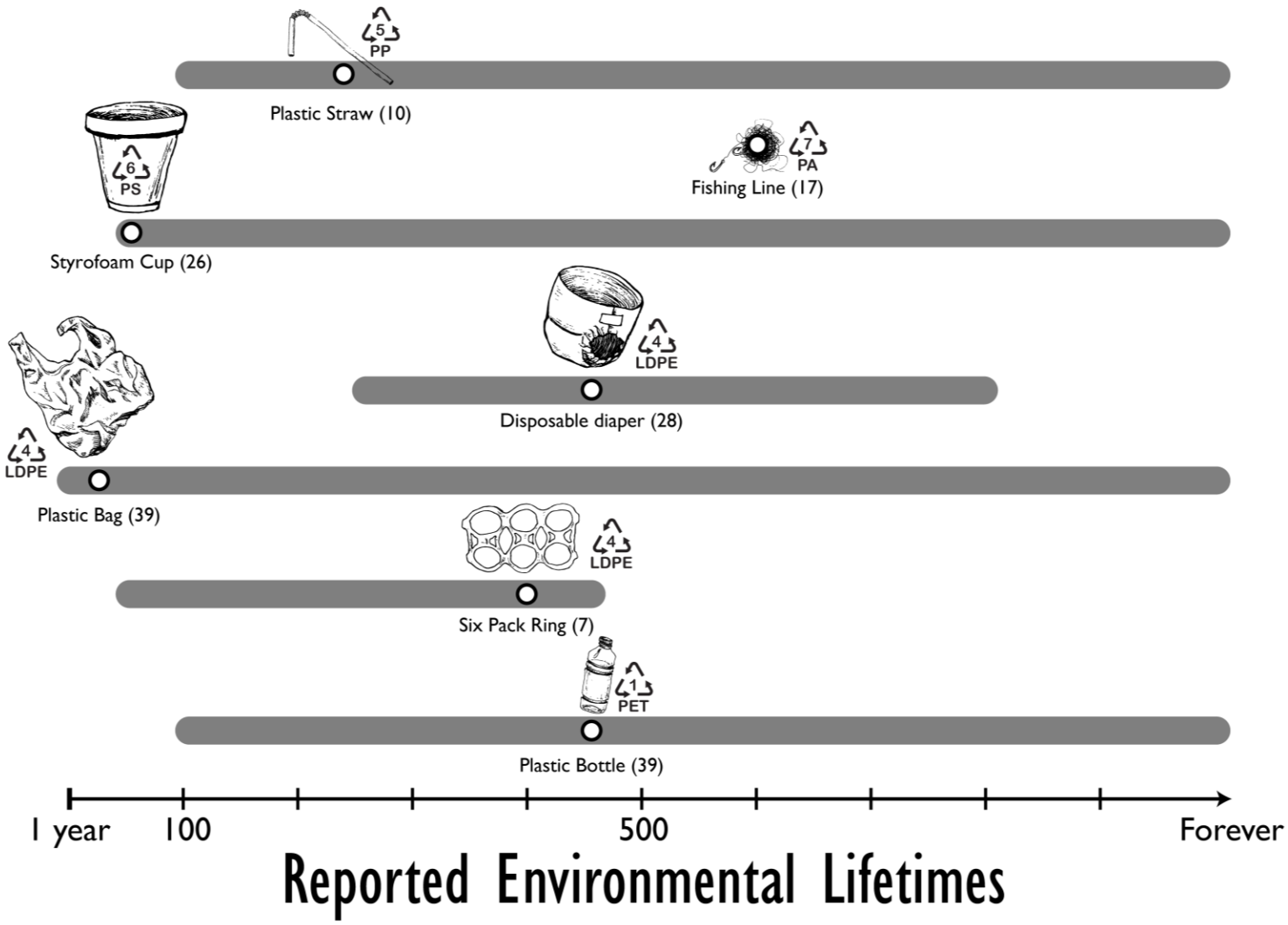
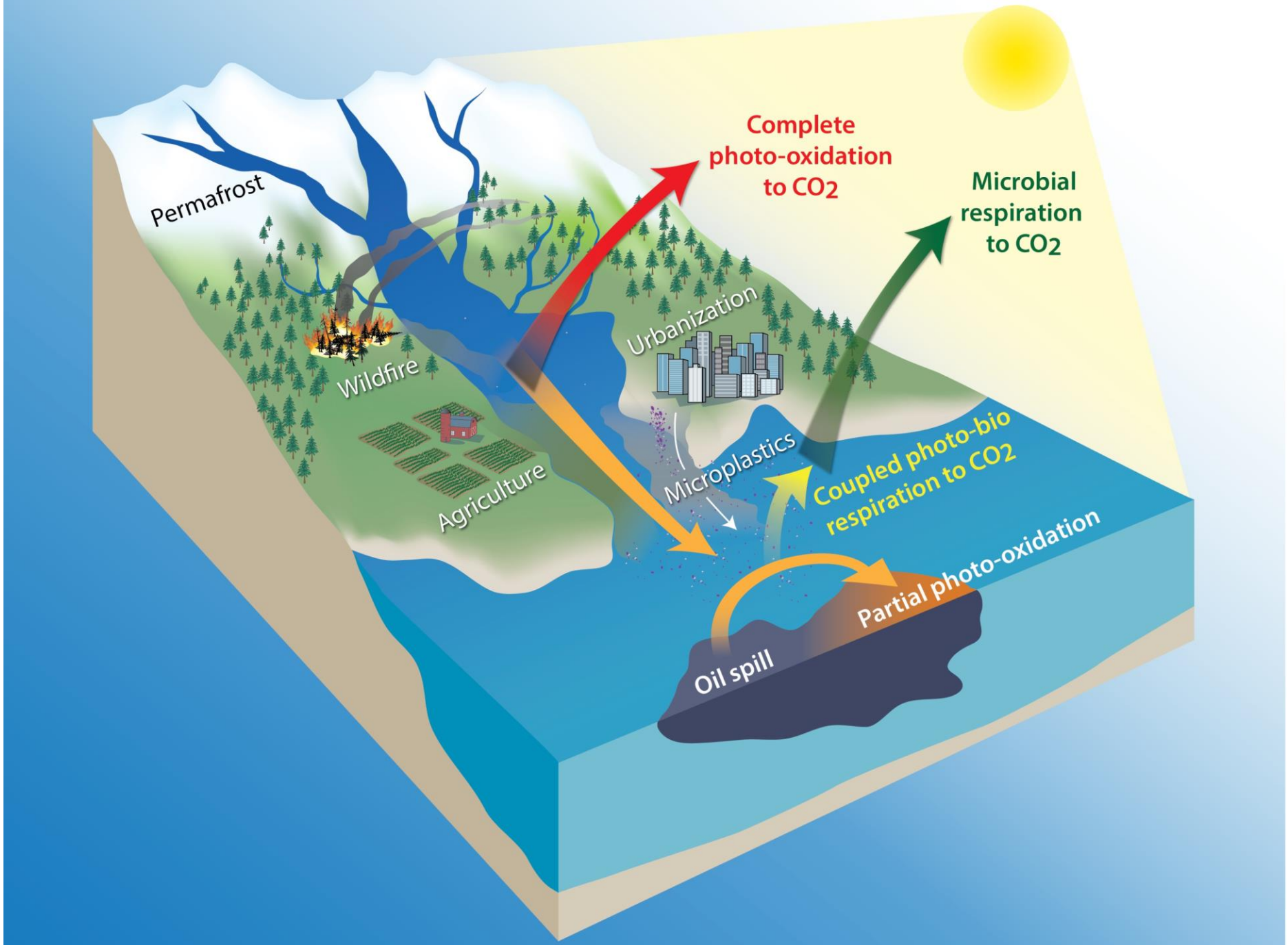
INSIGHTS INTO THE ENVIRONMENTAL FATE OF PLASTICS FROM THE NATURAL CARBON CYCLE

Collin Ward, Marine Chemistry & Geochemistry
Woods Hole Oceanographic Institution

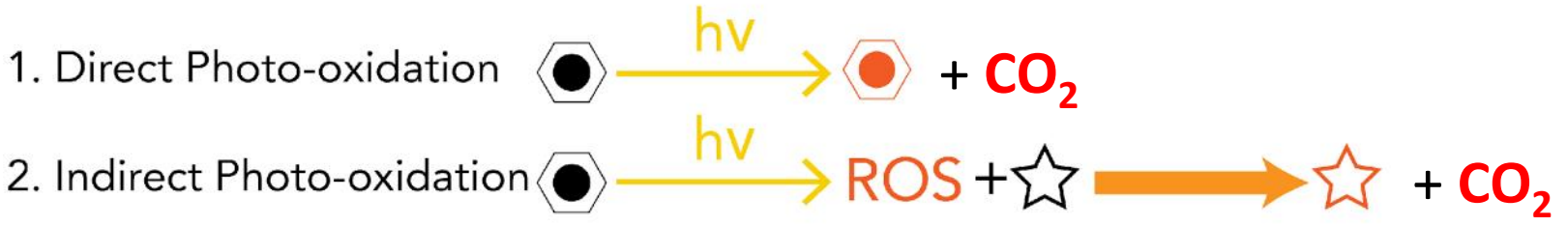
How long does plastic last in the environment?



