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Analysis of Floating Oil Under UV Light at Different Environmental Conditions

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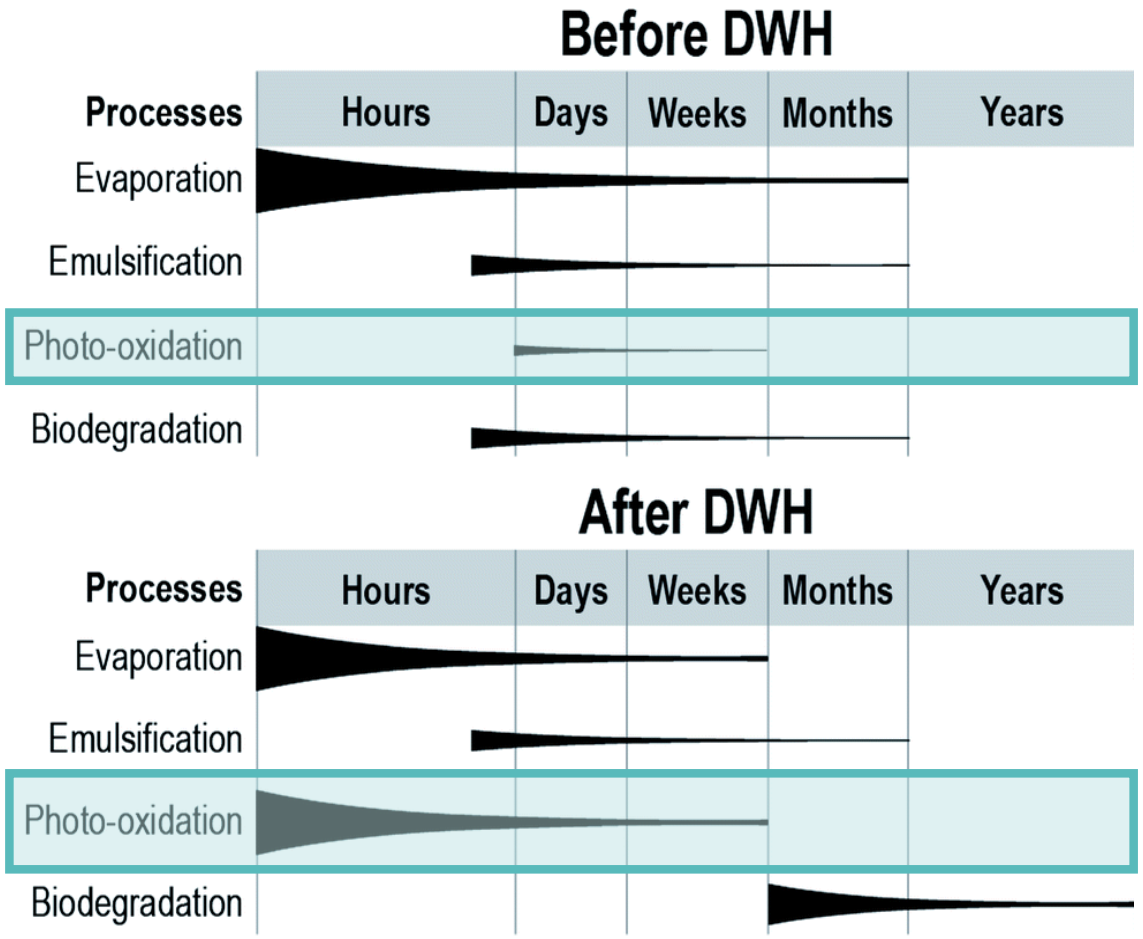
Introduction

- Recent shift in oil spill weathering paradigm
- Photo-oxidation still not well understood
  - Formation of oxygenated / more polar species
  - More soluble species?
  - What are these species?
- Lab studies show enhanced toxicity to estuarine organisms with thin oil sheens + UV exposure
- If we can better understand the photo-oxidation of oil, we can better understand the fate and transport of spilled oil in the environment



Ward and Overton 2020

Study Objectives

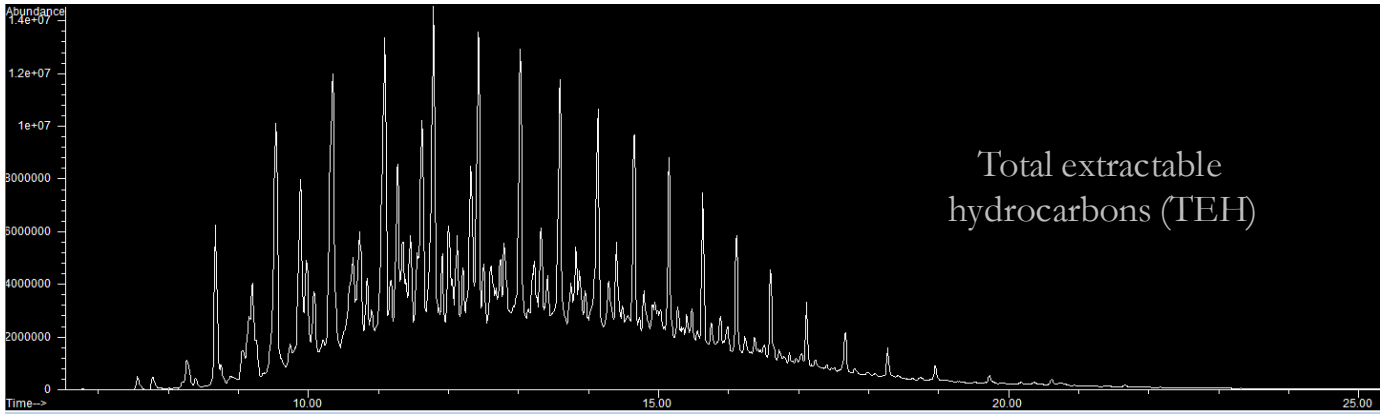
- How do the chemical and physical properties of oil change under different environmental conditions?
  - Ultraviolet Light (UV-A)
  - Temperature (10, 21, and 30°C)

