Qualitative impact of salinity, UV radiation and turbulence on leaching of organic plastic additives from four common plastics — A lab experiment

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ABSTRACT

Four common consumer plastic samples (polyethylene, polystyrene, polyethylene terephthalate, polyvinylchloride) were studied to investigate the impact of physical parameters such as turbulence, salinity and UV irradiance on leaching behavior of selected plastic components. Polymers were exposed to two different salinities (i.e. 0 and 35 g/kg), UV radiation and turbulence. Additives (e.g. bisphenol A, phthalates, citrates, and Irgafos® 168 phosphate) and oligomers were detected in initial plastics and aqueous extracts. Identification and quantification was performed by GC–FID/MS. Bisphenol A and citrate based additives are leached easier compared to phthalates. The print highly contributed to the chemical burden of the analyzed polyethylene bag. The study underlines a positive relationship between turbulence and magnitude of leaching. Salinity had a minor impact that differs for each analyte. Global annual release of additives from assessed plastics into marine environments is estimated to be between 35 and 917 tons, of which most are derived from plasticized polyvinylchloride.

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1. Introduction

Marine plastic pollution has become a growing threat to marine life in the past few decades (Andrady, 2011; Cole et al., 2011; Depledge et al., 2013; Derraik, 2002; Eriksen et al., 2013; Hammer et al., 2012; Ivar do Sul and Costa, 2014; Law et al., 2010; Moore et al., 2001). Plastic production itself has skyrocketed with the onset of large-scale production in the 50s and 60s. Between 1960 and 2000 plastic resin production increased by a factor of 25 (Moore, 2008). In 2013 as much as 299 million tons of plastic were produced (PlasticsEurope, 2015).

Besides the main polymer, most plastics contain a number of additives to improve product specifications like ductility, hardness, durability or resistance to weathering. Some of these additives, especially certain plasticizers, are suspected to be endocrine disruptors for animals as well as humans (Kang et al., 2006; Talsness et al., 2009). Consequently, dibutylphthalate (DBP) and diethylhexylphthalate (DEHP) are already on the OSPAR[1] list of priority compounds; bisphenol A (BPA) is suspect to review for possible identification as a priority substance. BPA is one of the most commonly produced chemicals worldwide (Vandenberg et al., 2007), and a central monomer in the production of polycarbonate (PC) plastics and epoxy resins (e.g. Aschberger et al., 2010; Chen et al., 2002; Munn et al., 2003). In polyvinylchloride (PVC)

production it is used as a reaction inhibitor, antioxidant for the PVC itself and antioxidant in the production of plasticizers used in PVC processing (e.g. Aschberger et al., 2010; Chen et al., 2002; Munn et al., 2003; Vandenberg et al., 2007; Yamamoto and Yasuhara, 1999). Prenatal exposure to BPA has been shown to alter the male and female genital tract, which may trigger early onset of certain diseases, mammary and prostate cancer and reduce fertility (Maffini et al., 2006). Despite their linkages to health conditions, phthalates are commonly used as plasticizers (Hauser and Calafat, 2005). Being endocrine disrupting chemicals (EDCs), they have been associated with conditions such as breast cancer (López-Carrillo et al., 2010), obesity (Teitelbaum et al., 2012) and DNA damage in human sperm (Hauser et al., 2007).

New, less toxic substitutes for classical additives aim for biological inertness, low migration potential and easier, quicker degradation under natural conditions. Two such alternatives may be tri-2-ethylhexyltrimellitate (TOTM) (Fischer et al., 2014; Kambia et al., 2001) and acetyltri-n-butyl citrate (ATBC), commercially available as Citroflex® A4 plasticizers (Rahman and Brazel, 2006). Other typical additives are UV-stabilizers and antioxidants such as Irganox® or Irgafos® (Dilettato and Arpino, 1991; Simoneit et al., 2005). Polyolefin oligomeric saturated hydrocarbons (POSH), linear, branched and cyclic hydrocarbons typically of C-numbers between C_{12} and C_{32}, are known to be released from polyethylene (PE) and polypropylene (PP) food packaging and coatings (Biedermann and Grob, 2012). Closely related to mineral oil-saturated hydrocarbons (MOSH), they are now a focus of research as food contaminants and potentially harmful compounds due to their resorption potential (e.g. EFSA, 2012)).

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[1] Oslo and Paris Conventions for the protection of the marine environment of the North-East Atlantic.

In case polymerization is incomplete, not only additives, but also mono- and oligomers of the basic plastic isomer may pose health problems. Styrene, as well as its di- and trimer, is of toxicological interest (METI, 2002; Nakai et al., 2014; Tatarazako et al., 2002). While styrene monomers are anticipated to be human carcinogens (NTP, 2014), its di- and trimers (SD and ST) appear to be of relatively low toxicity (METI, 2002; Nakai et al., 2014). Nevertheless, a negative impact of SD and ST on reproduction of freshwater crustaceans (daphnia) has been reported (Tatarazako et al., 2002). Their migration into food (Kawamura et al., 1998), but also into seawater as a consequence of polystyrene (PS) degradation, has been a focus of research recently (Saido et al., 2014).

A large part of consumer and industrial plastics are released into the environment every year. While general estimations suspect that up to 10% of all plastics produced end up in the oceans (Thompson, 2006), more recent calculations for 2010 suggest that 4.8 to 12.7 Mt of plastics have entered the oceans that year (Jambeck et al., 2015). Although the share of plastics in the waste production of humans is only about 10% of its mass (Barnes et al., 2009), it varies around 60–80% of waste items found in the marine environment (Derraik, 2002; Gregory and Ryan, 1997). In some areas the plastic fraction represents as much as 90–95% of all waste (Moore, 2008). Marine plastic debris covers a large variety of polymers and particle sizes. The composition of micro- and macro plastics differs due to different sources and varying degradation efficiencies of different polymers. Ocean surface samples mostly contain PP, PE and Styrofoam (expanded PS), as well as (not expanded) PS, PVC and PET (Andrady, 2015). The latter are denser than seawater and sink to the seafloor. This gravitational force competes with surface tension force of water and is directly related to particle size (Stolte et al., 2015). Variations in particle density, depending on polymer type and extent of biofouling, as well as in particle sizes lead to differences in pelagic and beach plastic debris (Morét-Ferguson et al., 2010). Near shore plastic content and proportion may vary from marine composition due to different regional sources such as river run off and tourism.

