

Microplastics in Sediment Cores from Asia and Africa as Indicators of Temporal Trends in Plastic Pollution

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Abstract Microplastics (<5 mm) were extracted from sediment cores collected in Japan, Thailand, Malaysia, and South Africa by density separation after hydrogen peroxide treatment to remove biofilms were and identified using FTIR. Carbonyl and vinyl indices were used to avoid counting biopolymers as plastics. Microplastics composed of variety of polymers, including polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethyleneterephthalates (PET), polyethylene-polypropylene copolymer (PEP), and polyacrylates (PAK), were identified in the sediment. We measured microplastics between 315 µm and 5 mm, most of which were in the range 315 µm–1 mm. The abundance of microplastics in surface sediment varied from 100 pieces/kg-dry sediment in a core collected in the Gulf of Thailand to 1900 pieces/kg-dry sediment in a core collected in a canal in Tokyo Bay. A far higher stock of PE and PP composed microplastics in sediment compared with

surface water samples collected in a canal in Tokyo Bay suggests that sediment is an important sink for microplastics. In dated sediment cores from Japan, microplastic pollution started in 1950s, and their abundance increased markedly toward the surface layer (i.e., 2000s). In all sediment cores from Japan, Thailand, Malaysia, and South Africa, the abundance of microplastics increased toward the surface, suggesting the global occurrence of and an increase in microplastic pollution over time.

Globally, approximately 300 million tons of plastic products are produced annually, of which about half are single-use products. Some plastics elude waste management systems and enter rivers and the ocean. While floating at the sea surface and when stranded on beaches, plastic products are exposed to UV radiation and in this manner are fragmented into smaller pieces (Andrady 2011). The fragments get smaller and smaller and eventually become microplastics (i.e., plastics <5 mm in size). Plastics do not readily biodegrade but persist in the marine environment for long periods. An estimated 5 trillion pieces of plastic are floating in the world's oceans (Eriksen et al. 2014) from the Arctic (Obbard et al. 2014) to Antarctic (Isobe et al. 2016).

In the ocean, plastic fragments may be ingested by marine organisms. Ingestion of large fragments (e.g., ~cm) by large marine organisms, such as whales, turtles, and seabirds, has been reported since the 1970s (Rothstein 1973). More recently, the ingestion of smaller plastics (i.e., microplastics) by shellfish (Li et al. 2015) and fish (Lusher et al. 2013; Tanaka and Takada 2016) has been reported. The ingested plastics may result in physical damage to these biota (Wright et al. 2013). In addition, plastics and microplastics in the marine environment contain hazardous

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chemicals derived from additives in their formulation products, whereas hydrophobic chemicals from surrounding seawater may adsorb onto their surface (Teuten et al. 2009). The latter process has been well documented by the International Pellet Watch programme (Ogata et al. 2009; Takada and Yamashita 2016). Thus, microplastics also present a chemical hazard in marine ecosystems. Understanding the behavior and fates of plastics in the marine environment is essential for the robust assessment of the risks posed by microplastics. This understanding, however, is still limited.

The amount of plastic entering the world's oceans is estimated at 5–13 million tons/year (Jambeck et al. 2015). However, the amount of plastics floating at the sea surface in the world's oceans is estimated to be 0.3 million tons (Eriksen et al. 2014). The significantly lower amount of floating plastic compared with plastic input suggests a missing sink for plastics in the marine environment. A missing sink also is suggested by disparities in the size of microplastics floating at the sea surface. There is a marked paucity of plastics <1 mm in size at the sea surface compared with that expected from the abundance of plastics >1 mm in size (Cózar et al. 2014; Isobe et al. 2015). Sedimentation is a plausible process that may explain this difference (Cózar et al. 2014; Law et al. 2010). Most microplastics, i.e., polyethylene (PE) and polypropylene (PP), are less dense than seawater (Morét-Ferguson et al. 2010) and thus float at the sea surface. However, while floating at the sea surface microplastics are colonized by microorganisms that form biofilms (Zettler et al. 2013). This increases the density and reduces the buoyancy of microplastics (Morét-Ferguson et al. 2010) and may be an important mechanism for their settlement from the water column onto the seabed. Recently, microplastics have been detected in marine snow (Zhao et al. 2017) and have been reported in sediment in both coastal shallow waters (Claessens et al. 2011; Vianello et al. 2013) and the deep sea (Van Cauwenberghe et al. 2013). However, studies on microplastics in marine sediment are limited, especially the identification of polymer types and the quantitative evaluation of sediments as a sink for microplastics in the marine environment. Even more limited is research on microplastics in stratified sediment cores. This is important, because stratified sediments provide a history of pollution (Smol 2002). The measurement of persistent contaminants in stratified sediment cores, for example, has been used to understand historical trends in contamination (Chow et al. 1973; Goldberg et al. 1976; Van Metre and Mahler 2005; Boonyatumanond et al. 2007).

This paper provides the results of the analysis of microplastic polymer types in sediment cores collected in the marine environment in parts of Asia and Africa and a quantitative evaluation of the role of sediment as a sink for

microplastics in marine ecosystems in these areas. This is important, because the measurement of microplastics in marine ecosystems is a relatively new science and thus time-series data are limited (Law et al. 2010). Some of the sediment cores have previously been dated using radio nuclides and man-made chemicals with well-documented histories of emission as geochronometers. Selected layers of sediment extracted from the cores were analyzed in the present study, as a preliminary study to demonstrate the utility of sediment cores for understanding the history of and trends in microplastic pollution.

