Surface Collecting/Herding Agents:

Ecofriendly Chemical Herders – BioDerived Oil Collecting Agents for Maritime Oil Spill Remediation

George John¹, Hao Zhou,² Charles Maldarelli,²
¹Department of Chemistry and Biochemistry
²Department of Chemical Engineering
The City College of New York – CUNY

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Why Does Oil Spread So Rapidly on a Sea Surface?

Surface and Interfacial Tension of the Oil

Surface Tension of the Water

\[
S = \frac{\gamma_{\text{sea}}}{\gamma_{w/o}} > 0
\]

\[
\gamma_{\text{air/sea}} = 55-65 \text{ mN/m}
\]

\[
\gamma_{w/o} = 18.4-27.4 \text{ mN/m}
\]

\[
\gamma_{o} = 25.2-28.8 \text{ mN/m}
\]
Current crude oil remediation methods

- burning
- dispersants
- booming
- skimming
- bio-remediation

SUSTAINABLE MOLECULAR MATERIALS FOR OIL-SPILL MITIGATION

PROJECT 1: PHASE SELECTIVE GELATION TECHNOLOGY –
Eco-friendly Gelators from Biomass

PROJECT 2: Herding Chemicals to "Fatten" the Spill for Burning –
Eco-friendly Herders from Biomass

Assemblies
Green Chemistry

Supramolecular Chemistry

PLANTS/CROPS

BIOCATALYSIS

CHEMICAL SYNTHESIS

VALUE-ADDED PRODUCTS

SENSORS

FIBERS / NANOTUBES

LIQUID CRYSTALS

AMPHIPHILES, MONOMERS (building blocks)

GELS

MICELLE/EMULSION, VESICLE

self-assembly

amphiphiles/
LMWGs

hydrophilic
likes water

lipophilic
likes oil

SELF-ASSEMBLY

amphiphiles/ LMWGs self-assembled structure of amphiphiles

OR

3D - Network

water
organic solvent

hydrogel
organogel
Raw Materials for New Amphiphiles

- Trehalose
- Amygdalin
- Closed chain sugars (calorific)

- Sorbitol
- Mannitol
- Xylitol
- Open chain sugars (non-calorific)

- Esculin
- Raspberry ketone glucoside
- Glucosides (e.g. organic scintillator, antioxidant)
Regioselective Biocatalysis
1: Non-Toxic Sugar-Based Phase Selective Gelators for Crude Oil Gels

Phase Selective Gelation of Crude Oil

Sugar-based Gelator/Recoverable/Biodegradable

Green Surfactants | Rheology Modifiers | Gel Forming Small Molecules | Biobased Chemical Herders
Phase Selective Gelation of Diesel

Sugar-based Gelator/Recoverable/Biodegradable

https://www.youtube.com/watch?v=8RXxRVRLdow

Representative picture of a typical gel formed via phase-selective gelation: 

a) a tilted vial containing crude oil gel alongside that containing liquid crude oil - the level of the gel is not perpendicular to the direction of pull of gravity while that of the liquid is observed to be so; b) verification of crude oil gel formation by inverting the vial upside down.
Herding Chemicals to "Fatten" the Spill for Burning – Eco-friendly Herders from Biomass
**Chemical Herders** are defined as oil collecting agents as they herd oil spilled on a sea surface into thickened slicks, so that they can be removed by in situ burning (ISB).

Figure A: Concept of herder function. **Top:** The oil slick spreads on the water surface into a thin slick that cannot be burned nor easily recovered.

**Bottom:** The application of herders reduces the surface tension of the water, allowing the slick to contract into a thick slick of oil that is more easily treated.

**Chemical Herders** are defined as oil collecting agents as they herd oil spilled on a sea surface into thickened slicks, so that they can be removed by in situ burning (ISB).
Surfactant in an organic solvent is sprayed at the periphery of the slick, where it lowers the air/sea tension causing the lens to retract.
Cartoon showing the herding process. Top view shows the sequence of events, starting from the spill of oil at water surface followed by addition of 20 µL of herder delivering 2.34 mg of herder based on standard dose of 150 mg/m² using a micro-pipette, alters the interfacial forces at the edge of oil slick thus retracting the oil slick.

**Top View of Herding Process**

Oil spilled on water

Spray herder around slick

Herded oil slick

Contraction of oil layer
Surfactant in an organic solvent is sprayed at the periphery of the slick, where it lowers the air/sea tension causing the lens to retract. Once it is retracted to a thickness of 3-5 mm, it can be burned.

\[ S = \frac{\text{sea}}{\text{w}} - \frac{\text{w/o}}{\text{a/o}} < 0 \]
Currently used chemical herders

[1]

[2] Thickslick 6535
Why chemical herding?

