.3–44.4)
D. tertiolecta	Growth	8	16	11.5	(10.7–12.2)
Species Sensitivity Distribution		–	–	1.4[b]	(0.6–4.4)

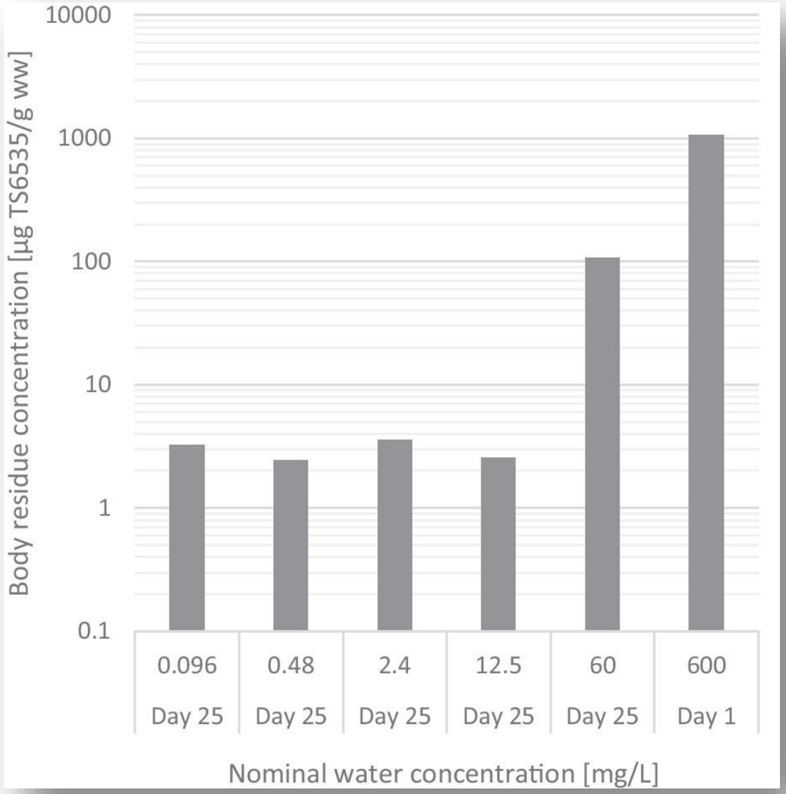
Table 2. Toxicity endpoint values (ppm) for seven species exposed to ThickSlick 6535

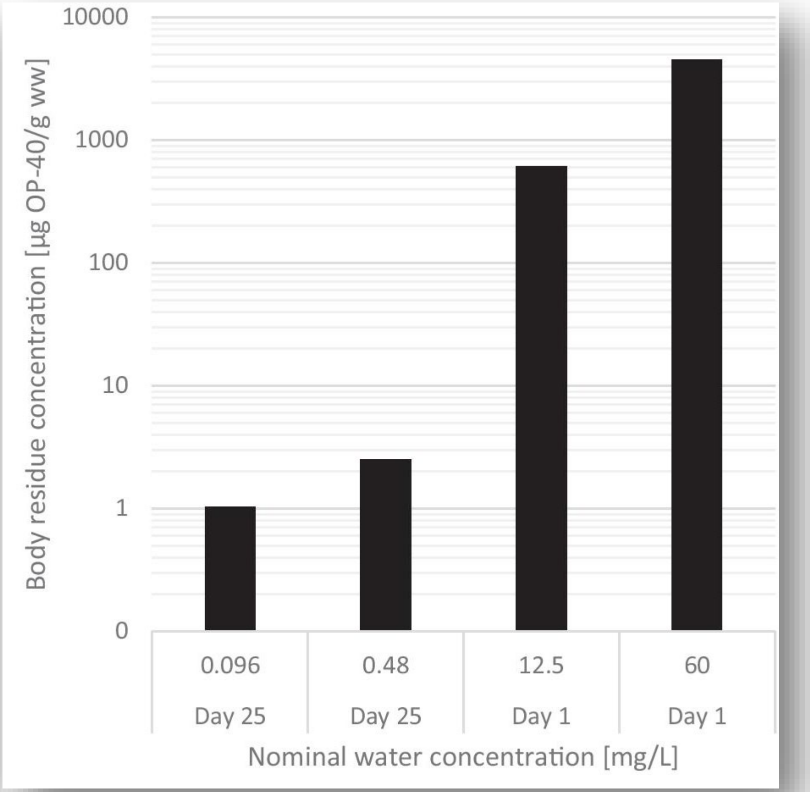
Species	Endpoint	NOEC	LOEC	LC/EC50 (95% confidence interval)	
P. promelas	Survival	30	60	53.7	(30.3–77.1)
M. beryllina	Survival	75	150	126.4	(35.6–217.2)
A. punctulata	Development	5	10	24.6	(6–43.3)
C. dubia	Survival	1	2	2.2	(2–2.3)
A. bahia	Survival	20	40	74.9	(68–81.7)
R. subcapitata	Growth	6.25	12.5	14.3	(13.8–14.8)
D. tertiolecta	Growth	0.25	0.5	12.7	(−11.7–37)
Species Sensitivity Distribution		–	–	2.6[a]	(0.6–17.7)

