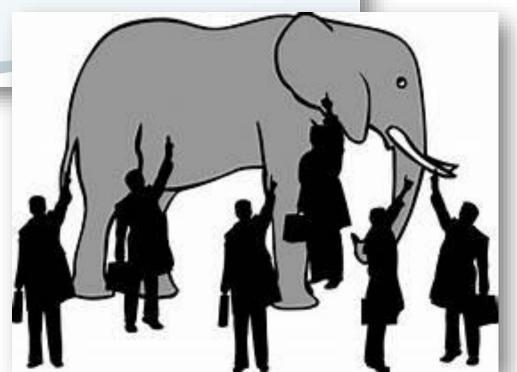
Marine oil snow formation: Insights into mechanisms

Towards a Synthesis

Uta Passow

Key Synthesis Questions

- What was the state of the science ("baseline") before Deepwater Horizon?
- What have we learned? (Critical assessment)
- What major gaps in knowledge still exist?
- How can we best apply what we have learned? (What will be the impact – how do we make a difference?)
- Where do we go from here?



MOSSFA = Marine Oil Snow Sedimentation and Flocculent Accumulation

Marine snow

Rachel Carson 1951 Visible to eye

What makes MOS MOS?

- Particle-Oil Associations
- Oil Incorporation
- Sinking velocities
 - Composition of MOS, EPS Chen
 - Microbial contributions Kai
 - OSAs –Ali

Oil-Particle Associations in the water

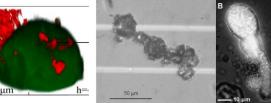
oil=green,

et al. 2017

sed.=red; Zhao

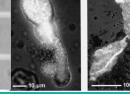
OMAs, OSAs, OPAs, oil-SPM:

- Droplets coated with mineral grains
- 3 types: droplet, solid, flake
- Small, e.g. 20 100 μm, but SOA, SRB
- Neutrally buoyant or sinking (<10 mm s⁻¹),
- Oil droplets, inorganic particles, traces of organic matter, non fractal

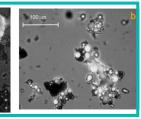


Khelifa et al.

2017



Lee et al. 2002



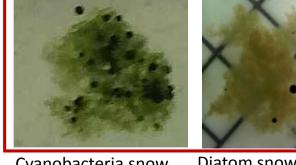
Khelifa et al. 2017

MOS, ORMS

- formed via aggregation/ coagulation:
- formed via biol. production:
- MS formed independent of oil and oil is inadvertently trapped in aggregates
- Larger 500 μm
- Sinking at 100's m d⁻¹)
- Porous & Fractal (P > 98%)
- Oil droplets < 50% (V/V)

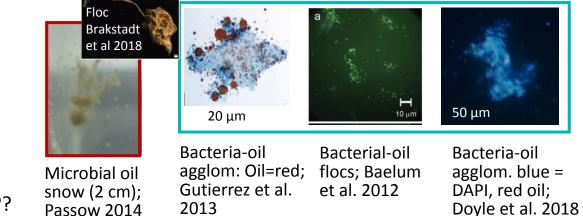
Bacteria-oil-agglomerations/ Microbial oil snow, MOS:

- Microbial response to oil exposure: Mucus production
- Formation of Biofilm-like structures
- Microbial consortia interspecies interactions
- Efficient hydrocarbon degradation??



Cyanobacteria snow, (1.5 cm) oil=black, cells=green; Wirth et al. 2018 Diatom snow fragment (500 μm); Ziervogel, unpubl. A B

Copepod fecal pellet filled with oil droplets. Almeda *et al.* 2015

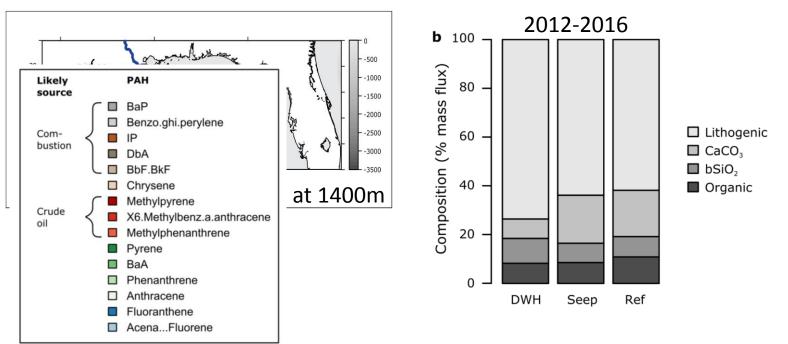


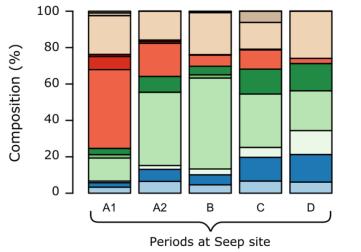
Marine snow: Composite particles > 0.5 mm

