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The role of plastics in the accumulation and release of trace elements in the environment

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Review

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Abstract

Plastics are an emerging class of environmental contaminants whose impacts are not yet fully understood. Trace elements, another class of environmental contaminant and commonly associated with plastics, have been widely researched and are known to be toxic to organisms. However, the combined impacts of these two contaminants on the environment remain unclear. Here, we reviewed the current knowledge of the types and concentrations of trace elements associated with plastics, the role of plastics in creating new exposure routes, the processes involved in the release of trace elements from plastics, and the transport of plastics through environmental compartments. Trace elements inherent in plastics, due to addition during manufacture for formation or functional properties, are typically present at higher concentrations than those that are acquired from the environment, and consequently are likely to have greater impacts. Trace elements are continuously released into environmental matrices from plastics but may be released at higher concentrations when exposed to rapid changes in environmental conditions (pH, ionic strength, redox potential, salinity, UV levels). Plastics potentially provide additional exposure routes for organisms to trace elements. For example, exposure to trace elements may occur when organisms ingest plastics, use them for shelter and nest building or as a surface to attach onto. Further research to improve our understanding of this complex contaminant should focus on environmentally relevant studies on trace element release and their effects.

Impact statement

This systematic review summarises current knowledge on toxic trace elements that are associated with plastics, including inherent trace elements (intentionally or non-intentionally added) as well as those acquired from the environment. It considers how, once in the environment, plastics cycle through ecosystem compartments and assesses the potential impacts of associated trace elements on the organisms they interact with. Mechanisms through which trace elements may be released into the environment or organisms were assessed along with the environmental fate of plastics to determine the impacts of plastic-associated trace elements and identify settings where impacts are likely to be higher. Routes through which organisms may be exposed to trace elements, that would not occur in the absence of plastics, were also identified. Key knowledge gaps were identified, and as plastics are ubiquitous environmental contaminants, further research on the environmental impacts of plastic-associated trace elements is urgently needed.

Introduction

Plastics are an emerging class of environmental pollutants which have been identified in all environmental compartments so far examined (air, biota, soil and water), including remote areas such as Antarctica (Furness, 1985; Reed et al., 2018; Webb et al., 2019; Pereira et al., 2020; Aves et al., 2022). Human reliance on plastic has been driven by its low cost and versatility in a wide range of applications. Plastic is used for packaging, building and construction materials, transport, electronics, medical supplies, and household, leisure and sporting equipment (PlasticsEurope, 2021).

More recently it has been acknowledged that plastics often contain trace elements (TEs) added during the production and manufacture of plastic items, as well as acquiring them from the environment (Turner and Filella, 2021). The potential for plastics to act as vectors of TEs over long distances and increase the exposure of organisms to TEs is of concern. Trace elements are non-degradable persistent contaminants and therefore may bioaccumulate and biomagnify in biota, thus resulting in greater effects on organisms higher up the food chain (Wu et al., 2016b).

The environmental fate of plastics and their cycling within and between environmental compartments is a key factor to be considered when assessing the impacts of plastic-associated TEs. Sources of plastic entering the environment include wastewater treatment plant (WWTP) discharges, landfill leachate and aerial resuspension, agriculture, fishing, illegal and accidental

littering, and the breakdown of large plastic materials through general wear and tear during usage (Wu et al., 2016a; Koelmans et al., 2019; Li et al., 2020; Ruffell et al., 2021). Once released into the environment there is a continuous flow of plastics between air, soil, biota, surface water, groundwater and sediments (Li et al., 2020). Major transport mechanisms include water cycling, deposition, wind erosion, incomplete incineration of plastic waste, wave action and sea turbulence, and interactions with biota (Ryan, 2015; Dris et al., 2017; Allen et al., 2020; Prinz and Korez, 2020; Watt et al., 2021; Weiss et al., 2021; Pantos, 2022). The transport of plastics can be affected by the density and the additives present, as well as the size and morphotype of each individual particle (Hoellein et al., 2019; Kumar et al., 2021; Shamskhany et al., 2021). These characteristics of individual particles can change depending on environmental conditions such as UV exposure, weathering and degree of biofouling, making it difficult to predict the fate of environmental plastics (Moret-Ferguson et al., 2010; Liço et al., 2014; Lagarde et al., 2016).

