The diverse metal composition of plastic items and its implications

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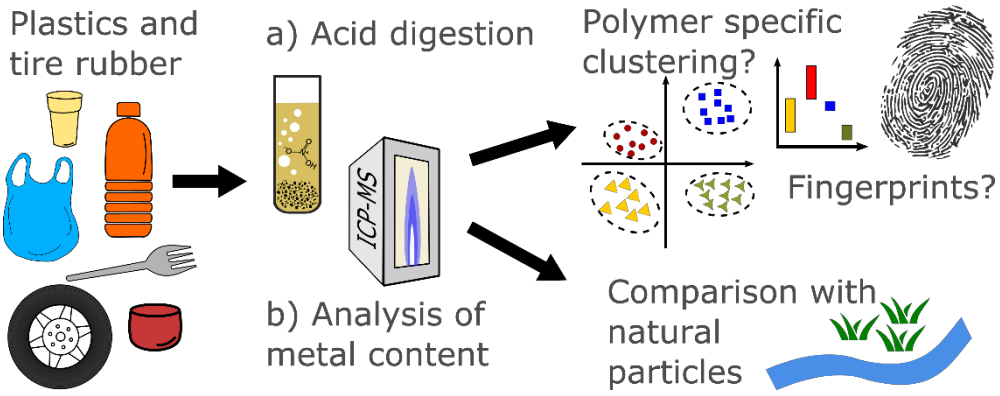
Graphical abstract:



Abstract

Plastic items from urban, freshwater and marine environments as well as from household items and electric supplies were analyzed for their metals and metalloids arsenic, barium, bismuth, cadmium, cobalt, chromium, copper, manganese, nickel, iron, lead, antimony, tin and zinc. Total metal contents ranged from 3 µg/kg (5^{th} percentile) up to up to 7 g/kg (95^{th} percentile). The median content of most metals was below 1 mg/kg and did not exceed legal limits. Iron and zinc were the metals with the highest contents, with medians of approximately 50 mg/kg. Multivariate statistics (k-means clustering and principal component analysis) did not reveal a polymer specific metal composition except for samples of tire tread rubber that was obtained from passenger car tires. Investigation on the potential origin of the metals in plastics revealed that pigments were the most likely source. In comparison to natural and anthropogenic materials in rivers, oceans and air, the metal content of plastic items was within the same order of magnitude, except for antimony and zinc contents. Literature data on the adsorption capacities of plastics suggested that the inherent content of barium, iron, antimony and zinc was dominating the total content in the studied samples. Compared to suspended sediments in rivers, the metal flux into marine environment transported with plastic items was found to be negligible due to the three orders of magnitude lower masses. The different properties, however, may consequently lead to the transport of plastics and their constituents into pristine and remote environments which natural particulate matter may not reach.

1. Introduction

Plastics are not only ubiquitous in daily life, but also in the environment. Plastic products have long been entering the environment for example due to mismanagement of waste, littering or wear and tear during their use phase (Jambeck et al., 2015; SAPEA, 2018; ter Halle et al., 2016). As a consequence, plastic debris has been detected in even the most remote and pristine locations such as in arctic deep-sea sediments (Bergmann et al., 2017), mountain lakes (Free et al., 2014) or remote islands (Martins et al., 2020).

One of the pressing questions is if and how this material class affects these different ecosystems. It is known that effects may be caused by the particle, by material constituents or by adsorbed chemicals (Triebskorn et al., 2019). Recently, a better assessment of the relation between effects and chemicals associated with plastic materials has been requested (Triebskorn et al., 2019). This assessment requires comprehensive information on material constituents and their behavior in the environment.

In order to tailor the plastic products to a variety of needs and applications, additives are essential. These chemicals are required for the production of the polymer (such as vulcanization, curing or blowing agents), or are used to achieve certain physical properties of the product (such as pigments, dyes, plasticizers), for safety and stability purposes (such as flame retardants, heat stabilizers, photo stabilizers, antioxidants, biocides), for better processability of raw materials (slip agents, lubricants), or to reduce costs (fillers such as for example calcium carbonate or silica) (Hahladakis et al., 2018; Murphy, 2001). Additives are used in large quantities on industrial scale. Recently, the European Chemicals Agency (ECHA) identified > 400 additives for plastic materials registered within REACH that are used in volumes of > 100 t/a in the EU (ECHA, 2019). Many of these high-volume chemicals are organic compounds such as phthalates or cyanines, but a large share are also inorganic compounds (e.g. TiO_2 as pigment) or organic compounds containing inorganic elements such

as stearate salts of zinc, cadmium or lead (ECHA, 2019). Metals can also be present in plastics as a relic of previous products due to recycling processes (Wäger et al., 2012).

Due to the potential hazard of some additive groups, their content is regulated, for example in different European legislations. The RoHS directive (Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic equipment) for instance limits the use of metals in electronic equipment. (Europan Parliament and Council, 2011), the “Toy safety directive” regulates the migration limits of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Sn, Zn in toys (European Parliament and Council, 2009) and directive 94/62/EC on packaging and packaging waste regulates the sum of Pb, Hg, Cd and Cr(VI) in packaging (European Parliament and Council, 1994).