Ward and Reddy, Unpublished; Review of 42 Informational Graphics (N = 158)

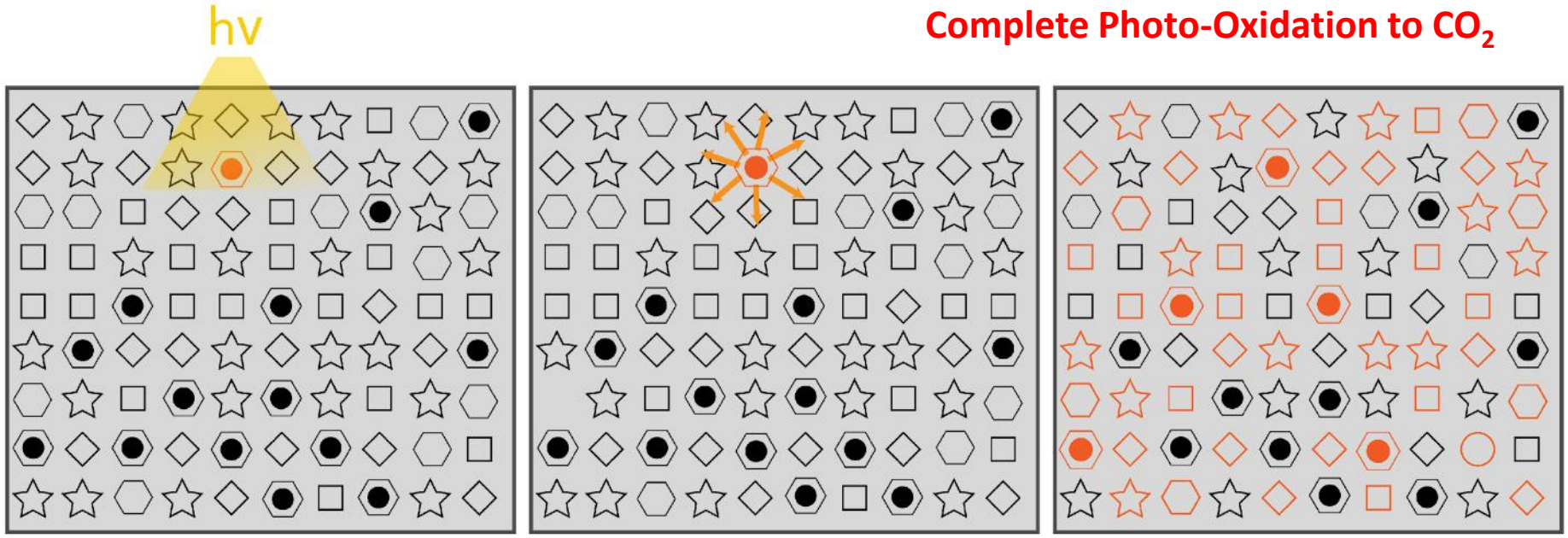

Permafrost
Wildfire
Agriculture
Urbanization
Microplastics
Complete photo-oxidation to CO_2
Microbial respiration to CO_2
Coupled photo-bio respiration to CO_2
Partial photo-oxidation
Oil spill

Direct and Indirect Photo-oxidation



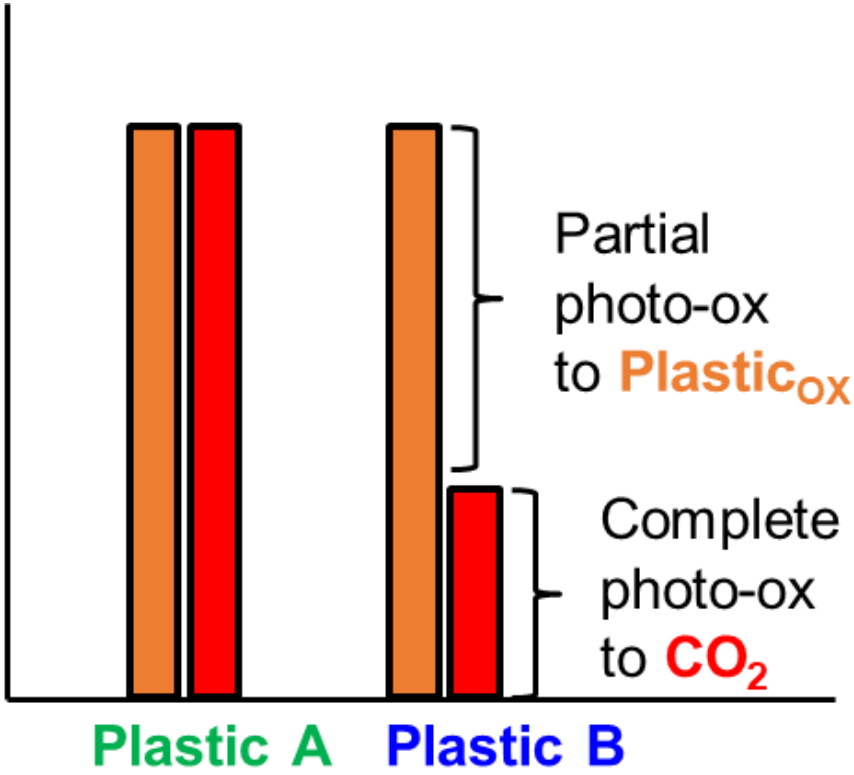
Partial Photo-Oxidation to $Plastic_{OX}$

Complete Photo-Oxidation to CO_2



Photochemical O_2:CO_2 as a diagnostic indicator

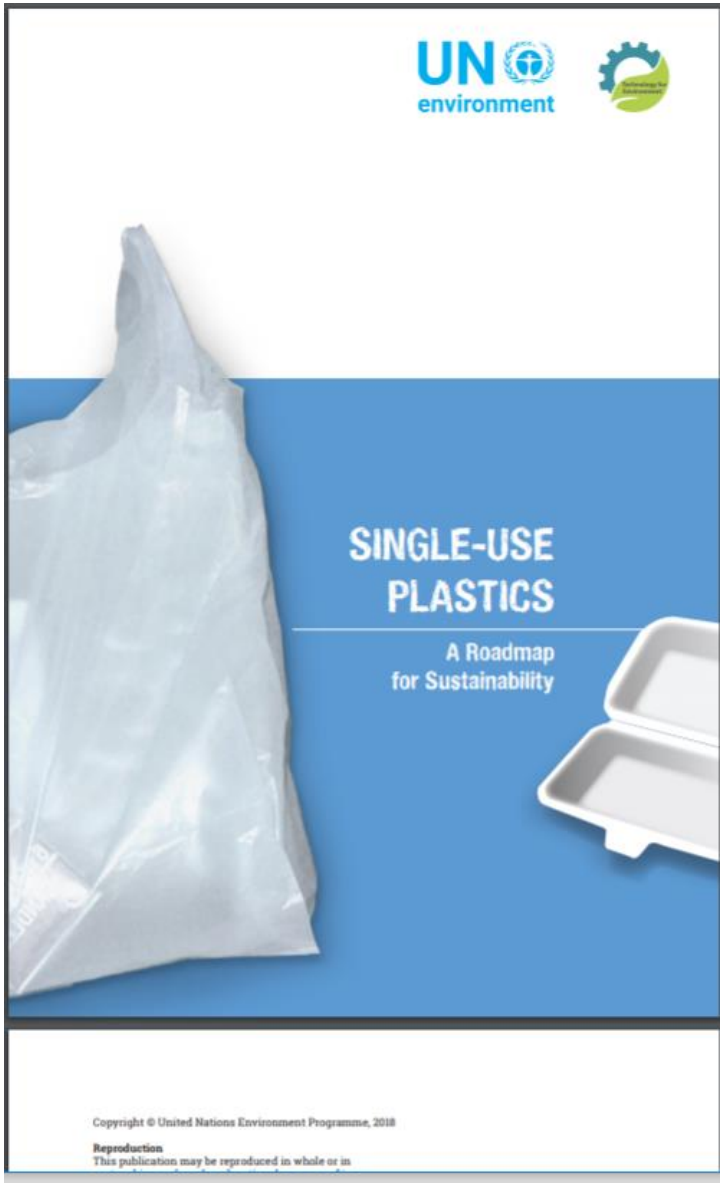
Photochemical
O_2 consumption
or
CO_2 production



