Photo-chemical production of dissolved organic carbon from North Pacific Gyre plastics (DOC) concentration and chemistry from laboratory experiments in natural seawater

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Project
» EAGER: Collaborative Research: Assessing the contribution of plastics to marine particulate organic carbon (Marine Plastic POC)
» Collaborative Research: CBET: The role of sunlight in determining the fate and microbial impact of microplastics in surface waters (Sunlight Microbial Microplastics)

Contributors	Affiliation	Role
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Abstract
Photo-chemical production of dissolved organic carbon from North Pacific Gyre plastics (DOC) concentration and chemistry from laboratory experiments in natural seawater. Results published in Zhu et al., 2020.

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Coverage

Spatial Extent: **N**:50 **E**:-76.9854 **S**:0 **W**:117.5162

Methods & Sampling

Experimental

2.1 Seawater and general sample handling

All sample handling and experimental procedures followed trace clean oceanic protocols for DOC[29]. All plasticware was cleaned by triple rinsing with ultrapure water (MilliQ), soaking overnight in ~pH 2 water (4:1000, v:v, 6N HCl:MilliQ), triple rinsing with MilliQ and then drying. Glassware and quartzware were cleaned as above and then ashed at 450 °C for 6 hours to remove any trace organics. Seawater (salinity ~35) was collected from ~5 m in the South Atlantic Bight using Niskin bottles aboard the RV *Savannah* and gravity-filtered (0.2 µm; AcroPakTM 1500, PALL) directly from Niskin bottles into pre-cleaned 20 L high density PE carboys. In order to remove natural, photochemically active organics before adding plastics, seawater was transferred to 2 L ashed quartz flasks and placed under germicidal ultraviolet-C light until colored dissolved organic matter was undetectable using an Aqualog spectrofluorometer (HORIBA Scientific) and the DOC concentration was stable.

2.2 Plastic preparation

Plastic particles collected from the North Pacific Gyre were provided by Algalita Marine Research and Education and the 5 Gyres Institute. The real-world North Pacific Gyre sample contained plastic-fragments with an average size of 5.9±3.1 mm (Fig. S1 in Zhu et al., 2020), including sub-5 mm microplastics and other small plastic fragments. Thus, we refer to this sample as containing plastic-fragments rather than using the more precise, operational term microplastics that refers specifically to particles under 5 mm[2]. Plastic particles were sonicated in MilliQ water for 10 minutes and then soaked in 1% H_2O_2 for two hours, and then triple sonicated for 5 minutes in MilliQ water. Once clean, the plastics were air dried prior to further analysis and use in experiments.

Postconsumer plastics were PE (RejoiceTM shampoo bottle), PP (NIVEA® facial cleanser bottle) and EPS (disposable lunch box). Postconsumer plastics were cut into small pieces (3.04±0.87 mm; Fig. S1B-D). In addition, a standard PE granule (PEstd) was purchased (diameter: 2 mm; Goodfellow, USA). Prior to further analysis and experiments, microplastics were cleaned by sonification in MilliQ water and dried.

The surface area and volume of each sample type was estimated as described in the Supplementary Methods. Surface area to volume ratios (SA:V) were for each sample type were then calculated (Table1 in Zhu et al., 2020).

Density of each postconsumer microplastics was assessed by the addition of microplastics to MilliQ water and then either calcium or ethanol was added to adjust the solution density until the microplastics maintained in a position of neutral buoyancy for 20 minutes[30]. 1 mL of the resultant solution was weighed to determine solution density. Measured densities are reported in Table S1 of Zhu et al. (2020). The density of EPS could not be determined via this method due to the presence of embedded air pockets. Therefore, data (0.01-0.05 g cm-3) from the manufacturer are reported (https://insulationcorp.com/eps/).

2.3 Irradiations

All plastics were cleaned by sonification in MilliQ water and dried prior to experiments to simulate prior exposure to water as expected for plastics found at sea. Four hundred and eighty cleaned pieces of each polymer type were randomly selected, weighed (XP26 DeltaRange, Mettler Toledo, readability is 0.01 mg), and divided into two groups (240 particles per group). For the North Pacific Gyre sample, plastic-fragments were evenly separated into two groups based on mass (AB265 S/FACT, Mettler Toledo, readability is 0.01 mg). This yielded a total of twelve plastic aliquots: 2×PE, 2×PE standard, 2×EPS, 2×PP and 2×North Pacific Gyre. Prior to irradiation these aliquots were rinsed three times with MilliQ, three times with seawater and then transferred into the 2 L ashed and ultraviolet-C sterilized spherical quartz irradiation flasks with 1 L of pre-photobleached seawater (two flasks for each plastic type = 10 flasks). Two control flasks were filled with pre-photobleached seawater, without plastics resulting in a total of 12 flasks. Half of the flasks (i.e. one of each treatment) were wrapped in heavy duty aluminum foil to provide dark controls. All flasks were then placed inside a solar simulator.

