

Analysis of Floating Oil Exposed to Ultraviolet Light Under Different Environmental Conditions: A Pilot Study



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Introduction

Upon release into the environment, oil is exposed to many weathering processes including photo-oxidation. The process of photo-oxidation has only recently become recognized as an important contributor to the breakdown of spilled oil. While research is limited on the products that are formed during photo-oxidation, it is thought that the transformation products are more polar and hence potentially more water soluble than their precursors. A more thorough understanding of how oil weathers via solar irradiation can help improve models that predict the fate and transport of oil during spills and enhance our understanding of cleanup/remediation techniques. The goal of this pilot study is to measure the chemical and physical changes that occur when oil is exposed to ultraviolet (UV) light at different temperatures and identify future

Methods

- Louisiana Sweet Crude (LSC) oil (200 µl) was pipetted as a surface slick onto 100 mL seawater in 600 mL beakers on an orbital shaker platform (70 rpm).
- Floating oil was exposed to either UV-A or fluorescent light (12h light/12h dark photoperiod, 7 day test duration); exposures were run at 21°C and 10° C.
- Average UV light intensity at 380nm: $0.058 \pm 0.004 \text{ mW/cm}^2$ Analyses were performed at 6h, 24h, 48h, and 7d.
- 3 reps/treatment/time point to analyze oil+water chemistry and 1 rep/treatment/time point to analyze water chemistry only
- Physical Changes \rightarrow Photography
- Chemical Changes \rightarrow Liquid/Liquid extraction + silica SPE fractionation
- Hydrocarbon fractions (biomarkers, total extractable hydrocarbons [TEH], polycyclic aromatic hydrocarbons [PAH]) via GC/MS, and polar fraction vis LC-MS/MS





These photos show the experimental setup for each exposure. The top left is floating oil under fluorescent (no UV) light, the bottom left is oil under UV-A light, and the top right photo shows the overall setup. Treatments were separated by hanging black plastic sheeting on all four sides. Overhead lights were turned off for the duration of the exposures.



Results

- Observed physical changes Oil in the UV light treatments formed tar ball-like substances within 7 days whereas oil in fluorescent (no UV) light treatments stayed more sheen-like (Figure 1) at both 21°C and 10°C.
- Measured chemistry Significant differences between fluorescent (no UV) and UV light treatments were only observed at select time points for measured hydrocarbon (PAH50, TEH, Σ Biomarker) concentrations (Figure 2).
 - \succ Student's t-test found significant differences in PAH50 concentrations at 24h/10°C (p=0.0172), TEH at 7d/10°C (p=0.0027), and Σ biomarkers at 7d/21°C (p=0.0196).
 - > Biomarker concentrations in both temperature exposures show an increasing trend over the duration of the exposure; it is unclear at this point in time why this is occurring.
- Percent changes in PAH50 composition over time at 21°C (Figure 3) show that mid to heavy molecular weight PAHs are degraded faster in the presence of UV light. At 10°C this trend is roughly observed but more variable.
- > Positive values in Figure 3 reflect a higher proportion of the PAH in the fluorescent (no UV) light treatment whereas negative values are indicative of a higher proportion in the UV light treatment
- PAHs only comprise $\sim 2\%$ of LSC oil, which is likely not responsible for the observed physical differences.... So what chemical change(s) are driving the observed physical differences?







Figure 1: From top to bottom, these are photos taken during the no UV (left)/UV (right) exposure at 21°C at 6h, 24h, 48h and 7d. One of the three replicates from each time point/treatment is shown. As previously noted, oil exposed to UV light (right) forms a tar ball-like substance within seven days while oil not exposed to UV light remains sheen-like (left).

Conclusions/Next Steps

Figure 2: Plotted hydrocarbon concentrations for no UV (fluorescent) versus UV treatments at each time point for exposures at 21°C (top) and 10°C (bottom). PAH50 is the sum of 50 parent and alkylated PAHs, TEH is a measurement of the total extractable hydrocarbons in the sample and Σ Biomarkers is a sum of 13 biomarker compounds (hopanes and steranes). "*" denotes a significant different observed between treatments at a time point using the Student's t-test. Error bars are one standard deviation.



48h

7d

- Exposure to UV light is a factor in tar ball formation. Measured chemistry from this study does not wholly support the observed physical changes.
- \triangleright Our next steps are to:
 - \blacktriangleright Run the 7 day exposure at 30°C
 - Analyze the "polar" fraction obtained from SPE, via FTIR and LC-MS/MS to characterize chemical compositional changes between fluorescent and UV light exposures
 - > Quantify the physical changes in the oil by measuring the surface area of the oil captured at each time point
 - Rerun exposures with a different oil (Fuel Oil #6)
- Follow-up questions include:
 - ➢ What chemical compositional changes are occurring during UV exposure that lead to tar ball formation?
 - ➢ How does the chemical composition of the water accommodated fraction change over time as floating oil is exposed to UV light?
 - How do the bulk physical properties of oil (e.g. density, viscosity) change under UV exposure?
 - > What is the relationship between UV intensity and tar ball formation?

Figure 3: Plotted percent (%) changes for PAHs at 21°C (top) and 10°C (bottom) with standard error bars for each time point. Analytes are plotted, from left to right, in the order of parents and their associated alkylated group from low molecular weight to high molecular weight. Positive values mean that the proportion of that PAH is higher in the no UV treatment while negative values mean that the PAH proportion is higher in the UV treatment for a time point.