The Occurrence and Degradation of Aquatic Plastic Litter Based on Polymer Physicochemical Properties: a Review

Tom Bond[1]*, Veronica Ferrandiz-Mas[2], Mónica Felipe-Sotelo[3] and Erik van Sebille[4]

1. Department of Civil and Environmental Engineering, University of Surrey, Guildford, GU2 7XH, United Kingdom
2. Department of Architecture and Civil Engineering, University of Bath, Bath, BA2 7AY, United Kingdom
3. Department of Chemistry, University of Surrey, Guildford, GU2 7XH, United Kingdom
4. Institute for Marine and Atmospheric Research, Utrecht University, 3584 CC Utrecht, The Netherlands

* Corresponding author, Tel: +44(0)1483684474, email: t.bond@surrey.ac.uk

Abstract

The whereabouts of the overwhelming majority of plastic estimated to enter the environment is unknown. This study's aim was to combine information about the environmental occurrence and physicochemical properties of widespread polymers to predict the fate of aquatic plastic litter. Polyethylene and polypropylene are common in the surface layer and shorelines; polyester and cellulosic fibres in sewage treatment works, estuarine and deep-sea sediments. Overall, non-buoyant polymers are underrepresented on the ocean surface. Three main explanations are proposed for the missing plastic. The first is accumulation of both buoyant and non-buoyant polymers in sewage treatment works, river and estuarine sediments and along shorelines. The second is settling of non-buoyant polymers into the deep-sea. The third is fragmentation of both buoyant and non-buoyant polymers into particles smaller than captured by existing experimental methods. Some isolation techniques may overrepresent larger, buoyant particles; methodological improvements are needed to capture the full size-range of plastic litter. When microplastics fragment they become neutrally-buoyant, thus nanoplastics are potentially widely dispersed in aquatic systems, both horizontally and vertically. Ultimately, over decades or longer, plastics are potentially solubilized and subsequently biodegraded. The rates at which these processes apply to plastic litter in different environmental compartments remain largely unknown.

Keywords: polyethylene, polypropylene, sedimentation, fragmentation, biodegradation.

1. Introduction

The prevalence of plastic litter in the environment is well known. Synthesis of decades of trawling data concluded that there are between 5 and 50 trillion plastic particles on the ocean surface, with a combined mass from 32,000 to 236,000 metric tonnes (van Sebille et al. 2015). It has been estimated that 8300 million metric tons (Mt) as of virgin plastics have been produced to date (Geyer et al. 2017). Packaging, i.e. items designed for single use and then disposed, represent ~42% of total non-fibre plastic production (Geyer et al. 2017).

Much of plastic litter is comprised of microplastics, typically defined as particles < 5 mm in diameter (GESAMP 2016). Plastics designed to be this size are referred to as primary microplastics, whereas secondary microplastics result from the fragmentation of larger pieces of plastic. Primary microplastics include microbeads used in cosmetic and cleaning products. The US has pledged to phase out use of microbeads in cosmetics and personal care products by 2019 (ChemistryWorld 2016), while the UK government has announced plans to ban microbeads by the end of 2017 (BBC 2016).

Microplastics in the marine environment can be distributed between the ocean surface, the water column, the seafloor, coastlines and coastal sediments and in biota (Hardesty et al. 2017). Approximately half of the floating marine plastic litter is found in subtropical gyres (van Sebille et al. 2015). Nonetheless, microplastics have also been observed in some of Earth's remotest marine environments, including surface waters of the Arctic (Cózar et al. 2017, Lusher et al. 2015), Arctic sea ice (Obbard et al. 2014) and around Antarctica (Barnes et al. 2010, Munari et al. 2017a).

The harmful impacts of microplastics on marine life have been the subject of many studies. Ingestion of microplastics has been recorded in over 100 species, from zooplankton upwards in size, including molluscs, crustaceans, fish and seabirds (GESAMP 2016, Wright et al. 2013). Microplastics can sorb persistent organic pollutants, including polychlorinated biphenyls, dichlorodiphenyltrichloroethane (DDT), polycyclic aromatic hydrocarbons, organochlorine pesticides, hexachlorobenzene and brominated/fluorinated flame retardants (Andrady 2017, Carpenter et al. 1972, GESAMP 2016, Teuten et al. 2009). In turn, there is concern about the potential for microplastics to act as agents for concentrating and transferring such hazardous chemicals to other organisms, including humans.

In recent years a number of studies have also identified microplastics in freshwater environments (Eerkes-Medrano et al. 2015), including rivers, estuaries, lakes and sewage treatment plants. Regarding the latter, of particular concern are the high concentrations of synthetic fibres that originate from laundering clothes: tests using domestic washing demonstrated that a single garment can produce >1900 fibres per wash (Browne et al. 2011). Synthetic plastic fibres have also been identified on the ocean floor (Woodall et al. 2014).

It has been estimated that the amount of plastic waste entering the ocean is one to three orders of magnitude greater than that floating on its surface (Jambeck et al. 2015). Another assessment indicated 99% or more of the plastic waste estimated to be present in the ocean is not captured by surface trawls and is thus currently unaccounted for (van Sebille et al. 2015). Analysis of the size distribution of plastic debris collected from the ocean surface showed a peak in abundance of particles ~2 mm in size and a pronounced lack of particles <1 mm (Cózar et al. 2014).

Given the above background, it is clear that the ultimate fate of plastic entering the environment is uncertain. Four main explanations for the missing marine plastic have been hypothesised: shore deposition, nanofragmentation, sinking, and ingestion by biota (Andrady 2011, Cózar et al. 2014, Hardesty et al. 2017, Law et al. 2010, van Sebille et al. 2015). In addition, generation of soluble low molecular-weight degradation products and mineralization, specifically production of carbon dioxide and water, by both biotic and abiotic pathways, have been demonstrated in laboratory-based studies using plastics. Together with sorption to sediments and sludge (Horton et al. 2017b), these represent further, unquantified, destinations for plastics in the environment.

The dominant compartments where different plastics accumulate is linked to polymer physicochemical characteristics, such as size, density and hydrophobicity (Andrady 2017). Therefore, the main aim of this study was to use information about the physicochemical properties of widespread polymers, combined with occurrence data for microplastics in seawater and freshwater, to inform a discussion about the predicted environmental fate of different types of plastics. A secondary aim was to highlight areas in which experimental methods used to isolate and identify polymers in environmental samples can be improved.

2. Methods of this review

Information about the properties, structure and applications of commonly-used polymers is given in Table 1-2 (ACD/Labs 2017, Berlins 1991, Chemspider 2015, Crawford 1998, Moret-Ferguson et al. 2010, PlasticsEurope 2017, USEPA 2011). Throughout the manuscript PET (polyethylene terephthalate) and PVC (polyvinyl chloride) are referred to by their abbreviations, which are in widespread use, whereas full names are used for the other polymers considered. Meanwhile, occurrence data from peer-reviewed publications which used spectroscopic techniques to identify the polymer type in samples collected from marine (Tables 3-4) and freshwater (Tables 3 and 5) environments were compiled. Given the limitations of existing methods (see section 3), comparing data from multiple sources requires caution. For this reason, in Tables 4-5 the principal measure of abundance used is whether a particular plastic was the first, second, third etc. most common polymer type identified. For the purposes of this review, sewage treatment works and estuaries are included with the freshwater studies (Table 5). Average (mean) values for occurrence in different environmental compartment were plotted along EU plastics demand data (Figure 1). This involved a number of assumptions, as detailed in the caption for Figure 1. In addition, note that % EU plastics demand values are based on the mass (in million tonnes) of each polymer resin, whereas the occurrence data is based on number of particles. Hence, this figure represents an initial estimation of the distribution of plastic litter relative to the demand for individual polymers.

3. Experimental methods used for analysis of plastics in environmental samples

The focus of this study is on using the abundance and physicochemical properties of commonly-used polymers (Tables 1-2) to assess their environmental fate. Hence, only literature which utilised spectroscopic methods to quantify the relative abundance of polymer-type of plastics isolated from environmental samples was included (Table 3)

Relevant peer-reviewed papers were highlighted by searching scientific databases (specifically Web of Science, ScienceDirect and ACS publications) for the terms "microplastic" and "microplastic and FTIR/FT-IR". In practice, spectroscopic methods typically mean various types of Fourier transform infrared (FTIR) spectroscopy. Less commonly other forms of IR spectroscopy, pyrolysis gas chromatography-mass spectrometry and Raman spectroscopy are also used (Table 3). While solely visual methods are commonly used to classify particles as plastics (Hidalgo-Ruz et al. 2012) this is associated with a risk of misidentification. As many as 70% of particles visually resembling microplastics may actually be non-plastic when analysed by FTIR spectroscopy (Hidalgo-Ruz et al. 2012). There are additional examples in literature of particles initially suspected to be plastics being subsequently re-identified as paint chips, presumably from ship hulls (Moret-Ferguson et al. 2010) or coal ash and coal fly ash (aluminium silicates) (Eriksen et al. 2013) when subjected to additional analysis. Even when spectroscopic methods are used to identify polymer type, visual inspection is often used as an isolation step (Table 3), which is likely to be biased in favour of large and brightly-coloured particles. Erni-Cassola et al. (2017) suggested that the lack of microplastics <1 mm highlighted by Cozar et al. (2014) and others can be at least partly explained by the deployment of visual sorting methods. As an alternative, Erni-Cassola et al. (2017) proposed a semi-automated procedure using the dye Nile red, fluorescence microscopy and image analysis software which was shown to be effective for the quantification of small polyethylene, polypropylene, polystyrene and nylon particles and does not rely on visual sorting.