This review examines the current state of knowledge around the interaction between plastic-associated TEs and the environment. The relative environmental hazards of TEs added during manufacture are compared to those of TEs acquired from the environment, and the composite contaminant that the TE-plastic combination forms. Potential exposure routes of organisms to TEs associated with plastics, and the role environmental conditions play in the level of risk are also examined. The knowledge gaps that need addressing to better understand the impacts and risk of plastics, a now ubiquitous class of anthropogenic contaminant, are identified.

Plastic-associated trace elements

Trace elements may either be inherent within plastics, due to their use in polymer manufacturing, used as additives for improving or adding desirable properties, or acquired from the surrounding environment through adsorption due to physicochemical surface properties of plastic (Bridson et al., 2021; Turner and Filella, 2021).

Inherent

Many toxic substances are inherent within plastic products, having been deliberately added in order to add or increase some desired properties of the plastic. These are referred to as additives (Bridson et al., 2021). Additives (organic or inorganic) are added to the base polymer during production for improving fire, UV and heat resistance; for adding specific or desirable colours; and as fillers for reducing cost or increasing hardness and stiffness (Gradin et al., 1989; Sendra et al., 2021). Plastics may also have other toxic substances incorporated within the polymer matrix during production, such as catalyst residues (e.g., antimony compounds used as a catalyst in the production of polyester) and impurities that are unintentionally added, referred to as non-intentionally added substances (NIAS) (Bridson et al., 2021). The amount of TE additives present in the final plastic product as a mass percentage varies between polymer and product types but can range from a few percent to half of the total mass, in the case of inorganic fillers (Hahladakis et al., 2018). Trace element use, commonly used compounds, and chemical formula are summarised in Table 1. Some inorganic additives have multiple purposes, such as zinc oxide (ZnO, filler and pigment) and antimony trioxide (Sb_2O_3, flame retardant and pigment) (Turner and Filella, 2021). These TEs are not chemically bound to the polymer matrix and as a result can diffuse throughout the polymer and into the surrounding environment due to concentration gradients (Wilson et al., 1982; Mercea et al., 2017; Chen et al., 2019; Mao et al., 2020). This creates concern regarding the impacts of TEs being released into the surrounding environment.

Acquired

The ubiquity of both TEs and plastic in the environment allows for interactions potentially resulting in TEs being acquired by plastics through adsorption. Factors determining the adsorption of TEs to plastics include polymer type, extent of weathering, particle size and concentration, salinity, pH, dissolved organic matter, and temperature (Yang et al., 2019; Wang et al., 2019a; Guo et al., 2020; Wang et al., 2020b; Aghilinasrollahabadi et al., 2021). The rate at which polymers adsorb TEs generally occurs rapidly, and there is a constant transfer of TEs between the plastics and matrices they are in contact with (Guo et al., 2020).

There are three key mechanisms by which TEs have been reported to accumulate in plastics (Figure 1). Firstly, sorption through surface complexation or electrostatic interactions can occur when charged TEs interact with polar or charged regions on plastic surfaces (Zhang et al., 2020a; Cao et al., 2021). Charged regions on polymer surfaces arise from the presence of alkene (C=C), carbonyl (C=O) and hydroxyl (-OH) functional groups which can result from environmental weathering (Bandow et al., 2017). Certain plastics (polystyrene [PS], polyethylene terephthalate [PET] and polyvinyl chloride [PVC]) contain polar regions inherent to the polymer chain (Brennecke et al., 2016; Liu et al., 2021). The presence of charged additives and other contaminants also results in charged regions on polymer surfaces enabling electrostatic interactions with TEs (Holmes et al., 2012; Lin et al., 2022). Liu et al. (2022) investigated the adsorption of cadmium (Cd), copper (Cu), chromium (Cr) and lead (Pb) to polypropylene (PP), PS and PVC microplastics (MPs) and identified that halogen bonds and π- π interactions also contribute to the adsorption of TE to plastics in addition to electrostatic interactions. Trace elements can also become associated with environmental plastics through sorption to biofilms and hydrous oxides on the surface of the plastics (Ashton et al., 2010; Guan et al., 2020).

