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The applicability of reflectance micro-Fourier-transform infrared spectroscopy for the detection of synthetic microplastics in marine sediments

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ABSTRACT

Synthetic microplastics (≤5-mm fragments) are globally distributed contaminants within coastal sediments that may transport organic pollutants and additives into food webs. Although micro-Fourier-transform infrared (micro-FT-IR) spectroscopy represents an ideal method for detecting microplastics in sediments, this technique lacks a standardized operating protocol. Herein, an optimized method for the micro-FT-IR analysis of microplastics in vacuum-filtered sediment retentates was developed. Reflectance micro-FT-IR analyses of polyethylene (PE) were compared with attenuated total reflectance FT-IR (ATR-FT-IR) measurements. Molecular mapping as a precursor to the imaging of microplastics was explored in the presence and absence of 150-μm PE fragments, added to sediment at concentrations of 10, 100, 500 and 1000 ppm. Subsequently, polymer spectra were assessed across plastic-spiked sediments from fifteen offshore sites. While all spectra obtained of evenly shaped plastics were typical to PE, reflectance micro-FT-IR measurements of irregularly shaped materials must account for refractive error. Additionally, we provide the first evidence that mapping successfully detects microplastics without their visual selection for characterization, despite this technique relying on spectra from small and spatially separated locations. Flotation of microplastics from sediments only enabled a fragment recovery rate of 61 (±31 S.D.) %. However, mapping 3-mm^2 areas (within 47-mm filters) detected PE at spiking concentrations of 100 ppm and above, displaying 69 (±12 S.D.) % of the fragments in these locations. Additionally, mapping detected a potential PE fragment in a non-spiked retentate. These data have important implications for research into the imaging of microplastics. Specifically, the sensitivity and spatial resolution of the present protocol may be improved by visualizing the entire filter with high-throughput detection techniques (e.g., focal plane array-based imaging). Additionally, since micro-FT-IR analyses depend on methods of sample collection, our results emphasize the urgency of developing efficient and reproducible techniques to separate microplastics from sediments.

1. Introduction

Synthetic microplastics (≤5-mm fragments) are globally distributed pollutants in marine ecosystems that have been discovered particularly in coastal sediments (Barnes et al., 2009; Browne et al., 2010; Claessens et al., 2011). Despite their ability to transport organic pollutants and additives into food webs, our understanding concerning the abundance and fate of microplastics is insufficient, owing to the difficulty of quantifying these contaminants (NOAA, 2009; GESAMP, 2010). Reflectance micro-Fourier-transform infrared (micro-FT-IR) spectroscopy represents an ideal method for the detection of microplastics due to its non-destructive nature, minimal need for sample preparation, and ability to produce IR absorption spectra for thick and opaque materials (Ojeda et al., 2009). To date, most attempts to employ FT-IR analyses for the detection of microplastics in sediments have been preceded by the flotation and filtration of buoyant materials in a saline solution, followed by the light microscopy-based separation of putative polymers for spectroscopy (Thompson et al., 2004; Ng and Obbard, 2006; Reddy et al., 2006; Corcoran et al., 2009; Claessens et al., 2011). However, this approach to the FT-IR analysis of microplastics is both labor-intensive and prone to error, due to its reliance on the visual selection of particles for characterization (Thompson et al., 2004; Ng and Obbard, 2006; Reddy et al., 2006; Corcoran et al., 2009). Additionally, spectroscopic approaches for the characterization of microplastics have not been evaluated across research groups and different types of marine habitats. Due to these challenges, limited confidence can be placed on estimates concerning the extent of microplastic pollution in the environment. Hence, the

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Abbreviations: ATR, attenuated total reflectance; LDPE, low-density polyethylene; FPA, focal plane array; FT-IR, Fourier-transform infrared; UHMW PE, ultra-high molecular weight polyethylene.

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development of reliable methods for the collection, detection and quantification of microplastics is pivotal to the advancement of research into the distribution, fate and impacts of plastic debris (NOAA, 2009; Ryan et al., 2009; GESAMP, 2010).

In order to form a basis for research into developing improved techniques for the FT-IR-based detection microplastics in the environment, this research assesses the applicability of reflectance micro-FT-IR analyses for the identification of synthetic microplastics in vacuum-filtered marine sediments. Following an optimization of instrumental scanning parameters, as described by Mastalerz and Bustin (1995) and Ojeda et al. (2009) for the analysis of opaque samples, the reliability of reflectance micro-FT-IR spectroscopy is compared with attenuated total reflectance FT-IR (ATR-FT-IR) analyses and with reference to evenly and unevenly shaped microplastics. Furthermore, we explore the potential for the molecular mapping of microplastics, as a step towards the spectral imaging of these pollutants without the need for visual selection of fragments for analysis (Levin and Bhargava, 2005). Finally, the variability of microplastic spectra across fifteen offshore sampling sites is investigated. Throughout the study, polyethylene (PE) is used as a model polymer due to its role as a dominant component of marine plastic debris (Barnes et al., 2009).

2. Materials and methods

2.1. Sediment sampling and analysis

Sediments were collected between April and July 2009 from Lowestoft, Spurn Point (within the Humber Estuary) and fifteen offshore sites (U.K.), with distances of 50–500 km between stations (Supplementary material, Fig. S1). Samples from Lowestoft and Spurn Point were collected from the surficial centimeter of the seabed at low tide using a stainless steel spatula. Offshore samples were obtained using bulk sediments collected a by 0.1 m^2 Day Grab. All sediments were stored at 4 °C until use. Offshore sediments were analyzed for organic carbon content as described by Sapp et al. (2010).