Spectra obtained from analysis of plastic particles are typically compared and matched with those of model samples from library databases. For example, in one study matches with quality index ≥ 0.7 were accepted, those with a quality index <0.6 were rejected and spectra with a quality index ≥ 0.6, but < 0.7 were individually interpreted (Woodall et al. 2014). In this case 1.0 would represent the best possible match between spectra from the sample and library database. However, since degradation processes can lead to changes in polymer chemical composition, for instance due to oxidation reactions, discrepancies between model spectra and those from environmental samples are expected and can complicate identification. Renner et al (2017) recently reported a chemometric method which increased the accuracy of identification of microplastics using Attenuated Total Reflection (ATR) FTIR from 76%, using a conventional library search, to 96%. Unfortunately, in other studies the criteria used to assign polymer type are not provided. Moreover, the analysis of smaller microplastics (as well as nanoplastics) is limited by the spatial resolution of the selected analytical method. A combination of ATR-FTIR and focal plane array (FPA)-based transmission micro-FTIR imaging were used to identify polymer particles and fibres down to a size of 20 μm (Mintenig et al. 2017), much smaller than possible without a microscope.

As suggested above, spectroscopic methods do not necessarily lead to unambiguous identification of polymer type. In particular, FTIR spectra of cellulose and the semi-synthetic polymer rayon/viscose are almost identical and reports of the latter in environmental samples (Tables 4 and 5) have been queried (Comnea-Stancu et al. 2017). This study indicated that ATR-FTIR, and application of ATR libraries are required to successfully distinguish between natural and man-made cellulosic fibres (Comnea-Stancu et al. 2017) while transmittance FTIR, associated with reports of rayon in both marine (Lusher et al. 2015, Woodall et al. 2014) (Table 4) and freshwater (Peng et al. 2017) (Table 5) environments is ineffective for this purpose.

Thus, it is recommended that future studies publish the precise criteria used to classify particles as different polymer types. This should include publication of spectra from environmental plastic samples, so that a representative picture can be developed of their variability and diagnostic features. Additives, pigments, coatings, polymer blends and novel polymers may also cause the spectra of environmental plastics to differ from model examples present in library databases. Use of plastics during sample processing and analysis should be limited and negative controls and/or blanks should also be included to evaluate and account for microplastic contamination during collection and laboratory processing of environmental samples, which is significant issue given the prevalence of plastics in everyday life (see Mintenig et al. (2017) and Murphy et al. (2016)).

Prior to identification with spectroscopic methods, it is necessary to separate and isolate plastic particles. The most common isolation density separation method was floatation using sodium chloride (NaCl) solution, which was deployed in 16 out of 48 studies (Table 3). The density of saturated sodium chloride solution is ~1.2 $g\cdot cm^{-3}$ (Carson et al. 2011), which is actually lower than that of PET (polyethylene terephthalate) and some types of PVC (polyvinyl chloride) (Table 2). This is likely to lead to these types of plastic being underrepresented where this type of density separation was used. In recent years the use of alternative density separation solutions, such as sodium iodide (density 1.6-1.8 $g\cdot cm^{-3}$, (Dekiff et al. 2014, Van Cauwenberghe et al. 2013)), sodium polytungstate solution (1.5 $g\cdot cm^{-3}$,(Corcoran et al. 2015)) and zinc chloride (density 1.6 $g\cdot cm^{-3}$, (Bergmann et al. 2017, Mintenig et al. 2017) have also been reported in literature, which will improve recovery of denser plastics, although it must be noted that the density of PVC is up to 1.7 $g\cdot cm^{-3}$ (Table 2).

Municipal wastewater (sewage), its associated residual solids (sewage sludge) and sediments are especially problematic matrices from which to isolate and analyse plastic particles. As can be seen from Table 3, additional steps are required when processing such samples. These include removal of organic matter through pre-treatment with hydrogen peroxide (H_2O_2) (Mintenig et al. 2017, Peng et al. 2017), hydrogen peroxide and sulphuric acid (H_2SO_4) (Klein et al. 2015), enzymes (Löder et al. 2017, Mintenig et al. 2017) or alkaline solution (Cole et al. 2014, Mintenig et al. 2017); while stains selective for natural particles (Rose-Bengal solution) (Ziajahromi et al. 2017) and Nile red (Erni-Cassola et al. 2017) have also been employed for identification purposes. Microplastic fibres occur at high concentrations in sewage treatment plants and are problematic to extract and analyse: Mintenig (2017) reported that to distinguish between natural and synthetic fibres in a subsample of wastewater required 10 h of processing.

Overall, the extraction and identification of plastic particles from environmental samples is complicated and time consuming. The methods summarised in Table 3 can simultaneously be viewed as being state-of-the-art (due to the inclusion of spectroscopic methods for polymer identification) and work in progress (due to sometimes being biased to certain types or sizes of plastic particles). Details of quality assurance protocols widely used in analytical chemistry, i.e. calibration and validation procedures, such as use of internal standards and control samples, are scarce in environmental surveys of microplastics, yet can help to improve the reliability of collected data. Additional improvements are also needed to capture the full spectrum of plastic particles in environmental samples, reduce the time and cost of analyses and increase the accuracy of specific chemical identification of polymer type. Remote sensing of macroplastics, using spectral light reflectance measurements collected by airborne or satellite sensors, may have a role to play in the future (Goddijn-Murphy et al. 2018).

4. Environmental occurrence and degradation of plastics

4.1 General weathering processes

Before moving onto polymer-specific processes, a general overview of weathering of plastics under environmentally-relevant conditions is provided. Most forms of weathering are initiated at the polymer surface. A surface layer of oxidised, embrittled and crazed plastics develops. Sometimes this is accompanied by discolouration. Thereafter the interior degradation proceeds by a diffusion-controlled process. Eventually it leads to loss of material properties and total disintegration (Vasile 2000). Consistent with this, imaging of plastic debris collected from Hawaiian beaches by scanning electron microscopy (SEM) revealed fractured, flaked, pitted and grooved surfaces (Cooper and Corcoran 2010). Particles collected from muddy shorelines had surfaces with less mechanical fracturing than those from sandy shorelines (Zbyszewski and Corcoran 2011). Mechanically degraded sites are susceptible to additional weathering, which weakens the surface and leads to embrittlement. Pits and grooves conforming to the shape of microorganisms have been reported from millimetre-sized marine plastics, suggesting biota may also be important to degradation (Reisser et al. 2014). Physically weathered plastics will have increased surface areas, relative to non-weathered plastics, which is expected to enhance interactions with persistent organic pollutants (Horton et al. 2017b, Teuten et al. 2009). The embrittled and weathered surface layer of plastic litter contains a high proportion of hydrophilic oxidation products (Kaczmarek et al. 2002) which, when exposed to repeated swell/dry cycles, such as on shorelines, is prone to disintegrate into microplastics (Andrady 2017). This process has been termed degradation by a surface-ablation mechanism (Andrady 2017).

Weathering of plastics floating in water is much slower than in air or on beaches, as the presence of water suppresses light-induced oxidative degradation (Andrady 2011). This can be attributed to lower temperatures, lower oxygen concentrations and reduced transmittance of UV irradiation in water, as well as increased biofilm formation. Biodegradation of plastics may occur, but generally requires fragments with relatively low molecular weight. Therefore abiotic degradation is expected to generally precede biodegradation (Gewert et al. 2015). Complete mineralisation of plastics, i.e. production of water and carbon dioxide, by biotic and abiotic pathways has been demonstrated for certain polymers under laboratory and/or field conditions (Table 6).

4.2 Polyethylene

Polyethylene is produced in high-, medium- and low-density forms, which share the same basic chemical composition, but differ in the amount of polymer branching (Table 1). Combined, the various forms of polyethylene have the highest EU plastics demand and have many domestic applications, including shopping bags, bottles and the microbeads used in many cosmetic products (Table 1). The various forms of polyethylene have a density from 0.91 – 0.96 $g \cdot cm^{-3}$ (Table 2), slightly lower than that of freshwater.

In environmental surveys, polyethylene is frequently the most abundant plastic in surface water and shorelines (Tables 4-5). On an average basis it is commoner in these compartments than expected on the basis of its EU plastics demand (Figure 1). For example, it was identified as the commonest plastic on beaches in Japan, Malta, Hawaii, the Maldives, Taiwan and Italy (Table 4). In the first three of these studies, significant quantities of plastic production pellets were observed, indicating an industrial, rather than domestic origin. In Hawaii, no local source for the virgin pellets was present, further signifying these pellets had travelled long distances. Moreover, polyethylene was either the commonest or joint-commonest plastic identified in inshore surface or subsurface waters in Brazil, Singapore, China and the Slovenian Adriatic, subsurface waters along a transect from the European Coast to the North Atlantic Subtropical Gyre (Table 4). Meanwhile, in fresh water surveys, polyethylene was identified as the most abundant type of plastic particle (excluding microfibres) in samples taken from beaches on the

North American Great Lakes, German sewage treatment plants and UK estuarine surface water, sediment and strandline samples (Table 5). Because polyethylene floats in water, it is expected to accumulate along shorelines and in the surface layer of water bodies, which broadly agrees with the data summarised in Figure 1. Conversely, its density can also explain its scarcity in water at intermediate depths and the deep sea (Figure 1).

As shown by $\log K_{ow}$ values for representative polyethylene substructures of 6.0 – 6.1 (Table 2) polyethylene is the most hydrophobic of the selected plastics and is predicted to sorb onto sediments and sewage sludge. Reports from tidal sediments, sediment cores and sewage treatment plant surveys are in agreement with this idea (Table 5). Mintenig (2017) reported that polyethylene was the commonest microplastic identified in sludge from six German sewage treatment plants. Furthermore, Murphy (2016) reported that polyethylene was the commonest plastic in sludge and residual grease from a Scottish sewage treatment plant. Another study reported on, on average, that 52% of microbeads extracted from cosmetic products, the majority polyethylene, were captured in activated sludge (Kalčíková et al. 2017). Smaller particles (up to 60-70 µm) were more effectively removed than larger particles. Nonetheless, while commonly recorded in sewage treatment plants (Table 5), the average abundance of polyethylene, relative to other polymers, in such samples is still less than expected on the basis of its EU plastics demand (Figure 1).