Materials and Methods

Sediment Cores

Sediment cores were collected in a canal in Tokyo Bay and in the Sakurada-bori Moat at the Imperial Palace in Tokyo in Japan, in the Gulf of Thailand, in the Straits of Johor in Malaysia, and in Durban Bay in South Africa. All sediment samples were collected using a gravity corer. The corer consists of an acrylic pipe (8-cm or 11-cm inner diameter \times 50-cm or 100-cm length) with a stainless-steel weight and stainless-steel catcher to prevent loss of the sediment. The corer was pushed into the sediment to its penetrable depth and then recovered. The sediment cores were sliced onsite into 1-cm to 5-cm intervals. The outer 1 cm of all layers was trimmed to prevent contamination from acrylic polymer of the corer. The trimmed sediment samples were stored in stainless-steel containers. Information on the core collection locations is provided in Table 1. The sediment core from the canal in Tokyo Bay was collected using a gravity corer of 11-cm i.d. and 50-cm length. The core was sliced at 5-cm intervals onsite. The slices were stored individually in stainless-steel containers and frozen until analysis. The canal receives river runoff, secondary effluent, and combined sewer overflows. Sediment in the canal is disturbed by biological processes (bioturbation), runoff, and dredging.

Sediment cores were collected in the Sakurada-bori Moat at the Imperial Palace in Tokyo in 1997 (Sanada et al. 1999) and 2001. Sediment was collected at the same site on both dates. The moat receives street runoff and combined sewer over flows. In 1997, sediment was collected using a gravity corer of 8-cm i.d. and 1-m length. The core was sliced at 2-cm intervals. The slices were stored individually and subsequently freeze dried. Slices from the 84–86 cm and 86–88 cm depths in the core were combined and used for this study. In 2001, a 40-cm long core was collected using a gravity corer of 11-cm i.d. and 50-cm length. The core was sliced at 2-cm intervals onsite. The slices were stored individually and subsequently freeze dried.

Table 1 Information on sediment core collection locations

Country	Area	Type	Site	Date of collection	Water column depth (m)	Latitude				Longitude				Altitude (m)
						D	M	S		D	M	S		
Japan	Tokyo Bay	Canal	Cn.21	Jul. 2012	5	N	35	35	46.2	E	139	44	51.5	0
Japan	Tokyo Bay	Canal	Cn.22	Jul. 2014	7	N	35	35	54.0	E	139	44	31.5	0
Japan	Imperial Palace	Moat	Sakurada-bori	May 1997	2	N	35	40	46.7	E	139	44	52.9	0
Japan	Nagano	Remote Mountain Lake	Ohnuma-ike	Nov. 2001	2	N	35	40	46.7	E	139	44	52.9	0
				Sep. 2001	25	N	36	42	18	E	138	31	37	~1700
Japan	Hokkaido	Remote Mountain Lake	Komadome-ko	Aug. 2001	5	N	43	15	24	E	143	5	37	~800
Thailand	Gulf of Thailand	Coastal zone	GT14	Jun. 2004	11	N	13	24	64	E	100	34	58	0
Thailand	Gulf of Thailand	Coastal zone	GT15	Jun. 2004	14	N	13	21	86	E	100	34	60	0
Thailand	Gulf of Thailand	Coastal zone	GT16	Jun. 2004	13	N	13	18	90	E	100	4	45	0
Thailand	Gulf of Thailand	Coastal zone	GT18	Jun. 2004	18	N	13	13	58	E	100	34	23	0
Malaysia	Straits of Johor	Coastal zone	JBEC3	Sep. 2006	14	N	1	28	31.3	E	103	49	51.2	0
South Africa	Durban Bay	Harbor	SADB-3	Sep. 2012	3	S	29	53	23	E	31	0	27	0

Sediment from the surface (0–2 cm) and middle (38–40 cm) of the core were used for this study.

Sediment cores were collected at four locations in the Gulf of Thailand in 2004 (Boonyatumanond et al. 2007), using a gravity corer of 11-cm i.d. and 1-m length. The cores were sliced at 1- or 2-cm intervals onsite. The slices were stored individually and subsequently freeze dried. Selected slices from the cores were analyzed for this study.

A sediment core was similarly collected in the Straits of Johor in Malaysia in 2006. Selected slices from the core were used for this study.

Sediment was collected in Durban Bay in South Africa in 2012 using a gravity corer of 11-cm i.d. and 50-cm length. The core was sliced at 2.5-cm intervals onsite and frozen until analysis. Slices at 2.5–5 cm and 20–22.5 cm depths were used for this study. The core was collected in a location that receives inflows from three rivers that receive stormwater runoff and effluent from wastewater works.