Alloy, M. M., Sundaravadivelu, D., Moso, E., Meyer, P., & Barron, M. G. (2022). Comparative toxicity of oil spill herding agents to aquatic species. *Environmental toxicology and chemistry*, *41*(5), 1311-1318.

Aquatic toxicity & bioaccumulation

- Toxicity, bioaccumulation and biodegradability of ThickSlick 6535 and Siltech OP-40 with Arctic water and the high Arctic copepod, *Calanus hyperboreus*.
- ThickSlick 6535 did not bioaccumulate in *Calanus hyperboreus* or affect grazing activity.
- Siltech OP-40 tends to bioaccumulate in *Calanus hyperboreus, with* sublethal effects (as reduced grazing activity).

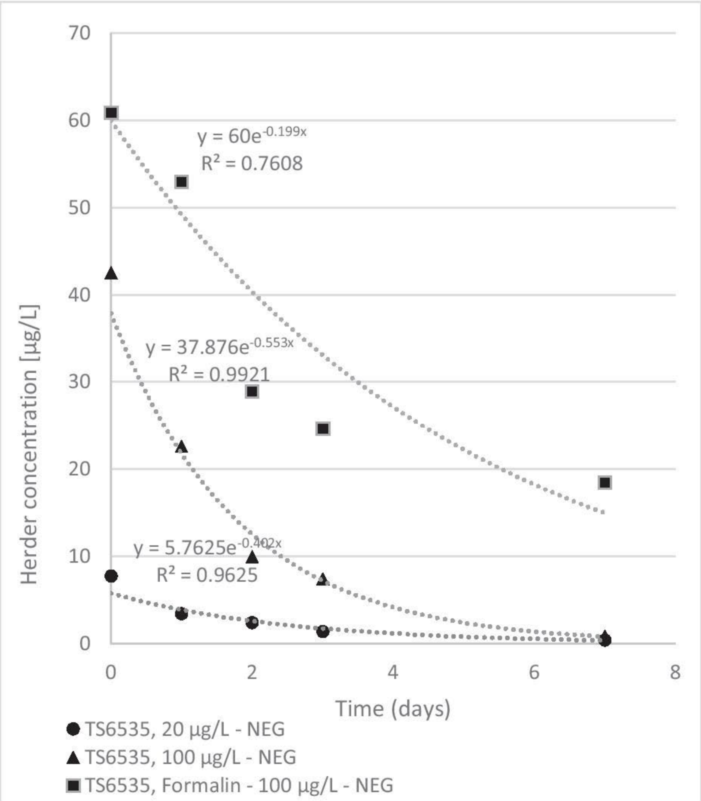


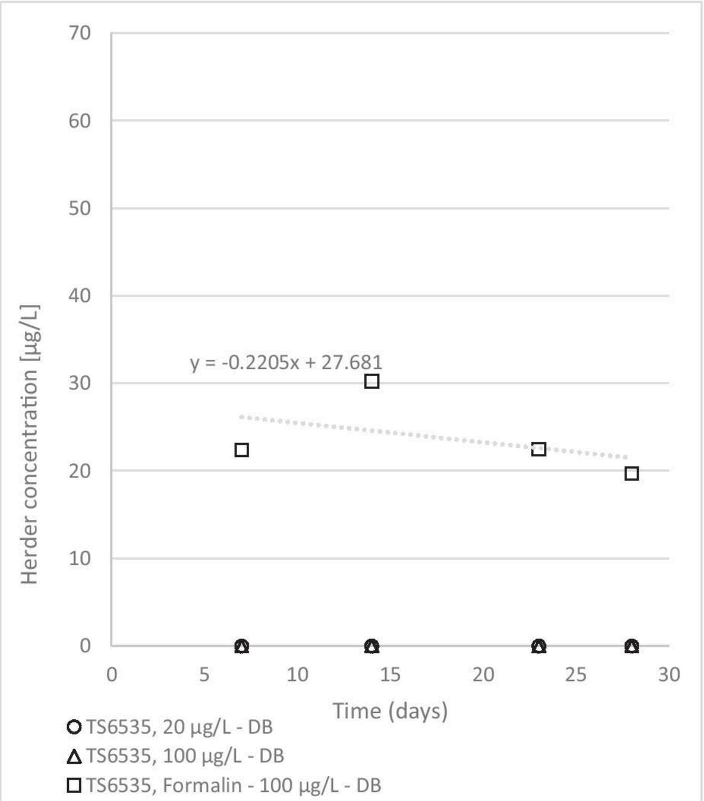


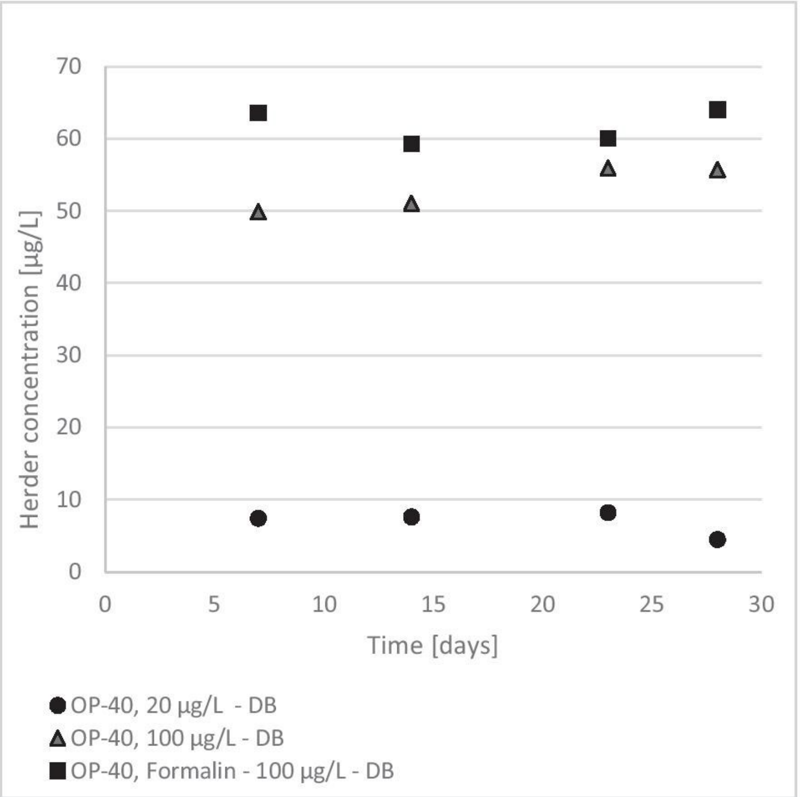
Fritt-Rasmussen, J., Møller, E. F., Kyhn, L. A., Wegeberg, S., Lassen, P., Cooper, D., & Gustavson, K. (2021). Biodegradation, bioaccumulation and toxicity of oil spill herding agents in arctic waters as part of an ecotoxicological screening. *Water, Air, & Soil Pollution*, *232*, 1-14.

Aquatic toxicity & biodegradation

- ThickSlick 6535 biodegradation within 7 days.
- Siltech OP-40 minimal or no biodegradation within 28 days.