Although the structure of polyethylene does not contain any chromophores (Table 1) photochemical oxidation by ultraviolet radiation is considered the initial and rate-determining step for environmental degradation (Gewert et al. 2015). This agrees with an accelerated weathering study, which found that neither polyethylene or polypropylene are likely to be fragmented by mechanical abrasion without photooxidation (Song et al. 2017). Photodegradation is assumed to initiate at locations with manufacturing impurities or imperfections (Vasile 2000). Thermoxidative degradation shares several steps with photooxidation (Vasile 2000). FTIR analysis of weathered polyethylene particles collected amongst Hawaiian beach debris indicated surfaces which had been highly oxidised (Cooper and Corcoran 2010). Similarly, in polyethylene pellets collected from Maltese beaches, the amount of yellowing corresponded with an increase in the carbonyl index and therefore indicated the amount of photochemical aging (Turner and Holmes 2011). This agrees with results from long-term field tests showing that the carbonyl peak increased during abiotic degradation and that photo-oxidation preceded biodegradation (Albertsson and Karlsson 1988). Photochemical degradation of polyethylene proceeds via the formation of hydroperoxide intermediates to form carbonyl compounds (Roy et al. 2011). A wide range of low molecular weight alkanes, alkenes, ketones, aldehydes and carboxylic acids have been observed as polyethylene degradation products (Table 6). In addition, hexacene and furanones have been reported (Table 6). Amongst these identified products, hydrophilic, low molecular-weight products, for example ketones, aldehydes and carboxylic acids, are readily biodegradable (Bond et al. 2011).

Polyethylene food bags submerged in seawater showed visible biofilm formation after one week and by three weeks the plastic began to sink and exhibit neutral buoyancy (Lobelle and Cunliffe 2011). A similar study demonstrated that the surface area of polyethylene carrier bags decreased by 2% over 40 weeks (O’Brine and Thompson 2010). Polyethylene film showed a 12% loss in ultimate extension, an indication of embrittlement, after 12 months (Pegram and Andrady 1989). For comparison, air exposed samples lost 95% of ultimate extension after six months (Pegram and Andrady 1989). The marine fungus *Zalerion maritimum* has been found to decrease the size and mass of polyethylene pellets (Paço et al. 2017), while marine bacteria isolated from the Arabian Sea were able to reduce the weight of polyethylene films by up to 1.75% after 30 days’ incubation (Harshvardhan and Jha 2013). It has also been demonstrated that bacteria in the guts of waxworms, or Indian mealmoths (the larvae of *Plodia* *interpunctella*) can eat polyethylene films (Yang et al. 2014). This work indicates photochemical degradation is not necessarily a prerequisite for biodegradation, as suggested elsewhere (Albertsson and Karlsson 1988). Both theoretical calculations and experimental measurements have shown that polyethylene accumulates more persistent organic pollutants than polypropylene and polyvinyl chloride, particularly hydrophobic compounds such as polychlorinated biphenyls (Teuten et al. 2009).

4.3 Polypropylene

With an EU plastics demand of 19.1%, polypropylene is the second most common plastic, excluding other plastics, and grouping the various types of polyethylene (Table 1). Typical applications include food containers; medicine bottles and automotive parts (Table 1). With a density of 0.90 – 0.91 $g \cdot cm^{-3}$, pristine polypropylene floats in freshwater and seawater. On an average basis, polypropylene is disproportionately common in surface waters, relative to its plastics demand (Figure 1). For example, it was the most abundant microplastic in Swedish, Chinese and Indonesian coastal waters, and in those from Hong Kong (Table 4). It is also common along shorelines and was recorded as the most abundant microplastic in beach sediments on Nordeney Island in the North Sea; Hawaiian, Japanese, Italian and Taiwanese beaches and in tidal sediments from the Lagoon of Venice (Table 4). In freshwater surveys, polypropylene was the commonest plastic on the surface of the Seine River, France, and the Three Gorges reservoir in China (Table 5). It was also the second most abundant plastic in seven beaches on Lake Huron, Canada, sediment cores from Lake Ontario, Canada, and tidal sediment samples from the Beijiang River, China (Table 5).

Reports of small amounts of polypropylene in sediments from Portuguese shelf waters, at depths from 8-27 m, the Arctic seafloor at a depth of 2500-5000 m and in sediments from the Adriatic at a depth of 7-142 m (Table 4) are unexpected given this polymer’s buoyancy.

Nonetheless, polypropylene is overall disproportionately scarce, relative to its EU plastics demand, in treated sewage, at intermediate water depths and in the deep sea (Figure 1).

In German sewage treatment works (Mintenig et al. 2017) polypropylene was the second commonest particle >500 µm and a major component of plastic particles in sludge. Thus, while both polyethylene and polypropylene float in both freshwater and seawater, data from Tables 4 and 5 shows this does not preclude their sorption to sludge or sediment, something aided by their hydrophobic nature (Table 2).

Due to the presence of tertiary carbons (Table 1), polypropylene is considered more susceptible to chemical degradation than polyethylene (Gewert et al. 2015). Once again, photodegradation is believed to be initiated at weak spots or due to the presence of light-absorbing impurities. Although polypropylene itself is resistant to biodegradation, its photooxidation products are more biodegradable. SEM imaging and FTIR analysis of plastics collected from North American Great Lakes beaches indicated that polypropylene pellets had experienced more chemical weathering and/or were less resistant to weathering than polyethylene samples (Zbyszewski and Corcoran 2011). Polypropylene tape in seawater lost 26% of ultimate extension after 12 months, whereas samples in air lost 90% (Pegram and Andrady 1989).

4.4 Polyvinyl chloride (PVC)

PVC has an EU plastics demand of 10.1%, making it the third most common plastic, excluding other plastics and grouping the various types of polyethylene (Table 1). Its applications include packaging, pipes, toys, hoses and clothing (Table 1). With a density from 1.2 – 1.7 $g{\cdot}cm^{-3}$ (Table 2), PVC is the densest of the commonly-used plastics. As this range is above that of saturated sodium chloride solution frequently used for floatation-based separation, PVC is likely to be incompletely extracted in many surveys.

PVC occurs less commonly in all environmental compartments than would be expected on the basis of its EU plastic demand (Figure 1). It was the fourth most common microplastic isolated from beach samples on Nordeney in the North Sea, eighth commonest plastic in tidal sediments from the Lagoon of Venice and a minor component of plastics from Italian beaches and subsurface waters between Germany and South Africa (Tables 4 and 5). It was also a minor proportion of microplastics identified in German river sediments, sediment samples from an Italian subalpine lake, UK estuarine waters and samples from Scottish and German sewage treatment plants (Table 5). Its relative scarcity in the environment is most likely because a high proportion of PVC is used for applications other than packaging, e.g. cable insulation, floor tiles and window frames (Table 1). Another contributory factor may be that its high density, up to 1.70 $g{\cdot}cm^{-3}$ (Table 2), means it is incompletely isolated by density separation methods (Table 3). Nonetheless, there are exceptions to this pattern: PVC was the second commonest component of particles under 1 mm in UK estuarine sediment and strandline samples, representing 26% of plastics in this category (Table 5).

PVC is susceptible to yellowing, associated with the formation of conjugated polyenes (Andrady et al. 1998). It is considered the most sensitive of the common polymers to UV irradiation (Gewert et al. 2015). As with polyethylene, photodegradation is associated with the presence of chemical impurities (Gewert et al. 2015) and proceeds in the absence of any intrinsic chromophores in the polymer structure (Table 1). Despite this, photodegradation is expected to be a crucial degradation pathway for PVC litter in the environment.

4.5 Polyesters, including PET

Polyester is the generic name for ester-containing polymers, the most prominent of which is PET (Table 1). PET is the fourth most commonly used plastic in the EU (excluding other plastics and grouping the various types of polyethylene), representing 7.1% of total demand,

and is typically used to make water, soft drink, juice and household cleaner bottles (Table 1). Based on the demand for PET relative to other plastics, it would be expected to comprise a minor proportion of plastic isolated from the environment, which, on an average basis, is consistent with studies sampling the surface waters (Figure 1).

In addition to the listed applications for PET, polyester fibres are also widely used in clothing, bed sheets, blankets and furniture upholstery. This, together with its high density, 1.36 – 1.37 $g \cdot cm^{-3}$ for PET (Table 2), explains why polyester is disproportionately abundant in sewage works and the deep sea, relative to its EU plastics demand (Figure 1). For example, polyester fibres have been reported as the most abundant plastics identified in Australian and Finnish sewage treatment plants and the commonest synthetic fibre in German sewage treatment plants (Table 5). Murphy and co-workers (2016) investigated the removal of microplastics throughout a Scottish sewage treatment plant and found that polyester was the commonest plastic in primary effluent and final effluent (Table 5).

Browne et al (2011) presented data from experiments using domestic washing machines that demonstrated that a single item of clothing can produce >1900 fibres per wash, which explains the prevalence of synthetic fibres in sewage. Because the proportion of polyester, relative to other synthetic fibres, found in marine sediments and sewage resembled that in textiles, the same authors highlighted washing clothes as the most plausible origin for such microplastics. It has been suggested that advanced wastewater treatment processes are required to effectively remove polyester fibres from sewage. Annual discharges of microplastic particles and fibres from 12 German sewage treatment plants were calculated to be from 9×10^7 to 4×10^9 (Mintenig et al. 2017). In one plant containing tertiary filtration with pile fabric 98% of synthetic fibres, predominantly polyester, were removed (Mintenig et al. 2017), but even such high levels of removal still leave a significant number of fibres entering the environment. Similarly, advanced wastewater treatment processes – a membrane bioreactor, rapid sand filter, dissolved air flotation – removed 95% or more of microplastics (Talvitie et al. 2017). All shapes of microplastics were effectively removed, including fibres, the majority of which were polyester.

In marine surveys, polyester fibres were also reported as the most abundant microplastic from 18 beaches sampled worldwide, five beaches in the Persian Gulf and seawater over 2 km deep west of Scotland (Table 4). Further, PET fibres were the second most abundant plastic in deep-sea sediments and coral samples from the Mediterranean Sea, Indian Ocean and Atlantic Ocean and in beaches from the southeastern USA (Table 4).