Dating

Sediment in the core collected in the Sakurada-bori Moat at the Imperial Palace in Tokyo was dated using the bulk density of individual sediment layers and sediment accumulation rate, which was estimated through the analysis of

anthropogenic compounds (i.e., polychlorinated biphenyls: PCBs) in the sediment. For the core collected in 2001, the highest PCB concentrations were found in the 30–32 cm layer. This sediment layer was ascribed to 1971, when PCB usage was highest in Japan. The cumulative weight of sediment layers between 0–31 cm (4.83 g/cm^2) over the 30-year time period (2001–1971) implied a sediment accumulation rate of $0.161 \text{ g/year/cm}^2$. Using this accumulation rate and the bulk density of the sediment, sediment from the 38–40 cm layer was estimated to have been deposited between 1952–1957 (1950s). The same sediment accumulation rate ($0.161 \text{ g/year/cm}^2$) was applied to the core collected in 1997, and sediment from the 84–88 cm layer in this core was estimated to have been deposited in the 1880s. Goldberg et al. (1976) reported a sedimentation rate of 2.0 cm/year for a sediment core collected at a different location of the Sakurada-bori Moat. Their rate is greater than our estimation, although it is in the same order of magnitude. This is probably due to the different core collection location, as discussed in Sanada et al. (1999).

Sediment in core GT-15 collected in the Gulf of Thailand was dated through the analysis of radio nuclides (^{137}Cs) and molecular markers (linear alkylbenzenes: LABs). Based on the details described in Boonyatumanond et al. (2007), the 44–46 and 6–12 cm layers were estimated

to have been deposited in the 1950s and 1990s, respectively. Cores collected from the Straits of Johor and from Durban Bay were not dated.

Measurement of Microplastics in Sediment

Ten grams of freeze-dried sediment or wet sediment corresponding to 10 g of dry sediment was analyzed for microplastics. To remove biofilms from the surface of microplastics, 150 mL of 30% H_2O_2 was added to the sediment in a glass beaker. After the reaction ceased, which was normally after ~ 1 week, the sediment was passed through a 315- μm , mesh-size nylon sieve. Particles retained in the sieve were suspended in 500 mL of 5.3 M NaI solution (density: 1.6 g/cm^3), stirred for 2 min, allowed to stand for 3 h, and a 100 mL aliquot of the supernatant was then removed. This process was repeated, and the combined supernatant was then centrifuged at 2000 rpm for 10 min. The supernatant was passed through a 5-mm, mesh-size, stainless-steel sieve and then through 1-mm, mesh-size, stainless-steel sieve and 315- μm , mesh-size nylon sieve. All the retained particles on the meshes were dried in a desiccator with activated silica gel for a week, picked-up one by one using stainless-steel tweezers, and subjected to Fourier transform infrared spectroscopy (FTIR) as follows.

Polymer types were identified using FTIR (NICOLET iS5, Thermofisher Scientific) with Attenuated Total Reflectance (ATR). The specifics of FTIR analysis were as follows: Spectrum resolution: 4 cm^{-1} ; number of scans: 10 per a sample; automatic adjustment for atmosphere: on; baseline correction: advanced ATR correction. HR Hummel Polymer and additives, HR Rubber compounding materials, and Sprouse polymer by ATR libraries were used for polymer identification. A hit quality $>60\%$ was used as the threshold for polymer types. A combination of a carbonyl index <1 and a vinyl index <0.2 was used to exclude biopolymers (discussed further in “[Results and Discussion](#)”). Reproducibility of counting microplastics was examined by the analysis of a sediment sample in duplicate (2.5–5-cm layer from sediment core collected in Durban Bay). The relative deviation was less than 10% for total microplastics (Table S1). Laboratory contamination was examined by analyzing surface sediment samples collected from remote mountain lakes (Lake Komadomeko and Lake Ohnumaike) in Japan.

Measurement of Microplastics in Surface Water

For comparative purposes, microplastics were measured in surface water collected in June 2013 and July 2014 in the same canal in Tokyo Bay as that in which the sediment core was collected. A Neuston net (30-cm i.d. and 1-m

length) of 315- μm nylon mesh size was deployed from the side of a boat at a speed of 2 miles per hour for 20 min. During deployment, half of the mouth of the net was submerged below the water surface. The contents trapped by the net were transferred to a glass bottle and transported to the laboratory. The contents were passed through a 5-mm, mesh-size, stainless-steel sieve, and then 1-mm, mesh-size, stainless-steel sieve and 315- μm , mesh-size nylon sieve. Particles retained by the sieves that were presumed to be microplastics were removed and identified using FTIR, in the same manner as for microplastics in sediment samples.

