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Masterarbeit / Master's Thesis

Titel der Masterarbeit / Title of the Master's Thesis

Salinity and turbulence influence the leaching process of DEHP from PVC microplastics

verfasst von / submitted by

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angestrebter akademischer Grad / in partial fulfilment of the requirements for the degree of

Master of Science (MSc)

Wien, 2021 / Vienna 2021

Studienkennzahl lt. Studienblatt / degree programme code as it appears on the student record sheet:	UA 066 299
Studienrichtung lt. Studienblatt / degree programme as it appears on the student record sheet:	Interdisziplinäres Masterstudium Environmental Sciences
Betreut von / Supervisor:	Univ.-Prof. Dr. Thilo Hofmann
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Affidavit

I hereby affirm that this Master's Thesis represents my own written work and that I have used no sources and aids other than those indicated. All passages quoted from publications or paraphrased from these sources are properly cited and attributed.

The thesis was not submitted in the same or in a substantially similar version to another examination board and was not published elsewhere.

Date: 20.03.2021 Signature: 

Acknowledgements

At this point I would like to take the opportunity to thank all those who have supported me in the preparation of this work.

I would like to thank Prof. Thilo Hofmann for the opportunity to write my thesis in his research group and for providing the needed devices and equipment in his laboratory. Furthermore, I would like to thank Petra Körner, Wolfgang Obermaier and Nathalie Tepe for their practical help in the laboratory. Special thanks goes to my supervisors Thorsten Hüffer and Charlotte Henkel who always helped me during the complete master thesis. They especially supported me by showing me general lab practices, giving me suggestions for my experiments and proofreading my thesis. Moreover, they were always accessible for discussions and questions.

I would also like to thank the other proofreaders for their patience. Finally, I would like to thank my parents and friends who made my studies possible in the first place.

Abstract

Since the beginning of plastic production in the 1950s, the pollution of the environment by plastic has been increasing, which is why the problem is being discussed in science and the public. Since 2004, particular attention is being paid to the effects of microplastics (MP) on the environment. MPs are particles of different polymer types with a diameter of 1 to < 1000 μm, although a uniform definition has yet not been established. During the production of plastic, partially harmful additives such as phthalates are added to increase the functionality and service life of plastics. They can be released into the environment from MPs through leaching. The aim of this work is to investigate the influence of salinity and turbulence on the leaching process since those factors can be assigned to particular environments that are involved in MP transport such as rivers or oceans. This would help to identify environments which are most susceptible to additive pollution. Leaching experiments were carried out with PVC since this polymer introduces the most phthalates into the environment.

The results of the thesis show that leaching processes of DEHP plasticized PVC MPs are limited by aqueous boundary layer diffusion (ABLD). Increasing turbulence increases the leaching rate. Based on model results describing the diffusion processes of the phthalate, the increased leaching rate can be attributed to a thinner ABL surrounding the MP pellet. Hence, the shorter diffusion distance through the thinner ABL increases the leaching rate. Further, it was found that higher salinity reduces the leaching rates, as an addition of salt displaces the slightly water-soluble phthalates from the aqueous solution. Thus, the partition coefficient of DEHP between the MP pellet and the aqueous phase increases. Further, the results of the ABLD model show that leaching half-lives increase with increasing salinity and decreasing turbulence. However, even at slow leaching conditions, leaching half-lives were estimated to be 416 years, while residence times of MPs in rivers range from days to weeks. The main fraction of DEHP will thus be released into the oceans.

This study provides first insights of the effects of two environmental factors on the leaching process of a phthalate from PVC. However, other environmental factors need to be considered when assessing the leaching of phthalates into the environment. Further research is thus obligatory to gain a better understanding of the leaching processes and pollutant interactions of MPs and the environment.

Zusammenfassung

Seit Beginn der Plastikproduktion in den 1950er Jahren nimmt die Verschmutzung der Umwelt durch Plastik zu. Seit 2004 wird ein besonderes Augenmerk auf die Erforschung der Auswirkungen von Mikroplastik (MP) auf die Umwelt gelegt. MP sind Partikel verschiedener Polymertypen mit einem Durchmesser von 1 bis < 1000 μm, wobei sich eine einheitliche Definition noch nicht durchgesetzt hat. Bei der Herstellung von Plastik werden teils schädliche Additive wie Phthalate zugesetzt, um die Funktionalität und Lebensdauer der Kunststoffe zu erhöhen. Sie können durch Auswaschung aus MP in die Umwelt gelangen. Ziel dieser Arbeit ist es daher, den Einfluss des Salzgehalts und der Turbulenz auf den Auslaugungsprozess zu untersuchen, da diese Faktoren bestimmten Umweltsystemen zugeordnet werden können, die am MP-Transport beteiligt sind wie beispielsweise Flüsse oder Ozeane. Dies würde helfen, gefährdete Ökosysteme für Additivverschmutzung zu identifizieren. Die Auslaugungsversuche wurden mit PVC durchgeführt, da dieses Polymer die meisten Phthalate in die Umwelt einbringt.

Die Ergebnisse der Arbeit zeigen, dass Auslaugvorgänge von DEHP aus PVC MP durch die Diffusion durch eine wässrige Grenzschicht (ABL) limitiert werden. Mit zunehmender Turbulenz erhöht sich die Auslaugungsrate. Basierend auf Modellergebnissen, die die Diffusionsprozesse des Phthalats beschreiben, kann die erhöhte Auslaugungsrate auf eine dünnere ABL, die das MP-Granulat umgibt, zurückgeführt werden. Die kürzere Diffusionsstrecke durch die dünnere ABL erhöht daher die Auslaugungsraten. Weiterhin wurde festgestellt, dass ein erhöhter Salzgehalt die Auslaugungsraten reduziert, da die Zugabe von Salz die schwer wasserlöslichen Phthalate aus der wässrigen Lösung drängt. Dadurch erhöht sich der Verteilungskoeffizient von DEHP zwischen MP und der wässrigen Phase. Weiterhin zeigen die Ergebnisse des ABLD-Modells auf, dass die Halbwertszeiten der Auslaugung mit zunehmendem Salzgehalt und abnehmender Turbulenz zunehmen. Allerdings wurden selbst bei Bedingungen niedriger Auslaugunsraten, Halbwertszeiten von 416 Jahren berechnet, während die Verweilzeiten von MP in Flüssen nur von Tagen bis Wochen reichen. Der Hauptanteil von DEHP wird daher in den Ozeanen freigesetzt.

Diese Studie liefert erste Erkenntnisse über die Auswirkungen von zwei Umweltfaktoren auf den Auslaugungsprozess eines Phthalats aus PVC. Bei der Bewertung der Auslaugung von Phthalaten in die Umwelt müssen jedoch weitere Umweltfaktoren berücksichtigt werden. Weitere Forschung ist daher obligatorisch, um ein besseres Verständnis der Auslaugungsprozesse und Schadstoffinteraktionen von MP und der Umwelt zu erlangen.

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List of abbreviations

ABL	Aqueous Boundary Layer
ASE	Accelerated Solvent Extraction
BPA	Bisphenol A
CAS	Chemical Abstract Service
DDT	Dichlorodiphenyltrichloroethane
DEP	Diethyl Phthalate
DEHP	Di(2-ethylhexyl)Phthalate
DMP	Dimethyl Phthalate
DOM	Dissolved Organic Matter
FDA	Food and Drug Administration, USA
GC	Gas Chromatograph
HCl	Hydrochloric Acid
HOC	Hydrophobic Organic Compounds
IPD	Intraparticle Diffusion
KCl	Potassium Chloride
MS	Mass Spectrometer
MP	Microplastics

PAE Phatalate Esters

PAH Polycyclic Aromatic Hydrocarbons

PCB Polychlorinated Biphenyls

PE Polyethylene

PET Polyethylene Terephthalate

POP Persistent Organic Pollutants

PP Polypropylene

PS Polystyrene

PVC Polyvinyl Chloride

REACH Registration, Evaluation, Authorisation and Restriction of Chemicals, EU law

rpm Rotation per Minute

SVHC Substance of very high Concern

TOC Total Organic Carbon

1 Introduction

Since the beginning of mass production of plastics in the 1950s, the annual plastic production volume has increased drastically (Geyer et al., 2017). The global plastic production has increased by an average of ∼10 tonnes per year since 2008 (Figure 1). According to Plasticseurope (2019), 359 million tons of plastic were produced worldwide in 2018. The plastic industry is of great importance for many economic sectors. In Europe for instance, the plastic industry represents the seventh largest industry, producing 61.8 million tons of plastics in 2018, which represents 17.2% of the global plastic production. This corresponds to a revenue of more than 360 billion euros (Plasticseurope, 2019). The rapid increase in global plastic production can be explained by numerous factors. One advantage of plastic is that it can be formed into various shapes. Therefore, it can be used in different ways and has become part of our everyday life. In addition, plastic is light, durable and offers a cheaper alternative compared to many other materials in various industries (Bergmann et al., 2008). Hence, it is used in numerous sectors, such as packaging, electrical and automotive industries, agriculture and construction. The sectors with the highest plastics consumption in Europe are found in the packaging and construction industry (Plasticseurope, 2019). Plastics helps saving energy, reduces transportation costs due to its light weight and improves our health through a variety of medical products (Thompson et al., 2009).

The pollution of the environment by plastic waste is receiving more and more attention in science and public. Special attention is given to the disposal of plastic and its sinks in the environment. In order to obtain the full benefit from the life cycle of a plastic object, disposal and recycling must be well organized (Rochman et al., 2013a). While Europe had a recycling rate of 42% in 2018 (Plasticseurope, 2019), 91% of the world's plastic waste is still not adequately managed (National Geographic, 2020). Since the beginning of mass production, plastic has accumulated in rivers and in the countryside (Buschmann

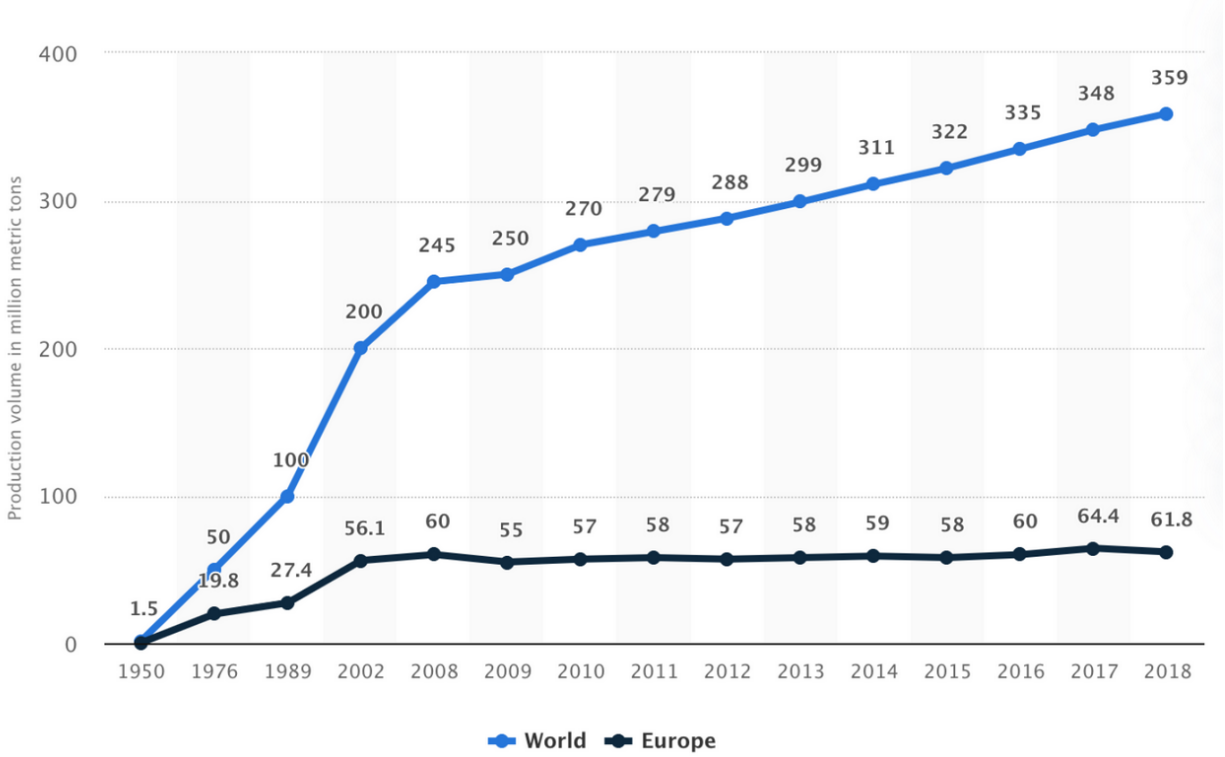

Figure 1: Rising plastic production from 1950 to 2018 in million tons per year worldwide (blue) and Europe (black) (Garside, 2020).

and Freund, 2019; Barnes et al., 2009). The biggest sink however, are the oceans, where approximately 10% of the plastic produced ends up (Thompson, 2006). Thereby, a share of 80% of the plastic waste which can be found in the sea is disposed off on land, where it is carried into oceans by wind and surface runoff (Andrady, 2011). In the ocean, plastics are transported by ocean currents a few hundred kilometres away from the coasts and ends up in large eddy currents, such as the *Great Pacific Garbage Patch*. Once there, it takes hundreds to thousands of years to decompose (Elias, 2018, Moore, 2008). For example, half of the plastic found in oceans is older than 13 years and 80% is older than 4 years (Koelmans et al., 2016). Plastic is therefore a long lasting pollutant and comes in various sizes and shapes.

Many of the in the ocean floating plastic fragments are leftovers from packaging, plastic bags, fishing equipment, shoes, cigarette filters and other household items (Derraik, 2002). Those plastic fragments include microplastics (MP). They refer to plastic fragments with

a size of 1 to < 5000 µm (MoE, 2015) although a uniform definition has yet not been established. Hartmann et al. (2019) propose a size definition according to the SI system of 1 to < 1000 µm. Due to their small size, they are highly bioavailable. The ingestion of those particles poses a risk to marine flora for several reasons. Supersaturation from MP blocks their gastro-intestinal passage, which may lead to death due to malnutrition (Moore et al., 2001). In addition to the physical hazards, there are rising concerns about the chemical hazards of MPs to the environment and its organisms. Thereby, MP is acting as a vector for various chemicals. On the one hand, MPs can sorb existent pollutants from the water and release them back to aquatic organisms. Compared to other environmental carrier media with higher abundance, such as suspended organic particulates or water, plastics however plays a negligible role as a transport vector to marine organisms for those compounds (Koelmans et al., 2016). On the other hand, various auxiliary compounds, so-called additives, can be introduced into the surrounding water. Additives are added during plastic production to increase its functionality and service life. These include dyes, UV stabilisers, flame retardants, as well as plasticisers such as phthalates and bisphenol A (BPA) and many other substances, which can act endocrine disrupting and carcinogenic (Talsness et al., 2009; Teuten et al., 2009).

