

Characterization of Inorganic Additives in and Photochemically Liberated from Consumer Plastics: Implications for Global and Local Biogeochemical Cycles

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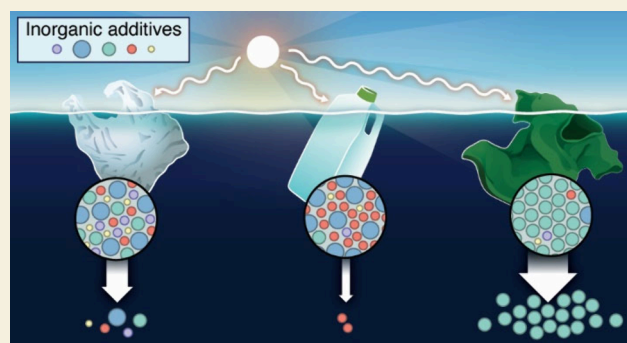


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ABSTRACT: The composition and environmental impacts of inorganic additives in consumer plastics have received little attention within the plastic pollution discipline relative to organic additives. In this work, X-ray fluorescence spectroscopy, loss-on-ignition, and inductively coupled plasma mass spectrometry were used to qualitatively and quantitatively characterize inorganic additives from up to 80 consumer plastic items. On average, consumer plastic goods contained ~8% inorganic additives by mass. Concentrations of each element often varied by orders of magnitude. The most common elements detected were from the alkali metal, alkaline earth metal, and first-row transition metal groups, with Ca, Ti, and Al being most abundant. The diversity and abundance of inorganic additives was notably higher in consumer-grade plastics than in standard plastics routinely used to assess the fate and impacts of plastic pollution. Sunlight exposure readily liberated most elements from consumer plastics, typically in the <10 and <1 μm fractions. However, the relative percent of photochemical liberation varied considerably across element and plastic articles, suggesting that formulation is a key control of their liberation from consumer plastics. Compared to average upper continental crust concentrations, Sb and Zn were most enriched, with median enrichment factors of 2 and 1 orders of magnitude, respectfully. Mass balance calculations indicate that plastic pollution may represent a substantial proportion of natural riverine elemental fluxes, particularly for Sb and Zn, which could reach ~13% and ~4% of the global natural riverine fluxes by 2060, respectively. Localized impacts in many small, highly polluted rivers could be even larger. However, such impacts are highly dependent on the riverine plastic loading rate to the ocean. Overall, these findings highlight the need for increased consideration of inorganic additives when assessing the fate and impacts of consumer plastics leaking into the environment.



KEYWORDS: Plastic Pollution, Consumer Plastics, Inorganic Additives, Aquatic Photochemistry, Trace Metal Biogeochemistry

1. INTRODUCTION

Consumer plastics are complex mixtures with widely varying formulations and subsequent environmental implications.^{1–4} Inorganic additives are prevalent; consumer plastics contain hundreds of inorganic additives, often in large quantities (i.e., up to 50% by mass for some fillers).¹ Their ubiquity results from their high utility, with applications as pigments, flame retardants, and fillers, which cheaply bulk up the material. Many of these additives—particularly photocatalytic ones, such as titanium dioxide (TiO_2)—have gained visibility due to their role in plastic degradation in the environment.^{3,5–7} However, specific consumer plastic formulations are largely unknown and unreported, hindering identification of particularly prevalent and/or impactful inorganic additives.² Furthermore, inorganic additives and their environmental implications have received substantially less attention than

the organic components (i.e., the polymer and organic additives) and even naturally occurring metals sorbed to plastics.^{8–11} As a result, the environmental release and implications of inorganic additives remain largely unknown, limiting our ability to assess and mitigate potentially major components of plastic pollution.

The existing literature suggests that many inorganic additives are released under environmental conditions, even without

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degradation of the surrounding polymer matrix.^{12,13} The migration of potentially toxic additives from plastics used for food and drink packaging and toys is particularly well-documented and regulated in several countries. While most studies have focused on organic additives,^{1,2} antimony (Sb), which is present as a residual catalyst, is well-known to leach from single-use polyethylene(terephthalate) (PET) water bottles.¹⁴ It can also leach from various plastics into seawater, leading to concentration in marine sediments.¹² Photodegradation, which occurs under environmental conditions on relevant time scales (i.e., weeks to months) in a variety of plastic formulations,^{3,7,15,16} can accelerate inorganic additive liberation by inducing additive dissolution¹³ or weakening and degrading away the surrounding polymer matrix.¹⁷ Six studies have examined the influence of sunlight exposure on additive release, consistently showing that sunlight accelerates additive release relative to leaching in the dark.^{13,18–22} While these works represent promising first steps, additional study is necessary to understand the magnitude of this process across consumer plastic formulations and the characteristics and implications of the released additives.