Adsorption of TEs is dependent on the polymer type and the TE. For example, adsorption of Cu was much greater for polyamide (PA) and polymethyl methacrylate (PMMA) (323.6 and 41.03 μg/g, respectively) compared to polyethylene (PE), PS, PET and PVC (<10 μg/g) (Yang et al., 2019). This enhanced adsorption was attributed to the polar surface functional groups of PA and PMMA. In contrast, greater amounts of strontium (Sr) adsorbed onto PP and PS than PA (52.4, 51.4 and 31.8 μg/g, respectively) (Guo et al., 2020). The extent of adsorption of Cu to UV-aged PA and PMMA was correlated with the change in C=O functional groups (Yang et al., 2019). Similarly, UV-ageing of PET increased the adsorption capacity for Cu from 51.2 to 178.2 μg/g, as well as Zn from 32.7 to 81.5 μg/g (Wang et al., 2020b).

In laboratory studies, it has been demonstrated that water chemistry plays a key role in the adsorption of TEs to plastics. Changing pH alters the adsorption of different TEs, with maximum adsorption generally reached at pH 6–10 for the studied TEs, Cd, Cu, Pb and Zn (Gao et al., 2019; Wang et al., 2019a; Wang et al., 2020b). At lower pH, adsorption was less due to the presence of H^+ ions which may outcompete positively charged TEs for binding sites. Conversely at higher pH, TEs begin to form hydroxyl complexes and precipitate, in some cases reducing adsorption (Wang

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Table 1. Trace elements used as additives within plastics products, including the most commonly used compounds and chemical formula

Use	Metal	Compound	Chemical formula	Reference
Antioxidants and UV stabilisers	Ti	Titanium oxide	TiO	(Ambrogi et al., 2017)
	Ni	Nickel chelates		(Ambrogi et al., 2017)
Biocides	Ag, As, Cd, Co, Cu, Mn, Ni, Zn	Inert matrix containing metal ion		(Hahladakis et al., 2018; Prunier et al., 2019)
Catalyst	Sb	Antimony trioxide	Sb_2O_3	(Turner and Filella, 2021)
	Cr	Chromium trioxide	Cr_2O_3	(Prunier et al., 2019)
	Ti	Titanium chloride	$TiCl_4$/$TiCl_3$ (with $MgCl_2$)	(Prunier et al., 2019)
	Co	Cobalt diacetate	$Co(CH_3CO_2)_2$	(Hawkins, 2001)
	Ge	Germanium dioxide	GeO_2	(Rosenberg, 2008)
	Sn	Tin octanoate	$C_{16}H_{30}O_4Sn$	(Masutani and Kimura, 2014)
Filler	Ba	Barium sulfate	$BaSO_4$	(Prunier et al., 2019; Turner and Filella, 2021)
	Ca	Calcium carbonate	$CaCO_4$	(Turner and Filella, 2021)
	Mg	Talc	$Mg_3Si_4O_{10}(OH)_2$	(Turner and Filella, 2021)
	Zn	Zinc oxide	ZnO	(Prunier et al., 2019)
Flame retardants	Br, Cl, F, I	Halogen based		(Ambrogi et al., 2017)
	Al	Metal hydrates	$Al(OH)_3$	(Ambrogi et al., 2017; Hahladakis et al., 2018)
	Mg	Metal hydrates		(Ambrogi et al., 2017)
	Sb	Antimony trioxide	Sb_2O_3	(Filella and Turner, 2018)
Heat stabilisers	Sn	Organotin		(Ambrogi et al., 2017)
	Ba, Ca, Cd, Pb, Zn	Metallic salts		(Ambrogi et al., 2017; Turner and Filella, 2021)
Pigments	Ce, Cs, Cr, Cu, Fe, Hg, Mo, Pb, Sb, Se, Ti, Zn	Various inorganic compounds		(Berte, 2001; Charvat, 2003; Ambrogi et al., 2017; Filella and Turner, 2018; Filella et al., 2020; Catrouillet et al., 2021; Pfaff, 2021, 2022; Turner and Filella, 2021)

et al., 2020b). Changes in salinity and ionic strength can alter the adsorption of metal ions to plastics (Wang et al., 2019a). Adsorption of Cd to high-density polyethylene (HDPE) was reduced from approximately 68 μg/g to 11 μg/g by the addition of 1 mg/L sodium chloride (NaCl) due to Na outcompeting Cd for binding sites on the surface and Cl complexing with Cd (Wang et al., 2019a). This increased ionic strength of high saline conditions also compresses the electrical double layer surrounding plastic particles, lowering repulsive forces and increasing aggregation of plastics, leading to a decrease in surface area and hence adsorption capacity (Alimi et al., 2018). While increased dissolved organic matter (DOM) concentration in solution increased the sorption of Ag to PS MPs, the increased sorption was attributed to greater adsorption of silver (Ag) to DOM bound to PS MPs (Abdolahpur Monikh et al., 2020).