As soon as plastic particles are released into the environment, they not only carry their original components with them, but they also interact with the surrounding media with the result that metals can be adsorbed on or desorbed from their surfaces (Yu et al., 2019) or leached from the plastics (Hahladakis et al., 2018). With prolonged exposure to environmental conditions, aging processes change the physicochemical properties of plastics and may lead to embrittlement and subsequent mechanical degradation (ter Halle et al., 2016). Adsorption depends on properties of the sorbent such as surface charge, degree of aging, coating with organic matter or surface to volume ratio of the sorbate (e.g. metal oxidation status, concentration in solution) and on the conditions of the surrounding media such as pH, salinity, temperature or organic matter content (Bradney et al., 2019). Thus, the extent to which adsorption contributes to the metal load of plastic depends on time and location and is still under discussion.

Knowing the multitude of additives and the plastic mass in the environment, the question arises to what extent plastic contributes to metal emissions and distribution in the environment. The high mass of floating plastic debris in the oceans (Eriksen et al., (2014) estimated >250'000 tons) would suggest plastic as a relevant source for metals in the marine environments. It is thus

of high importance to assess the contribution of metals from these anthropogenic materials compared to natural particles.

Furthermore, given the variety of metals added to different polymers, an identification of metal fingerprints specific for polymer types or sources of plastic items would help in characterization of plastic items found in the environment. In a recent study it was demonstrated that plastics have a distinct bulk elemental composition (C, N, H, S) compared to natural material (Mallow et al., 2020). Multi-metal fingerprints could even make it possible to quantify the polymer content of a sample if metal contents were sufficiently different, both compared to the metal composition of the background matrix and between polymers.

In this study, plastic samples from different origins were obtained: household items and electric supplies as well as marine, urban and lake litter and tire tread rubber samples. The samples were analyzed for the metals and metalloids As, Ba, Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Sn, and Zn. In the following text, these elements are referred to as metals and no differentiation between transition metals or post-transition metals (Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn, and Zn), alkaline earth metals (Ba) and metalloids (As, Sb) is made. This data set was evaluated to identify potential metal fingerprints, assess the metal contents in plastic in relation to other particulate matter and compare the determined content with the adsorption capacity of plastics. Since rivers contribute substantially to the marine plastic budget (Schmidt et al., 2017), suspended river sediments were selected as reference for natural particles. The following hypotheses were investigated: i) metal fingerprints can be obtained for different plastic items due to differences in additive application for different polymers and applications, ii) the metal contents in plastic are elevated compared to natural particles and iii) the inherent load of investigated metals in plastics is higher than the adsorbed fraction.

2. Materials and Methods

2.1. Sampling

Samples from passenger car tires were obtained by cutting tread pieces from used discarded tires (n=9, "tires"). Components required for electric installations were obtained from a local hardware shop (n=18, "electrics"). Samples from a lake reservoir (Muldestausee, Saxony-Anhalt, Germany) were obtained by collection from the shoreline (n=24, "lake reservoir", sampling 08th - 09th May 2019). During the expedition SO268/3 with RV SONNE across the Pacific Ocean from May 25th to July 5th 2019, floating marine debris was collected with a net (n=44, "marine litter"). Household items were obtained from a local supermarket (n=12, "household"). Urban litter was collected in the city of Leipzig (n=45, "urban litter"). A total of 152 samples was analyzed. Further details on all samples can be found in the supporting information (Table S10).

2.2. Polymer identification

Polymer identification was conducted using Fourier-transform infrared (FT-IR) spectroscopy (Cary 670 spectrometer, Cary 620 microscope, Agilent Technologies, Santa Clara, CA, USA) with a germanium attenuated total reflection crystal (Ge ATR, Agilent Technologies, Santa Clara, CA, USA). Obtained spectra were compared to those of reference materials using the software MPHunter v2.0 (Liu et al., 2019) to ensure correct identification of the polymer type. If the polymer type could not be identified, the samples were classified as “unknown”. If the polymer type was indicated on the item, spectroscopy was not performed.

2.3. Microwave assisted acid digestion

Samples were rinsed with ultrapure water (Milli-Q integral, Merck, Darmstadt, Germany), cut with a ceramic knife on a glass plate to a size of 1-2 mm pieces and approximately 500 mg were digested in a microwave (Multiwave, Rotor 8NXF100, Anton Paar, Graz, Austria) with the use of nitric acid (HNO_3, Chemsolute, superpure grade, 67-70%, Th. Geyer, Renningen, Germany),

hydrogen peroxide (H_2O_2, Suprapur, 30%, Merck, Darmstadt, Germany) and hydrochloric acid (HCl, Emsure, 37%, Merck, Darmstadt, Germany). For digestion of PE, PET, PA, PP, PS and PU, a mixture of 5 – 8 mL HNO_3 and 0.5 – 2 mL HCl was used. A mixture of 6 mL HNO_3 and 2 mL H_2O_2 was used for rubber digestion. PVC was digested by a mixture of 5 mL HNO_3, 1 mL HCl and 1 mL H_2O_2 (see also Table S1). After digestion, samples were diluted to a final volume of 50 mL with ultrapure water and centrifuged. Microwave programs were chosen polymer dependent according to suggested protocols from the manufacturer (T_{max} = 240 °C, p_{max} = 60 bar).

2.4. Elemental analysis

Inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) were used for determination of elemental concentrations in solution after digestion. ICP-MS was used for the determination of As, Ba, Bi, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb and Sn, while ICP-OES was used for the determination of Al, Ca, Fe, K, Mg, Na, S, Si, Ti and Zn. Contents of Al, Ca, K, Mg, Na, S, Si, Ti were not included in the data evaluation in this study. Results for the metal doped polyethylene reference materials EC-680m and EC-681m (EC-JRC, Geel, Belgium) can be found in Table S2. Details on the instrumental parameters and calibration standards are summarized in Table S3.