Once released into the environment, inorganic additives may have wide-ranging effects on organisms and ecosystems as well as geochemical processes and cycles. Through the release of other inorganic materials, human activities such as mining, fossil fuel/biomass burning, and construction have disrupted several element cycles²³ and left signals tracing decades of release in river,²⁴ lake,²⁵ and marine sediments.²⁶ Given the massive and growing release of plastic to the environment, which is estimated at ~8 million metric tons in 2010 and expected to quadruple by 2060 under current production and release trends,^{27,28} plastic-derived inputs of inorganic additives may be substantial. Moreover, plastics are not evenly distributed in the environment, with hotspots in rivers near urban centers, especially those with lower waste management capabilities,²⁹ and the subtropical gyres, where ocean currents accumulate plastics at the surface.³⁰ Thus, localized impacts from inorganic additives may be even more pronounced. For example, the amount of zinc (Zn) released from tire wear particles to urban and suburban watersheds in the United States may be more than atmospheric sources.³¹ However, the magnitude and distribution of plastic-derived inputs are largely unknown for most elements and environmental compartments.

In this work, we aimed to determine the prevalence and photochemical release of inorganic additives and the metals comprising them in consumer plastics entering the environment. Using this information, we assessed the implications of inorganic additives within a broader geochemical context, focusing on riverine inputs to the ocean. To do this, we selected nearly 80 plastic items based on their detection frequency in ocean surveys^{32–34} and/or potential for significant incidental release (e.g., tire wear particles)^{31,33,35,36} and analyzed their overall inorganic additive contents. For a subset of these plastics, we measured the major, trace, and rare earth element compositions of the additives. Next, we performed photodegradation experiments to assess the potential environmental release of inorganic additives and the size ranges in which the additives are released. Finally, using elemental abundances in consumer plastic goods, we assessed the potential influence of plastic-derived inputs on riverine element fluxes. Overall, the findings from this study indicate that inorganic additives are essential components of consumer plastics, with a potentially sizable and under-

appreciated influence on the fate and impacts of plastic pollution.

2. METHODS

2.1. Selection of Consumer Plastic Goods for Analysis

Sample selection was based on two main objectives: (1) representativeness of plastics leaked to the ocean based on detection frequency in beach clean-ups and marine litter inventories,^{32–34} production volume,^{32,33,35,37} usage type (e.g., industrial sector, single- or long-term-use),³⁷ and other factors that may suggest leakage into the environment (e.g., shedding of tire rubber or shoe sole)^{31,33,35,36} and (2) representativeness of the diverse array of additive compositions and amounts.¹ Particular attention was also paid to include samples with a wide, representative range of Sb and Zn concentrations, as determined via X-ray fluorescence (XRF) measurements and past measurements of these elements.^{38,39} A variety of common consumer plastic goods ($n = 103$) were purchased and prescreened using XRF (Oxford Instruments X-MET 7500) (Table S1). In some cases, the spatial variability of additive compositions was tested, yielding a data set of 127 XRF spectra (Table S1). From this data set, 77 plastic items were selected for loss on ignition (LOI) measurements based on the criteria described above (Table S2) and, from those, 56 plastic items were selected for inductively coupled plasma mass spectrometry (ICP-MS) analysis (Table S3). Finally, three plastics from the group analyzed via ICP-MS were selected for photochemical additive liberation experiments based on their additive contents, diversity, representativeness of the group as a whole, and likelihood of leakage to the environment.^{31–34}

2.2. Analysis of Consumer Plastic Additive Compositions and Potential Impacts on Environmental Systems

Inorganic additives in plastics were isolated and quantified after combustion at 500 °C for 8 h based on methods described previously³ and in section S2. In addition to the removal of any organic material, this step was also a means of making LOI measurements to determine the inorganic contents of the plastics. Several plastics were analyzed in duplicate or triplicate to (a) acquire enough inorganic material for inductively coupled plasma mass spectrometry (ICP-MS) analysis and/or (b) determine the variability of additives within the polymer. In both cases, the inorganic material from all replicates was combined. Subsequent acid digestion of the inorganic material also followed established methods (section S2).⁴⁰ All samples were analyzed for 48 elements (Table S3) via ICP-MS at the Woods Hole Oceanographic Institution Plasma Facility. Instrument specifications, quality control procedures, and results are described in section S3.

2.3. Determination of Additive Liberation during Photodegradation

Liberation of additives from consumer plastics was studied for three of the samples analyzed via ICP-MS: the conventional CVS bag, the rubber mulch, and the power strip. Plastic-free light-exposed and dark control flasks were also included to assess background contamination. All plastic data are reported with their corresponding plastic-free blanks subtracted out. Plastics were cut into small (~0.1–1 cm) pieces, mixed to ensure homogeneity, and weighed. Next, ~2 g of the rubber mulch and power strip and ~0.1 g of the postconsumer CVS bag were placed in 60 mL quartz bomb flasks with ~50 mL of Milli-Q water, for which photodegradation rates appear comparable to seawater.³ Ample headspace was left in the flasks to ensure that the system remained oxygenated throughout the experiment. The flasks were irradiated for 10 days at room temperature using a 308 nm LED array similar to those described previously (section S4).⁴¹ At 3 and 6 days, 5 mL subsamples were taken and replaced with 5 mL of fresh Milli-Q water. Each day, the flasks were opened and shaken to ensure oxygenation. Replicate samples were taken for one filter fraction of each sample at the final time point. After each time point, samples were filtered with 1.0 and 10 μm (Omnipore hydrophilic PTFE membranes) filters, using acid-washed PFA, PP, and quartz materials to avoid metal contamination. A filter blank (i.e., fresh Milli-Q water