Results and Discussion

Identification and Quantitative Measurement of Plastics and Polymer Type

Results of the identification of microplastics in sediment from the core collected in the canal in Tokyo Bay are provided in Table S1. Microplastics in the sediment were comprised of various polymers, including polyethylene (PE), polypropylene (PP), polyethylene propylene copolymer (PEP), polystyrene (PS), polyethyleneterephthalates (PET), polyvinyl chloride (PVC), polyamide (PA), ethylvinyl acetate (EVA), polyacrylates (PAK), and polycaprolactone (PCL). Figures S1 and S2 provide typical photos and the typical IR spectrum of microplastics in sediment collected from the canal and corresponding polymers. PE was characterized by doublet absorption of stretching vibration of the C–H bond in ethylene structure at 2925 and 2855 cm^{-1} and absorption of bending vibration of the C–H bond in ethylene structure at 1465 and 725 cm^{-1} , while PP had additional absorptions around 2900 and 1380 cm^{-1} , 1000 and 975 cm^{-1} , which were ascribed to the methyl group ($-\text{CH}_3$). PEP showed an intermediate spectrum between PE and PP. PVC was characterized by absorption at 620, 630, and 690 cm^{-1} specific to vibration of the C–Cl bond. IR spectrum of PS showed absorption around 2950, 760, and 700 cm^{-1} , which are derived from their aromatic structure. PET, EVA, PCL, and PAK had absorption at 1715 cm^{-1} , which is specific to carbonyl ($\text{C}=\text{O}$). They were differentiated by absorptions in the range 1100 to 1300 cm^{-1} (i.e., 1240 cm^{-1} for EVA; 1100 and 1265 cm^{-1} for PET, 1240 cm^{-1} for PAK, 1175 cm^{-1} and vicinities for PCL), which is characterized as bending vibration of the C–O bond in ester structure. PET showed further specific absorption of the aromatic C–H bond at 725 and 730 cm^{-1} . Polyamide (PA) has a $\text{C}=\text{O}$ bond, but it is in an amide structure that shifted absorption of the $\text{C}=\text{O}$ bond to 1635 cm^{-1} . PA also had absorptions caused by the N–H

bond at 3300 and 1565 cm^{-1} . Our identification of microplastics was based on the comparison of their IR spectrum to those in HR Hummel Polymer and Additives, HR Rubber Compounding Materials, Spouse Polymer by ATR library. Highest agreement (hit quality) of a spectrum was assigned as the polymer in cases where the hit quality was higher than 60%.

In the case of polymers with normal alkyl chains, such as polyethylene (PE), polyethylene propylene diene (PEPD), polyethylene propylene copolymer (PEP), and poly(ethylene:1-butane), we introduced a criterion for their identification as synthetic polymers, because a straight alkyl chain is common in natural polymers. For example, the IR spectrum of H_2O_2 -treated leaves of the plant *Zelkova serrata* is similar to that of polyethylene with hit quality of 74% (Fig. S3). This requires a criterion to distinguish plastics from natural polymers. Natural polymers with straight alkyl chains sometimes have a carbonyl functional group, such as fatty acid moiety. Oxidative treatment using H_2O_2 may introduce a carbonyl functional group into the n-alkane structure of natural polymers. The IR spectrum of H_2O_2 -treated leaves had a prominent peak at 1715 cm^{-1} , indicating the presence of carbonyl group that might be an original constituent of a biopolymer or might be an oxidative-product during H_2O_2 -treatment. Based on these considerations, absorbance of the carbonyl group (i.e., carbonyl index defined as a ratio of absorbance of carbonyl at 1715 cm^{-1} to that of ethylene at 1465 cm^{-1}) was utilized as the criterion to distinguish natural and synthetic polymers. For leaves, the carbonyl index was ~ 1 . Therefore, samples with a carbonyl index >1 were ascribed to biopolymers. However, the carbonyl index has been used as an indicator of the degree of weathering of polyethylene (Satoto et al. 1997), because oxidation of PE introduces a carbonyl group into the polymer. Thus, our criterion could exclude weathered plastics and, therefore, may lead to an underestimation of PE in samples.

Another peak was observed at 1640 cm^{-1} in the IR spectrum of H_2O_2 -treated leaves. This is ascribed to a vinyl structure ($\text{C}=\text{C}$), which may be contained in biopolymers or can be produced by H_2O_2 treatment. A vinyl structure is not normally produced by UV photolysis. To examine the threshold of the vinyl index, which is defined as a ratio of absorbance of vinyl at 1640 cm^{-1} to that of ethylene at 1465 cm^{-1} , a cross plot of carbonyl and vinyl indices for suspected microplastics in surface sediment from Sakurada-bori Moat at the Imperial Palace in Tokyo was prepared (Fig. 1). Based on the vinyl index, suspected microplastics fell into two groups: those with an index >0.5 and those with an index <0.2 . This suggests two distinct sources, that is, biogenic and synthetic polymers. Thus, a sample with vinyl index >0.2 was ascribed as a biopolymer. Samples with a carbonyl index <1 and a vinyl index

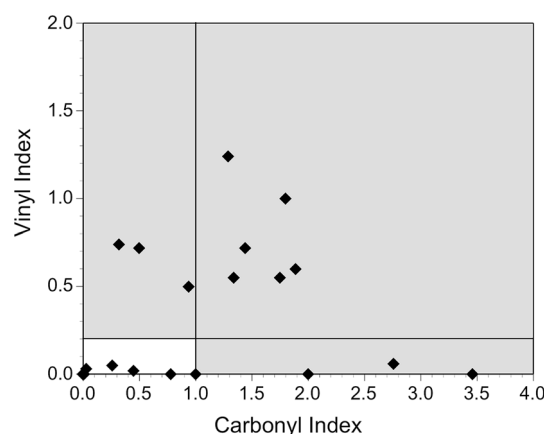


Fig. 1 Carbonyl Index–Vinyl Index cross plot for microplastics in sediment. Sample: 0–2-cm layer of sediment from core collected in the Sakurada-bori Moat at the Imperial Palace in Tokyo, Japan. Carbonyl Index: ratio of absorbance of carbonyl at 1715 cm^{-1} to that of ethylene at 1465 cm^{-1} ; Vinyl Index: ratio of absorbance of vinyl at 1640 cm^{-1} to that of ethylene at 1465 cm^{-1}