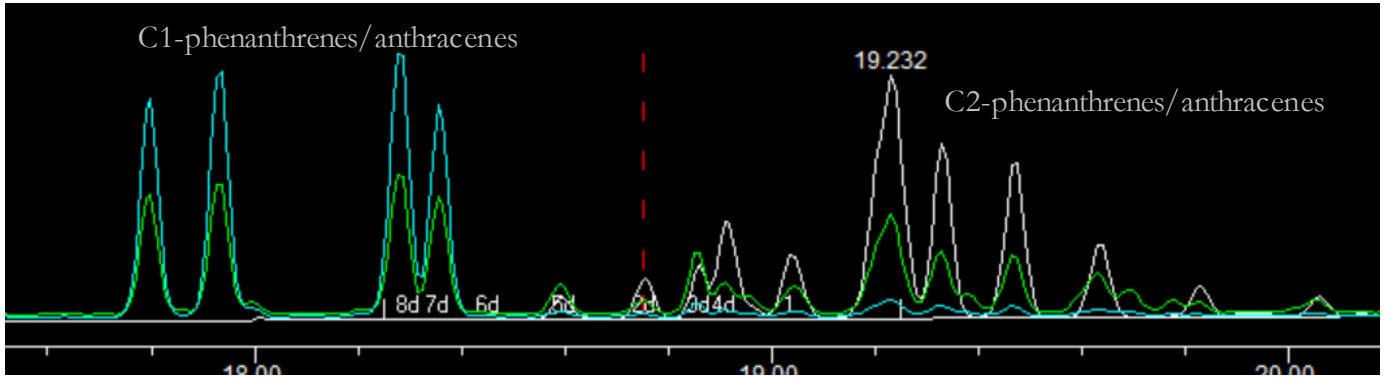
Methodology

- Environmental chamber
  - UV-A and fluorescent (no UV) light treatments
- 7 d test exposure; 12 h light / 12 h dark photoperiod
  - At 10, 21 and 30°C
  - Avg. UV intensity at 380nm: 0.058 ± 0.004 mW/cm^2 ≈ spring day in Southern US
- Oil (Louisiana Sweet Crude; LSC)
  - ~33 µm slick applied to 100 ml seawater, orbital shaker (70 rpm)
  - 3 reps/treatment/time point (oil + water)

Methodology

- Chemical / Physical measurements at 6h, 24h, 48h and 7d
- Photography (physical measurements)
- PAHs, TEH, hopanes / steranes (biomarkers)
    - L/L extraction + silica SPE, GC/MS





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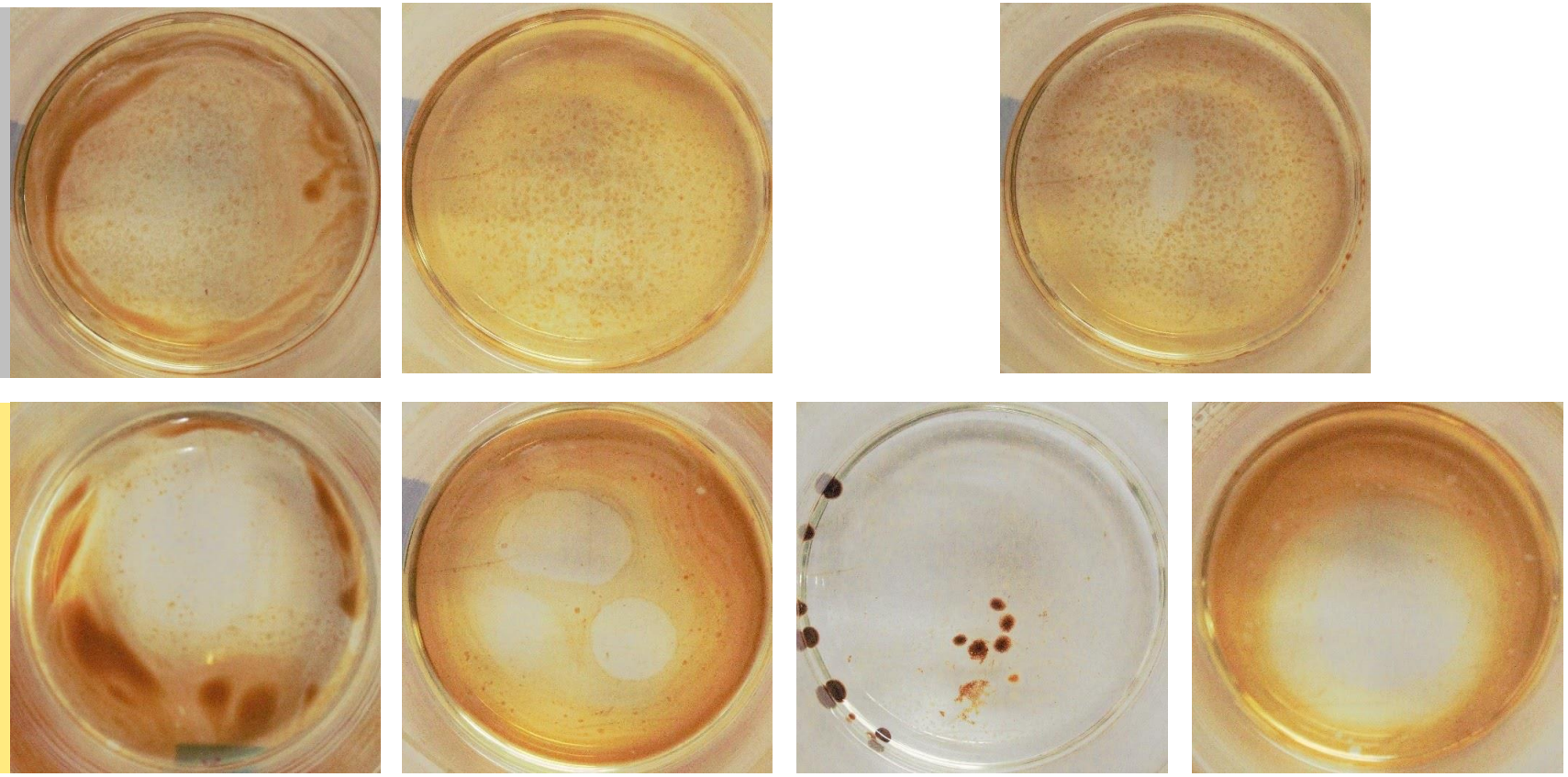
Results
10°C

