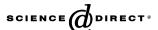


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Prevalence of microplastics in Singapore's coastal marine environment

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Abstract

Microplastics have been recently identified as marine pollutants of significant concern due to their persistence, ubiquity and potential to act as vectors for the transfer and exposure of persistent organic pollutants to marine organisms. This study documents, for the first time, the presence and abundance of microplastics (>1.6 μ m) in Singapore's coastal environment. An optimized sampling protocol for the collection and analysis of microplastics was developed, and beach sediments and seawater (surface microlayer and subsurface layer) samples were collected from nine different locations around the coastline. Low density microplastics were separated from sediments by flotation and polymer types were identified using Fourier transform infrared (FTIR) spectrometry. Synthetic polymer microplastics identified in beach sediments included polyethylene, polypropylene, polystyrene, nylon, polyvinyl alcohol and acrylonitrile butadiene styrene. Microplastics were detected in samples from four out of seven beach environments, with the greatest quantity found in sediments from two popular beaches in the eastern part of Singapore. Polyethylene, polypropylene and polystyrene microplastics were also found in the surface microlayer (50–60 μ m) and subsurface layer (1 m) of coastal waters. The presence of microplastics in sediments and seawater is likely due to on-going waste disposal practices from industries and recreational activities, and discharge from shipping.

Keywords: Microplastics; Marine environment; Singapore; Beach sediments; IR spectroscopy

1. Introduction

For centuries, humans have been disposing of waste into the sea where it eventually deposits on the coastline or the seabed. Plastic product production was estimated at 2.63 billion kg in 2004 in the United States alone (Schlechter, 2005) and increasing consumption over time is coupled to escalating levels of plastic in the marine environment via industrial discharge, littering and terrestrial runoff. Most polymers are highly persistent in the marine environment and only degrade slowly via photocatalysis when exposed to ultra-violet radiation (Dixon and Dixon, 1981). The lifetime of plastics at sea is not accurately known, but is estimated to range from years to decades, depending on the physical and chemical properties of the polymer (Gregory, 1978). Plastics at sea eventually undergo fragmentation,

leading to the formation of microscopic particulates of plastic or so called 'microplastics'. Due to their buoyant and persistent properties, microplastics have the potential to become widely dispersed in the marine environment via hydrodynamic processes and ocean currents.

The harmful effects of microplastics on marine life are still largely speculative, but adverse effects on marine invertebrates has been recently reported. In an article by Thompson et al. (2004) in the journal 'Science' entitled 'Lost at Sea: Where is all the Plastic?' the prevalence of microplastics in the world's oceans was highlighted, together with their propensity for ingestion by marine organisms. Microplastics are composed of a wide range of polymers derived from multiple sources, and may act as a transfer medium for toxic substances, including persistent man-made chemicals such as pesticides and polychlorinated biphenyls (PCBs). As such, there is a justified interest in their impact on the marine ecosystem (Khordagui and Abu-Hilal, 1994).

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Singapore is an island located in Southeast Asia between Malaysia and Indonesia (see Fig. 1) with a land area of less than 700 km² and a population of 4 million people. The nation is fully industrialized, being home to one of the world's busiest shipping ports and the world's third largest petroleum refinery. As such, the coastal and marine ecosystems are heavily disturbed and have been extensively modified by coastal development, reclamation and the port industry development. Plastic resins are transported to Singapore for onward distribution to trading companies in the region, and are also used in domestic plastic industries.

In this study, sediment and seawater samples were collected from Singapore's coastline to establish the first documented evidence for the presence of microplastics in the Asian marine environment. The initial objective was to establish a suitable sampling protocol for the collection and analysis of microplastics from beach sediments and seawater. This was followed by identification of the types of microplastic polymers in samples using Fourier transform infrared (FTIR) spectrometry, followed by an evaluation of spatial variability in the types and prevalence of microplastics in Singapore's coastal environment.