<0.2 were ascribed as plastics (Fig. 1). This criterion was applied to PE, PEP, and poly(ethylene:1-butane). However, even using these criteria, it was impossible to distinguish PEPD from natural rubber. Thus, PEPD was excluded from consideration. This study may have underestimated the number of PE, PEP, and poly(ethylene:1-butane) microplastics, because the threshold may have excluded weathered microplastics. Furthermore, the approach may have excluded PE, PEP, and poly(ethylene:1-butane) with additives consisting of carbonyl and/or vinyl moieties. A more accurate approach to identify synthetic polymers must be developed in future studies.

Our procedures gave rise to some potential sources of laboratory contamination. For example, nylon sieves used in the separation of microplastics from sediment are a potential source of polyamides. However, no microplastics, including polyamides, were detected in sediment cores from the remote mountain lakes, indicating that laboratory contamination was not significant, if at all important. We did not examine the recovery of the analytical procedure by spiking sediment samples with microplastics. However, we checked the extraction efficiency of density separation, the most critical part of the process. We did this by analyzing residual deposits after density separation, as follows. A sediment sample from Tokyo Bay canal (Cn.22) was analyzed for microplastics using the normal procedure. Supernatants were decanted after density separation by using NaI. Thereafter, the residual deposits (which were discarded in our normal procedure) were analyzed for microplastics. The number of microplastics in the supernatants (sum of first and second supernatants) was 243 pieces per 10 g dry weight of sediment, whereas the total number of microplastics in the residual deposit was 18

pieces per 10 g dry weight of sediment (Table SI-2). This indicated that the majority (93%) of microplastics were recovered from the sediment by density separation. There was a much higher number of nonplastic particles in the residual sediment deposit, i.e., 499 pieces of nonplastic particles versus 18 microplastics. On this basis, we only analyzed the supernatants for microplastics.

We detected microplastics composed of light (e.g., PE and PP) to heavy (e.g., PVC and PET) polymers in the sediment core collected in the canal in Tokyo Bay (Fig. 2). In contrast, microplastics in one of the surface water samples collected in the canal were composed predominantly of light polymers (i.e., PE and PP) (Table 2). The detection of microplastics composed of PVC, PET, and PAK in sediment is reasonable considering their density is 1.17–1.45 times greater than that of seawater. PCL (polycaprolactones), one of the “biodegradable” plastics, were among the heavier microplastics detected. This can probably be explained by the fact that the biodegradation of “biodegradable” plastics is depressed under anaerobic conditions in sediment.

As stated earlier, microplastics composed of PE and PP, which are less dense than seawater, were detected in sediment. This may be due to an increase in the density of microplastics composed of these polymers through fouling by biofilms and their subsequent settling from water column due to the biofilm-induced increase in density. Morét-Ferguson et al. (2010) observed an increase in the density of PE and PP plastic debris in surface waters, which they ascribed to biofouling. Microbial colonization on microplastics also has been demonstrated by Zettler et al. (2013), as has the settling of microplastics in marine snow by Zhao et al. (2017). An additional way that microplastics may be transported to the seabed is in the fecal pellets of organisms that may have ingested the microplastics (e.g., large zooplankters, shellfish, and fish).

The abundance of microplastics in various layers of the sediment core collected in the canal in Tokyo Bay ranged from 1845–5385 pieces/kg-dry sediment (Fig. 2). There was, however, no consistent trend in microplastic

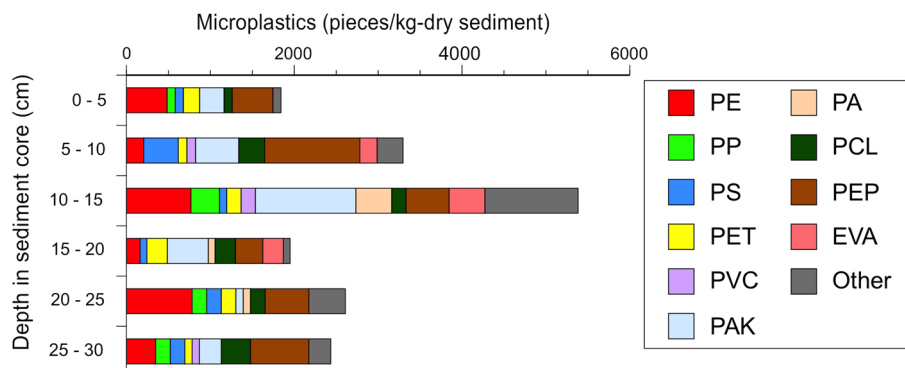
Table 2 Abundance of microplastics (315 μm –1 mm) in sediment extracted from a core and in surface water samples collected in a canal (Cn.21) in Tokyo Bay