In the ocean, plastic particles are subject to a series of physical, chemical and biological interactions. The wide range of detrimental biological interactions such as entanglement, ingestion and assimilation by plankton is well reviewed (Cole et al., 2013, 2011; Gall and Thompson, 2015; Wright et al., 2013). Wave action stimulates physical degradation and breakdown of macro- to micro- and nanoplastics (Andrady and Neal, 2009; Cózar et al., 2014), which is intensified in coastal environments due to increased wave action, abrasion and sand/coastline induced mechanical weathering and UV contact (Corcoran et al., 2009). This transfer from macro- to nanoplastics concurs with a progressive increase of particle surface area, with direct implications for additive leaching and interactions with solved compounds. Persistent organic pollutants (POPs) are known to be enriched on plastic surfaces (Derraik, 2002; Rios et al., 2007; Teuten et al., 2009; Zarfl and Matthies, 2010). Apparent adsorption coefficients of POPs to plastic surfaces are in the order of 10^5–10^6 (Mato et al., 2001) and vary for each POP-plastic combination (Rochman et al., 2013a; Teuten et al., 2009). This results in an ongoing discussion of microplastic ingestion being a vector for POP intake (Browne et al., 2013; Koelmans et al., 2014; Tanaka et al., 2013).

While the impact of POPs adsorbed on plastic particles and ingested at different levels of the food web is object of major interest in several studies (e.g. Besseling et al., 2013; Rochman et al., 2013b; Ryan et al., 1988; Tanaka et al., 2013; Teuten et al., 2009), less is understood about the impact of POPs, oligomers and technical additives that leach from plastic particles into the ocean and are taken up into the food web directly from the aqueous phase. The impact of leached additives might be of similar relevance as POP enrichment on plastic surfaces since polymers contain on average 20 additives that make up between less than 1% and 60% of the plastic material (Fischer et al., 2014; Oers et al., 2012). While there is some research about migration of BPA into seawater (Sajiki and Yonekubo, 2003), studies about other plastic

additives and byproducts are usually related to drinking water (e.g. Amiridou and Voutsa, 2011; Bosnir et al., 2007; Erythropel et al., 2014; Wagner and Oehlmann, 2009), urban waste water systems (Björklund et al., 2009), landfill leachates (e.g. Bauer and Herrmann, 1998; Kalmykova et al., 2013; Kjeldsen et al., 2002; Paxéus, 2000; Yasuhara et al., 1999), food (e.g. Biedermann and Grob, 2012; Bosnir et al., 2003; Dopico-García et al., 2007; Erythropel et al., 2014; Farhoodi et al., 2008; Kawamura et al., 1998; Montuori et al., 2008; Nakai et al., 2014; Shen, 2005) or toys and hospital equipment (e.g. Erythropel et al., 2014). Accordingly, this laboratory experiment focuses on the leaching potential of four common, widely used and often discharged user plastics (plasticized PVC, not expanded PS, PE and PET) with respect to their additives and byproducts released into seawater in particular. Furthermore, the impact of oceanographic parameters such as turbulence, salinity and UV irradiance on leaching processes were included in simplified basic attempts.

2. Materials and methods

To investigate leaching of additives from common plastics, low density (LD-)PE (shopping bag with a print), PET (mineral water bottle), PS (disposable drinking cup) and PVC (pond building foil) were chosen for their prominence in marine debris and large production volume (54% of European plastic demand (PlasticsEurope, 2015)). LDPE, PET (the most common polyester), and PS are commonly used in the packaging sector and often of short term use. This increases their probability to end up in the environment. Flexible PVC is widely used as a waterproof membrane and in a wide range of other fields like medical equipment, clothing, toys and sports goods (e.g. Fischer et al., 2014). Furthermore, these plastics represent a mix of plastics with supposedly high (e.g. flexible PVC) and low additive loads (e.g. PE or PET).

2.1. Experimental setup

The polymer surfaces were cleaned with a wet cloth and cut into pieces of approximately 5 mm × 5 mm. Four experiments were performed with each type of plastic at room temperature; one in deionized (DI) water (generated with an ultrapure water system, Satorius, Germany) and three in salt water with a salinity of 35 g/kg water (prepared with DI water and sea salt from Seequasal GmbH, Germany). The saltwater experiments were run with salt water only (SW condition), continuously stirred with a magnetic stirrer at about 150 rpm (TURB condition), and constantly exposed to UV radiation (JBL ReptileDesert UV 300 15 w lamp, Neuhofen, Germany; UV condition) for each polymer. All conditions were kept in the same room with the non-UV conditions placed in a closed shelf in complete darkness. Temperature effects of the UV lamp and magnetic stirrer are neglected, as potential temperature variations are minute compared to intense UV or turbulence exposure. The magnetic stirrer fish was covered with Teflon, which is supposed to be chemically inert. No detectable compounds could be leached with DCM. As the stirrer fishes were the same, but none of the targeted analytes (explained below) was detected in leachates of all plastics, contamination from the stirrer fish can be ruled out.

For each experiment 5 g of plastic (i.e. multiple pieces adding up to a total weight of 5 g) were placed in 1 L Erlenmeyer flasks containing 500 mL DI or salt water. The flasks were capped with a beaker to avoid airborne contamination. Before usage all equipment was rinsed with nanograde n-hexane and dichloromethane (DCM).

2.2. Sampling

Sampling frequencies were high in the starting period and decreased with time. In the case of PVC and PS, aqueous phases were sampled after 1, 8, 22 and 57 days, in the case of PE and PET after 2, 14, 42 and 78 days. The experiments for PVC and PS were run in parallel, as were the PE and

PET experiments. In both setups a blank for each condition was treated, sampled and analyzed simultaneously. The different sampling points and experiment lengths were due to expected differences in additive load and practical aspects. Since PE and PET were expected to have less leachable compounds, experiments were run longer to achieve quantifiable additive amounts in aqueous phases. At each sampling time 10 different samples — (2 blanks and 4 samples for each of the 2 plastics) were processed. Since the focus was on the general leaching trend and order of magnitude of leached compounds only, the experiments were conducted without replicates.

2.3. Extraction and analysis

To analyze relative composition and quantity of leached additives, the aqueous phases were decanted into a separation funnel and replaced by 500 ml of new DI or salt water to generate juvenile leaching conditions. The leachates were spiked with butylbenzylphthalate (BBT), an additive not contained in the specific polymers chosen, as the internal standard. Next, organic compounds were extracted via liquid–liquid phase extraction thrice, using 20 ml, 10 ml, and 10 ml of DCM. The combined organic phases were dried with sodium sulphate (Na_2SO_4), filtered over solvent extracted cotton and reduced under vacuum to 1 ml. The samples were analyzed by gas chromatography (GC) combined with a flame ionization detector (FID) and mass spectrometry (MS, EI conditions). In all cases compound identification corresponded to standards (if available), the NIST 2.0 Mass Spectral Database and comparison with literature data. Identification was restricted to selected, representative constituents either known from prior studies (e.g. plasticizers like phthalates), structurally similar to the polymer (oligomers), or evident as conspicuous signals from GC chromatograms. All available standards were quantified on the base of their FID-signal via calibration curves (internal standardization). Other compounds were quantified by using closely related standard compounds or in relation to the internal standard signal. To investigate their initial additive composition, the plastics were dissolved in their corresponding solvents (PVC in tetrahydrofurane (THF), PS in DCM, PE in xylol (boiled under reflux) and PET in m-cresol (warmed in sand bath to 120 °C)). The polymers were precipitated with methanol and the supernatant was analyzed with GCFID and GCMS.