Since additives can leach into their surrounding during the life span of plastics, leaching processes of additives into aquatic systems are currently in the focus of science (Koelmans et al., 2014; Luo et al., 2019a). While the main focus is put on additive release from medical items (Rose et al., 2012; Gayathri et al., 2004) and food packaging (Fang et al., 2017; Keresztes et al., 2013), only little research exists on the influence of various environmental factors influencing leaching. Those include salinity, turbulence, temperature, dissolved organic matter (DOM) content and the formation of biofilms on the plastic surface. Understanding how these factors influence the leaching process would be relevant for the environmental risk assessment for these materials. This would help identifying aquatic ecosystems which are most susceptible to additive pollution. Among the aforementioned environmental factors, turbulence and salinity can be assigned to particular

environments that are involved in MP transport. For instance, oceans and rivers have higher turbulence compared to lakes due to wave movements and river currents, while rivers and lakes have a lower salinity compared to oceans. Analysing the impact of salinity and turbulence on the leaching process of additives is therefore of importance to identify environments which are most susceptible to additive leaching. Such findings are practically relevant for environmental risk assessment.

2 State of Knowledge, Aims and Hypothesis

2.1 State of Knowledge

Microplastics are a risk for the aquatic environment

Plastics consist of polymers, whereby countless polymer types exist today. The most used polymers include polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polystyrene (PS) and polyethylene (PE) (Plasticseurope, 2019). Ocean surface samples mostly contain PP, PE, PVC, PET and styrofoam (expanded PS) which occur in various sizes such as MPs (Andrady, 2015).

MPs are divided into primary and secondary MP according to their origin (Cole et al., 2011). Primary MPs are produced in their final form for direct consumption and are used in a wide range of applications. For instance, plastic granules which are used as a basic material in the plastic industry for plastic production are considered as primary MPs (Do Sul et al., 2009). While primary MPs are produced in small units for special purposes, secondary MPs have various sources originating from fragmentation of larger plastic elements. Fragmentation involves physical, biological and chemical processes that reduce the structural integrity of the plastic. Most of the secondary MPs in the environment are degraded by photolytic degradation through the sun's UV radiation or physical abrasion, for instance due to wave movements (Andrady, 2011). Other sources of secondary MPs are the abrasion of car tyres and shoes which end up in the wastewater (Moore, 2008). Moreover, up to 1900 plastic fibres from synthetic textiles can be flushed into the sewage system per washing cycle (Browne et al., 2011). Once there, secondary MPs can pass wastewater treatment

plants and hence end up in rivers and finally in oceans (Mason et al., 2016).

MPs are found in high concentrations in the environment. For instance, in Belgian ports concentrations of up to 390 MP particles per kilogram of beach sediment have been measured (Claessens et al., 2011). Such a high presence of MPs in aquatic habitats has numerous effects on the environment and its creatures. Due to their small size, MPs can be ingested by even the smallest organisms such as zooplankton and are therefore bioavailable. Moreover, MPs are consumed by larger creatures such as worms, echinoderms, bryozoans, sea cucumbers and crustaceans as they only partially select their food (Ward and Shumway, 2004). Small organisms suffer in particular from the uptake of MPs, as the smaller gastro-intestinal passage can be blocked more easily. This can lead to death due to malnutrition (Moore et al., 2001). However, larger organisms such as fish and seabirds which seek their food on the water surface suffer from the intake of MPs as well (Moore et al., 2001). The ingested MP particles can lead to cell death, reduced fertility, inflammations and wounds in the intestines and can accumulate in tissues of the organisms (Rochman et al., 2015a). A study by Rochman et al. (2015b) discovered that MPs in the form of particles and fibres can be found in 67% of all stomachs of commercially purchased fish in the US. Since MPs reach humans at the end of the food chain, there is currently increasing concern about the effects of MPs on human health.

The capability for MPs to act as a sorbent for hydrophobic organic compounds (HOC) has been demonstrated in several studies (Teuten et al., 2007; Rochman et al., 2013b; Lohmann, 2012). Sorption is the phase transfer process of a substance from one phase to another (Atkins and De Paula, 2013). While absorption describes the transfer into a different phase, adsorption is the accumulation at the interface between two phases. Due their small size, MPs have a high surface-to-volume ratio compared to bigger plastic particles, which increases the frequency of interactions with HOC. Those include pharmaceuticals, fertilisers and pesticides (herbicides, insecticides, fungicides) which are released into the environment for instance from wastewater and agricultural activities (UBA, 2017). They accumulate in the groundwater, rivers, oceans (Luo et al., 2019b), soils (Corradini

et al., 2019) and in the air (Gasperi et al., 2018). These substances include polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT), polycyclic aromatic hydrocarbons (PAHs), various drugs and other organic substances (Lohmann, 2011). Toxicological effects have been demonstrated for many of them. They can interfere with the hormonal system of organisms, influence metabolism and reproduction, damage organs and have carcinogenic effects (Rönnefahrt et al., 2012; UBA, 2017). Moreover, due to the hydrophobic character of those substances and the non-polar structure of most polymers such as PS, PE and PVC, MP is particularly favourable to the sorption of HOC (Mayer et al., 2003; Seidensticker et al., 2018). For instance, Hüffer and Hofmann (2016) found a strong relationship between sorption coefficient of MPs of four different polymer types (PA, PE, PVC and PS) and the hydrophobicity of seven aliphatic and aromatic organic sorbates. Therefore, hydrophobic interactions are of major importance which is why non-polar polymers can be used for passive sampling (Namieśnik et al., 2005). After sorption, the concentration of these substances can be several orders of magnitude higher in MP than in the surrounding medium. This depends on the residence time of MPs in water (Mato et al., 2001) and the difference in fugacity between the MP pellet and its surrounding (Kwon et al., 2017). Sorbed HOC can then be transported over long distances to the most remote regions, such as the arctic (Do Sul et al., 2009; Zarfl and Matthies, 2010).

While sorption of organic substances on MPs is undisputed in science, the effect of MPs as a transport vector to organisms via ingestion is yet not understood (Koelmans et al., 2016; Browne et al., 2013). Although MPs have a higher sorption affinity for HOC compared to other carrier media, such as natural organic and inorganic particulates or water, they are still present in much lower concentrations (Kershaw, 2015). Koelmans et al. (2016) estimates that only $\sim$0.001‰ of HOC bound to environmental media in the ocean is bound to plastics. Therefore, they argue that MPs play a negligible role as a transport vector for foreign organic substances to organisms. Moreover, Kwon et al. (2017) argue that HOC have a high fugacity in the water phase and a low fugacity in MP. This is why MPs should

be considered as a final sink and not as a source of HOC. For instance, Beckingham and Ghosh (2017) have shown that the transport of PCBs to the worm *L. variegatus* can be reduced by the presence of plastic. This is caused by the so-called cleaning effect of MPs which can reduce the body burden of HOC. Similar results have been shown by the modelling approach of Bakir et al. (2016).

Additives

MPs are considered a source of additives to the aquatic environment (Kwon et al., 2017) since additives have a low fugacity in the water phase compared to a high fugacity in plastic (Karapanagioti et al., 2011). Compared to the vector function of MP, where foreign HOCs from the water phase are transported, additives are introduced by MP into the environment. Therefore, science focuses more and more on the processes of additive release since desorption of chemicals from MPs has been far less studied then sorption and might play a more important role as a vector for HOC to aquatic organisms than previously assumed.

Especially phthalates which are added to polymers as plasticizers have been linked to diseases such as breast cancer (López-Carrillo et al., 2010), DNA damage to human sperm (Hauser et al., 2007), liver damage (Kambia et al., 2001), obesity (Teitelbaum et al., 2012) and environmental hazards (Staples et al., 1997). One of the most used groups of phthalates are phthalate esters (PAE), which are used since the 1930s to plasticise brittle PVC to increase its durability and flexibility by lowering its glass transition temperature (Graham, 1973; Staples et al., 1997). Many PAEs have raised concerns regarding human health and environmental impacts which is why they are listed as priority pollutants in the EU, US and Canada (Ventrice et al., 2013; EPA, 2014). One of the most applied phthalate esters is the colorless, non-volatile and odorless, viscous liquid Di-2-ethylhexyl phthalate (DEHP) (Figure 2). With more than half of the phthalate production worldwide, it is considered the most used PVC plasticizer (Carlson, 2010).

DEHP is considered a high performance phthalate an is used to produce highly elastic PVC.

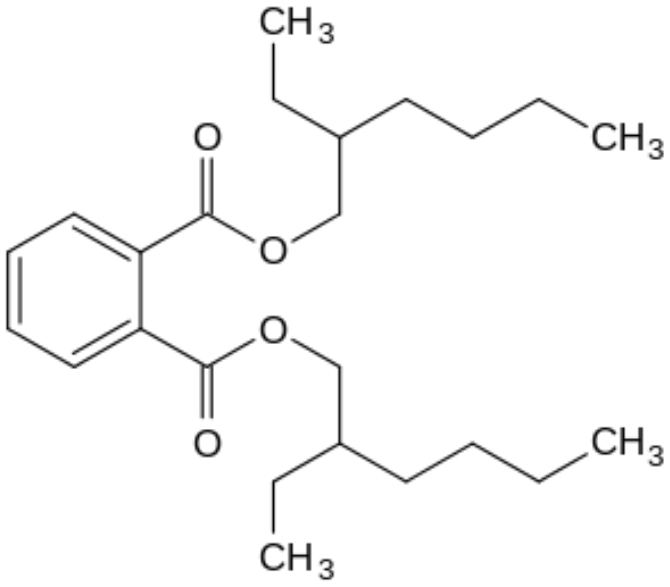

Figure 2: Chemical structure of the ortho-phthalate DEHP ($C_{24}H_{38}O_4$) (SpecialChem, 2017).

It offers good gelling and shows reasonable good flexibility at low temperatures and resistance to high temperatures (SpecialChem, 2017). In addition, its low costs lead to a widespread use of DEHP-plasticized PVC in commercial products such as tubings, packaging material, clothing, roofing, flooring and medical applications like blood containers. (Tickner et al., 2001; Shea et al., 2003). Products made out of plasticized PVC contain up to 40% DEHP (Wilkes et al., 2005). A common DEHP content for flexible PVC is ∼30% (Stark et al., 2005). Due to its adverse effects on humans and the environment some countries like the US limited its share to 0.1% in special items such as toys since the additive is especially toxic for children (SpecialChem, 2017). Moreover, DEHP is listed as a substance of very high concern (SVHC) under the European REACH legislation (Registration, Evaluation, Authorisation and Restriction of Chemicals). This is why its application is prohibited in Europe since 2014 (ECHA, 2020). The US Food and Drug Administration (FDA) limited its usage in food packaging for fatty foods, since DEHP easily extracts into non-polar solvents (SpecialChem, 2017). Even though DEHP consumption is currently decreasing due to the concerns about its adverse effects, it is still the most commonly used phthalate in the world (Carlson, 2010; SpecialChem, 2017). Therefore, DEHP can be considered a

model phthalate since a lot of data has been collected on it.

DEHP is commonly found in waters and sediments in the environment due to its high production volume, its worldwide use and its leachability (Helm, 2007). Since DEHP has a low water solubility of 3 µg/L (ECHA, 2020), it is often linked with particles but can also be detected in water samples. For instance, Peijnenburg and Struijs (2006) found DEHP concentrations of up to 2.35 µg/L in Lake Bergum and 19,200 µg/kg in sediments in the Nordsea Canal. Moreover, DEHP was found in several river and seawater samples worldwide (Zhang et al., 2018; Eremina et al., 2016; Liu et al., 2012). Once in the environment, DEHP has shown to be persistent and is therefore assigned to the group of persistent organic pollutants (POP) (ECHA, 2020). Even though mineralization of DEHP has been observed in anaerobic environments (Staples et al., 1997), biodegradation of DEHP is generally an extremely slow process due to the strong bonding to organic matter (Feng et al., 2002). Additionally, abiotic factors do not play an important role in the environmental degradation of DEHP. For instance, photolysis through natural UV-radiation (Lertsirisopon et al., 2009) as well as hydrolysis seem to be negligible (Lertsirisopon et al., 2009; Chang et al., 2005). Given the high persistence of DEHP in the environment, it is important to understand its input pathways and hence the corresponding leaching processes.

Leaching Process from spherical Particles

Leaching is the process of the extraction of a solute from a solid by dissolving it in a liquid solvent (Richardson et al., 2002). In this study, leaching of DEHP from spherical MP into aqueous environments is examined (Figure 3). Leaching can be divided into two parallel sub-steps. Firstly, the solute diffuses through the pores or matrix of the carrier substance to reach its surface which is called intraparticle diffusion (IPD). Secondly, the solute is transferred through an aqueous boundary layer (ABL) with its thickness δ. This process is called aqueous boundary layer diffusion (ABLD) and includes the partitioning of the solute between the carrier substance and the solvent (Grathwohl, 2014).