2. Materials and methods

2.1. Sample collection

Samples of beach sediments and seawater were collected from around Singapore's between August and December 2004. Seawater samples included both the ocean surface microlayer (50–60 μ m) and the subsurface layer (1 m). Beach sediments were collected from St John Island,

Changi, Pasir Ris, East Coast, Kallang River, Sembawang and Sentosa Island (see Fig. 1). All sediment samples were collected 0.5 m away from the ocean tideline. In total, 16 kg of sediments were collected from St John's Island for method development, and this included 2 kg samples taken from eight separate points, four of which were at the beach surface (top 1 cm) and four at a depth of 10–11 cm. Subsequently, 3 kg sediment was collected from Changi, Pasir Ris, East Coast, Kallang River, Sembawang and Sentosa beaches, where 1 kg of sediment was taken from three separate points at the beach surface (top 1 cm) and homogenised. Each sample was divided into three portions for replicate analysis. Each 1 kg sample was then further divided into three portions for replicate analysis.

Surface microlayer (SML) and subsurface water samples were also collected from Kranji and the Republic of Singapore Yacht Club (RSYC) (see Fig. 2) using a rotating drum sampler, as developed by Harvey (1966) and Carlson et al. (1988). Ten litres of SML and subsurface water was collected from each of the two locations and split into five samples per site, respectively. The SML is collected under capillary force by the rotating glass drum (diameter 300 mm, length 500 mm) and collected in a 101 glass container. The sampler is to collect SML samples to a depth of 50-60 µm and comprises stainless steel, anodized aluminum and teflon materials. Simultaneously, a 12 V DC Teflon pump was used to collect 101 of subsurface water from a depth of 1 m from each location. The sampler was attached to a small a research vessel by a 5 m long aluminum boom located starboard. Further details on SML sampling are given in Wurl and Obbard (2005).

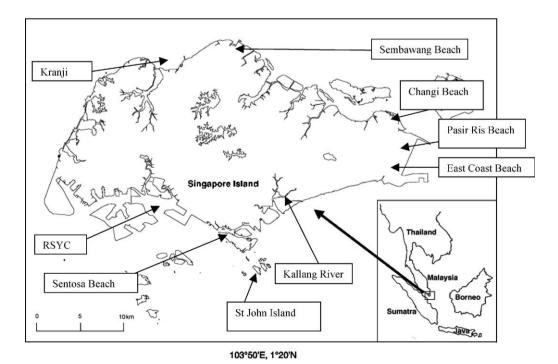


Fig. 1. Geographical location of Singapore and sampling locations.

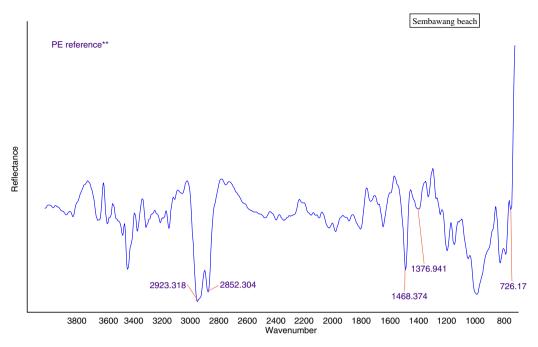


Fig. 2. IR spectra of an unknown particle in saline solution (artificial seawater) spiked with polyethylene.

2.2. Analytical method development

As this was the first investigation of microplastics in Singapore's coastal environment, a sampling protocol was adapted from the procedure given by Thompson et al. (2004). Separation of microplastic particulates from samples was achieved via flotation in a 1.2 kg l⁻¹ hypersaturated saline solution, whereby buoyant particulates float to the surface of the saline solution and are then collected onto filter paper following filtration of the sediment/saline mixture.

For homogenized sediment samples, 500 ml of saline solution was added to 250 g (dry wt. equivalent) of sediment in a 11 conical flask. The mixture was then shaken on a GEL® shaker for 1 min at 200 rpm. The supernatant was then poured into a second 500 ml conical flask and allowed to settle for 6 h before the final supernatant was filtered through a GF/A Whatman® glass microfibre filter paper (pore size 1.6 μ m) under vacuum filtration. The filter paper was placed into a petri dish inside a desiccator for 12 h. Each sample was divided into three portions for replicate analysis.

For the SML and subsurface water, 101 samples were shaken manually for 5 min and 11 of sample was filtered through a GF/A Whatman[®] glass microfibre filter paper (pore size $1.6 \mu m$) under vacuum filtration. The filter paper was then placed in a petri dish in a desiccator for 12 h. Seawater samples were analysed in triplicate.