While PET is considered highly resistant to biodegradation (Müller et al. 2001) the presence of chromophores and ester linkages mean it is susceptible to photochemical and hydrolytic degradation respectively (Wiles 1973). Photodegradation leads to the formation of carboxylic acid groups on the surface layer, as well as decreased surface tensile strength (Blais et al. 1973). Hydrolysis is considered the dominant degradation pathway (McMahon et al. 1959) Table 6). Eventually this can lead to the generation of water, carbon dioxide (CO_2), carbon monoxide (CO) and a range of low molecular-weight aldehydes and carboxylic acids as the end products of degradation ((Day and Wiles 1972, Singh et al. 2015): Table 6)). In a study under controlled laboratory conditions, as degradation proceeded increases in polymer density were noted, presumably associated with changes in chemical composition of the surface layer; subsequently formation of voids reduced density (McMahon et al. 1959). Such changes in polymer density are not highlighted in recent literature on microplastics, but are important, as they show that physicochemical weathering processing can modify polymer density and in turn buoyancy in water. PET samples kept at a depth of 1 m for one year in seawater showed biofilm formation and a weight loss of 7%. Accompanying FTIR analysis showed decreases in carbonyl/oxidation indices, indicative of biodegradation (Muthukumar et al. 2011). ATR-FTIR analysis of PET bottles collected from the bottom of the Mediterranean Sea showed that older bottles (over ~15 years) had cracked surfaces and showed significant changes in FTIR spectra (Ioakeimidis et al.

2016). These data illustrate that biodegradation of PET in the marine environment does occur, but over a time period of decades. By screening samples collected from sediments, soil, wastewater, and a PET bottle recycling facility Yoshida et al. (2016), were able to isolate a novel bacterium that can use PET as its major energy and carbon source.

4.6 Polystyrene

Polystyrene, the plastic with the fifth highest EU plastics demand, is typically used for food packaging, disposable cups and plates and for building insulation (Table 1). Expanded polystyrene has a far lower density than other plastics, <0.05 $g{\cdot}cm^{-3}$, while standard polystyrene has a density of 1.04 – 1.07 $g{\cdot}cm^{-3}$. Typically, environmental surveys do not specify which type of polystyrene was identified. Based on its density, expanded polystyrene should accumulate in surface waters and shorelines. Meanwhile, standard polystyrene has a density slightly above that of both freshwater (0.999 $g{\cdot}cm^{-3}$) and seawater (1.026 $g{\cdot}cm^{-3}$) (Metcalf & Eddy et al. 2014)). Polystyrene spherules were reported as widespread in coastal waters of southern New England in the early 1970s (Table 4), one of the earliest reports of plastic litter in marine environments (Carpenter et al. 1972). Their origin was thought to be from a manufacturing facility. More recently, polystyrene was observed to be the joint-commonest plastic in the surface microlayer of coastal waters off Singapore, and from the second to fourth commonest in beaches from the Maldives, Hawaii, Taiwan, Italy and Nordeney Island in the North Sea, as well as the fifth commonest in tidal sediments from the Lagoon of Venice (Table 4).

Polystyrene was also found to be the commonest plastic in sediment samples from beaches of an Italian subalpine lake and the second most abundant in UK estuarine surface waters (Table 5). It was also the third most frequently identified component of plastic particles <500 µm in German sewage plants, of plastic particles >500 µm from UK estuarine sediment and strandline samples and of all plastic particles from surface waters from Chinese reservoirs (Table 5). In a Scottish sewage treatment plant, polystyrene was found to be the most abundant plastic in effluent from grit/grease removal, the second commonest in sludge and a minor component of plastics in other samples (Table 5), which indicates a high level of removal during sewage treatment. Overall, the abundance of polystyrene in surface waters, shorelines and sewage works is rather similar to its EU plastics demand (Figure 1) and it does not have a clearly defined occurrence pattern.

Polystyrene is more susceptible to outdoor weathering than polyethylene or polypropylene, yet is considered more resistant to biodegradation (Gewert et al. 2015).When exposed to UV irradiation, rapid yellowing and gradual embrittlement occurs (Yousif and Haddad 2013). Samples from a disposable polystyrene coffee cup lid placed in deionised water and exposed to UV irradiation in a weathering chamber generated nanoplastics at a concentration of 1.26×10^8 particles$\cdot$mL^{-1} (mean size 224 nm), compared with 0.41×10^8 particles$\cdot$mL^{-1} in the control sample without polystyrene (Lambert and Wagner 2016a). Mealworms (the larvae of *Tenebrio molitor*) were found to efficiently eat Styrofoam, a type of expanded polystyrene, and survived over one month when fed solely on Styrofoam (Yang et al. 2015a). A related study showed the essential role played by gut bacteria in the biodegradation and mineralization of polystyrene (Yang et al. 2015b). In a laboratory degradation study using a weathering chamber, a polystyrene (PS) coffee-to-go lid produced more particles in the size range 30 nm - 60 µm than the six other polymers investigated, 92,465 particles$\cdot$mL^{-1} (Lambert and Wagner 2016b). In another weathering study, abrasion of expanded polystyrene pellets with sand led to fragmentation (Song et al. 2017).

4.7 Other plastics

Combined, ‘other plastics’ represent nearly 20% of EU plastics demand. Selected examples of plastics which have been recorded at relatively high concentration in environmental samples are given in Tables 4 and 5. In marine samples rayon, a semi-synthetic fibre made from natural fibres (purified cellulose) was reported as the commonest plastic in deep sea sediments and coral samples from the Mediterranean Sea, SW Indian Ocean and NE Atlantic Ocean, Arctic surface and subsurface seawater samples, subsurface waters between Germany and South Africa, coastal sediments from Portuguese shelf waters and in sediment samples from a Chinese estuary (Tables 4 and 5). Rayon has a density of 1.50 $g{\cdot}cm^{-3}$ (Osswald et al. 2006), higher than that of any of widespread polymers listed in Table 1. Note that these identifications have been questioned (Comnea-Stancu et al. 2017) and another study reported such fibres as “cellulosic materials” including rayon (Yu et al. 2018). Natural fibres, including cotton, flax, hemp and sisal and widely used for clothing, domestic woven fabrics and ropes and can be confused with manmade rayon/viscose when analysed by transmittance FTIR (Comnea-Stancu et al. 2017). Therefore, rayon reported from environmental samples (Tables 4 and 5) could also plausibly be natural fibres.

Alkyd, a polyester used in paints and casting moulds, has been reported as the commonest plastic in the surface microlayer of Korean coastal waters (Table 4) and was believed to originate from ship coatings (Song et al. 2014). Nylon was the commonest plastic identified in samples from sediments collected from the Adriatic (Table 4). In sediment samples from the Ross sea, Antarctica, styrene-butadiene-styrene, widely used in pneumatic tires, was the commonest plastic (Table 4). Polytetrafluoroethylene (PTFE) (density 2.10−2.30 $g{\cdot}cm^{-3}$) was the commonest plastic reported in Arctic deep-sea sediments and Scottish intertidal sediments (Table 4). Other plastics recorded at lower concentrations in environmental samples are polyvinyl alcohol, polyamides and acrylic (Tables 4 and 5).

5 Discussion – fate of aquatic plastic litter

The above information is helpful when addressing the question of what happens to plastic debris in seawater and freshwater. Analysis of data from environmental surveys reveals that both polyethylene and polypropylene are disproportionately abundant, relative to their EU plastics demand, in surface waters and also occur commonly on shorelines (Figure 1). This pattern is explicable in terms of their buoyancy in water (Table 2). Less expected are reports that polyethylene and polypropylene were the 1st or 2nd most abundant microplastics in tidal sediments from the Lagoon of Venice and the bottom of Lake Ontario, Singaporean subsurface waters, subsurface (3 m deep) waters between Europe, the North Atlantic Subtropical Gyre, Chinese and UK estuarine sediments and sewage sludge (Tables 4 and 5; Figure 1). Sorption/aggregation with natural particles is likely to play a role in these reports, given their hydrophobic nature (Table 2). Overall, the abundance of polyethylene and polypropylene, relative to other polymers, declines with water depth (Figure 1). Thus, their abundance ranged from not reported to the second most abundant microplastic in coastal sediments from Portuguese shelf waters (7-27 m deep, (Frias et al. 2016), sediments in the Adriatic (7-142 m deep, (Mistri et al. 2017) and subsurface waters between Germany and South Africa (11 m deep, (Kanhai et al. 2017) (Table 4). Of three surveys that sampled microplastics from the deep sea (Bergmann et al. 2017, Courtene-Jones et al. 2017, Woodall et al. 2014) (Table 4), two reported small amounts of polyethylene or polypropylene from two, while the other did not report either. Note that chlorinated polyethylene, the most abundant microplastic in sediments from the Arctic seafloor (Bergmann et al. 2017) has a density of 1.16 $g \cdot cm^{-3}$ (AZoM 2017), above that of seawater. Thus, available evidence does not indicate significant amounts of conventional polyethylene or polypropylene, which together represent ~50% of EU plastics demand (Table 1), are accumulating on the seafloor (Figure 2). Conversely, selected studies from Tables 4 and 5 indicate significant quantities of polyethylene and polypropylene can be associated with tidal sediments, lake sediments and sewage sludge. These are therefore predicted to be significant final destinations for polyethylene and polypropylene litter. The same also presumably applies to freshwater sediments in general. The ultimate fate of the large amounts of plastic removed during sewage treatment will vary with sludge disposal methods. Where treated sewage sludge is reused in agriculture this represents a route for microplastics to enter the terrestrial environment (Horton et al. 2017b).

Reports of buoyant polymers in deep water can only be explained by some form of environmental processing causing them to sink. Possible mechanisms include biofouling, changes in chemical composition caused by weathering, as has been shown for PET under laboratory conditions (see section 5.3, (McMahon et al. 1959), aggregation with natural particles or phytoplankton (Andrady 2017, Long et al. 2015) or ingestion by aquatic organisms. Surface biofouling/encrustation by marine microorganisms can increase the density of non-buoyant plastic particles (Andrady 2011, Ye and Andrady 1991). Biofouling is predicted to be more rapid for smaller plastic particles, as these have relatively high surface area to volume ratios (Ryan 2015). This is expected to precede defouling in deeper water, which causes particles with density lower than seawater to rise again (Andrady 2011). The first part of this process has been demonstrated experimentally by Fazey and Ryan (2016), who found that 50% of high density and low density polyethylene sheets, cut into squares up to 50×50 mm in size, sank after 17-62 days in seawater; while smaller samples lost buoyancy more rapidly. Meanwhile, a modelling study predicted that biofouling causes spherical polyethylene and polypropylene particles with radii from 1-10 mm to sink after 24 to 26 days in seawater and thereafter oscillate vertically as biofouling reduces and then increases once more (Kooi et al. 2017).