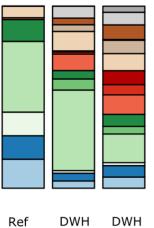
- Trap results
- Experimental Results:
 - Microbial oil snow (response of bacteria to oil)
 & MOS formed via incorporation of oil into MS
 - Oil incorporation
 - Effect of Corexit
 - Sinking velocity



Sinking MOS in situ: Mineral & Oil Contribution



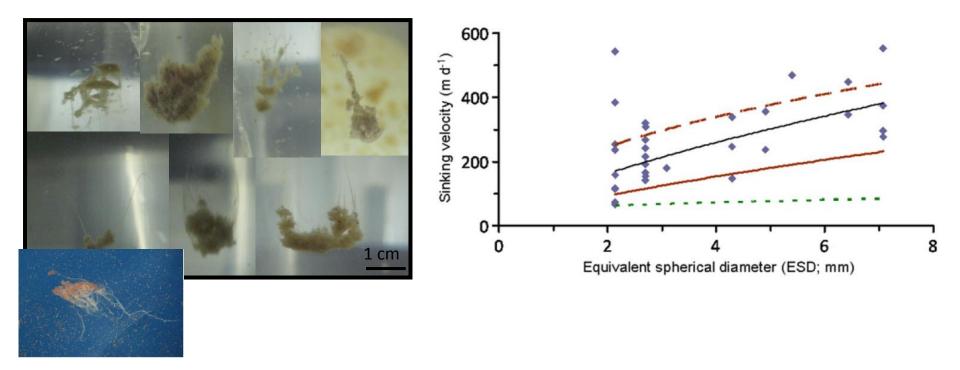




(2012) (2010)

- Lithogenic minerals cosediment with MS
- Hydrocarbons also cosediment, e.g. with diatom aggregates

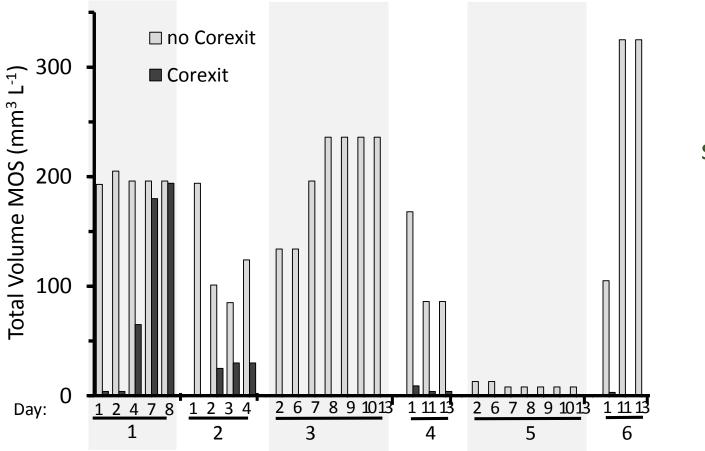
MOS: Microbial Oil Snow



- Microbial OS formed in the **absence of particles**
- Carbon in Microbial OS was derived to ~100 % from oil
- Biofilm formation without solid surface
- Microbial OS sank rapidly, similar to MS

Passow DSR 2014, Passow *et al* ERL 2012, Ziervogel et al. 2012

Microbial Oil Snow: Role of Corexit



COREXIT impedes the formation of Microbial oil snow, because it disperses EPS.

Dispersant addition protocol and DOM *very* important

10 µL Corexit 9500A to 1 mL oil & 1 L seawater

Passow DSR 2014

MOS: Phytoplankton Aggregates

WAF (1 mL oil/ L)

