Degradation Processes of Microplastics

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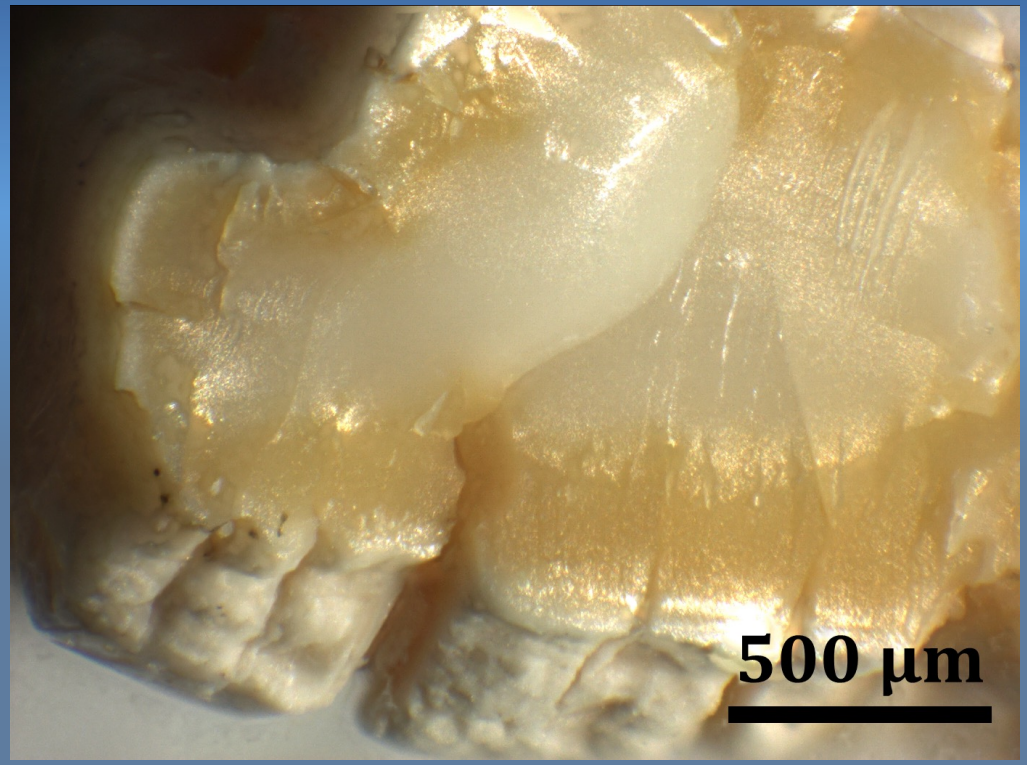
Sea Education Association Dow Chemical



MARII Workshop
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Degradation of plastics

plastic = synthetic polymer + chemical additives

Definition of degradation (materials science):

Changes in material properties resulting in reduced performance and/or loss of function

- Changes in chemical composition and/or chemical structure (polymer microstructure)
- Classified by type of chemical reactions within the polymer, and the initiating mechanisms

Note: Changes due to leaching of additives from, or adsorption of chemicals (including water) into the material can also affect plastic properties.

Why should we study degradation processes?

1. Lifetime in the environment / Time scale of contamination
   - How long before large item becomes MPs?
     - Informs time scale of efficient capture (cleanup)