2.5. Statistical analysis

Rstudio (v. 1.2.1335) was used for data analysis. Plots were created using ggplot2 (v. 3.3.1). The following descriptive statistic values were calculated: 05^{th}, 25^{th}, 75^{th} and 95^{th} percentiles, median (50^{th} percentile) and maximum. The detection frequency was calculated by dividing the number of observations >LOQ by the number of samples that were analyzed for the respective metal.

For k-means analyses, values below LOQ were replaced with 0.5*LOQ and data was centered by subtracting the column mean and scaled by dividing the centered column with the standard

deviation before analysis. K-means clustering (factoextra, v.1.0.7) was performed on a dataset excluding Fe, Mn and Ni because for these metals, the number of analyzed samples was lower and the algorithm cannot deal with missing values. For PCA, missing values were imputed by the regularized iterative PCA algorithm ("imputePCA", FactoMineR v. 2.3).

A subset of 113 samples was analyzed for differences between polymer types. A Kruskal-Wallis and Dunn's post hoc test were performed (ggpubr v. 0.3.0) for statistically significant differences from the median.

3. Results - The metal content of plastic items

Plastic items from household and electric supplies, environmental plastics obtained from the marine environment, from a lake reservoir and from urban terrestrial environment as well as rubber samples obtained from tire tread of passenger car tires were analyzed in the present study. The 152 samples comprised of 7 expanded polystyrene (EPS), 46 polyethylene (PE), 36 polypropylene (PP), 5 polystyrene (PS), 10 polyvinylchloride (PVC), 9 tire tread rubber, 4 polyurethane (PUR), 1 polyester epoxide (PES), 1 styrene acrylonitrile (SAN) and 1 polyethyleneterephtalate (PET) sample as identified via FT-IR spectroscopy or as indicated on the sample. For 32 samples, polymer type was not identified and these are described as "unknown".

Metal contents were highly variable, ranging from 0.0026 mg/kg (5^{th} percentile, Co) up to 7,000 mg/kg (95^{th} percentile, Zn) (Table 1). Most metals were present in median contents below 1 mg/kg except for Cu, Fe and Zn, with the lowest median contents observed for Cd and Co. Fe and Zn were present in by far the highest median contents with 51 and 45 mg/kg, respectively. The other metals were present in median contents between 0.1 - 1 mg/kg. The majority of metals was detected at a frequency of >80% throughout the samples (Ba, Co, Cr, Cu, Mn, Ni, Pb and Zn; Table 1).

Table 1: Descriptive statistics of the whole dataset; values are provided in mg/kg

	As	Ba	Bi	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Sn	Zn
5th percentile	0.022	0.14	0.017	0.0030	0.0026	0.076	0.13	7.8	0.051	0.058	0.034	0.013	0.062	0.89
25th percentile	0.09	0.64	0.042	0.014	0.012	0.35	0.45	16	0.15	0.25	0.13	0.058	0.26	7.2
Median	0.18	3.4	0.13	0.041	0.06	0.95	1.8	51	0.49	0.6	0.34	0.32	0.61	45
75th percentile	0.53	10	0.25	0.14	0.30	2.9	7.0	160	4.0	1.5	1.8	5.2	2.2	150
95th percentile	3.1	480	2.8	4.6	5.9	13	75	990	51	5.3	38	1800	16	7000
Maximum	11	14000	5900	71	28	180	2100	15000	290	19	760	7400	1200	8500
Samples analyzed	152	152	152	152	152	152	152	104	95	104	152	152	152	152
Detection frequency	66%	100%	20%	70%	89%	99%	99%	79%	100%	100%	97%	33%	57%	82%

Multivariate statistics was applied in order to find metal fingerprints that allow the identification of the polymer or sample origin. For the identification of metal markers, two methods of multivariate statistics were applied: k-means clustering, which would allow the distinct grouping of samples with similar composition, and principal component analysis (PCA), which would help in identifying the metals that explain most of the sample variance and also allow the identification of similarities between samples.

K-means cluster analysis was set to aim for 10 clusters, which was considered appropriate based on the within-sum-of-squares (WSS) plot (Figure S3). Since clusters were hard to identify in the cluster plot (Figure S4), the cluster affiliation of each sample was summarized in a histogram (Figure 1a), allowing the identification of homogenous clusters. One cluster was clearly different from the others and consisted exclusively of tire tread rubber, indicating that their metal composition was sufficiently specific to allow a differentiation to the other samples. Another cluster included all polymer types except tire tread rubber, indicating that the samples were not sufficiently different in terms of metal composition. The remaining clusters consisted of either very low numbers of samples or the polymer types were present in other clusters as well.

In addition to k-means analysis, a PCA was performed (Figure 1b). The first two principal components were not sufficient to cover the variation in the dataset: PC1 explained only 26.2% of the variation, while PC2 accounted for 17.6% (Figure 1b). Clustering of tire tread rubber samples is only visible when changing axis scales (Figure S6) as all samples are close to the origin in the biplot. The other samples did again not show distinct grouping.