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

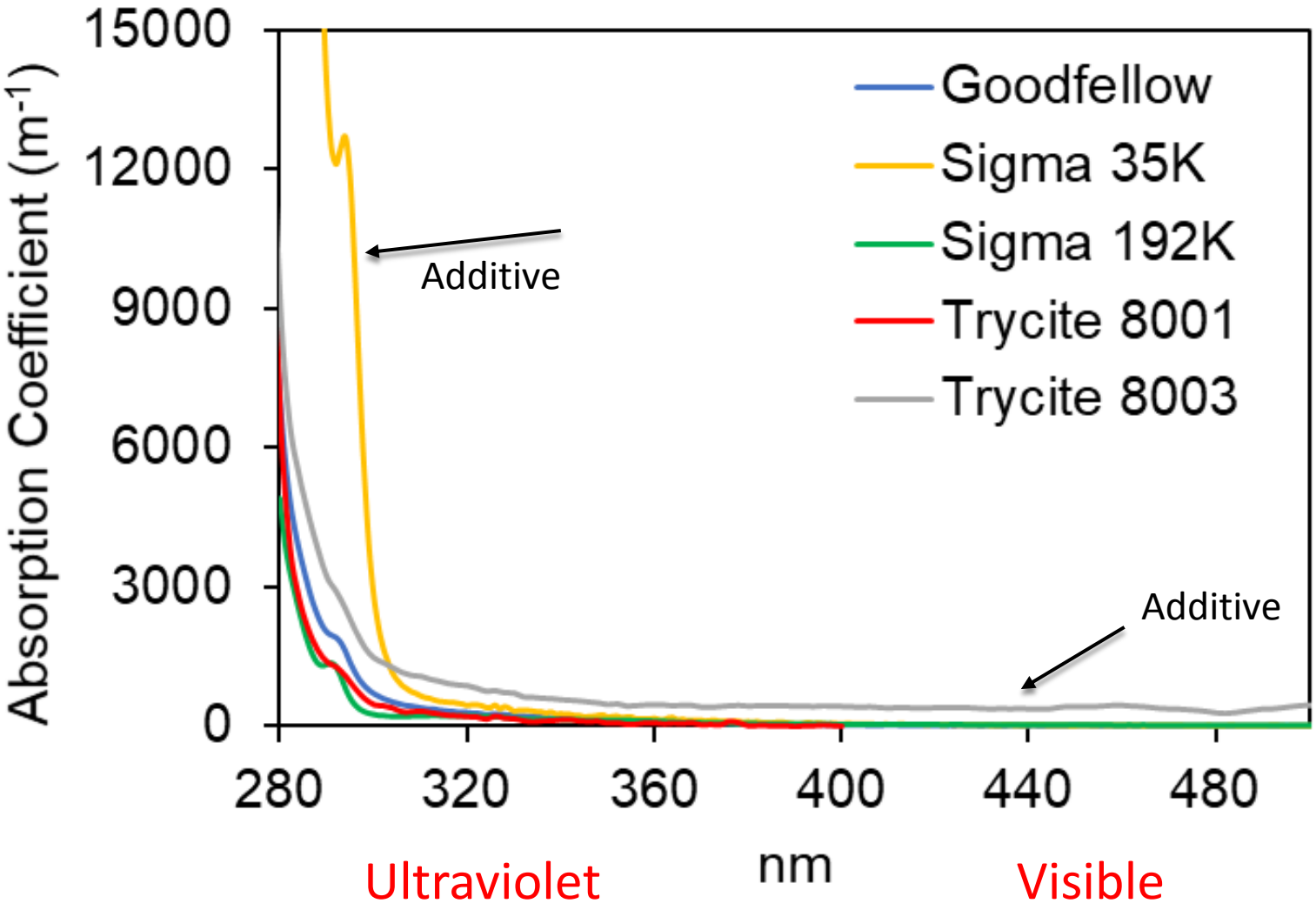
Ward et al., 2014, 2017, 2018, 2019;
Cory et al., 2014;
Ward and Cory 2016,

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



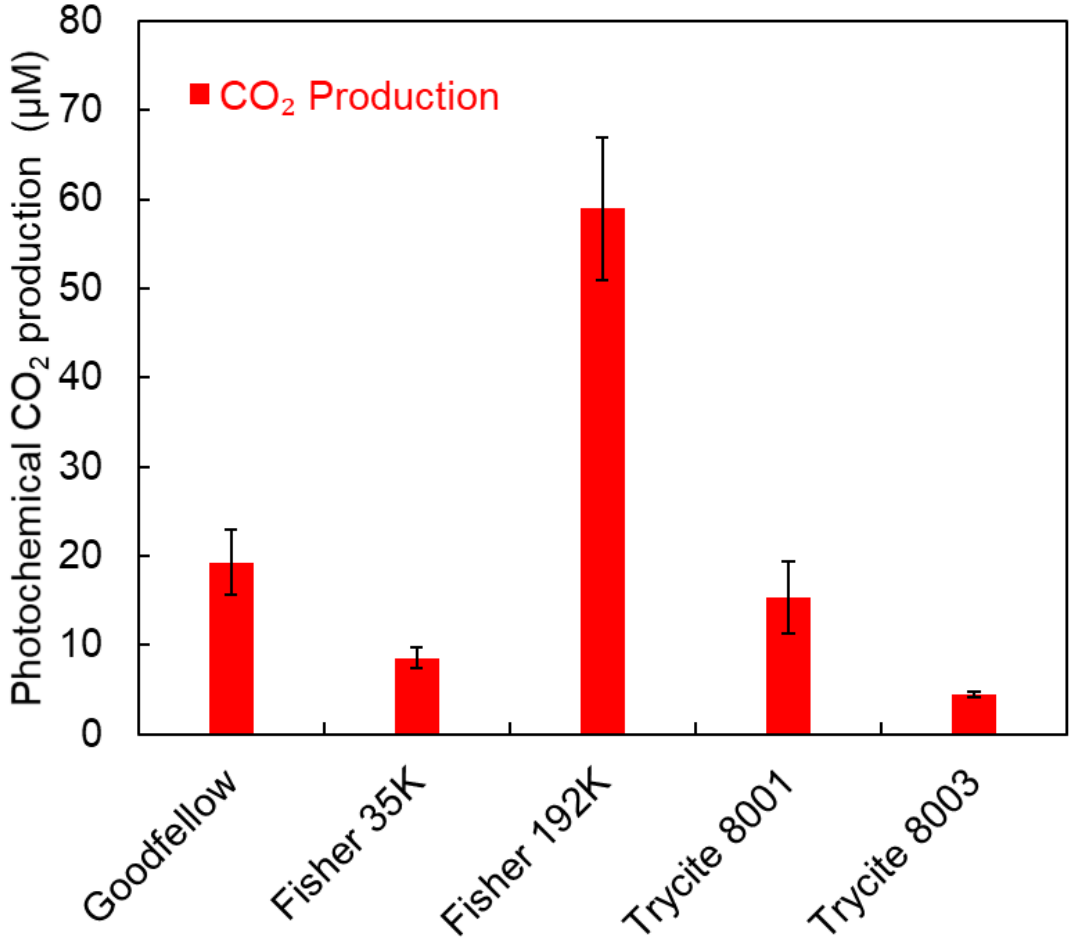
“numerous heterogeneous microbial communities failed to affect biodegradation of the plastic tested.” Kaplan et al., 1979

