Pyrolysis-GC/MS grouped compound information

Website: https://www.bco-dmo.org/dataset/943291

Data Type: experimental

Version: 1

Version Date: 2024-11-12

Project

» <u>EAGER: Collaborative Research: NSF2026: Is Plastic Degradation Occurring in the Deep Ocean Water</u> Column? (Deep Ocean Plastic Degradation)

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Abstract

The photodegradation of macroplastics in the marine environment remains poorly understood. Here, we investigated the weathering of commercially available plastics (tabs $1.3 \times 4.4 \times 0.16$ cm), including high-density polyethylene, low-density polyethylene, polypropylene, polystyrene, and polycarbonate, in seawater under laboratory-simulated ultraviolet A radiation for 3–9 months, equivalent to 25–75 years of natural sunlight exposure without considering other confounding factors. After the exposure, the physical integrity and thermal stability of the tabs remained relatively intact, suggesting that the bulk polymer chains were not severely altered despite strong irradiation, likely due to their low specific surface area. In contrast, the surface layer ($\sim 1~\mu m$) of the tabs was highly oxidized and eroded after 9 months of accelerated weathering. Several antioxidant additives were identified in the plastics through low temperature pyrolysis coupled with gas chromatography/mass spectrometry (Pyr-GC/MS) analysis. The Pyr-GC/MS results also revealed many new oxygen-containing compounds formed during photodegradation, and these compounds indicated the dominance of chain scission reactions during weathering. These findings highlight the strong resistance of industrial macroplastics to weathering, emphasizing the need for a broader range of plastics with varying properties and sizes to accurately estimate plastic degradation in the marine environment.

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Coverage

Temporal Extent: 2020-10-01 - 2022-09-01

Methods & Sampling

Materials: High-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), and polycarbonate (PC) plastic sheets, as the primary plastic without weathering previously, were obtained from McMaster-Carr Supply Company (USA). These polymers were chosen because of their large-scale global production and their widespread presence in the marine environment. The plastic sheets (122 cm

 \times 61 cm) had a thickness of 1.6 mm. The exact formula and additive information were not provided by the vendor. However, plastic additives in various concentrations were confirmed in different plastics through Pyr-GC/MS. Plastic sheets were cut into small tabs (1.3 cm \times 4.4 cm) and then cleaned with DI water and dried in a laminar-flow hood before further use.

Weathering Experiment: To simulate long-term weathering conditions in the marine environment, plastic tabs underwent a controlled experimental setup. Four plastic tabs of each polymer type were placed within a 10 cm Pyrex crystallizing dish filled with 200 mL of filtered natural seawater (1 μm spiral wound cartridge filter, Pall, USA, salinity 32 psu) and maintained at 55 °C with three replicates. Additionally, approximately 10,000 glass beads (1 mm diameter) were introduced to the dish, covering 80% of the dish's bottom surface area, with continuous agitation provided by a rotary table (stroke length 10 cm, speed 60 rpm) to simulate the effects of physical contact with sediment particles in coastal water. UVA lighting (315–400 nm) was applied using three overhead LED UV lamps (Isuerfy, 120 W, F120W-UV-US), positioned 3 cm above the dishes, with an intensity of 230 W/m2 each, verified by a UV light meter (UV513AB, General Tools). UVA was selected due to its prevalence and deeper penetration depth over the other UV bands. On average, the simulated UVA irradiance was approximately 50 times that of natural UVA strength, estimated at 4.5 W/m2 reaching the earth on a global average, i.e., 3 months of continuous light exposure in this experiment equals approximately 25 years of natural diel UVA exposure in the ocean. To maintain constant salinity and water levels, distilled water was replenished every other day.

The plastic tabs were subsampled at four different time points: T0 (before weathering), T1 (3 months ≈ 25 years), T2 (6 months ≈ 50 years), and T3 (9 months ≈ 75 years). These time points were chosen to capture the progressive changes in the plastic tabs over the course of the weathering process. The experimental design, involving the coincubation of plastic tabs of the same polymer with agitation, posed challenges for tracking the weight change of a specific tab at a given time point. Additionally, due to incubation in seawater, effectively removing all sea salt adhered to the plastic surface through water rinsing was difficult. Thus, we did not measure the weight loss of the tabs with the exposure time.

