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## An airborne remote sensing case study of synthetic hydrocarbon detection using short wave infrared absorption features identified from marineharvested macro- and microplastics



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#### ABSTRACT

The abundance and distribution of plastic debris in natural waters is largely unknown due to limited comprehensive monitoring. Here, optical properties of dry and wet marine-harvested plastic debris were quantified to explore the feasibility of plastic debris optical remote sensing in the natural environment. We measured the spectral reflectance of microplastics (< 5 mm) from the North Atlantic Ocean, macroplastics (> 5 mm) washed ashore along the USA west coast and virgin plastic pellets over a wavelength range from 350 to 2500 nm. Compared to the spectral variability of multi-colored dry macroplastics, the measured dry marine-harvested microplastic reflectance spectra could be represented as a single bulk average spectrum with notable absorption features at ~931, 1215, 1417 and 1732 nm. The wet marine-harvested microplastics had similar spectral features to the dry microplastics but the magnitude was lower over the measured spectrum. When spectrally matched to the reference library of typical dry virgin pellets, the mean dry marine-harvested microplastics reflectance had moderate similarities to low-density polyethylene, polyethylene terephthalate, polypropylene and polymethyl methacrylate. This composition was consistent with the subset sampled with the Fourier Transform Infrared (FTIR) spectrometer and what has been reported globally. The absorption features at 1215 and 1732 nm were observable through an intervening atmosphere and used to map the distributions of synthetic hydrocarbons at a landfill and on man-made structures from airborne visible-infrared imaging spectrometer (AVIRIS) imagery, indicating the potential to remotely sense dry washed ashore and land-origin plastics. These same absorption features were identifiable on wet marine-harvested microplastics, but the ability to conduct remote sensing of microplastics at the ocean surface layer will require more detailed radiative transfer analysis and development of high signal-to-noise sensors. The spectral measurements presented here provide a foundation for such advances towards remote detection of plastics from various platforms.

#### 1. Introduction

Plastic pollution in the ocean has been identified as a threat for benthic, pelagic and littoral zones (Bergmann et al., 2015; Carpenter et al., 1972; Carpenter and Smith, 1972; Colton et al., 1974; Eerkes-Medrano et al., 2015; GESAMP, 2015; Thevenon et al., 2014; USEPA, 2011). A wide variety of marine organisms can ingest or become entangled in these plastic products with direct and often deadly effects (Carpenter et al., 1972; Cole et al., 2013; Eriksen et al., 2014; Ryan and Moloney, 1993; Thompson et al., 2004). Although large concentrations of floating or suspended plastic debris are being observed or modeled across aquatic habitats from inland to the open ocean, a comprehensive analysis of the spatial extent and abundance of debris is lacking and the monitoring tools are not well developed to assess global distributions (Bergmann et al., 2015; Carpenter and Smith, 1972; Eerkes-Medrano et al., 2015; Eriksen et al., 2014; GESAMP, 2015; Jambeck et al., 2015; Law et al., 2010; Ryan and Moloney, 1993; Thompson et al., 2004; van Sebille et al., 2015). Remote sensing imagery with moderate to high temporal, spectral and spatial resolution would provide an excellent ancillary tool to quantitatively explore the distributions of floating marine plastic debris (Maximenko et al., 2016; Moller et al., 2016).

Interdisciplinary scientific knowledge on plastic debris in the natural environment is required to document the dramatic increase in global uses of plastic over the last half century (Bergmann et al., 2015; SEP, 2011; Wang et al., 2016). Recent publications have outlined several methodological and analytical challenges to assessing marine

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plastic size ranges, abundance and polymer types (Eerkes-Medrano et al., 2015; Filella, 2015; Galgani et al., 2013; GESAMP, 2015; Hidalgo-Ruz et al., 2012; Lenz et al., 2015; SEP, 2011; Thevenon et al., 2014; Wang et al., 2016). Despite this, researchers have proposed provisional working terms, sampling and analytical techniques that are used in this investigation. Macroplastics include all particles > 5 mm in diameter and microplastics range from 0.33 to 5 mm in diameter (GESAMP, 2015; Thevenon et al., 2014; USEPA, 2011). The primary sampling method at sea involves deploying neuston nets with a mesh size of  $\sim 0.33$  mm in the surface layers from a research vessel (Carpenter and Smith, 1972; Law et al., 2010; Masura et al., 2015; Reisser et al., 2013). Harvested plastics are identified and sorted by visual inspection also using a microscope. Polymer composition and type of individual microplastic particles is obtained typically from density separation with subsequent C:H:N analysis, pyrolysis-gas chromatography and Fourier Transform Infrared or Raman spectroscopy (Bergmann et al., 2015; Hidalgo-Ruz et al., 2012; Thevenon et al., 2014).

However, there is a need for integrative direct and indirect monitoring approaches such as remote sensing (Mace, 2012; Maximenko et al., 2016; Slonecker et al., 2010). Remote sensing potentially provides the necessary spatial and temporal coverage of the ocean surface for estimating the global abundance of near sea surface plastics. However, enhanced reflectance due to marine plastics in ocean color imagery may not be observable due to standard processing techniques that remove portions of the signal influenced by atmospheric and sea surface perturbations (Bailey et al., 2010; Gordon and Wang, 1994). Additionally, limited sea-truth information on naturally harvested plastics has constrained the development of quantitative algorithms to remotely detect marine plastics. Therefore, a better understanding of the optical properties of marine plastics and their contributions to the visible and infrared wavelengths is important to assess how these features can be detected and quantified with current and future remote sensing tools.