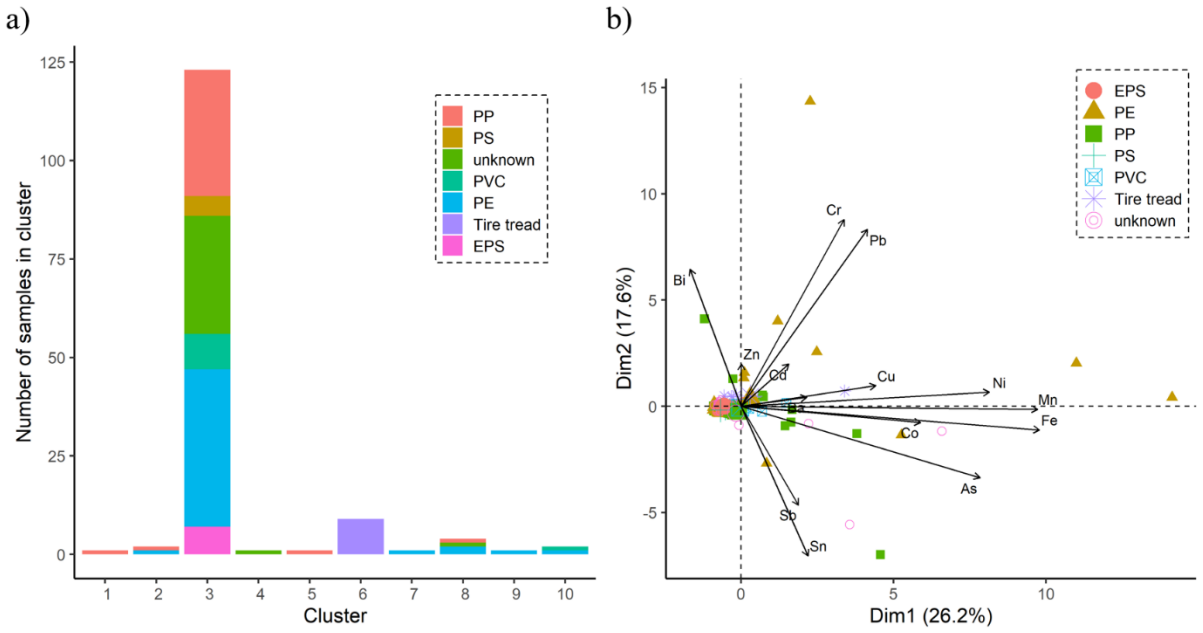


Figure 1: a) Histogram of cluster affiliations after k-means analysis. The colors indicate polymer type, while on the x-axis the determined clusters and on the y-axis the number of samples within each cluster are shown. b) Results of PCA.

Since from multivariate statistics, only few differences between the polymers could be identified, the results of the metal analysis were considered individually for each metal and resolved for the polymer type (Figure 2). Statistically significant differences in the median contents of the individual polymer type compared to the median content of the total sample set was only found for EPS, PVC and tire tread rubber. EPS had significantly lower contents of As, Ba, Cd, Cu, Pb and Sn. In contrast, PVC had lower concentrations for As and Bi, but higher concentrations for Fe, Mn and Zn. Tire tread rubber was only below the median in the case of Sb, but exceeded the median for the metals Cd, Cr, Ni, Pb and Zn. Co was the only metal were

no statistical difference between any polymer groups was determined. Similarities between polymer types were strongest between PE and PP, which had similar median contents. PS was relatively similar to PE and PP but the median was occasionally up to 85% lower (e.g. As, Ba, Cd, Mn, Ni) or up to 270% higher (e.g. Co in PE).

