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Abstract

Historically, many additives and catalysts used in plastics were based on compounds of toxic metals (and metalloids), like arsenic, cadmium, chromium(VI) and lead. Despite subsequent restrictions, hazardous additives remain in plastics in societal circulation because of the pervasiveness of many products and the more general contamination of recycled goods. However, little is understood about their presence and impacts in the environment, with most studies focusing on the role of plastics in acquiring metals from their surrounding through, for example, adsorption. Accordingly, this paper provides a review of the uses of hazardous, metal-based additives in plastics, the relevant European regulations that have been introduced to restrict or prohibit usage in various sectors, and the likely environmental impacts of hazardous additives once plastics are lost in nature. Examination of the literature reveals widespread occurrence of hazardous metals in environmental plastics, with impacts ranging from contamination of the waste stream to increasing the density and settling rates of material in aquatic systems. A potential concern from an ecotoxicological perspective is the diffusion of metals from the matrix of micro- and nanoplastics under certain physico-chemical conditions, and especially favorable here are the acidic environments encountered in the digestive tract of many animals (birds, fish, mammals) that inadvertently consume plastics. For instance, in vitro studies have shown that the mobilization of Cd and Pb from historical microplastics can greatly exceed concentrations deemed to be safe according to migration limits specified by the current European Toy Safety Directive (17 mg kg^{-1} and 23 mg kg^{-1}, respectively). When compared with concentrations of metals typically adsorbed to plastics from the environment, the risks from pervasive, historical additives are far more significant.

Keywords: plastics; hazardous additives; metals; regulations; recycling; environmental impacts

1. Introduction

Plastics contain not only polymers or copolymers but chemicals that have been deliberately added for some functionality or that remain as residues or contaminants from the manufacturing process. Functional additives are many and varied include plasticizers, stabilizers, pigments for color, fillers and extenders, flame retardants, blowing agents, antioxidants, impact modifiers, lubricants and antimicrobial agents, while residues include monomers, intermediates and catalysts arising from polymerization and legacy contaminants introduced through material recycling (Murphy, 2001; Hahladakis et al., 2018).

From an environmental perspective, the focus of much recent research has been on the impacts resulting from the mobilization of potentially harmful additives and residues into aqueous media and their subsequent propensity for bioaccumulation. However, the emphasis has been on endocrine-disrupting organic compounds, and in particular phthalate-based plasticizers, bisphenol A, alkylphenols and brominated flame retardants (Engler, 2012; Tanaka et al., 2013; Koelmans et al., 2014; Suhrhoff and Scholz-Böttcher, 2016; De Frond et al., 2019; Schmidt et al., 2019). Significantly, in many recent review and perspective articles where additives are generally discussed, there is little or no mention of chemicals in plastics that contain metals or metalloids known to be harmful (Li et al., 2016; Kwon et al., 2017; Gallo et al., 2018; Franzellitti et al., 2019; Fred-Ahmadu et al., 2020a). This is surprising given the well-established and widespread regulations and restrictions in place for such chemicals in plastics but is perhaps attributable to the misconception that plastics are more significant carriers of adsorbed metals than sources of matrix-bound additive metals (Vedolin et al., 2018; Bradney et al., 2019; Wang et al., 2019; Naqash et al., 2020; Zhang and Chen, 2020).

In the present paper, we describe the historical uses of plastic additives based on metals and metalloids (hereafter collectively referred to as metals) that are deemed to be hazardous; that is, those that have been incorporated into regulations on plastics based on their known or suspected toxicities. Accordingly, we also define relevant, current European regulations for hazardous metals in plastics that are in place for consumer and environmental protection, and discuss shortfalls in these regulations and in circular economies that result in the introduction and dispersion of metals into newer products through material recycling. However, the main focus is a critical evaluation of the role of hazardous metal additives on the environmental behavior and impacts of plastics, including microplastics, that are lost in nature. Here, we also compare concentrations of hazardous metals added to plastics with those acquired from the environment, and make recommendations for risk evaluation based on appropriate European regulations involving metal migration. The intention of this review is that future research will focus on metals and plastics that pose the greatest potential

harm rather than generate results that fail to demonstrate environmental or ecotoxicological significance.

2. Metal additives in plastics

Metals may remain in plastics as catalytic or reaction residues, with a well-documented example being catalytic Sb contaminating polyethylene terephthalate (Takahashi et al., 2008; Filella, 2020). The principal primary source of metals in plastics more generally, however, is functional additives. Metal-based additives may be insoluble inorganic compounds, partially soluble organic compounds or organometallic liquids or salts. Inorganic and organometallic compounds have superior heat resistance and weathering properties and are cheaper, but concerns about their impacts on human health and the environment have resulted in a gradual shift towards organic compounds or non-metal-based alternatives in many sectors (Tolinski, 2015). Metal concentrations in the final product depend on the type of polymer, the nature of the additive and the desired effect (e.g. opacity, depth of shade, thickness of article or intended environment of usage) but can often reach values of several percent on a weight basis (with some inorganic compounds contributing up to one half of the final product mass; Hahladakis et al., 2018).