The presence of additives within the polymer may also play a role in the adsorption of TEs. For example, adding the flame retardant hexabromocyclododecane to virgin PS increased the adsorption of Cu, nickel (Ni) and Zn (Lin et al., 2022). The enhanced adsorption was attributed to the polar bromine groups within the flame retardant. No other studies considering the effects of additives on TE adsorption were able to be found.

The ambient temperature may determine the extent of adsorption of TEs to plastics as TE adsorption is endothermic (Liu et al., 2021). In a laboratory study, increasing the temperature from 288 K to 318 K increased the adsorption of Zn from 74.8 to 153.7 μg/g and Cu from 119.4 to 268.4 μg/g onto PET (Wang et al., 2020b). Similarly, increasing the temperature was also reported to increase the adsorption of Pb and aluminium (Al) onto PET, PA and ethylene vinyl acetate (EVA), albeit to a lesser extent (Öz et al., 2019). In agreement with the laboratory studies, a marine field-based study off the coast of China related the higher concentration of Cd and arsenic (As) adsorbed at one of the three sites to the higher temperatures (Gao et al., 2019).

The study by Gao et al. (2019) is currently the only published field study measuring the accumulation of TEs onto plastics. Peak concentrations for As, Cd, Cr, Cu, manganese (Mn), Pb and Zn were 0.037, 0.023, 0.084, 0.223, 31.3, 0.441 and 0.014 μg/g, respectively, over 9 months. Chromium and Pb had the greatest adsorption to both plastics, peaking at 3 months and plateauing thereafter. The concentration of TEs adsorbed changed with respect to changing concentration in the surrounding water, showing a dynamic equilibrium between the two. Exceptions were Cu and Mn accumulation, having no correlation to the surrounding water concentrations.

Trace element concentrations of environmental plastics

The concentrations of TEs associated with environmental plastics for a range of environmental compartments from multiple studies are summarised in Table 2. Factors identified as influencing the sorption of TEs to environmental plastics include polymer type, population density, nearby land uses and ambient TE concentrations (Ashton et al., 2010; Yang et al., 2019; Carbery et al., 2020).

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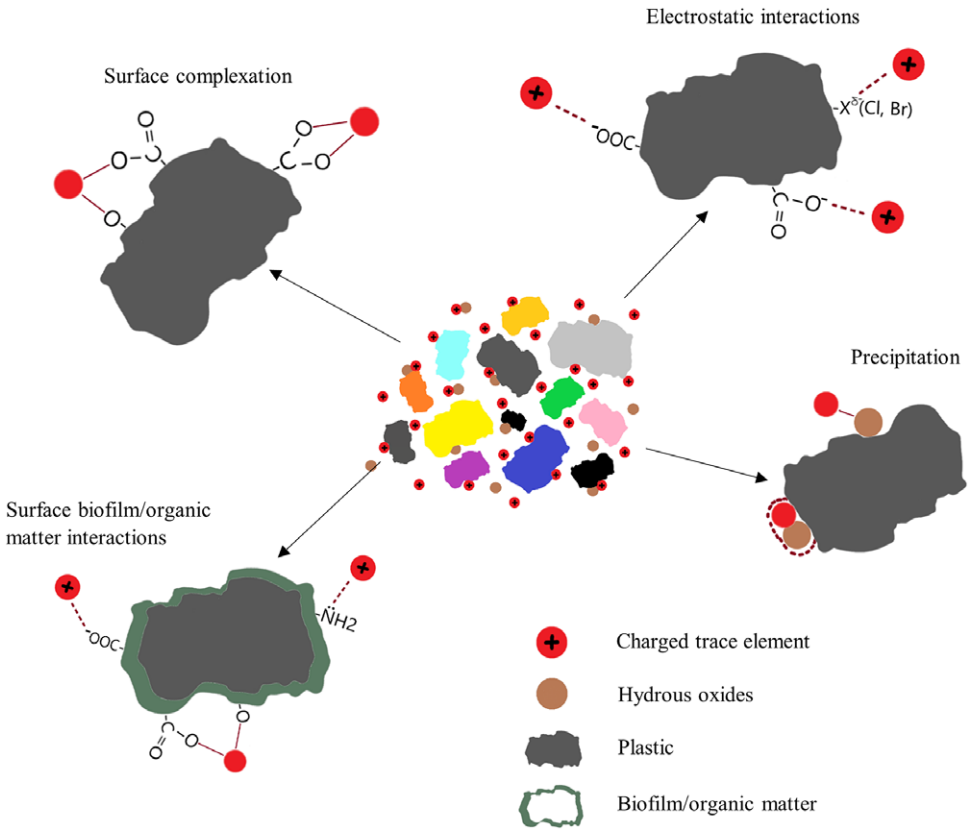