	PE	PP
Surface water (pieces/m ²)		
June 2013	3.2	Not measured
July 2014	1.7	0.7
Bottom sediment (pieces/m ²)		
	6×10^4	2×10^4

abundance through the core. This may be due to a combination of temporally variable inputs of microplastics to the canal, the rapid rate of sedimentation in the canal (2–3.5 cm/year; Simura 1985), and the high degree of natural (e.g., bioturbation) and anthropogenic (e.g., dredging) disturbance of sediment in the canal. Stocks of microplastics per unit area (i.e., m²) are compared between bottom sediment and surface water. Based on the dry bulk density (0.37–0.49 g/cm³) and number of PE and PP microplastics in layers of the core, the total number of PE and PP microplastics in the core (0–30 cm) was calculated as 6×10^4 pieces/m² and 2×10^4 pieces/m² respectively (Table 2). The abundance of PE and PP microplastics in surface water samples collected in the same canal was calculated at 1.7–3.2 pieces/m² and 0.7 pieces/m² respectively. The stock of PE and PP microplastics in the core was thus four orders of magnitude higher than in the water column (Table 2). This suggests that sediment is a significant sink for microplastics in the canal.

Microplastics in sediment from the canal were categorized into two size classes: 0.3–1 mm and 1–5 mm. Most microplastics were in the 0.3–1-mm size class, with particles of 1–5 mm present in trace amounts. The high abundance and size of microplastics is consistent with the findings of Cózar et al. (2014) and Isobe et al. (2015), who suggested that sediment is the missing sink for microplastics based on their observation of size distribution of microplastics in surface water. They found a smaller

Fig. 2 Profile of microplastics in the sediment core collected from a canal (Cn.21) in Tokyo Bay. Detailed data are available in Tables S1-1 to S1-6



number of microplastics <1 mm than expected based on the number of microplastics >1 mm and suggested that small microplastics were being removed from water column by unknown processes. Our results suggest that sedimentation may account for the missing range of microplastics.

Microplastics of various shapes were identified in sediment from the canal, including films/sheets, fibers, fragments, and beads. Fragments were numerically dominant (75%), followed by fibers (15%) and beads (4%; Fig. 3a). These ratios are similar to those for microplastics found in the digestive tract of anchovy caught in Tokyo Bay (Tanaka and Takada 2016). Considering PET alone, fibers were the dominant form (80%; Fig. 3b). This is consistent with the abundance of PET fibers typically found in laundry wastewater (Browne et al. 2011) and their significant contribution to microplastics in aquatic habitats (Napper and Thompson 2016). However, fragments of PET also were detected in significant abundances, implying that fragmentation of PET products (e.g., PET bottles) cannot be ignored. Microplastics in the sediment were of various colors. Most were white (57%), followed by brown (17%) and black (14%), but red, blue, and green microplastics

also were detected (Fig. 3c). However, predominance of white plastics may be overestimated, because colored plastics may have been bleached by H_2O_2 used to remove biofilms from the microplastics.

Vianello et al. (2013) reported a similar variety of microplastic polymer types and dominance of microplastic fragments in sediment from Venice Lagoon in Italy. However, they report a higher abundance of light (i.e., PE and PP) than heavy polymers. PE and PP represented 63–89% of microplastics in sediment in the lagoon. Different sources, routes of introduction, and depositional environments (intertidal lagoon vs. sublittoral bottom) may be responsible for the difference in the proportion of polymers. The abundance of microplastics in sediment collected from the canal in Tokyo Bay (~1800 pieces/kg-dry sediment) is similar to the abundance reported for surficial sediment in Venice Lagoon (672–2175 pieces/kg-dry sediment) but is one to two orders of magnitude higher than the abundance reported for sediment from the Belgian coast by Claessens et al. (2011) (Harbor: 67–391 pieces/kg-dry sediment; continental shelf: 71–270 pieces/kg-dry sediment). Proximity to rivers, sewage outfalls, and combined sewers is likely to influence the abundance of microplastics in sediment.

Fig. 3 Shapes (a, b) and color (c) of microplastics in sediment core collected in a canal (Cn.21) in Tokyo Bay, Japan. $n = 198$ for all polymers (a, c) and $n = 11$ for PET (b)