Additives Impact Optical Properties



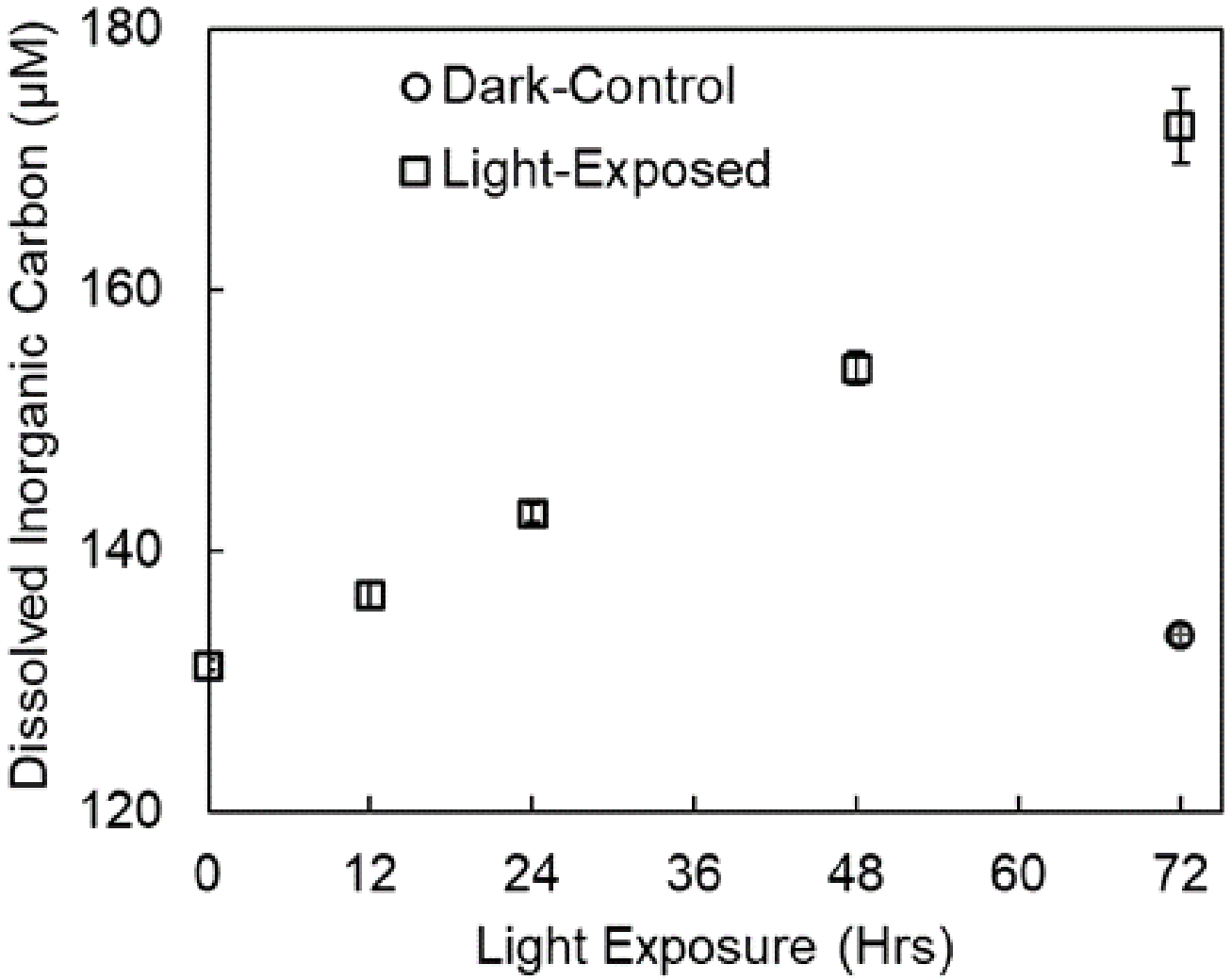
Five Sources, All Converted to CO_2

"It is only with the intervention of microorganisms that the polymer will start to break down into its component elements."
GESAMP 2019

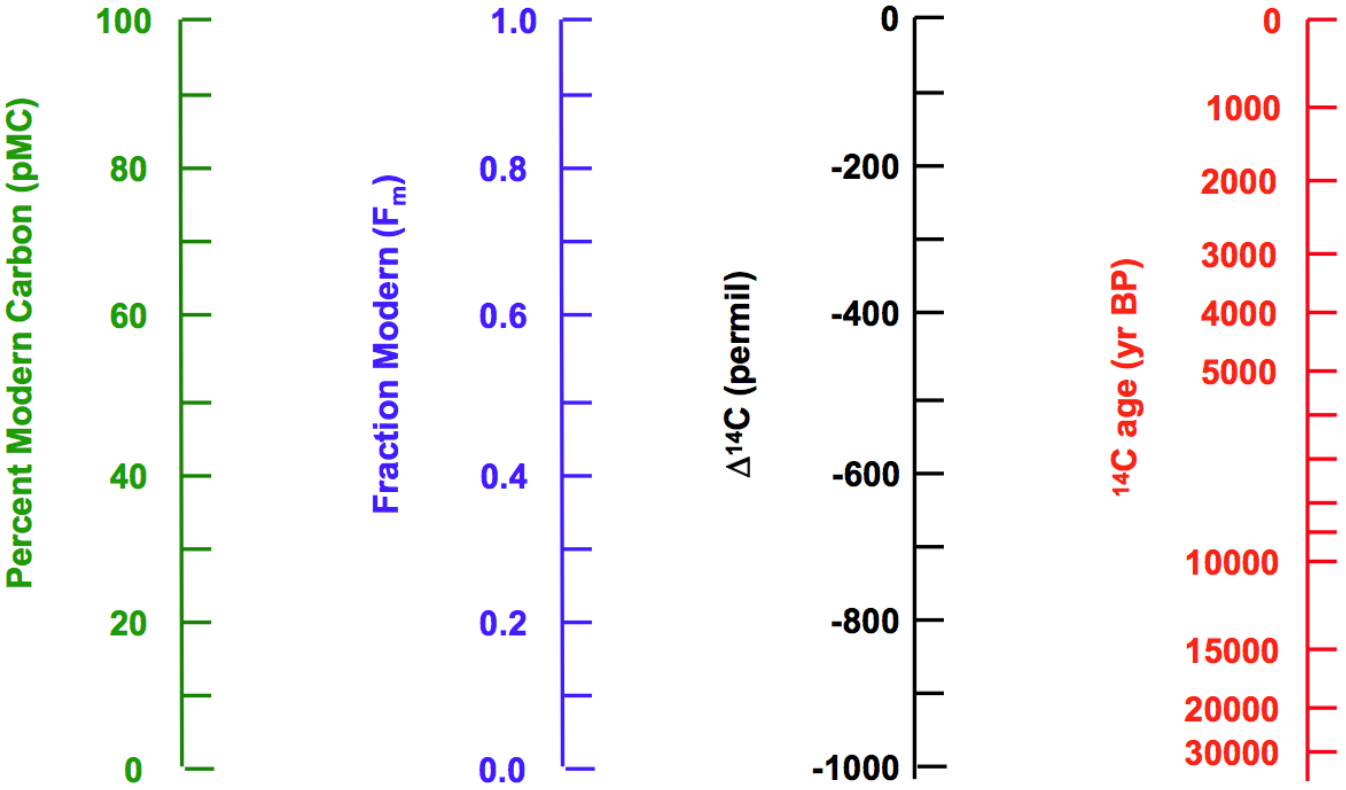


Exposure times equivalent to ≤ one-week at mid-latitudes.

More Light, More Mineralization to CO_2



Natural Abundance Radiocarbon as a Natural Tracer



$T_{1/2}$ (^{14}C) = 5730 years

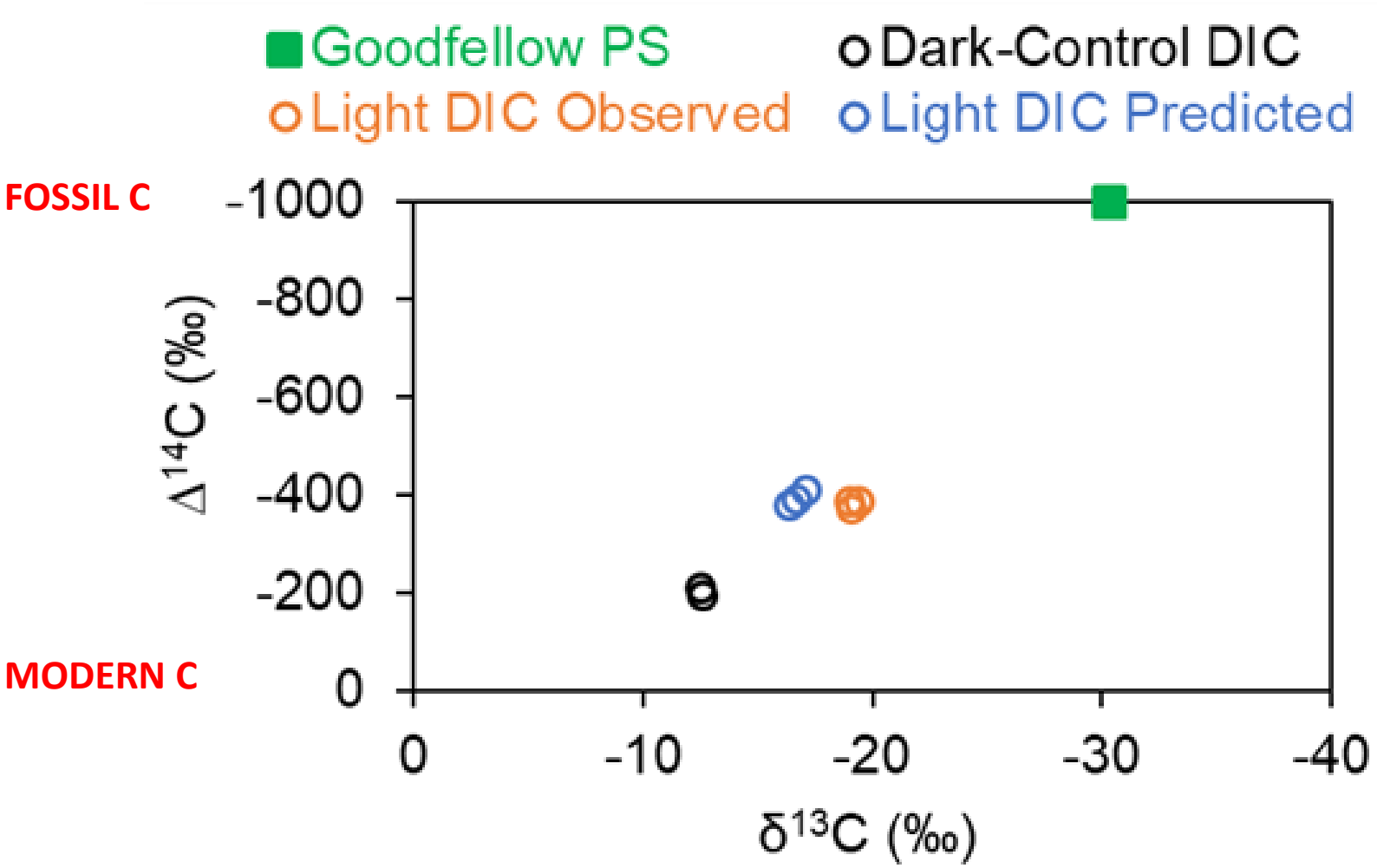
"Radiocarbon dating is limited to 50,000 yrs or so.." Libby (1967)