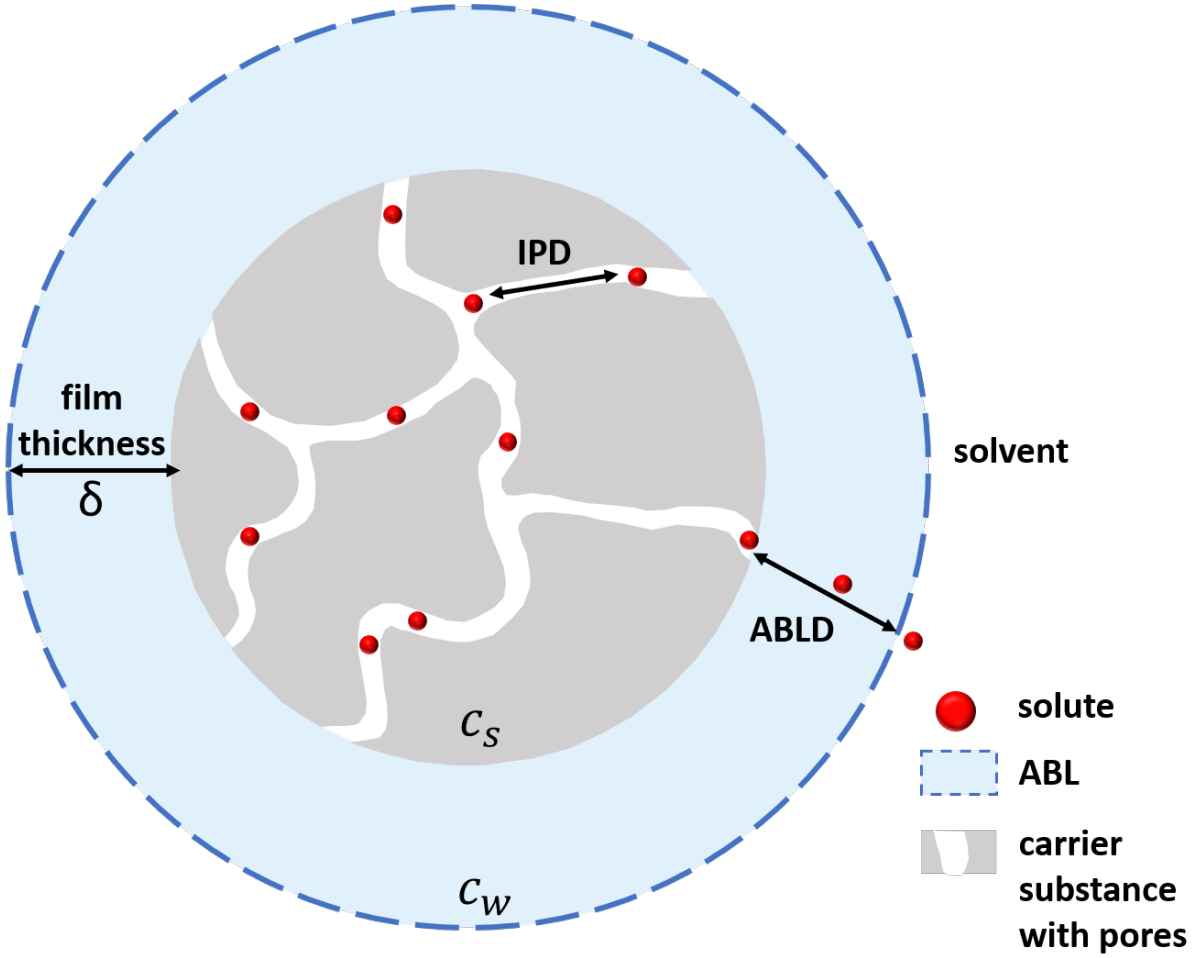

Figure 3: Leaching process, showing the IPD of the solute within the pores of the carrier substance and the diffusion through the ABL with its film thickness δ into the solvent. C_S [µg/kg] and C_W [µg/L] describe the concentrations in equilibrium of the solid and liquid phase.

The equilibrium distribution of a substance between two different phases is described by a partition coefficient. It is specific to the respective substance and is also called the Nernst distribution coefficient (Schwarzenbach et al., 2002, p. 59). The distribution of the substance between two different phases represents a dynamic equilibrium. An important variant of the Nernst distribution coefficient is the n-octanol-water coefficient K_{OW} which represents the distribution of a substance between an organic phase and water. It is particularly relevant for lipophilic and hydrophobic substances (Schwarzenbach et al., 2002, p. 223). Besides K_{OW}, the distribution value between a solid phase and a liquid phase, K_D

[L/kg] can be defined by the equation

$$\mathrm{K}_D = \frac{\mathrm{C}_S}{\mathrm{C}_W} \tag{2.1}$$

where C_S [µg/kg] and C_W [µg/L] describe the equilibrium concentration of the compound in the solid and liquid phase respectively (Schwarzenbach et al., 2002, p. 93). If the general solid phase S in Formula 2.1 is replaced by the specific solid PVC, the distribution coefficient between PVC and water

$$\mathrm{K}_{PVC-W} = \frac{\mathrm{C}_{PVC}}{\mathrm{C}_W} \tag{2.2}$$

is obtained. The time until equilibrium between the PVC and water phase is established depends on molecular properties of the solute and the particle, as well as on the basic parameters of the liquid phase (Thompson et al., 2009). The release of the solute is controlled by the kinetics of the IPD and ABLD, whereby the slower process controls the overall diffusion process (Grathwohl, 2014).

Intraparticle Diffusion (IPD)

The IPD describes the internal mass transfer mechanism of a compound in the pore structure and matrix of a spherical particle (Wu et al., 2009). In case the IPD is more slowly than the ABLD, the overall leaching kinetics are limited by the IPD and can be described as

$$\mathrm{f}_{desorbed}(t) = 1 - \frac{M_t}{M_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2}\ exp\ (-\frac{n^2\ \pi^2\ t\ D_{PVC}}{R^2}) \tag{2.3}$$

where $\mathrm{f}_{desorbed}$(t) describes the cumulative fraction of a solute leached from the PVC particle over time (Endo et al., 2013b). The parameter M_t represents the mass of the solute in the PVC particle at time t, and M_0 expresses the initial mass. The radius of the PVC particle is described by R and the diffusion coefficient in PVC is expressed by D_{PVC} which

is the only solute specific parameter of the model (Kwon et al., 2007). The coefficient D_{PVC} is influenced by various internal factors, such as the molecular weight of the solute. Molecules with a low weight have higher diffusion coefficients since this facilitates the migration through the porous medium (Stark et al., 2005). In order to diffuse through a solid matrix, a compound needs to change its position in the grid by overcoming an energy barrier. This process is enhanced at higher temperatures, which increases diffusion coefficients (Richardson et al., 2002). This is known as the Arrhenius-relation (Mehrer, 2007). As shown in experiments from Kim et al. (2003), who examined the extraction of DEHP from thin PVC sheets at different temperatures, this fact also applies to the leaching process of DEHP-plasticized PVC.

The polymer PVC is made of vinyl chloride monomers (C_2H_3Cl). During the PVC production, the vinyl chloride molecules combine to form long PVC chains in a chemical reaction known as polymerization. A distinction is made between unplasticized PVC and plasticized PVC. During the production of DEHP-plasticized PVC, DEHP penetrates into the molecular space of PVC chains. As DEHP is an external plasticizer, it does not from chemical bonds with PVC but rather forms weaker physical interactions (Kastner et al., 2012). Those interactions include polar orientations, which reduce the intermolecular forces between the polymer chains such that the plastic becomes soft and flexible (Gilbert, 2016, p.353). The polar carbonyl groups of DEHP interact with the polar carbon chloride bonds of PVC polymer chains which makes them compatible. However, it is weakened by the absence of interactions between the non-polar parts of the plasticizer. Consequently, the long PVC chains become more flexible due to less interaction between each other (Wilkes et al., 2005). At high levels of DEHP, the intramolecular interactions between the polymer chains diminish, resulting in a decrease in overall binding strength. This leads to higher release rates of DEHP from PVC over time. The migration of DEHP is therefore proportional to the amount of added DEHP (Kim et al., 2003).

Aqueous Boundary Layer Diffusion (ABLD)

The ABLD can be described by Fick's first law (Endo et al., 2013b) which describes a steady-state diffusion (Schwarzenbach et al., 2002, p. 786). In case the ABLD in the PVC particle is more slowly than the IPD, the leaching kinetics of a solute are controlled by the ABLD (Kwon et al., 2007; Endo et al., 2013a). The process can be described as

$$\mathrm{f}_{desorbed}(t) = 1 - \frac{M_t}{M_0} = 1 - exp\ (-\frac{D_W\ A_{PVC}\ t}{\delta\ V_{PVC}\ K_{PVC-W}}) \tag{2.4}$$

where A_{PVC} is the surface area of the PVC particle, δ describes the thickness of the ABL and V_{PVC} expresses the volume of the PVC particle. The parameter D_W [m^2/s] describes the diffusion coefficient of the solute in water and can be calculated from the relationship with its molecular weight M [g/mol] (Schwarzenbach et al., 2002) by

$$\mathrm{D}_W = \frac{2.7\ \mathrm{x}\ 10^{-8}}{M^{0.71}}. \tag{2.5}$$

The coefficients D_W and K_{PVC-W} represent the only solute specific parameters in the ABLD model, where K_{PVC-W} is considered the most important parameter for the assessment of ABLD dominated leaching processes from MPs (Kwon et al., 2017; Kastner et al., 2012). For instance, substances like DEHP which are hydrophobic ($log\mathrm{K}_{OW} = 7.5$) and have a low water solubility desorb more slowly. Consequently, the probability of ABLD dominated leaching kinetics is high for substances with a high K_{PVC-W}. For more polar solutes, leaching rates have been observed to be more IPD-controlled since the diffusion into the solvent is facilitated (Kwon et al., 2006).

In contrast, a higher salt content of the aqueous solution can impede leaching into the surrounding medium on neutral organic solutes, which is called the Setschenow relationship or salting-out effect. The dissolved salt increases the cohesive energy of the surrounding aqueous solution and therefore increases the cavity formation energy cost, when a compound is transferred through the ABL (Schwarzenbach et al., 2002). Hence, higher salinities

may alter distribution coefficients. Furthermore, dissolved organic matter (DOM) can increase distribution coefficients of organic compounds and therefore increase leaching rates (Seidensticker et al., 2017; Smith et al., 2011). Leaching is therefore enhanced by the DOM facilitated transport of organic compounds through the ABL (Ter Laak et al., 2009). Another factor which changes leaching rates of phthalates from MPs is turbulence. Suhrhoff and Scholz-Böttcher (2016) have shown that leaching rates of various phthalates increase with increasing turbulence. Similar results have been found by Rakowska et al. (2017), who examined the desorption of PAHs under turbulent conditions. Results show that turbulence increases desorption by a reduction of particle aggregate size through induced shear forces. However, little is known about whether turbulence alters ABLD or IPD processes of phthalates from PVC MPs.

There are several studies investigating leaching of phthalates from PVC and PS. The main focus is put on phthalate release from medical items, such as infusion sets (Rose et al., 2012; Bagel-Boithias et al., 2005; Tickner et al., 2001) and blood storage bags (Gayathri et al., 2004). For instance, Latini et al. (2010) were examining the leaching of DEHP from PVC into medical devices. They found, that the main factors determining to what extent DEHP migrates from medical items are the share of DEHP, storage time and the degree of PVC degradation. Additionally, Rose et al. (2012) found that leaching of DEHP from PVC into infusion sets increased with higher temperatures. Moreover, studies are analyzing phthalate release from food packaging such as food containers (Fang et al., 2017; Fasano et al., 2012) with a focus on leaching into fatty foods (Yuan et al., 2020) since the hydrophobic character of phthalates increases their solubility in fatty solvents (Hamdani and Feigenbaum, 1996). However, little is known how environmental factors can influence the leaching process of phthalates from PVC MPs in aqueous environments.

While Suhrhoff and Scholz-Böttcher (2016) have shown the influence of some environmental factors (salinity, turbulence, UV-radiation) on leaching of DEHP from PVC sheets, little is known about the governing process determining the leaching process of spher-

ical DEHP plasticized PVC particles such as MP and its release kinetics. Identifying the governing leaching process would allow to calculate leaching half-lives, which are important in order to understand when and where leaching mainly takes place. Short leaching half-lives ranging from days to weeks would indicate that the main part of additives would be released in rivers, where MP is entering via sewage treatment plants (Mason et al., 2016). River residence times for MP in the river Rhine for instance can be up to 10 days (Mani et al., 2015). In contrast, higher leaching half-lives would point out that leaching mainly takes place in the oceans. However, environmental factors could influence or even change the governing leaching process, leading to a shift in leaching half-lives. Salinity and turbulence are particularly important in this context since they can alter leaching processes as mentioned before. While temperature and DOM-content are not associated to a particular ecosystem, salinity and turbulence are. For instance, rivers are more turbulent than lakes, while oceans have a higher salinity than rivers, but are similarly turbulent. Knowing their impact would help to understand and predict which aquatic ecosystems are most susceptible to additive pollution and are therefore highly important for an environmental risk assessment.

Since DEHP is very hydrophobic and has a very low water solubility of 3 µg/L water (ECHA, 2020), it is challenging to investigate the corresponding leaching processes. Therefore, an infinite sink developed by Henkel et al. (2019) is used for the leaching experiments. It is intended to take up DEHP from the aqueous phase in order to keep its concentration well below its water solubility. This is important since the equilibrium would gradually shift more towards the MP pellet as the concentration in the water phase rises if an infinite sink would not be applied. Hence, it ensures concentration gradients on the polymer surface during the leaching experiments. This is especially important for long term experiments since the governing leaching process could not be identified, when reaching a concentration of 3 µg/L water. The infinite sink therefore assures that leaching processes remain unaffected from solubility problems and helps determining the governing leaching processes. Moreover, this approach is a step towards a more environmentally realistic scenario since water bodies in nature can be considered as an infinite sink as well.

2.2 Aims and Hypotheses

The preceding discussion demonstrated that there are no known studies that examine the leaching process of DEHP plasticized PVC MPs with an infinite sink and modelling approach. Moreover, it is not known how salinity and turbulence alter the leaching processes. This however would be important to better understand where and when DEHP enters aquatic environments, due to the adverse effects of DEHP on the environment and its wide use as a plasticizer for PVC. Special attention should be payed to MP particles, since they are highly bioavailable and a source of plasticizers to aquatic ecosystems (Kwon et al., 2017). Consequently, the following research question is defined: *How do the two environmental factors, turbulence and salinity, influence the leaching process of DEHP from PVC MPs into aqueous solutions?* To answer this question, batch experiments were carried out in the lab.

To show whether ABLD or IPD is the limiting factor of the leaching process, the generated data is compared to the previously presented diffusion models. Since MP particles with a large diameter (∼5 mm) are used in this study, the leaching process could be limited by IPD. This can be explained by the fact that the diffusion distance that DEHP has to travel in the particle to the surface is increased. The amount that can be released at the surface could therefore be limited by IPD. However, studies indicate that compounds with high K_{OW} partition coefficients like DEHP are usually limited by ABLD due to their low diffusion rates in water. Therefore, leaching rates are highly dependent on K_{PVC-W}, as the most important variable (Lampert et al., 2015; Kastner et al., 2012; Seidensticker et al., 2017). In contrast, leaching kinetics of compounds with low hydrophobicity can be controlled by IPD (Fries and Zarfl, 2012; Teuten et al., 2009).

Hypothesis 1: The leaching process of DEHP plasticized PVC MPs is dominated by ABLD.