Rick Loomis/L.A. Times

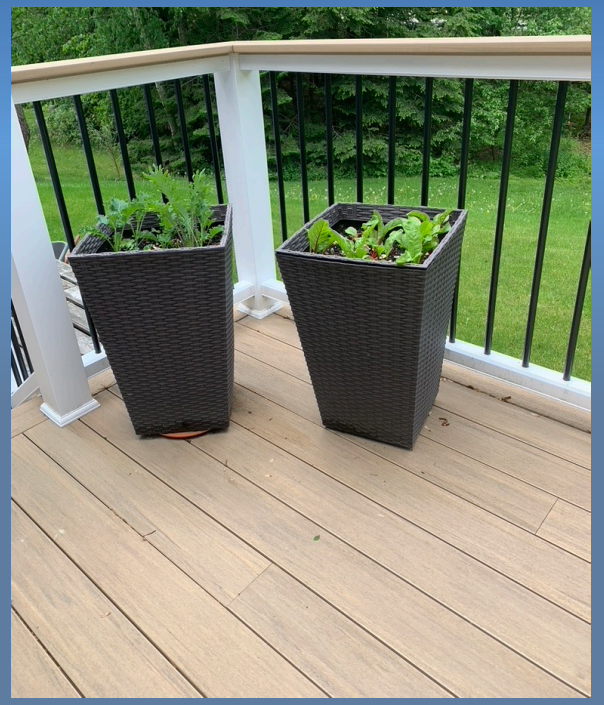
Nicholas Mallos/Ocean Conservancy

Sea Education Association

Why should we study degradation processes?

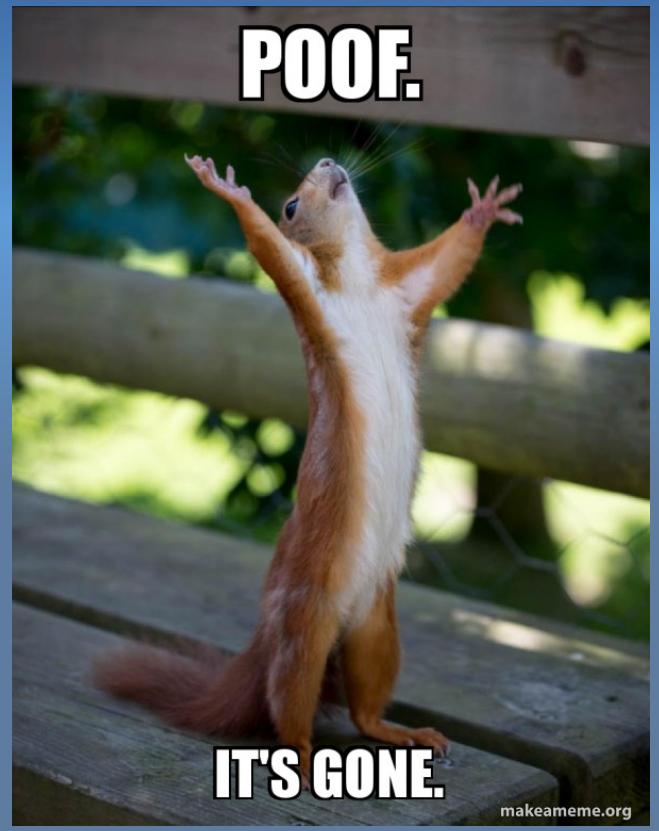
1. Lifetime in the environment / Time scale of contamination
   - Time scale of NP generation
     - Informs risk assessment for wildlife and human health

Nanoplastics?



Why should we study degradation processes?

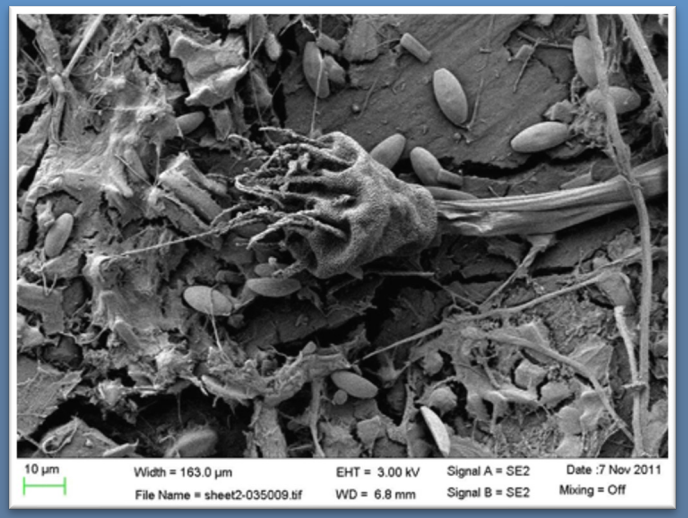
1. Lifetime in the environment / Time scale of contamination
   - Time scale of mineralization
     - Elimination of contamination and risk



Why should we study degradation processes?