Figure 1. Interactions of trace elements with surface functional groups and charged regions of plastics in the environment. Adapted from Cao et al. (2021).

Colour was reported multiple times to be the source of high concentrations of many TEs (Cd, Cr, Cu, molybdenum [Mo], Pb, Sb and selenium [Se]) due to the presence of TE-based pigments inherent in the polymer (Filella and Turner, 2018; Fernandes et al., 2020; Catrouillet et al., 2021). A key finding is that the concentrations of TEs acquired from the environment are, in most cases, orders of magnitude lower than those that are inherently present. For example, barium (Ba), Cd, Cr, mercury (Hg), Pb, Sb and Zn are common additives to plastics. The maximum concentrations (μg/g) for acquired and inherent TEs, respectively, were Ba (59 and 143,000), Cd (11 and 6,760), Cr (14.2 and 77,100), Hg (0.1 and 810), Pb (151 and 23,500), Sb (0.5 and 27,100) and Zn (288 and 26,700). The orders of magnitude differences between adsorbed and inherent TE concentrations (Table 2) highlight that intentionally added TEs present a greater threat to the environment. Concentrations of TEs adsorbed on environmental plastics are lower than laboratory-based studies, indicating the adsorption capacities of plastics demonstrated in the laboratory are not environmentally relevant.

Release of plastic-associated trace elements

Trace elements can be released from plastics due to changes to either plastic properties (weathering and fragmentation) or environmental conditions (UV exposure, temperature, pH, salinity, and ionic strength). The extent of desorption will depend on the source of the TE (acquired vs inherent) as well as the environmental setting. As the concentrations of some TEs (Cd, Cr, Hg, Mn, Pb, Sb, Se and Zn) inherent within plastics can be elevated, these TEs will diffuse from the plastic into the surrounding environment due to the concentration gradient (Bridson et al., 2021). For example, inherent Cu, Mn, Ni, Pb and Zn were released from virgin PVC incubated in alkaline paddy soils (Meng et al., 2021) and Sb is leached from PET bottles into bottled water (Westerhoff et al., 2008).

The extent of environmental weathering will determine the proportion of inherent TEs released, as weathering exposes more of the interior of the plastic. For example, the release of a Cd-containing pigment was greater from acrylonitrile butadiene styrene (ABS) particles that were mechanically abraded (0.64 μg/mL) compared to new particles (0.112 μg/mL) (Fowles, 1977). Correspondingly more adsorbed Zn was released from aged low-density polyethylene (LDPE) (71.9%) compared to unaged LDPE (10.8%) into an artificial stormwater solution (Aghilinasrollahabadi et al., 2021).

UV exposure will also alter the proportion of inherent TEs released, especially for photosensitive compounds such as cadmium sulfide (CdS) and cadmium selenide (CdSe) (Halpin and Carroll, 1974), two commonly used pigments. UV irradiation of ABS increased Cd release from 0.332–2.26 to 5.6–17.6 μg/mL (Fowles, 1977). Similarly, 6 hours of UV exposure resulted in four to five times greater release of Sb from PET bottles compared to bottles with no UV exposure (Westerhoff et al., 2008). This enhanced release of Sb was attributed to the oxidation of the catalyst residue in PET, Sb_2O_3 (oxidation state Sb(III)), likely to $Sb(OH)_6^-$ (oxidation state Sb(V)), thus increasing its solubility (Hu et al., 2014). Increased temperature can also enhance the release of TEs. For example, higher concentrations of Sb were released from PET at 80 °C (7.8–9.7 ppb) compared to 22 °C (0.5–0.64 ppb) (Westerhoff et al., 2008) as well as greater release of Cd at 37.5 °C (0.332–0.64 μg/mL) compared to 19 °C (0.124–0.22 μg/mL) (Fowles, 1977).

