The role of titanium dioxide on the behaviour and fate of plastics in the aquatic environment

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HIGHLIGHTS

- Titanium dioxide pigment widely distributed in plastics at varying concentrations.
- Rutile appears to be most common polymorph in non-fibrous plastics.
- Ti concentrations above ~38,000 mg kg^{-1} can affect buoyancy of polyolefins.
- Nature of pigment surface modification significantly impacts photo-oxidation of plastic.
- On aging, leaching of titania can occur but bioactivity of particles released unclear.

GRAPHICAL ABSTRACT
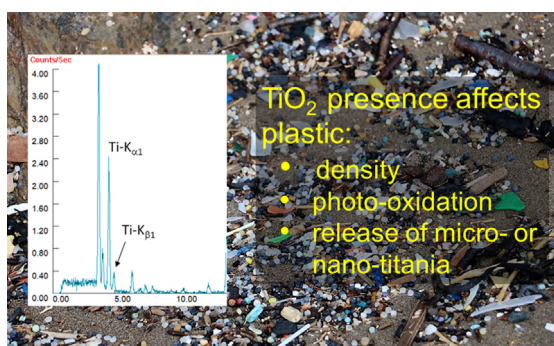
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ABSTRACT

Although titanium dioxide (TiO$_2$) is the most widely used pigment in plastics, there is limited quantitative information available for consumer goods and environmental samples. Moreover, and despite its photocatalytic activity, the potential impacts of TiO$_2$ on the behaviour and fate of environmental plastics has received little attention. This paper compiles measurements of Ti in plastic samples from aquatic environments and in consumer goods that are known to make important contributions to environmental pollution. These data, along with a critical evaluation of experimental studies using TiO$_2$-pigmented plastics, are used to formulate an understanding of how the pigment modifies the properties and persistence of environmental plastics. Titanium is heterogeneously distributed amongst different categories and sources of plastic, with concentrations ranging from <1 mg kg^{-1} in transparent-translucent materials to over 50,000 mg kg^{-1} in brightly coloured samples. Concentrations towards the higher end are sufficient to change positively buoyant polyolefins into negatively buoyant plastics, suggesting that environmental fractionation based on Ti content might occur. Accelerated leaching of TiO$_2$ from aged plastic has been demonstrated empirically, and while mobilised particles are reported within a size range greater than biotically-active titania nanoparticles, modelling studies suggest that the latter could be derived from TiO$_2$ pigments in the environment. Although rutile appears to be the most important polymorph of TiO$_2$ in non-fibrous plastics, the degree and type of engineered surface modification in consumer and environmental plastics are generally unknown. Surface modification is likely to have a significant impact on the photo-oxidative degradation of plastics and the mobilisation of fine (and, possibly, nano-sized) TiO$_2$ particles and requires further research.

1. Introduction

Additives are incorporated into most plastics in order to ensure efficient processing of materials and to engender specific properties to the finished product (Dufton, 1998). Additives are critical for colour, flame retardancy, flexibility, impact modification and light stabilisation, for example, but may also remain as residues from catalysis, crosslinking and lubrication (Pritchard, 1998). The precise chemicals and materials employed as additives have evolved with consumer requirements, legislation relating to environmental and health risks, and technical developments, but thousands remain on the global market according to a recent assessment by Wiesinger et al. (2021).

One of the major concerns with additives, and especially those known to be harmful, is their release during the lifetime of the plastic (Kuang et al., 2018; Schmid and Welle, 2020) or after its disposal by landfill or incineration (Ranta-Korpi et al., 2014; Kwan and Takada, 2016). In the marine environment, widely regarded to be one of the most important, ultimate receptors of plastic waste (Lebreton et al., 2017; Schwarz et al., 2019), attention has been directed at the slow migration of additives into the aqueous phase and their enhanced release into the digestive fluids of plastic-consuming animals (Koelmans et al., 2014; Tanaka et al., 2015; Martin and Turner, 2019; Smith and Turner, 2020).

Less well studied, however, are the effects that additives may have on the behaviour of the plastic itself once emitted directly into the environment. For example, Turner and Filella (2020a, 2020b) addressed the potential for a dense additive, like $BaSO_4$, to alter the buoyancy of light, marine plastics (like polypropylene and polyethylene), and lead to their fractionation (through settlement) based on additive content. In a similar fashion, the presence and amount of additives designed for protection, including flame retardancy or photo-oxidative breakdown, might be expected to have a significant impact on the fate of plastics, including their propensity to fragment into micro- and nanoplastics (Khaled et al., 2018; Ward et al., 2019). For instance, food packaging is designed to be single use and immediate waste, whereas building materials must be designed to last for decades (Wagner and Schlummer, 2020).

Because of its high light scattering efficiency, inertness, thermal stability, dispersability and cost-effectiveness, titanium dioxide (TiO_2) is the most widely employed pigment in plastics (Kemp and McIntyre, 2001). Two polymorphic forms of TiO_2 are used: rutile (refractive index = 2.61) and anatase (refractive index = 2.56). The TiO_2 content of pre-consumer plastics ranges from 10 % (100,000 mg kg^{-1}) or more where strong white colouration is required, to as low as 0.01 % (100 mg kg^{-1}) for tinting a deep shade, but typical concentrations range from 0.5 to 5 % (Day, 1990).