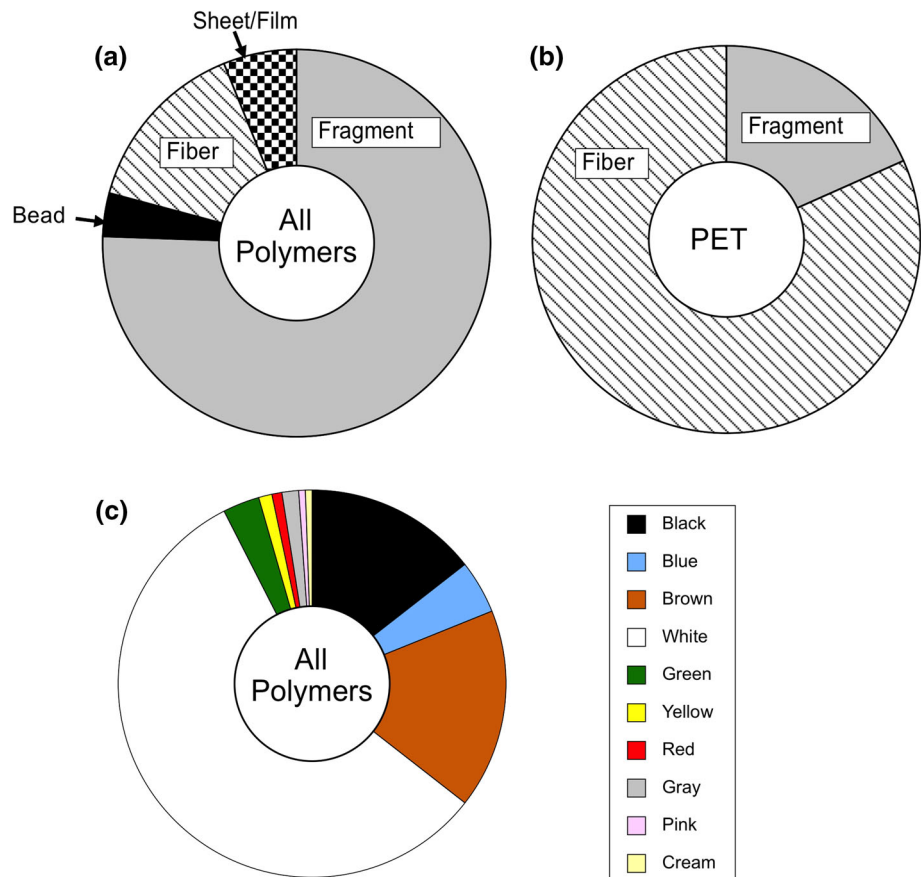


Fig. 4 Vertical profile of microplastics in sediment core collected in the Sakurada-bori Moat at the Imperial Palace in Tokyo, Japan. Detailed data are available in Tables S1-7 to S1-9

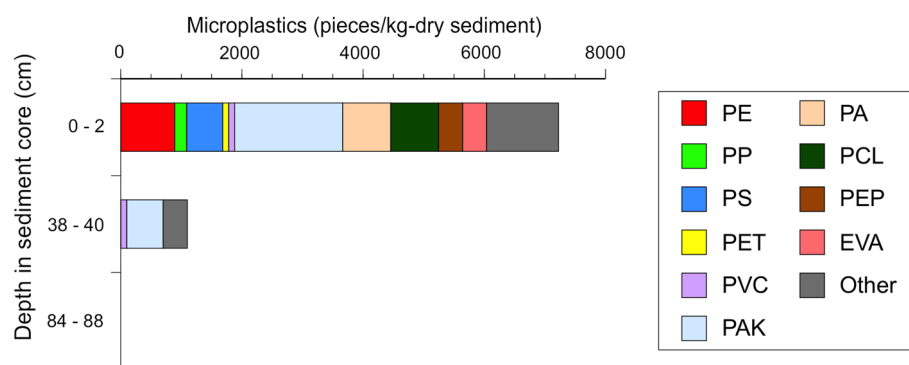
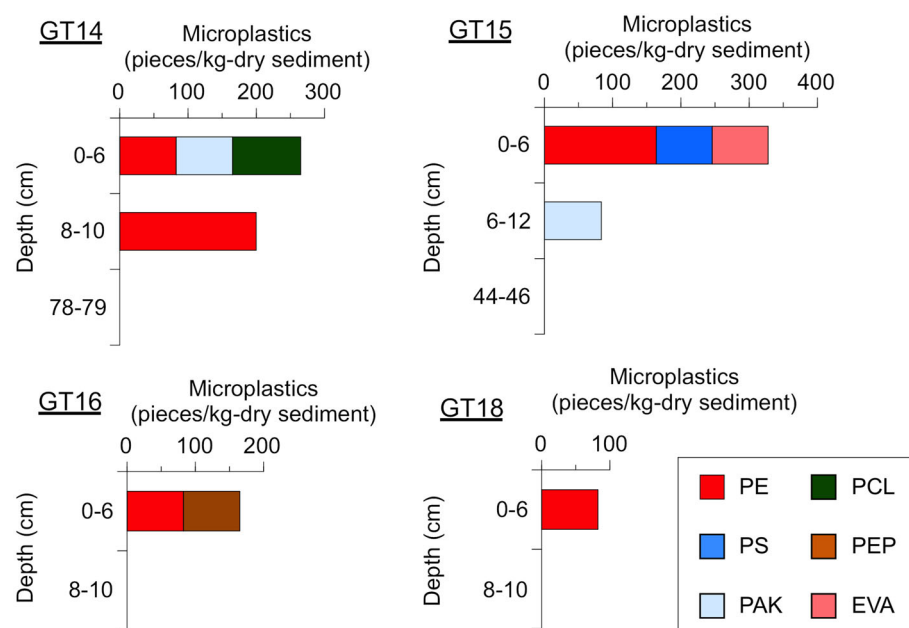


Fig. 5 Profile of microplastics in the sediment core collected from Gulf of Thailand, Thailand. Detailed data are available in Tables S1-13 to S1-22



Profiles of Microplastics in Sediment Cores

There was a marked increase in the abundance of microplastics from the deeper to surface layers of the sediment core collected from the Sakurada-bori Moat at the Imperial Palace in Tokyo (Fig. 4). In the deepest layer of the core (84–88 cm), no plastics were detected. This is understandable considering this layer corresponds to a date before 1900 (i.e., before plastic production). In the middle layer (38–40 cm), dated to the 1950s, a small yet significant number of microplastics (~1100 pieces/kg-dry sediment) were detected. These included PVC and acrylics, whose industrial production started in the 1950s in Japan (The Japan Plastics Industry Federation 2008). The surface layer (0–2 cm), which was dated to the early 2000s, contained by far the greatest abundance of microplastics (~7000 pieces/kg-dry sediment) and included PE, PP, PS, PET, PVC, acrylics, polyamides, polylactones, PEP, and EVA. These plastics are derived from street runoff and

combined sewer overflows. The marked increase in the number of microplastics from the middle layer (1950s) to the surface (early 2000s) is consistent with the increase in plastic production in Japan during this period. Microplastics in sediment increased by a factor of 7 during this period, while plastic production increased by a factor of 30. Future analysis of additional sediment layers from the core will allow a more detailed assessment of microplastic pollution with time.