NOSAMS | NATIONAL OCEAN SCIENCES ACCELERATOR MASS SPECTROMETRY

Woods Hole Oceanographic Institution

Courtesy of Ulrich Hanke

Sunlight Converts Polystyrene Into CO_2

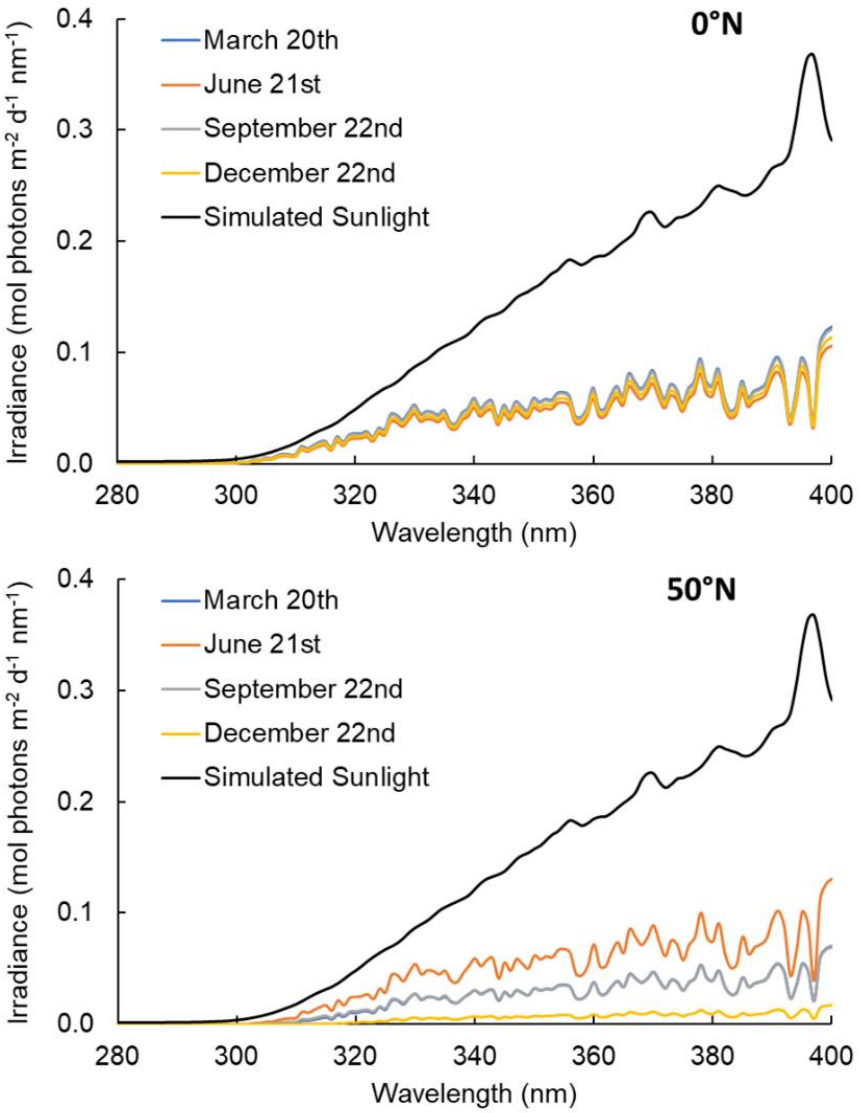


Exposure times equivalent to
≤ one-week at mid-latitudes

Woods Hole Oceanographic Institution

Experiment conducted in triplicate;
error bars smaller than symbol

Lifetimes of photomineralization are on centennial timescales



Lifetimes average 300 to 400 years for complete mineralization of polystyrene into CO_2 by sunlight

This isn't surprising…

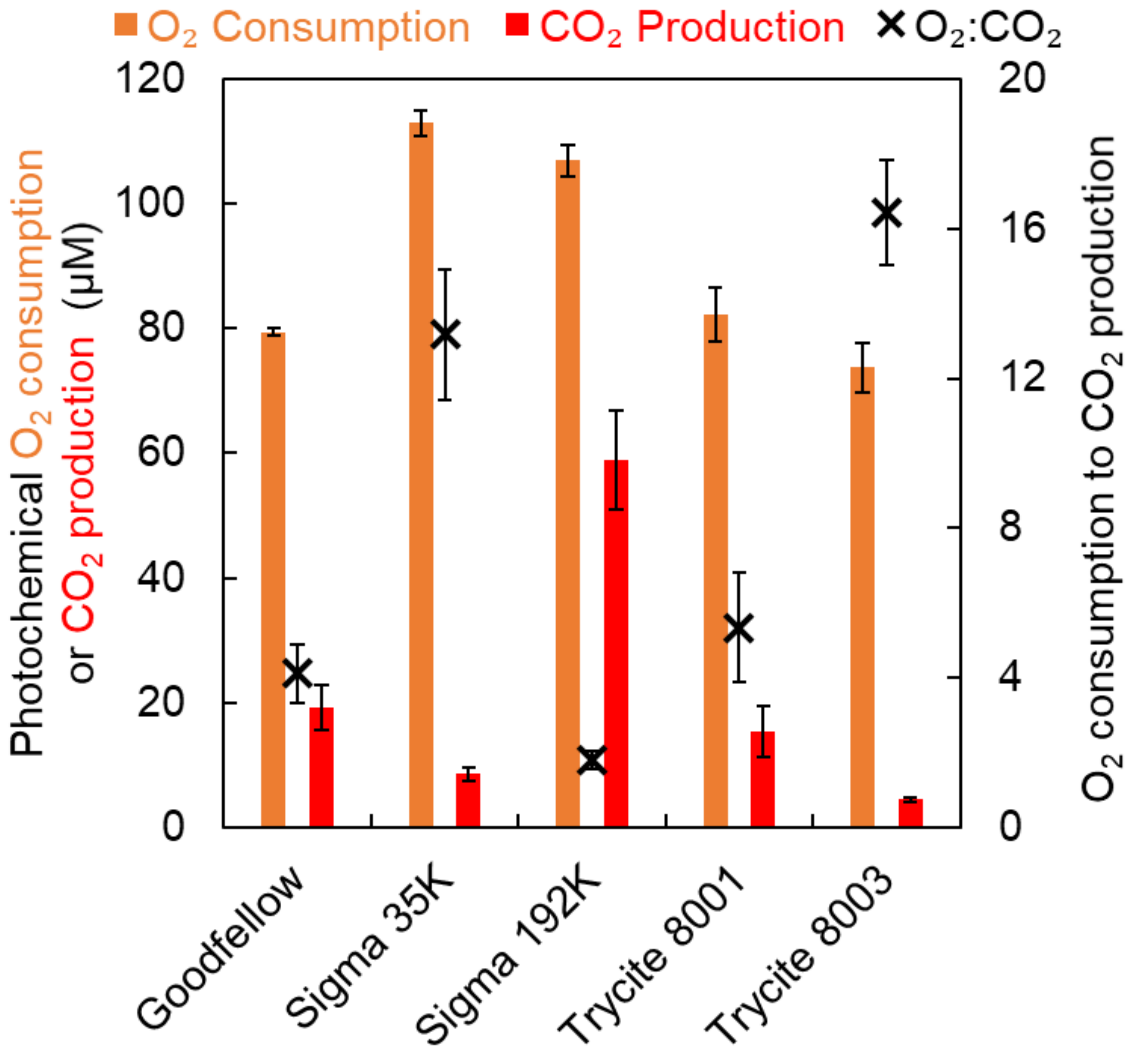
GEOPHYSICAL RESEARCH LETTERS, VOL. 22, NO. 4, PAGES 417-420, FEBRUARY 15, 1995