With semi-conducting properties and a band gap of 370 nm (anatase) or 400 nm (rutile), TiO_2 also acts as a photocatalyst in the ultraviolet region (Worsley and Searle, 2002). This results in reactions at the pigment surface that may accelerate the degradation (chalking and loss of gloss and flexibility) of the surrounding polymer (Bolt et al., 2005). Accordingly, and in particular for plastics for outdoor use, the base crystal is often surface treated (commonly with silica, alumina or zirconia) to minimise this activity (IARC, 2010). The form of TiO_2, its concentration and its degree of surface modification are, therefore, critical factors in the manufacture of plastics designed for different purposes (Day, 1990; Worsley and Searle, 2002). For example, high durability grades may have coating contents of up to 10 % but this may reduce pigment dispersability and opacity, whereas most consumer and general purpose plastics employ lightly coated (1–7 %) rutiles; anatase or uncoated rutile are not often used in plastics but are widely used in rubbers.

Despite the widespread use of TiO_2 as a pigment and its significance to polymer degradation, there exists very little information in the scientific literature on Ti in consumer or environmental plastics. For example, in an estimation of the mass of chemicals associated with ocean plastics, De Frond et al. (2018) neglect TiO_2 but consider other, less commonly used metal and metalloid oxides, while a general overview of additives in plastics by Hahladakis et al. (2018) only refers to TiO_2 amongst a list of inorganic additives. In the environment, and to our knowledge, quantitative data for Ti in plastic or a recognition of the potential significance of TiO_2 to the fate of plastic is limited to a handful of papers (Windler et al., 2012; Fries et al., 2013; Imhof et al., 2016; Turner and Solman, 2016; Bayo et al., 2017; Prunier et al., 2019; Dong et al., 2020; Walsh et al., 2021; Scott et al., 2022; Filella et al., 2022; Habib et al., 2022).

The purpose of the present study is to compile a dataset on the Ti content of consumer and waste/environmental plastics (including rubbers and expanded-extruded materials but excluding paints). Regarding environmental plastics, we focus on the aquatic environment where measurements of chemicals in plastics and microplastics (<5 mm in size) are most available, while for consumer plastics we focus on products purchased or sourced elsewhere but that are known to make an important contribution to the aquatic plastic litter pool. We then explore the potential impacts that TiO_2 has on the behaviour and fate of environmental plastics, including density-buoyancy and photodegradation, as well as the hypothesis that pigmented plastics may act as a source of fine particles and nanoparticles.

2. Methodology

Materials in the present study include beached and trawled (suspended) marine plastics, fishing waste, textiles and lint representative of microfibres, packaging, expanded and extruded plastics, and rubbers.

The majority of data were obtained from the authors' studies, and include cases where Ti was (i) reported directly in the literature (e.g., Turner and Solman, 2016), (ii) measured as part of the analysis but not reported (e.g., Turner and Filella, 2017; Filella et al., 2021), or (iii) determined specifically for the purposes of the present work. Briefly, all plastics, including films, rubbers and foams, were measured non-destructively using a Niton energy-dispersive X-ray fluorescence (XRF) spectrometer (model XL3t 950 He GOLDD+) configured in a laboratory test stand. Samples were analysed in a plastics mode and with thickness correction (50 μm to >13 mm) for a period of 30 to 120 s, comprising successive counting periods at 20 kV/100 μA and 50 kV/40 μA. Concentrations of Ti were calculated by fundamental parameters and using NDT software from secondary X-ray peak intensities at 4.51 keV ($K_{\alpha 1}$) and 4.93 keV ($K_{\beta 1}$). Limits of detection, defined as three counting errors, varied depending on sample thickness, porosity and composition but were generally between 4 and 20 mg kg^{-1}.

Other data for Ti in environmental and consumer plastics was derived from wavelength-dispersive XRF (Bayo et al., 2017), or by inductively coupled plasma-mass spectrometry following digestion in concentrated mineral acid (e.g., Imhof et al., 2016; Prunier et al., 2019; Walsh et al., 2021) or after combustion (Loaeza et al., 2021). In one case, Ti content appears to have been supplied by the manufacturer (Luo et al., 2020).

Pigments in various Ti-rich consumer and environmental plastics were examined under a scanning electron microscope (SEM) coupled with an energy dispersive X-ray (EDX) spectrometer. We employed a JEOL JSM-6610 SEM operated with an accelerating voltage of 15 kV and in a low vacuum mode outfitted with an Oxford Instruments EDX spectrometer and AZtec software.

3. Results

3.1. Measured Ti concentrations in plastics

Table 1 provides a description of the type of consumer plastics, including packaging, for which Ti concentrations are available in the literature or within the authors' datasets and that potentially make important contributions to the plastic litter pool of aquatic systems. Note that the number of samples analysed (*n*) in each category does not reflect production figures but the quantity selected for different research projects. Within the analytical constraints of the instruments employed, and in particular the XRF, the frequency of Ti detection and summary statistics for Ti concentrations are provided for each category. Where determined spectroscopically or noted from resin codes, polymers included polyamides (mainly nylon), polyesters (mainly polyethylene terephthalate; PET), polyethylene, polypropylene,

Table 1
Detection frequency and summary statistics for Ti concentrations (in mg kg^{-1}) and, for TiO$_2$, calculated medians, in consumer and general use plastics that make important contributions to the aquatic litter pool (shown in chronological order of publication). The polymer is indicated where a single material was present. Where an asterisk is shown by a reference, Ti data were not directly reported but the metal was measured amongst a suite of other elements.