No UV

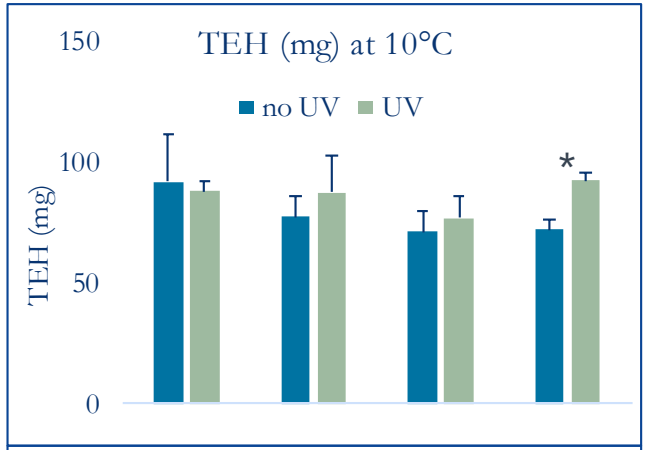
UV

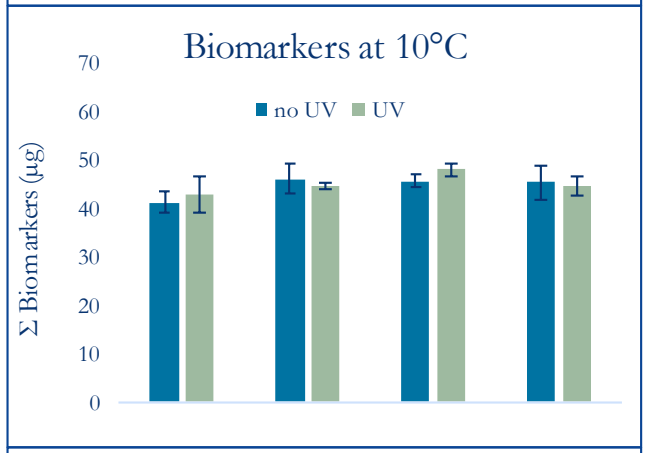


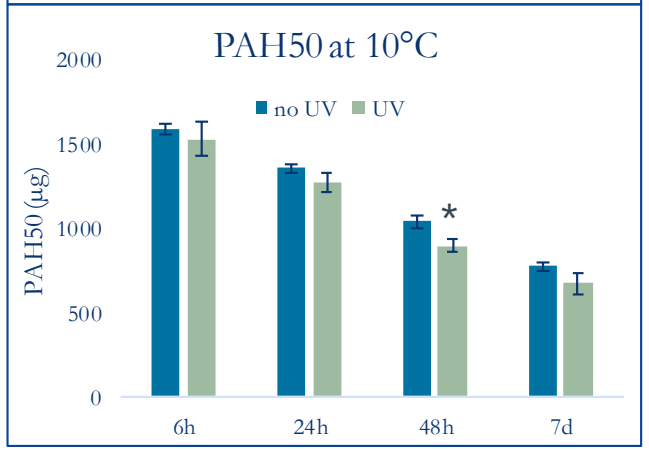
6 h

24 h

48 h







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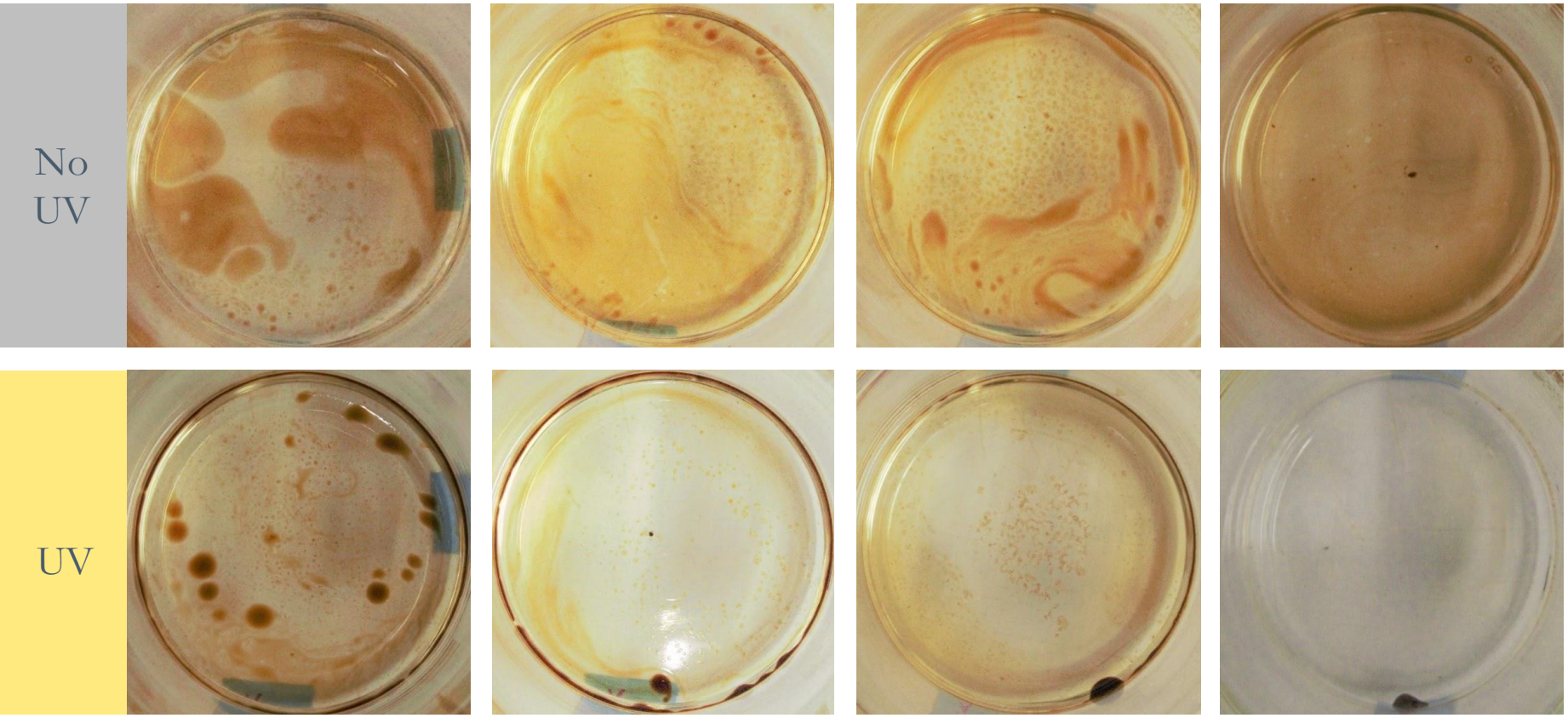
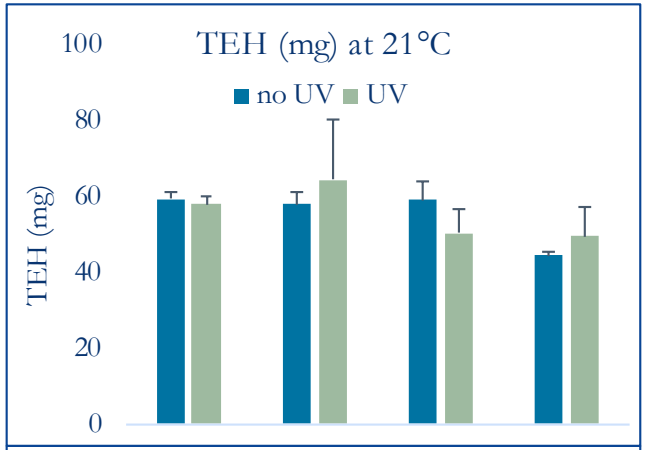
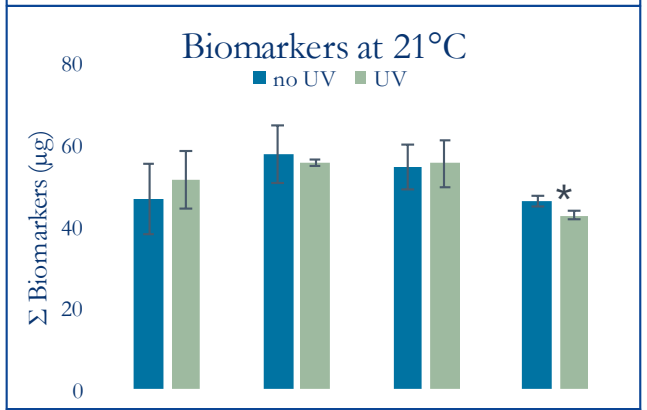
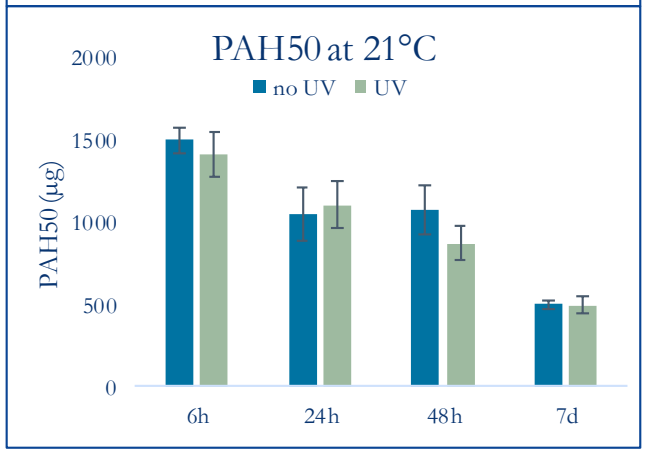
Results
21°C