2.2. Spiking of sediments with microplastics

For all analyses with the exception of molecular mapping, 10 g of wet homogenized sediment from each site was mixed with a single, evenly shaped $1 \times 5 \times 5$-mm LDPE square (Goodfellow, U.K.) and 50 ± 5 mg of unevenly shaped 1-mm LDPE granules (Goodfellow, U.K.). For molecular mapping, sediment from a single sampling site (Lowestoft, U.K.) was spiked with 10, 100, 500 or 1000 ppm of unevenly shaped 150-μm ultra-high molecular weight (UHMW) PE granules (Goodfellow). Non-spiked sediment retentates were also examined, using sediment collected from Lowestoft and Spurn Point, Humber Estuary (U.K.). All samples were prepared in triplicate.

2.3. Vacuum filtrations of plastic-spiked sediments

Microplastic-spiked sediments were stored at 4 °C for 48 h and covered up to 50 ml with hypersaturated artificial seawater prepared using 1.2 kg l^{-1} of a standard salt mixture (ZM Systems, U.K.) (Thompson et al., 2004; Ng and Obbard, 2006; Browne et al., 2010). The samples were mixed by inversion, vortexed for 30 s at 40 Hz and kept overnight at 4 °C. The resulting supernatants (30 ml) were vacuum-filtered through 47-mm Isopore™ polycarbonate membrane filters with a pore size of 0.2 μm (Millipore, U.S.A). The filters were air-dried and stored at room temperature until analysis.

2.4. Recovery of microplastics

Recovery (%) of artificially added microplastics was calculated using sediments spiked with 150-μm UHMW PE fragments ($n = 3$). The mean mass of non-plastic residues on the filter (determined using retentates of sediment and water only; $n = 3$) was subtracted from the total mass of materials retained on the filter surfaces following vacuum filtration.

2.5. FT-IR spectroscopy

Fourier-transform infrared measurements were performed using reflectance micro-FT-IR spectroscopy and attenuated total reflectance FT-IR (ATR-FT-IR) spectroscopy. Spectra were collected of artificially added microplastics within sediment retentates and of the membrane filter surface following vacuum filtration (Sections 2.2 and 2.3), using a Perkin-Elmer Spotlight imaging system and a Perkin-Elmer Spectrum One FT-IR spectroscope (Ojeda et al., 2009). For ATR-FT-IR measurements, a Specac Silver Gate ATR accessory was used, consisting of a germanium crystal at an incidence angle of 45°. Scans were performed using a spectral resolution of 4 cm^{-1}. Reflectance spectra were Kramers–Kronig-transformed to correct for specular reflection (Mastalerz and Bustin, 1995, 1996; Hacura et al., 2003). The micro-FT-IR analyses were performed individually or by molecular mapping. Individual measurements were obtained for randomly selected positions on the sample surface. Molecular micrographs were obtained for randomly selected areas of 3 mm^2, with spectra collected at intervals of 150 μm.

3. Results and discussion

Although micro-FT-IR spectroscopy represents an ideal method for the detection of microplastics in environmental samples (Thompson et al., 2004; Ng and Obbard, 2006; Ojeda et al., 2009), this method has not been experimentally evaluated. This study assessed the applicability of reflectance micro-FT-IR analyses for the detection of synthetic microplastics in retentates of vacuum-filtered marine sediments, using polyethylene as a model plastic. Following an examination of polymer spectra as a function of aperture size and the frequency of scans, reflectance micro-FT-IR analyses were compared with ATR-FT-IR measurements. Molecular mapping analyses were explored as a step towards the spectral imaging of microplastics. Finally, the spectra of plastics were compared across fifteen offshore sampling sites.

3.1. Signal-to-noise ratio as a function of aperture size and the frequency of scans

Despite previous attempts to detect synthetic microplastics in marine sediments (Thompson et al., 2004; Ng and Obbard, 2006; Reddy et al., 2006; Corcoran et al., 2009), the instrumental parameters for the reflectance micro-FT-IR analysis of microplastics have not been optimized. Therefore, we collected the spectra of granule- and square-shaped LDPE fragments within a vacuum-filtered retentate of plastic-spiked sediment (Lowestoft, U.K.; Supplementary material, Fig. S1) and of the polycarbonate membrane following filtration, using 100 co-added scans at aperture sizes of 10, 15, 20 and 50 μm^2 (Fig. 1). The filtration step did not affect the positions of absorbance bands, as shown by a comparison with spectra collected prior to filtration (Supplementary material, Fig. S2). The positions of absorbance bands and the ratios between peaks were consistent for all samples when examined as a function of aperture size. No interference was detected from the background signal originating from the polycarbonate membrane when collecting spectra for LDPE (Fig. 1). Although the signal-to-noise ratios of the spectra improved with increasing aperture size, large apertures may limit the detection of small plastic particles in heterogeneous matrices. Small aperture sizes provide high spatial resolution and are likely to facilitate the molecular mapping of microplastics, favoring the use of small apertures during spectral collection. It was observed that an aperture size of 15×15 μm