Photochemical production of dissolved inorganic carbon from terrestrial organic matter: Significance to the oceanic organic carbon cycle

William L. Miller[1] and Richard G. Zepp
Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia

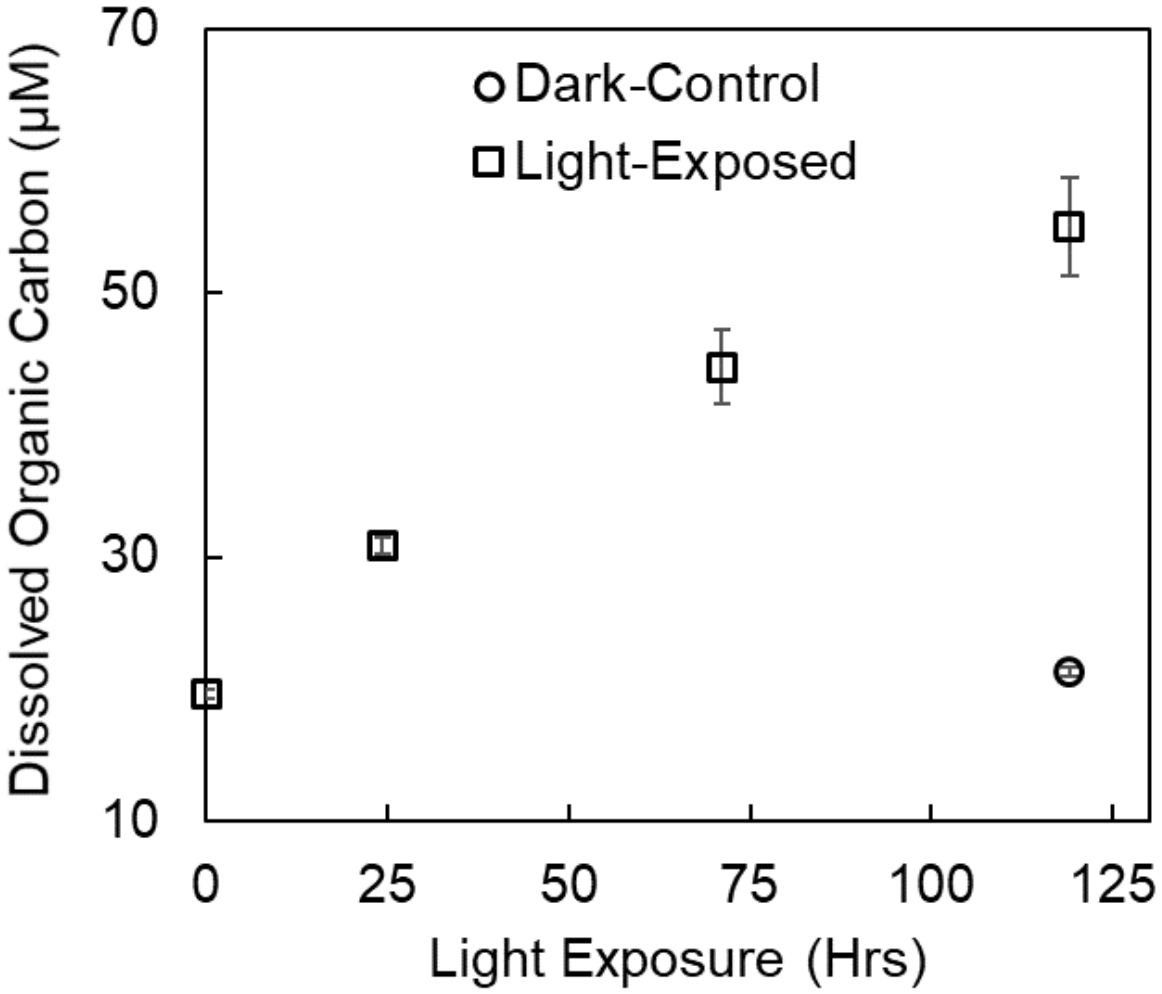
"This important process is not included in earlier estimates of photochemical conversions in natural waters and implies that the residence time for terrestrial carbon in the ocean is notably shorter than previously proposed."

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

Water and Gas Phase PS Transformation Products

ENVIRONMENTAL Science & Technology

Article

Cite This: *Environ. Sci. Technol.* 2018, 52, 11123−11131

pubs.acs.org/est

Phototransformation of Plastic Containing Brominated Flame Retardants: Enhanced Fragmentation and Release of Photoproducts to Water and Air

Amina Khaled,[†] Agnès Rivaton,*[,†] Claire Richard,[†] Farouk Jaber,[‡] and Mohamad Sleiman*[,†]

[†]Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de Clermont-Ferrand, F-63000 Clermont−Ferrand, France

[‡]Laboratory of Analysis of Organic Compounds (509), Faculty of Sciences I, Lebanese University, Hadath, Beirut, Lebanon

"Plastic fragments will have similar structural properties as larger items of the same polymer." GESAMP 2019

ENVIRONMENTAL Science & Technology LETTERS

ACS AuthorChoice

Letter

Cite This: *Environ. Sci. Technol. Lett.* 2018, 5, 272−276

pubs.acs.org/journal/estlcu

Identification of Chain Scission Products Released to Water by Plastic Exposed to Ultraviolet Light

Berit Gewert, Merle Plassmann, Oskar Sandblom, and Matthew MacLeod*

Department of Environmental Science and Analytical Chemistry, Stockholm University, Svante Arrhenius väg 8, 11418 Stockholm, Sweden

This isn't surprising…

Limnol. Oceanogr., 51(2), 2006, 1064–1071

Photodissolution of particulate organic matter from sediments

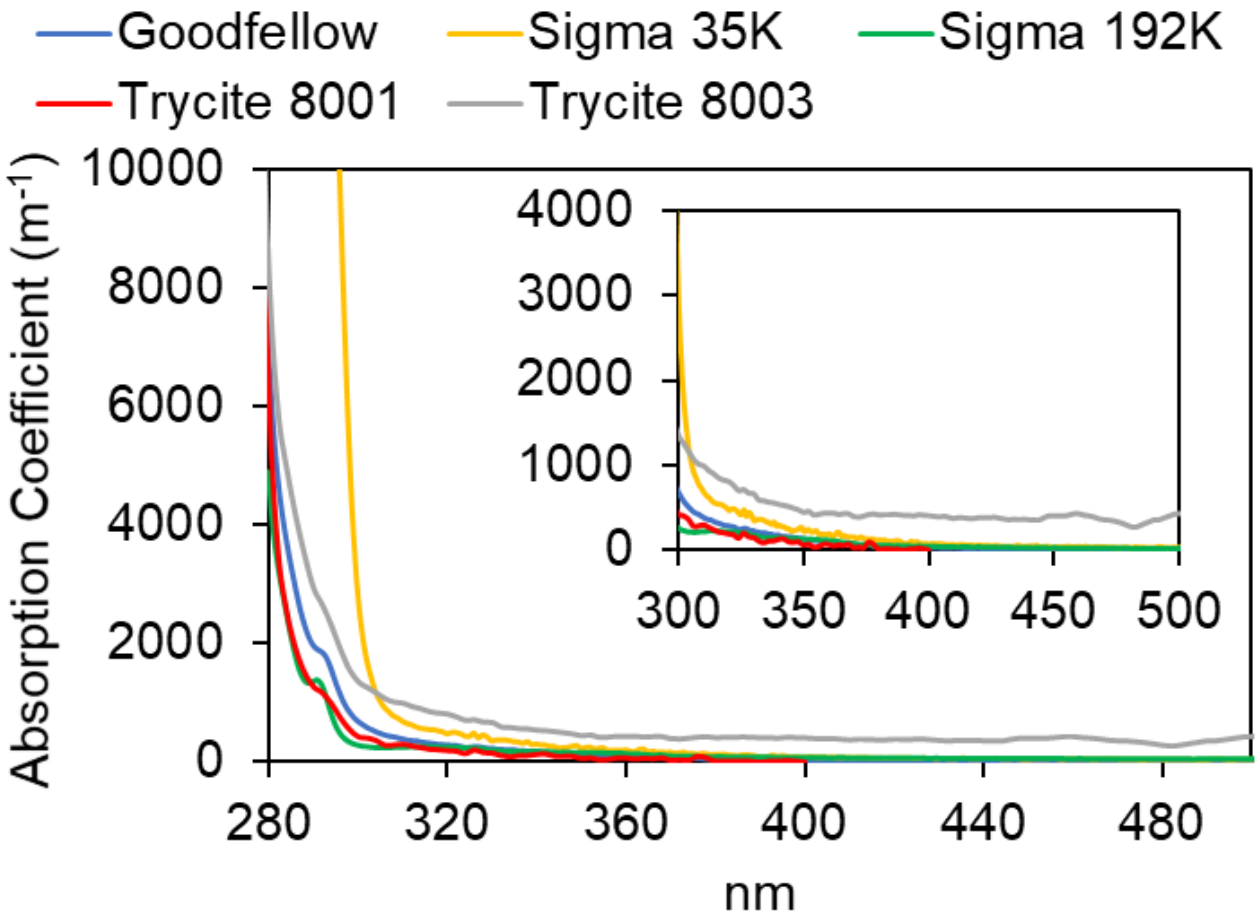
Lawrence M. Mayer,[1] Linda L. Schick, and Krysia Skorko
School of Marine Sciences, University of Maine, Walpole, Maine 04573