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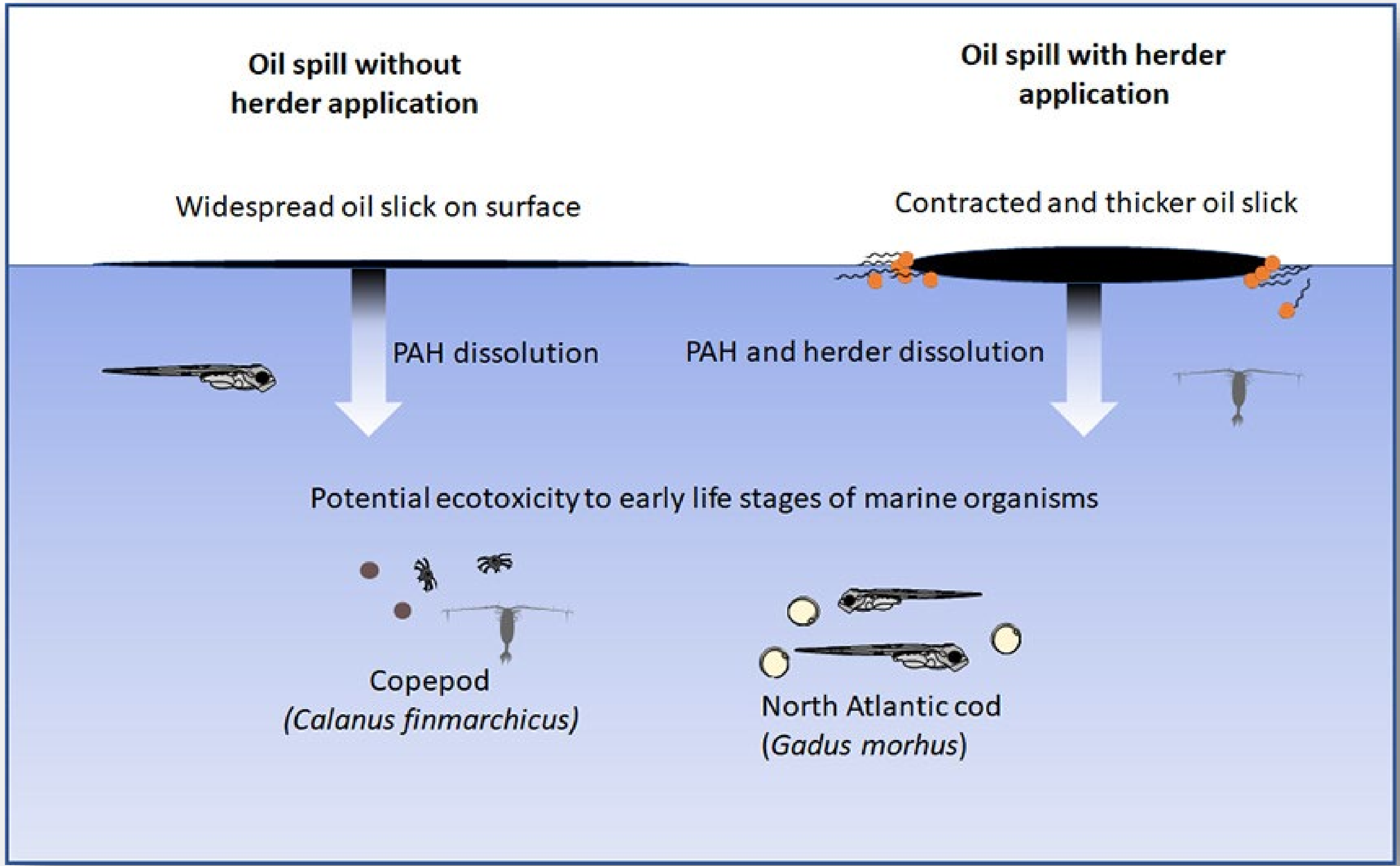
Aquatic toxicity of herders and oil

- Acute toxicity of Siltech OP-40 and ThickSlick 6535 with and without oil was tested on cold-water marine organisms.
- Low-energy WAFs prepared with and without herders displayed comparable ecotoxicity.
- No significant differences in toxicity thresholds between treatments to LE-WAFs generated with oil alone and oil treated with herders.
- Herders tested displayed acute toxicity at concentrations well above what would be expected following field application.



Hansen, B. H., Nordtug, T., Øverjordet, I. B., Altin, D., Farkas, J., Daling, P. S., ... & Faksness, L. G. (2022). Application of chemical herders do not increase acute crude oil toxicity to cold-water marine species. *Science of the Total Environment*, *823*, 153779.