1. Lifetime in the environment / Time scale of contamination

2. Nature of plastics interaction with biota
   - Changes in surface properties that affect biofilm formation (e.g. hydrophobicity), additive leaching, ingestion (particle size, surface chemistry)



Polymer characteristics affecting degradation

1. Chemical composition: bond energies, intermolecular forces
2. Polymer microstructure: crystallinity, cross-linking, branching
3. Plastic properties (macroscopic material characteristics): Initially determined by 1. and 2., and affected by processing and external conditions (weathering)

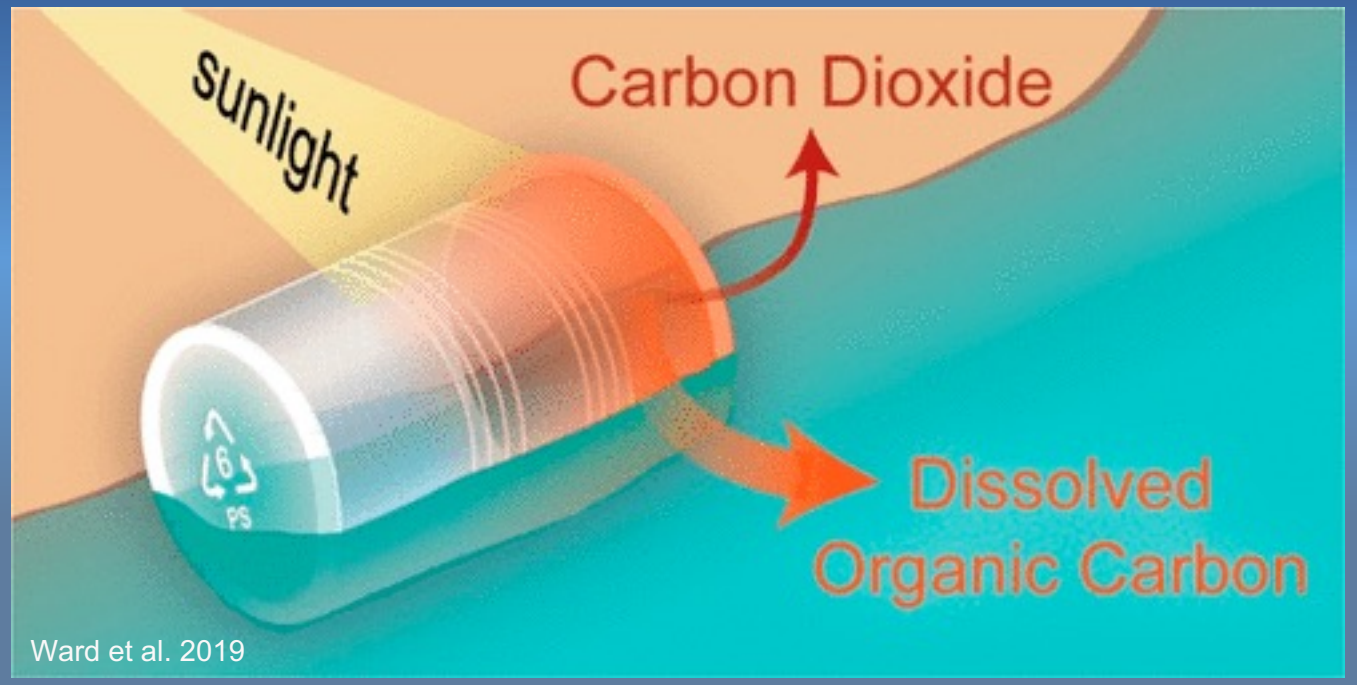
Photochemical degradation

Initiated when UV-Vis light absorbed by chromophores causes excitation

- Chromophores are typically present in plastics due to impurities, defects or additives
  - Photo- or UV-stabilizers contain chromophore groups that absorb UV to prevent this reaction in the polymer itself
- Excitation, in presence of oxygen, drives oxidation reaction (at polymer surface, to depths ~100s microns)
  - Rate is temperature and oxygen dependent