put through each filter) was included for each pore size to assess potential background contamination from the filtering step alone, which was near or below the LOD across elements for both sizes (section S5). An unfiltered sample was also prepared for the final time point. Samples were then aliquoted into iCAP vials and diluted with 2% nitric acid (Optima grade, Fisher Chemical). ICP-MS analysis paralleled the methods described above (section S3), but the list of elements analyzed was narrowed to 13 of those most abundant in plastics and the most environmentally relevant.

2.4. Estimating the Influence of Plastic-Derived Inputs on Riverine Element Fluxes

Plastic elemental compositions were compared to those in the Post-Archaean Australian Shale (PAAS). PAAS generally represents the composition of the upper continental crust and, therefore, many marine sediments and other environmental media.⁴² Thus, elements enriched in plastics relative to PAAS may have greater potential to be perturbed in natural systems due to plastic inputs.

Using estimated plastic inputs to the ocean for 2010²⁷ and predicted inputs for 2060, plastic-derived fluxes for each element to the ocean were computed. The 2060 estimate uses the OECD projection for mismanaged waste²⁸ and the median proportion of such waste entering the ocean.²⁷ While these represent the most widely used (based on the number of citations) estimates of plastic inputs to the ocean, estimates vary substantially (i.e., orders of magnitude),⁴³ so other highly cited estimates were also used to determine a range of potential inputs. These elemental fluxes were compared with the corresponding riverine fluxes, which dominate input to the ocean.²³ Thus, any plastic-derived input approaching the riverine input could signify a large perturbation.

Similar estimates were made for specific rivers to understand the potential for localized impacts. These calculations were based on 2017–2020 annual rates of riverine plastic discharge to the ocean²⁹ and corresponding annual water discharge rates.⁴⁴ As before, plastic fluxes were scaled to the average element concentrations determined in the present work. These plastic-derived element fluxes were then compared to natural riverine element fluxes (combined particulate and dissolved), determined using annual water discharge rates and worldwide average riverine element concentrations.⁴⁵ Estimates were also made for 2060, assuming riverine plastic concentrations increase proportionally to overall mismanaged waste entering the ocean.²⁷ Among the top 200 plastic-discharging rivers, sufficient data were available for only the Pasig (Philippines; ranking: 1), the Ganges (India; ranking: 8), the Huangpu (China; ranking: 18), and the Zhujiang (China; ranking: 39).

3. RESULTS

3.1. Inorganic Additive Contents of Consumer Plastics

All plastics analyzed contained measurable quantities of inorganic additives (Figure 1), with an average mass loss on ignition of $92 \pm 13\%$ (± 1 SD, $n = 77$; Table S2). Accordingly, the average inorganic additive content of the consumer plastics was 8%. The range of inorganic contents was wide: 14% of plastics contained >25% inorganic additives, 10% contained 10–25%, 34% contained 1–10%, 30% contained 0.1–1%, and 12% contained <0.1%.

All of the elements measured were present above the limit of detection in at least one item (Figure 2 and Table S3). Nearly three-quarters of the plastic items (40 of 56) contained all elements measured, with concentrations spanning 6 orders of magnitude. The most common elements detected were from the alkali metal, alkaline earth metal, and first-row transition metal groups. Even for individual elements, concentrations often varied by orders of magnitude. Ca, Ti, and Al were above the detection limit in all items and had the highest average concentrations at 19.5 ± 40.7 , 5.4 ± 8.7 , and 2.4 ± 13.9 mg/g, respectively.

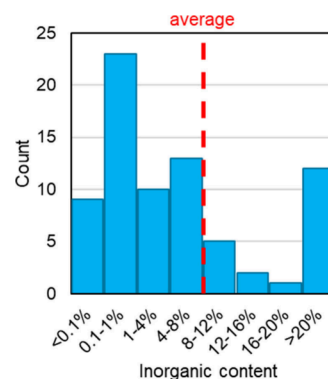


Figure 1. Histogram showing the inorganic contents of the consumer plastic goods in this study determined by LOI. The overall average is denoted by the red dashed line.

The abundance of Sb was the highest relative to PAAS (Figure 2b), with an average enrichment factor of nearly 5 orders of magnitude and a median of 2 orders of magnitude. Zn also showed notable enrichment, with an average of 2 orders of magnitude greater than PAAS and a median of 1 order of magnitude greater than PAAS. Moderate enrichment relative to PAAS (around 1 order of magnitude for mean and/or median) was observed for P, Ca, Ti, Cu, Mo, Sn, and Pb. Most other elements were depleted relative to PAAS. The rare earth elements, in particular, were consistently at least an order of magnitude less abundant in the plastic additives than PAAS.