Further, leaching rates of DEHP from PVC MPs in aqueous systems may decrease with increasing salinity. This assumption is supported by the previously presented salting out effect and especially holds true for neutral organic substances due to their high cavity formation energy costs. Moreover, the salting out effect is large for substances with high K_{OW} values

like DEHP, since they are more susceptible to an increase in cohesive energy (Endo et al., 2012). This is further supported by Sajiki and Yonekubo (2003), who found out that leaching rates of the common plasticizer BPA are slower to seawater than to river water. In case the leaching process is ABLD limited, a possible shift of the partition coefficient K_{PVC-W} for DEHP shall be determined with the help of the ABLD model. However, there are also findings which do not align with this hypothesis. For instance, Suhrhoff and Scholz-Böttcher (2016) showed that salinity did not show a distinct trend in phthalate release from PVC MPs. However, leaching rates differed for each phthalate. The main reasons for that are that salinity variations induce complex changes in compound and water chemistry and have impacts on ionic strength, polarity, dipole moment and pH. However, Endo et al. (2012) argues that the relevance of the salting out effect is low, but existent.

Hypothesis 2: Leaching rates of DEHP from PVC MPs in aqueous systems are decreasing with increasing salinity.

Even though Suhrhoff and Scholz-Böttcher (2016) indicate a clear positive relationship between leaching rates and turbulence, little is known about whether turbulence alters ABLD or IPD processes. We hypothesize that turbulence decreases the thickness of the ABL which causes a faster diffusion through the film and therefore leads to a higher external mass transfer. IPD might be unaffected by a change in turbulence.

Hypothesis 3: Leaching rates of DEHP from PVC MPs in aqueous systems increase with increasing turbulence.

3 Material and Methods

3.1 Used Materials and Preparations

PVC Pellets

The PVC pellets used in this study (Industrie Generali spa, Italy) had a DEHP content of ∼35% as the only phthalate as stated by the manufacturer (Figure 4). They had a diameter of ∼5 mm and weighed between 27.75 and 29.25 mg.

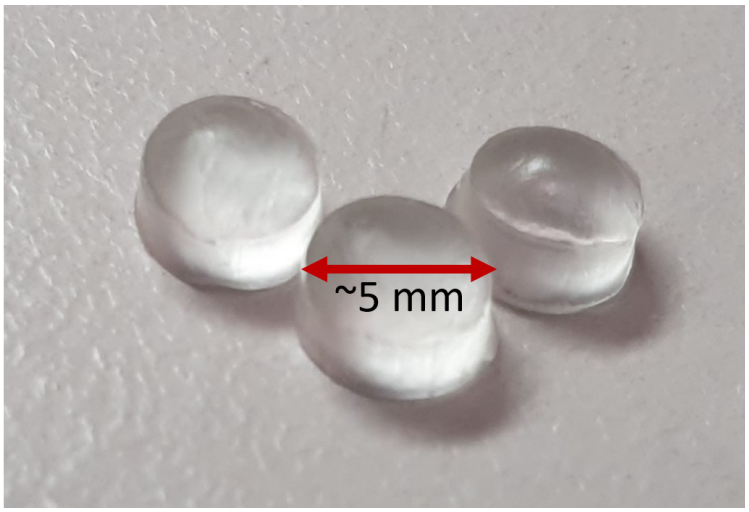

Figure 4: PVC MP pellets with a diameter of ∼5 mm.

Infinite Sinks

The infinite sink (Figure 5) was made of 10 mg activated carbon powder packed in a 4 x 4 cm piece of filter paper, stabilized with a stainless steel wire according to Henkel et al. (2019). Before the sinks were built, wires were wiped with acetone and placed in n-hexane for at least 10 minutes to ensure that the wires were free of organics. The material specifications used for the infinite sinks are listed in Table A1 in the appendix.

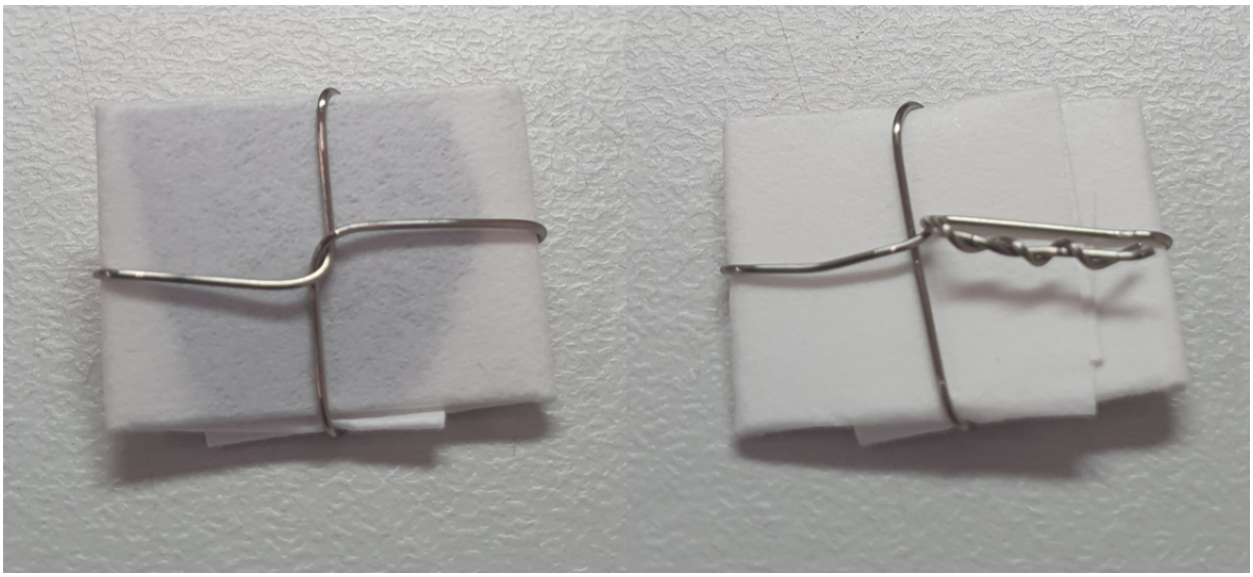

Figure 5: Infinite sink from the front (left) and bottom (right). It consists of 10 mg activated carbon powder packed in a 4 x 4 cm piece of Grade 50 filter paper stabilized with a stainless steel wire.

Saline background Solutions

Three solutions with graded salt contents (1 mM potassium chloride (KCl), EPA moderate hard water, artificial sea saltwater) were prepared. 1 mM KCl solutions were used for the turbulence leaching experiments to be able to measure the pH-value. The salts used for the solutions are listed in Table A2 in the appendix.

To prepare the 1 mM KCl solution, 74.55 mg KCl were mixed with 1 L ultrapure water in a 1 L bottle and shaken until the salt was completely dissolved. Any glassware used was rinsed three times with acetone and then muffled at 550°C for 5 hours. The moderate hard water solution was made following the EPA guideline (EPA, 2002). 60 mg calcium sulphate dihydrate ($CaSO_4$*2 H_2O), 60 mg magnesium sulfate ($MgSO_4$), 4 mg potassium chloride (KCl) and 96 mg sodium hydrogen carbonate ($NaHCO_3$) were mixed with 1 L ultrapure water and shaken until the salts were completely dissolved. To prepare the artificial saltwater solution (EPA, 2002), 38 g of sea salt were mixed with ∼0.7 L ultrapure water in a 1 L volumetric flask and shaken until the salt was completely dissolved. Then the volumetric flask was filled up to 1 L with ultrapure water. The solution was transferred to a 1 L bottle.

Since more than 1 L of each solution was needed per leaching experiment, several solutions were prepared and stored in a fridge at 4°C to prevent biofilm formation.

Furthermore, the total organic carbon (TOC) content, pH value and electric conductivity were measured to ensure stable and uniform conditions. For the TOC-analysis, samples of the solution were measured using a TOC-analyzer (Shimadzu, Duisburg, Germany). First, the samples were acidified to pH < 2 with hydrochloric acid (HCl). Then, they were oxidized at 680°C with subsequent NDIR detection. Electric conductivity and pH values were measured using a Multi 9620 IDS multiparameter benchtop meter (WTW, Weilheim, Germany). The TOC content, electric conductivity and pH value for each prepared solution were stable (Table A4 in the appendix).

3.2 Leaching Experiments

Following, the procedure of the leaching experiments is shown by means of the four steps execution, sampling, extraction and measurement (Figure 6).

Execution of the Leaching Experiments

The experiments were carried based on the procedure of the leaching experiments of Henkel et al. (2019). Therefore, 60 mL vials, which were previously rinsed three times with acetone and muffled at 550°C for 5 hours, were filled with 40 mL of the respective background solution (depending on the experiment). Furthermore, an infinite sink was added to each vial and shaken on a horizontal shaker at 125 rpm for at least 24 hours at room temperature. This ensured a pre-equilibration of the infinite sink and the respective solution. Each leaching experiment was carried out for eight different run-times (1, 3, 5, 9, 15, 30, 50 and 80 days). At the time the experiments were started, three PVC pellets with a total weight of 85-86 mg were added to the prepared vials and put on a horizontal shaker. The pellets had a similar size, shape and weight and hence similar surface area. Experiments were run at room temperature and in the dark to prevent photodegradation. Each experiment was carried out

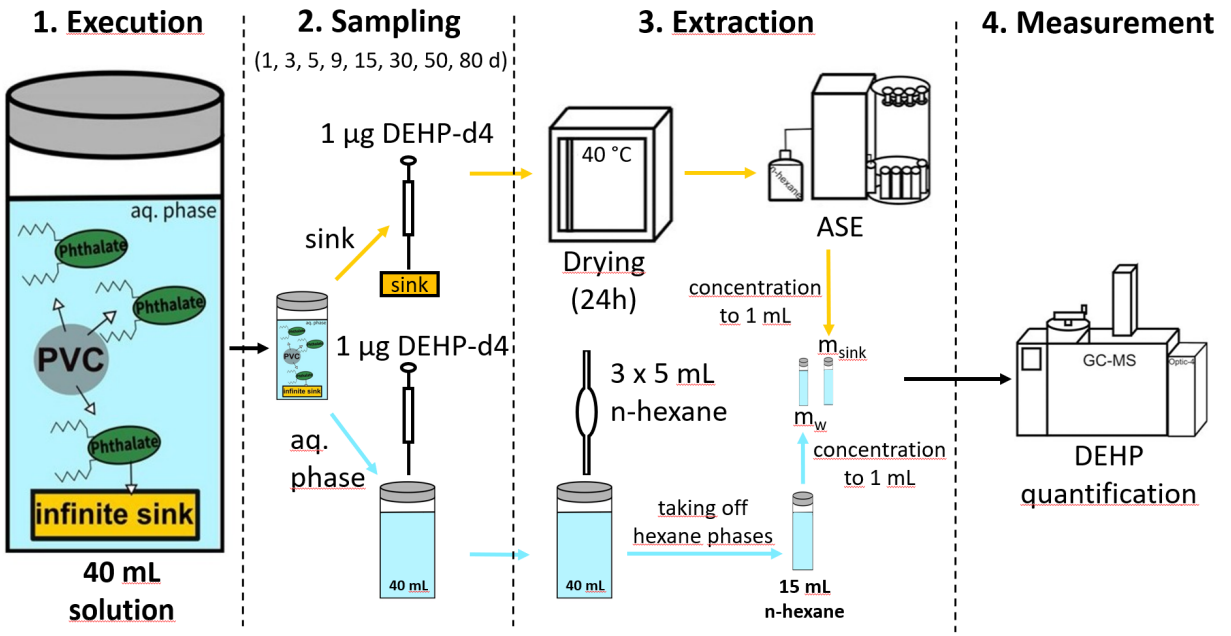

Figure 6: The experimental procedure is divided into four steps: Execution, sampling, extraction and measurement. Graphic based on Henkel et al. (2019).

in triplicates.

The three turbulence experiments were carried out at different shaking speeds (125, 25 and 0 rpm) on a horizontal shaker to analyze a graded sequence of turbulence effects. The used background solution in this experimental setup was the 1 mM KCl solution. In contrast, the three salinity experiments were carried out with different solutions (1 mM KCl, EPA moderate hard water, artificial sea saltwater) on a horizontal shaker at 125 rpm.

Sampling

Samples were taken at the respective time intervals. First the PVC pellets and then the infinite sink were removed with tweezers. To quantify DEHP in the aqueous phase and in the infinite sink, both phases were spiked with 20 µL of an internal 50 µg/L 2-propanol DEHP-d4 standard. The inifnite sinks were dried for at least 12 h at 40°C in an oven and then stored in a desiccator until extraction. After the aqueous phase was spiked, the vials were placed on a horizontal shaker for at least 24 h until extraction to ensure homogeneity

of the internal standard and the solution.

Liquid-liquid Extraction

Based on Henkel et al. (2019), DEHP was extracted from the aqueous phase. Therefore, 5 mL of n-hexane were added to the aqueous phase and shaken by hand for two minutes. The vials containing both phases were then placed in a fridge at 4°C for 30 minutes until the n-hexane phases separated. The n-hexane phases were then taken off with glass pipettes and transferred into a 20 mL glass vial. This procedure was repeated three times, resulting in ∼15 mL extracted n-hexane which were pooled in the same vial. Subsequently, the n-hexane extracts were concentrated to ∼1 mL. Therefore, the extracts were aerated with nitrogen at 40°C using a laboratory evaporator (Barkey vapotherm basic mobil, Germany; Figure 7). The concentrated extracts were then transferred with glass pipettes into 1.5 mL brown glass measurement vials and stored at room temperature until measurement.