An increase in the abundance of microplastics toward the upper layers was observed in all other sediment cores. No microplastics were detected in the 44–46 cm layer (1950s) of sediment core GT15 collected from the Gulf of Thailand (Fig. 5). This may suggest that the onset of large-scale consumption of plastics in Thailand occurred in the 1960s. The significant increase in abundance of microplastics in sediment from the 6–12-cm layer (1990s) to the surface layer (2000s) is undoubtedly related to an increase in plastic consumption in Thailand. Microplastics

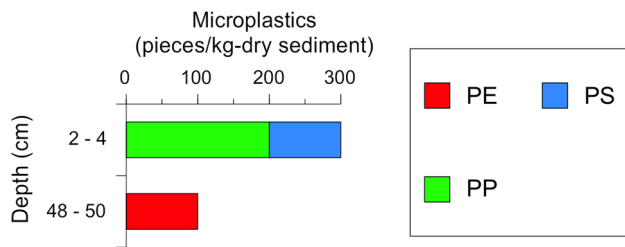


Fig. 6 Profile of microplastics in the sediment core collected from Straits of Johor, Malaysia. Detailed data are available in Table S1-23 to S1-24

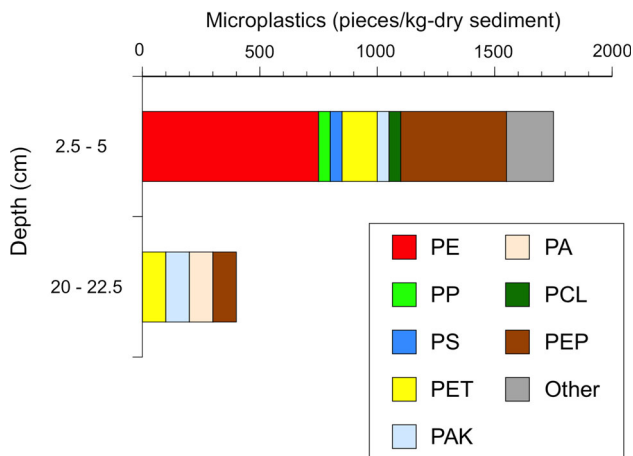


Fig. 7 Profile of microplastics in the sediment core collected from Durban Bay, South Africa. Detailed data are available in Tables S1-10 to S1-12

were detected in the surface layer of all other (nondated) sediment cores collected in the Gulf of Thailand but were not detected in the deepest layers. A higher abundance of microplastics was detected in the 2–4-cm layer than in the 48–50-cm layer of the sediment core collected from the Straits of Johor, Malaysia (Fig. 6).

Increase in microplastic pollution also was observed in the sediment core collected in Durban Bay, South Africa. A considerably higher abundance of microplastics was observed in the surface layer (2.5–5 cm) than the deeper layer (20–22.5 cm; Fig. 7). Microplastics comprised of PE and PEP polymers were more abundant than in sediment from the core collected in the canal in Tokyo Bay. Many factors, including patterns of polymer composition of formulation-plastics and routes of microplastic introduction, could have contributed to the difference in the polymer composition of microplastics between these study areas. More samples must be analyzed in future studies to develop a better understanding of the controlling factors. The results nevertheless indicate that microplastic pollution of sediment in the areas where cores were collected in Japan, Thailand, Malaysia, and South Africa has increased significantly over time. Similar trends in microplastic

abundance in beach sediment from Belgium were reported by Claessens et al. (2011). Trends in microplastic abundance through the cores are consistent with the increase in global plastic production and suggest the global occurrence of microplastics in sediment.

Conclusions

Microplastics composed of a variety of polymers, including PE, PP, PS, PET, PVC, acrylics, polyamide, polyethylene propylene copolymer, ethylvinyl acetate, and polycaprolactone, were identified in sediment cores collected in marine environments in several Asian countries and South Africa. The abundance of microplastics in sediment collected in a canal in Tokyo Bay was several orders of magnitude higher than the abundance in surface water samples collected in the canal. This suggests that sediment is a significant sink for microplastics in the marine environment. The abundance of microplastics in sediment in all cores increased from the deeper (older) to surface (younger) layers of the sediment. In dated cores, profiles of microplastics through the cores were consistent with the history of plastic production. The results indicate the global increase of microplastic pollution. The results are in accordance with the Anthropocene being an epoch when human activities significantly impacted Earth's geology, atmosphere, and ecosystems (Crutzen and Stoermer 2000; Waters et al. 2016).

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