Several strong positive correlations were apparent between elements (Figure S1), including Ca and the lanthanides and Y (i.e., the rare earth elements; REEs) (Pearson correlation coefficients >0.6); Fe, Co, and Ni (Pearson correlation coefficients >0.6); and Al, Ga, and V (Pearson correlation coefficients >0.9). Strong negative correlations were not observed. Sb was most strongly associated with fibers, textiles, and electronics (Table S2). Zn is especially prominent in plastics with transportation-related uses. However, for many elements, no clear patterns were apparent (Table S2).

3.2. Additive Liberation during Plastic Photodegradation

All plastics showed evidence of the photochemical liberation of inorganic additives (Figures 3 and S2–4). By day 10, light-exposed treatments exceeded dark controls across all filter fractions for 100% of elements analyzed in the rubber mulch, 67% of those in the power strip, and 69% of those in the postconsumer CVS bag. The elements liberated in the largest quantities for the rubber mulch in the unfiltered day 10 time points of the light and dark treatments were Zn, Ca, and K. For the power strip, the most abundant elements in light-exposed samples were Ca, Mg, and Zn, and those in dark samples were Ca, Mg, and K. For the postconsumer CVS bag, the most abundant elements in both light and dark samples were Ca, Mg, and K.

In most cases the unfiltered, 10 μm filtered, and 1 μm filtered element concentrations were similar, indicating that most of the liberated additives were <10 and 1 μm in size. (Figures 3a, Tables S6–S11). The 1 μm fraction comprised >50% of the 10 μm fraction for Cu, Sn, and Sb across plastic types, treatments, and time points. This was also observed across treatments and time points for Mn, Co, Zn, and Mo in the rubber mulch; Mg, K, Ca, and Zn in the power strip; and Mn in the postconsumer CVS bag. The 10 μm fractions typically comprised an even larger fraction of the unfiltered

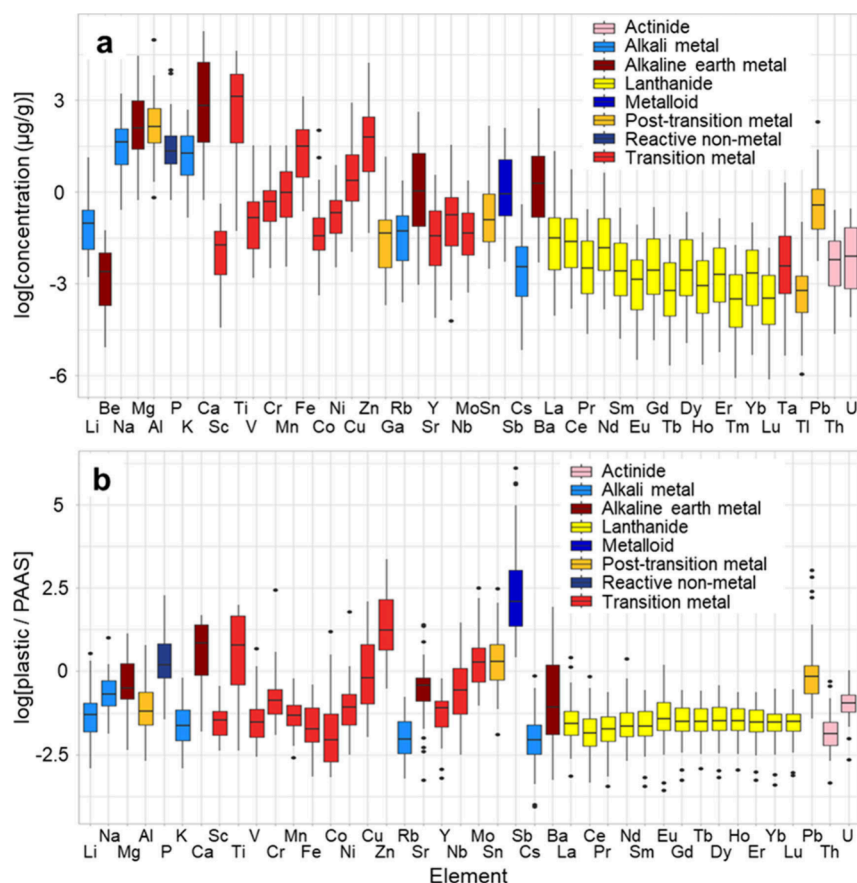


Figure 2. Box and whisker plots showing (a) elemental concentrations for plastics in this study and (b) element abundances in inorganic additives relative to PAAS. Color coding is based on series or subseries on the periodic table.