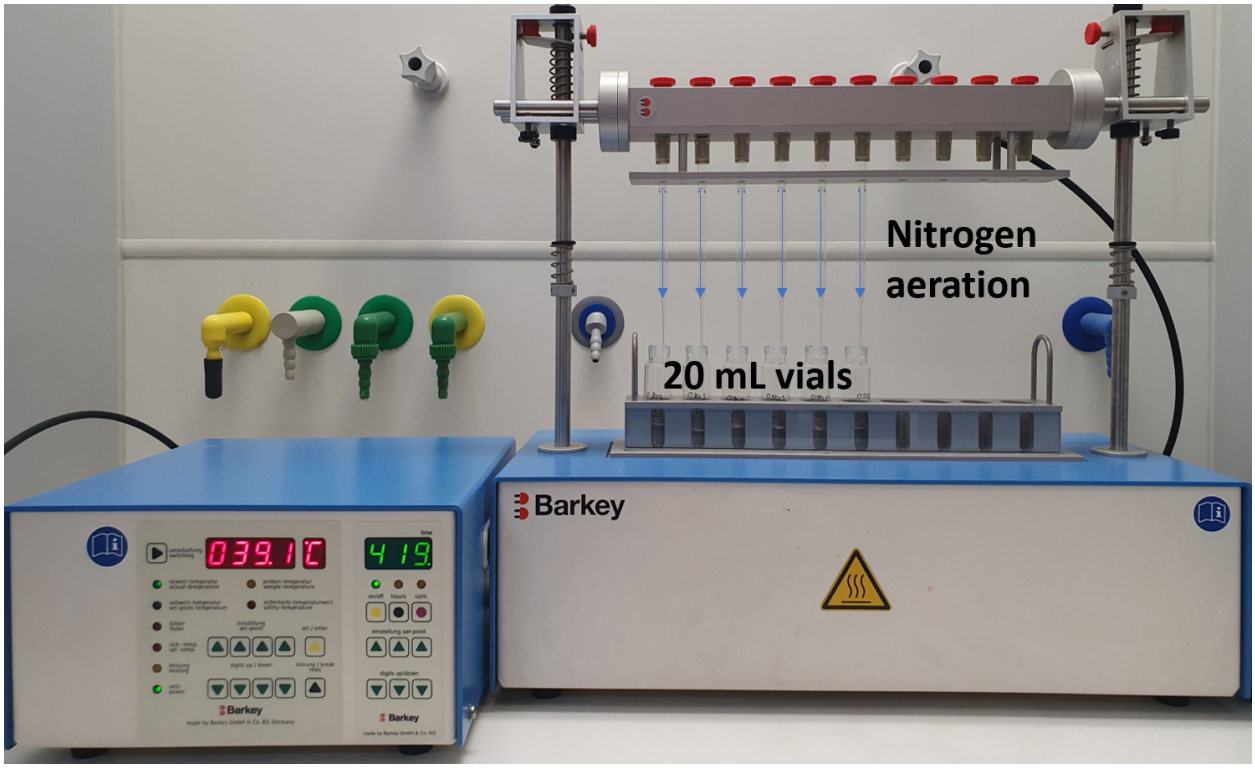

Figure 7: A Barkey vapotherm basic mobil was used to concentrate n-hexane extracts. Therefore the 20 mL vials were placed under a 40°C nitrogen aeration stream.

Accelerated Solvent Extraction

Before the sinks were extracted, they were taken out of the desiccator and dried at 40°C for 24 h to ensure that the moisture content between the infinite sinks was similar. Next, the infinite sinks were placed in stainless steel cylinders with a volume of 10 mL (Figure 8). To extract DEHP from the infinite sinks, an Accelerated Solvent Extractor (ASE 350, Thermo Fisher scientific Dionex, USA) was used. The sinks were extracted at 120°C and 103 bar for 7 minutes using n-hexane. The cylinders were then flushed with n-hexane at 60% of their volume resulting in a total volume of ∼16 mL n-hexane extract for each sample. The n-hexane extracts were collected in 60 mL vials. Between each extraction the ASE is rinsed with 5 mL n-hexane. The extracts were transferred from the 60 mL vial into a 20 mL glass vial and concentrated to ∼1 mL using a laboratory evaporator (Figure 7). The concentrated extracts were then transferred into 2 mL brown glass measurement vials and stored at room temperature until measurement (Henkel et al., 2019).

Figure 8: Stainless steel cylinders with a volume of 11 mL (left) and the ASE 350 (right).

GC-MS Measurement

To quantify the DEHP concentrations, samples were measured with GC-MS. The GC-MS system and the corresponding measuring program are listed in Table A3 in the appendix. When measuring with GC-MS, the sample is first vaporized by an oven and absorbed by a carrier gas (here helium), the so-called mobile phase. The gas is then passed through a separation column coated with an absorbent liquid phase. This is called stationary phase. On its way through the separation column, DEHP is distributed between the mobile and stationary phases. The time required for DEHP to pass through the separation column is substance-specific and is called retention time (Schwedt, 2007). DEHP is then ionised, fragmented and separated in the mass spectrometer (MS) according to its mass-to-charge ratio. Following, DEHP fragments were identified, resulting in a mass spectrum that could be compared with a database.

Calibration solutions were prepared in n-hexane to determine the concentrations of DEHP extracts. Therefore, ten 2 mL calibration solutions with DEHP concentrations of 15, 12, 10, 7, 5, 3, 1, 0.5, 0.25 and 0.1 µg/mL were prepared from three stock solutions (500, 50 and 5 µg/mL 2-propanol). In addition, 40 µL of the internal 50 µg/mL 2-propanol DEHP-d4 standard were added to each calibration solution. To determine the concentration of DEHP, signals of the samples were compared with the signal of the internal standard. This allowed the quantification of DEHP in the samples.

To calculate the DEHP concentration of the samples, the response factors

$$rf = \frac{\mathrm{A}_{DEHP}/\mathrm{C}_{DEHP}}{\mathrm{A}_{DEHP-d4}/\mathrm{C}_{DEHP-d4}} \tag{3.1}$$

were determined. The peak areas of DEHP and the internal DEHP-d4 standard are denoted by A_{DEHP} and $\mathrm{A}_{DEHP-d4}$, respectively. The corresponding concentrations are C_{DEHP} [µg/mL] and $\mathrm{C}_{DEHP-d4}$ [µg/mL]. With the known mass of the internal standard in the sample $\mathrm{M}_{DEHP-d4,S}$ [µg] and the response factor, the mass of DEHP in the sample $\mathrm{M}_{DEHP,S}$ [µg]

can be calculated by

$$\mathrm{M}_{DEHP,S} = \frac{\mathrm{A}_{DEHP,S} \cdot \mathrm{M}_{DEHP-d4,S}}{\mathrm{A}_{DEHP-d4,S} \cdot rf} \tag{3.2}$$

where $\mathrm{A}_{DEHP,S}$ and $\mathrm{A}_{DEHP-d4,S}$ describe the peak area of DEHP and the internal standard in the sample, while $\mathrm{M}_{DEHP-d4,S}$ denotes the mass of the internal standard. To eliminate background concentrations, the concentrations of the respective blanks were subtracted from the calculated masses of DEHP. The measurement data is listed in Section 7.3 in the appendix.

3.3 Calculation of leaching Models and leaching Half-life

Model Parameters

To compute the ABLD and IPD model, their different parameters had to be determined. The radius of the PVC pellet R was measured using a measuring tape. The partition coefficient K_{PVC-W} was calculated based on the molecular structure of DEHP and PVC, the respective solution, temperature and pressure using the SPARC-calculator[1]. While the diffusion coefficient of DEHP in PVC D_{PVC} was obtained from literature (Griffiths et al., 1983), the diffusion coefficient of DEHP in water D_W was calculated from its molecular weight described in Equation 2.5 using Excel.

ABLD model parameter fitting: Turbulence experiments

The ABL thickness

$$\delta = \frac{-3\ D_W\ t}{R\ K_{PVC-W}\ ln(-\mathrm{f}_{desorbed}(t) + 1)} \tag{3.3}$$

was derived by matching the results of experimental data ($f_{desorbed}(t)$ & t) with Equation 3.3

[1]SPARC online calculator from the University of Georgia, http://archemcalc.com/sparc, based on Carreira and Karickhoff (1994)

and therefore served as a fitting parameter. This was done using Excel for all eight sampling times. The mean of the eight ABL thicknesses was then used to plot the ABLD model using the software `R` (R Core Team, 2013, V. 4.0.3) with the package `ggplot2` (Wickham, 2011), for each experiment (0, 25, 125 rpm) respectively. The corresponding `R` script can be found in Section 7.2 in the appendix. The choice of δ as a fitting parameter and the sensitivity of the model results are discussed in the result section.

ABLD model parameter fitting: Salinity experiments

As all salinity experiments were run at 125 rpm on a horizontal shaker, the ABL thickness δ was assumed to be constant. We hypothesize that changing salinities cause a shift of the partition coefficient K_{PVC-W}. Starting from the calculated K_{PVC-W} value from SPARC for the 1 mM KCl solution, partition coefficients

$$K_{PVC-W} = \frac{-3\ D_W\ t}{R\ \delta\ ln(-\mathrm{f}_{desorbed}(t) + 1)} \tag{3.4}$$

for the moderate hard water and artificial saltwater experiments were derived by matching the experimental data ($f_{desorbed}(t)$ & t) with Equation 3.4. Therefore, K_{PVC-W} served as a fitting parameter for the moderate hard water and artificial saltwater experiments. This was done using Excel for all eight sampling times. The mean of the eight distribution coefficients K_{PVC-W} was then used to plot the ABLD model using `R` for both experiments (moderate hard water and artificial sea saltwater). The corresponding `R` script for the ABLD modelling can be found in Section 7.2 in the appendix.

Calculation of the IPD model

The IPD model (Equation 2.3) was plotted with $t = 1 : 1{,}000{,}000$ d and the obtained parameters described above. The upper limit of the summation index n, was manually increased until the point of convergence had been reached at a value of 1,000,000. The corresponding `R` script for the IPD modelling can be found in Section 7.2 in the appendix.

Leaching half-life

Leaching half-lives

$$t_{1/2} = \frac{R\ \delta\ K_{PVC-W}\ ln(2)}{3\ D_W} \tag{3.5}$$

were calculated by rearranging Equation 2.4 using Excel for each ABLD limited experiment.

4 Results and Discussion

Infinite Sink Validation

The results of the experiments show that the infinite sink developed by Henkel et al. (2019) works for our experimental setup. The DEHP concentrations in the water phase were kept below water solubility. Even after 80 days, the infinite sinks were still absorbing DEHP. The highest measured values in the infinite sink were four orders of magnitude lower than in the PVC pellets. For the 125 rpm experiment, DEHP masses in the water phase were lower than in the sink for <5 days (Table A5 in the appendix). After 5 days, concentrations in the water phase were constant and lower than in the sink. This indicates an equilibrium between the water phase and the infinite sink. In contrast, the response time for the 0 rpm experiment was >80 days since concentrations in the water phase were always higher than in the sink (Table A7 in the appendix). This indicates slower kinetics towards equilibrium due to the missing water movement. In this case DEHP transport is dominated by Brownian intrinsic movement, which is generally slow.

4.1 Diffusion Processes of DEHP plasticized MPs are limited by ABLD

The total mass leached increased linear over time for the 125 rpm (1 mM KCl) experiment (Figure 9) with 130 ng/d. It is illustrated in Figure 9A by the trend line which runs through the origin since initial leaching is neglected. Since the aqueous diffusion coefficient D_W ($3.9*10^{-10}$ m^2/s) and the partition coefficient between PVC and water K_{PVC-W} ($2.34*10^8$ L/kg) were calculated, the thickness of the ABL δ served as a fitting parameter for the ABLD model. While δ is directly proportional to D_W, it is inversely proportional

to K_{PVC-W}. An average δ of 38 ± 13 µm over all sampling points was calculated. This number is in accordance with findings of Seidensticker et al. (2017) and Endo et al. (2013b). Seidensticker et al. (2017) found an ABL thickness of 10 µm for PE MP pellets with a diameter of 260 µm and a shaking speed of 150 rpm on a rotational shaker. Endo et al. (2013b) found an ABL thickness of 30 µm for approximately spherical shaped MP PE pellets from the field at 120 rpm. Hence, the aforementioned studies had similar experimental setups and calculated ABL thicknesses δ. Further, they determined the ABLD as the limiting process in their experiments. Therefore, we conclude that the diffusion process in our experimental setup (r=250 µm, 125 rpm) is limited by the ABLD as well.

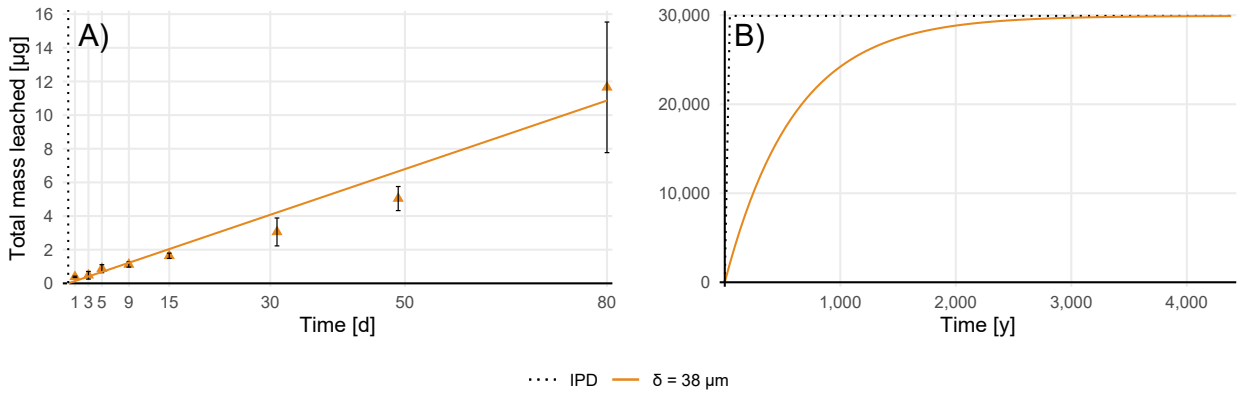

Figure 9: Total mass leached (sum of the extracted mass of DEHP from the aqueous phase and infinite sink) over time for the 125 rpm experiment (A). Each data point represents a blank corrected triplicate with ± standard deviations. The black error bars indicate absolute standard deviations. The *orange* line represents the ABLD model for an ABL of 38 µm, while the *dotted* line shows the IPD model. Graph (B) shows the models for higher x- and y-values.

When comparing the ABLD model to the IPD model in Figure 9B, it becomes clear that the ABLD is the slower process. Since the diffusion processes are limited by ABLD, the pellet would be in equilibrium with the aqueous phase after approximately 4000 years at 125 rpm. For an IPD limited process, this would take only ∼500 days (see Figure 9). Therefore, the IPD model overestimates the experimental leaching curves. This further supports the finding that the ABLD is the governing mechanism for leaching of DEHP from PVC pellets and agrees with studies examining leaching of other highly hydrophobic substances (Endo

et al., 2013b; Seidensticker et al., 2017). For instance, Seidensticker et al. (2017) found that sorption/desorption processes for typical wastewater pollutants like the hydrophobic phenanthrene (water solubility of 1.15 mg/L, ECHA (2020)) from PE MP pellets are limited by ABLD. For less hydrophobic additives or setups with more non-polar solvents, IPD might play a more important role (Kwon et al., 2006; Teuten et al., 2009; Fries and Zarfl, 2012) since ABLD is facilitated due to a lower cavity formation energy.

