INSIGHTS INTO THE ENVIRONMENTAL FATE OF PLASTICS FROM THE NATURAL CARBON CYCLE

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How long does plastic last in the environment?

Ward and Reddy, Unpublished; Review of 42 Informational Graphics (N = 158)
Direct and Indirect Photo-oxidation

1. Direct Photo-oxidation

2. Indirect Photo-oxidation

Partial Photo-Oxidation to Plastic_{OX}

Complete Photo-Oxidation to CO_{2}
Photochemical $O_2:CO_2$ as a diagnostic indicator

**Photochemical $O_2$ consumption or $CO_2$ production**

**Plastic B** is more susceptible to partial photo-oxidation than **Plastic A**

Ward et al., 2014, 2017, 2018, 2019; Cory et al., 2014; Ward and Cory 2016,

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“Polystyrene can take up to thousands of years to decompose”

“numerous heterogeneous microbial communities failed to affect biodegradation of the plastic tested.” Kaplan et al., 1979
Additives Impact Optical Properties

The graph shows the absorption coefficient (m⁻¹) for different additives across the ultraviolet and visible light spectrum. The x-axis represents the wavelength in nanometers (nm). The y-axis represents the absorption coefficient. The graph compares the performance of Goodfellow, Sigma 35K, Sigma 192K, Trycite 8001, and Trycite 8003 additives. The graph highlights the impact of additives on optical properties in both the ultraviolet and visible regions of the spectrum.
“It is only with the intervention of microorganisms that the polymer will start to break down into its component elements.”
GESAMP 2019

Exposure times equivalent to ≤ one-week at mid-latitudes.
More Light, More Mineralization to CO$_2$
Radiocarbon dating is limited to 50,000 yrs or so..” Libby (1967)

\[ T_{1/2} \left( ^{14}C \right) = 5730 \text{ years} \]
Sunlight Converts Polystyrene Into CO$_2$

- Experiment conducted in triplicate; error bars smaller than symbol
- Exposure times equivalent to ≤ one-week at mid-latitudes

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Lifetimes of photomineralization are on centennial timescales. Lifetimes average 300 to 400 years for complete mineralization of polystyrene into CO₂ by sunlight.
Photochemical production of dissolved inorganic carbon from terrestrial organic matter: Significance to the oceanic organic carbon cycle

William L. Miller and Richard G. Zepp
Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia

“This important process is not included in earlier estimates of photochemical conversions in natural waters and implies that the residence time for terrestrial carbon in the ocean is notably shorter than previously proposed.”
Partial Oxidation is the Dominant Fate

Exposure times equivalent to < one-week at mid-latitudes
More Light, More Dissolved Organic Carbon

Lifetimes of partial photo-oxidation occur on decadal timescales.

Operationally defined at 0.7 µm
“Plastic fragments will have similar structural properties as larger items of the same polymer.”
GESAMP 2019
Photodissolution of particulate organic matter from sediments

Lawrence M. Mayer, Linda L. Schick, and Krysia Skorko
School of Marine Sciences, University of Maine, Walpole, Maine 04573

Emmanuel Boss
School of Marine Sciences, University of Maine, Orono, Maine 04469

“These results point to a heretofore ignored role for photodissolution of particulate organic matter at the Earth’s surface.”
Mayer et al., 2006
We assume that visible light is irrelevant.

“Fragmentation will occur if plastics are subject to UV radiation”
GESAMP 2019
Additives can drive oxidation by visible light.
10x more Vis Light, 10x greater depth penetration
“Visible light was the principal contributor to POM based CO photoproduction.”
Song et al., 2015
Conclusions

1. Sunlight exposure appears to be a governing control of the environmental persistence of polystyrene.

2. Photochemical oxidation is a viable pathway for the mineralization of polystyrene.

3. Fragmentation is more complicated than Large $\rightarrow$ Small
   - Transformation to water and gas phase products

4. Additives can accelerate oxidation by expanding reactivity into the visible region.

5. Leveraging knowledge from the natural carbon cycling will help us understand the fate of plastics in the environment.
GUIDELINES FOR THE MONITORING AND ASSESSMENT OF PLASTIC LITTER IN THE OCEAN
Plastic fragmentation

Most conventional plastics will persist in the marine environment for a considerable time. Fragmentation will occur if plastics are subject to UV radiation, causing the surface to become brittle, and physical abrasion, such as on exposed shorelines or at the sea surface (GESAMP 2015). If plastics are deposited on the seafloor or buried in sediments then they are likely to remain intact indefinitely. Plastic fragments will have similar structural properties as larger items of the same polymer. It is only with the intervention of microorganisms that the polymer will start to break down into its component elements. This is an extremely slow process in the ocean, even for polymers that may be marketed as ‘biodegradable’. A fuller discussion on biodegradable and compostable materials can be found in (UNEP 2015).

GESAMP 2019
How long does plastic last in the environment?

- Plastic Straw (10) lasts 3 years
- Styrofoam Cup (26) lasts 4 years
- Fishing Line (17) lasts 17 years
- Disposable diaper (28) lasts 28 years
- Plastic Bag (39) lasts 39 years
- Six Pack Ring (7) lasts 7 years
- Plastic Bottle (39) lasts 39 years

Reported Environmental Lifetimes

Review of 42 informational graphics (N = 158)
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GESAMP 2019
We Need Algorithms to Incorporate Photochemistry into Global Fate Models

\[
\text{Photo-oxidation} \ (\text{mol PRODUCT m}^{-2} \text{ d}^{-1}) = \int_{280}^{700} \Phi_\lambda \times R_{a\lambda} \ d\lambda
\]

How efficiently is plastic altered by light?
\(\Phi_{PO,\lambda}\) Apparent quantum yield: mol of PRODUCT per mol of photons absorbed

How much light does plastic absorb?
\(R_{a\lambda}\) Rate of light absorption: mol photons absorbed by plastic

\[
R_{a\lambda} \ (\text{mol photons m}^{-2} \text{ d}^{-1} \text{ nm}^{-1}) = E_{ds\lambda} \left(1 - e^{-K_{d\lambda}z}\right)
\]

How much light is available at the sea surface?
\(E_{ds\lambda}\) Downwelling scaling irradiance: mol of photons m\(^{-2}\)

How strongly does plastic absorb light?
\(K_{d\lambda}\) Light attenuation coefficient of plastic: m\(^{-1}\)

How thick is the plastic particle?
\(z\) Pathlength: m

Woods Hole Oceanographic Institution
Why does partial photo-oxidation matter?

- Impacts to the marine plastic budget
  - Gas- and aqueous-phase products omitted from budget (Khaled et al., 2018, Gerwet et al., 2018)
  - Lability to microbial respiration unknown
Testing the photo-reactivity of polystyrene

- 5 polystyrene sources varying in composition

- Measurements of:
  - Light absorption spectra
  - Partial and complete photo-oxidation
  - Wavelength and Temperautre dependence

WHOI/MIT Joint Program Grad Student Anna Walsh Characterizing Optical Properties of Plastic Films