For quality control purposes, both reverse-phase HPLC grade polyethylene and chromatographic grade polypropylene were spiked separately into sediment and concentrated saline solution at a density 1.2 kg l⁻¹ (representing artificial seawater) and then subjected to the extraction

procedure. These particles are spherical and 3.45 µm in size. Precision and particle recovery of the method was ascertained by comparing infrared spectra obtained against the polymer frequencies and library spectra for both polyethylene and polypropylene standards.

Infrared (IR) spectroscopy was performed on microplastics captured on filter papers (pore size 1.6 µm) for both sediment and seawater samples using a Bio Rad IR microscope UMA-500 attached to a Bio Rad Excalibur series FTS 3500. The instrument was operated in scanning reflection mode at a velocity of 5 kHZ, a mid-IR range of between 700 and 4000 cm⁻¹ and a resolution of 4 cm⁻¹ at four scans per analysis. The mercury cadmium telluride (MCT) detector in the instrument was liquid nitrogen cooled. Surface analysis of the sample on the filter paper was conducted using diffuse reflectance which is, generally, a non-destructive method requiring only minimum sample preparation. Although diffuse reflectance is useful for rapid and reproducible analysis, it may not provide a true spectrum of the sample as severe band distortions can arise as a result of complex surface and refractive index phenomena. Therefore, a background spectrum of sediment was taken and automatically subtracted from each sample spectrum obtained. The presence of characteristic frequencies in the spectra of seawater and sediment samples spiked with polyethylene and polypropylene were used as the reference spectra for microplastic identification in sediments and seawater samples. For identification of other unknown microplastics without reference material, interpretation was based on the correlation of absorption bands in the spectra of the samples to known absorption frequencies for specific chemical bonds types of relevant polymers (Kuptsov, 1998).

For extracted sediment and seawater sample filter papers, five randomly selected areas of 3 mm² on each filter paper. Within each area a visual observation scan was conducted using an FTIR microscope, at 1000× magnification to identify all potential microplastic particulates present. For all suspected microplastic particulates, FTIR analysis was performed using an 8-10 µm diameter laser beam to determine the polymer type of the particulate. Generally, the quality of the IR spectra of specific polymers is dependant on the preparation method of samples. A certain degree of error may be expected for IR spectra analysis of environmental samples due to the micron size range of naturally present particulates. False radiation may occur as variable diffraction phenomena in particulates may cause the apparent intensity of IR absorption bands to be too small for identification. In such cases, an exact match of the IR spectra against known reference polymer spectra may be difficult, unless the reference spectra for all polymer types are available.

3. Results and discussion

3.1. Reference spectra for microplastic identification

Polyethylene,—[CH₂—CH₂]_n—has distinct absorption bands for CH and CH₂ groups. Thus, peaks with wave numbers 2850–2960 cm⁻¹, 1450–1470 cm⁻¹ and 720–730 cm⁻¹ must be present for a positive identification. As shown in Fig. 2, a polyethylene spiked in an artificial seawater sample, these peaks were present in the spectra for the particulates analysed using FTIR, thereby confirming the presence of polyethylene.

Polypropylene

$$[CH_2$$
-- $CH]_n$ --- has absorption bands for CH , CH_2 and CH_3 .

Thus, peaks near wavenumbers 2850–2960 cm⁻¹, 1450–1470 cm⁻¹ and 1360–1380 should be present. Generally, the bands between 700 and 770 cm⁻¹ are due to rocking modes of the CH₂ groups. Unlike polyethylene, amorphous and crystalline polypropylene will not show any absorption at all in this region. Hence, the presence of peaks in this region serves to distinguish between polyethylene and polypropylene. For polypropylene, the 968 cm⁻¹ band is assigned to the methyl-rocking mode, mixed with CH₂ and CH rocking vibration. Moreover, absorption at 1380 cm⁻¹, presumably due to methyl group vibrations, is related to polypropylene. As shown in Fig. 3, in a polypropylene spiked sediment sample, these peaks were present in the spectra for the particulates analysed using FTIR, thereby confirming the presence of polypropylene.