However there are also studies that could indicate an IPD restrictive diffusion process for our experimental setup. For instance, Lampert et al. (2015) found that sorption by passive samplers under field conditions are limited by ABLD for substances with high K_{OW} like DEHP. A reason for that might be that passive samplers are mostly thin PE sheets (Lohmann, 2012). Hence, IPD could not limit the diffusion process, since the majority of the additive is rather at the surface than in the interior of the sheet. In our study however, pellets were used. Therefore, IPD becomes more important for particles due to longer diffusion distances from the core to the surface. Since leaching rates are related to the surface to volume ratio, bigger particles could be limited even more by IPD. Moreover, PVC has a higher glass transition temperature as the commonly used PE for passive samplers (Bergmann et al., 2008). Hence, DEHP has a lower diffusion coefficient in PVC than in PE (George and Thomas, 2001), which leads to more IPD restricted diffusion processes. However, neither the particle size nor the higher glass transition temperature of PVC led to an IPD limited diffusion process in our experimental setup. A reason for that might be the high share of DEHP (~35%) in the PVC pellets compared to a common DEHP content for flexible PVC of ~25 - 30% (Stark et al., 2005). Masses of only ~12 µg DEHP of the total DEHP (29925 µg) content of the three MP pellets leached during 80 days. Hence, the amount leached over the experimental time was not sufficient to create a concentration gradient in the PVC pellet. The outer surface of the pellet might not have experienced a decrease in DEHP concentration, which is why IPD could not limit the overall leaching process. For pellets with a lower share of DEHP however, IPD might dominate the

overall leaching kinetics. Because of decreasing DEHP contents, this would also apply for the pellets used in this experiment if the leaching time had been increased. In practice, it is recommended to compare the ABLD and IPD models for each case in order to check which diffusion process controls the overall leaching kinetics.

4.2 Increasing Turbulence increases Leaching rates of DEHP from PVC MPs

The experimental data (Figure 10, experimental data listed in Tables A5 to A7 in the appendix) show higher leaching rates with increasing turbulence. Leaching rates at 0 rpm (5.18 ng/d) (Figure 10C) were 2.80 times lower than at 25 rpm (14.5 ng/d) (Figure 10B) and 25.1 times lower compared to the 125 rpm experiment (130 ng/d) (Figure 10A). These findings agree with Suhrhoff and Scholz-Böttcher (2016), who show that leaching rates of DEHP from PVC consumer plastic samples (5x5 mm) increase by 40 times, when increasing rotation speed with a magnetic stirrer from 0 to 150 rpm. A general trend towards higher leaching rates with increasing turbulence could therefore be determined in both studies. However, the increase in leaching rates with increasing turbulence were 1.60 times higher compared to our findings, which can have various reasons. For instance, the different shape of the used plastic sheets have a higher surface area compared to the MP particles used in this study. This might have increased the potential for increasing leaching rates due to increasing turbulence. Moreover, the higher rotation speed of 25 rotations more per minute might have increased leaching rates.

The regression functions and coefficients of determination (R^2) are shown below the linear trend lines. Comparing the R^2s reveals that the experiments with low turbulence show a poorer fit. This especially holds true for the 0 rpm experiment, which is due to a less homogeneous setup compared to the 125 rpm experiment. Since some MP pellets were initially floating on the water surface, they had to be transferred into the water phase by gentle shaking, which may have increased initial leaching rates. This effect is weaker for the

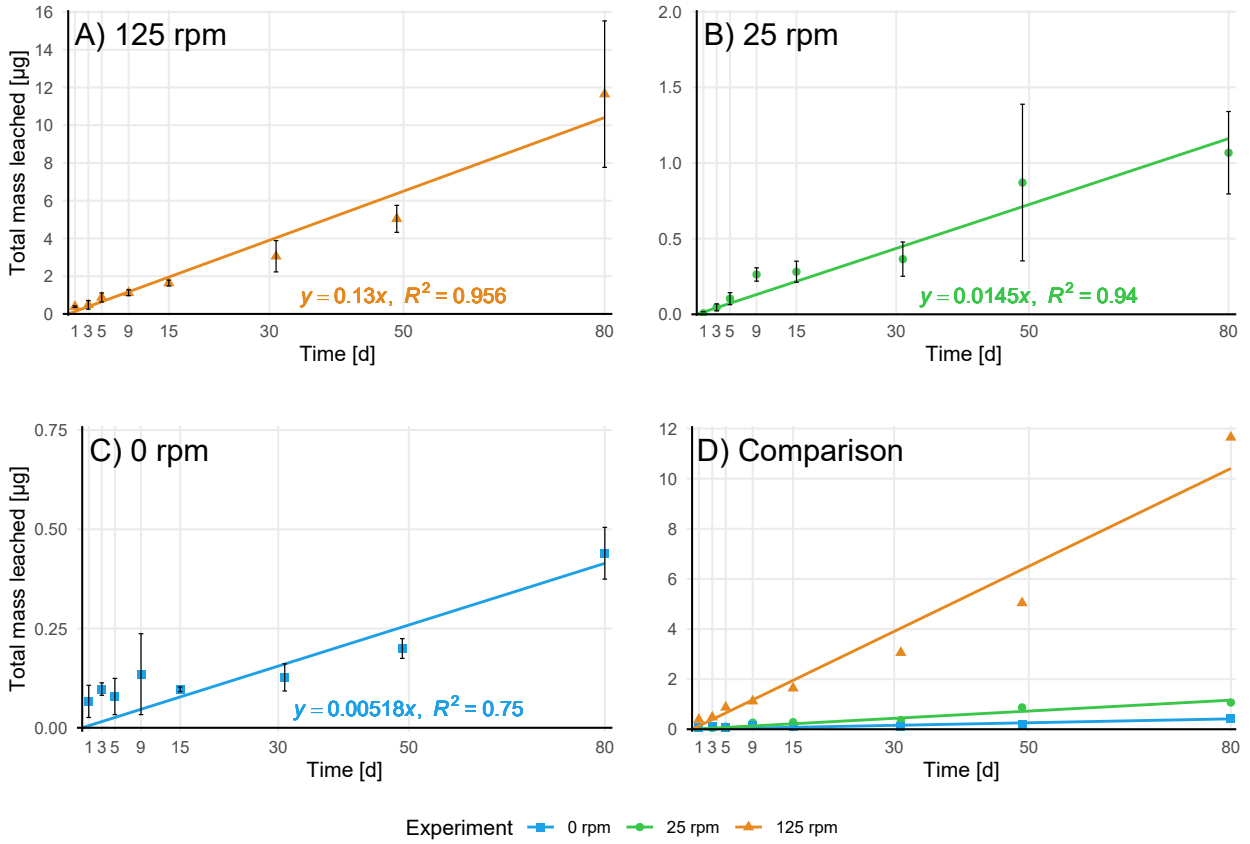

Figure 10: Total mass leached (sum of the extracted mass of DEHP from the aqueous phase and infinite sink) over time for experiments with different turbulence (A,B,C). Each data point represents a blank corrected triplicate with ± standard deviations. The black error bars indicate absolute standard deviations. They are generally higher with increasing time and total mass leached. Plot D shows a comparison of A,B and C.

25 and 125 rpm experiment since those vials were put on the horizontal shaker afterwards. The variations within the triplicates can originate from deviations of the handmade infinite sinks, cross-contamination or the standard error of the GC-MS. The latter influenced each sample and can therefore be neglected due to a compensation within the triplicates.

The model results show that with thicker ABLs the leaching rate of DEHP decreases (Figure 11). By increasing the ABL thickness in the model (indicated by dotted line), leaching rates become much lower as indicated by the lower slope (Figure 11A - C). This can be explained by a longer diffusion through the ABL. Different leaching rates can therefore be well explained

by changes of the ABL thickness. When fitting the models of the 25 and 0 rpm experiment to the experimental data (Figure 11B and C), ABL thicknesses increase by a factor of 10 for 25 rpm (370 µm) and by a factor of 20 for 0 rpm (770 µm). This can be explained by lower shear forces acting on the ABL caused by less water movement, which might keep the ABL thicker. The IPD model (dotted line in Figure 11D) is not capable to cover any experimental data due to overestimation.

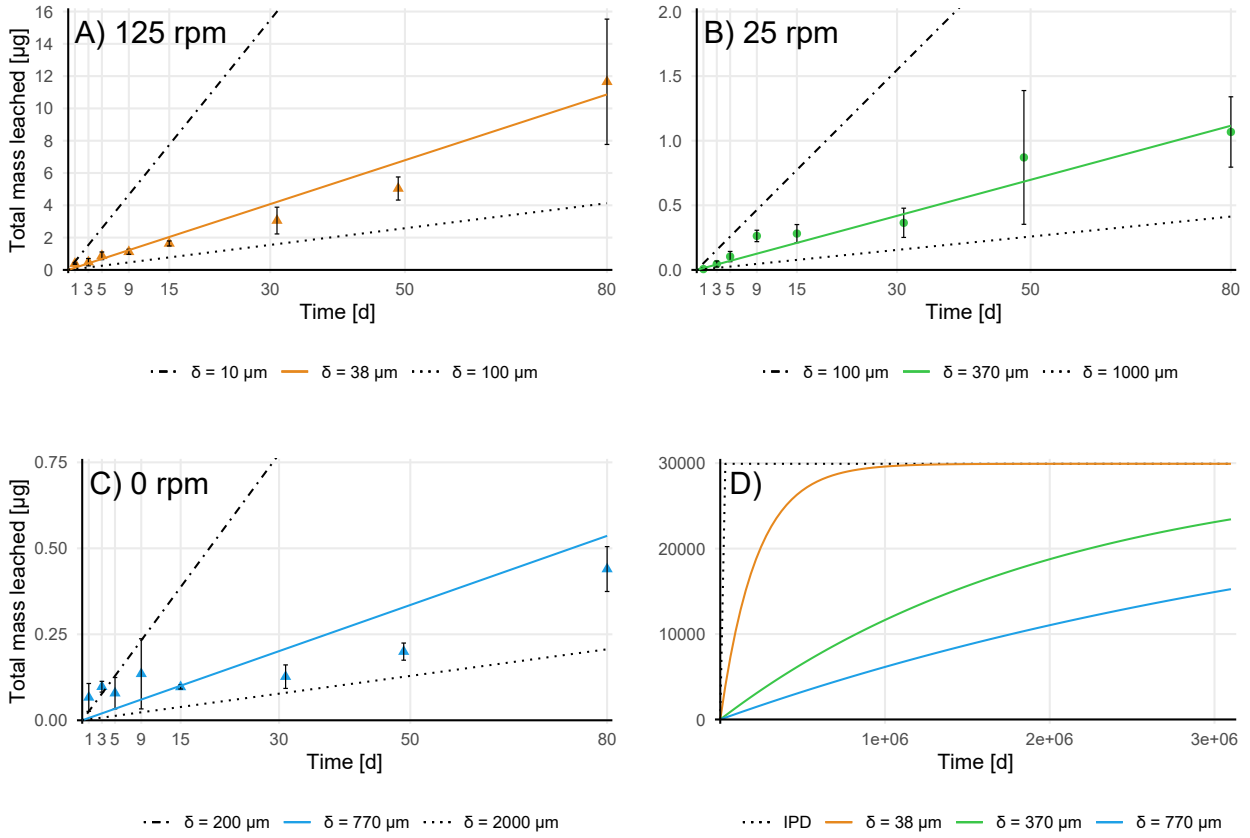

Figure 11: Total mass leached (sum of the extracted mass of DEHP from the aqueous phase and infinite sink) over time for experiments with different turbulence intensities. The data points show the average of of each triplicate with ± standard deviations. The plots A,B and C show the measurement values and the ABLD model with varying ABL thicknesses δ for the three turbulence intensities. Plot D compares the most fitting ABLD models of the three experiments with the IPD model.

Based on the fit of the kinetic data using the ABLD model, leaching half-lives $t_{1/2}$ were calculated. According to Equation 3.5, the leaching half-lives of the turbulence experiments

range from 416 years (125 rpm) over 4063 years (25 rpm) to 7121 years (0 rpm). These results indicate that leaching of DEHP from PVC pellets is generally slow, particularly in environments with little turbulence. With progressing leaching duration, however, the leaching process might finally be limited by IPD due to a lower share of DEHP, which causes the formation of a concentration gradient within the pellet. This might decrease leaching rates for depleted particles even more, since longer diffusion distances from the inside of the particle to the outer surface could lead to an IPD limited and slow diffusion process. The point in time at which the PVC pellet is in equilibrium with its surrounding environment is therefore difficult to estimate. However, it is likely that it will take much longer than the estimated leaching half-lives.

As demonstrated, the ABLD model can well approximate the leaching kinetics of DEHP from PVC pellets into water. The model requires values of K_{PVC-W}, D_W and δ. While K_{PVC-W} and D_W can be estimated, the ABL thickness δ for environmental conditions is difficult to calculate and requires further investigations.

4.3 Increasing Salinity decreases Leaching rates of DEHP from PVC MPs

The experimental data (Figure 12, experimental data listed in Tables A5, A8 and A9 in the appendix) show lower leaching rates with increasing salinity. Leaching rates of the 1 mM KCl (130 ng/l) and moderate hard water (131 ng/l) experiments do not differ significantly (t-test for difference of slopes $p = 0.952$). In contrast, the leaching rate of the artificial sea saltwater experiment (81.6 ng/d) is significantly lower than in the two aforementioned experiments (both $p < 0.001$). While the 1 mM KCl and moderate hard water experiments have similar ion concentrations (1 mM and 4 mM), the artificial sea saltwater experiment has a much higher ionic strength of ~700 mM. Hence, DEHP molecules have to overcome a higher cohesive energy when entering the aqueous solution. This increases the cavity formation energy costs, which shifts the equilibrium towards the PVC pellets and finally

leads to lower leaching rates. Therefore, the partition coefficient K_{PVC-W} is considered the most important parameter for the assessment of leaching (Seidensticker et al., 2017). The salting-out effect is particularly pronounced with non-polar compounds (Endo et al., 2012) like DEHP due to the repulsion forces of the increasingly polar solvent.