In contrast, once in the open sea, non-buoyant particles, including PET/polyester, standard polystyrene, PVC and rayon are expected to start sinking immediately (Kooi et al. 2017). Settling velocity is proportional to particle size, with larger particles settling more rapidly. For example, Kooi et al. (2017) calculated that a particle of 10 mm particle of PVC requires only 1.6 mins to sink to the ocean floor (4000 m). The equivalent times for 0.1 mm and 1 µm particles are 10 days and 278 years (Kooi et al. 2017). Another theoretical simulation estimated that 99.8% of the plastic that had entered the ocean since 1950 had settled below the surface layer by 2016 (Koelmans et al. 2017). This explains why the occurrence of PVC and PET/polyester in surface waters is far lower than expected based on their EU plastics demand (Figure 1). The most abundant polymers recorded from deep sea surveys are chlorinated polyethylene, polyamide, PTFE, polyester, PET and cellulosic fibres (Table 4), all of which are non-buoyant. Polyester/PET fibres and polystyrene also accumulate along both marine (Table 4) and freshwater (Table 5) shorelines. Polyester fibres are also among the more abundant plastics in sewage sludge (Table 5).

Overall, the environmental occurrence of larger plastic particles (over ˜200 µm) is largely explicable in terms of their density. As sedimentation theory predicts that both buoyant and non-buoyant plastic particles become neutrally-buoyant as they decrease in size, the ultimate fate of smaller microplastics and nanoplastics remains enigmatic (Figure 2). Calculations undertaken by Kooi et al. (2017) predict that non-buoyant plastics ≤10 µm settle so slowly that they could be present anywhere in the water column; their location is likely to be affected by seawater density, which itself depends on temperature and salinity. A similar point was made by Enders et al. (2015) who indicated that smaller microplastic fragments in the ocean are dispersed both vertically and horizontally; plastics <200 µm were spread through the surface mixed layer of the ocean. This means plastic particles which pass through nets used for surface sampling, which typically have a mesh size from 112 – 300 µm (Table 3) would not be confined to the surface layer and will become increasingly difficult to sample. Contrary to other literature (e.g. Cózar et al. (2014), both Enders el al. (2015) and Erni-Cassola et al. (2017) reported that the abundance of microplastics did actually increase with decreasing particle size. The implication is that isolation methods that reply upon visual identification of microplastics are biased in favour of larger, more brightly coloured, plastic particles, which causes the relative abundance of such particles to be overrepresented in many studies.

It is assumed that nanoplastics exist widely within the pool of secondary microplastics. Due to their small size and bioavailability, they are potentially the most hazardous, yet poorly understood, class of plastic litter. They have not yet been unequivocally identified in environmental samples, due to analytical difficulties associated with their isolation and identification (Andrady 2011, GESAMP 2016). As nanoplastics can be of similar size to the phytoplankton, which constitutes the diet of zooplankton such as krill, this represents an obvious pathway for them to enter to the food chain (Andrady 2011). In the absence of environmental data that can be used to evaluate the hazards they pose, studies on engineered nanoparticles can provide potentially relevant insights. These frequently have properties that significantly differ from the bulk material, which relate to their relatively high surface area. Due to a paucity of sensitive and selective methods for their detection in complex natural matrices, the behaviour of engineered nanoparticles is predominantly investigated through laboratory based-experiments and modelling (Troester et al. 2016). The higher surface area to volume ratios of nanoplastics will increase surface interactions and thus the potential for binding with persistent organic pollutants (Horton et al. 2017b).

While the stability of nanoplastics is also unknown, it is plausible they continue to degrade until soluble, low molecular-weight, degradation products are released (Table 6). This would facilitate access to another pathway for environmental processing of plastic litter: mineralisation, by either biotic or abiotic pathways (Table 6). Polystyrene, PET and polyethylene can all be directly biodegraded by a variety of microorganisms (section 4), while UV irradiation can precede mineralisation of PET and polyethylene (Table 6). Long-term investigations of polymer degradation indicate these processes occur over periods of decades or more for macroplastics. For example, after 10 years in soil, only small indications of the complete structural deterioration, signalling the onset of mineralisation, of low density polyethylene film were noted (Albertsson and Karlsson 1988). Moreover, the surfaces of PET water bottles were reported to remain intact for over 15 years in the marine environment (Ioakeimidis et al. 2016). It is thought that plastics can persist for 100s of years on the surface of the ocean and probably for far longer in the deep sea (Ioakeimidis et al. 2016). Conversely, owing to high exposure to UV irradiation and mechanical abrasion, fragmentation is rapider on shorelines (Andrady 2011, Andrady 2017). Given the variability in size of aquatic plastic litter, and of conditions they experience in different environmental compartments, notably exposure to UV irradiation and populations of microorganisms which can directly biodegrade polymers, it is hard to draw conclusions about the relevance of biodegradation and mineralisation for explaining the fate of the missing plastics. However, it can somewhat speculatively be predicted that biodegradation and mineralisation in aquatic systems, with the possible exception of UV-initiated processes on shorelines, are so slow relative the amounts of plastic entering the environment that they are insignificant. Conversely, it is important to note that most interaction between plastic and marine organisms happens close to coastlines, where marine life is most abundant, e.g. (Schuyler et al. 2016, Wilcox et al. 2015). Plastic items that fragment faster (i.e. closer to coastlines) may therefore have a larger impact on marine ecosystems. Similarly, interactions between persistent organic pollutants and plastic litter are likely to be more important in freshwaters with high pollutant concentrations, i.e. those close to industrialised and populated areas (Eerkes-Medrano et al. 2015, Horton et al. 2017b).

Direct ingestion by marine organisms, including fish and seabirds, is potentially more important over shorter time scales For example, it has been estimated that 59% of seabird species studied between 1962 and 2012 had ingested plastic, and, on an average basis, 29% of individual seabirds had plastic in their gut (Wilcox et al. 2015). Which marine organisms are prone to ingest which polymer types is linked to the extent of overlap between their environmental distributions. Zooplankton prevalent in gyres and coastal regions, such as echinoderm larvae, calanoid copepods and chaetognaths, are likely to be particularly susceptible to the effects of ingesting buoyant microplastics (Wright et al. 2013), notably polyethylene and polypropylene particles. In contrast, benthic deposit feeders, benthic scavengers and benthic suspension feeders are all more likely ingest non-buoyant polymer particles such as PVC, polyesters (including PET) and cellulosic materials. For instance, four species of sea cucumbers were found to selectively ingest PVC and nylon fragments over sediment particles. See Wright et al., 2013 for more detail. Nonetheless, the extent to which direct ingestion can explain the fate of aquatic plastic litter is unclear. Estimates of its contribution are complicated by the fact that ingestion does not necessarily represent a final destination for plastic litter. Ingested plastic can be excreted back into the environment and residence time in the gut can be highly variable between different species, at least for seabirds (Wilcox et al. 2015).

One strategy to reduce plastic pollution is to replace established polymers (Table 1) with those which degrade relatively quickly in the environment and which are often described as green, biodegradable and/or oxo-degradable (UNEP 2015). However, while these approaches may help mitigate the problems of plastic litter, it is also vital to have a comprehensive picture of the identity and ecotoxicity of degradation products, as well as how rapidly they form, to properly assess the risk they pose and their susceptibility to biodegradation. For example, furanones, which can be readily converted into potentially carcinogenic furans, were identified following exposure of polyethylene to UV irradiation and heat (Hakkarainen et al. 1997). At present there is no balance of information to suggest that biodegradable plastics reduce the risk posed by marine litter (UNEP 2015), which is not to say this will not be forthcoming once more work is undertaken. Nonetheless, caution is required, especially as definitions of plastic biodegradability are typically based on behaviour in an industrial composting facility at 50 °C (UNEP 2015), which may not correspond to fate in aquatic systems.

Given the abundance and geographical spread of aquatic plastic litter, combined with rising levels of plastics production, there is unlikely to be one single solution to the hazards they pose. Instead, multiple interventions should be targeted, including raising public awareness of littering, boosting the circular economy for plastic products, increased taxes on certain plastics, developing alternatives to plastic products, improving solid waste management and removing plastic pollution in bottlenecks where high concentrations occur, for example, washing machines, sewage works and coastlines (van Sebille et al. 2016). Innovative and sustainable plastic formulations also have a role to play. However, direct comparison with established plastics under representative conditions is required to prove the former do actually fragment more rapidly and into more benign products than the latter.

6 Conclusions

Literature indicates that 99% of plastic entering the ocean is unaccounted for. The main aim of this study was to combine information about the occurrence in seawater and freshwater of widespread polymers, together with their physicochemical properties, to predict the environmental fate of aquatic plastic litter. Three major explanations are proposed for the missing plastic.

Together, polyethylene and polypropylene represent ~50% of plastics demand, therefore any assessment of the missing plastic litter also needs to address their fate. Both are buoyant in water and are frequently the most abundant polymers recorded in the surface layer and on shorelines, as well as in sewage treatment works, tidal sediments and freshwater sediments. Substructures of both polymers are more hydrophobic than for other commonly–used plastics, aiding partitioning into sediments and sludge, in turn predicted to represent a significant destination for polyethylene and polypropylene in the environment. There are reports of small amounts of these polymers in deeper water, explicable by environmental processing leading to density increases. Nonetheless, available evidence does not support the idea that significant proportions of polyethylene and polypropylene accumulate in the deep sea.

The occurrence of PET/polyester and cellulosic fibres in sewage treatment works, river and estuarine sediments and along shorelines are also disproportionately high, relative to the overall demand for these polymers. Therefore, the first proposed explanation for the missing plastic is accumulation of both buoyant and non-buoyant polymers in such locations.