The identification of microplastic polymers in seawater and sediment samples was completed by comparison of the spectra of polyethylene and polypropylene with the spectra obtained from unknown particulates. If the samples did not contain either polyethylene or polypropylene, the spectra obtained was then examined with respect to the available library reference spectra for functional groups of other polymer types.

3.2. Microplastics in beach sediment and seawater samples

All sediment and seawater samples collected from the various locations were prepared for IR scanning. The IR spectra were analysed to identify the presence of specific polymers.

Fig. 4 shows a typical example of an IR spectra subjected to analysis (RSYC, SML seawater sample). The IR spectra (black line) coincide with the reference spectrum, for polyethylene (blue line). Thus, it can be deduced that the particle analysed is indeed a polyethylene microplastic. The incidences of polyethylene microplastics in sediment and seawater samples are given in Tables 1 and 2.

Microplastics of six different types were identified in four out of seven sediment samples. The incidence of microplastics when detected in sample replicates can be considered as low (ranging from 0 to 4 particulates per sample replicate). However, a number of different polymer types were found including the reference polymers polyethylene and polypropylene, as well as other such as polyvinyl alcohol, acrylonitrile butadiene styrene, polystyrene and nylon.

Two out of the three sediment samples collected from Pasir Ris and East Coast, and four of the sediment samples collected from St John Island, were found to contain microplastics. The St John Island samples were collected during the southwest monsoon period with low rainfall and light winds, whereby currents from the Malacca Straits move westwards to Singapore and the west coast of Malaysia. The predominant water circulation brings water masses up from the south during low tide, allowing the accumulation of sediments and solid particulates along the coastline of St John's Island. Similar weather and tidal conditions prevailed at the Pasir Ris and East Coast sample locations during sample collection. The higher proportion of samples containing microplastics from East Coast and Pasir Ris relative to St John's island is most likely linked to the level of public usage of beaches. The Pasir Ris and East Coast beaches comprise the largest recreational areas in Singapore and are heavily visited, especially during weekends. This is associated with increased incidence of litter and accumulation of plastic debris. Gregory (1978) estimated that complete degradation of plastics on beaches takes up to 50 years, and much longer at sea. Hence, the presence of microplastics may be due to the plastic disposal years, or even decades previously, although faster degradation rates may be expected in warm tropical seas. One third of the

¹ For interpretation of color in Fig. 4, the reader is referred to the web version of this article.

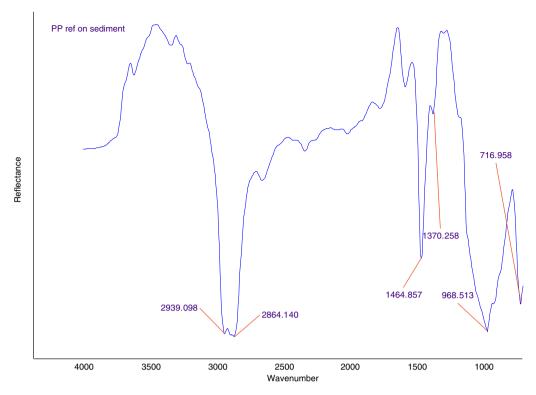


Fig. 3. IR spectra of an unknown particle in sediments spiked with polypropylene.

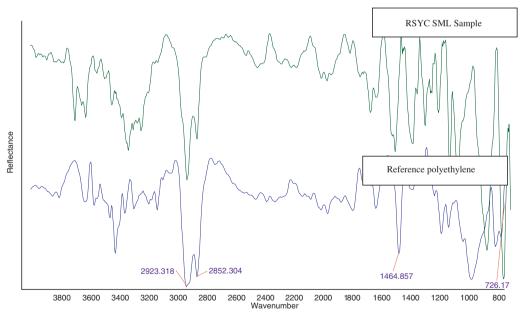


Fig. 4. RSYC SML sample spectra (upper line) with the overlay spectrum of reference polyethylene (lower line).

sediment samples collected from Kallang River were found to contain microplastic debris. Kallang Basin receives the drainage discharge from five rivers, namely the Rochor River, Kallang River, Geylang River, Whampoa River and Pelton Canal which drain major urbanized areas of Singapore. Up to 1980s, uncontrolled discharge of wastewater and solid debris flowed into basin, before a major clean-up operation in 1977. However littering is still a pre-

valent problem, where plastic fragments following degradation will persist in the sediments. In contrast, no microplastic particulates were detected in beach sediments from Changi, Sembawang and Sentosa beaches, although results do not prove that microplastics are completely absent due to the limited sampling.