Further information about GCFID and GCMS conditions, set up and software are listed in the supplementary material (Tables S2 and S3).

2.4. Conversion from weight to surface data

To generate plots normalized to surface area (Chapter 3.4.), five plastic particles were weighted for each polymer type to average out deviations from their ideal 5 × 5 mm size and their surface was calculated using thicknesses of 1 mm for PVC, 0.5 mm for PS and 0.05 mm for PE. Thickness was measured using a sliding caliper with accuracy of 0.05 mm. The resulting surface to weight ratio was used to transform the plot from leaching per plastic weight to leaching per plastic surface (Fig. 3).

3. Results and discussion

3.1. Additive inventory of the different polymers

Indicator additives and byproducts used for further studies were determined from the selected plastics after solving and precipitating the respective polymer. These selected compounds and calculated initial concentrations are summarized in Table 1.

3.1.1. PVC

A big variety of plastic additives, dominated by phthalates, was identified in the plastic sample. Detected phthalates are a technical mixture of di-*iso*-nonylphthalate (tech DiNP) and di-*iso*-decylphthalate (tech DiDP),

two didecylphthaltes (DDP1, DDP2), decyldodecylphthalatephthalate (DDoP), and DEHP in decreasing order of concentration (cf. Table 1). The technical mixture shows a dispersed signal, as a result of various nonyl and decyl isomers, and was quantified subtracting DDP1 from the accumulated peak area eluting in the same time window. Besides phthalates, two trioctyl trimellitates (TOTM1, TOTM2) were identified. Referring to their mass spectra, a match with tri(2-ethylhexyl)-trimellitate (TEHTM) isomers is most likely. TOTMs are a plasticizer group commonly used in PVC (Lai et al., 2012), which has safer toxicokinetic properties compared to phthalates such as DEHP (Kambia et al., 2001) and low migration potential (Fischer et al., 2014). Additionally, traces of several trialkyl trimellitates (TATM, cf. "T" in Fig. S3 and Table S1) of higher C numbers were identified from EI and CI mass spectrometric information. Information about characteristic MS mass fragments of all targeted analytes can be found in Table S1 of the supplementary material. For most phthalates and trimelliates, only the length of the alkyl side chain in terms of C numbers, disregarding possible branches, could be distinguished in default of reference standards

All detected additives combined correspond to 26% of the weight of the PVC sample. Of the additives, technical DiDP/DiNP mixtures (39%) and DDP1 (34%) are the most prominent constituents, followed by TOTMs with 10% (cf. Table 1). With about one per mill of the total plastic weight, DEHP and BPA are minor components of this PVC foil.

An additive content of around 30% is common for flexible PVC used e.g. as geomembranes (Stark et al., 2005). Whereas the high percentage of plasticizers is rather constant for this type of membrane and characterizes its mechanical properties, its compounding (type, chain length and structure) varies depending on its application (e.g. Fischer et al., 2014; Stark et al., 2005). In a similar pond foil analyzed in the early stages of the experiments, the authors quantified the same plasticizer proportion. However, in this foil less and partially different plasticizers were used (DEHP 78% of total plasticizer load, diethylhexyltherephthalate (DEHT) 11%, techn. DiDP 9% and diethylhexyladipate (DEHA) 2%). This illustrates that PVC composition is not only highly variable with regard to different applications, but also depends on the producers and their unique additive mix.

3.1.2. PS

Compounds detected after complete PS dissolution were identified as oligomers of the PS monomer, indicating incomplete polymerization in the production process or thermal degeneration during PS processing. Besides two polystyrene dimers (SD 1&2), a trimer (ST1), two tetramers (STe a&b) and two pentamers (SP a&b) were detected in the extract. Additionally, two groups of trimer isomers (ST2 a–d, ST3 a&b) were detected. Trimers, i.e. the sum of ST1, ST2 a–d, ST3 a&b, were the most abundant analytes compared to other oligomers. Table 1 summarizes all individual signals for each oligomer group; more information about the oligomers can be found in supplementary Table S1. The chromatogram of the dissolved PS is nearly superimposable with chromatograms of aqueous extractions given as an example in supplementary Fig. S2. The styrene monomer was not analyzed as it elutes within the solvent peak region (GC-FID) or sleep time of the GC–MS. Combined, the detected oligomers represent about one percent of the plastic mass. Distinct signals of typical plastic additives like plasticizers or antioxidants were absent or in blank value range of the chromatogram.

3.1.3. PE

To determine the additive load of the print, both a print free, white piece of the plastic bag and a piece containing green print were dissolved and compared.

The most prominent component in the chromatogram (1,2-di(p-tolyl)ethane, DTE) was most likely a thermal reaction product of xylene used for solving the PE polymer, already described under more harsh, pyrolytic conditions (Auspos et al., 1955), and not derived from PE itself.

The second most prominent compound was acetyl tri-*n*-butyl citrate (ATBC, commercially available as e.g. Citroflex A4®). It belongs to a

Table 1

The columns represent concentration of selected additives in the initial plastic, the fraction of the initial concentration leached under ambient saltwater conditions and ratios demonstrating the impact of (no) salinity (DI condition), UV radiation (UV) and turbulence (TURB) on leaching relative to the ambient seawater condition (SW). DHAA and related compounds could not be detected in the dissolved PE, hence leaching is not given as a fraction of initial concentration, but the total concentration measured in aqueous leachates. Information about mass fragments from MS and full names can be found in Table S1 of the supplementary material. *TBC and TBA are not detected in the initial plastics either, but are degradation products of ATBC. TBC and TBA amounts detected in leachates are given as ATBC mass equivalents transferred via molar mass in relation to initial ATBC concentrations. n.a. = not analyzed, n.d. = not detected.

	Analyte	Initial concentration in mg/g plastic (Chapter 3.1.)	Total % of initial concentration leached in SW after 57/78 days (Chapter 3.2)	Leaching ratio (Chapter 3.3.)								
				DI to SW			UV to SW			TURB to SW		
				<1	~1	>1	<1	~1	>1	<1	~1	>1
PVC	BPA	1.4	3.8	X			X					X
	DEHP	1.2	0.083	X			X					>40
	Tech DiNP + tech DiDP	101	0.0096		X		X					>15
	DDP 1	89.7	0.011	X			X					>50
	DDP 2	8.8	0.00044		X		X					>40
	DDoP	3.6	0.0012	X					X			>70
	Σ TOTM	26.5	0.028	X			X					>60
PS	Σ SD	1.1	0.07		X		X					X
	ST1	2.8	0.14		X		X					X
	Σ ST2	5.7	0.06		X		X					X
	Σ ST3	0.5	0.05		X		X					X
	STe	0.1	0.07		X		X					X
	SP	0.3	0.09		X		X					X
PE	ATBC	1.16 (0.16)	4.87		X				X			X
	TBC	n.d.	5.4*	X			X			X		
	TBA	n.d.	0.083*	X					X			>10
	DHAA and related compounds	n.d.	556 µg/g plastic	X				X			X	
	Irgafos® 168 phosphate	0.56 (0.43)	0.05	X				X				>190
PET	DBP	0.07	0.37	n.a.			n.a.			n.a.		

group of supposedly only marginally toxic (Rahman and Brazel, 2006) and non-persistent "green" plasticizers that are becoming more common. ATBC concentrations were about 7 times higher in the solution of the printed PE compared to the white PE sample.