Overall, non-buoyant polymers are poorly represented in surveys sampling the ocean surface, while several have been reported in the deep-sea. The latter therefore represents the second proposed explanation for the missing plastic. In all types of environmental samples PVC is less abundant than expected based on its plastics demand.

Whatever their chemical composition, plastic particles <~200 µm become increasing neutrally-buoyant as they fragment. In turn, they can become widely dispersed, both vertically and horizontally, through aquatic systems. Therefore, the third predicted fate for a substantial portion of the missing plastic is fragmentation into particles smaller than captured by existing experimental methods, i.e. nanoplastics and small microplastics. Ultimately, over decades or longer, such plastics are potentially solubilized and subsequently biodegraded. The rates at which these processes apply to microplastics and nanoplastics in different environmental compartments, and their associated environmental impacts, remain largely unknown.

A secondary aim of the study was to discuss how experimental methods used to isolate and identify polymers in environmental samples can be improved. Alternative density separation methods are beneficial for increasing the recovery of denser plastics such as PVC. It is crucial that methods used to identify polymers in environmental samples are explicitly detailed. Further modifications are required to capture the full spectrum of plastic particles in environmental samples, reduce the time and cost of analyses and increase the accuracy of specific chemical identification of polymer type.

7 Acknowledgments

Erik van Sebille was supported through the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No 715386)

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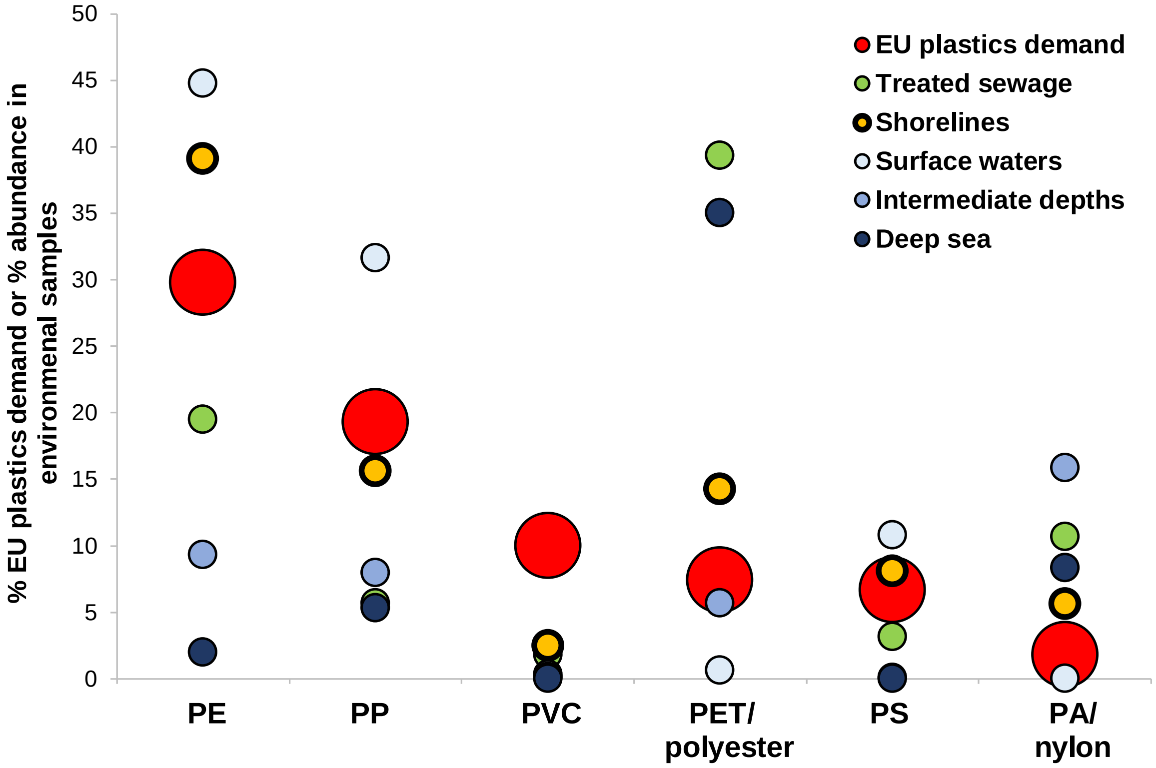

Figure 1: comparing the plastics demand of specific polymers with their abundance in different environmental compartments. PE = polyethylene, PP = polypropylene, PVC = polyvinyl chloride, PET = polyethylene terephthalate, PS = polystyrene, PA = polyamide. Raw data from Tables 1, 4 & 5. Plastics demand for PE is sum of HDPE and LDPE. Plastics demand values for PET/polyester and PA/nylon are for PET and PA only, respectively. Abundance data are mean values across the different environmental compartments. Minor but unquantified assumed to be 3%. Where studies provided separate data for different particles size classes, these data are treated as separate studies when calculating mean values. See section 2 for additional detail.

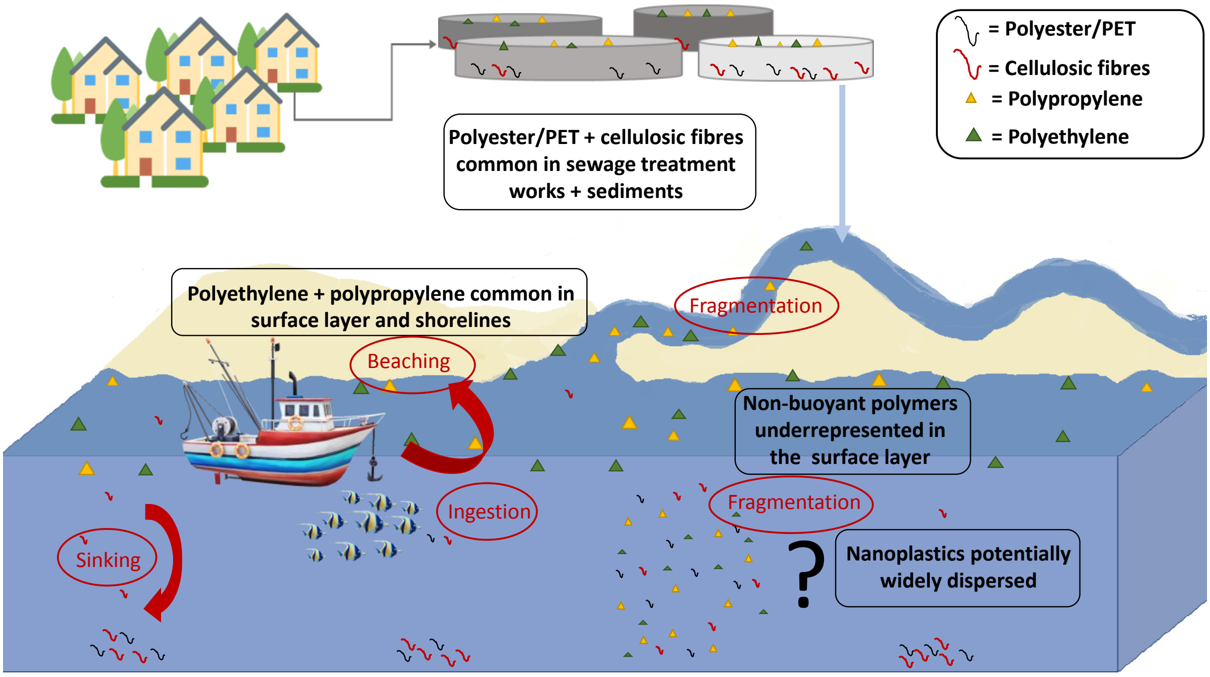

Figure 2: schematic showing fate of commonly-used polymers in aquatic systems.

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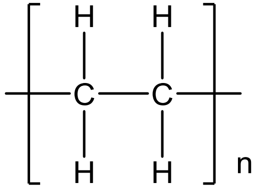
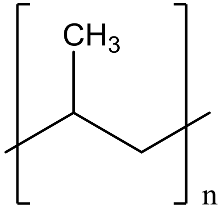
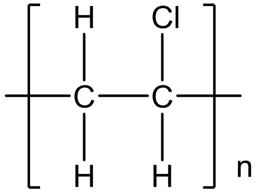
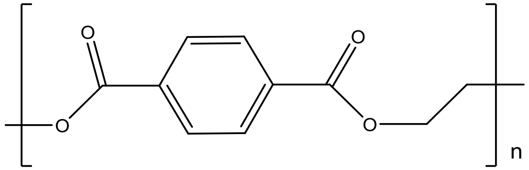
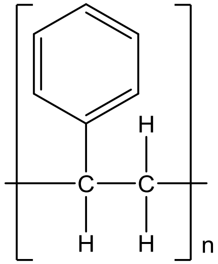
Table 1: structure, demand and applications of commonly-used plastics. See section 3 for references.

Plastic code	Name (abbreviation)	Structure	% EU plastics demand*	Applications
2	High-density polyethylene (HDPE)	 $\left[-\mathrm{CH_2}-\mathrm{CH_2}-\right]_n$ With less branching than LDPE	12.3% (for high and medium density polyethylene).	Toys; milk and shampoo bottles; yoghurt & margarine containers; cereal box liners; shopping bags; microbeads.
4	Low-density polyethylene (LDPE)	As HDPE, though with more branching	17.5% (for low density and linear low density polyethylene).	Food bags; six pack rings; squeezable bottles; tubing; microbeads.
5	Polypropylene (PP)		19.3%	Ketchup bottles; yoghurt and margarine containers; medicine bottles; automotive parts; dishware; microbeads.
3	Polyvinyl chloride (PVC)	 $\left[-\mathrm{CH_2}-\mathrm{CHCl}-\right]_n$	10.0%	Food and non-food packaging; pipes; floor tiles; carpet backing; window frames; children's toys; hoses; cable insulation; clothing.
1	Polyethylene terephthalate (PET). Polyester is a generic name for ester-containing polymers, including PET.		7.4% (for PET)	Bottles for water, soft drinks, juices, cleaners.