Irradiations were conducted in a solar simulator system equipped with 12 UVA-340 bulbs (Q-Panel) which provides light with a spectral shape and flux approximating natural sunlight irradiance from 295 to 365 nm[31]. This wavelength range is responsible for the majority of environmental polymer photochemical reactions[32-34]. The integrated irradiance (14±0.7 W m-2) in the solar simulator was quantified using a spectroradiometer (OL 756, Optronic Laboratories) fitted with a quartz fiber optic cable and 2-inch diameter integrating sphere which was calibrated with a National Institute of Standards and Technology (NIST) standard lamp (OL752-10 irradiance standard)[34]. Twenty four hours irradiation under these conditions approximates one solar day of photochemical exposure in the subtropical ocean gyre surface waters[20] where microplastics accumulate. A side mounted fan maintained temperatures between 25°C and 30°C. The flasks were repositioned daily to average out potential spatial variation in the light flux under the solar simulator. Throughout the seawater incubations DOC was monitored providing a time-series of DOC release and accumulation. In detail, liquid samples were drawn from the flasks using ashed glass Pasteur pipettes. Duplicate DOC samples (~10 mL aliquots) per time point were collected into pre-combusted 24 mL glass vials at 0 d, 2 d, 5 d, 10 d, 14 d, 22 d, 35 d, 49 d, 68 d for the North Pacific Gyre sample and 0 d, 0.5 d, 1 d, 3 d, 6 d, 10 d, 15 d, 22 d, 35 d, 54 d for postconsumer and standard plastic samples. Samples for bacteria counts (1 mL aliquots in sterile Nalgene cryovials) were collected at 0 d, 1 d, 15 d and 54 d for postconsumer and standard microplastics and at 0 d, 2 d, 5 d, 10 d, 14 d, 22 d, 35 d, 49 d, 68 d for the North Pacific Gyre sample, fixed with 0.1 % glutaraldehyde, and frozen at -80 °C until analysis. The remaining volume of each sample for the next time point irradiation was determined based on weight. Plastics were recovered from the flasks by filtering through 0.22 µm filters (GVWP04700, Millipore). After 54 days, fragments were dried, weighed and further analyzed for carbon content, and via optical and electron microscopy, and Fourier transform infrared (FTIR) spectroscopy.

2.7 Dissolved organic carbon (DOC)

Samples for DOC analysis were acidified to pH < 2 using HCl (p.a.) before analysis using a Shimadzu TOC-VCPH total organic carbon analyzer[29]. Certified DOC standards (low carbon seawater, LSW and deep seawater reference material, DSR) from the Consensus Reference Materials (CRM, University of Miami) were measured to confirm precision and accuracy. Measured DSR values were consistent with the consensus value (0.49-0.53 mg L-1, http://yyy.rsmas.miami.edu/groups/biogeochem/Table1.htm) with a standard deviation <5%. Routine minimum DOC detection limits using the above configuration are 0.034±0.0036 mg L-1 and standard errors are typically 1.7±0.5 % of the DOC concentration[29].

Plastic carbon mass normalized DOC accumulation was calculated following Equation 1 (Zhu et al., 2020).

Where, *PDOC* is the accumulation of DOC produced during the photo-dissolution of microplastics; *n* is the total number of samplings; *i* is each time point; *V* and *C* are the sample volume and concentration at each time point, respectively, and; *MC initial* denoted the total plastic carbon mass (g) of plastic particles at the start of each experiment. Measurement uncertainties were propagated to calculate final errors[38].

Note about locations:

The seawater was from the Southern Atlantic Bight but the location is not relevant to the interpretation or use of this dataset.

The plastics were collected from the North Pacific Gyre by non-profits (Algalita and 5 Gyres) studying the area. The exact sampling locations are unknown. They were provided as representative samples.

Data Processing Description

BCO-DMO Data Manager Processing Notes:
* Source file "DOC production for BCO-DMO_Data.csv" was imported into the BCO-DMO data system with values "#N/A" as missing data values.
** Missing data values are displayed differently based on the file format you download. They are blank in csv files, "NaN" in MatLab files, etc.
* Column names adjusted to conform to BCO-DMO naming conventions designed to support broad re-use by a variety of research tools and scripting languages. [Only numbers, letters, and underscores. Can not start with a number]

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Related Publications

Zhu, L., Zhao, S., Bittar, T. B., Stubbins, A., & Li, D. (2020). Photochemical dissolution of buoyant microplastics to dissolved organic carbon: Rates and microbial impacts. Journal of Hazardous Materials, 383, 121065. https://doi.org/10.1016/j.jhazmat.2019.121065
Results

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Parameters

Parameter	Description	Units
Sample_name	Sample name	unitless
Irradiated_Time	Time under solar simulator in light	Days
Initial_Weight_of_Plastic	Initial Weight of Plastic Irradiated	grams (g)
Carbon_Content	Percentage of initial plastic that was carbon (C) by mass	pecent (%)
DOC_sample1	Dissolved organic carbon concentration in duplicate irradation 1	micromolar (uM)
DOC_sample2	Dissolved organic carbon concentration in duplicate irradation 2	micromolar (uM)
Volume	Volume of water in irradiation flask	milliters (mL)
Percent_Plastic_Loss	Percentage of initial plastic carbon (C) that was converted to DOC	percent (%)
DOC_production	Rate of DOC production	mg-DOC g-C-1 d-1
Propagated_Error	Error associated with measurement of DOC production	mg-DOC g-C-1 d-1