Photochemical Dissolution

- Dissolved Organic Carbon (DOC)



Ward et al. 2019

Romera-Castillo et al. 2018

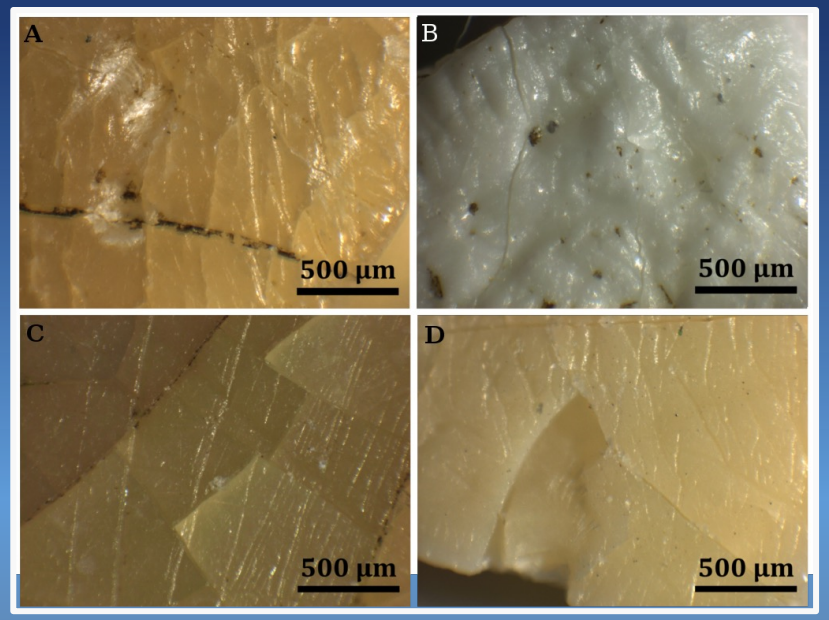
Ward et al. 2019

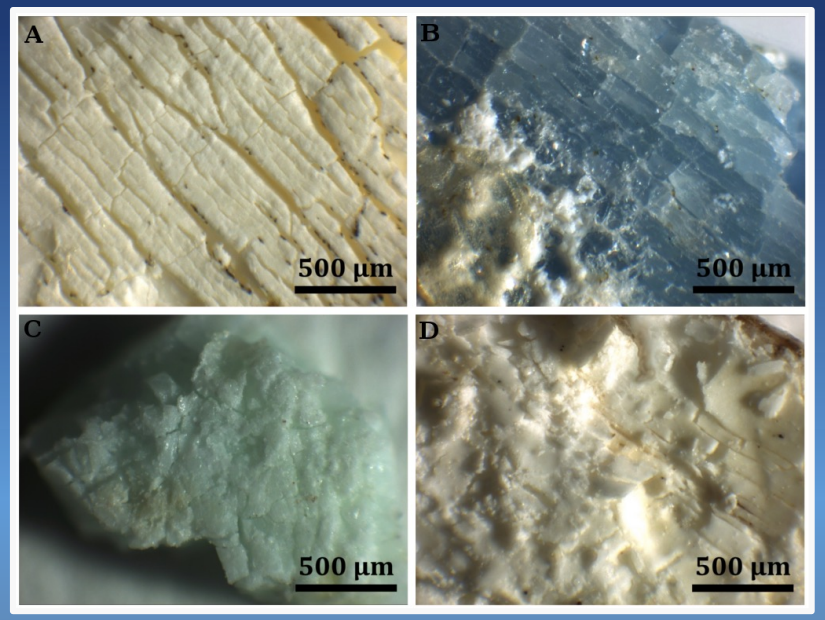
Zhu et al. 2020

Other degradation processes

- Thermo-oxidative degradation
  - Can proceed following photo-oxidative reactions
- Thermal degradation
  - At high (non-environmentally relevant) temperatures
  - Relevant for some waste management processes
- Chemical degradation
  - Being explored for depolymerization processes
- Biodegradation
  - Dependent on plastic, microbe, environmental conditions