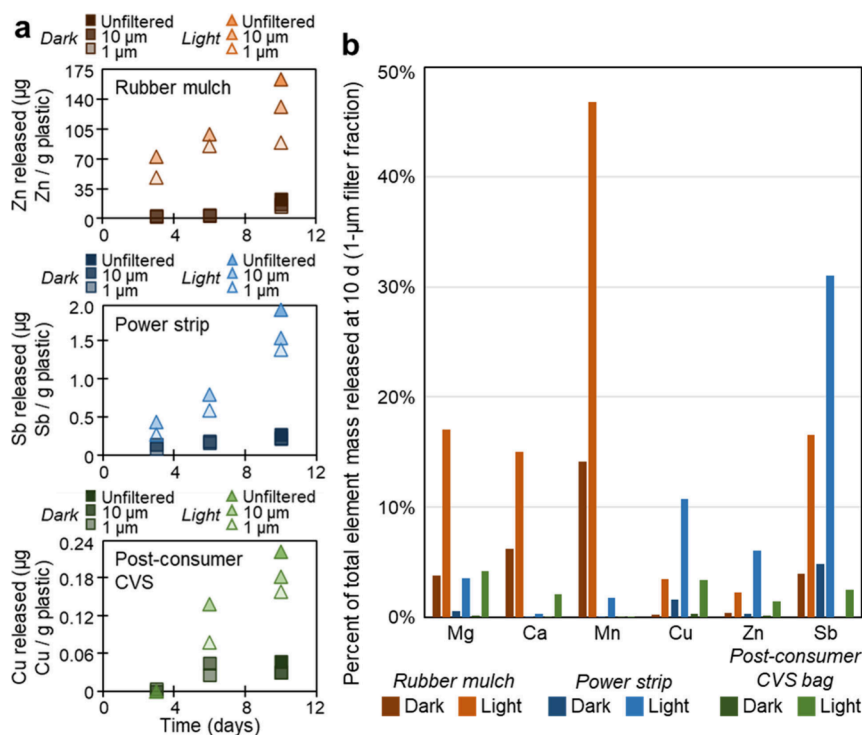


Figure 3. (a) Release of select elements from each plastic across all time points, filter fractions, and light/dark treatments. Element release is normalized to plastic mass. (b) Percent of the total element mass in each plastic type released after 10 days in the 1 μm filter fraction for light and dark treatments for select elements. These elements were selected for their relatively high release in at least two of the plastic types.

samples, at >50% across plastic types and treatments for P, K, Mn, Co, Cu, Zn, Sn, and Sb. This was also observed across treatments for Mg in the rubber mulch and power strip and Ti and Fe in the postconsumer CVS bag. In contrast, some elements became more abundant by over a factor of 2 in the large size fractions as they were irradiated relative to shorter irradiation times and/or dark controls. This was true for K, Ca, and Ti in the rubber mulch and Ti in the power strip and postconsumer CVS bag. The opposite relationship (i.e., a decrease in the large size fraction over irradiation time and/or in the dark controls) was observed for Mg and P in the rubber mulch, P in the power strip, and Mg and P in the postconsumer CVS bag.

3.3. Estimating Plastic-Derived Inputs to Environmental Systems

When scaled to the most widely used estimates of plastic leakage to the ocean,^{27,28} potential plastic-derived element fluxes to the ocean spanned several orders of magnitude. The most abundant elements in the plastics (Ca, Ti, Mg, and Al) had the highest potential fluxes, on the order of gigagrams (Gg) for 2010 and tens of Gg for 2060. Relative to riverine inputs—the primary natural input of most elements to the ocean—two elements were notably high: Sb and Zn (Figures 2 and S5). Plastic-derived Sb and Zn inputs were 3% and 1% of natural riverine inputs, respectfully. By 2060, these numbers are expected to increase ~4-fold to 13% and 4%, respectively. However, when other widely cited estimates for plastic leakage to the environment⁴³ are used, element fluxes are, on average, ~6 times smaller and span ~3 orders of magnitude.

On a regional scale, plastic-derived element fluxes varied widely across elements and the four river systems. The Pasig River (Philippines) was estimated to discharge the greatest quantity of plastic in 2020 and correspondingly had the greatest plastic-derived element inputs by mass and relative to natural fluxes. Sb and Zn had the highest annual plastic-derived discharges at 1 and 86 Mg, respectively, equating to 6% and 5% of natural fluxes, respectively. Element fluxes for the Zhujiang, Huangpu, and Ganges Rivers were ~10 times smaller and represented smaller proportions relative to natural fluxes: plastic-derived Sb fluxes were 0.37%, 0.18%, and 0.01% of natural fluxes, and Zn fluxes were 0.33%, 0.15%, and 0.01%, respectively. By 2060, plastic-derived Sb and Zn fluxes are estimated to become substantial for the Pasig River, representing 21% and 18%, respectively, of natural fluxes. Other elements, including Ti, Ca, and Cu, approach or exceed 1% of natural fluxes in this system. In the Zhujiang River, Sb and Zn also exceed 1% of natural flux by 2060.