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Table 2. Comparison of trace elements acquired from the environment and total (acquired and inherent) for plastics collected from different environments

		Trace element concentration environmentally acquired (ppm)										Total trace element concentration, acquired and inherent (ppm)							
	As	–	0.05–1.53	–	–	–	–	–	0.08–0.11	2.55	1.7–26.4	–	3.08–6.92	–	4–21	–	<LOD-0.1856	–	–
Trace Element	Ba	–	2.42–59.08	–	–	–	–	–	–	–	–	–	–	–	236–143000	–	–	0.4–1.8	20–42.7
	Cd	0.6	<LOD-11.46	10.15–54.3		0.002–0.01	0.0013–0.00544	<LOD-0.492	0.04–0.16	8.43	23–6760	–	3.4–8.2	0.003–4285	117–4640	25–147	0.0077–0.5083	0.1–0.2	0.2–815
	Co	–	–	–	–	0.025–0.101		<LOD-0.787	–	3.82	–	–	0.09–0.11	0.002–0.1	–	–	–	0.01–0.1	0.5–2.7
	Cr	14.2	<LOD-2.77	–	–	0.019–0.151	0.03–0.74	<LOD-7.97	0.07–0.1	67.56	17–77100	–	1.9–2.5	0.3–2541	21–1240	2.7–46	–	0.2–0.8	5.7–94.1
	Cu	13.7	0.09–142.66	24	0.1–1	0.06–0.61	0.08–0.61	<LOD-7.73	0.07–0.11	28.13	–	0.012–0.365	0.22–0.24	0.1–31.9	9.9–718	7.9–123	1.0692–4.0634	0.7–11.7	16.6–111
	Hg	0.1	–	0.007–0.015	–	–	–	–	–	–	3.3–810	–	–	–	54–273	–	0.0001–0.0008	–	–
	Mn	14.5	0.02–174.84	–	<LOD-9	1.28–8.31	0.19–8.25	0.075–308	0.11–1.77	–	–	–	4.1–4.7		–	–	–	0.1–3.9	42.5–437
	Mo	–	–	–	–	0.007–0.015	–	–	–	–	–	–	<LOD-0.5	0.001–2.1	–	–	–	0.3–0.4	1–1.4
	Ni	–		–	–	–	0.04–0.27	<LOD-0.562	0.04–0.09	23.52	–	–	0.29–0.33	0.05–23	17–555	8.4–173	<LOD-0.0952	1.2–1.3	6.2–14.9
	Pb	13.1	0.01–18.37	10.3–151.3	–	0.15–1.08	0.04–0.85	<LOD-10.3	0.15–0.85	34.23	5.9–23500	0.152–2218	3.3–5.3	0.01–8314	6.3–17500	3.4–47	0.0313–1.4048	0.2–1.2	5.4–418
	Sb	0.5	–	–	–	0.006–0.017	–	–	–	18.43	33.1–27100	–	–	0.0001–240.3	154–12600	31–243	–	0.1	0.3–27.5
	Se	–	<LOD-0.031	–	–	–	–	–	0.07–0.1	1.3	156–1670	–	–	–	214–563	–	–	0.1–0.2	0.1–3.2
	Sn	–	–	–	–	0.018–0.114	–	–	–	10.21	–	–	–	–	34–2090	–	–	0.1–1.4	0.5–0.6
	Zn	–	0.23–95.2	0.55–0.657	0.3–8	0.42–2.34	0.6–3.61	<LOD-288	0.07–0.1	94.63	–	–	5.2–10.6	1.2–327.8	5.1–26700	6.4–36	1.66–4.28	9.6–322	107–540
Environment type		Terrestrial	Marine	Marine	Marine	Marine	Marine	Marine	Marine	Terrestrial	Freshwater	Freshwater	Marine	Marine	Marine	Marine	Marine	Freshwater	Freshwater
Sampling Location		China	Australia	Vancouver	Brazil	England	Croatia	England	Nigeria	Germany	Lake Geneva	Malaysia	Northeast Atlantic	North Atlantic gyre	England	England	Malaysia	Italy	Italy
Sample Type		MPs	Debris	Debris	Pellets	Pellets	Pellets	Pellets	Debris	Plastic >5 mm	Debris	MPs	Debris	Debris	Debris	Debris	Plastics <10 mm	Pellets	MPs
Study		(Zhou et al., 2019)	(Carbery et al., 2020)	(Fernandes et al., 2020)	(Vedolin et al., 2018)	(Ashton et al., 2010)	(Maršić-Lučić et al., 2018)	(Holmes et al., 2012)	(Fred-Ahmadu et al., 2022)	(Weber et al., 2022)	(Filella and Turner, 2018)	(Purwiyanto et al., 2020)	(Martins et al., 2020)	(Prunier et al., 2019)	(Turner, 2016)	(Turner and Solman, 2016)	(Noik et al., 2015)	(Campanale et al., 2022)	(Campanale et al., 2022)