Metal-based additives have a wide range of functions in plastics and may act as, for example, biocides, antimicrobial agents, lubricants and flame retardants. However, their principal uses are as inert fillers, pigments for color and stabilizers (Murphy, 2001; Janssen et al., 2016). Fillers increase the stiffness and hardness of plastic and often reduce the cost of the product as they are generally cheaper than the base polymer. Industrial mineral fillers include barium sulfate (barytes), calcium carbonate (calcite) and hydrated magnesium silicate (talc). Synthetic organic pigments include phthalocyanines, coordination complexes of copper that mimic the structures of porphyrins, while inorganic pigments include a range of compounds but mainly oxides and sulfides. Some inorganic pigments are multifunctional, with ZnO and Sb_2O_3, for example, both acting as white pigments but also serving as a fungicide and flame retardant synergist, respectively.

As heat stabilizers, metal-based compounds have found extensive use in the versatile, and widely used thermoplastic, polyvinyl chloride (PVC). This material decomposes at a temperature lower than its processing temperature and countering thermo-oxidative degradation requires chemicals that can substitute stable groups for labile chlorine atoms in the polymer and react with HCl generated by the degradation process. To this end, the most important stabilizers are metal soaps, including Pb-, Cd-, Ba-, Ca- and Zn-dicarboxylates, and various organotin compounds (Liu et al., 2007).

Additives are normally mixed with the polymer melt as liquids or solids, with the latter incorporated as fine particles of average diameters on the order of a few micrometers or a few hundred nanometers that disperse in the matrix (Murphy, 2001). Particles larger than this may impact on the strength and appearance of the finished product while smaller particles are subject to agglomeration. Particles are generally prepared by precipitation, calcination (if the compound is sufficiently heat-stable) and grinding. In theory, metal compounds added to plastics as particles, and at least those in inorganic form, should not migrate from the matrix and, therefore, pose little risk to the consumer or, under appropriate disposal conditions, the environment. However, empirical studies undertaken in the 1970s demonstrated the release of insoluble cadmium compounds from micronized particles of acrylonitrile butadiene styrene (ABS), a plastic commonly used in toys, under conditions representative of the human digestive system (Fowles et al., 1977). Concerns about the more general migration of metals that are toxic resulted in regulations and voluntary commitments that restricted the use, concentration or mobility of certain metals in consumer and industrial plastics.

3. Current European regulations on the use of metal additives in plastics and definition of hazardous metals

3.1. European regulations

Table 1 lists metals that are used or that have been used as additives in plastics where European regulatory directives are now in place. Note that many of these directives are adopted or form the basis of regulations in the wider international community (ACCC, 2008; Horn, 2016).

The Toy Safety (TS) Directive and its amendments lay down criteria that toys must meet before being marketed in the EU (European Parliament and Council of the EU, 2009; Council of the European Union, 2017). For materials that can be 'scraped off', including plastics, concentration limits on the migration of eighteen species of sixteen metals in 0.07 M HCl at 37 ^{o}C for 2 h are stipulated. In contrast, the Restriction of Hazardous Substances (RoHS) Directive, that includes electronic and electrical plastic housings and insulation (European Parliament and Council, 2003; 2011), and the End-of-Life Vehicles (ELV) Directive, that encompasses plastic components of vehicles (European Parliament and of the Council, 2000; Commission Directive, 2017), set total concentration limits for four metals (1000 mg kg^{-1} for Cr(VI), Hg and Pb, and 100 mg kg^{-1} for Cd). The Packaging and Packaging Waste (PPW) Directive is also restricted to these metals but sets a combined total concentration limit of 100 mg kg^{-1} (European Parliament and Council of the EU, 1994) while the Directive relating to plastics intended to come into contact with foodstuffs (CFS) stipulates different but substantially lower total concentration limits for five metals (Commission Directive, 2002). An

amendment to a Council Directive dealing with the marketing and use of dangerous substances (Council Directive, 1976) now specifically restricts the use of di- and tri-substituted organotin compounds to 1000 mg kg^{-1} by weight of Sn in plastics, and is particularly relevant to PVC (Commission Decision, 2009).

3.2. Voluntary commitments for PVC

Because of the more specific health and sustainability concerns about the production, use and disposal of PVC, regulations for this particular plastic were called for. However, European producers and stake-holders proposed a series of voluntary measures that included phasing out the intentional introduction of Cd- and Pb-based stabilizers in the EU through a series of charters, like "Vinyl 2010". Thus, manufacture of Cd used as a stearate or laurate and combined with a Ba ester was discontinued in the EU-27 in 2007, while Pb compounds, including stearates and basic sulfates, were discontinued in the EU-28 in December 2015 and replaced by safer Ca-based alternatives (VinylPlus, 2014). This approach exemplifies how successful voluntary commitments from industry can be without the usual control enforcement from regulatory authorities (Buekens and Sevenster, 2010).

3.3. Hazardous metal additives in plastics

Also identified in Table 1 are metals in plastics that are considered "hazardous"; that is, metals that are currently included in at least two of the aforementioned directives and are defined in the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) Candidate list of substances of very high concern (SVHC) by the European Chemicals Agency (ECHA). Specific compounds of these metals that have commonly been used in plastics, and in particular in Europe, are defined and characterized in Table 2 along with best estimates of their concentration range in finished products. Note that while most compounds are additives, the list also includes catalysts arising from the manufacturing process that remain in certain plastics.