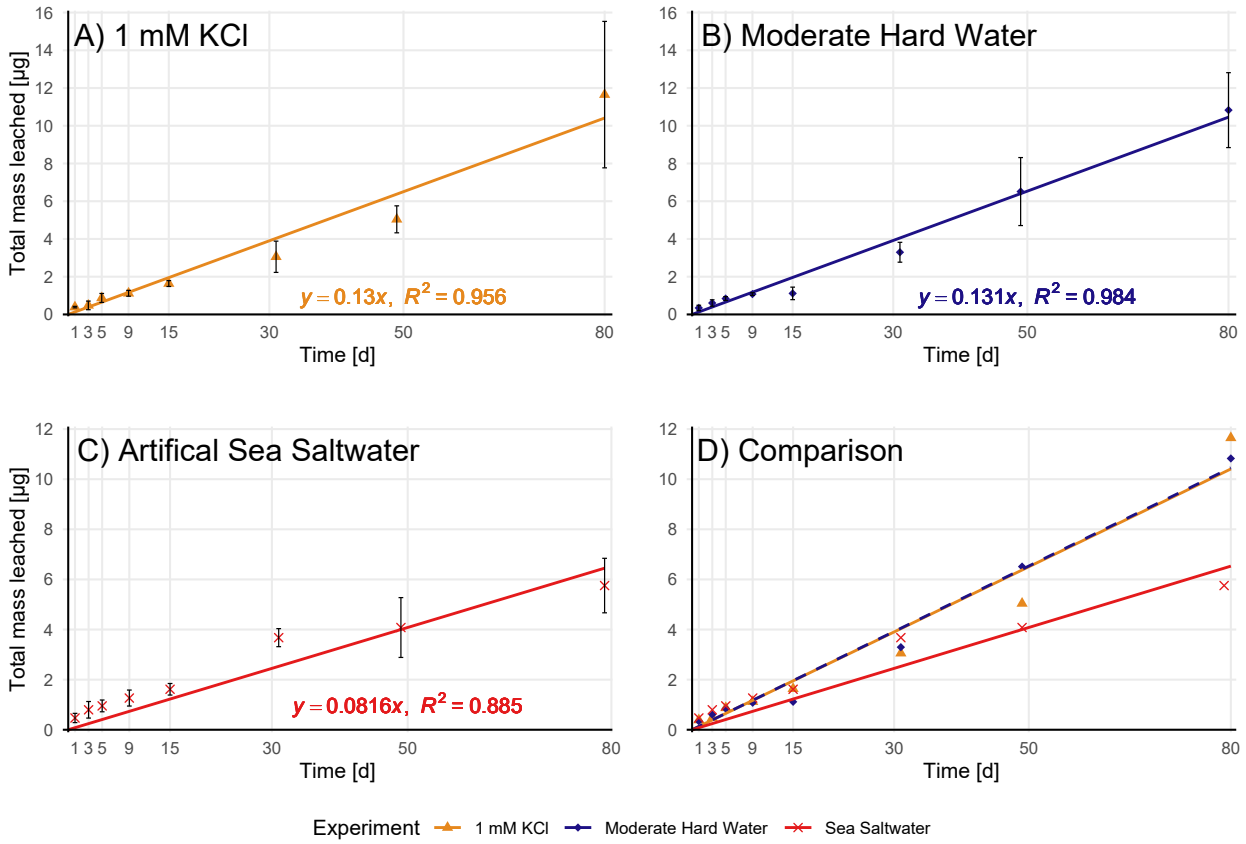

Figure 12: Total mass leached (sum of the extracted mass of DEHP from the aqueous phase and infinite sink) over time for experiments with different salinities (A,B,C). Each data point represents a blank corrected triplicate with ± standard deviations. The black error bars indicate absolute standard deviations. They are generally higher with increasing time and total mass leached. Plot D shows a comparison of A,B and C.

Comparing the solubility of various organic compounds such as Phenanthrene or Toluene, Xie et al. (1997) experimentally determined an average solubility reduction by a factor of 1.36 between water and saltwater. The results are in line with this finding since we observe a solubility decrease of DEHP in our 1 mM KCl and the artificial sea saltwater experiment

with a factor of 1.32. However, our findings contradict with the results of Suhrhoff and Scholz-Böttcher (2016), who found that DEHP leaching rates from PVC pellets did not change with increasing salinity. Moreover, the authors found that most PVC additives have higher leaching rates in saltwater, depending on the substance chemistry. Nonetheless, the cited study is the only one showing that leaching of hydrophobic substances increases with increasing salinity. In general, comparing the salting out effect of various compounds cannot be generalized since fluctuations in salinity lead to various changes in water and compound chemistry such as polarity, dipole moment, ionic strength and pH.

The model results show that a decrease in leaching rates of DEHP cause higher partition coefficients between PVC and water K_{PVC-W} (Figure 13) since the fugacity of DEHP in the particle increases. To compute the ABLD model, the partition coefficient between PVC and water K_{PVC-W} served as a fitting parameter. The thickness of the ABL δ was assumed to be 38 µm for all three experiments as the turbulence was kept at 125 rpm. Since the thickness of the ABL δ was previously calculated based on the partition coefficient for the 1 mM KCl using SPARC-calculator, only partition coefficients for the moderate hard water and artificial sea saltwater experiments were fitted.

By increasing the partition coefficients in the model (indicated by dotted line), leaching rates become much lower as indicated by the lower slope. This is due to a shift of the equilibrium towards PVC. In contrast, when decreasing partition coefficients (indicated by dashed-dotted line) leaching rates increase. Hence, the relationship between decreasing leaching rates and increasing salinity can be explained by a shift of the partition coefficient K_{PVC-W}. The partition coefficient for moderate hard water increased slightly to $2.39*10^8$ compared to the calculated value for 1 mM KCl using SPARC ($2.34*10^8$). For the artificial sea saltwater experiment however, the partition coefficient increased by a factor of 1.32 to $3.09*10^8$ as discussed above. In general, the data can be well described by the ABLD model.

According to Equation 3.5, the leaching half-lives of the salinity experiments range from 416 years (1 mM KCl) over 426 years (moderate hard water) to 461 years (artificial sea saltwater). Therefore, leaching half-lives increase with increasing salinity due to slower

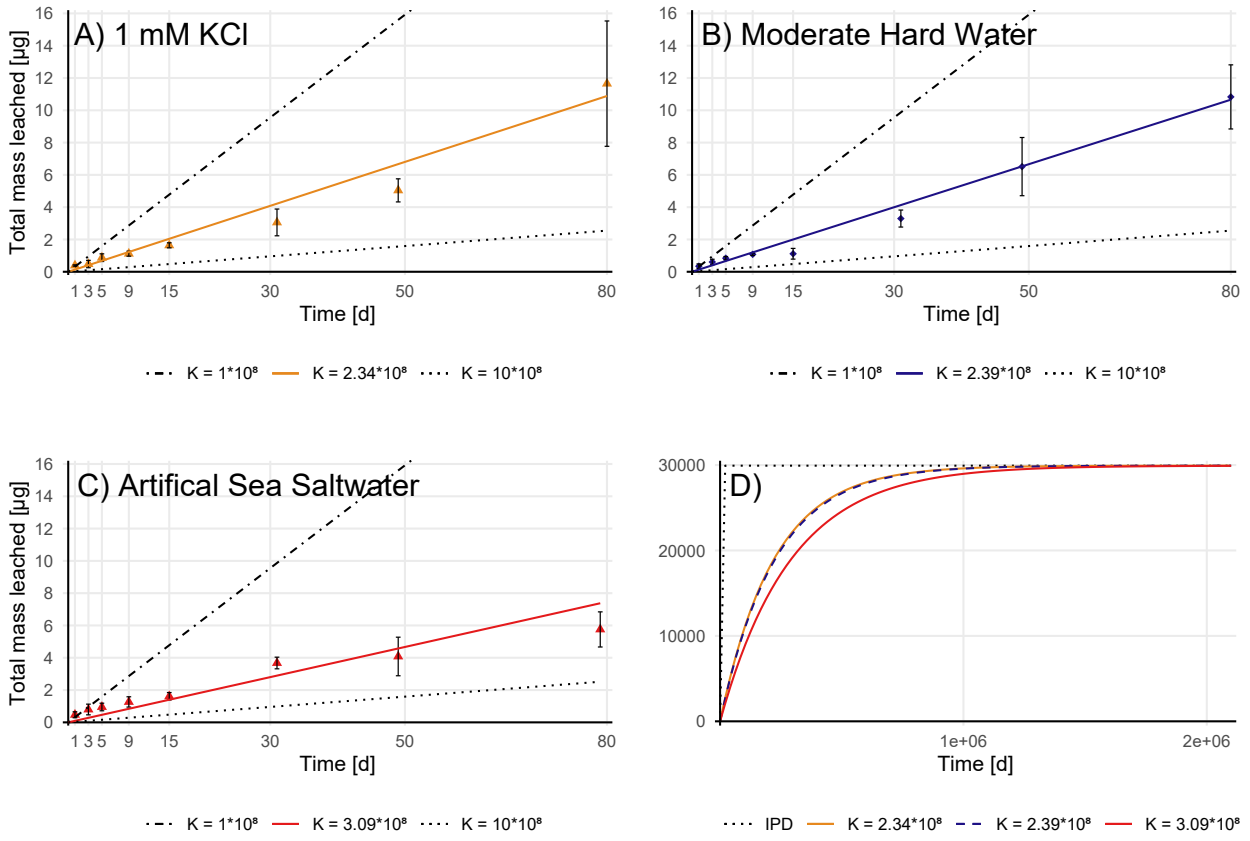

Figure 13: Total mass leached (sum of the extracted mass of DEHP from the aqueous phase and infinite sink) over time for experiments with different salinities. The data points show the average of of each triplicate with ± standard deviations. The plots A,B and C show the measurement values and the ABLD model with varying partition coefficients K_{PVC-W} for the three salinities. Plot D compares the most fitting ABLD models of the three experiments with the IPD model.

leaching. However, differences in leaching half-lives between different salinities are much smaller compared to the turbulence experiments. Hence, salinity has a smaller impact on leaching half-lives than turbulence.

4.4 Environmental Implications

This study has shown that leaching of DEHP from PVC pellets varies between different environments. When looking at environments with high leaching potential of DEHP from

PVC MPs, rivers seem to be especially susceptible due to high turbulence and low salinity. However, leaching half-lives at such conditions were estimated to be 416 years, while residence times of MPs in rivers range only from days to weeks. The main fraction of DEHP will therefore be released into the oceans. The high salinity in oceans will further reduce leaching rates in those ecosystems. PVC MP particles can be considered as a long lasting source of DEHP in the oceans.

However, MP pellets could settle in rivers before entering the oceans. This especially holds true for less plasticized PVC, since the density of DEHP (0.99 g/cm^3, ECHA (2020)) is lower than of PVC (1.2 - 1.4 g/cm^3, ECHA (2020)). Once there, leaching rates can be smaller than in the water phase. Fragmentation of particles at the bottom of rivers may be reduced due to the lack of physical impacts. This however depends on the respective river regime. While rivers with high flow velocities may enhance physical degradation of MP due to friction with other sediments, mixing and re-suspension might not occur in slow rivers. Hence, MP pellets might not reduce in size in such environments. When looking at the ABLD model (see Equation 2.4) it becomes clear that larger pellets have higher leaching half-lives than smaller pellets. Furthermore, less turbulence keeps the ABL thicker, which leads to slower leaching rates, as shown in this study. Consequently, less plasticized MP pellets can also act as a long lasting source of DEHP in river beds. However, the lighter and more plasticized MPs, which are reaching the oceans, might sediment as well due to biofilm formation. For instance, Kaiser et al. (2017) found that after 6 weeks of biofilm formation on MP pellets, sinking velocities of MPs increased by 81% in salt water.

Hence, PVC MP pellets will either end up in river or sea beds. The released DEHP will then most likely be adsorbed by adjacent sediments close to the pellets. This results in DEHP concentrations, which can be more than 10,000 times higher than in the water phase (Peijnenburg and Struijs, 2006). Worms and filter feeders often feed unselectively on sediments (Ward and Shumway, 2004), which leads to the ingestion of MPs (Koelmans et al., 2014) and sediments with elevated DEHP concentrations. Therefore, the aquatic community living in sediments is particularly vulnerable to the endocrine disrupting and

cancer inducing DEHP. In contrast, the exposure of additives to fish by MP ingestion seems to be negligible (Koelmans et al., 2014). Additionally, fish do not seem to be strongly exposed to DEHP from water due to the low concentrations of DEHP found in the oceans.

For further understanding of leaching of DEHP from PVC MPs in the environment, other environmental factors such as DOM facilitated transfer or temperature need to be considered as well. For instance, DOM can increase leaching rates of ABLD limited leaching processes (Seidensticker et al., 2017; Smith et al., 2011) since DOM facilitates the transport of organic compounds through the ABL (Ter Laak et al., 2009). High DOM concentrations could therefore decrease leaching half-lives, which increases the amount of additives released during the residence time of MP pellets in rivers. If the leaching half-lives would decrease drastically to days or weeks, rivers could be more susceptible to additive pollution than indicated by this work. Therefore, further experiments and modeling work for the assessment of leaching of DEHP is recommended. However, due to the increasing amount of plastic in the environment, only a reduction of plastic emissions into ecosystems can be seen as a sustainable solution for the future.

5 Conclusion and Outlook

In five batch experiments, using an infinite sink, the influence of turbulence and salinity on the leaching process of DEHP-plasticized MP was investigated. The experiments have shown a positive relationship between turbulence and leaching. Leaching rates increased by a factor of 25 when increasing the turbulence from 0 to 125 rpm. As shown by the ABLD model, this can be explained by a reduction of shear forces acting on the ABL, leading to a decrease in ABL thickness from 770 to 38 µm. This causes a longer diffusion through the ABL and therefore lower leaching rates.

In contrast, a negative relationship between salinity and leaching has been determined. Leaching rates were decreasing by one half when increasing the ionic strength of the solution from 1 to 700 mM. Therefore, DEHP molecules have to overcome a higher cohesive energy when entering the aqueous solution, which increases the cavity formation energy costs. This shifts the equilibrium towards the PVC pellets and leads to lower leaching rates. However, compared to the effect of turbulence on leaching of DEHP, salinity had a minor impact.

The applied diffusion models clearly showed that for the leaching of DEHP from PVC MPs, the ABLD is the overall rate-limiting step since the IPD model overestimates the experimental leaching curves. A reduction in the additive content could increase the likelihood of an IPD-limiting leaching process, since this leads to a stronger DEHP gradient within the particle. Moreover, the presented models do not consider facilitated transfer mechanisms. For instance, DOM can act as a vector for additives through the ABL. Nevertheless, the models can be used to demonstrate the upper and lower limits of leaching rates. Since facilitated transfer via DOM can only accelerate ABLD, the IPD model represents the fastest leaching possible while the ABLD model represents the slowest leaching process. According to the ABLD model, the estimated leaching half-lives indicate that leaching of DEHP is slow, especially for non turbulent environments (7121 years). Leaching will therefore mainly

take place in the oceans, since residence times of MPs in rivers are much smaller.