Sample type (no. samples)	Polymer	Source	No. detected	Min, Ti	Max, Ti	Median, Ti	Median, TiO$_2$	Reference
Yarn ($n = 1$)	Polyamide	Purchased in EU	1			117	197	Windler et al. (2012)
Outdoor clothing ($n = 6$)	Various	Purchased in EU	6	2150	8540	5630	9490	von Goetz et al. (2013)
Packaging ($n = 17$)	Various	Purchased in EU	17	30.5	14,100	701	1180	Imhof et al. (2016)
Microbeads from facial cleansers ($n = 4$)	Polyethylene	Purchased in EU	4	6.0	5430	48.0	80.9	Bayo et al. (2017)
Household waste and post-consumer plastics ($n = 82$)	Various	Purchased in EU	70	<3.9	13,800	1330	2240	Eriksen et al. (2018)
Food packaging ($n = 108$)	Various	Purchased in UK	75	3.8	10,300	1064	1790	Turner and Filella (2017)*
Packaging ($n = 23$)	Polyethylene	Purchased in EU	23	0.4	850	141	238	Prunier et al. (2019)
Dryer lint microfibres ($n = 18$)	Unknown	Plymouth households	18	58.5	2610	732	1230	Turner (2019)*
Clothing textiles ($n = 72$)	Various	Purchased in UK	61	14.9	5500	1090	1840	Turner (2019)*
Pre-consumer plastic ($n = 1$)	Polyethylene	Sourced in China	1			360,000	600,000	Luo et al. (2020)
Post-consumer plastic ($n = 1$)	Polyethylene terephthalate	Waste recycling company in EU	1			8690	14,700	Loaeza et al. (2021)
Carrier bags ($n = 4$)	Polyethylene	Sourced in USA	4	700	13,000	11,000	18,300	Walsh et al. (2021)
Food packaging ($n = 3$)	Polyethylene	Purchased in USA	3	720	13,000	10,700	18,000	Nelson et al. (2021)
Cleaning cloth textiles ($n = 81$)	Various	Purchased in EU and UK	78	25.7	12,400	3730	6290	Filella et al. (2022)
Virgin plastic ($n = 1$)	Polyethylene	Sourced in EU	1			2.7	5	Núñez et al. (2022)
Post-consumer plastics ($n = 5$)	Polyethylene	Sourced in EU	5	19	100	88	148	Núñez et al. (2022)
Rubber consumer products ($n = 19$)	Unknown	Purchased in UK and EU	15	22.6	9660	911	1540	Unpublished data
Exterior construction products ($n = 18$)	Various	Sourced in EU	18	235	61,200	8710	14,700	Unpublished data

polystyrene (including extruded and expanded forms), polyvinyl chloride (PVC) and various rubbers.

Titanium was detected widely across textiles and fibres, packaging, post-consumer plastics and rubbers, with an overall frequency of about 86 % (401 out of 464 samples). Concentrations also varied widely across most categories, with a range often spanning about three orders of magnitude. Median concentrations were generally greater for polyolefin and PVC-based exterior plastics and polyethylene packaging sourced from the USA than various types of polyolefin and PET-based packaging sourced from Europe; note, however, an exceptionally high Ti content for a single, pre-consumer polyethylene obtained from China. The lowest concentrations and non-detects were associated with transparent or translucent samples that were usually (but not always) colourless, while concentrations above 5000 mg kg^{-1} were generally encountered in textile fibres, films

(<100 μm) and thicker plastics and rubbers that were white or brightly coloured.

Table 2 categorises environmental plastics by location and characteristics (e.g., plastic fragments, foamed plastics, rubbers) or original use (e.g., fishing, industry), and provides detection frequencies and summary statistics for Ti concentrations according to information in the literature or the authors' datasets. As above, the number of samples analysed (n) in each category does not reflect environmental abundance but the quantity selected for different research projects. Polymers identified here include all of those encompassed by consumer plastics, but with greater proportions of polyolefins, cellulose acetate (cigarette filters; not included in published beach surveys) and foamed polyurethane and polystyrene.

Like consumer plastics, Ti was detected widely across each category, with an overall frequency of about 91 % (2123 out of 2325 samples),

Table 2
Detection frequency and summary statistics for Ti concentrations (in mg kg^{-1}) and, for TiO$_2$, calculated medians, in environmental plastics (and shown in chronological order of publication). Polymer/s are indicated where one or two materials were present. Where an asterisk is shown by a reference, Ti data were not directly provided but the metal was measured amongst a suite of other elements.