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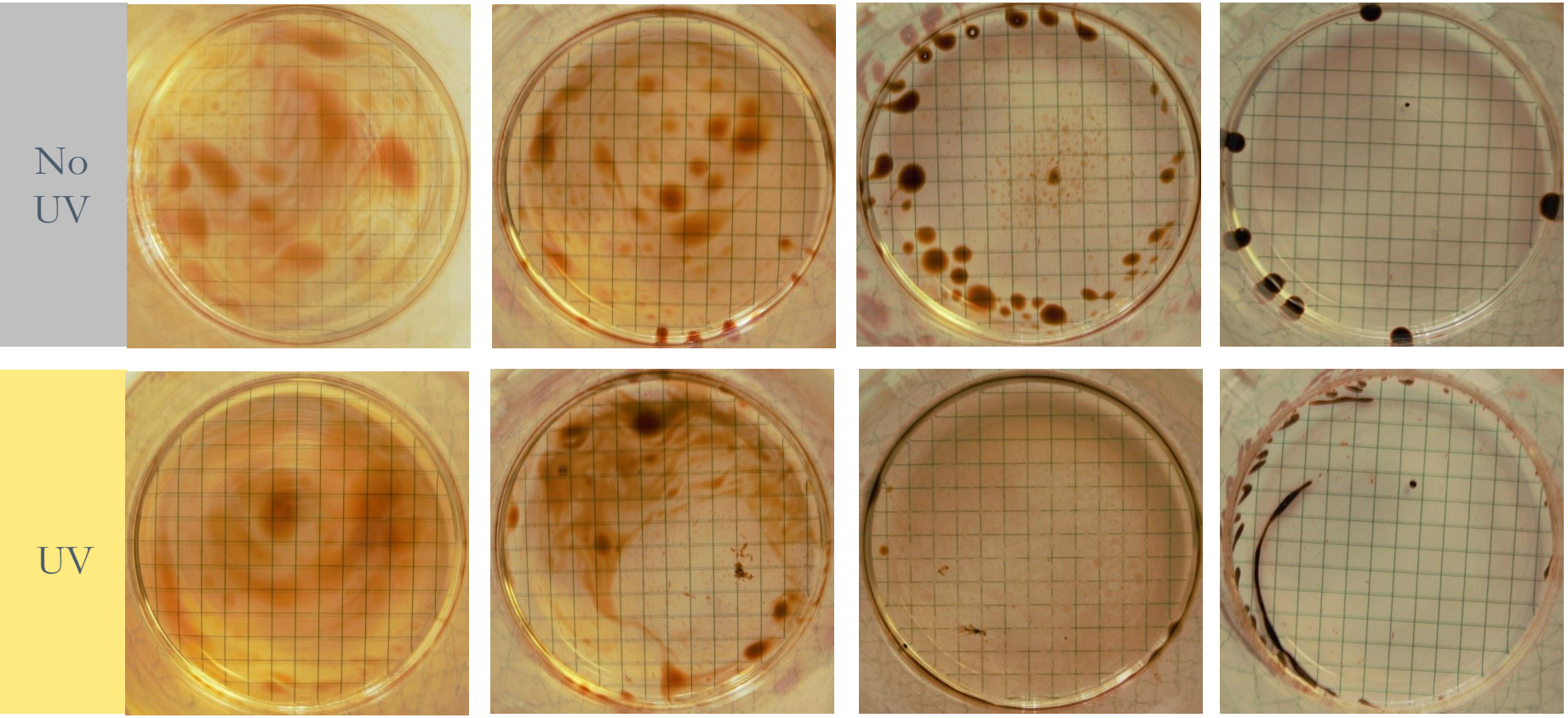
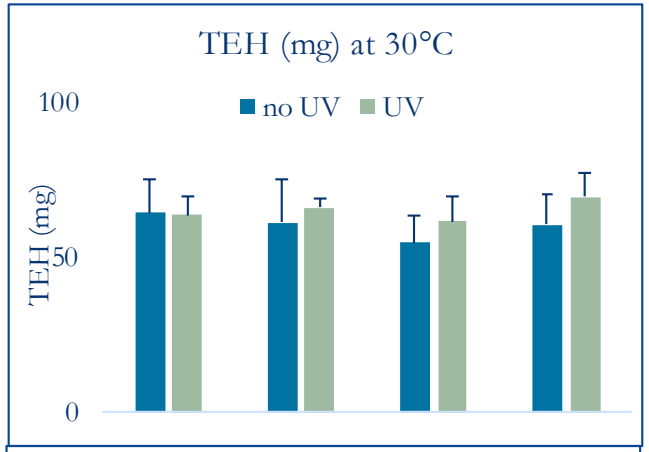
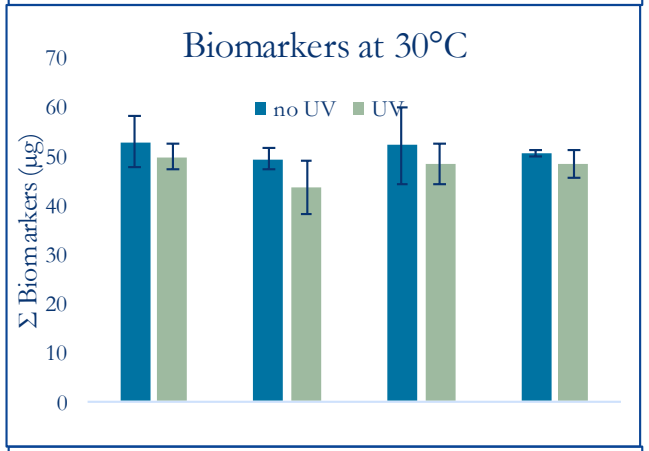
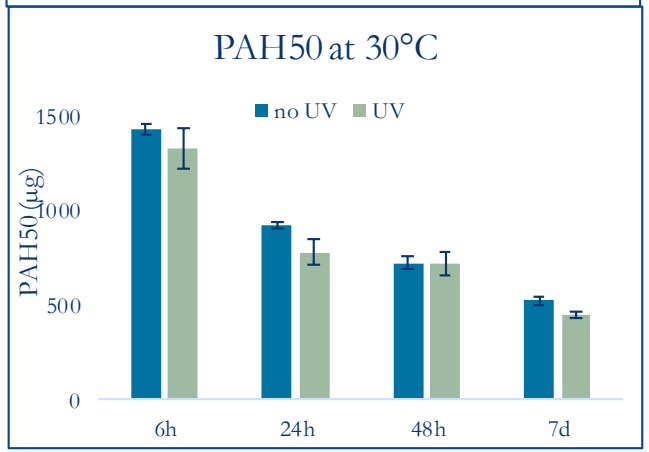
Results
30°C