4. DISCUSSION

4.1. Occurrence and Compositions of Inorganic Additives in Consumer Plastic Goods

Inorganic additives comprise a substantial proportion of the plastics entering the environment (Figure 1), yet their presence, diversity, and environmental implications have been largely overlooked. The plastics analyzed in this study, which were selected based on production volume, frequency of detection in environmental surveys, and potential for leakage into the environment,^{32,33,35–37} contained 8% inorganic additives by mass, on average (Figure 1). Previous estimates put overall additive contents, which include both organic and inorganic additives, at 7%.³⁷ This slight mismatch may be due to the difficulty of finding the necessary information for such

estimates, which the authors themselves noted;³⁷ it may suggest that the plastics most likely to be leaked to the environment contain more inorganic additives than the average plastic; or it may indicate that inorganic additive use has increased since the aforementioned study was published in 2017. Expanding upon the survey presented here to examine more plastic articles and additive types and characteristics (e.g., use categories, chemical compositions, size ranges, etc.) is necessary to better account for inorganic additives in the future.

The use of ICP-MS for measuring a suite of elements at trace (parts per trillion to parts per billion) concentrations enabled new insights into plastic elemental compositions. Inorganic additives were diverse, with most plastic articles containing nearly 50 different elements at widely varying concentrations (Figure 2, Table S3). Consistent with past reports,^{1,46} elements in fillers and pigments were the most abundant (up to ~20% by mass; Figure 2a) across most plastic types (Table S3). Other elements appeared to be present unintentionally, by association with other additives: the strong correlation of Ca with REEs (Figure S1) is consistent with limestone,^{47–50} the primary source of calcium carbonate fillers.⁵¹ This may explain previous observations of trace REEs in plastics, for which the origin was unclear.⁵² Source mineral impurities may also explain the correlations between Fe, Co, and Ni (Figure S1), which co-occur in many minerals due to their magnetic properties,⁵³ and Al, Ga, and V (Figure S1), which are common in bauxite, the main source of Al additives.⁵⁴ While past studies have surveyed specific elements in plastics,^{38,39,52,55–58} most relied on XRF, which is less sensitive and accurate than ICP-MS (Figure S6).³⁸ ICP-MS techniques employed in this work are routine in many fields⁵⁹ and thus may yield valuable information about inorganic additives in consumer plastics. Because detailed information on inorganic additive compositions is unreported, unregulated in the US, and largely unavailable,⁴⁶ even, at times, to the companies selling the plastics,² such studies remain essential to identifying additives that may be important from the perspective of environmental fate and impacts.

Comparisons of inorganic additives with environmental media suggest that the natural cycling of certain elements may be disproportionately impacted and offer new tools for distinguishing plastic-derived elements from their natural counterparts. First, Sb, Zn and, to a lesser extent, Ti, Ca, and Cu were disproportionately abundant in consumer plastics relative to the upper continental crust (Figure 2b).⁴² Sb and Zn were widely detected across plastic types and characteristics, likely due to their high utility in multiple forms. Sb is routinely observed in PET as a residual polymerization catalyst,³⁸ consistent with the observed trace concentrations in and associations with fibers and textiles (Tables S2 and S3). Its higher concentrations and association with electronics (Tables S2 and S3) are more consistent with its use as a flame retardant as antimony trioxide (Sb₂O₃).³⁸ Zn is widely used as a filler and in slip agents, pigments, and many other applications.¹ Notably, it is prevalent in tire rubber, usually as zinc oxide, at concentrations comparable to those observed in the rubber mulch (up to ~3%; Table S3).^{31,60} These differences in elemental compositions may offer valuable lines of evidence in environmental monitoring efforts for inorganic additives and the plastics themselves.

4.2. Implications of Inorganic Additives on Consumer Plastic Environmental Fate and Impacts. These findings

underline the importance of looking beyond polymers and organic additives in plastics. Inorganic additives appear to be equally, if not more, abundant in consumer plastics.^{1,37} However, they were scarcely, if at all, mentioned in several widely cited reviews that aimed to comprehensively outline plastic's influence in the broader geochemical context,¹⁰ its potential harmful effects on ecosystems and organisms,^{8,9} and the “grand challenges” for the field in understanding and addressing plastic pollution, more broadly.¹¹ In contrast, organic additives in plastics and metals sorbed to plastics were discussed extensively in most of the reviews. Studies on organic additives are often justified based on abundance, potential toxicity, bioactivity, and/or photoactivity,^{8,9} yet many inorganic additives possess the same characteristics.² For example, Sb is ubiquitous, photocatalytic, and widely known for its toxicity to humans in many forms (e.g., Sb₂O₃).^{38,57,61,62} Zn, which is even more abundant in plastics, is photocatalytic and an important micronutrient for marine phytoplankton.^{63,64} Overall, integrating inorganic additive characterization into experimental frameworks may enhance our understanding of plastic's environmental fate and impacts.