Organometallic forms of As, Hg and Sn found in plastics include 10,10'-oxybisphenoxarsine, a broad spectrum fungicide and antimicrobial agent used mainly in unplasticized PVC, various phenylmercury compounds used in the production of polyurethane, of which phenylmercury neodecanoate appears to have had the most widespread use in Europe (ECHA, 2010), and dibutyl tins used as stabilizers for PVC when Pb compounds are not suitable or as catalysts in the production of polyurethane. Organic metal compounds (mainly organic acid salts) include the blue pigment, Co(II) diacetate, used for coloring polyethylene terephthalate, and various soaps of Cd used to heat- and light-stabilize PVC. Inorganic compounds include chromium(VI) trioxide, used in the production of polyethylene, various basic salts of Pb used to stabilize and lubricate PVC (note that Pb soaps have had less use in the

European PVC market; ECHA, 2016), and pigments based on compounds of Cd, Hg and Pb (with the latter often employed in combination with Cr(VI)).

Inorganic pigments are centered around the intensely colored, calcined compounds of CdS and $PbCrO_4$. Cadmium sulfide is bright yellow, with excellent thermal stability, light and weather fastness and chemical resistance. Yellow pigments are achieved with solid solutions of CdS and ZnS while oranges and reds are prepared with solid solutions of CdS and CdSe. Although solid solutions of CdS and HgS can also engender a similar color range (Tamaddon and Hogland, 1993), relatively poor light-fastness and heat stability of the latter sulfide has resulted in limited use of this combination in plastics since the 1950s (Rangos, 2004; Filella and Turner, 2018). Lead chromate is also bright yellow and characterized by high fastness and heat stability, and can be mixed with $PbSO_4$ and $PbMoO_4$ (where S and Mo are incorporated into the crystal lattice of the chromate) and, sometimes, PbO, to create a range of colors similar to Cd-based solid solutions. Although chromates are generally applicable in thermoplastics, some polymers require suitable surface treatment of the pigments through, for example, stabilization by silicate or alumina (Ranta-Korpi et al., 2014). Pigments of both Cd and Pb can also be modified or mixed with other pigments to expand the color range to greens and browns.

4. Hazardous metal additives in society and in the environment

4.1. Plastics in societal circulation

In theory, hazardous metal-based additives are no longer intentionally incorporated into contemporary plastics, at least in Europe (Ranta-Korpi et al., 2014). However, recent research suggests that such additives are still illegally employed in certain consumer goods available in the EU (but not necessarily manufactured there) and that historical, industrial plastics containing hazardous metals have been used to manufacture consumer goods with the intention of being environmentally positive (Turner and Filella, 2021). More generally, because of the durability of many plastics, historical products in circulation (like toys) or employed for construction or plumbing (such as PVC window frames and piping) may contain high levels of restricted metals (Turner, 2018b; Turner, 2019; Klöckner et al., 2020; Wagner and Schlummer, 2020). Significantly, Tamaddon and Hogland (1993) suggest that consumer plastics may have lifetimes up to 40 years, a timeframe that significantly predates all regulations given in Table 1. A more recent and detailed product lifetime analysis by Geyer et al. (2017) suggests mean values of 35 years and 20 years for building-construction and industrial-machinery plastics, respectively, with upper estimates exceeding 50 years in both cases.

More broadly, the recycling of plastics, and especially poorly managed or dismantled electronic plastics both within and outside of the EU, has introduced traces of restricted additives into a wider range of contemporary products in both the consumer and industrial sectors (Guzzonato et al., 2017; Turner and Filella, 2017; Eriksen et al., 2018). From a health perspective, this is a particular problem for food-contact plastics or toys designed for young children (Chen et al., 2009; Kuang et al., 2018). Although it has been suggested that plastics known or suspected to contain hazardous additives be recycled into products where human exposure is minimal (e.g. pallets, lumber, refuse facilities, guttering, road signs; Turner, 2018a), identification and sorting of such materials on an industrial scale is not yet feasible.

4.2. Plastics in the environment

In general, the makeup of plastics in the environment reflects that of plastics used by consumers and by industry (neglecting, for now, any chemical modifications incurred by chemical acquisition from the surroundings). However, the plastic stock in the environment is predicted to be more contaminated by restricted additives than the stock in societal circulation, and certainly than in societal plastics manufactured over the past twenty years that reflect the clear decline in the use of hazardous substances (Janssen et al., 2016). This discrepancy may be attributed to a number of factors. Thus, first, plastics have been subject to uncontrolled discharge to the environment since their manufacture began several decades ago, and residence times for terminal or temporary receptors of many products (e.g. sediments and soils) are likely to greatly exceed timeframes of production (Geyer et al., 2017). Second, the historical use of many heavy metal-based additives for thermal and light protection means that such plastics are predicted to be more persistent in the environment relative to plastics that are newer, that contain no additives or that contain additives that degrade. In support of this contention, Prunier et al. (2019) found relatively high concentrations of Ti in plastics sampled from the surface waters of North Atlantic Gyre and proposed that their persistence is related to the UV–absorbing properties of TiO_2. Third, significant point sources of historical and unregulated plastics exist, such as poorly maintained and managed, collapsing coastal landfills (Pope et al., 2012). Fourth, and despite restrictions and regulations in place (see Table 1), many current industrial practices appear to employ plastics that contain hazardous metal-based additives.