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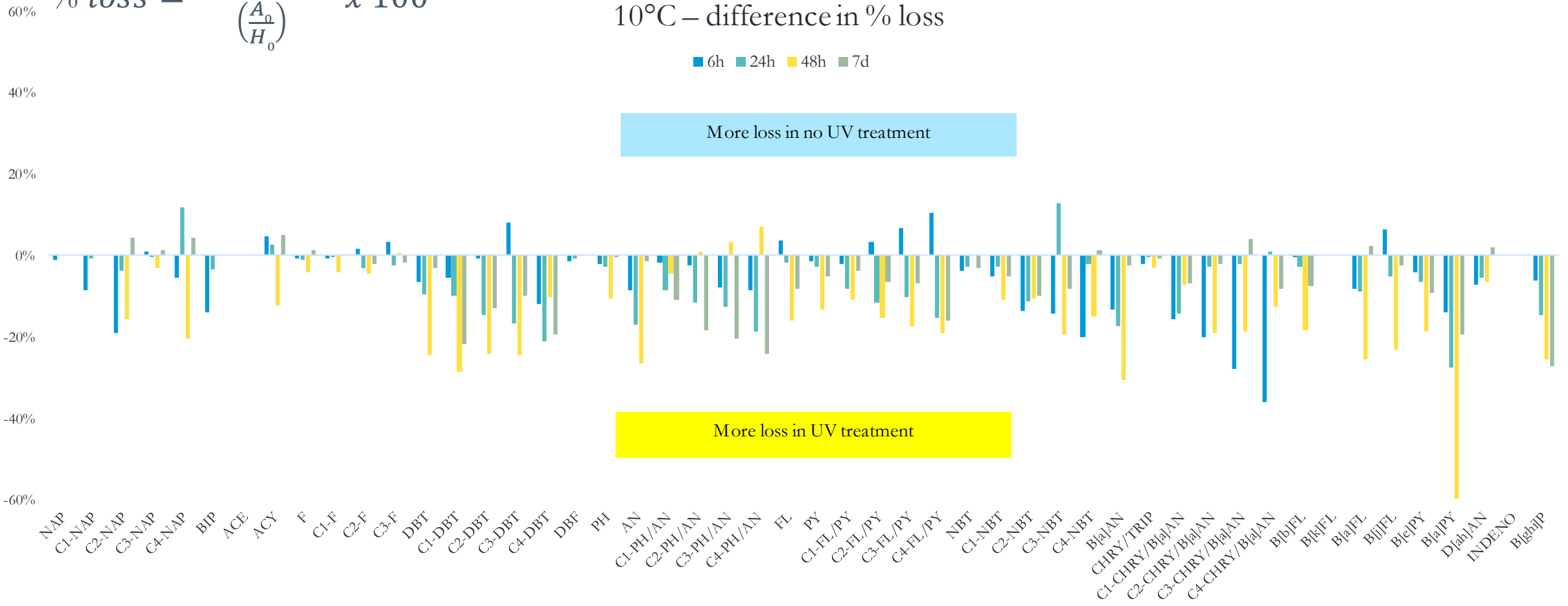
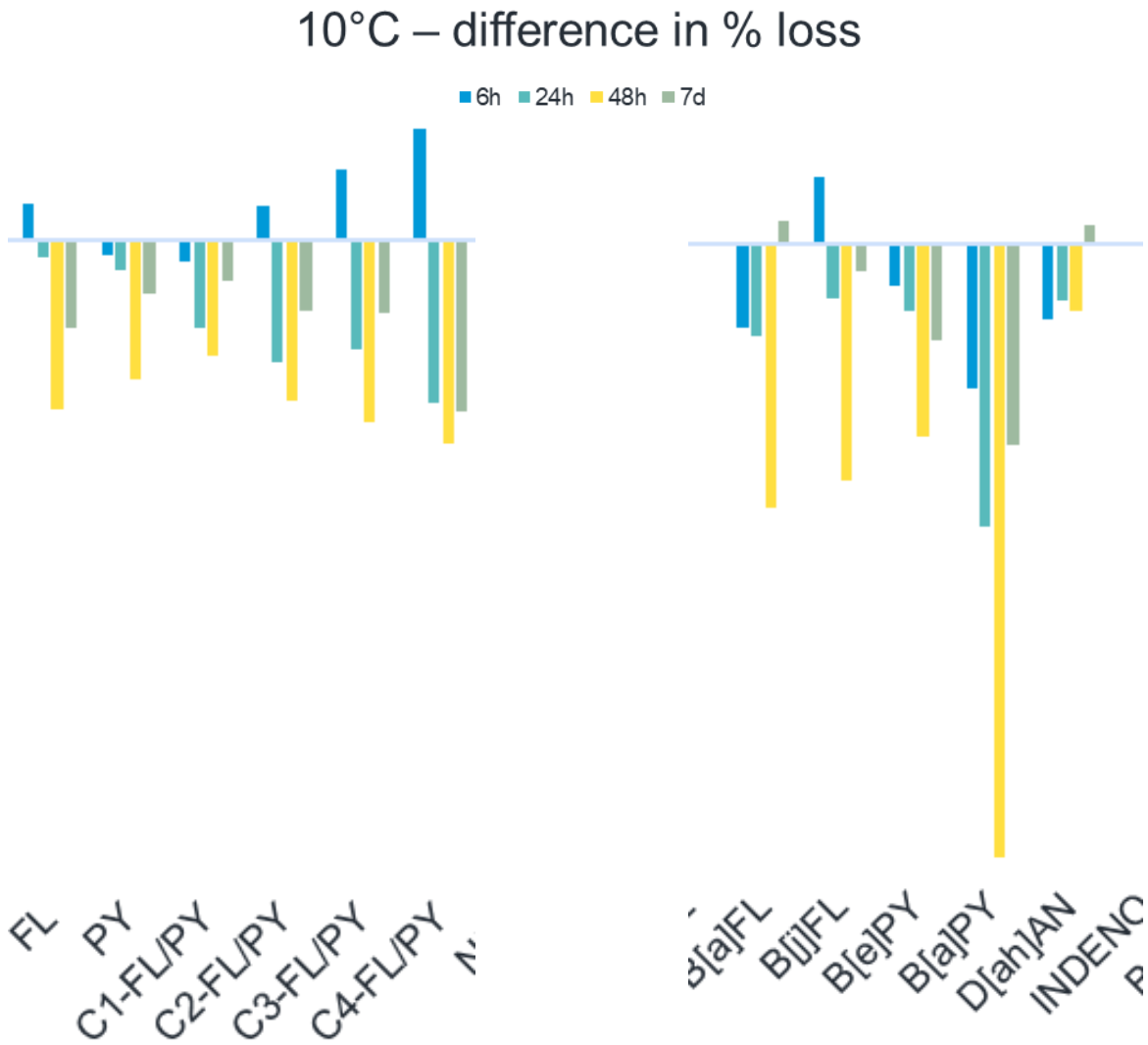
H_0 = 17α(H)21β(H)hopane concentration in fresh oil
A_0 = PAH concentration in fresh oil
H_t = 17α(H)21β(H)hopane concentration at desired time point/treatment
A_t = PAH concentration at desired time point/treatment