Plastics have unique inherent optical characteristics in the near infrared (NIR) to shortwave infrared (SWIR) spectrum that have been used in automated optical sorting of waste in the recycling industry (Huth-Fehre et al., 1995; Masoumi et al., 2012; Moroni et al., 2015; Wienke et al., 1995). While reflectance in the visible to near infrared spectrum 400 to 900 nm has been measured on select pieces of macroplastic garbage (Hu et al., 2015), we are not aware of any studies characterizing the spectral properties of marine-harvested macro- and microplastics from the visible to SWIR wavelengths. However, there is a rising interest in the potential applications of remote sensing in detecting hydrocarbons such as oil, plastics and methane utilizing the absorption features in the ultra-violet to longwave infrared spectrum (Asadzadeh and de Souza Filho, 2017; Maximenko et al., 2016; Scafutto et al., 2017).

In this study, we aim to broaden the available information on the spectral properties of macro- and microplastics by conducting analysis on debris harvested from the North Atlantic Ocean and coastal ecosystems along the USA west coast as well as virgin pellets. We investigate the spectral bands and resolution specific to dry and wet marine-harvested plastics. Furthermore, we explore the potential for remote sensing algorithms of plastics using identified inherent plastic absorption bands. The results from this work have applications to sensor design and technology, as well as providing a foundation for more intensive radiative transfer modeling of plastics and experiments in marine ecosystems.

#### 2. Methods and materials

#### 2.1. Reflectance sampling

Spectral reflectance of dry marine-harvested macroplastics was measured outdoors at the Mystic Aquarium in Connecticut, USA on 25 March 2015 around midday (Fig. 1). These macroplastics were collected by the Washed Ashore team of volunteers along the beaches in Oregon and other areas on the west coastline of the USA. No further laboratory analyses were completed on the dry samples because they are part of an ongoing plastic pollution awareness art exhibition called Washed Ashore: Art to Save the Sea.

These specimens represent a wide range of harvested macroplastic debris that have undergone environmental weathering, but do not necessarily represent the most frequently found macroplastic debris on the beaches. Therefore, the spectra should be considered as representative of what might be found, but cannot be statistically aggregated into an "average" bulk signal or type of plastic. Identifiable items included buoys, handles, bottle caps, containers, styrofoam, ropes, toys, diving fins and nets. Item colors included yellow, green, peach, orange, dark brown, beige, light blue, clear, white, glossy white and pale green.

Reflectance measurements were also conducted on microplastics harvested by Sea Education Association team from the top 0.25 m of western North Atlantic waters with a neuston net mesh size of  $335 \, \mu m$ (Law et al., 2010). These samples were dried, separated by hand and stored in glass scintillation vials. Samples were further separated by size using successive filters from large to small metal sieves with mesh sizes: 1.68-2.00 mm, 2.00-2.38 mm, 2.38-2.83 mm, 2.83-3.36 mm, 3.36-4.00 mm (Fig. 2). Additional information on refractive indices of known virgin pellets as well as size, color and roundness of these specimens is presented (Supplementary Material Tables S1 and S2). Samples smaller than 1.68 mm were not included because the quantity was not sufficient to obtain a reasonable spectral signal or an optically dense target. Another set of microplastic samples from Kamilo Point, Hawaii, USA was prepared as above but was not of sufficient quantity to separate into size classes and was identified only as particles < 5 mm.

Eleven types of dry virgin pellets were also measured to establish a spectral reference library: polyvinyl chloride (PVC), polyamide or nylon (PA 6.6 and PA 6), low-density polyethylene (LDPE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), fluorinated ethylene propylene teflon (FEP), terpolymer lustran 752 (ABS), Merlon, polymethyl methacrylate (PMMA). The dry virgin pellets were not co-lored but had varying opacity (Supplementary Material Fig. S1). Selection of the dry virgin pellets was based on polymer type analysis from prior extensive investigations on sediment and marine-harvested plastic debris (Andrady, 2011; GESAMP, 2015; Hidalgo-Ruz et al., 2012).

A PANalytical Boulder ASD FieldSpec 4 spectroradiometer with a wavelength range from 350 to 2500 nm interpolated to a 1 nm resolution was utilized to measure spectral reflectance of the samples under ambient sunlight during clear sky conditions. Dry microplastics and the virgin pellets were aggregated into an optically dense target on a black rubber mat for a bulk spectral measurement of the sample (Fig. 2). The black rubber used as background material had negligible reflectance. A 1° fore optic pointed vertically downwards was outfitted on the spectrometer at 8 cm above the microplastics along with a 75%Labsphere white Spectralon plaque. For the dry macroplastics, an 8.5° fore optic was pointed at a nadir angle of 45° to the sample at a distance of 10 cm with a 99% white Spectralon plaque. Effects of instrument and user shading on measurements were minimal at this geometry and distance. A measurement was taken over Spectralon followed by 5 (macroplastic) or 10 (microplastic) measurements over the sample and finally another measurement over Spectralon. For the macroplastics, spectra were recorded from five different spots on the stationary art sample. For the microplastics, the sample was gently mixed to rearrange the location and orientation of the particles for each of the 10 replicate bulk measurements. The spectral reflectance of wet microplastics floating on filtered seawater with salinity 30 ppt was also collected following the same methods as above (Supplementary Material Fig. S2). Lambertian-equivalent reflectance (R) was then calculated as the spectrum of the sample normalized to the spectrum obtained over the Lambertian Spectralon plaque. A representative R was determined

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