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

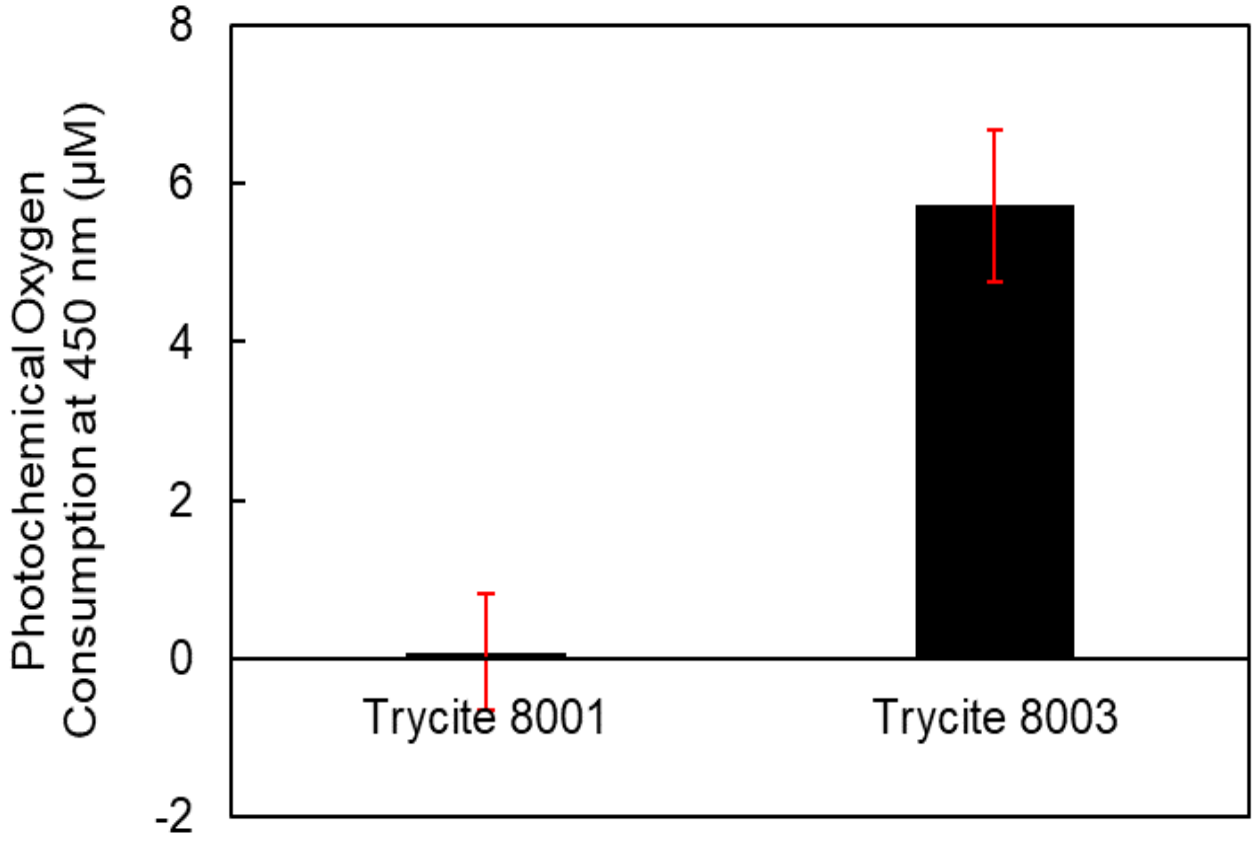
"These results point to a heretofore ignored role for photodissolution of particulate organic matter at the Earth's surface."
Mayer et al., 2006

We assume that visible light is irrelevant

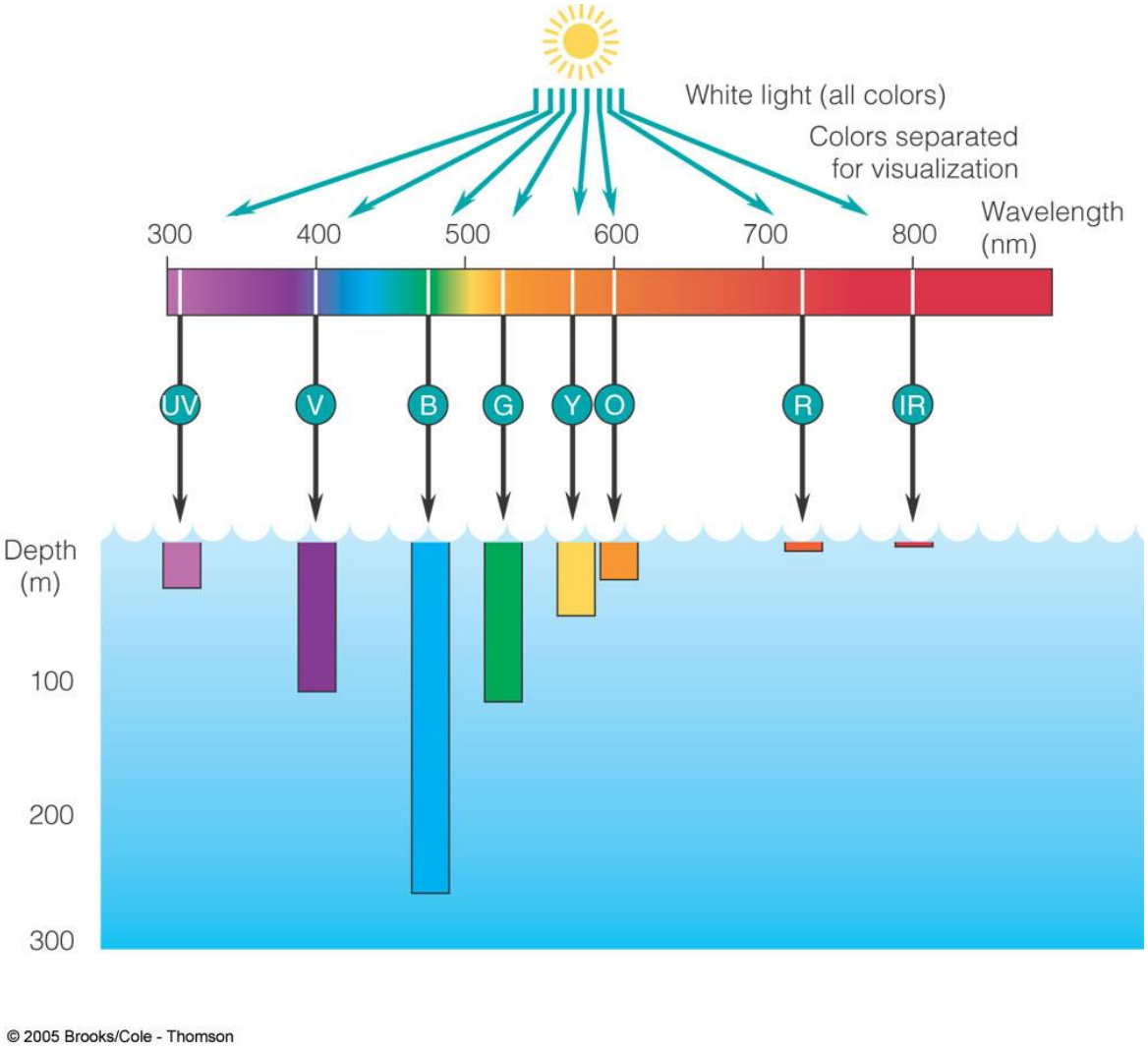
"Fragmentation will occur if plastics are subject to UV radiation"
GESAMP 2019