POSH, here mainly even chain homologous of *n*-alkanes (between C_{12} and C_{32}, with maximum at *n*-C_{18}), were detected in both samples. The printed PE sample contained about 38% more *n*-alkane homologous than the unprinted section. These even *n*-alkanes represent low-molecular weight oligomers originating from the ethylene polymerization process (Dilettato and Arpino, 1991; Simoneit et al., 2005). The higher *n*-alkane content of the printed sample originates most likely from print contents, possibly of mineral oil origin.

Another major analyte detected in the solution is *tris* (2,4-di-*tert*-butylphenyl) phosphate, also known as e.g. Irgafos® 168 phosphate. It is an oxidation product of the common PE and PP additive Irgafos® 168 (Dopico-García et al., 2007; Simoneit et al., 2005), that is used as an antioxidant (Marcato et al., 2003) and lubricant/antiadhesive (Simoneit et al., 2005). Irgafos® 168 itself was detectable only at trace levels.

All detected additives and oligomers represent 2.25 mg (printed) or 0.97 mg (white) per gram PE. The combination of plasticizer (in their case DEHP), antioxidant (Irgafos®168 and its oxidation product) as well as even chain *n*-alkanes were already described as representative additives for PE bags (Simoneit et al., 2005). In good accordance with our data, Simoneit et al. determined a sum of 1.35 mg per gram in surface extracts of a Chilean PE shopping bag.

A labeled chromatogram of soluble compounds after dissolution and polymer precipitation of the PE sample is given in the supplementary material (Fig. S5).

3.1.4. PET

PET could not be completely dissolved, only strongly leached, although heated in *m*-cresol under reflux conditions. The only typical plastic additive detected was di-*n*-butyl phthalate (DBP), identified from the standard mixture. DBP makes up about 70 micrograms per gram PET sample. Other signals in the chromatogram resulting from this relatively harsh treatment are strongly related to PET itself and

were characterized as typical mass fragments of the terephthalate moiety. They were tentatively identified as PET oligomers.

3.2. Composition of plastic leachates under ambient seawater conditions

Leaching rates of additives from polymers were high in the beginning and usually decreased with time. In most cases cumulative additive concentrations in aqueous phases followed a saturation curve as shown in Fig. 1. A representative leachate chromatogram of each plastic type is given in the supplementary material (Figs. S1–S4).
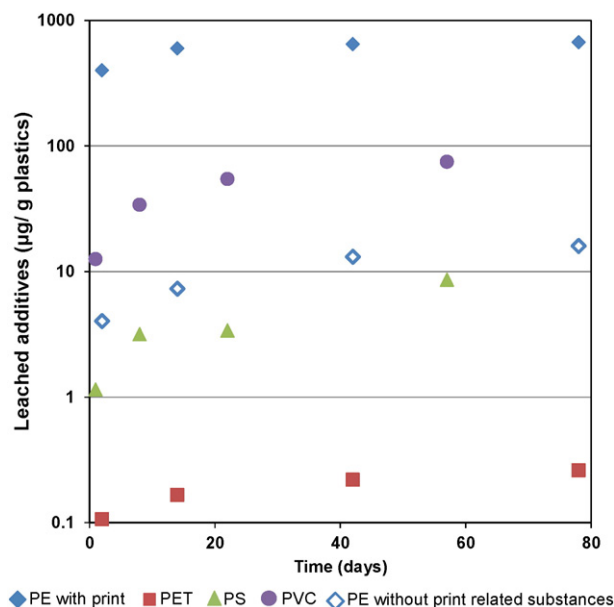

Fig. 1. Sum of selected additives leached from different plastic polymers into salt water (SW condition) illustrated as leached additives per gram plastic versus leaching time. PE = polyethylene, PET = polyethylene terephthalate, PS = polystyrene, PVC = polyvinylchloride.

Since the leaching behavior of polymers in ambient seawater (SW condition) constitutes the basis of reference for the other experimental conditions it is discussed first (cf. Fig. 1 and Table 1).

3.2.1. PVC

Although only a minor additive of PVC, BPA is the dominant additive leached into aqueous phases. With about 53 micrograms of BPA leached per gram PVC after 57 days, its concentrations in ambient salt water exceeded those of major additives like DiDP/DiNP and DDP1 by more than an order of magnitude. 3.8% of the initial BPA content was released during the experiments, while other additives stayed below 0.1% (DEHP). Only 0.006% of the technical DiDP/DiNP mixture and 0.011% DDP were released into the aqueous phase. This is in accordance with declining leaching potential with increasing aliphatic chain length (Kastner et al., 2012) and lower migration with higher plasticizer molecular weight (Stark et al., 2005). TOTM was only detected in trace levels under ambient seawater conditions.

3.2.2. PS

Between 0.07% and 0.14% of PS oligomers were released into saltwater. Compounds identified in the leachates mirrored those detected after complete PS dissolution in both identity (oligomers detected) and relative amounts, with trimers as most abundant styrene oligomers. This implies that all oligomers have a comparable solubility, reflected in a similar percentage of the initial concentrations leached during the experiments (cf. Table 1). Their release is most likely related to the polymer surface given.

In the marine environment, oligomer concentrations are reportedly much higher in sediments than in water itself (Saido et al., 2014). This points to a high surface or particle affinity of oligomers and to sediment as a potential sink.