$$\% \; loss = \frac{\left[\left(\frac{A_0}{H_0}\right) - \left(\frac{A_t}{H_t}\right)\right]}{\left(\frac{A_0}{H_0}\right)} \; x \; 100$$

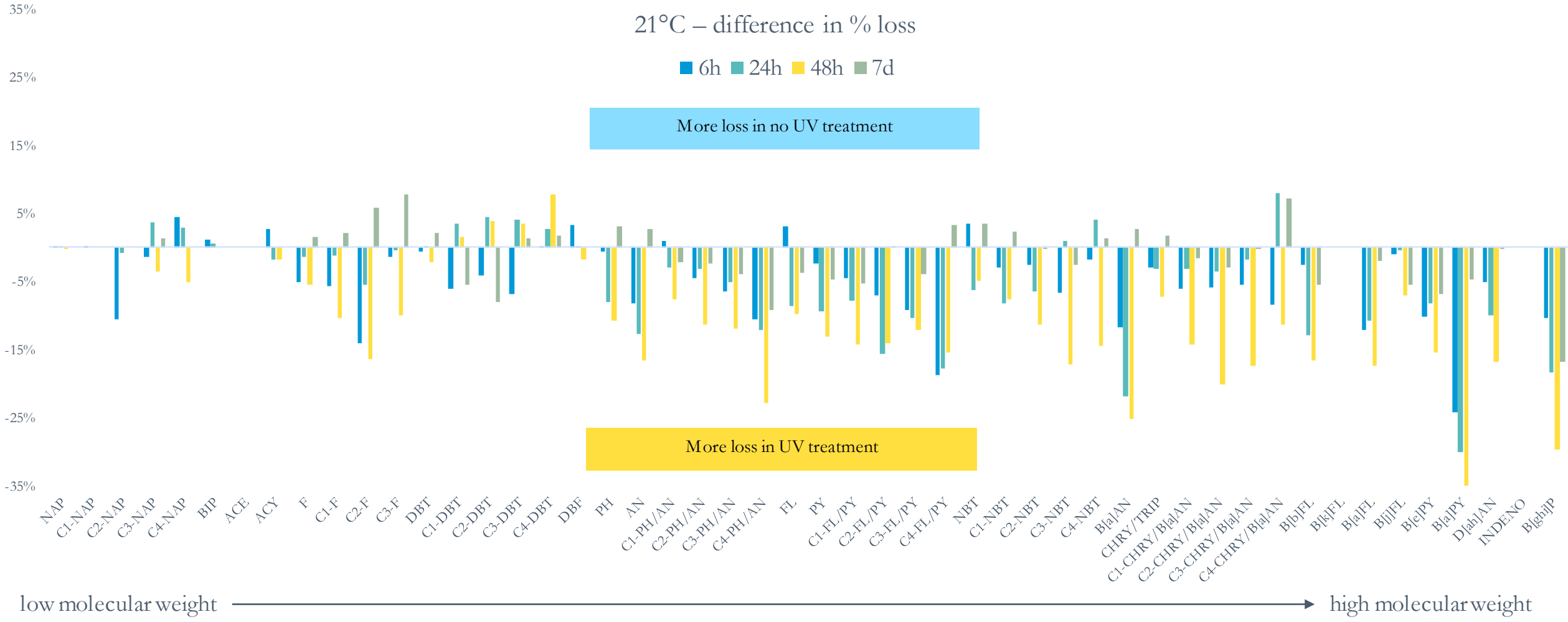


low molecular weight → high molecular weight

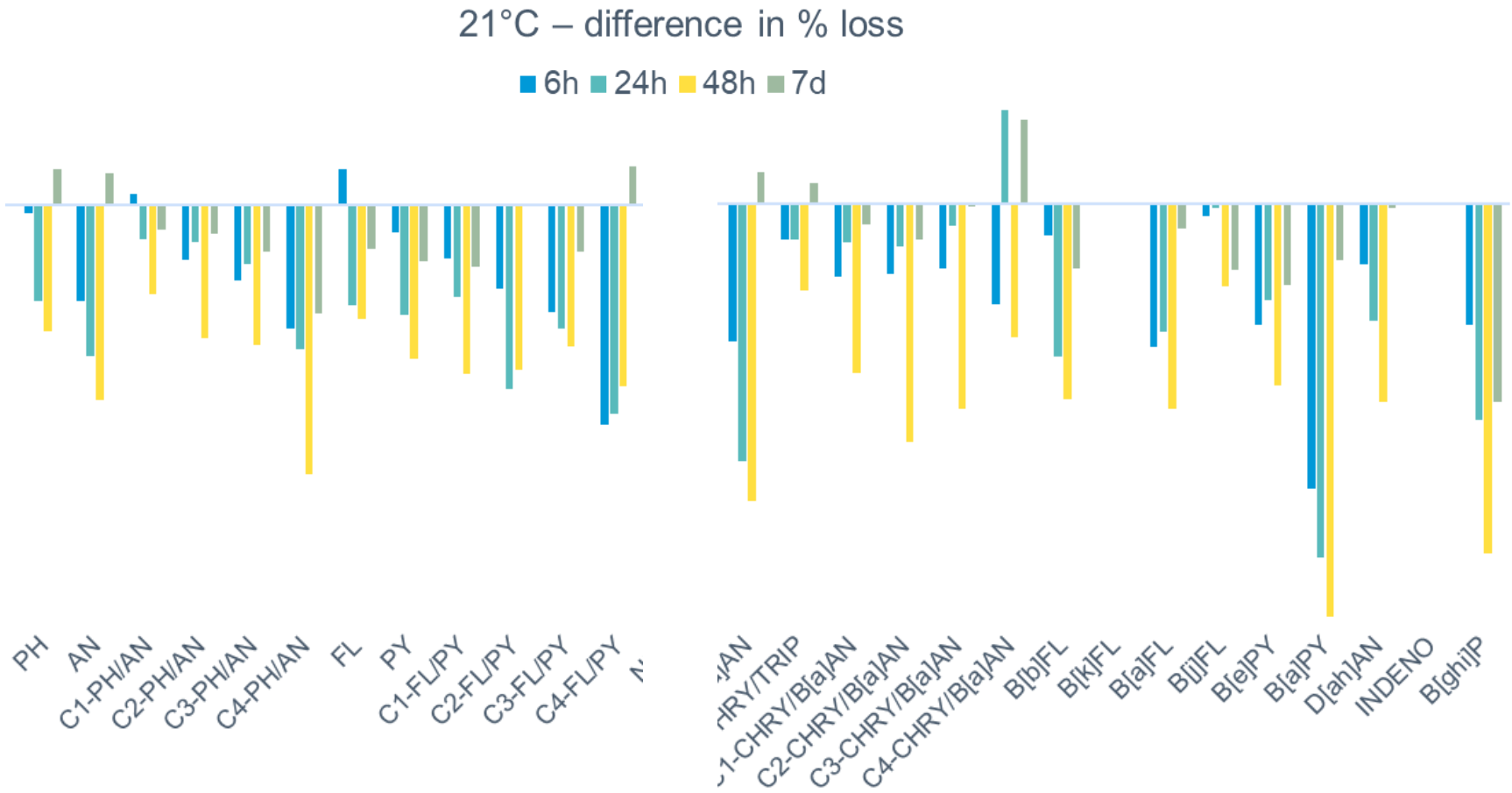


Note of interest