Sample type (no. samples)	Polymer	Location	No. detected	Min, Ti	Max, Ti	Median, Ti	Median, TiO$_2$	Reference
Beached plastic fragments ($n = 9$)	Various	Lake Garda	9	1050	175,000	3430	5780	Imhof et al. (2016)
Beached plastic foam fragments ($n = 149$)	Mainly polystyrene/ polyurethane	SW coast of England	143	18	30,400	867	1460	Turner and Solman (2016)
Beached fishing waste ($n = 68$)	Various	SW coast of England	67	16.8	3140	386	651	Turner and Solman (2016)
Beached plastic fragments and objects ($n = 144$)[a]	Various	SW coast of England	131	5.6	63,900	382	644	Turner and Solman (2016)*
Beached plastic fragments and objects ($n = 597$)	Various	Lake Geneva	544	1.5	48,700	587	989	Filella and Turner (2018)*
Beached plastic foam fragments ($n = 53$)	Mainly polystyrene/ polyurethane	Lake Geneva	53	48.4	16,200	1060	1790	Filella and Turner (2018)*
Beached rubbers ($n = 9$)	Unknown	Lake Geneva	6	5.8	13,100	1120	1890	Filella and Turner (2018)*
Beached fishing waste ($n = 12$)	Various	Lake Geneva	10	14.6	55,300	3940	6640	Filella and Turner (2018)*
Suspended mesofragments ($n = 13$)	Polyethylene	North Atlantic Gyre	13	8.8	7350	51.3	86.5	Prunier et al. (2019)
Suspended microfragments ($n = 4$)	Polyethylene	North Atlantic Gyre	4	497	2010	1040	1750	Prunier et al. (2019)
Beached industrial beads ($n = 497$)	Polyethylene/ polypropylene	coastlines of NW Europe	487	59.0	35,100	4460	7520	Turner (2019)
Beached plastics and foams ($n = 598$)	Mainly polystyrene/ polyurethane	various Swiss lakes	520	4.9	177,000	799	1350	Filella et al. (2021)
Beached nurdles and pellets ($n = 119$)	Polyethylene/ polypropylene	SW coast of England	113	3.2	30,700	792	1340	Unpublished data
Beached rubbers ($n = 13$)	Unknown	SW coast of England	6	9.1	5028	50.0	84.3	Turner and Solman (2016); unpublished data
Littered cigarette filters ($n = 40$)	Cellulose acetate	Plymouth streets	17	22.5	8910	6850	11,500	Unpublished data

[a] Samples exclude nurdles, pellets and rubbers from original data.

concentrations varied widely across all categories, with a range spanning two to four orders of magnitude, and the highest concentrations were associated with white or brightly coloured plastics. Overall, there was no significant difference in the median Ti concentrations of consumer and environmental plastics ($p > 0.05$ according to a Mann-Whitney U test performed in Minitab v19).

3.2. Concentration and form of TiO_2 in plastics

Also shown in Tables 1 and 2 are the calculated median concentrations of TiO_2 for each sample category, assuming that all Ti is present as the dioxide. Median concentrations range from about 80 mg kg^{-1} to 18,000 mg kg^{-1} in consumer plastics (with the exception of a single, pre-consumer polyethylene) and from about 80 mg kg^{-1} to 11,500 mg kg^{-1} in environmental plastics, with individual values (not shown) exhibiting a broader range and from <1 mg kg^{-1} to 600,000 mg kg^{-1} in consumer plastics and about 2.5 mg kg^{-1} to 280,000 mg kg^{-1} for environmental samples. The TiO_2 content of the majority of samples falls within the indicative range reported by Day (1990) where the pigment is used for tinting (~100 mg kg^{-1}) and bright white colouration (up to 50,000 mg kg^{-1}). However, in many cases where TiO_2 is present below the lower value, we suspect its presence may reflect contamination arising from manufacture (including recycling; Matxinandiarena et al., 2019) or, for environmental plastics, acquisition of aqueous and particulate forms of Ti from the environment (Ashton et al., 2010).

Amongst the studies summarised in Tables 1 and 2, only a limited number appear to have considered the crystal polymorphs of TiO_2. Walsh et al. (2021) used powder X-ray diffraction to establish that rutile was present in polyethylene carrier bags. More commonly, however, rutile and anatase have been identified by Raman spectroscopy and from characteristic peaks at 241, 445 and 610 nm and 143, 397, 516 and 638 nm, respectively (Nava et al., 2021). Thus, Imhof et al. (2016) analysed selected beached microplastics from Lake Garda constructed of polyethylene, polypropylene and polystyrene ($n = 12$) and found that rutile and anatase were present in three cases each. More recently, Filella et al. (2022) established that anatase, but not rutile, was present in various polyester-polyamide microfibrous cleaning cloths. Lenz et al. (2015) and Luo et al. (2020) also refer to the presence of TiO_2 in an ethylene vinyl acetate microplastic trawled from the English Channel and a pre-consumer polyethylene, respectively, that exhibited peaks characteristics of rutile.

Rutile is the preferred and most commonly encountered form of TiO_2 in the majority of polymers because of its greater stability and light scattering efficiency and a lower propensity to catalyse photodegradation, with stabilised and surface-treated grades offering particularly good weather and photochemical stability (Worsley and Searle, 2002; Danish Ministry of the Environment, 2014). Untreated or surface-treated anatase may offer high tinting strength, brightness and dispersability and is less abrasive and costly but is not recommended for outdoor applications unless chalking is required to mask discoloration of near-whites in sunlight (Day, 1990). Anatase is, however, preferred in rubber and as a delustrant for synthetic fibres (Puchowicz and Cieslak, 2021). It is clear, therefore, that both forms of TiO_2 are present in environmental plastics (including microfibres), with the precise form and its concentration in any given sample dependent on the original or intended function of the plastic.

3.3. Impact of TiO_2 on degradation of environmental plastics

In the aquatic setting, the physical breakdown (e.g., embrittlement, cracking, flaking) and chemical degradation (oxidation or hydrolysis) of plastics is dependent on a number of factors. These include polymer type (molecular weight, hydrophobicity, presence of functional groups), sample thickness, surface area and shape, and environmental conditions, such as whether material is beached or suspended or is subject to biofouling. In a critical examination of published experimental data on thermoplastics in the marine environment, and ranging in thickness from 100 μm to 10 mm, Chamas et al. (2020) report specific surface degradation rates

ranging from about 5 to 110 μm year^{-1} and estimated half-lives from about 1.4 to >2500 years.