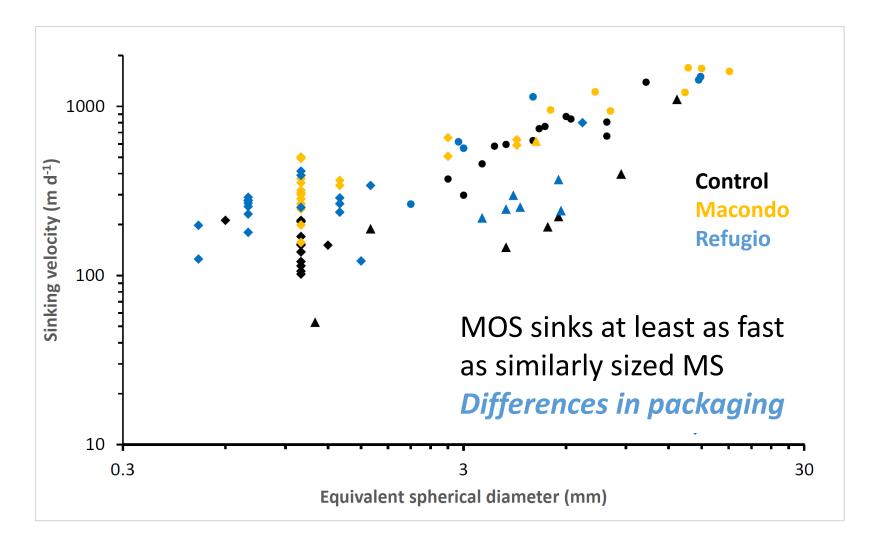
Marine snow (exp)	Oil type	% C
Skeletonema grethae	Macondo-WAF	5
Odontella aurita	Macondo-WAF	6
Odontella aurita	Refugio-WAF	15
Chaetoceros sp	Refugio-WAF	42
Thalassiosira pseudonana	Refugio-WAF	35

200 • WAF_{Mac} 180 EOE: PON in aggregates • WAF_{REF} 160 (ng Oil (µg PON)⁻¹) 140 ********* 120 100 80 60 y = 0.17x + 32.5440 $R^2 = 0.71$ 20 0 100 200 300 400 500 600 700 0 Initial EOE concentration (µg Oil L⁻¹)

Incorporation rate of oil is largely a function of oil concentration in the water and aggregate concentration.

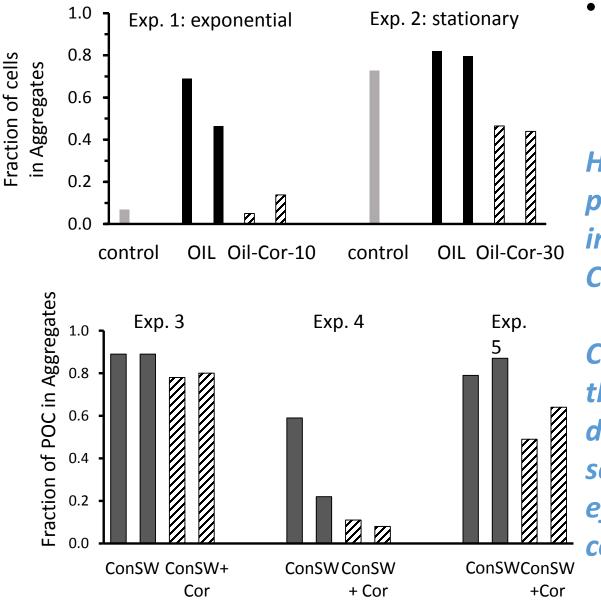
Passow 2016, Passow et al. MEPS in revision

MOS: Phytoplankton Aggregates: Sinking Velocity



Passow et al. MEPS in revision

Phytopl. & Detrital MOS: The Effect of Corexit



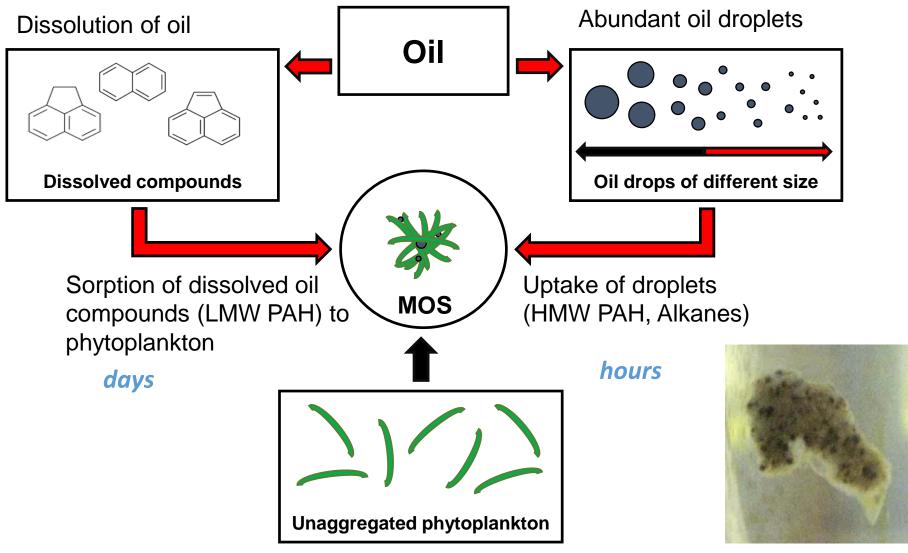
 The addition of Corexit inhibits aggregation

However, oil content per aggregate is higher in the presence of Corexit.