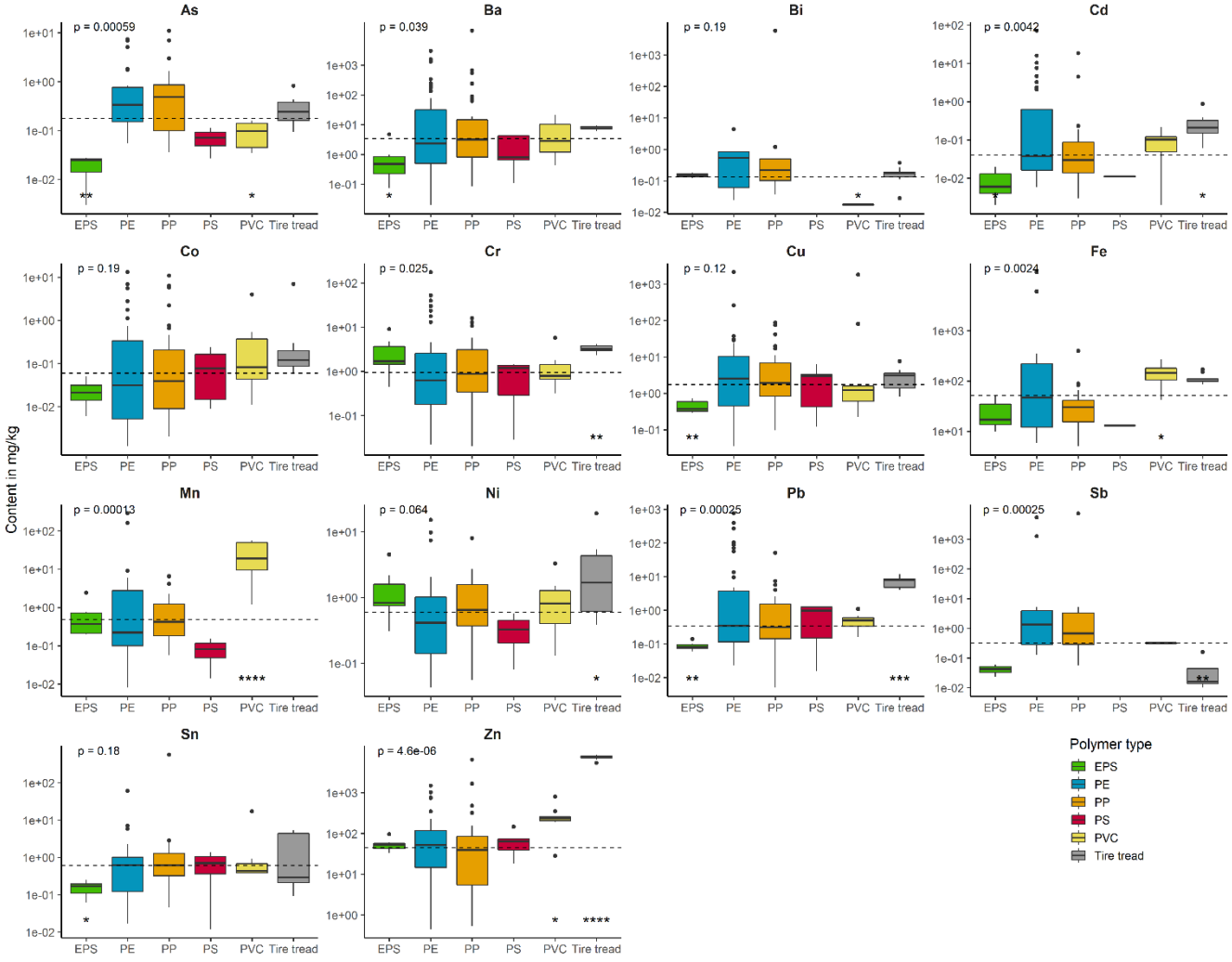


Figure 2: Contents of metals in different polymer types. The dashed lines show the median of the whole dataset. A Kruskal-Wallis and Dunn's post hoc test were performed for statistically significant differences from the median. Significant differences are indicated with * (p≤0.05), ** (p≤0.01), * (p≤0.001), **** (p≤0.0001). The sample size for this assessment was n=113 with 7 EPS, 46 PE, 36 PP, 5 PS, 10 PVC and 9 tire tread rubber samples. PUR, PES, SAN and PET and unknown samples were not included in this analysis. For Fe and Ni, sample size was n=86 (7 EPS, 33 PE, 25PP, 2 PS, 10 PVC, 9 tire tread rubber) and for Mn sample size was n=77 (similar polymers as Fe and Ni but no tire tread rubber).**

When comparing the samples obtained from the marine environment with samples from another origin and of the same polymer type (PE and PP), barely any differences in metal content could be observed (Figure S1, Figure S2). Co content in PP samples was significantly lower in marine samples compared to the other samples, while in PE samples the content was also lower (but not significant). A tendency (albeit not statistically significant) of elevated Zn contents could be observed for both PE and PP samples in marine plastic samples.

4. Discussion

4.1. Metal content of plastic items compared to literature data and regulatory threshold values

Before analyzing whether a metal fingerprint specific for different polymers exists, the metal contents were compared to literature data on total metal contents of environmental plastics (Table S6) and threshold values from legislation. As, Ba, Bi, Cd, Cr, Mn, Pb, Sb and Sn were present in comparably low median contents in the present dataset, and even the 95th percentiles were occasionally lower than median contents reported in literature (Ba, Bi and Cr). Co, Cu, Fe, and Zn were present in median contents similar to the median of literature data or within the ranges reported. The 95th percentiles of these metals occasionally exceeded the ranges of single studies, but for all these metals also higher contents have already been published. For tire tread rubber, As, Bi, Cd, Ni and Sb determined in the present study are up to three orders of magnitude lower than tire treads analyzed in previous studies, whereas Cr, Cu, Fe, Pb and Zn are present in approximately equal content (Kocher et al., 2010; Kreider et al., 2010).

In general, the samples of this study are considered representative for environmental samples. It is obvious that these samples can only represent a fraction of the high number of plastic items present in the environment. Further uncertainties are also associated with the limited samples

numbers of some polymers (e.g. for PS (n = 5) or EPS (n=7)). However, the metal content of environmental plastics would be expected to span broad concentration ranges due to the very diverse applications of plastic products. Despite these uncertainties, the sample set was considered to sufficiently depict the heterogeneity of environmental plastics.

Concerning the regulatory values of metals in plastic items, none of the samples exceeded the limits defined in the RoHS directive (Europan Parliament and Council, 2011) of 1000 mg/kg (Pb, Cr) and 100 mg/kg (Cd). The limits defined in Council Directive 94/62/EC on packaging and packaging waste are 100 mg/kg for the sum of Pb, Cd, Hg and Cr(VI). In the present study, Hg was not included and no differentiation between Cr species was made. However, four of the marine litter samples and one household item had a sum of Pb and Cd > 100 mg/kg.

4.2. The metal fingerprint of plastic items for polymer identification

The metal composition may depend on the polymer type, material additives present in the sample and material age. The type of additive present in the plastic material may be polymer dependent allowing an indirect identification of the polymer based on metal fingerprints. Based on the metal composition, no polymer specific fingerprints were obtained; thus, polymer types cannot be reliably identified by their metal pattern, except in the case of tire tread rubber (Figure 1a). Even though the present dataset is limited regarding the number of samples considered, this observation is justified because the ranges of determined contents in this study and in literature are large and the metal composition is characterized by a high heterogeneity (Figure 2).

Regarding tire tread rubber, note that the present samples were obtained from used passenger car tires and that truck tires may have a different elemental composition. The presence of encrusted mineral particles in the tire tread rubber samples was not expected to alter the

elemental composition since the layer potentially containing particles would be negligible compared to the overall sample thickness.