These assertions are consistent with high, total or extractable concentrations of restricted metals in many primary objects and secondary fragments of plastic litter on coastal and lacustrine beaches and in freshwater sediment and agricultural fields (Nakashima et al., 2012a; 2012b; Imhof et al., 2016; Turner and Solman, 2016; Turner, 2017; Filella and Turner, 2018, 2021; Munier and Bendell,

2018; Prunier et al., 2019; Santos-Echeandía et al., 2020; Turner et al., 2019). Amongst contaminated litter in these studies are (presumably) historical consumer plastics, including toys, cartridges, bottle tops and compost packaging, fragments of PVC and polyurethane whose origin is usually unknown, and industrial plastics like fragments of fishing line, netting and floats, and polyethylene microbeads ("biobeads"; Turner et al., 2019) used in many modern municipal water treatment plants. Table 3 provides examples of the maximum, total concentrations of Cd and Pb (two of the most widely occurring restricted metals) reported in plastic litter from a range of environments and as determined non-destructively by X-ray fluorescence (XRF) spectrometry or, following sample digestion in nitric acid, by inductively coupled plasma-mass spectrometry. Although the frequency of detection and distribution of concentrations are not always available, the data are entirely consistent with the quantitative information given in Table 2 and serve to illustrate how widespread hazardous additives are in environmental plastics.

Regarding the specific hazardous metals and compounds present in environmental plastics reported in the literature and determined by XRF spectrometry (and exemplified in Figure 1), these are largely in agreement with the information presented in Table 2, but with some significant exceptions and additions. Thus, in many colored objects, Pb is present with Cr and Cd is present alone or with Se or, occasionally, Hg, as inorganic pigments, with Pb and Cd concentrations up to a few thousand mg kg^{-1} and Pb and Cr usually present in a ratio similar to that in $PbCrO_4$ (~ 4:1 on a mass basis) (Turner and Solman, 2016; Filella and Turner, 2018). In PVC, Sn or Cd are sometimes present at concentrations of a few thousand mg kg^{-1} but Pb is more commonly encountered and at concentrations of up to 25,000 mg kg^{-1} and As is rarely detected (Turner and Solman, 2016; Filella and Turner, 2018). Environmental plastics that are colored black can also contain significant quantities of Pb and, less frequently, Cd. Here, their presence results from the inability to sort dark colored polymers by near infra-red technology and the consequent illegal recycling of black electronic plastics into a wide range of consumer and industrial products (Turner, 2018a; Shaw and Turner, 2019).

5. Potential environmental impacts of hazardous metals in plastics

5.1. Material disposal and recycling

Conventional disposal and energy-from-waste practices involving metal-rich products result in the contamination of landfill leachate, fly ash and bottom ash, with consequent constraints on the use or safe disposal of the latter materials (Mangialardi, 2003; Krausova et al., 2016). In this context, the occurrence or importance of hazardous metals in historical or recycled plastic waste has often been overlooked (Ranti-Korpa et al., 2014). Nakamura et al. (1996) estimated the metal content of component materials in the Japanese municipal and commercial waste stream and suggested that

about 0.5% and 2.4% of total cadmium and lead, respectively, were derived from plastics. In contrast, estimates of metals in the more general, contemporary waste stream suggest that plastic is the main material carrier of total cadmium (almost 50%) and a highly significant carrier of total lead (about 17%) (Viczek et al., 2020). Presumably, the increase in hazardous metal contributions from plastics is attributable to the improved regulation and management of low abundant articles of high metal content, like batteries, paints and electronic equipment, coupled with the pervasiveness of many non-recyclable, historical plastic items. To further significantly reduce the metal content of waste would, therefore, require a means of identifying and eliminating plastics containing hazardous additives that can operate on an industrial scale.

5.2. Density modification

Additives based on heavy metals like Cd and Pb can increase the density of plastic by small but significant amounts. This effect has been employed in the recycling industry in order to separate denser and more harmful additive-laden plastics from "cleaner", additive-free materials, and in particular for isolating and eliminating plastics enriched in brominated flame retardants (Retegan et al., 2010; Haarman and Gasser, 2016). For polymers whose inherent density is similar to but lower than that of fresh water or seawater (ρ = 1 to 1.03 g cm^{-3}), like polyethylene or polypropylene (ρ ~ 0.90 to 0.97 g cm^{-3}), a small increase arising from the addition of lead chromate (ρ = 6.12 g cm^{-3}; Table 2), for example, can result in plastic that sinks rather than floats. While this may be inconsequential for products while in use, in the aquatic environment a small increase in density could markedly modify its transport, fate and bioavailability. To this end, it has been proposed that there may be some kind of fractionation (settling versus floating) of polyolefins in the freshwater and marine environments based on their hazardous metal additive content, and that shore-based sampling of stranded, lighter materials may underestimate the environmental stock of metal-rich plastics (Turner and Filella, 2020).

5.3. Metal diffusion from plastics

Because metal additives are generally not chemically bound to polymers, they have the propensity to mobilize from the matrix via diffusion and mass transfer into the surrounding aqueous phase (Wilson et al., 1982; Mercea et al., 2018; Chen et al., 2019; Mao et al., 2020). This effect is often considered in regulations by fixing a maximum concentration of a chemical allowed to be released when empirical tests are applied. These tests are not based on any mechanistic approach but rather employ simplified and standardized extractant solutions that attempt to mimic realistic conditions, such as those encountered in the human digestive environment (European Parliament and Council of the EU, 2009) or in human sweat (OEKO-TEX Association, 2020; Biver et al., 2021), or those that

303 simulate the migration of food during storage or cooking (Conti, 2008; van Putten, 2011; Kao, 2012;
304 Schmid and Welle, 2020).