For a given polymer, thickness and geometry, a factor that has been acknowledged but often overlooked quantitatively in the environmental literature is the effect of additives, and in particular those like TiO_2 that are photocatalytic, on plastic degradation. Table 3 reproduces data reported by Day (1990) for the embrittlement times (as hours to 50 % reduction in elongation break) of 100 μm thick polyethylene films that had been impregnated with different forms, grades and contents of TiO_2 and subsequently exposed to UV light under controlled, experimental conditions. The pigmented plastics failed more quickly than unpigmented polyethylene and in an order consistent with pigment grade, and degradation increased with increasing pigment content between 20,000 and 80,000 mg kg^{-1}. Overall, embrittlement times vary by more than an order of magnitude, and while a relatively high concentration of uncoated or coated anatase or lightly coated rutile accelerates weathering, a relatively low concentration of "superdurable" (highly coated) rutile effects greatest polymer stability.

More recently, Walsh et al. (2021) studied the degradation of pieces of polyethylene carrier bags and pure polyethylene film immersed in Milli-Q water and subject to simulated solar radiation. Compared with pure polyethylene, the consumer plastics produced dissolved organic carbon more rapidly and generated a greater number of chemical products. This was attributed to the presence and photocatalytic activity of rutile TiO_2 in the carrier bags (although no information on surface modification of the pigment crystal was referred to).

Clearly, the characteristics and content of TiO_2 in plastics will play an important role in the rate and nature of plastic degradation in the environment. Thus, plastics not intended for outdoor use and pigmented with high concentrations of anatase or lightly treated rutile for colour, brightness and opacity are predicted to degrade much more quickly than plastics specifically designed for outdoor use (Zheng and Nowack, 2021). Significantly, recent research in polymer engineering has deliberately aimed to enhance the photodegradation of plastic waste through the incorporation of customised, photoactive TiO_2 pigments (Colburn et al., 2020; Lee and Li, 2021; Nabi et al., 2021).

While the analysis of the TiO_2 content of plastics, either destructively or non-destructively, is relatively straightforward, and the determination of its polymorphic form is possible, albeit more challenging, a critical measurement is the nature and degree of pigment coating or surface modification. A specific, potential marker of engineered surface modification of TiO_2 is zirconium (for zirconia). This is commonly employed in paints but is also used in highly durable plastics, including polyolefins and PVC for building exteriors, agricultural films and outdoor furniture; zirconia is not, however, employed by all plastic manufacturers (Titan Group Innovative, 2020).

Fig. 1 shows XRF spectra for four samples of polyethylene of broadly similar (<1 cm) dimensions collected from the strandline of coastal beaches in southwest England. Titanium is detectable in all samples, with clear secondary X-ray peaks at 4.51 keV (K$_{\alpha 1}$) and 4.93 keV (K$_{\beta 1}$) and concentrations annotated. By contrast, the peak for Zr at 15.78 keV (K$_{\alpha 1}$) is only evident in two cases (note that the Niton XRF is not calibrated for Zr in

Table 3

Embrittlement times, in hours of UV exposure to reach 50 % reduction in elongation at break, for polyethylene sheeting impregnated with different grades and quantities (in mg kg^{-1}) of TiO_2 (Day, 1990).

Pigment	0	20,000	50,000	80,000
Uncoated anatase		225	125	125
Coated anatase			250	
Lightly coated fine crystal rutile		800	475	450
Lightly coated rutile			525	
Highly durable fine crystal rutile		1100	950	850
Highly durable rutile		1250	875	850
Superdurable rutile		1700	1300	950
Unpigmented	>2000			

plastic and concentrations are not calculated). Presumably, therefore, the polyethylene of the coloured fragments in (a) and (b) was originally employed for exterior use, while the white production pellet and black industrial biobead in (c) and (d), respectively, were destined for or derived from polyethylene intended for more general purpose usage. On this basis, and for equivalent environmental exposures, we would predict the former samples to be more persistent in the marine environment.

With respect to the samples in Table 2 analysed by energy-dispersive XRF spectrometry, and where Ti was detected and spectra were available for inspection, we encountered 18 out of about 350 (or about 5 % in total) that exhibited a discernible Zr peak. This may, however, represent an underestimate because of the amount of noise present in this part of the XRF spectrum for many of the smaller and thinner samples. Nevertheless, and where zirconia is used individually or in combination with other minerals to modify the pigment crystal surface, the concurrent determination of Ti and Zr in environmental samples has the potential to probe, at least qualitatively, differences in degradation rates of plastics.

Alumina and silica are also commonly employed in the surface treatment of TiO₂ pigment particles. However, and despite the ready determination of Al and Si, these elements have multiple uses in plastics, including alumina trihydrate as a flame retardant, aluminium stearate as a lubricant, aluminium silicate as a filler, and a multitude of siloxanes serving a variety of functions (Pritchard, 1998). Accordingly, techniques are required that target the surface of TiO₂ pigments. These include examination under a scanning/transmission electron microscopy (S/TEM) coupled with elemental mapping obtained by EDX (where a less powerful and penetrating X-ray beam is used than in XRF). S/TEM-EDX applied to road paints is able to discriminate between silica-coated and untreated crocoite pigments, as well as estimate the thickness, hence contribution, of the amorphous coating (Lee et al., 2018; O'Shea et al., 2021), and has potential for the analysis of pigments in plastics.

We examined various Ti-rich consumer and environmental plastics by SEM-EDX and images and results are exemplified in Fig. 2. Thus, when pigment particles in a white, polypropylene yoghurt pot were targeted, Ti was returned with traces of Ca and sometimes Na. Pigment particles in an offcut of a PVC house siding, however, returned Ti (and Ca) along with traces of Al and Si. While these results are only qualitative and lack the spatial resolution required to probe pigment surface morphology and structure (the resolution of the X-ray beam was about 1 μm), they are consistent with the chemical makeup of pure or lightly coated rutile versus more highly coated and durable rutile.