Corexit application may thus increase or decrease the sedimentation efficiency of oilcompounds

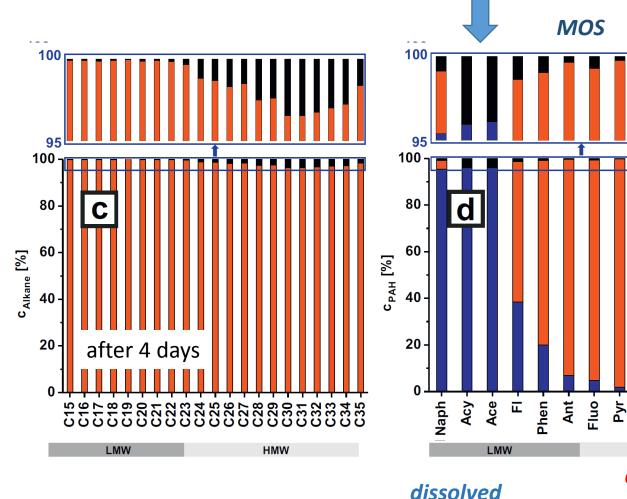
Passow et al. Mar Pol. Bul. 2017

Phytoplankton MOS: Mechanisms of Oil Incorporation



Wirth et al. 2018

Phytoplankton MOS: Mechanisms of Oil Incorporation



Immediate: Insoluble compounds in MOS: Linear correlation between those compounds in droplets and MOS (LMW PAH absent) After day additionally sorption of LMW PAH to phytoplankton (unaggregated and MOS). Linear relationship of LMW PAHs in dissolved vs particulate phases.

droplets & unaggregated particle

BB Bb

Ba

HMW

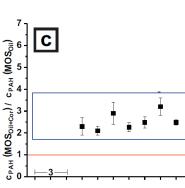
Wirth et al. 2018

Phytoplankton MOS: Impact of Corexit for Oil Incorporation

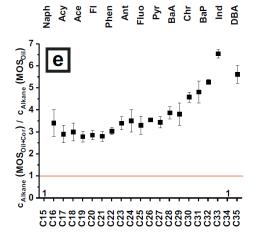
COREXIT

- <u>increases dispersion (more smaller droplets)</u> and <u>accelerates dissolution</u> (compound specific):
- increased amount of oil droplets in MOS (consistent with coagulation theory)
- enrichment of HMW compounds in droplets (LMW compounds dissolve faster)
- > 1 day, additionally sorption of LMW PAH (enhanced availability outweighing decreased sorption potential)
- Biodegradation after 4 days, especially in MOS

MS sinks (rather than remain in oil layer for 4 days): Timing between aggregation/ Corexit addition and oil contamination essential in determining which compounds enriched in MOS



1 day exp.



Synthesis:

Both, *microbial oil snow*, which forms because of oil contamination, and natural *marine snow* that inadvertently incorporates oil, may act as a <u>transport vehicle for oil</u> compounds, rapidly transferring oil residues to the seafloor at > 1400m. The presence of oil does not lead to reduced sinking velocities.

The interactions between oil or oil + Corexit with marine snow (biologically mediated process) are extremely complex. But general rules begin to emerge that make this a potentially predictable event if one considers the "ecosystem state".

The amount of oil incorporated into MOS depends on the <u>concentrations of both</u>, <u>oil and</u> <u>marine snow</u> (linear function).

Corexit disperses not only oil but also exopolymeric substances that play an important role for marine snow formation: Corexit may inhibit both types of MOS formation

Synthesis:

Oil compounds are incorporated into marine snow as *droplets and sorbed* to cells. Physicochemical properties of oil compounds largely determine the partitioning: Droplet incorporation is proportional to droplet concentration. Sorption is proportional to the aqueous concentration. Droplet incorporation is immediate, sorption takes > 1 day.

The relative timing of the encounter between marine snow, oil, and dispersant are essential in determining the formation of MOS and the incorporation of oil compounds into sinking MOS, but should be principally predictable

Biodegradation enhanced in MOS compared to dispersed or dissolved oil

Thank you!

for listening & for the invitation