305 Fluxes of metals in plastics can be theoretically described by Fick's first law provided that diffusion
306 coefficients for the metals and their compounds actually present in the polymers are known
307 (PlasticsEurope, undated; Barnes et al., 2007). Published diffusion coefficients are sparse and often
308 limited to specific problems such as migration into potable water or food (Hampe and Piringer, 1998;
309 Adams et al., 2011; Fang and Vitrac, 2017) but a recent compilation of estimates obtained at or
310 around room temperature and relevant in the context of metal migration from environmental
311 plastics is given by Town et al. (2018). Here, values are 1.5 x 10^{-20} m^2 s^{-1} for Pb acetate in low density
312 polyethylene, about 10^{-15} m^2 s^{-1} for species of dibutyl tin in polypropylene, 1.7 x 10^{-17} to 5 x 10^{-20} m^2 s^{-1} for Cd stearate in PVC, and 6 x 10^{-17} to 4 x 10^{-23} m^2 s^{-1} for Pb stearate and dibasic Pb phosphite in
314 PVC. By comparison, diffusion coefficients for metal ions in aqueous media are on the order of 5 to
315 20 x 10^{-10} m^2 s^{-1}.

316 The rate at which mobilization by molecular diffusion takes place is proportional to the square of the
317 distance to travel. This means that the complete release of metals or metallic compounds from very
318 small particles or thin sheets (of nanometer to micrometer dimensions) is predicted to take place
319 over timescales of hours to days, and nanoplastics exposed to the environment are predicted to be
320 rapidly depleted of metal additives. On the other hand, the complete metal release from larger
321 particles (hundreds of micrometers to millimeter dimensions) is predicted to take years to decades
322 or longer. In practice, however, studies often reveal that metal release from plastics of this size
323 range is significantly more rapid, with rates of mobilization flattening after a period of time (Martin
324 and Turner, 2019; Smith and Turner, 2020; see Figure 2). This suggests that there may be a pulse of
325 initial metal release, possibly due to the presence of a "leachable" layer at the surface of the plastic,
326 followed by much slower diffusion. Such an effect has recently been invoked to explain the nature
327 and kinetics of Sb release from PET bottles (Filella, 2020).

328 *5.4. Mobilization of metals from plastics in the environment*

329 The rate of metal mobilization from plastic will increase if conditions favor the dissociation of metal
330 compounds in the matrix or alter the speciation in the aqueous phase and maintain or enhance the
331 concentration gradient of the diffusing metal species. Such conditions include a reduction in pH and
332 the introduction of complexants to the aqueous phase, and may be particularly significant in the
333 extracellular (e.g. stomach) or intracellular (e.g. lysosomes) digestive environments of many
334 organisms (Zhong et al., 2006; Smith and Turner, 2020). Some hazardous additives, including
335 cadmium sulfoselenide pigments, are also photoactive and undergo more ready dissociation and

diffusion when exposed to visible and ultraviolet light compared with dark conditions (Fowles et al., 1977; Liu et al., 2017). Consequently, a clear increase in Cd mobilization from microplastics is observed when aqueous suspensions are irradiated by artificial sunlight (Liu et al., 2020). Organotin compounds in PVC exhibit both greater mobilization and photodegradation under visible and ultraviolet light but increasing salinity appears to inhibit these effects (Chen et al., 2019).

More generally, metal mobilization is expected to increase when the plastic is weathered or degraded in the environment, presumably because of the associated increase in porosity and surface area of the aged matrix (Zhang et al., 2018). Experiments performed by Nakashima et al. (2016) on newly purchased PVC fishing floats containing Pb stearate as a stabilizer have provided mechanistic and quantitative insights into the effect of surface damage on metal mobilization into pure water. Thus, release is initially rapid, and in particular during the first 24 h, because of diffusion from the surface layer whose thickness is about 1 μm. This is, presumably, equivalent to the leachable layer referred to above and accounts for about 0.1% of total Pb. Thereafter, mobilization tails off as this layer becomes depleted of Pb but is accelerated when the plastic surface is scarified by sandpaper, simulating erosion when beached, for example, and exposes areas of a new leachable layer.

Figure 2 shows results of timed experiments in which two micronized plastics (PVC piping and polycarbonate-ABS reconstituted from electronic waste and containing added Pb and contaminating Cd, respectively) were exposed to conditions designed to replicate the residence time and chemistries of the digestive system of a seabird (Smith and Turner, 2020). Note the relatively rapid release of metals in the early stages of the experiments, consistent with the initial pulse and leachable layer described above. Exposure to neutral saline solution (0.1 mol L^{-1} NaCl) at 40°C results in limited but not insignificant mobilization of Pb and Cd; specifically, the percentage of Pb mobilized from PVC is similar to that reported in pure water by Nakashima et al. (2016). The dissolution of compounded inorganic additives is dramatically increased by reducing the pH of the solution to 2.5 (and in the presence of the digestive enzyme, pepsin), and the further addition of menhaden fish oil, mimicking the presence of a dietary component, increases the dissolution of Pb but decreases the release of Cd, presumably by affecting the integrity of the polymer or acting to block diffusing species, respectively. At the end of the exposures, the maximum Pb and Cd concentrations mobilized were about 1800 mg kg^{-1} and 20 mg kg^{-1}, respectively. Relative to total metal concentrations in the plastics (and as annotated), this represents respective bioaccessibilities of about 9% and over 60%. Clearly, therefore, significant quantities of hazardous metals have the potential to be mobilized from historical and recycled plastics under certain environmental or physiological conditions, and in particular those representative of the acidic digestive system of birds, mammals and fish.