Under environmental conditions, abraded tire tread particles are expected to form agglomerates with other particles to form an entity that has been described as tire and road wear particle (TRWP, Kreider et al., 2010; Wagner et al., 2018). Even though TRWPs have a lower Zn content than pure tire tread (Kreider et al., 2010), the Zn content of TRWPs would still be an order of magnitude higher compared to the other plastic samples (i.e. 3000 mg Zn/kg TRWP (Kreider et al., 2010) compared to the 75^{th} percentile of the present dataset of 150 mg Zn/kg; Table 1).

Furthermore, the Zn content of tire tread rubber or TRWPs may be subject to change, as Zn may leach from the particles (Councell et al., 2004). Whether a differentiation in elemental fingerprints between aged tire tread or TRWPs and the other samples could be obtained is beyond the scope of this work and would require further research.

The strong similarities in metal composition of PE and PP is most likely because both these polymers are polyolefins and similar additives can be used for both polymers in many cases (ECHA, 2019).

Apart from metals, other elements have been tested for their suitability as plastic fingerprints. In a previous study, analysis of organic and inorganic C, H, N, S, and O in combination with overdetermined equations allowed a quantification of microplastic content (Mallow et al., 2020). Here, microplastics could be distinguished from inert and biogenic material, but differentiation between polymer types was not possible. The method required knowledge on the composition of the biogenic and plastic composition and would be applicable in places with constant conditions, such as industrial wastewaters, only. A differentiation between polymer types based on elemental composition has successfully been performed by Morét-Ferguson et al. (2010). The study was based on the content of C, H and N of single plastic items isolated

306 from the marine environment and allowed differentiation between PS, Nylon 6, PVC, PET and
307 PP/PE. No differentiation between PP and PE could be made due to similar CHN composition.
308
309 As material weathering may also change the metal content of plastic particles it was expected
310 that the marine plastic samples may exhibit a distinct metal composition, because they were
311 highly weathered and are expected to have undergone long and continuous aging compared to
312 the other samples. Taking this into account, two possible effects on the metal contents could be
313 expected: i) the contents of metals are lower than in less intensively weathered samples due to
314 leaching of additives (Frond et al., 2019) or ii) the contents are elevated due to adsorption, since
315 aged polymers where shown to have significantly higher adsorption capacities than pristine
316 plastic materials (Bradney et al., 2019). While the current dataset provides some indications
317 towards these processes in the case of Co and Zn (Figure S1, S2), it does not allow drawing a
318 firm conclusion. Rather, the metal compositions of the marine litter samples are remarkably
319 similar to the other sample groups. This contrasts with a recent study that found an increase of
320 metal contents in marine debris compared to new items (Prunier et al., 2019).
321 Since the samples of the present study were only mildly washed, the total metal content may
322 also have been affected by adsorbed metals (see chapter 4.5), biofilms attached to the surface
323 or particles attached to the surface as encrustations. Biofilms were shown to play a role in metal
324 accumulation on the surface of marine plastics (Richard et al., 2019), but the extent to which
325 biofilms contribute to the total metal load of environmental plastics is yet unclear. In the present
326 study, macroplastics (>5 mm) were analyzed and the mass contribution of attached biofilms
327 remaining after cleaning was considered of little importance compared to the total sample mass.
328

4.3. The metal fingerprints for additive identification

Metal composition may also provide information on material additives in the plastic. It is suggested that the wide ranges of metal content found in the present study are due to the high number of plastic additives in use. Considering that all of the metals determined in this study except As are present in at least one pigment with an annual application of > 100 t in Europe (ECHA, 2019, Table S4, Table S9), this additive class represents the most likely origin for some of the determined metals in the plastic samples. This also goes hand in hand with the particularly low contents of several metals in EPS (Figure 2): since these samples were white, the difference may be explained with a lower pigment content. However, this was not sufficient to group the EPS samples in the cluster analysis (Figure 1a).

Regarding the metals with the highest contents (Figure 2), Fe and Zn are present in a broad range of pigments; Zn is also present in antioxidants, plasticizers, flame retardants and other additives. (Table S4, S9). Particularly in PVC products that require electrical insulation, Zn is commonly contained in heat stabilizers (Murphy, 2001). Since the PVC samples in this study were obtained from cable sheaths, their elevated Zn content (Figure 2) compared to other polymer types is obvious. The elevated Fe and Mn contents in PVC may in turn be attributed to pigments or additives that are not contained in the list provided by ECHA but have been reported to be used for PVC such as for Fe in flame retardants (Carty, 1998).

The apparent correlations between some elements (e.g. Cr~Pb, Sb~Sn, Co~Mn~Fe or Ba~Cu~Ni; Figure 1b) may be due to the co-occurrence in high-volume additives. Pb and Cr for example may originate from Lead sulfochromate yellow (CAS 1344-37-2), while Fe and Mn may be applied as Iron manganese trioxide (CAS 12062-81-6). Co and Fe are contained in the additive Iron cobalt chromite black spinel (CAS 68186-97-0). This additive however also contains Cr, which did not correlate with Co and Fe in the PCA biplot (Figure 1b).

The differentiation of tire tread rubber from the plastic items is due to the significantly higher Zn content of the tire tread rubber samples compared to others, as well as elevated Cr, Cu and Pb contents (Figure 2, Table S5). Zn is a well-known ingredient of tire tread rubber as ZnO is required for the production and is added at quantities of approximately 1%wt (Smolders and Degryse, 2002).