6	Polystyrene (PS)		6.7% (for both polystyrene and expanded polystyrene).	Insulation board; meat trays; egg cartons; cups; plates; building insulation.
7	Other plastics, e.g. acrylic, nylon, polycarbonate, polylactic acid and polyurethane.	Variable	19.3%	Large water bottles; fruit juice and ketchup.

*Plastics demand data excludes PET fibres, polyamide fibres, PP fibres and polyacryls fibres.

Table 2: properties of plastic polymers and monomers. See section 2 for references.

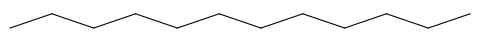
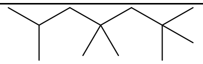
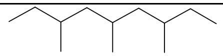
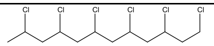
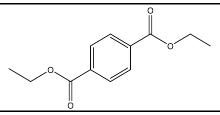
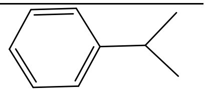
Polymer	**High-density polyethylene**	**Low-density polyethylene**	**Polypropylene**	**PVC**	**PET**	**Polystyrene**
Density (g·cm^{-3}) (Virgin resin)	0.95 – 0.96 (0.94 –0.97)	0.91 – 0.93 (0.89 – 0.93)	0.90 – 0.91 (0.85 – 0.92)	1.20 – 1.70 (flexible) or 1.30 – 1.70 (rigid) (1.16 –1.41)	1.36 -1.37 (1.38 –1.41)	1.04 – 1.07 (1.04 – 1.08) Expanded PS <0.05
Representative substructure (C_{9-12})	n-Dodecane	2,2,4,4,6-Pentamethylheptane	3,5,7-Trimethylnonane	1,3,5,7,9,11-Hexachlorododecane	1,4-Benzenedicarboxylic acid, diethyl ester (Ethyl terephthalate)	2-Phenyl-2-propanyl
Structure						
Substructure logK$_{ow}$	6.10	5.94	6.01	5.74	2.65	3.66

Table 3: experimental methods used for isolation and analysis of plastics in environmental samples

Reference	**Isolation**	**Analysis**
Marine studies (see Table 4 for main findings)		
Shorelines & sediments		
Blumenröder 2017	Density separation (NaCl), filtration, visual examination with microscope.	FTIR
Browne 2011 (beach samples)	Three sequential density separations (NaCl solution)	Transmittance FTIR
Carson 2011	Density separation (NaCl solution); sieving.	FTIR
Cooper 2010	Washed in ultrasonic bath; dried at 35 °C.	Micro ATR FTIR
Dekiff 2014	Sieving; fraction > 1mm examined visually; fraction < 1 mm two-step air-induced overflow extraction (NaCl then NaI solutions)	Thermal desorption pyrolysis gas chromatography-mass spectrometry
Imhof 2017	Sieving, density separation in seawater, visual examination with microscope.	ATR FTIR
Kunz 2016	Sieving, density separation (NaCl), visual examination with microscope, HCl.	ATR micro FTIR and synchrotron-based micro FTIR (SR-FTIR)
Kuriyama 2002	Visual inspection of beaches.	Near IR
Matsuguma 2017	H_2O_2, sieving, density separation (NaI), centrifugation, sieving	ATR FTIR
Munari 2017b	Drying, visual examination with microscope	ATR FTIR on subset of particles
Naji 2017a	Air-induced overflow using NaCl then NaI; filtration	FTIR absorption on a subset of 81 particles
Naji 2017b	Air-induced overflow using NaCl then NaI; filtration.	Absorption FTIR on a subset of 68 particles
Turner 2011	Visual	Transmittance FTIR
Vianello 2013	Flotation (NaCl solution), sieving; filtration; drying.	Reflectance micro FTIR
Yu 2018	Drying, density separation (NaCl), filtration.	Transmittance FTIR
Surface & subsurface waters		
Carpenter 1972b	Plankton tows. Mesh size 333 μm	IR spectrophotometry
Castro 2016	Filtration then visual examination with microscope.	ATR FTIR on a subset of 30 particles.
Enders 2015	Filtration, drying, density separation (sodium dodecylsulfate)	Raman micro-spectrometry on a subset of samples
Gajšt 2016	Visual examination with microscope	Near IR
Gewert 2017	Visual separation for larger pieces. Filtration, H_2O_2, microscope.	ATR FTIR on a subset of 59 particles.
Lusher 2015	Filtration then visual examination with microscope.	FTIR on a subset of 30 particles
Ng 2006	Density separation (NaCl solution) then filtration.	IR with microscope.
Song 2014	Filtration; drying.	Micro FTIR
Syakti 2017	Visual separation.	ATR FTIR
Tsang 2017	Sieving, density separation (NaCl), filtration, drying	ATR FTIR on a subset of samples
Zhang 2017	Sieving, H_2O_2 and Fe (II) to remove natural organic matter, filtration	ATR FTIR
Intermediate depths (7-142 m)		

Frias 2016	Density separation (NaCl solution); filtration.	Micro FTIR
Kanhai 2017	Filtration, visual examination with microscope.	Micro FTIR
Mistri 2017	Visual examination with microscope	ATR FTIR
Munari 2017a	Visual examination with microscope	ATR FTIR on subset of particles
Deep sea		
Bergmann 2017	Density separation ($ZnCl_2$), filtration, microscope (particles >500 µm), Fenton's reagent (particles <500 µm). Fibres not analysed.	ATR FTIR and micro FTIR
Courtene-Jones 2017	Deep-sea filters, visual examination with microscope	ATR FTIR
Woodall 2014	Variable between samples.	Transmittance FTIR
Freshwater studies (see Table 5 for main findings)		
Sewage works		
Browne 2011 (sewage effluent samples)	Filtration	Transmittance FTIR
Mintenig 2017	Enzymatic-oxidation, density separation ($ZnCl_2$ solution)	ATR FTIR and focal plane micro FTIR
Murphy 2016	Filtration then visual examination with microscope	Reflectance FTIR
Talvitie 2017	Filtration then visual inspection with a microscope	Transmittance FTIR
Ziajahromi 2017	Density separation (NaI); centrifugation; staining (Rose-Bengal solution)	ATR FTIR
Shorelines & sediments		
Browne 2010	Density separation (NaCl solution).	Transmittance FTIR
Corcoran 2015	Drying, sieving, density separation (water then sodium polytungstate solution); microscope.	ATR micro FTIR
Horton 2017	Sieving, visual inspection, density separation ($ZnCl_2$ solution), visual inspection. Only particles from 1-4 mm considered.	Raman spectroscopy on a 20% subset of particles.
Imhof 2013	"Density separation"	Raman microspectroscopy
Klein 2015	Density separation (NaCl solution); filtration. Natural organic matter removed with H_2O_2 and H_2SO_4.	ATR FTIR
Peng 2017	Density separation (NaCl solution); H_2O_2; filtration; microscope	Micro transmittance FTIR
Wang 2017	Drying, density separation (NaCl), filtration, drying, visual inspection with microscope.	Micro reflectance FTIR
Zbyszewski 2011	Dried, separated by hand, sonicated, dried.	Micro ATR FTIR
Surface waters		
Gasperi 2014	Floating plastic debris sorted manually.	ATR FTIR
Sadri 2014	Sieving.	FTIR
Zhang 2015	Net with with 112 µm mesh. Sieving, drying.	ATR FTIR

Attenuated Total Reflection: ATR. Fourier Transform Infrared Spectroscopy: FTIR

Table 4: polymer abundance during marine field surveys for microplastics, including coastal beaches. Abundance of 1 means most common polymer identified; 2 second most common etc. % means percentage of particles identified as this polymer. Minor means not quantified but comprising a small proportion of microplastics

Reference	Location and sample type	Polymer abundance
Shorelines & sediments		
Blumenröder 2017	Surface layer (top 3 cm) of intertidal sediments from Orkney Islands, Scotland.	PTFE 1 (45%), PE or polyvinylidine 2 (15%), PA 3 (10%), PES 4 (8%)
Browne 2011	18 beaches worldwide	PES fibres 1 (56%), acrylic 2 (23%), PP 3 (7%), PE 4 (6%), PA fibres 5 (3%)
Carson 2011	Hawaii. Beach sediments	PE 1 (85%), PP 2 (14%), PS or PU 3 (1%)
Cooper 2010	Hawaii. Five beaches. Visible plastics from surface layer, plus sediment from < 3 cm	PE 1 (80%), PP 2 (20%)
Dekiff 2014	Norderney Island, North Sea (Germany). Beach sediments.	PP 1 (40%), PE 2 (27%), PET 3 (13%). PVC =4 (7%). PS =4 (7%). PA =4 (7%)
Imhof 2017	Surface layer (~1 cm) of beaches in the Maldives	PE 1 (54%), PS 2 (31%), PP 3 (13%)
Kunz 2016	Top 10 cm of beaches in Taiwan	PE 1 (44%), PP 2 (43%), PS 3 (12%)
Kuriyama 2002	Japan. 30 beaches.	PE 1 (60%) and PP 2 (35%) of identified pellets
Munari 2017b	Top 5 cm of 5 beaches of the Italian Adriatic	PE 1 (38%), PP 2 (35%), nylon 3 (12%), PS 4 (10%), PET 5 (4%) PVC 6 (2%)
Naji 2017a	Persian Gulf, Iran. Beach surfaces.	PET 1 (47%), mainly as fibres, PE 2 (32%), nylon fibres 3 (21%)
Naji 2017b	Tidal sediments in the Persian Gulf.	PET 1 (41%), PE 2 (31%), nylon 3 (16%)
Turner 2011	Malta. Surface layer of sandy beaches.	PE 1 (100% of production pellets)
Vianello 2013	Italy, Lagoon of Venice. Tidal sediments.	PE 1 (48%), PP 2 (34%), PES 4 (4%), PS 5 (3.5%), Alkyd 7 (1.4%), PVC 8 (0.5%), Polyvinyl alcohol 9 (0.4%), PA 10 (0.3%)
Yu 2018	Surface layer of 18 beaches in southeastern USA.	68% of fibres “cellulosic materials” including rayon, PET fibres 2 (24%)
Surface & subsurface waters		
Carpenter 1972b	Coastal waters of southern New England, USA.	PS spherules up to an average of 1 sphere/m^3
Castro 2016	Brasil. Surface of estuarine waters with 150 µm mesh net.	PE 1 (72%), PP 2 (26%)
Enders 2015	Subsurface (3 m deep) waters between European Coast and the North Atlantic Subtropical Gyre	PE 1 (42%), PA 3 (11%), PP =4 (6%), PES =4 (6%), PS 5 (4%), PVC 7 (2%)
Gajšt 2016	Surface sampling of Slovenian Adriatic with 300 µm mesh net	PE 1 (82%), PP 3 (2%), PS (0%) and PVC (0%) =5
Gewert 2017	Surface layer of Swedish waters with 335 µm mesh net.	PP 1 (53%), PE 2 (24%)
Lusher 2015	Surface (top 16 cm) and subsurface (6 m) Arctic waters near Svalbard.	Rayon 1 (30%), PA =2 (15%), PES =2 (15%)