Toxicity of ThickSlick 6535 to Atlantic shallow-water corals

Austin Blakeslee, MSc candidate, Nova Southeastern University, Halmos College of Arts and Sciences

- 96-hour static-renewal toxicity assays with ThickSlick 6535.
- Two species of shallow-water hermatypic corals (typically occur in <5 m depth): *Porites divaricata* and *Acropora cervicornis* (Atlantic staghorn coral, ESA-listed species).
- All nominal thresholds > than the 10 mg/L regulatory threshold.
- Healthy corals resilient to ThickSlick 6535 exposure, *Acropora cervicornis* the most sensitive coral tested.

Acropora cervicornis

Porites divaricata

	Acropora cervicornis			*Porites divaricata*		
	NOEC	LOEC	96-h	NOEC	LOEC	96-h
Mortality (LC50)	300 mg/L	600 mg/L	285 mg/L	300 mg/L	600 mg/L	330 mg/L
Physical changes (coral condition) ($EC50_{Condition}$)	150 mg/L	300 mg/L	194 mg/L	150 mg/L	300 mg/L	106 mg/L
Photosynthetic efficiency (PAM) ($IC50_{Photo}$)	150 mg/L	300 mg/L	610 mg/L	300 mg/L	600 mg/L	838 mg/L

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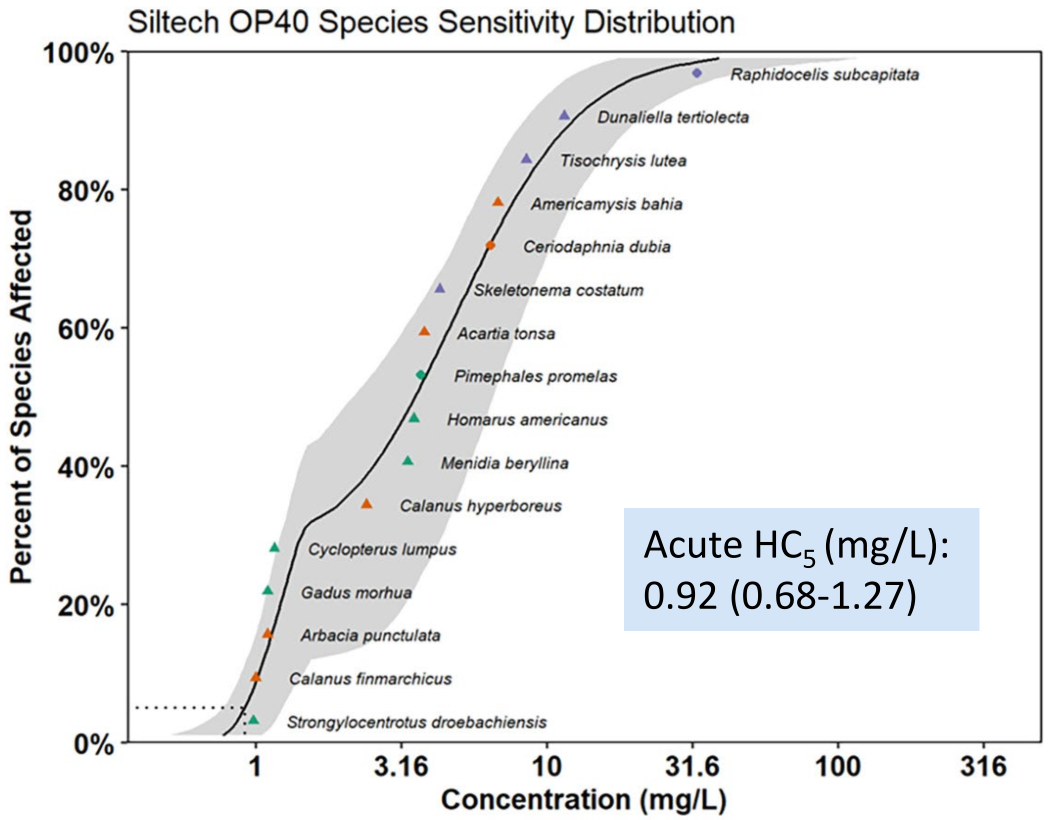
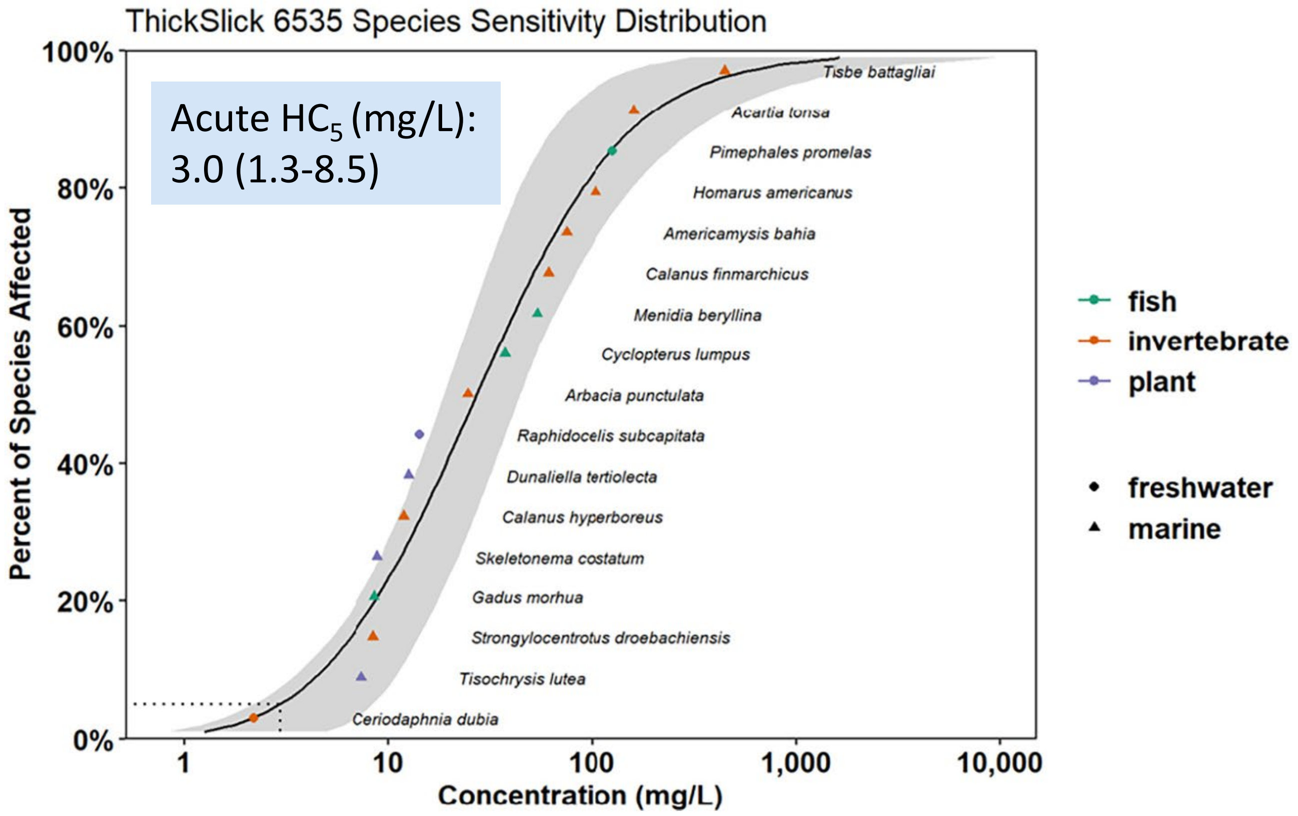
Aquatic toxicity of herders





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Summary

- Considerable aquatic toxicity data are available that provide technical basis to establish water quality objectives to protect aquatic life.
- Aquatic hazard of ThickSlick 6535 is lower than Siltech OP-40.
- Toxicity of ThickSlick 6535 dictated by surfactant, not solvent component.
- Herder application results in very low and short duration water column exposures.
- ThickSlick 6535 is not persistent and biodegrades.
- Application of chemical herders to oil slicks is not expected to add significant effects to that of the oil for cold-water marine species exposed to herder-treated oil slicks.
- Predicted herder concentrations expected to pose minimal risk to aquatic resources.