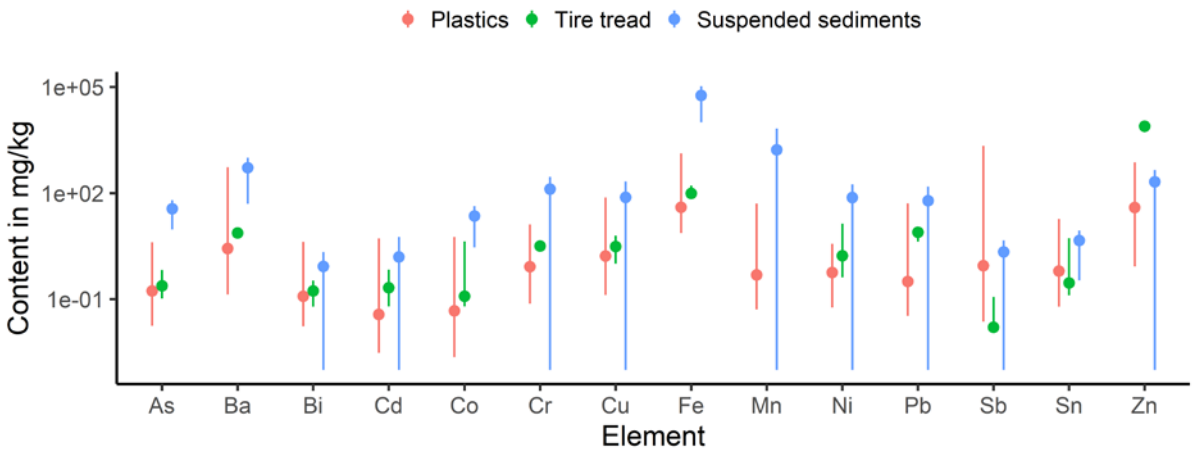
Given the high heterogeneity of metals in plastic additives, metals cannot be certainly assigned to specific additives, except in the case of tire tread rubber.

4.4. Comparison of metal content in plastic with natural suspended matter, biogenic material and airborne particles

Rivers are a major transport pathway of suspended material including plastics and natural particulate material into estuaries and marine environments (Lebreton et al., 2017; Schmidt et al., 2017). Therefore, metal contents of plastic and tire tread rubber samples were compared to metal contents of suspended river sediments. A review study by Viers et al. (2009) summarized the global average metal composition of suspended river sediments. Given the high heterogeneity of the metal contents in plastic samples, generalization is difficult. On the one hand, the median contents in plastic samples in the present dataset never exceeded the reported global average contents of the sediments for any of the metals considered in this study (Figure 3). This indicates that the majority of plastics in the environment is not expected to contain higher contents of potentially harmful metals than suspended river sediments. For the tire tread rubber samples, only the median Zn content was higher than the mean content in suspended sediments. As such, the presence of plastics and tire tread rubber in suspended sediment has little influence on the total metal content, except in the case of Zn for tire tread rubber.

On the other hand, as indicated by the large ranges determined, the average contents of sediment may be exceeded by single plastic items. The 95th percentile of the plastics dataset exceeded

379 the range (median + standard deviation) of the sediment data in the following cases: Bi, Sb, Sn
380 and Zn (Figure 3). For the tire tread rubber samples, the only metal exceeding the range of
381 sediments was Zn (both in 95th percentile and maximum value). This means that single plastic
382 items or particles may contain higher contents of potentially toxic metal than suspended river
383 sediments.
384



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386 **Figure 3: Metal content of 143 plastic samples, 9 tire tread rubber samples and of suspended river sediments (Viers et**
387 **al., 2009). For plastic and tire tread rubber samples, median values are displayed by points while the lines show the**
388 **range from the 5th to the 95th percentile. For sediments, mean ± one standard deviation is provided.**

389 In a study of Ashton et al. (2010), the content of Cd, Co, Cr, Cu, Pb, Sb, Sn and Zn (among
390 others) in plastic pellets collected from beaches were also mostly lower but within the same
391 order of magnitude as the particulate matrix surrounding the pellets. Only for Cd and Pb, higher
392 contents were determined in the plastic samples compared to the particulate matrix. The authors
393 concluded, that pellets were not an important reservoir for metals and that metals may adsorb
394 to the surface of the pellets. Similar observations have also been reported for soils. For example,
395 the metal contents of Cr, Pb, Cu, Sb (among others) in the study of Zhou et al. (2019) were
396 lower in the analyzed plastic samples than in the soil matrix; only Cd was higher in plastics
397 than in soil.

Since the metal composition of the random sample set in this study was similar to earlier studies, the elemental contents shall be used here to extrapolate global inputs of plastic-associated metals into the oceans. The global plastic load transported by rivers into the oceans has been estimated between 0.41 x 10^6 - 12.7 x 10^6 t plastic/a (Jambeck et al., 2015; Schmidt et al., 2017). For the marine environment, approximately 2% of total TRWP emissions were estimated to reach the estuary as modelled for the Seine watershed (Unice et al., 2019). Assuming global TRWP emissions of 5.9x10^6 t TRWP/a (Kole et al., 2017), this would result in 1.2x10^5 t TRWP/a reaching estuaries.