Ng 2006	Singapore. Surface microlayer (50-60 µm) and subsurface layer (1 m) of coastal waters	PE =1 (50%) of surface + 1 (67%) of subsurface layer. PS =1 (50%) of surface microlayer. PP 2 (33%) of subsurface layer
Song 2014	South Korea. Surface microlayer of coastal waters.	Alkyd 1 (81%)
Syakti 2017	Surface sampling of Indonesian coastal waters.	PP 1 (68%), LDPE 2 (11%)
Tsang 2017	Sediment and surface water samples from coastal Hong Kong	PP 1 (51%), PE 2 (45%)
Zhang 2017	Surface layer of Bohai sea, China with 330 µm mesh net	PE 1 (51%), PP 2 (29%), PS 3 (16%), PET 4 (3%)
Intermediate depths (7-142 m)		
Frias 2016	Portugal. Coastal sediments from shelf waters. 7-27 m deep.	Rayon fibres 1 (81%), PP fragments 2 (19%)
Kanhai 2017	Subsurface waters (11 m deep) between Germany and South Africa	Rayon 1 (63%), PES 2 (17%), PA minor (0.8%), PVC minor (0.4%), Acrylic minor (0.4%), PS minor (0.2%)
Mistri 2017	Sediments from 140 km transect of Adriatic, depth 7-142 m	Nylon 1 (47%), PE 2 (28%), PP 4 (5%)
Munari 2017a	Sediment samples from the Ross sea, Antarctica, 25-140 m deep.	Styrene-butadiene-styrene 1 (94% by weight)
Deep sea		
Bergmann 2017	Sediments from Arctic seafloor at 2500–5500 m depth	Chlorinated PE 1 (38%), PA 2 (22%) and PP 3 (16%) particles <500 µm. PTFE all particles >500 µm
Courtene-Jones 2017	Rockall Trough, west of Scotland, UK, 2227 m deep.	PES 1 (65%), PET 2 (17%), PE minor (6%)
Woodall 2014	Mediterranean, Indian Ocean and Atlantic. Deep sea sediments and coral samples. Mostly ~1000 m.	Rayon fibres 1 (57%), PES fibres 2 (23%), acrylic 4 (12%), PA minor.

PE = polyethylene, PP = polypropylene, PVC = polyvinyl chloride, PET= polyethylene terephthalate, PES = polyester, PS = polystyrene, PA = polyamide, PTFE = polytetrafluoroethylene, PU = polyurethane.

Table 5: polymer abundance during freshwater field surveys for microplastics, including sewage treatment works and estuaries. Abundance of 1 means most common polymer; 2 second most common etc. % means percentage of particles identified as this polymer. Minor means not quantified but comprising a small proportion of microplastics.

Reference	Location and sample type	Polyethylene	Polypropylene
Sewage works			
Browne 2011	Australia. Effluent from 2 sewage works.	PES fibres 1 (67%), acrylic fibres 2 (17%, including 16% PA)	
Mintenig 2017	Germany. Effluent from 12 sewage works. Sludge from six.	PE 1 of particles > 500 µm (59%) and particles < 500 µm (40%). Major in sludge. PP 2 (16%) of particles >500 µm; minor % of particles <500 µm. 3 (9%) of synthetic fibres. Major in sludge. PES 1 of synthetic fibres (74%). PS =3 (8%) of particles <500 µm. Minor % of particles >500 µm. PA =3 (8%) of particles <500 µm. Minor % of particles >500 µm. 2 (17%) of fibres. PET minor % of particles <500 µm. PVC minor in particles <500 µm and >500 µm. Polyvinyl alcohol 2 (16%) of particles <500 µm	
Murphy 2016	Effluent and sludge from Scottish sewage works.	PE =5 (4%) in final effluent, 1 (32%) in residual grease and 1 (33%) in residual sludge. Equivalent values for PP: =3 (12%), 5 (5%), 0%. Equivalent values for PS: =5, (4), =6 (2%), =2 (17%). Equivalent values for PES: 1 (28%), 2 (24%), =2 (17%). Equivalent values for PET: =5 (4%), =3 (14%), 0%. Equivalent values for PA: 2 (20%), 0%, 0%	
Talvitie 2017	Four Finnish sewage treatment works	PES 1 (60%), PE 2 (14%), polyacrylates 3 (7%), PVC 4 (5%), PS 5 (4%) and PP 6 (3%)	
Ziajahromi 2017	Sydney, Australia. Three sewage works.	PET fibres and PE particles most common microplastics	
Shorelines & sediments			
Browne 2010	Tamar estuary, UK. Estuarine sediment and strandline samples	PE 1 (32%), PP 2 (28%) and PS 3 (23%) of particles > 1 mm. PES 1 (35%), PVC 2 (26%) and PA 3 (18%) of particles < 1 mm	
Corcoran 2015	Sediment cores from bottom of Lake Ontario, North America.	PE 1 (74%), PP 2 (17%)	
Horton 2017	Sediments from four sites in the Thames Basin, UK.	PET/polyester 1 (41%), PP 2 (15%), PE 3 (6%), PS =4 (3%), PVC =4 (3%).	
Imhof 2013	Italy. Sediments from beaches on subalpine Lake Garda	PS 1 (46%), PE 2 (43%) and PP 3 (10%). PVC and PA minor in 9-500 µm size range	
Klein 2015	Germany. Top 2-3 cm of river sediments.	PE, PP and PS >75% of microplastics. PET, PVC and acrylic minor	
Peng 2017	Changjiang Estuary, China. Sediment from 53 locations.	Rayon 1 (63%), PES 2 (19%), acrylic 3 (14%)	
Wang 2017	Sediment samples from tidal zone of Beijiang River, China.	PE 1 (54%), PP 2 (25%)	

Zbyszewski 2011	Lake Huron, Canada. Surface sampling from 7 beaches	PE 1 (71%), PP 2 (27%), PET 3 (2%)
Surface waters		
Gasperi 2014	Floating debris on the Seine river, France.	PP 1 (35%), PE 2 (26%)
Sadri 2014	Tamar estuary, UK. Surface waters with 330 µm mesh net	PE 1 (40%), PS 2 (25%), PP 3 (19%). PES, PVC and nylon all minor
Zhang 2015	Three Gorges reservoir, China. Surface waters with 112 µm mesh net	PP 1 (42 - 63%), PE 2 (37 – 57%), PS 3 (0 - 13%)

PE = polyethylene, PP = polypropylene, PVC = polyvinyl chloride, PET= polyethylene terephthalate, PES = polyester, PS = polystyrene, PA = polyamide.

Table 6: low molecular-weight plastic degradation products identified during experimental studies of plastic degradation and comments about degradation pathways

Reference	Products identified and comments about degradation pathways
PET (polyethylene terephthalate)	
Day and Wiles 1972	CO, CO_2 and carboxylic acids predominant products.
Singh 2008	Formaldehyde, acetaldehyde, formic acid, acetic acid, CO_2 and H_2O
McMahon 1959	Hydrolysis faster than oxidation and thermal degradation. Degradation initially increases density. Subsequently void formation reduces density.
Polyethylene	
Vasile 2000	Numerous low molecular weight alkanes, alkenes, ketones, aldehydes Also hexacene (fused aryl)
Albertsson 1987	CO_2 and H_2O end products of LDPE biodegradation. Carbonyl peak, as monitored by IR spectroscopy, increased and decreased during abiotic and biotic degradation, respectively. Photo-oxidation precedes biodegradation.
Hakkarainen 1997 J Env Polym Deg	Homologous series of low molecular-weight carboxylic acids, ketones and furanones produced from UV irradiation (100 h), then 5 weeks at 80 °C.
Hakkarainen 1997 J Appl Polym Sci	Mono- and dicarboxylic acids major products in water and air. Ketoacids formed in both water and air. Ketones and hydrocarbons only in air.
Karlsson 1997	Hydrocarbons, ketones, carboxylic acids and dicarboxylic acids initial products from photo-oxidation. More dicarboxylic acids from prolonged photo-oxidation.
Hoff 1982	Most common products from thermooxidative degradation fatty acids, eg, formic acid and acetic acid, followed by aldehydes, eg, formaldehyde and acetaldehyde. Over 44 volatile products detected by GC and GC-MS
Polypropylene	
Frostling 1984	Formaldehyde, acetaldehyde, α-methylacrolein, acetic acid, and acetone major products from thermooxidative degradation.
Vasile 2000	Photooxdiation reduces chain length and forms carbonyls and hydroperoxides.
Vasile 2000	Numerous low molecular-weight alcohols, aldehydes, hydroperoxides, ketones and alkanes are major products from thermooxidative degradation. Also trimethylbenzenes detected.
Polystyrene	
Singh 2008	Chain cleavage generates ketones and alkenes
Hoff 1982	Theromoxidative degradation led to dimers and trimers of styrene, benzaldehyde, benzoic acid and acetophenone; then acids and aldehydes as stable products.

GC = gas chromatography. GC-MS = gas chromatography with mass spectrometry.