Photochemical release of inorganic additives into water was substantial but varies with article type and element, indicating that plastic formulation plays an important role. Consistent with past findings,^{12,18} release rates and proportions varied across elements and plastic types for light-exposed and dark treatments (Figures 3 and S2–4 and Tables S6–11). Several elements (e.g., Mg, Ca, Mn, Cu, Zn, and Sb) showed substantial release from multiple plastic articles in the dark and light but to a greater extent in the latter. This may be due to the concentration of these additives at the plastic surface, higher solubility, and/or greater mobility within the polymer.^{1,18,65} Light exposure also induced release in cases in which dark release was minimal or not observed. The effect was most substantial for Ti, which had among the lowest proportions of the bulk element released across plastics. This limited release may be due to its presence in the particulate phase⁶⁶ and low solubility,⁶⁷ which are unfavorable for release without degradation of the surrounding polymer matrix.¹⁷ In general, substantial variation was observed in the proportions of elements released by each plastic type. For example, while the power strip and rubber mulch had similar Sb contents and lost ~6% after 10 days in the dark, the power strip released double the proportion after 10 days of irradiation (43% vs 20% in the unfiltered sample). Past studies have shown that plastic surface area influences photochemical additive release,¹³ although formulation-driven differences in plastic photo-degradation rates^{3,7,15,20} and subsequent deterioration of the surrounding matrix are likely also important.¹⁷ Additionally, environmental variables, including salinity and organic matter, influence the release of metal-containing additives, although only one study appears to have examined their effects.¹⁹ Further work is, therefore, necessary to parse out controls and determine release rates for various plastic formulations under realistic environmental conditions.

The widespread presence and diversity of inorganic additives in consumer plastics, as well as the evidence that plastic formulation is a control of additive liberation, strongly suggests that future studies focused on the fate and impacts of plastic pollution should use consumer-grade materials in their experimental designs. The formulation of plastics, including their inorganic additive contents, can impact the density and thus buoyancy of plastics,⁶⁸ the extent of biofouling,⁶⁹

wavelength dependence and degradation rates,^{3,7,15} and photoproduct composition³ and toxicity.⁷⁰ Therefore, using consumer grade materials in experimental frameworks is critical to advance the environmental relevance of plastic pollution studies. However, compared to plastic standards routinely used in experimental plastic pollution research,⁷¹ the abundance and diversity of inorganic elements is notably higher in consumer-grade materials. For example, in nearly half of the commercially available plastic standards, Ti, Al, and Zn were not detected.⁷¹ In the current study, however, Ti, Al, and Zn were present in nearly all items tested, often at abundances at or approaching weight percent. This discrepancy reinforces previous sentiments³ that the research community should strive to use plastic formulations in their experiments that are comparable to those leaking into the environment, thereby ensuring findings at the bench- and mesocosm-scale better reflect what may happen in nature.

4.3. Implications for Global and Local Biogeochemical Cycles. Plastic-derived element fluxes to the ocean have the potential to be substantial, but estimates varied widely depending on the element and the model used to predict overall plastic inputs. Consistent with their high abundance relative to the upper continental crust, Sb and Zn had the highest predicted inputs relative to natural inputs (Figures 2b and 4). Based on the most-cited yet highest estimate of plastic inputs to the ocean,⁷² Sb and Zn inputs may be ~3% and ~1% of riverine inputs, respectfully. This puts plastic-derived Sb inputs to the ocean at ~15% of total anthropogenic atmospheric Sb emissions, comparable to several widely studied Sb-emitting processes, such as brake wear and pig iron and steel production.⁷³ If current production and leakage

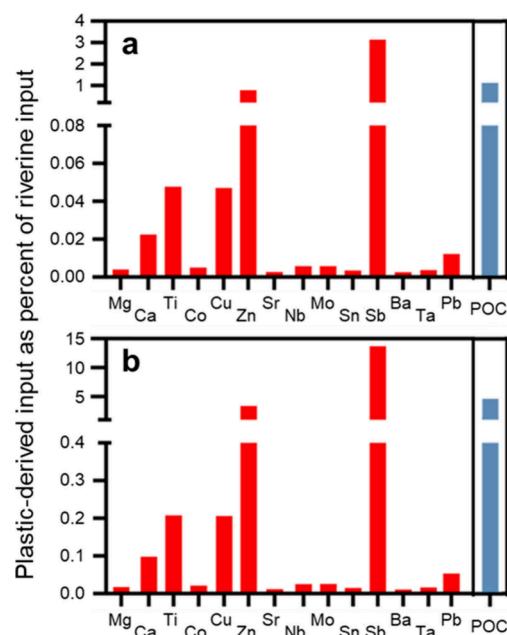


Figure 4. Percentage of select (i.e., those $\geq 0.003\%$ of riverine fluxes) elements (red) released to the ocean from plastics leaked to the environment relative to corresponding riverine inputs based on average element concentrations in consumer plastics and projected inputs of plastics to the ocean in (a) 2010 and (b) 2060. Corresponding estimates for organic carbon (OC) from plastic as a percent of riverine particulate OC (POC) flux, taken as the average of the range reported by Stubbins et al., are included (blue) for comparison.¹⁰

patterns continue, plastic-derived inputs of Sb and Zn would quadruple to ~13% and ~4% by 2060, respectively, resulting in potentially significant perturbations to these element cycles.