3.2.3. PE with print

During the experimental period of 78 days, about 4.9% of ATBC was leached into saltwater. This is the highest value observed for all investigated analytes. Besides ATBC, tributyl citrate (TBC) and tributyl aconite (TBA) were detected in aqueous leachates. As they were absent in direct PE dissolutions, their generation from ATBC degradation during the experiment is most plausible. They are not interpreted as additives but degradation products, however their ATBC mass equivalents (calculated via molar masses) show how much additional ATBC was leached to generate the detected amounts of TBC/TBA. While TBC forms via acetyl ester hydrolysis, occurrence of TBA could be explained by loss of acetic acid from ATBC or loss of a water molecule from TBC. According to our data, the latter seems to be more likely, as in conditions where TBA concentrations were high, TBC concentrations were low (cf. Fig. S8 a) and b)). This could indicate that parts of TBC already degraded to TBA. A mass equivalent of 5.4% of the initial ATBC content was detected as TBC, another 0.083% as TBA. Hence, more than half of the total ATBC leached is already degraded by the time of measurement and detected as TBC. Only 1.4% is detected as TBA

A large hump of compounds was present in the seawater leachate chromatograms (cf. "18" in Fig. S3) but not in those of methanolic supernatants after PE precipitation. One prominent compound of this hump was tentatively identified as dehydroabietic acid (DHAA) according to GC–MS data. Initially comprised of DHAA exclusively, during the leaching experiments other resin related compounds were detected in the hump. Together with DHAA they are termed as "DHAA and related compounds" without further identification. DHAA is present in commercial products e.g. in Burez® resin soaps used for emulsion polymerization, organic pigment production and wet glue formulations (Lawter Inc., 2011).

The absence of DHAA and related compounds in the dissolution experiments is surprising. Most likely methanol, used to precipitate plastic polymers after PE dissolution, might be a too polar solvent for terpenic acids, whereas DCM, used during the liquid–liquid phase extraction of

leachates, solves them from exfoliated paint particles that stay in suspension after the PE particles were filtered out.

Assuming that all DHAA and 86% of ATBC and its degradation products are derived from the print (cf. Table 1), the amount of leached additives that are derived from the polymer itself, not the print, was calculated. The print is responsible for 98% of all the additives leached from printed PE.

Only 0.05% (0.12 mg/g PE) of the Irgafos® 168 phosphate content was leached after 78 days under ambient seawater conditions. POSH are present only in trace amounts and could be detected on their specific mass trace (m/z 85) only.

3.2.4. PET

DBP was the only prominent signal in aqueous leachates. In ambient seawater its concentrations were extremely low and in the range of the blank values (cf. Figs. 2 and S8 f). Consequently, and because PET was not completely chemically dissolved, impacts of turbulence, salinity and UV radiation on leaching of distinct compounds from PET will not be included in further discussions

In conclusion, significant amounts of plastic borne organic pollutants are leached from printed PE bags, plasticized PVC foil and PS drinking cups with saltwater and in traces from PET (Fig. 1). Detected levels fall apart by about more than three orders of magnitude, with printed PE having the highest and PET the lowest leaching potential.

The general leaching trend of all compounds considered in this analysis is very similar to the one observed for plasticizer loss from PVC geomembranes used for canal liners (Stark et al., 2005). The authors discuss two general mechanisms of this migration process. Firstly low molecular weight solvents diffuse into the polymer, extract compounds (e.g. plasticizer) and the solution diffuses back to the polymer's surface and surrounding solvent. The second process considers high molecular lipophilic solvents. In this case the additive migrates to the polymer surface and dissolves in the surrounding liquid. For the given experimental set up the first scenario is more plausible. An evident loss of polymer transparency and an obvious swelling of particles point to a penetration of water into the polymer structure. Except for the styrene oligomers (cf. Fig. S7), the leached compounds are close to a steady state at the end of the experiment. The decreasing leachable amount of additives indicates a depletion of the surface layer and the buildup of a concentration gradient where penetration depth and diffusion rate of the additive in the polymer determine the leaching process. The trend of this process seems to be similar for the relatively low molecular weight compounds included in this study, independent of their chemical composition.

Whereas phthalates, mellitates, styrene oligomers and Irgafos® 168 phosphate are leached well below 0.1% of their initial concentrations in their respective source plastic, the extent of leaching reaches more than 10% for ATBC and its derived compounds and 3.8% for BPA, (cf. Table 1). This has to be taken into account regarding the respective source plastics and their impact on release low molecular additives into the environment.

3.3. Impact of salinity, UV radiation and turbulence

Knowledge of the impact of physical parameters like salinity, UV radiation and turbulence on leaching behavior of plastic additives is important, as it improves our understanding of the spatial distribution of released plastic related compounds in the marine environment.

The impact of the three parameters is expressed as the ratio of additive released 1) into deionized (DI) water (salinity), 2) under UV conditions (UV radiation) and 3) under TURB conditions (turbulence) compared to saltwater (SW) conditions already discussed (3.2). A ratio below 1 indicates weaker and ratios above 1 stronger leaching compared to SW conditions. Ratios between 0.9 and 1.1 were interpreted as approximately 1 (~1) and accordingly not being affected by the condition studied. The respective ratios are given in Table 1. The
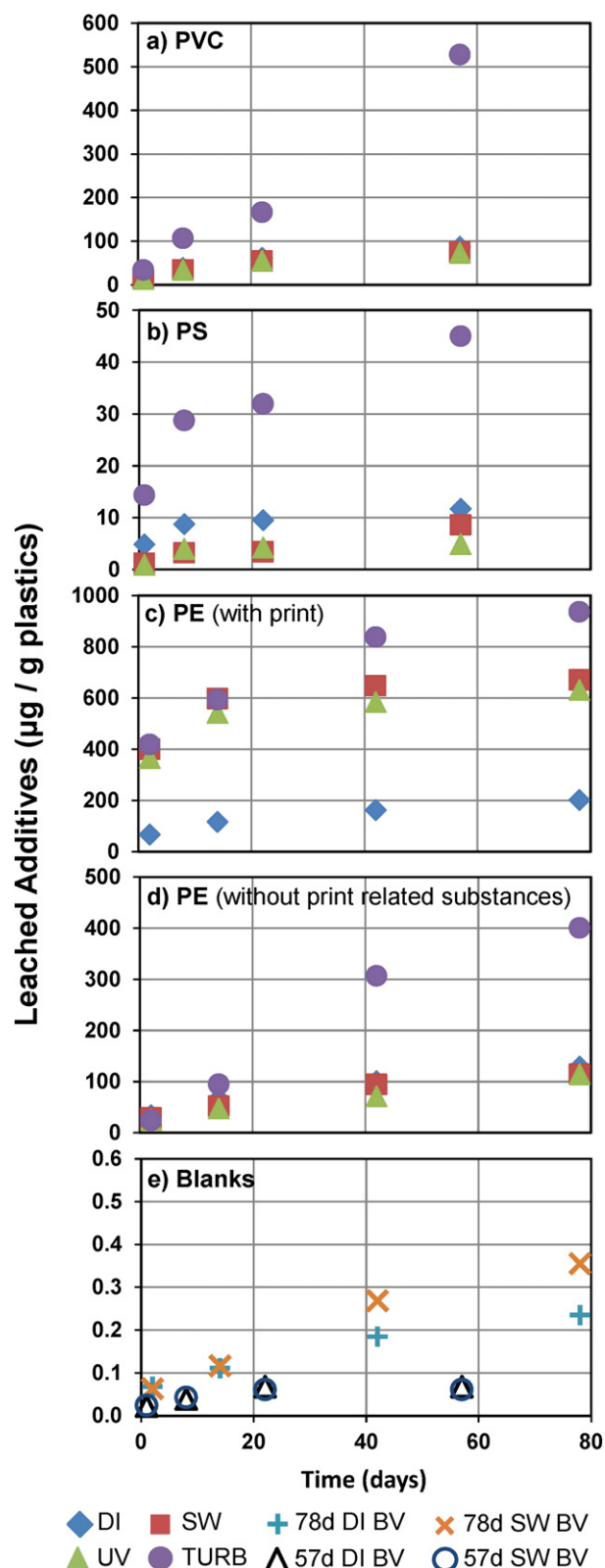
impact of experimental conditions on the leaching yield (sum of all indicative additives) of the plastics chosen is graphically summarized in Fig. 2.