3.4. Impact of TiO₂ content on plastic density

The densities of anatase ($\rho_{a\text{-TiO2}} = 3.90$ g cm^{-3}) and rutile ($\rho_{r\text{-TiO2}} = 4.27$ g cm^{-3}) are considerably greater than the densities of common polymers ($\rho_p \sim 0.85$ to 1.5 g cm^{-3}). This means that, in theory, the density of a plastic, ρ_{plast}, will increase by increasing the volume fraction of pigment present, f_{TiO2}:

$$\rho_{plast} = \left(1 - f_{TiO_2}\right)\rho_p + f_{TiO_2}\,\rho_{TiO_2} \tag{1}$$
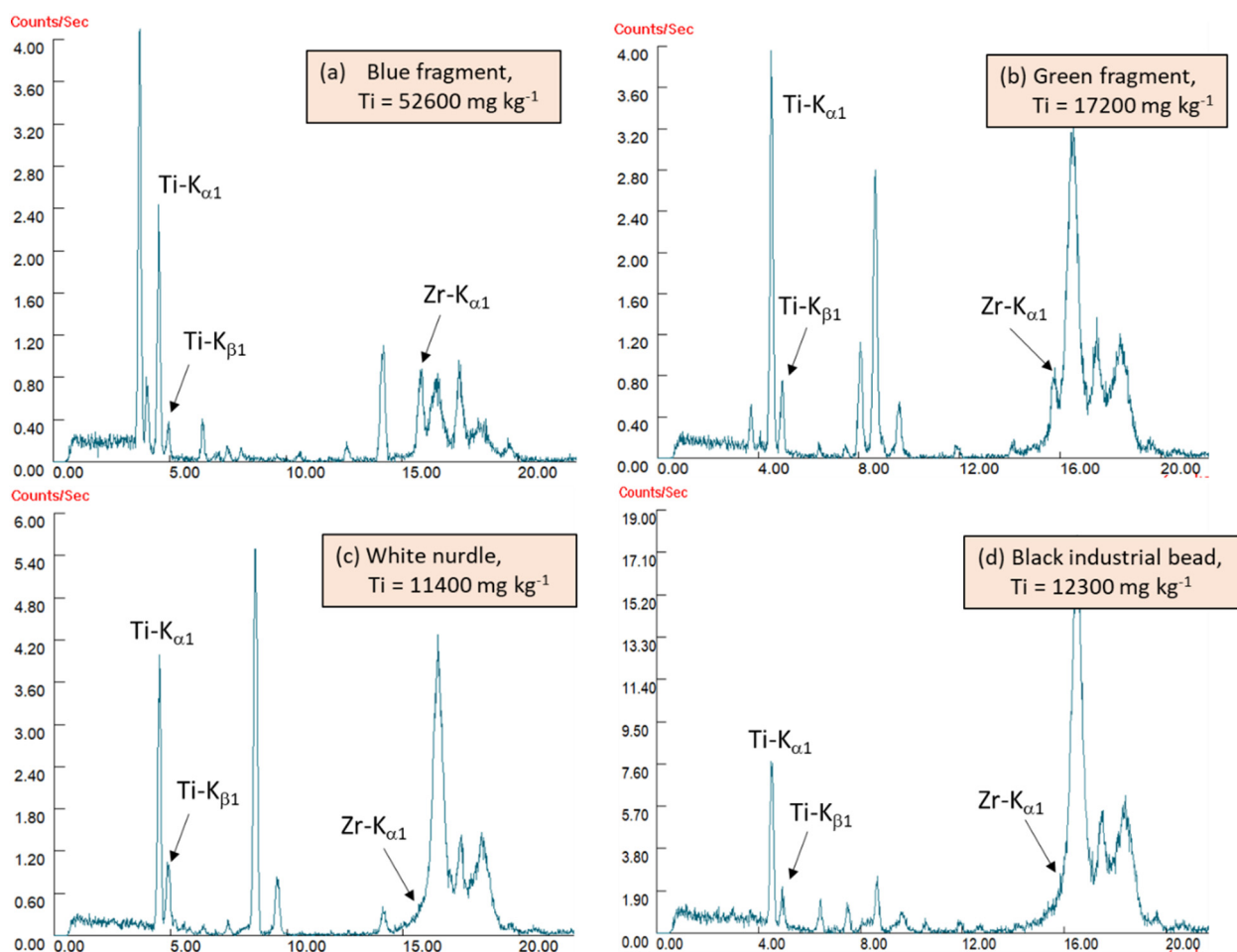