Data Processing Description

Pyrolysis analysis was conducted using a multishot pyrrolyzer (EGA/Py-3030D, Frontier Laboratories Ltd.) coupled with a GC/MS system (Shimadzu GCMS-TQ8040). To monitor potential cross-contamination, sample carryover, and instrument-related contamination, each sample run was followed by three blank runs before the next sample. A tab subsample, weighing 2–5 mg, was randomly cut by rinsed metal scissors and placed in a pyrolyzer cup. Two temperature modes were applied: high temperature (600 °C for 0.3 min) and low temperature (350 °C for 0.3 min) pyrolysis modes. For the low temperature mode, the GC inlet temperature was set at 300 °C, and the split ratio was 5:1. An Ultra ALLOY Capillary Column UA+-5 (30 m length, 0.25 mm I.D., and 0.25 μ m film thickness consisting of 95% polydimethylsiloxane and 5% polydiphenyldimethylsiloxane stationary phase, Frontier Laboratories Ltd.) was employed, with helium as the carrier gas at a flow rate of 1 mL/min. The GC oven program was set as follows: 50 °C (hold 1 min) \rightarrow 8 °C/min \rightarrow 130 °C (hold 4 min) \rightarrow 50 °C/min \rightarrow 320 °C (hold 5 min). Pyrolyzate chemical structures were identified by comparing them with the NIST17 library via LabSolution software (Shimadzu). Triplicate samples for each plastic type were analyzed.

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Parameters

Parameters for this dataset have not yet been identified

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Project Information

EAGER: Collaborative Research: NSF2026: Is Plastic Degradation Occurring in the Deep Ocean Water Column? (Deep Ocean Plastic Degradation)

Coverage: Sargasso Sea

NSF Award Abstract:

With support from the NSF 2026 program in the NSF Office of Integrated Activities, a team of researchers from four institutions will investigate the processes that affect plastic debris and its ultimate fate once it enters the ocean interior. Since 1950, global production of plastic has grown exponentially. An estimated 5 to 13 million metric tons of plastic flows from the land and enters the ocean each year. However, model assessment indicates that 99% or more of the plastic entering the ocean is currently unaccounted for. The goal of the project is to understand the physical modification and biochemical transformation of plastic debris by microbial communities in the mid- and deep-waters of the open ocean near Bermuda. The project directly addresses two of the top thirty-three Idea Machine entries: "Imagine a Life With Clean Oceans" and "Global Microbiome in a Changing Planet." The investigators will deploy incubators to evaluate plastic degradation at 600 meters and 3600 meters water depth at the NSF-funded Oceanic Flux Program (OFP) mooring site. Results from this project will further understanding of the mechanistic processes that govern decomposition of plastic particles in the mid-depth (600 meters) and deeper (3600 meters) ocean, as well as the microbial communities involved with biodegradation of plastics at those depths. The results will have broad implications to the fields of ocean biogeochemistry, environmental sciences, and microbial ecology. With the deep-sea incubator deployed inline on the OFP mooring being a new method to study plastic polymer degradation processes in situ, this research contributes significantly to technology development for oceanographic research. Results from this project will also provide insights into the global budget of plastics, potentially filling the knowledge gap on the fate of plastic and thus affecting plastic management policies. Knowledge of the role of deep ocean microbial communities in the degradation of synthetic plastic polymers will be very valuable information for industry and policymakers. The collaboration of the American Chemistry Council, which is providing polymers for the project, will strengthen the cooperation between academia and industry. Education is an essential part of this project, which includes one postdoctoral researcher and multiple undergraduate students. Project results will be incorporated into undergraduate courses and communicated through outreach activities for the broader public.

The investigators propose to test three sets of hypotheses: (1) Different polymers promote the assembly of distinct microbiomes, and these microbiomes differ between the mesopelagic and bathypelagic ocean regimes; (2) Plastics are degraded within the ocean interior, different plastic polymer types are degraded at different rates, and these rates differ between the mesopelagic and bathypelagic ocean regimes; and (3) Deep ocean microbiomes actively degrade plastics and utilize plastic polymers as a carbon source. These hypotheses will be tested deploying custom-built deep-sea incubators at 600 m and 3600 m containing well-defined plastic polymer films and fibers on the OFP mooring, located in the northern Sargasso Sea about 75 km south-east of Bermuda. The polymers deployed will represent the diversity of plastics found in the marine environment and have different stabilities against microbial degradation (e.g., polyethylene, polyethylene terephthalate, and others). This project will combine state-of-the-art polymer chemistry analyses (pyrolysis-GCMS and Raman, and micro-FTIR) with microscopy, and lipid (GCMS and GCirMS) and nucleic acid sequencing analyses, to determine if microbial communities can degrade polymers in the deep mesopelagic and bathypelagic ocean. The results will determine if microbial communities living within the aphotic ocean interior actively degrade and utilize the synthetic carbon polymers that make up plastics, and thus play an important role in the removal of global plastics.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

Project Location:

The study area of this project is the Oceanic Flux Program Site in the northern Sargasso Sea, located approximately 75 km southeast of Bermuda (31°50'N, 64°10'W).

This NSF collaborative grant brings together an interdisciplinary research team including Principal Investigator Pedrosa Pàmies (Marine Biological Laboratory, MBL) and Co-Principal Investigators Zhanfei Liu (University of Texas at Austin, Marine Science Institute), Alexander Bochdansky (Old Dominion University), Emil Ruff (MBL), PI of MBL subaward Scott Gallagher (Coastal Ocean Vision), and collaborators Jessica Mark Welch (MBL) and Maureen Conte (Bermuda Institute of Ocean Sciences/MBL).

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-2033828

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