Fragmentation: reduction in particle size





Requires physical forces (normal/shear stress) to cause material breakage

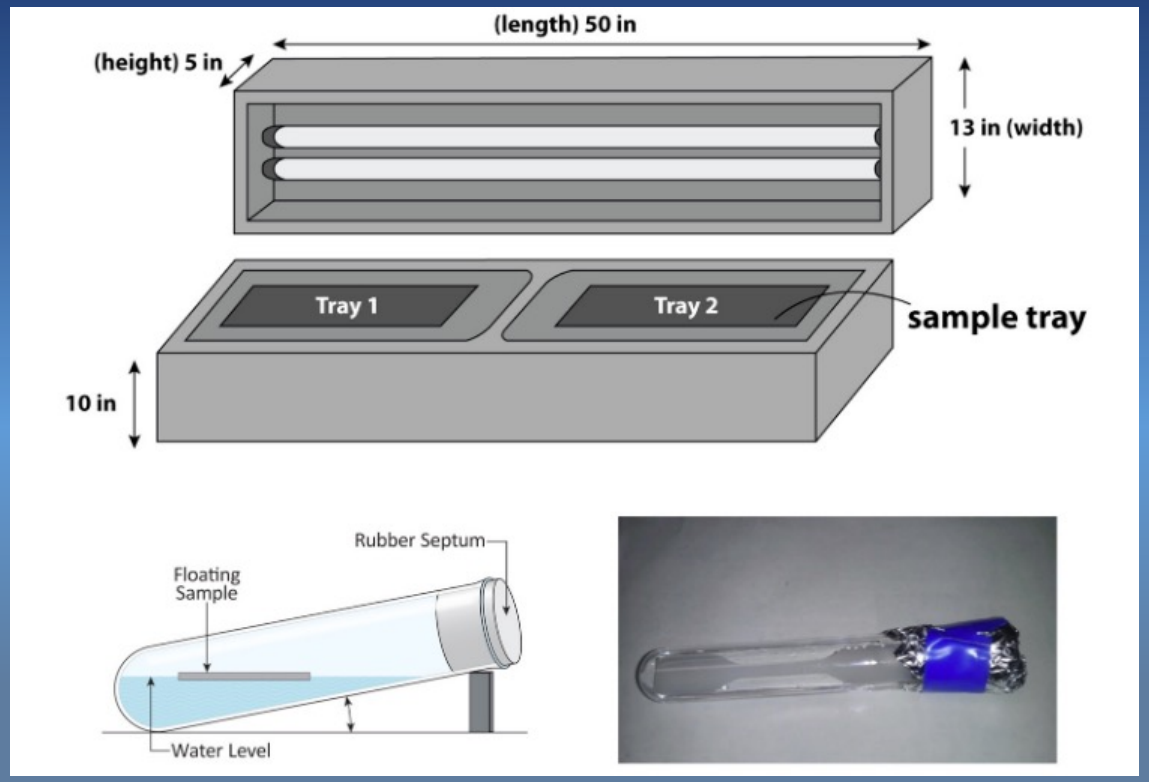
- Abrasion (sand/sediment)
- Biological action (biting, chewing, grinding)

Weathering Factors

- UV radiation
- Temperature
- Oxygen
- Water
- pH
- Chemical compounds
- Biological activity
  - fouling, enzymatic

Mitimiti coast in Northland, Moerewa Point in the foreground (Credit: Raewyn Peart)

Understanding Weathering
Laboratory ⟷ Environmental



Mitimiti coast in Northland, Moerewa Point in the foreground (Credit: Raewyn Peart)