Additives can drive oxidation by visible light



10x more Vis Light, 10x greater depth penetration



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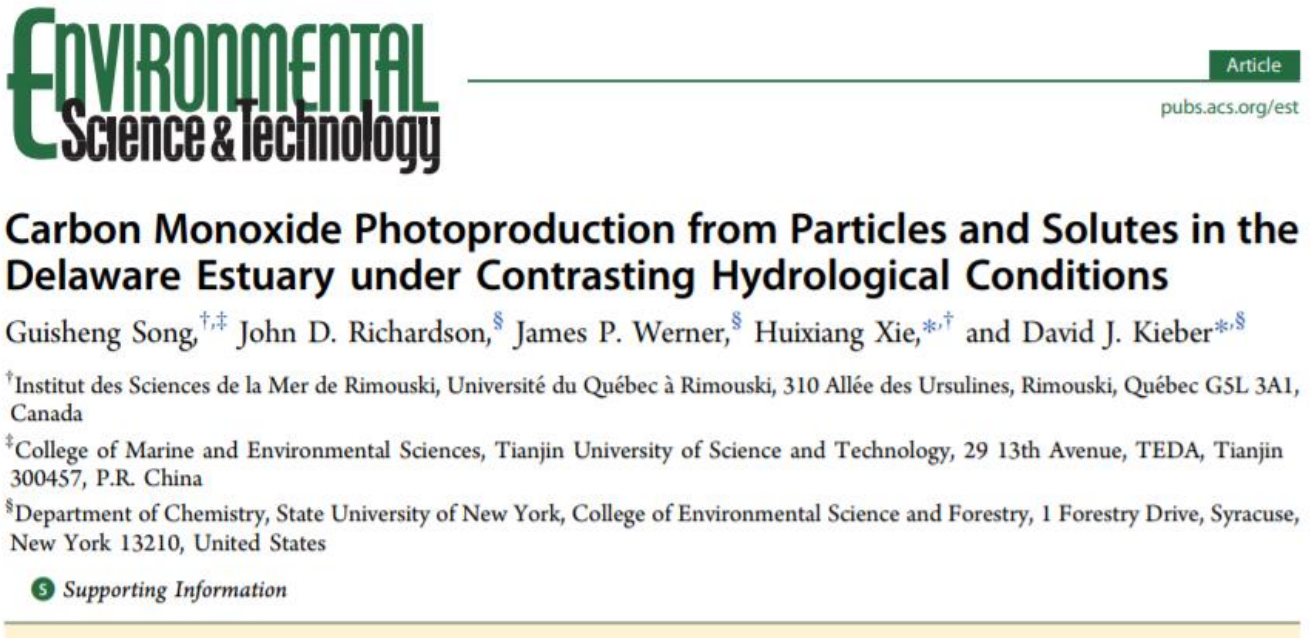

ENVIRONMENTAL Science & Technology

Article

pubs.acs.org/est

Carbon Monoxide Photoproduction from Particles and Solutes in the Delaware Estuary under Contrasting Hydrological Conditions

Guisheng Song,[†,‡] John D. Richardson,[§] James P. Werner,[§] Huixiang Xie,[*,†] and David J. Kieber[*,§]

[†]Institut des Sciences de la Mer de Rimouski, Université du Québec à Rimouski, 310 Allée des Ursulines, Rimouski, Québec G5L 3A1, Canada

[‡]College of Marine and Environmental Sciences, Tianjin University of Science and Technology, 29 13th Avenue, TEDA, Tianjin 300457, P.R. China

[§]Department of Chemistry, State University of New York, College of Environmental Science and Forestry, 1 Forestry Drive, Syracuse, New York 13210, United States

Supporting Information

"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 → 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

EXTRA

99

REPORTS AND STUDIES

GESAMP
Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection

GUIDELINES FOR THE MONITORING AND ASSESSMENT OF PLASTIC LITTER IN THE OCEAN

IMO FAO UNESCO IOC WMO UNIDO IAEA UN UN ENVIRONMENT UNDP IGA

1) Only microbes can mineralize plastics

2) Smaller particles look like larger particles

3) Only UV light is relevant

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).

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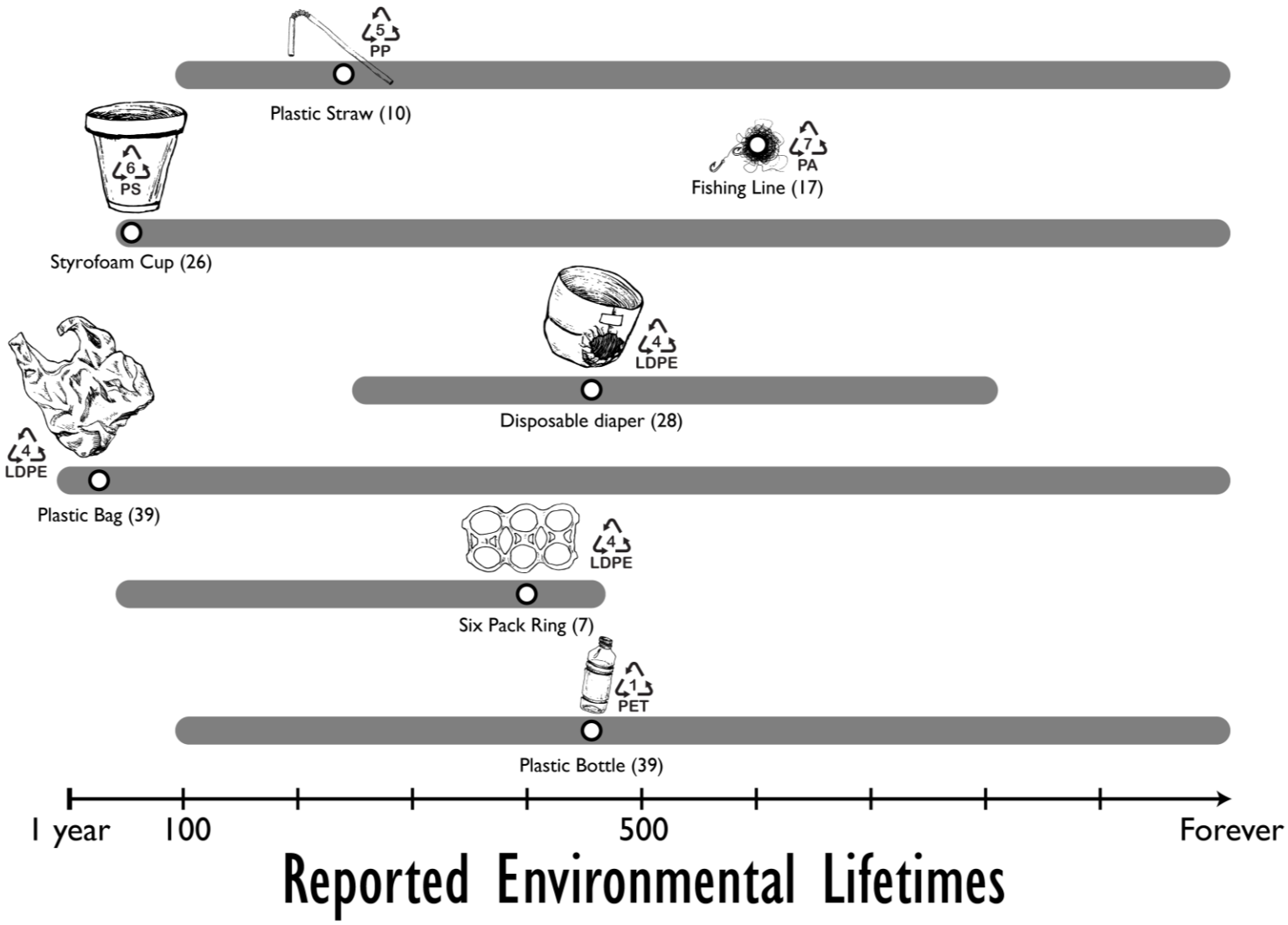

Review of 42 informational graphics (N = 158)

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We Need Algorithms to Incorporate Photochemistry into Global Fate Models

$$Photo-oxidation\ (mol\ PRODUCT\ m^{-2}\ d^{-1}) = \int_{280}^{700} \Phi_\lambda * R_{a\lambda}\ d\lambda$$

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

$$R_{a\lambda}\ (mol\ photons\ m^{-2}\ d^{-1}\ nm^{-1}) = E_{ds\lambda}(1 - e^{-K_{d\lambda}z})$$

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

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