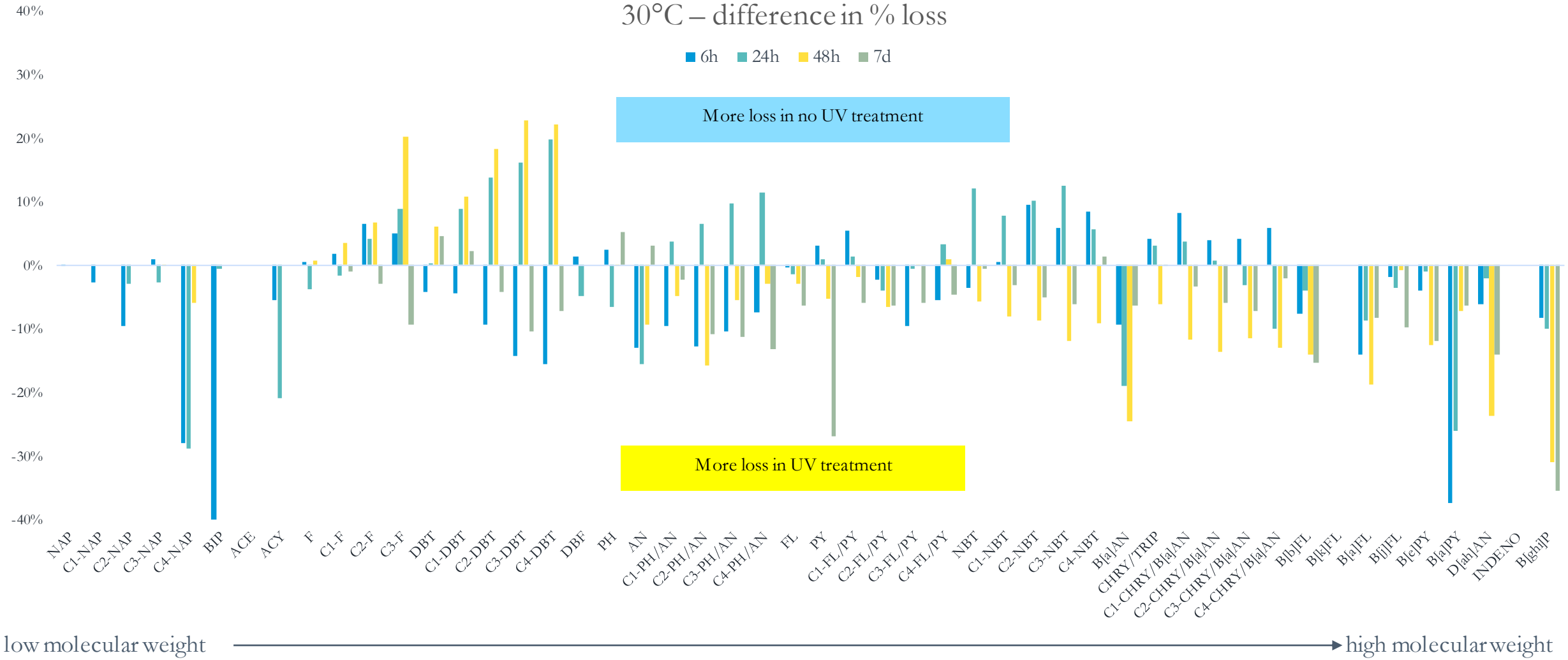
- The greatest difference in % loss tends to occur ~48h, not at 7d
- We think this may be related to when the tar ball forms in the UV treatment
- The tar ball has this "skin-like" feature surrounding it which likely slows weathering