3.3.1. Salinity

Most PVC additives leached more, or to a similar extent, into salt water. Only the technical DiNP/DiDP mix was relatively enriched in DI water. For PS oligomers the trend was reversed. All of them, except ST1, were leached more effectively into DI water. PE additives and their degradation products were enriched in salt water except ATBC, which has a ratio DI/SW >1, which could also indicate a less efficient degradation of ATBC to TBC and TBA under DI conditions. Leaching behavior of phthalates varies and seems to depend rather on the specific properties of each compound than on water salinity

In general we see that marine conditions do affect many analytes, however this effect depends on the inherent properties of each analyte and cannot be generalized for compound groups. This is due to the fact that salinity variations result in complex changes in water and compound chemistry and have an effect on pH, ionic strength, polarity, dipole moment and other parameters.

3.3.2. UV radiation

The UV lamp used for the experiment is rich in UV-A and UV-B radiation. Since the transmission of boron silicate glass is high above wavelengths of 300 nm, the light spectrum reaching the plastic particles during the experiment is close to natural conditions on Earth surface. Therefore, observed results should mirror UV-A induced effects in the marine environmental on a basic scale

The observed effect of UV radiation on the leaching potential of additives is heterogeneous. The aqueous phase remained relatively transparent, however stronger visual alterations of plastic particles compared to other experimental conditions could be observed for PET, PVC and PS. The formerly clear PET, and even more the PS pieces, turned whitish opaque, more so than in saline non-UV conditions. The blackish PVC surfaces became whitish. These observable changes might be induced by distension caused by incorporation of water into the polymers, discussed already. There was no visible change in shape of the polymers within the timescale of the experiment.

No positive effect of UV radiation on leaching efficiency of additives compared to ambient seawater was determined, except in cases of ATBC from printed PE and DDoP from PVC. All other compounds were either not affected, or detected levels of analytes in aqueous phases were lower when exposed to UV radiation (cf. Table 1). This could be due to surface changes of plastic particles (e.g. swelling) generating a leaching barrier. Another effect might be photodegradation of leached plastic additives in the aqueous phase, since many of the additives are UV-sensitive. Once leached into water, UV radiation might increase their decay into compounds not analyzed and a potential UV induced increase in leaching efficiency might be compensated by UV degradation prior to analysis. The direct analysis of additives retained in the polymer after UV-treatment compared to the starting material might lead to more reliable leaching rates.

TBC levels leached from PE are lower while TBA concentrations are higher when subjected to UV radiation, which might point to a more effective conversion of TBC into TBA. Although more ATBC is detected in aqueous phase (6.3% of the initial content), the sum of the ATBC mass equivalents of TBC and TBA are lower. This could indicate that degradation to TBC is rather slow or that TBA decays into products not detected (cf. Fig. S8 a–c).

3.3.3. Turbulence

Our data provide strong evidence that turbulence increases leaching of additives (cf. Table 1). When subjected to turbulence, detected additive concentrations in aqueous phase rose for all plastics tested

Saltwater leaching of BPA from PVC is only about 11% stronger when subjected to turbulence (cf. Fig. S6 f). Most likely this is due to its

Fig. 2. Sum of selected additives leached from different plastic polymers under different experimental conditions illustrated as leached additives per gram plastic versus leaching time. PE = polyethylene, PET = polyethylene terephthalate, PS = polystyrene, PVC = polyvinylchloride, DI = DI water condition, SW = seawater condition, UV = seawater + UV condition, TURB = seawater + turbulence condition, DI BV = DI water blank value, SW BV = seawater blank value, 57d corresponds to the 57 days PVC and PS experiments, 78d to the 78 days PE and PET experiments.

relatively high solubility in water (300 $\pm$ 5 mg·L^{-1} (Shareef et al., 2006)). A comparably high proportion of BPA is leached into the water already. Consequently, there is little potential for turbulence to make the leaching process more efficient. All other PVC additives leached between 20 and 79 times stronger under turbulent conditions. This is also the case for higher alkylated trimellitates (cf. "T" in Fig. S1 and Table S1). Phthalates, in contrast to BPA, are much less soluble in water. Their solubility reaches from 0.020 to 121 mg/L, dependent on the alkyl chain length or structure (Defoe et al., 1990)). Hence, turbulence increases their solution by avoiding a local steady state of dissolution between the polymer surface and the surrounding water phase. The strongest impact of turbulence was observed with the leaching of Irgafos® 168 phosphate from PE. Here an increase by a factor of 190 compared to SW conditions was observed, and almost 10% of the initial content was leached. Although Irgafos® 168 has a very low water solubility (0.005 mg/l, 20 °C (USEPA, 2009), cited in DFG, 2013), that of its oxidation product seems to be much higher, at least under turbulent conditions. No data could be found in literature, but the leaching experiments indicate that solubility of Irgafos® 168 phosphate is at least 0.3 mg/L (cf. Fig. S8 e).

Under turbulent conditions 0.94‰ of the initial printed PE weight was detected as additives in leachates.

27.5% of the initial ATBC content was leached into the aqueous phase after stirring, much more than in other experimental set ups. Compared to SW conditions, a tenfold increase of TBA concentrations was detected; however, TBC levels were so low that the sum of ATBC degradation products is lower than in other saltwater conditions (cf. Fig. S8 a, b and c). Apparently TBC is not stable under turbulent conditions, or ATBC degrades directly to tributyl aconite.

About 89% of the additives leached from printed PE under turbulent conditions are print derived. Of these 89%, about two thirds are DHAA and related compounds (cf. Fig. S8 d).

In conclusion, the effect of saline conditions on leaching behavior depends on specific compound properties of each distinct analyte and could not be jointly discussed for compound groups. Using this experimental set up and time span, UV-conditions have no, or diminishing, effects on leaching for most of the analyzed compounds. This could be due to UV-induced degradation of analytes in aqueous phase prior to their measurement, rather than to the effect of UV radiation itself.