For SML samples, samples from RSYC, situated in the western part of Singapore, had a greater prevalence of

Table 1 Incidence of microplastic polymers in sediment samples

Sample location St John Island	Date/time of collection 25 Aug 2004/11.30 am	Sample number	Sample replicates and number microplastic particulates present			Types of microplastic particle identified
			0	0	0	
		2	0	0	0	
		3	0	2	0	Acrylonitrile Butadiene Styrene
		4	1	1	0	Polystyrene
		5	2	0	0	Polystyrene
		6	0	0	0	
		7	0	2	0	Nylon
		8	0	0	0	
Pasir Ris	20 Sept 2004/11 am	1	1	0	1	Polystyrene
	•	2	0	0	0	
		3	0	3	1	Polystyrene/Polyethylene
East Coast	20 Sept 2004/5.30 pm	1	0	0	0	
	•	2	0	2	0	Polyvinyl alcohol
		3	1	0	0	Polypropylene
Changi	20 Sept 2004/9 am	1	0	0	0	
	_	2	0	0	0	
		3	0	0	0	
Kallang River	04 Dec 2004/7.30 am	1	4	2	2	Polyethylene
		2	0	0	0	
		3	0	0	0	
Sembawang	04 Dec 2004/2.30 pm	1	0	0	0	
		2	0	0	0	
		3	0	0	0	
Sentosa island	21 Sept 2004/1 pm	1	0	0	0	
	•	2	0	0	0	
		3	0	0	0	

Table 2 Incidence of microplastic polymers in seawater samples

Sample location	Date/time of collection 3 Dec 2004/1.57 pm	Sample number	Sample replicates and number microplastic particulates present			Types of microplastic particle identified
RSYC surface ocean microlayer			2	_	_	Polyethylene
		2	0	-	-	
		3	0	-	-	Polystyrene
		4	0	-	-	
		5	2	_	_	
RSYC sub-surface layer		1	0	_	_	
		2	0	_	_	
		3	2	_	_	Polyethylene
		4	2	_	_	Polyethylene
		5	0	_	_	
Kranji surface ocean microlayer	1 Dec 2004/12.30 pm	1	0	_	_	
	_	2	0	_	_	
		3	2	_	_	Polyethylene
		4	0	_	_	
		5	2	_	_	Polystyrene
Kranji sub-surface layer		1	0	_	_	
		2	0	_	-	
		3	0	_	-	
		4	1	_	-	Polypropylene
		5	0	_	_	

microplastics compared to Kranji, which is situated in the northern part of Singapore. Two out of five of the SML and subsurface samples collected from RSYC were found to contain microplastic debris, while two of the SML and only one of the subsurface samples from Kranji contained microplastics. This may be attributed to the presence of major large-scale plastic manufacturing based industries adjacent to the RSYC and the high density of shipping traffic nearby. As for Kranji, the presence of microplastic contaminants may be due to the northeastern currents transporting micro-debris from regional sources to Singapore. The most common microplastic detected in the SML samples from both RSYC and Kranji was polyethylene, where its presence was confirmed by comparison to the reference spectra of the spiked samples.

4. Conclusion

Study data are consistent with an earlier study that identified the widespread accumulation of microscopic plastic debris in marine sediments (Thompson et al., 2004). This study has shown, for the first time that synthetic polymer microplastics including polyethylene, polypropylene, polystyrene, nylon, polyvinyl alcohol and acrylonitrile butadiene styrene are prevalent in both seawater and sediment in the Asian marine environment. It is likely that these microplastics are derived from the physical and chemical fragmentation of larger plastic debris in the coastal environment. Both polystyrene and polyethylene were found to be common, where polystyrene was most readily

detected in sediments. Polyethylene was more prevalent in subsurface waters. Thompson et al. (2004) suggested that microplastics are a potential threat to marine biodiversity via particle ingestion and their potential to act as vectors for persistent man-made chemicals. Given the ubiquity and prevalence of microplastics in the marine environment further ecotoxicological investigation is warranted.

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