low molecular weight → high molecular weight



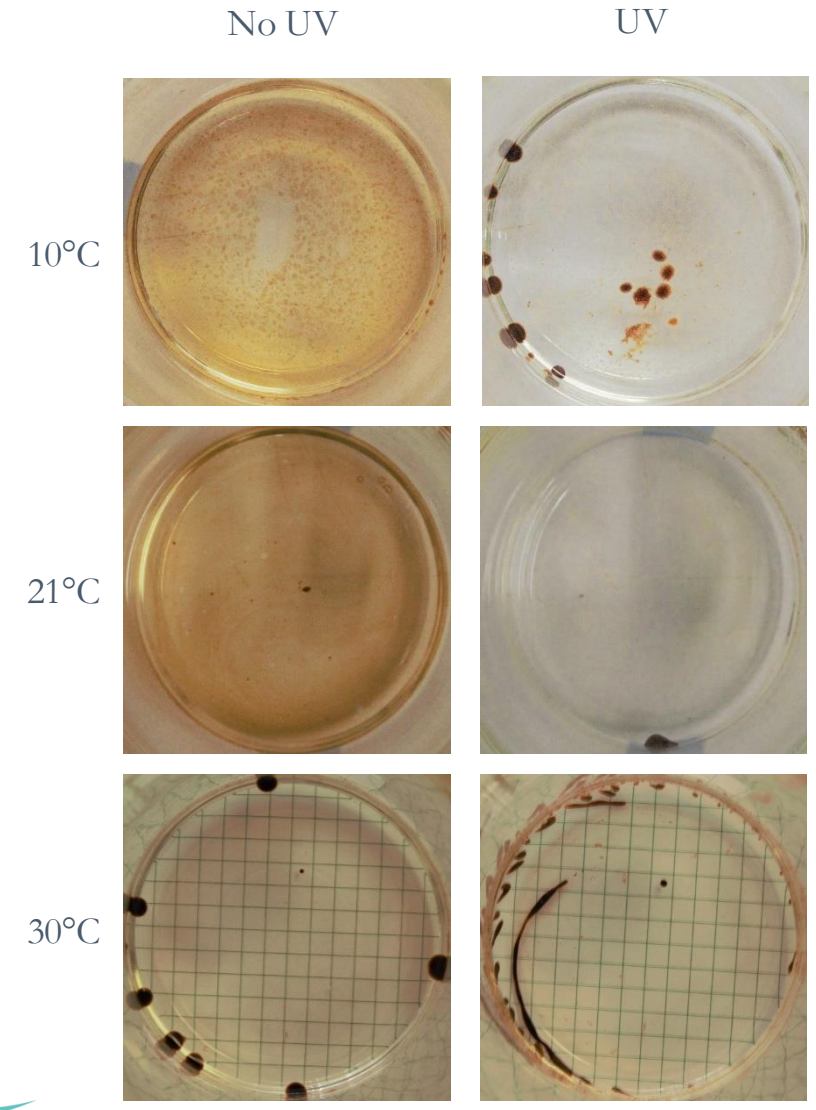
Again, we see similar trends in that the greatest difference in % loss occurs at 48h



low molecular weight → high molecular weight

Conclusions

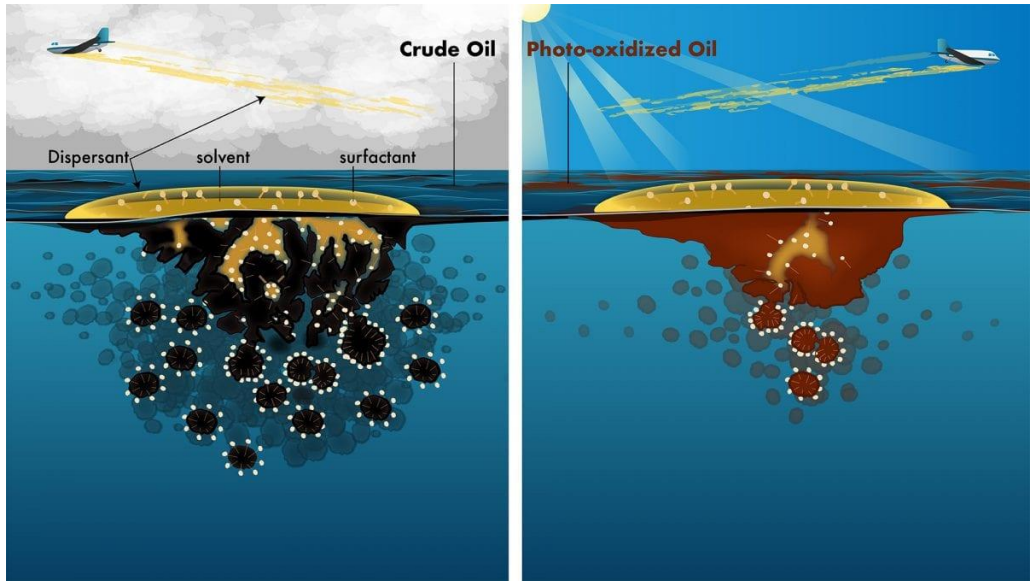
- UV light is a factor in tar ball formation
- Physical changes
  - UV → tar ball; no UV → sheen-like
- Chemical changes
  - TEH and Biomarkers: UV ≈ no UV
  - PAHs: high molecular weight / more alkylated PAHs affected by UV light
    - LSC oil composition ~1-2% PAHs; vast majority are low molecular weight



Future Directions

Additional Questions / Planned Experiments

- Does tar ball formation happen with other oil types?
  - Repeat exposure with Fuel Oil #2
- What products are being formed during photolysis?
  - Polar scans, non target analysis (LC-MS/MS, FTIR)
  - SARA analysis
- Does the time at which tar balls form differ between temperatures?
  - Add sampling time points 48 h – 7 d
  - Use ImageJ to analyze photos
- Does UV intensity affect tar ball formation?
- How do the bulk physical properties of oil change when exposed to UV light?
  - e.g., density, viscosity
- Is the chemistry of the underlying water changing?
  - pH, DO, chemical composition



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