A strong increase in leaching of all plastic additives was observed under turbulent conditions. With a 190 fold increase of leaching compared to ambient seawater conditions this effect was the largest for Irgafos® 168 phosphate and ranged between >15 and >70 for phthalates and mellitates (cf. Table 1). Turbulent conditions prevent concentration gradients on the polymer surface during the experiment because a continuous mixture with the water column exists. The relatively low molecular weight compounds diffuse into solution as no steady state equilibrium can develop at the polymer-water interface.

In the given experimental setup, the largest increase of leaching under turbulent conditions was observed for PVC plasticizers (cf. Fig. S6 a–e, g) and PE antioxidant (cf. Fig. S8 e), whereas the effect is less pronounced for PS oligomers (cf. Fig. S7 a–f). Since PVC and PE were much more flexible than the PS used in the experiment, a higher flexibility of the polymers might additionally increase the additive release under turbulent conditions due to easier mechanical deformation.

The remarkable loss of plasticizers from PVC and of antioxidant (Irgafos® 168 phosphate) from PE under turbulent conditions implies a loss in polymer stability in the long term due to increased chemical oxidation and subsequent fragmentation to microplastics. This process could be even more pronounced when polymers are additionally exposed to UV radiation. A study of a co-exposure to both UV radiation and turbulence would lead to further insights in this regard.

Under environmental conditions bio-fouling processes on plastic surfaces occur rapidly (e.g. Lobelle and Cunliffe, 2011) and might have an additional, possibly decelerating, influence on the leaching behavior of polymers.

3.4. Weight vs. surface

The mass of the different plastic samples in the experimental set up was identical. But as the polymers used in the experiments vary in density and the samples in thickness, there are considerable differences in surface area that is in contact with the aqueous phase. Fig. 3 shows leaching of all additives from PE, PS and PVC polymers normalized to weight (3a) and to surface area (3b) for the turbulent conditions.

Normalized to surface area, flexible PVC shows the highest leaching rate for additives followed by PS and printed PE, which are both lower by a factor of 10. PE without print releases nearly 160 times less additives than flexible PVC (cf. Fig. 3b). Differences in leaching rates are less pronounced and differ in order when normalized to weight (cf. Fig. 3a). Since most polymers are applied as hollow molds or foils, surface interactions with the surrounding liquid are of higher relevance regarding leaching behavior than the weight of the individual plastic item.

3.5. Assessment of potential global release of plastic related compounds into marine environments

3.5.1. Set up of the model calculation

Assuming the consumer plastic samples used for the leaching experiments to be representative for their respective polymer group, a global additive release into the oceans can be calculated. In 2013, 299 Mt. of plastics were produced worldwide. 29.6% were PE (HD- & LD-PE together), 6.9% PET, 7.1% PS and 10.4% PVC (Plastics Europe, 2015). The current content of plastic debris in the marine environment is still unknown and subject to ongoing discussion (Cózar et al., 2014; Eriksen et al., 2014; Law and Thompson, 2014). Based on plastic data from 2010, Jambeck et al. (2015) calculated that between 4.8 and 12.7 Mt. were introduced into the oceans that year. Combining these masses with the data from our experiments and the plastic production data from 2013, minimum and maximum amounts of plastic related compounds released from not printed PE, PS and flexible PVC into saline aqueous environments within the first 57, or 78 days, respectively, were calculated (cf. Table 2). This calculation is based on the assumption that plastics discarded into the oceans reflect the same relative proportions as in the production numbers and that our data for LD-PE concerning the antioxidant content, as prints were not taken into consideration, can also be applied to HD-PE.

It should be mentioned that some model calculations estimate much lower masses of plastics in the surface of the oceans. Based on globally collected data sets, Eriksen et al. (2014) estimate only 268,940 tons of floating plastic debris in the upper surface layer (0.5 to 200 m). Cózar et al. (2014) calculate between 7000 and 35,000 tons from surface tows. However, these estimates account for the surface layers and not the ocean as a whole and consequently assess only buoyant plastics. The large gap between plastics entering the ocean, much lower amounts actually found in surface samples and the global models derived from these measurements originates from the still only rudimentary understanding of the total input into the oceans, distribution and accumulation behavior of plastics, fragmentation behavior and the resulting size distribution. For the sake of this model the estimated minimum (4.8 Mt) and maximum (12.7 Mt) input of plastic calculated by Jambeck et al. (2015) is used.

Of the assessed plastics in the experiment, only PVC was responsible for the major portion of plasticizer release. In 2010, under ambient saltwater conditions, PVC leaching would result in a discharge of 7.1 to 18.7 tons of phthalates. Under turbulent conditions the phthalate release would increase to as much as 193 to 510 tons and additional 33 to 87.4 tons of TOTMs. Regardless of the experimental conditions, between 26.1 and 77.4 BPA per year could hypothetically be leached from flexible PVC. Other potential sources, mainly polycarbonates, not included in this study, enhance this input. Additives released from PVC make up 91.4% (SW condition), 94.4% (UV) and 73.6 (TURB condition)
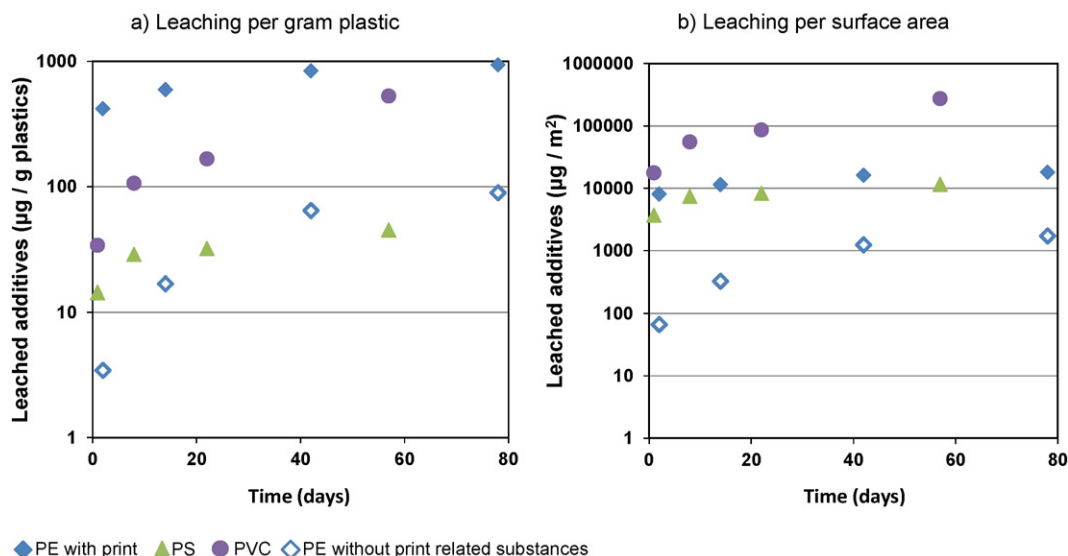
Fig. 3. Sum of selected additives leached from different plastic polymers into stirred salt water (TURB condition), illustrated as leached additives normalized to the weight of plastic versus leaching time (3a) and to plastic surface area (3b). PE = polyethylene, PS = polystyrene, PVC = polyvinylchloride.

of plastic related compounds from all plastics assessed in this model calculation respectively.