In addition to solution pH having a key role in the adsorption of TEs, it also determines the extent of release of TEs from plastics. At low pH values, H^+ ions exchange with TEs already adsorbed to the plastic, and at high pH, TEs can form insoluble hydroxides. Similar competition between ions for binding sites is observed with increased salinity, mainly increased NaCl concentrations (Holmes et al., 2014; Wang et al., 2019a). The smaller hydrated ion radius of Na^+ results in the exchange with many TEs adsorbed to plastics, such as Cd (Nightingale, 1959; Wang et al., 2019a). The formation of Cl complexes with inherent TEs can also result in the release of TEs in saline conditions.

Ingestion of plastics by organisms can result in a greater and more rapid release of TEs and release TEs that may otherwise not be released due to extreme gut conditions such as lower pH and increased surface area resulting from chewing or grinding. The elevated concentrations of inherent TEs may also result in acute exposures (Jones and Turner, 2010; Holmes et al., 2020; Smith and Turner, 2020). Simulated gastric fluids of marine seabirds have been demonstrated to release significant proportions of TEs from <1–78% of Cd, cobalt (Co), Cr, iron (Fe), Mn, Pb and Sb (Turner and Lau, 2016; Shaw and Turner, 2019; Holmes et al., 2020; Smith and Turner, 2020; Turner et al., 2020). These studies had incubation times from 120 to 220 hours; however, a large proportion of each TE was released rapidly followed by a gradual release to steady-state. Release of Pb was the most rapid, reaching a steady-state within the first time point (0.25 hours) (Holmes et al., 2020). Similarly, Cd (0.009–0.53%), Cu (14–19%) and Zn (14–16%) were released from plastics into simulated gastric fluids of marine invertebrates over a 5- to 6-hour period (Jones and Turner, 2010; Martin and Turner, 2019). Again, a rapid release of TEs occurred, with steady-state reached within 30 minutes in some cases, with the exclusion of the continual release of Cu over the 5-hour period (Jones and Turner, 2010). In addition to organisms ingesting plastic and associated TEs in a single region, they can also be transported long distances by organisms. For example, shearwaters (family Procellariidae) can travel over 1,700 km to forage for food for their chicks, and frequently consume plastic (Skira, 1986). This foraging behaviour can result in the translocation of plastics and associated TEs between significantly different ambient environmental contamination levels circumventing gradual loss across gradients. Consequently, this may result in food contaminated with high TE loading relative to the local environment being fed to their young in addition to uptake into the foraging adult. Further research on the bioavailability of plastic-associated TEs to organisms is needed. The majority of studies to date have used simple gastric simulants. The more complex nature of digestive tracts also needs to be considered including short-term release due to regurgitation, release into other parts of the digestive tract and more studies on the complex nature of seabird guts, including high lipid contents (Smith and Turner, 2020).