Fig. 1. XRF spectra (counts per second versus energy, keV) for four polyethylene samples collected from beaches of southwest England. Titanium peaks are present in all cases (with Ti concentrations annotated) but Zr is only evident in (a) and (b).
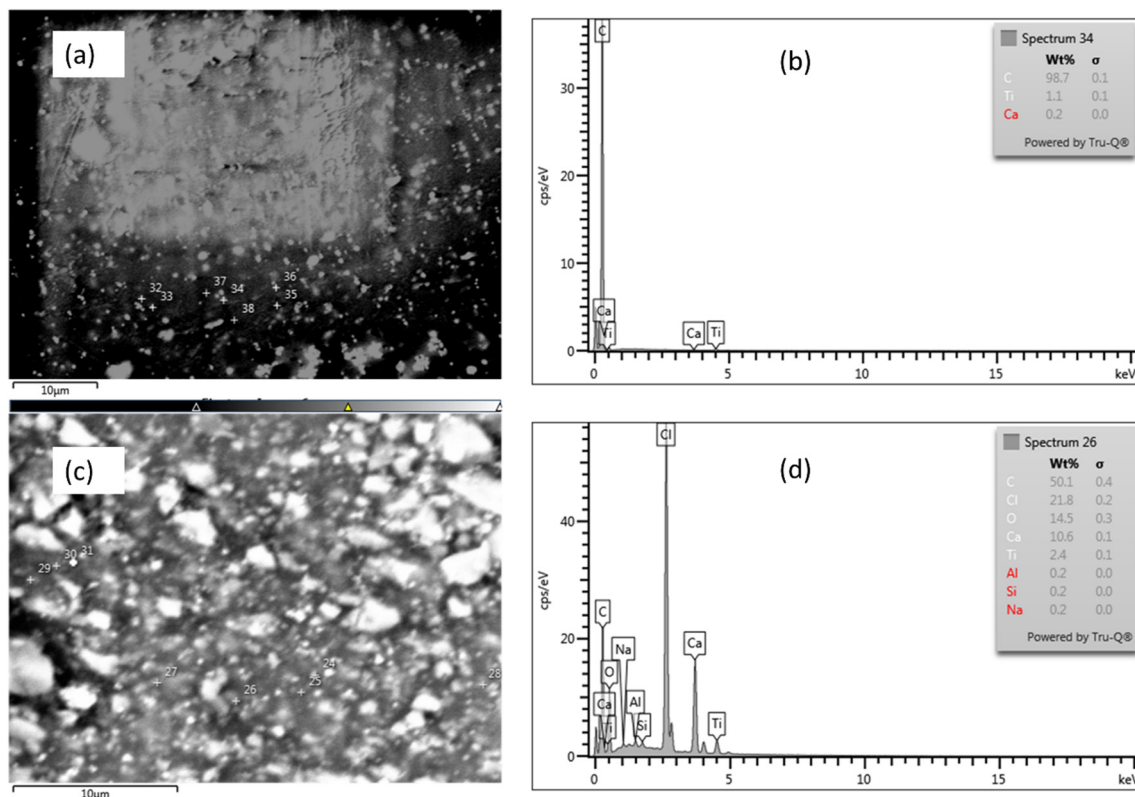
Fig. 2. SEM images of (a) a polypropylene yoghurt pot and (c) a PVC house siding and examples of EDX spectra that targeted individual TiO$_2$ pigments (b and d). Note that EDX concentrations are indicative only.

On a mass basis, and for a concentration of Ti in mg kg^{-1}, Eq. (1) can be rewritten as follows (Turner and Filella, 2020b):

$$\rho_{\text{plast}} = \rho_p \rho_{\text{TiO}_2} / \left(\left([\text{Ti}]/5.99 \times 10^5 \right) \left(\rho_p - \rho_{\text{TiO}_2} \right) + \rho_{\text{TiO}_2} \right) \quad (2)$$

where 5.99×10^5 accounts for both the conversion of mg kg^{-1} to a mass fraction and the mass contribution of Ti to TiO$_2$.

Critical in the aquatic environment is the quantity of TiO$_2$ that increases the density of a polymer sufficiently to alter the sign of its buoyancy. For light polymers that have a slight inherent positive buoyancy, including polyolefins ($\rho_p \sim 0.90$ to 0.98 g cm^{-3}), negative buoyancy may be effected in freshwater when density increases to above 1 g cm^{-3} and in coastal waters when density increases to above about 1.02 g cm^{-3}. Fig. 3 illustrates the calculated density for polymers of inherent densities ranging from 0.90 to 0.98 g cm^{-3} with increasing quantities of Ti, as rutile pigment, up to 100,000 mg kg^{-1}. Here, values of ρ_{plast} of 1 g cm^{-3} and 1.02 g cm^{-3} are attained with Ti additions ranging from about 75,000 mg kg^{-1} and 90,000 mg kg^{-1} and from 15,000 mg kg^{-1} to 30,000 mg kg^{-1}, respectively. These concentrations are exceeded for many environmental samples in Table 2 and for certain construction plastics given in Table 1, suggesting that polyolefins in the environment may be subject to fractionation (i.e., in suspension versus settled) and different fates (e.g., exposed to and shielded from sunlight; available to epipelagic or benthic organisms) according to Ti content.

In reality, net plastic densities are more complex and calculated values shown in Fig. 3 are likely underestimates. This is because Ti measurements neglect the presence of minerals that modify the pigment surface (that is, the total pigment content is underestimated) and other inorganic functional additives and fillers. Nevertheless, the presence of high quantities of dense additives more generally may explain, at least in part, why polyethylene is often reported in bed sediment (Vianello et al., 2013; Cheang et al., 2018).

Unfortunately, elemental or compositional analyses of benthic plastics is lacking but would be required to verify this assertion.