From PE only the leached antioxidant oxidation product Irgafos® 168 phosphate was included in the model calculation. Under turbulent conditions it represents around 22% of the calculated leaching burden, about 20 times more than in SW and UV conditions.

As additive compositions of plastics are highly variable even within one polymer type, the calculated model is only a rough estimate. However, it facilitates an approximation of the order of magnitude of annual additive and oligomer loads released from plastics into aqueous environments, which have to be considered as an additional stress factor for the ecosystem.

3.5.2. Comparison to concentrations found in the ocean

From the compounds analyzed, only phthalates, BPA and styrene oligomers were studied in ocean waters in a few studies. For Irgafos® 168, its phosphate and TOTM no marine literature values were found for comparison.

Typical concentrations of monoalkyl phthalate esters (MPEs), as common phthalate metabolites, in seawater range from 1 to 600 ng L^{-1} (Blair et al., 2009). In Chinese coastal waters, concentrations of phthalate esters average around 82 ng L^{-1}, with a range of 19–192 ng L^{-1} (Zhuang et al., 2011). The BPA content detected in seawater samples off the North West coast of Spain is 35 ng L^{-1} (Salgueiro-González et al., 2012). ST1 concentrations in Japanese coastal waters

are only present in trace amounts; in one location an average of 2.65 µg L^{-1} has been detected (Saido et al., 2014).

Assuming all additives remain in the top 200 m of the water column of the Earth's oceans with an even distribution of plastics and leached compounds, the additives and oligomers released within 57/78 days from plastics investigated in this study into ambient seawater lead to phthalate concentrations between 0.1 and 0.3 pg L^{-1} (low/high estimate), BPA concentrations between 0.37 and 0.97 pg L^{-1} and PS oligomer concentrations between 0.04 and 0.11 pg L^{-1}. Turbulent condition would enhance concentrations to ranges between 2.7 and 7.0 pg L^{-1} phthalates, 0.40 and 1.1 pg L^{-1} BPA and 0.21 and 0.56 pg L^{-1} PS oligomers, respectively. These calculations are based on a sea surface area of 361.84 × 10^6 km^2 (Charette and Smith, 2010) and neglect that some of these areas are shallower than 200 m.

These estimated values are all about three to six orders of magnitude lower than concentrations in the marine environment, but are related to less than three months of leaching and only 54% of the total 2010 plastic input. Over the last half of the century, around 6.1 billion tons of plastics have been produced (extrapolated from Plastics Europe (2015)). Together with other sources for the modeled compounds, e.g. ship paint, as well as riverine transport from land born sources and local accumulation zones, chemical leaching adds to the chemical pool and contributes to the concentrations reported in literature.

A uniform distribution of plastics and leached compounds can be omitted; local concentration and accumulation zones e.g. at coastal areas and gyre centers are prone to occur. Even if concentrations of chemicals derived from plastics in the marine environment are very low when averaged globally, their local impact in areas with higher plastic concentrations and high turbulence might be significant.

4. Conclusion

None of the plastics investigated are chemically inert. Release of additives or oligomers was observed in all cases. Leaching in ambient seawater is highest for printed PE, when normalized to the weight of initial plastic and almost 1‰ of the total plastic weight was released under turbulence conditions. When normalized to surface area, flexible PVC shows the highest leaching susceptibility. However, compared to compounds such as phthalates and BPA found in PVC, the leached compounds, such as ATBC (and its derivatives), are of lower concern from a toxicological point of view (Rahman and Brazel, 2006).

Table 2

Projected masses (in tons) of additives leached within the first 57/78 days from plastics analyzed in this study into the oceans in 2010. The low and high estimates are based on the minimum/maximum amount of plastics added to the oceans in 2010 as calculated by Jambeck et al. (2015). *Only Irgafos® 168 from the polymer itself, without considering the print. Information about mass fragments from MS and full names can be found in Table S1 of the supplementary material.

	Analytes, all values in tons	SW		UV		TURB	
		Low	High	Low	High	Low	High
From PVC	Σ phthalates	7.1	18.7	6.7	17.8	193	510
	BPA	26.5	70.0	26.1	69.0	29.3	77.4
	Σ TOTM	0.49	1.3	0.43	1.1	33.0	87.4
From PS	Σ PS oligomers	2.9	7.7	1.7	4.4	15.3	40.5
From PE*	Irgafos® 168 phosphate	0.40	1.1	0.37	1.0	76.3	202
	Σ all	37.3	98.8	35.2	93.2	347	917

About 89–98% of the additives leaching from PE bags investigated are derived from the print. Since prints strongly contribute to the chemical burden of plastics they should be avoided wherever possible. An appropriate abdication would avoid a high impact of additives into the environment without constriction in the principle use of the polymer.

Our experiments have shown a strong, positive relationship between turbulence and leaching. This indicates a more efficient release of plastic related compounds in areas of high turbulence such as coastlines. While having an impact, salinity alone, or combined with UV, did not show a distinct trend on additive release. Whether these factors increase or decrease leaching efficiency differs for each additive, pointing to additional factors not further discussed here.

During the first 57/78 days of their residence in the sea, between 35.2 and 917 t of plastic additives are potentially released into the oceans from the combined annual PVC, PS and PE load, depending on the true plastic input and local factors like UV radiation and turbulence. Unexpectedly, a very high mobilization of the major PE antioxidant was observed under turbulent conditions. Here, Irgafos® 168 phosphate represented 22% of the total additive load. Most likely the intensive loss of plasticizers and antioxidative components under turbulent conditions will have an effect on the polymers' fragmentation behavior in the marine environment on a longer time scale.

As a result of the model calculations, flexible PVC is responsible for the quantitative major portion (74–94%) of additives released from plastics assessed in this study into the marine environment. PVC releases high amounts of phthalates and BPA, which are toxicologically of particular concern. As also suggested in the PVC-Petition of the Environmental Protection Agency (EPA) (Andiman et al., 2014), it is ecologically worthwhile to restrict its use to a minimum and strictly avoid its disposal.

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Appendix A. Supplementary data

The supplementary material contains:

- A labeled GC chromatogram of saltwater leachates under turbulent conditions for each plastic type (Figs. S1–S4) and the corresponding table with compound names for each label and further characteristic mass spectrometric information (Table S1).
- A chromatogram of dissolved PE (Fig. S5).
- Plots for leaching behavior of individual additives under all conditions analyzed (Figs. S6–S8); data can be provided upon request.
- Two tables with details about the used GCMS and GCFID methods (Tables S2 and S3).

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