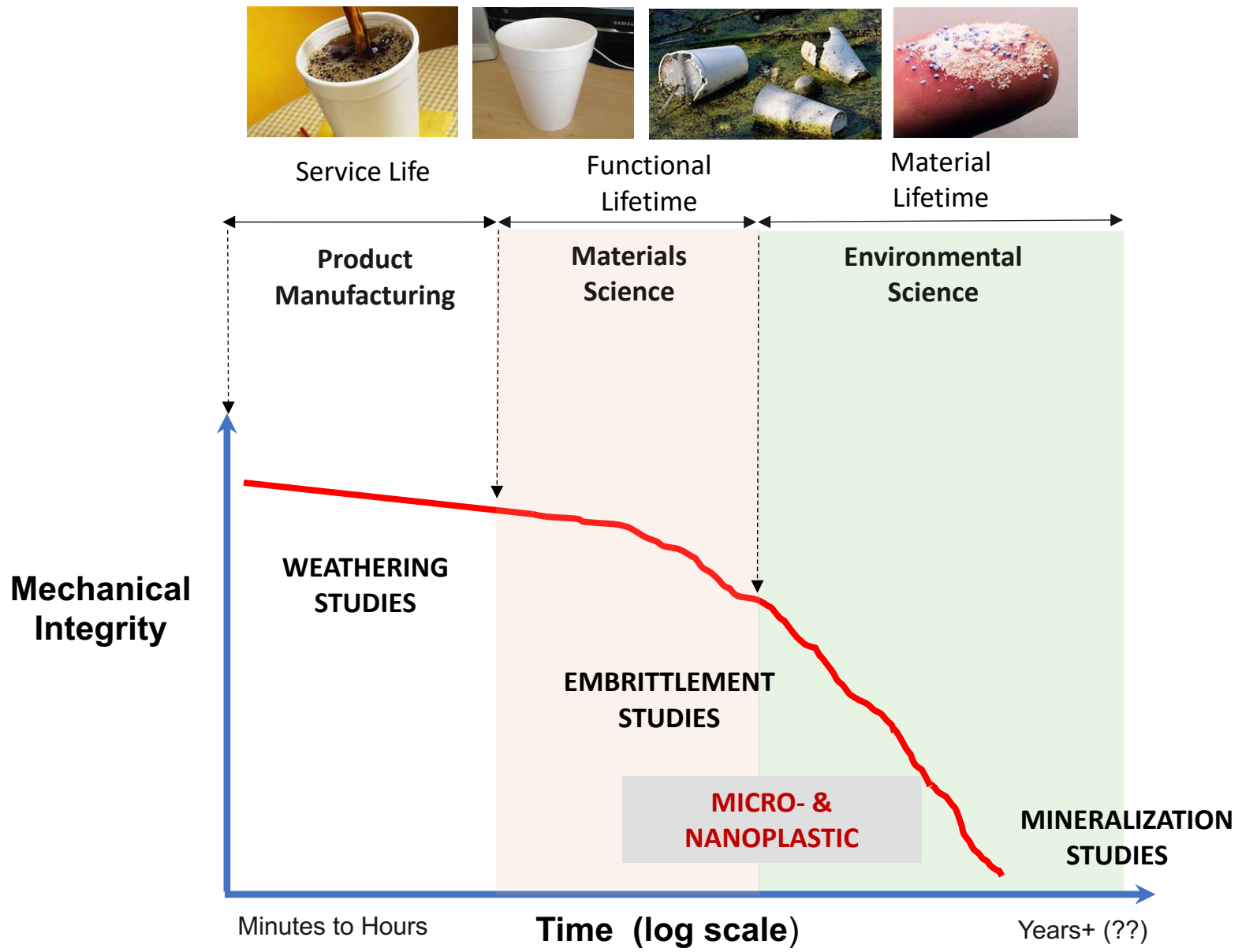


Figure adapted from A. Andrady

Today's session

Microplastics in the Ocean	Anthony Andrady
Linking Formulation to the Fate and Impacts of Plastics in Sunlit Surface Waters	Bryan James
Biological Degradation	Melissa Duhaime
Predicting Plastic Fragmentation in the Environment	Sam Harrison