3.5. Plastic pigmented with TiO$_2$ as a source of fine particles and nanoparticles

In a study of additives in plastics sampled from North Sea sediments, Fries et al. (2013) first addressed the possibility of microplastics acting as a source of TiO$_2$ nanoparticles in the marine environment. Strictly, nanoparticles are considered as objects with at least one dimension in the range 1 to 100 nm (Shi et al., 2013). By contrast, to optimise the scattering
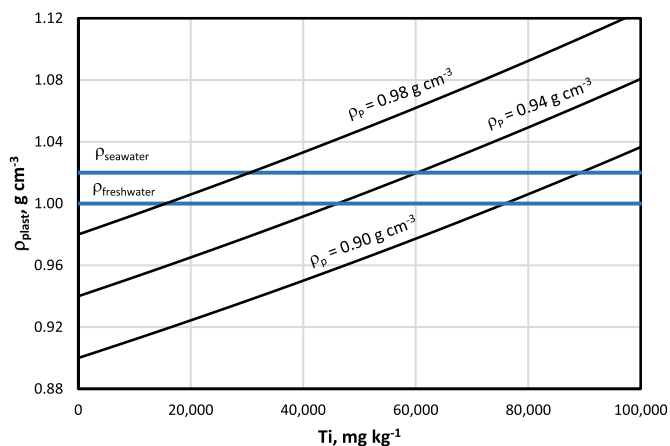

Fig. 3. Calculated density of plastic (ρ_{plast}) with increasing Ti concentration (as rutile TiO$_2$) added to polymers of inherent densities (ρ_p) ranging from 0.90 g cm^{-3} to 0.98 g cm^{-3}. Annotated in blue are the densities of freshwater and coastal seawater. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of light in plastics, pigment diameter should be just below one-half of the wavelength to be scattered. With the eye most sensitive to light of about 0.55 μm in wavelength, typical commercial TiO_2 pigments are between about 0.2 and 0.3 μm in size (Chemours, 2018). Although this size distribution renders TiO_2 pigment particles larger than TiO_2 nanoparticles, their effective sizes may be similar during experimental delivery unless stringent precautions are undertaken because of aggregation and agglomeration (IARC, 2008). Nevertheless, from a toxicological standpoint, individual particle size is critical: fine, pigmented particles are believed to be chemically inert, whereas nanoparticles are considered bioactive and potentially toxic because of their higher surface area, greater proportion of atoms localised at the particle surface, and ability to be taken up by endocytosis and diffusion (Skocaj et al., 2011). Recently, and because of the abundance of particles in the nano-size range, the European Food Safety Authority considered TiO_2 (as E171) no longer safe as a food additive (EFSA, 2021).

Luo et al. (2020) determined the leaching of rutile TiO_2 into deionised water and tap water from bright white, low-density polyethylene that had been powdered to <500 μm and subject to accelerated aging for different periods. After a twelve-hour period of leaching, unaged plastic released 8.8 ± 0.1 mg L^{-1} and 3.0 ± 0.1 mg L^{-1} in deionised water and tap water, respectively. By contrast, plastic aged for six weeks released 139 ± 1.4 mg L^{-1} and 136 ± 7.7 mg L^{-1} in the respective media. On a particle number basis, unaged and aged polyethylene microplastics released about 70×10^5 L^{-1} and 1100×10^5 L^{-1} into both media, respectively. Moreover, aged polyethylene tended to release a higher proportion of larger TiO_2 particles (>5 μm) and a lower proportion of smaller particles (< 5 μm) than unaged polyethylene. The authors suggested that the fragmentation and cracking of polyethylene particles on aging creates a larger contact area for TiO_2 with water and facilitates the release of more and larger particles. Significantly, however, the size distribution reported indicates that TiO_2 particle release is restricted to or dominated by chemically inert fines rather than bioactive nanoparticles.

By contrast, the recent application of a material flow analysis to TiO_2 by Zheng and Nowack (2021) that accounted for particle size and crystalline forms established that nanosized particles had been released to the environment from various products, that included plastics, well before the introduction of engineered nanomaterials in 2000. This observation requires that TiO_2 nanoparticles are also derived from conventional titania pigments and suggests that a complete risk assessment of TiO_2 in the environment should also consider pigmented particles.

Clearly, further experiments using a variety of polymers and grades or surface modifications of pigment particles are required for a better understanding of the mechanisms and kinetics involved in TiO_2 leaching and its subsequent toxicological impacts. Specifically, central questions to be addressed are how pigment photoactivity affects the release of TiO_2 (in addition to the degradation of the polymer itself), and whether the presence of other inorganic and organic additives affect this process (Allen et al., 1998; Gesenhues and Hocken, 2000).

3.6. Summary and perspectives

The compilation of Ti data in consumer and environmental plastics reveals a heterogeneous distribution of concentrations amongst each category, source or polymer type. However, the highest concentrations are associated with bright plastics (that are not always white) and the lowest (trace) concentrations are found in transparent or translucent materials or samples where external contamination may have arisen.

In addition to Ti content, the results and critical analysis presented here suggest that the polymorphic form and engineered modification of TiO_2 pigment particles have significant impacts on the behaviour and fate of a range of plastics in the aquatic environment. For instance, light plastics with quantities of relatively photoactive TiO_2 that are insufficient to effect sinking are predicted to degrade most quickly while in suspension or beached which, in turn, facilitates the mobilisation of TiO_2 pigment particles. By contrast, plastics containing high quantities of modified TiO_2 particles may settle out of suspension and become partially shaded from UV light

and are, therefore, predicted to be more persistent. Titanium should, therefore, be recognised as a critical element in environmental plastics that merits more widespread monitoring and greater scientific study.

A more general conclusion of this study is that experimental studies involving pure polymers may not lead to accurate data or inferences regarding the behaviour, persistence and fate of plastics in the aquatic environment.

CRediT authorship contribution statement

Andrew Turner: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Montserrat Filella:** Conceptualization, Investigation, Writing – review & editing.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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