✔ **Speed**: In minutes the lens can be retracted to a thickness for which the lens can be burned. Dispersants can take several days to weeks to break up the spill.

✔ **Low Application Rates**: Because herding agent is applied to the periphery, it consumes less surfactant than dispersants which are applied over the entire spill.

✔ **Ease of Use**: Aerial Spraying allows use in environments difficult for booms to work in, such as the Arctic.
What properties must the chemical herder have to be effective and acceptable?

- Must be able to penetrate and lower the air/sea surface biofilm and lower the air/sea surface tension to below 30 mN/m:
  \[ S = \frac{\text{sea}}{w} - \frac{\text{w/o}}{a/o} < 0 \]

- Must be able to remain on the surface to maintain herding action.

- Must be environmentally benign.
We designed an amphiphile which easily penetrates into the biofilm and is eco-friendly by using tails made of phytol, a isoprene chain abundant in the marine environment and present in the biofilm, and attach a polar aromatic group (through an ester linkage) to anchor the herder onto the interface (A Sacrificial Amphiphile – degrades after use!)
HERDING IN WARM OCEAN
What properties must the chemical herder have to be effective and acceptable?

- Must form a stable monolayer in the presence of surface wave action
- An advantage would be to have a large surface dilatational viscosity to dampen wave action
- Herding monolayers tend to disintegrate in seas with waves. Can binding of the monolayer to polysaccharides in the sea surface microlayer improve stability and increase dilatational viscosity
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Surfactants in Thylakoid Membranes of a Chloroplast

- MGDG and phytanic acid are constituents of the thylakoid membrane of higher plant chloroplasts.

![Diagram of a chloroplast showing the structure of MGDG and phytanic acid.](image)
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\[
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\]
Palmitic Acid vs Phytanic Acid
Surface Pressure Isotherms

Phytanic Acid

Palmitic Acid

Langmuir–Blodgett (LB) Method
Dilatational Viscosity Measurements Using the Pendant Drop Technique

Oscillating Pendant drop method for Measuring Surface Tension and the Dilatational Viscosity

A water drop is made in air, chemical herders are spread onto the drop surface and the shape is imaged to obtain the surface tension. Then the water drop is oscillated to obtain the dilatational viscosity.
λ Carrageenan is a polysaccharide extracted from red seaweed. It is one of the polysaccharides in the biofilm of ocean surface.

Polar group of MGDG entangles with the λ carrageenan in the water phase.
Small Pan Scale Oil Spill Remediation Experiments

- Fast video camera
- Ring for initial containment of oil
- Wilhelmy Plate
- Milled teflon trough
Crude Oil on Pure Water
Crude Oil on Pure Water with MGDG at Surface Pressure 35mN/m
Crude Oil on Pure Water with MGDG at Surface Pressure 10mN/m
Crude Oil on 0.05 wt% $\lambda$-Carrageenan with MGDG at Surface Pressure 41mN/m
Herding Capability of MGDG

The pan scale experiments have shown that MGDG are capable for oil spill remediation and the balance water-air interface tension is around 47 mN/m
Acknowledgements:
Large scale wave tank oil spill remediation experiments of single component chemical herder and synergism

0.4m x 0.4m x 6m (mini wave tank)

2.4m x 2.4m x 12m (Cold Regions Research and Engineering Laboratory [CRREL] wave tank)
MGDG as a Chemical Herder

MGDG, due to its unsaturated chain and large galactose headgroup, forms, like phytanic acid, a compressible liquid monolayer which should remain intact under wave action during herding.

MGDG binds strongly to the polysaccharides naturally present in the sea surface microlayer by hydrogen binding of the galactose head group to the polysaccharide. This increases the surface pressure, enhancing herding action.

X-ray reflectivity and fluorescence experiments have quantitatively shown that with the presence of MGDG molecules on the water-air interface, λ-Carrageenan, a natural polysaccharide in the sea surface will be recruited to the interface and three times more calcium cations are bonded to λ-Carrageenan molecules.

At similar surface concentrations, the dilatation viscosity of MGDG monolayer is larger than that of phytanic acid because the size of polar group of MGDG is larger than phytanic acid.
Edible Oleogels

Personal Care Applications

Solid Bilayer Membranes

Drug Delivery

Encapsulation of Bioactives

Stimuli Responsive Lipids

Antimicrobial Coatings

Oil-Spill Recovery Materials

Chemicals, Building Blocks

Hybrid Materials

Catalysis

Biobased Electrodes & Gel Electrolytes

Sustainable Molecular Design – Biomass Platform

Food, Energy, Cosmetics, Drug-delivery, Hybrid materials, Soft matter

Self-assembly

Enzyme catalysis

Biorefinery