However, the global estimates for sediment fluxes into the oceans have commonly been between 15 and 20 x10^9 t sediment/a (Walling, 2006), with more recent studies suggesting 13-15x10^9 t sediment/a (Li et al., 2020; Syvitski and Kettner, 2011). Given the flux of plastic items entering the oceans is about four orders of magnitude lower than that of suspended sediments, the masses of metals transported with the plastic items into the oceans can be considered negligible. As described above, plastics may still serve as a vector for certain metals due to the different transport behavior and exposure to biota compared to sediments.

If the metal contents of plastic items are compared to biogenic natural materials, a similar picture emerges. A review study recently summarized the contents of As, Cd, Cr, Cu, Mn, Ni, Pb and Zn in marine macroalgae and seagrass from the Mediterranean Sea (Bonanno and Orlando-Bonaca (2018) and citations therein). Of these metals, the 95th percentile of plastic items was within the ranges described for the seagrasses and macroalgae. Again, the Zn content of tire tread rubber samples was an order of magnitude higher.

The inhalative exposure to airborne plastic particles is gaining increased attention and adverse effects on human health may be expected (Prata, 2018). Compared to studies reporting metal contents of other airborne particulate matter, Sb and Zn would again be considerably higher

concentrated in the samples of the present study (up to two orders of magnitude; Table S8), whereas for all the other metals, the contents were similar or lower.

The EU Directives 2008/50/EC (European Parliament and Council, 2008) and 2004/107/EC (European Parliament and Council, 2004) limit the contents of PM_{10} (40 µg/m³), $PM_{2.5}$ (25 µg/m³), Pb (500 ng/m³), As (6 ng/m³), Cd (5 ng/m³) and Ni (20 ng/m³) in ambient air. Under the assumption that metal content does not change with decreasing particle size, these limit values would not be reached if PM_{10} or $PM_{2.5}$ particles had a metal content as high as the 95th percentile in the present dataset (Table S7), i.e. if the PM_{10} consisted only of plastic particles. The WHO Air Quality Guidelines for Europe state that exposure to Cr(VI) at a concentration of 0.25 ng/m³ would be associated with an excess lifetime risk of 1:100'000 (World Health Organization, 2000). This concentration would be exceeded by the samples of the present study if the determined total Cr would consist only of Cr(VI). This, however, is unlikely.

4.5. Comparison with adsorption capacity

The contributions of adsorbed metals and metals contained within the polymers to the total metal load are still unclear. In literature, the reported ranges on the adsorption capacities of polymers for metals vary over seven orders of magnitude (Table S9), depending on the polymer type, concentration of metal in surrounding media, exposure time, and degree of aging, among other parameters.

While in the present study, no differentiation between the adsorbed fraction and the metal constituents of the polymer could be made, it seems that the inherent load of Fe and Zn would substantially exceed the adsorbed fraction, because the 95th percentiles of these metals (Table 1) exceeded the reported values for adsorption capacities by up to one order of magnitude (Brennecke et al., 2016; Rochman et al., 2014; Qian Wang et al., 2020). Even though no

adsorption data was available, the same would also be expected for Ba and Sb simply due to the high contents determined in the samples (Table 1).

For As, the adsorbed fraction may be more relevant because application of additives containing As is limited (As was not contained in a compound in the ECHA list of additives with application doses of >100 t/a) and the 95th percentile of the present study was three orders of magnitude lower than literature values for adsorption (Dong et al., 2020, 2019). For Cd, Co, Cu, Cr, Mn, Ni and Pb contents of the present samples either the adsorbed fraction or the inherent load could be dominant in single items as the reported ranges for adsorption and the determined contents were variable. For Ba, Bi, Sb and Sn, no adsorption data was available in literature.

While plastic particles have the potential to adsorb metals, this is highly dependent on the surrounding media, the presence of organic matter on the particles, the particle surface and the metal concentration (Yu et al., 2019). In natural environments, the adsorbed fraction may be small compared to the content within the polymer. Turner et al. (2020) for example found that the amount of Pb added to plastic material during manufacturing may exceed the adsorbed amount by several orders of magnitude.

Whether a differentiation between the adsorbed and inherent fractions is meaningful, or whether determination of the total load is sufficient, is yet to be discussed. For environmental plastics, an assessment of both fractions would provide only a temporary information because additives in polymers are commonly not chemically bound and may migrate to the plastic surface, where they may become part of the adsorbed fraction (Hahladakis et al., 2018). While the adsorbed fraction can be released after uptake into organisms and induce toxic effects (Bradney et al., 2019), also additive-associated metals may be released (Bandow et al., 2017). Under environmental conditions, the total metal load of plastic items would always be a combination of both fractions, and availability to organisms is not restricted to either of them.

5. Conclusions

The presented findings show that the metal composition of plastic items is characterized by high heterogeneity, large content ranges and little differences between polymer types. Apart from tire tread rubber, which had a distinct composition and for which the deviations in metal content were lower, the metal composition was not sufficiently specific for polymer types or sample origin. Compared to natural suspended sediments, the majority of plastic items did not contain higher contents of metals. However, because the total metal load of single items can be high and due to different transportation behavior than sediments, exposure to marine life may still be significant. For remote and pristine habitats for example, accumulation of plastic items that were transported over long distances may lead to an elevated metal content if the background metal content of particulate matter would be low and if the input of particulate matter would be lower than the plastic input. This aspect could be addressed in future studies in order to further assess the role of metals in environmental plastics.

The metal load transported with plastics represents an important facet of the global plastic pollution. The use of pigments for example is not limited to plastic items. Rather, pigments may enter the environment via a range of applications. The release and occurrence in the environment of such anthropogenic material constituents deserve further attention.

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