Bioaccessibility is not necessarily equivalent to bioavailability and by itself does not provide evidence that metallic additives in plastics exert toxicity. However, the adverse impacts of certain metals (including Pb and Sn) in PVC on aquatic life have been demonstrated empirically, albeit at environmentally unrealistic plastic concentrations. Thus, Lithner et al. (2012) attributed the leaching of metals (including Sn) from PVC products exposed to deionized water for three days at 50 ^{o}C to be responsible for toxicity to *Daphnia magna*. More recently, Boyle et al. (2020) found that exposure of up to 500 mg L^{-1} of PVC particles (mean diameter = 150 μm) to the larvae of zebrafish (*Danio rerio*) increased expression of metallothionein 2, a metal-binding protein, but no expression changes were observed in biomarkers of estrogenic or organic contaminants. Subsequent leachate analysis revealed that Pb mobilized from the plastic was responsible and that aqueous concentrations reached over 80 μg L^{-1} over a 24 h period.

5.5. Hazardous metals added during manufacture versus accumulated from the environment

Much recent research into or mention of metals and microplastics in the environment refers to material acting as a vector for the transport and bioaccumulation of ions or complexes acquired from the surrounding environment (Vedolin et al., 2018; Bradney et al., 2019; Li et al., 2020; Ta and Babel, 2020; Purwiyanto et al., 2020; Yu et al., 2020). A compilation of concentrations of acid-extractable Cd and Pb associated with various plastics retrieved directly from aquatic settings (as opposed to being exposed to metals under controlled laboratory conditions) is given in Table 4. Note that direct comparisons are hampered by the use of different extractants by the various authors (no standard protocol exists in the literature; Hildebrand et al., 2020) and that in many cases the metals are likely adsorbed onto or co-precipitated with iron oxy(hydroxides) and organic precipitates and associated with surface-bound detritus rather than being directly adsorbed to the plastic itself. Nevertheless, it is clear that these concentrations are orders of magnitude lower than measured or indicative Cd- and Pb-based additive contents in historical or recycled plastics (Tables 2 and 3) and the concentrations of these additives that are potentially mobile (Figure 2). Significantly, and unlike the case for added metals (e.g. Boyle et al., 2020), there is no evidence that adsorbed metals exert any adverse effects on wildlife at concentrations encountered in the environment.

6. Application of regulations to hazardous metals in environmental plastics

The directives described in Table 1 that apply to new or newly recycled products are now well-recognized and widely enforced in the EU. However, the period between production-use and disposal or loss of consumer plastics means that many historical or recycled plastics in the environment are non-compliant with respect to current standards or regulatory limits. More generally, there appear to be important loopholes that enable plastics defined as hazardous in one

sector to be recycled into new (compliant or otherwise) goods in another sector that evade regulation or where regulation is less clear. For instance, electrical and electronic plastic containing concentrations of Cd and Pb in excess of the respective RoHS limits of 100 mg kg^{-1} and 1000 mg kg^{-1} appears to be recycled widely into consumer goods (Turner, 2018a; Turner and Filella, 2021) and into industrial plastics that are used in water treatment (Turner et al., 2019).

In order to evaluate the risk of such plastics, the accumulation and ecotoxicological implications of metals need to be addressed through studies of bioavailability (or at least bioaccessibility). Chemical bioavailability is a critical component of the TS Directive, with limits stipulated for various metals that are extractable from articles (including plastic toys) under chemical and physiological conditions representative of an infant's stomach; namely, 100 mg of material of < 6 mm in diameter in 5 mL of 0.07 M HCl for 2 h at 37°C and in the dark (British Standard, 1995). Threshold limits are based on the assumption of ingestion of 8 mg material per day and are shown in Table 1.

Rochman et al. (2013) argued for environmental plastics to be classified as hazardous based on more general physical and chemical characteristics but here we propose that more objective and quantitative criteria are available that relate metal concentrations to existing or modified regulations. For example, the northern fulmar (*Fulmarus glacialis*), an indicator species of plastic pollution according to the Oslo-Paris Convention for the North-East Atlantic (OSPAR, 2008), ingests plastics of size comparable to that stipulated by the TS Directive (Van Frankener et al., 2011) and has a digestive chemistry and physiology that is broadly similar to that of the human stomach (Hilton et al., 2020). Critically, however, non-food items can remain trapped in the proventriculus-gizzard for weeks to months as they are ground down to a size small enough to transit into the gut (Avery-Gomm et al., 2012) and the digestive system may contain, additionally, significant quantities of dietary-derived oils (Tanaka et al., 2015). Assuming that the size of plastic particles ingested or ground down in the gizzard are similar to those mechanically micronized as part of British Standard (1995), and assuming that *F. glacialis* ingests an average of 8 mg of plastic per day, one could argue that the current TS Directive limits for metals are applicable for an extended digestive test conducted in the presence of fish oil. The results shown in Figure 2 for acidified saline solution in the presence of fish oil essentially reflect the kinetics of Cd and Pb release from plastics subject to this digestive process. Thus, concentrations of Pb mobilized from PVC in Figure 2 exceed the toy safety limit of 23 mg kg^{-1} by one or two orders of magnitude throughout the time course while the concentration of Cd mobilized from PC-ABS marginally exceeds the limit of 17 mg kg^{-1} at the termination of the experiment.