Regional impacts may be even higher than global impacts due to the uneven distribution of plastic in the environment. Broadening monitoring efforts to include areas hit hardest by plastic pollution is, therefore, essential to understanding and mitigating impacts. “Hot spots” include highly polluted rivers,²⁹ subtropical gyres,³⁰ and, potentially, marine sediments.⁷⁴ Small urban rivers in Southeast Asia and West Africa discharge disproportionately large amounts of plastic to the ocean,²⁹ resulting in high potential impacts on element fluxes. The Pasig River that bisects Manila (Philippines)—the 17th largest city in the world—is estimated to discharge the most plastic of any river globally,²⁹ and its plastic-derived Sb and Zn fluxes are currently estimated to be ~5% of natural ones, with expected growth to ~20% by 2060. This is already a potentially significant perturbation, yet the Pasig and other small, highly polluted rivers have received little attention: only four studies^{75–78} appear to have focused on plastic in the Pasig River, whereas hundreds of studies have focused on the North Pacific alone. Natural element cycling studies in these small rivers are scarce, further hindering accurate estimates of such potential perturbations.

Disruptions to several trace elements may rival or even exceed disruptions to major elements including carbon. Carbon from plastic has received substantial attention, with studies covering its implications in various environmental systems and processes.^{10,79,80} Plastic-derived carbon is estimated to comprise 0.2–2% of global riverine POC emissions (Figure 2).¹⁰ This estimate assumes that all riverine plastic is (a) pure polymers and (b) present in the particulate organic form,¹⁰ which may be a flawed assumption given the abundance of inorganic additives and the known transformation processes (e.g., photodegradation) that convert plastic to DOC and DIC on time scales relevant to transit in surface waters.^{3,15,16} Furthermore, POC is only 23% of the global average riverine carbon flux,⁸¹ meaning that contributions to the overall carbon flux is ~4 times lower. Thus, the contribution of plastic-derived inputs to the respective element flux may be over an order of magnitude greater than that of carbon for Sb, several times greater for Zn, and comparable for Ti and Cu. Yet these elements have been widely overlooked by the community,^{10,79,80,82} thereby calling for a reframing of our understanding of the potential for plastic pollution to impact global and local biogeochemical cycles, as well as strategies for mitigating such impacts.

Despite these potential disruptions to natural biogeochemical cycles from inorganic additives in plastics, it is critical to note that, because estimates of plastic inputs to the ocean vary substantially,⁴³ the uncertainty in element fluxes from plastics is high. Other highly cited estimates⁴³ resulted in plastic-derived element fluxes up to 3 orders of magnitude lower, substantially reducing their potential for harmful effects and the list of elemental cycles that may be perturbed. Thus, it is difficult to assess the true magnitude of plastic-derived element flows to the ocean—and their implications—without first refining overall plastic flows to the ocean.

4.4. Implications for Next-Generation Circular Materials. As society moves toward more sustainable and circular plastic use, basing the next steps on realistic formulations (i.e., those containing inorganic additives) is critical to effectively mitigating impacts. Lifecycle assessments of additives are

currently limited due to the lack of detailed, publicly available information surrounding their usage and the scarcity of studies on their environmental release.⁴⁶ Yet considering inorganic additives and their impacts may even open doors to more efficient solutions: while the plastic field has primarily focused on the polymers themselves in designing more benign and circular next-generation plastics,⁸³ modifying use patterns of inorganic additives may offer a short-term strategy for reducing environmental impacts within the current production framework. Ultimately, additives that are “lost by design” (i.e., those added to materials expected to be landfilled, incinerated, or leaked into the environment with no viable means of recovery/recycling) are incompatible with plastic circularity;⁸⁴ the impacts of these additives once released adds yet another layer of unsustainability. Yet, the plastic industry appears unlikely to transition away from additives in the foreseeable future due to their considerable benefits to performance, aesthetics, and cost.⁸⁵ Thus, narrowing our use of inorganic additives to those with lower potential for environmental impacts and compatibility with future circularity scenarios is essential as we move to reduce the impacts of society’s continued and growing reliance on plastic.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenvironau.4c00130>.

Prescreening of consumer plastic using XRF, preparation of consumer plastic goods for LOI and ICP-MS analysis, ICP-MS analytical procedure for bulk plastics and plastic additive liberation experiments, LED spectral characteristics, and additive liberation experiment quality controls (PDF)

XRF and ICP-MS measurements for select consumer plastic goods, and LOD for elements measured in consumer plastic goods and water via ICP-MS (XLSX)

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Notes

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