Impacts of plastics and trace elements

Understanding the potential impacts of plastic-associated TEs is critical for determining the threat plastic pollution pose to ecosystems. There is however a significant knowledge gap in this area. Studies examining the impacts of plastic and TEs have, to date, focused on the determination of the interactions between plastics and TEs through co-exposure experiments (plastics and TEs added together as separate contaminants) rather than using plastics with bound TEs (either acquired or inherent). Such experiments do not accurately represent real-life exposure conditions resulting from plastic pollution. No synergistic negative effects were reported for the majority of these studies (Oliveira et al., 2018; Fu et al., 2019; Wang et al., 2019b; Lian et al., 2020; Sıkdokur et al., 2020; Zhang et al., 2020b; Cheng et al., 2021; Dong et al., 2021; Yang et al., 2022). However, some did see significant reduction in plant root mass, decreased growth and increased TE accumulation in tissues, bioavailability and mortality rate (Lu et al., 2018; Abbasi et al., 2020; Dong et al., 2020; Tunali et al., 2020; Zhou et al., 2020; Wang et al., 2020a; Li et al., 2021). The key difference between the majority of studies reporting impacts and those that reported no effect was the choice of polymer. Most studies reporting reduced or no adverse toxicological effects used polymers with active surface functional groups (PS, PET and PVC). On mixing, the TEs may have adsorbed to the plastics, potentially reducing their bioavailability and consequently the toxicological effect of the TEs themselves (Dong et al., 2021). This is not environmentally relevant as the surface functional groups of plastics will become fully saturated soon after entering the environment (Guo et al., 2020). Therefore, the presence of plastics would not decrease the exposure of TEs to organisms as suggested in the cited studies as the majority of TEs will likely remain waterborne. In contrast, toxic effects of TEs were more frequently reported for studies using PE, which has a low level of surface functional groups. In addition, the above studies also do not take into account TEs that are possibly inherent within the virgin plastic used which could be causing effects as well.

There is a significant lack of data on the impacts of plastic-associated TEs on organisms. To date, only two studies on the impacts due to plastic-associated TEs have been published (Wang et al., 2020c). Polyethylene MPs with sorbed Cd were more toxic to water fleas (*Moina monogolica)* in comparison to virgin PE-MPs. Exposure of virgin PVC to zebrafish (*Danio rerio)* resulted in increased metallothionen levels, a metal-binding protein, due to the release of inherent Pb (Boyle et al., 2020). The paucity of data on the toxicity of plastic-associated TEs is a critical data gap as inherent TEs can be present at elevated concentrations.

The environmental impacts of TEs adsorbed to plastics are likely to be lower than for inherent TEs. When considering the impacts of adsorbed TEs on the environment it could be assumed that they have comparable impacts to TEs sorbed to natural organic matter as natural organic matter and plastics have similar environmental cycling and fate. The higher concentrations of inherent TEs are of greater environmental concern. These TEs are released over time and in some cases rapidly. Environmental conditions that can change rapidly leading to greater release include pH, ionic strength, redox potential, UV exposure and salinity. Settings where these rapid changes can happen include plastic release from sediment to water, transport from freshwater to saltwater, rapid biofilm removal, discharges from WWTPs and landfills, and ingestion. Ingestion should also be highlighted as a significant source of high TE exposure as organisms may incorrectly select plastic as food based on colour (Okamoto et al., 2022) and high inherent TE concentrations are frequently due to their use as pigments. Conversely, environments where these conditions are more stable, such as sediments and groundwater, will slow down the release of TEs, resulting in lesser impacts.

New routes by which organisms are exposed to plastic-associated TEs are of further concern. This includes the above ingestion pathway, but also from direct chemical transfer to organisms without the protection of an exoskeleton that uses environmental plastics for shelter, for nest building or as a surface to live on (Reynolds et al., 2019). Even if the TE exposure is low relative to

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other pathways, it is an additional exposure route that would not occur in the absence of plastic and the TEs that they contain.

More environmentally relevant studies are required to address the significant knowledge gaps that exist. This includes the departure from the use of virgin plastics with no adsorbed TEs and unknown inherent TEs, to the use of plastics containing known levels of inherent or acquired TEs under ecologically relevant conditions.

Conclusions

Trace elements that are deliberately added or inherent within plastics are present at much higher concentrations than those acquired in the environment and may therefore have a greater impact on organisms and the environment due to continuous release over time. Factors that determine the extent of TE release include the source of TEs, properties of the associated plastic, the extent of weathering and environmental conditions such as pH and redox potential. Key knowledge gaps identified by this review include the significance of the release of inherent TEs from plastics into environmental matrices over long periods of time, how rapid changes in conditions may cause localised TE hotspots, determining the bioavailable portion of released TEs into marine organisms, determining if plastics provide previously unrecognised exposure pathways to organisms, including direct chemical transfer to organisms in contact with plastics and associated TEs, and lastly determining the impacts of inherent TEs and environmentally acquired TEs towards organisms. As plastics are now considered to be ubiquitous environmental contaminants, further research on the environmental impacts of plastic-associated TEs is urgently needed.

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