Although historical or recycled plastics clearly pose a risk to wildlife whose digestive chemistry favors the mobilization of hazardous metals, information on the abundance and availability of contaminated plastics in the environment is also required. To this end, two recent studies have provided a valuable insight into the prevalence of Cd and Pb in beached plastic litter (summarized in Table 4). Thus, first, analysis of polyolefin-based microplastic pellets and fragments (< 5 mm) collected from the strandlines of coastal beaches in southwest England by Massos and Turner (2017) revealed that over 100 out of 924 samples contained total Cd or Pb (or both) above the respective TS Directive limits. Second, analysis of a wider range of plastics collected from the shores of Lake Geneva by Filella and Turner (2018) revealed that over 200 out of 678 plastics contained total Cd or Pb (or both) above the respective limits. It would appear, therefore, that between about 10 and 30% of environmental plastics that are beached are potentially harmful with regard to a modified toy safety test. Concentrations of Cd and Pb reported by Prunier et al. (2019) for a more limited number of meso- and microplastics in the North Atlantic gyre (summarized in Table 4) suggests that a similar degree of "non-compliance" may also exist in the open ocean.

In addition to the abundance of contaminated plastics, exposure and risk may also be modified by the selection or avoidance of plastics based on color that is, for example, similar or dissimilar to natural prey (Ory et al., 2017; Duncan et al., 2019). Specifically, and as discussed above, cadmium sulfide and lead chromate and their derivatives are bright yellow, red or orange, while an array of metals are encountered in recycled electronic plastics that tend to be black (Turner, 2018a; Shaw and Turner, 2019).

7. Conclusions

Hazardous metal additives have served various functions in historical plastics (mainly as pigments for color and stabilizers in PVC) but are now restricted under a number of consumer and sustainability regulations. Despite these regulations and the consequent development of safer alternative additives, however, hazardous metals have become dispersed amongst contemporary consumer goods through material recycling. Moreover, because of the pervasiveness of plastics, poor management and disposal of historical plastics and the apparent recent use of restricted additives in marine and industrial applications, hazardous metals widely contaminate plastics lost in nature. Unfortunately, relatively little attention has been paid to hazardous metals in environmental plastics, with the main focus (and misconception) in this setting related to the importance of relatively low concentrations of metals acquired (e.g. adsorbed) from the surroundings. Concentrations of additive-bound metals that can be mobilized from historical plastics under conditions that simulate the digestive environment can be orders of magnitude higher than metal concentrations adsorbed to plastics. Accordingly, it is proposed that the risks posed by these plastics

468 to wildlife could be evaluated by comparing empirically-derived mobilized concentrations with
469 corresponding migration safety limits defined for hazardous metals in consumer products like toys.

470

471 **Declaration of interest statement**

472 The authors declare that they have no conflicts of interest.

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475 **References**

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804 **Tables**

805

806 Table 1: Metals in plastics that are regulated in Europe and current limit values according to various
807 directives. TS = migration limits in 0.07 M HCl specified by the Toy Safety Directive; RoHS, ELV, PPW,
808 CFS and OTC = total concentrations specified by directives relating to the Restriction of Hazardous
809 Substances, End-of-Life Vehicles, Packaging and Packaging Waste, contact with foodstuffs and
810 organotin compounds, respectively; hazardous classification is based on inclusion in at least two
811 directives and defined in REACH as a SVHC.

Metal	TS mg kg^{-1} (0.07M HCl)	RoHS mg kg^{-1} (total)	ELV mg kg^{-1} (total)	PPW mg kg^{-1} (total)	CFS mg kg^{-1} (total)	OTC mg kg^{-1} (total)	hazardous
Al	70,000						
As	47				1		yes
Ba	18,750						
Cd	17	100	100	100[a]			yes
Cr(III)	460						
Cr(IV)	0.2	1000	1000	100[a]	1[b]		yes
Co	130						yes
Cu	7700				5		
Hg	160	1000	1000	100[a]			yes
Mn	15,400						
Ni	930						
Pb	23	1000	1000	100[a]	2		yes
Sb	560						
Se	460						
Sn	180,000						
Sn (organic)	12					1000	yes
Sr	56,000						
Zn	46,000				100		

812

813 [a]The combined limit for all four metals is 100 mg kg^{-1}.

814 [b]The oxidation state of Cr is not specified but assumed to be VI.

815

816

Table 2: Examples of hazardous metal-based compounds that have been commonly employed in plastics, and in particular in Europe, along with their physico-chemical properties; nd = no data found. Sources of information: ChemicalBook CAS DataBase; ECHA (2009; 2010; 2011; 2012; 2016; 2017); Filella and Turner (2018); Hansen et al. (2013); Haynes (2015); Lofrano et al. (2018); Malik and Jain (1969); Piver (1973); Ranta-Korpi et al. (2014); RPA (2005); Zitko, 1999). PE = polyethylene; PET = polyethylene terephthalate; PP = polypropylene; PU = polyurethane; PVC = polyvinyl chloride.