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Project Information

EAGER: Collaborative Research: Assessing the contribution of plastics to marine particulate organic carbon (Marine Plastic POC)

Coverage: Boston Harbor, North Shore of Massachusetts, and Bermuda

NSF abstract:

Like life and the natural organic material life leaves behind, plastics are carbon-based. In use, plastics remain a wonder material, facilitating technological advancement. However, once discarded, their durability allows plastics to accumulate. One place that plastics are accumulating is at the surface of the open ocean. This project will collect samples from the open ocean and measure both natural organic carbon and plastic-carbon concentrations. The team hypothesize that in some places at the surface ocean there will be as much or even more plastic-carbon than natural organic carbon. If the team are correct, this will change how they and other ocean scientists interpret the carbon signatures observed in ocean samples and indicate our surface oceans have been fundamentally changed by plastic pollution.

Plastics are carbon-based polymers and an emergent component of the carbon-cycle. Data for plastics and organic carbon at sea are collected by different scientific communities, using different methods. Comparing data from these two communities suggests plastic-carbon may now rival concentrations of biogenic OC at the surface of the ocean. In this EArly-concept Grant for Exploratory Research (EAGER) project, the team will conduct an interdisciplinary study combining analysis of plastic-carbon and organic carbon for the same samples. Doing so in the Atlantic Ocean at BATS/Hydrostation “S” will test the hypothesis that plastic-carbon is now a significant fraction of total organic carbon at the sea surface. The project will deliver new methods for plastic-carbon analysis, including for nanoplastics down to 0.2 microns in size, and reveal whether ocean scientists now need to consider the role of plastic-carbon as an analyte in their samples and as an active component of the biogeochemistry and ecology of the surface ocean.

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.

Planned field sites:

Boston Harbor and the N. Shore of Mass. (near Nahant).

Ocean fieldwork is planned for summer of 2023 out of BiOS (Bermuda). Work will be conducted by small boat in coastal waters and near or at Hydrostation-S / BATS, and possibly a BATS cruise.

Collaborative Research: CBET: The role of sunlight in determining the fate and microbial impact of microplastics in surface waters (Sunlight Microbial Microplastics)

Coverage: Laboratory and North Atlantic

NSF abstract:
Microplastics are plastic particles smaller than 5 mm in size. Microplastics mostly originate from fragmentation of larger plastic objects and are now found globally from drinking water to rivers, lakes and streams, and the oceans. An estimated 8 million tonnes of plastic waste enter the oceans from land each year, yet only a fraction of this material is accounted for by floating microplastics. One hypothesis for the missing microplastic is that exposure to sunlight degrades them to dissolved carbon. This project will assess whether sunlight-driven photochemical reactions release dissolved organic carbon from plastics, resulting in removal of the plastics from the water. A second objective of this project will test whether the chemicals released affect bacterial growth and survivability in natural waters. Results will improve our understanding of the fate of floating plastics in natural waters. This project will have significant broader impacts in the fields of environmental microbiology and photochemistry. Results will be incorporated into high school classroom learning geared towards middle and high school students, to increase the Nation's scientific literacy and educate the next generation of environmental engineers and scientists. In addition, the results will inform society on how to prioritize plastic waste management to protect human and ecological health.

Microplastics are plastic particles smaller than 5 mm in size and originate from fragmentation of larger plastic objects released to the environment. Microplastics are found globally from drinking water to rivers, lakes and streams, and the oceans, where more than 98% of all buoyant microplastics are unaccounted for in loading estimates. The hypothesis for this research is that sunlight is responsible for degrading floating microplastics to dissolved organic carbon (DOC) on relatively short time scales (years). This hypothesis will be tested through a series of field, experimental, and analytical studies. The second hypothesis is that DOC released from photochemical breakdown will impact microbial growth. This hypothesis will be tested through bioassays with natural marine and freshwater microbes to assess the degradation kinetics (dissolution, fragmentation, and oxidation) of microplastics in seawater and freshwater in the light and dark, and with and without microbes. Experiments with plastics of variable polymer chemistry, size, and previous oxidation history will reveal the role of these factors in explaining variability in degradation rates to inform future modeling studies of plastic loss. The project brings together scientists with complementary educational, field, experimental, and analytical skills to transform our understanding of the fate and impact of buoyant microplastics in surface waters. Results will be disseminated to other scientists, the press, and incorporated into high school classroom learning via publication in the Science Journal for Kids, an open access journal which adapts primary, peer-reviewed research papers with age-appropriate language and illustrations geared towards middle and high school students.

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.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-2127669
Chemical, Bioengineering, Environmental and Transport Systems (CBET)	CBET-1910621

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