metal	compound	chemical formula	description	molecular mass	aq. solubility @ 20°C, mg L^{-1}	density, g mL^{-1}	plastic types	function	conc. in plastic, mg kg^{-1}
As	10,10'-oxybisphenoxarsine	$C_{24}H_{16}As_2O_3$	organometallic liquid	502.23	5.0	1.40-1.42	PVC	bacterioside/fungicide	300-500
Cd	cadmium sulphide	CdS	inorganic solid	144.48	1.3	4.83	all	pigment (yellow)	100-25,000
	cadmium selenide	CdSe	inorganic solid	191.38	"insoluble"	5.82	all	pigment (red)	100-25,000
	cadmium stearate	$C_{36}H_{70}CdO_4$	organic acid salt	679.40	"insoluble"	1.28	PVC	stabiliser	1000
	cadmium dodecanoate	$C_{24}H_{46}CdO_4$	organic acid salt	511.04	"insoluble"	nd	PVC	stabiliser	1000
Co	cobalt(II) diacetate	$C_4H_6CoO_4$	organic acid salt	177.02	"readily soluble"	1.71	PET	pigment (blue)	<10,000
Cr(VI)	chromium(VI) trioxide	CrO_3	inorganic solid	99.99	"soluble"	2.70	PE	catalyst	<5
	see also lead chromate								
Hg	phenylmercury compounds	$C_x H_y Hg_2O_4$ or $C_x H_y HgO_2$	organometallic solids	336.75-837.80	0.14-1843	nd	PU	catalyst	1000-3000
	mercury sulphide	HgS	inorganic solid	232.66	"insoluble"	8.10	PE, PP	pigment (red)	<1000
Pb	lead chromate	$PbCrO_4$	inorganic solid	323.19	0.2	6.12	all	pigment (yellow)	<50,000
	lead sulfate	$PbSO_4$	inorganic solid	303.26	44.5	6.29	all	pigment (red)	<50,000
	lead molybdate	$PbMoO_4$	inorganic solid	367.13	0.16	6.92	all	pigment (red)	<50,000
	tetralead trioxide sulfate	$3PbO{\cdot}PbSO_4$	inorganic solid	972.86	"insoluble"	6.40	PVC	stabiliser	25,000
	trilead bis(carbonate) dihydroxide	$Pb_3(CO_3)_2(OH)_2$	inorganic solid	775.90	"insoluble"	6.14	PVC	stabiliser	25,000
	trilead dioxide phosphonate	$PbHPO_3{\cdot}2(PbO)$	inorganic solid	733.58	"insoluble"	6.90	PVC	stabiliser	25,000
Sn	dibutyltin dilaureate	$C_{32}H_{64}O_4Sn$	organometallic liquid	631.56	<1.43	1.07	PVC and PU	stabiliser and catalyst	500-3000
	dibutyltin maleate	$C_{12}H_{20}O_4Sn$	organometallic liquid	346.99	"immiscible"	1.32	PVC	stabiliser	10-10,000

824 Table 3: Maximum concentrations of Cd and Pb reported in plastic litter from various environments,
825 along with the polymer in which maximum concentrations were observed (PE = polyethylene, PP =
826 polypropylene; PVC = polyvinyl chloride).

location	litter type (no. samples)	Cd, mg kg^{-1}	Pb, mg kg^{-1}	polymer	source
Lake Geneva	beached plastic litter (*n* = 670)	6760	23,500	PE, PVC	Filella and Turner (2018)
North Atlantic subtropical Gyre	mesoplastics (*n* = 13)	4280	8310	PE	Prunier et al. (2019)
	microplastics (*n* = 4)	105	112	PE	
NW Europe	water treatment beads (*n* = 537)	312	5380	PE	Turner et al. (2019)
Ookushi beach, Japan	fishing floats (*n* = 17)	nd[a]	21,900[b]	PVC	Nakashami et al. (2012b)
SW England	beached microplastic pellets (*n* = 752)	3390	5330	PP, PE	Massos and Turner (2017)
	beached microplastic fragments (*n* = 172)	2620	4820	PP, PE	

827

828 [a]Not detected

829 [b]Concentration represents the sum of the mean and error provided.

830

831 Table 4: Concentrations of Cd and Pb acquired by various environmental plastics from their

832 surroundings and evaluated by acid extraction.

location	description	measure	Cd, mg kg^{-1}	Pb, mg kg^{-1}	source
Australian coast	beached microplastics	max	0.088	0.50	Carbery et al. (2020)
Azores, N Atlantic	beached microplastics	mean	5.8	4.3	Martins et al. (2020)
Chao Phraya River, Thailand	sediment microplastics	mean		17.6	Ta and Babel (2020)
Chennai coast, India	beached plastics	max		1.85	Suman et al. (2020)
Hong Kong coast	beached microplastics	median	0.04		Li et al. (2020)
Musi River, Indonesia	suspended microplastics	mean		0.47	Purwiyanto et al. (2020)
Nigerian coast	beached microplastics	max	0.10	2.51	Fred-Ahmadu et al. (2020a)
SW English coast	beached pellets	max	0.01	1.08	Ashton et al. (2010)
Vis Island, Croatia	beached pellets	max	0.005	8.5	Jasna et al. (2019)

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836 Figure legends

837

838 Figure 1: Energy-dispersive XRF spectra, as counts per second versus energy in keV, of different
839 environmental plastics (of ~ 2 to 8 cm in length) containing hazardous metal-based additives
840 (unpublished data of the authors derived from direct sample analysis using a Niton XLt3+ portable
841 XRF). (a) An irregular fragment of plastic from a beach in SW England pigmented with Cd_2SSe, (b) a
842 piece of wrapping from agricultural land in central Spain pigmented with $PbCrO_4$, (c) PVC-film from a
843 beach on Lake Geneva with a Sn-based stabilizer and (d) a curved PVC fragment from a beach in Lake
844 Geneva with a Pb-based stabilizer.

845

846 Figure 2: Mobilization of (a) Cd from 100 mg L^{-1} of micronized (< 1 mm in two dimensions) polyvinyl
847 chloride (PVC) and (b) Pb from 100 mg L^{-1} of micronized polycarbonate-acryl nitro butadiene (PC-
848 ABS) into different solutions mimicking the digestive environments of a seabird (replotted from
849 Smith and Turner, 2020). The red dashed lines denote the respective Toy Safety Directive migration
850 limits.

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