This master's thesis provides first insights on the influence of two environmental factors on the leaching process of DEHP-plasticized PVC. However, when assessing leaching of phthalates into the environment, more factors such as DOM concentration, temperature or pH need to be considered. Therefore, further experiments and modeling work for the assessment of leaching of DEHP is recommended to improve our understanding of leaching processes and contaminant interactions in the environment. Those could include the investigation of the aforementioned factors with the same infinite sink approach applied in this study or experiments examining different polymers types and compounds. Also, an inspection of the depletion of additives at the outer surface of MP particles during leaching processes with spectroscopic approaches could help to determine additive gradients in the pellet. This would further improve our understanding of the involved leaching processes. In addition, findings of environmental sciences need to find their way into legislation to protect the most susceptible environments from additive pollution. This could include a reduction of plastic emissions to the environment by mandatory recycling rates and improved waste management. Moreover, further restrictions and substitutions of harmful additives could help to protect the aquatic environment.

Bibliography

Andrady, A. L. (2011). Microplastics in the marine environment. *Marine pollution bulletin*, 62(8):1596–1605.

Andrady, A. L. (2015). Persistence of plastic litter in the oceans. In *Marine anthropogenic litter*, pages 57–72. Springer, Cham.

Atkins, P. and De Paula, J. (2013). *Elements of physical chemistry*. Oxford University Press, USA.

Bagel-Boithias, S., Sautou-Miranda, V., Bourdeaux, D., Tramier, V., Boyer, A., and Chopineau, J. (2005). Leaching of diethylhexyl phthalate from multilayer tubing into etoposide infusion solutions. *American journal of health-system pharmacy*, 62(2):182–188.

Bakir, A., O'Connor, I. A., Rowland, S. J., Hendriks, A. J., and Thompson, R. C. (2016). Relative importance of microplastics as a pathway for the transfer of hydrophobic organic chemicals to marine life. *Environmental Pollution*, 219:56–65.

Barnes, D. K., Galgani, F., Thompson, R. C., and Barlaz, M. (2009). Accumulation and fragmentation of plastic debris in global environments. *Philosophical Transactions of the Royal Society of London B: Biological Sciences*, 364(1526):1985–1998.

Beckingham, B. and Ghosh, U. (2017). Differential bioavailability of polychlorinated biphenyls associated with environmental particles: Microplastic in comparison to wood, coal and biochar. *Environmental Pollution*, 220:150–158.

Bergmann, M., Gutow, L., and Klages, M. (2008). *Polymer Engineering : Technologien und Praxis*. VDI-Buch. Springer-Verlag, Berlin, Heidelberg.

Browne, M. A., Crump, P., Niven, S. J., Teuten, E., Tonkin, A., Galloway, T., and Thompson, R. (2011). Accumulation of microplastic on shorelines woldwide: sources and sinks. *Environmental science & technology*, 45(21):9175–9179.

Browne, M. A., Niven, S. J., Galloway, T. S., Rowland, S. J., and Thompson, R. C. (2013). Microplastic moves pollutants and additives to worms, reducing functions linked to health and biodiversity. *Current biology*, 23(23):2388–2392.

Buschmann, R. and Freund, J. (2019). BUND, Der Plastikatlas 2019 - Daten und Fakten über eine Welt voller Kunststoff, 2. Auflage, Juli 2019. *Chemie, Ressourcen Technik, Nachhaltigkeit*.

Carlson, K. (2010). Toxicity review of di (2-ethylhexyl) phthalate (dehp). *United States Consumer Product Safety Commission (Memorandum), Bethesda, MD, USA*.

Carreira, L. A., S. H. and Karickhoff, S. W. (1994). *Estimation of Chemical Reactivity Parameters and Physica Properties of Organic Molecules Using SPARC,Theoretical and Computational Chemistry, Quantitative Treatment of Solute/Solvent Interactions*. Elsevier Publishers.

Chang, B., Liao, C., and Yuan, S. (2005). Anaerobic degradation of diethyl phthalate, di-n-butyl phthalate, and di-(2-ethylhexyl) phthalate from river sediment in taiwan. *Chemosphere*, 58(11):1601–1607.

Claessens, M., De Meester, S., Van Landuyt, L., De Clerck, K., and Janssen, C. R. (2011). Occurrence and distribution of microplastics in marine sediments along the Belgian coast. *Marine Pollution Bulletin*, 62(10):2199–2204.

Cole, M., Lindeque, P., Halsband, C., and Galloway, T. S. (2011). Microplastics as contaminants in the marine environment: a review. *Marine pollution bulletin*, 62(12):2588–2597.

Corradini, F., Meza, P., Eguiluz, R., Casado, F., Huerta-Lwanga, E., and Geissen, V. (2019). Evidence of microplastic accumulation in agricultural soils from sewage sludge disposal. *Science of the Total Environment*, 671:411–420.

Derraik, J. G. (2002). The pollution of the marine environment by plastic debris: a review. *Marine pollution bulletin*, 44(9):842–852.

Do Sul, J. A. I., Spengler, Â., and Costa, M. F. (2009). Here, there and everywhere. Small plastic fragments and pellets on beaches of Fernando de Noronha (Equatorial Western Atlantic). *Marine Pollution Bulletin*, 58(8):1236–1238.

ECHA (2020). European Chemicals Agency, Substance information. `https://echa.europa.eu/de/`. Viewed on 08.06.2020.

Elias, S. A. (2018). Plastics in the ocean. *Encycl. Anthropocene*, 1:133–149.

Endo, S., Mewburn, B., and Escher, B. I. (2013a). Liposome and protein–water partitioning of polybrominated diphenyl ethers (pbdes). *Chemosphere*, 90(2):505–511.

Endo, S., Pfennigsdorff, A., and Goss, K.-U. (2012). Salting-out effect in aqueous nacl solutions: trends with size and polarity of solute molecules. *Environmental science & technology*, 46(3):1496–1503.

Endo, S., Yuyama, M., and Takada, H. (2013b). Desorption kinetics of hydrophobic organic contaminants from marine plastic pellets. *Marine Pollution Bulletin*, 74(1):125–131.

EPA (2002). Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms. `https://www.epa.gov/sites/production/files/2015-08/documents/short-term-chronic-freshwater-wet-manual_2002.pdf`.

EPA (2014). Environmental Protection Agency US, Priority Pollutant list. `https://www.epa.gov/sites/production/files/2015-09/documents/priority-pollutant-list-epa.pdf`. Viewed on 25.11.2020.

Eremina, N., Paschke, A., Mazlova, E. A., and Schüürmann, G. (2016). Distribution of polychlorinated biphenyls, phthalic acid esters, polycyclic aromatic hydrocarbons and organochlorine substances in the moscow river, russia. *Environmental Pollution*, 210:409–418.

Fang, H., Wang, J., and Lynch, R. A. (2017). Migration of di (2-ethylhexyl) phthalate (dehp) and di-n-butylphthalate (dbp) from polypropylene food containers. *Food Control*, 73:1298–1302.

Fasano, E., Bono-Blay, F., Cirillo, T., Montuori, P., and Lacorte, S. (2012). Migration of phthalates, alkylphenols, bisphenol a and di (2-ethylhexyl) adipate from food packaging. *Food Control*, 27(1):132–138.

Feng, Z., Kunyan, C., Jiamo, F., Guoying, S., and Huifang, Y. (2002). Biodegradability of di (2-ethylhexyl) phthalate by pseudomonas fluorescens fs1. *Water, Air, and Soil Pollution*, 140(1-4):297–305.

Fries, E. and Zarfl, C. (2012). Sorption of polycyclic aromatic hydrocarbons (pahs) to low and high density polyethylene (pe). *Environmental Science and Pollution Research*, 19(4):1296–1304.

Garside, M. (2020). Statista.com, Global plastic production 1950-2018. `https://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/#statisticContainer`. Viewed on 12.11.2020.

Gasperi, J., Wright, S. L., Dris, R., Collard, F., Mandin, C., Guerrouache, M., Langlois, V., Kelly, F. J., and Tassin, B. (2018). Microplastics in air: are we breathing it in? *Current Opinion in Environmental Science & Health*, 1:1–5.

Gayathri, N., Dhanya, C., Indu, A., and Kurup, P. (2004). Changes in some hormones by low doses of di (2-ethyl hexyl) phthalate (dehp), a commonly used plasticizer in pvc blood storage bags & medical tubing. *Indian Journal of Medical Research*, 119(4):139.

George, S. C. and Thomas, S. (2001). Transport phenomena through polymeric systems. *Progress in Polymer science*, 26(6):985–1017.

Geyer, R., Jambeck, J. R., and Law, K. L. (2017). Production, use, and fate of all plastics ever made. *Science advances*, 3(7):e1700782.

Gilbert, M. (2016). *Brydson's plastics materials*. William Andrew.

Graham, P. (1973). Phthalate ester plasticizers–why and how they are used. *Environmental health perspectives*, 3:3–12.

Grathwohl, P. (2014). On equilibration of pore water in column leaching tests. *Waste Management*, 34(5):908–918.

Griffiths, P., Krikor, K., and Park, G. (1983). Diffusion of additives and plasticizers in poly (vinyl chloride): 4. a programmed temperature technique for the determination of the diffusion parameters of three dialkylphthalates. *Polymer*, 24(7):831–833.

Hamdani, M. and Feigenbaum, A. (1996). Migration from plasticized poly (vinyl chloride) into fatty media: importance of simulant selectivity for the choice of volatile fatty simulants. *Food Additives & Contaminants*, 13(6):717–729.

Hartmann, N. B., Huffer, T., Thompson, R. C., Hassellov, M., Verschoor, A., Daugaard, A. E., Rist, S., Karlsson, T., Brennholt, N., Cole, M., et al. (2019). Are we speaking the same language? recommendations for a definition and categorization framework for plastic debris.

Hauser, R., Meeker, J., Singh, N., Silva, M., Ryan, L., Duty, S., and Calafat, A. (2007). Dna damage in human sperm is related to urinary levels of phthalate monoester and oxidative metabolites. *Human Reproduction*, 22(3):688–695.

Helm, D. (2007). Correlation between production amounts of dehp and daily intake. *Science of the total environment*, 388(1-3):389–391.

Henkel, C., Hüffer, T., and Hofmann, T. (2019). The leaching of phthalates from pvc can be determined with an infinite sink approach. *MethodsX*, 6:2729–2734.

Hüffer, T. and Hofmann, T. (2016). Sorption of non-polar organic compounds by micro-sized plastic particles in aqueous solution. *Environmental pollution*, 214:194–201.

Kaiser, D., Kowalski, N., and Waniek, J. J. (2017). Effects of biofouling on the sinking behavior of microplastics. *Environmental Research Letters*, 12(12):124003.

Kambia, K., Dine, T., Azar, R., Gressier, B., Luyckx, M., and Brunet, C. (2001). Comparative study of the leachability of di (2-ethylhexyl) phthalate and tri (2-ethylhexyl) trimellitate from haemodialysis tubing. *International journal of pharmaceutics*, 229(1-2):139–146.

Karapanagioti, H., Endo, S., Ogata, Y., and Takada, H. (2011). Diffuse pollution by persistent organic pollutants as measured in plastic pellets sampled from various beaches in greece. *Marine Pollution Bulletin*, 62(2):312–317.

Kastner, J., Cooper, D. G., Marić, M., Dodd, P., and Yargeau, V. (2012). Aqueous leaching of di-2-ethylhexyl phthalate and "green" plasticizers from poly (vinyl chloride). *Science of the total environment*, 432:357–364.

Keresztes, S., Tatár, E., Czégény, Z., Záray, G., and Mihucz, V. G. (2013). Study on the leaching of phthalates from polyethylene terephthalate bottles into mineral water. *Science of the total environment*, 458:451–458.

Kershaw, P. (2015). Sources, fate and effects of microplastics in the marine environment: A global assessment. *Rep. Stud. GESAMP*, 90(10.13140).

Kim, J.-H., Kim, S.-H., Lee, C.-H., Nah, J.-W., and Hahn, A. (2003). Dehp migration behavior from excessively plasticized pvc sheets. *Bulletin of the Korean Chemical Society*, 24(3):345–349.

Koelmans, A. A., Bakir, A., Burton, G. A., and Janssen, C. R. (2016). Microplastic as a vector for chemicals in the aquatic environment: critical review and model-supported reinterpretation of empirical studies. *Environmental science & technology*, 50(7):3315–3326.

Koelmans, A. A., Besseling, E., and Foekema, E. M. (2014). Leaching of plastic additives to marine organisms. *Environmental Pollution*, 187:49–54.

Kwon, J.-H., Chang, S., Hong, S. H., and Shim, W. J. (2017). Microplastics as a vector of hydrophobic contaminants: Importance of hydrophobic additives. *Integrated Environmental Assessment and Management*, 13(3):494–499.

Kwon, J.-H., Liljestrand, H. M., and Katz, L. E. (2006). Partitioning of moderately hydrophobic endocrine disruptors between water and synthetic membrane vesicles. *Environmental Toxicology and Chemistry: An International Journal*, 25(8):1984–1992.

Kwon, J.-H., Wuethrich, T., Mayer, P., and Escher, B. I. (2007). Dynamic permeation method to determine partition coefficients of highly hydrophobic chemicals between poly (dimethylsiloxane) and water. *Analytical chemistry*, 79(17):6816–6822.

Lampert, D., Thomas, C., and Reible, D. (2015). Internal and external transport significance for predicting contaminant uptake rates in passive samplers. *Chemosphere*, 119:910–916.

Latini, G., Ferri, M., and Chiellini, F. (2010). Materials degradation in pvc medical devices, dehp leaching and neonatal outcomes. *Current medicinal chemistry*, 17(26):2979–2989.

Lertsirisopon, R., Soda, S., Sei, K., and Ike, M. (2009). Abiotic degradation of four phthalic acid esters in aqueous phase under natural sunlight irradiation. *Journal of environmental sciences*, 21(3):285–290.

Liu, L., Bao, H., Liu, F., Zhang, J., and Shen, H. (2012). Phthalates exposure of chinese reproductive age couples and its effect on male semen quality, a primary study. *Environment international*, 42:78–83.

Lohmann, R. (2011). Critical review of low-density polyethylene's partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. *Environmental science & technology*, 46(2):606–618.

Lohmann, R. (2012). Critical review of low-density polyethylene's partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. *Environmental science & technology*, 46(2):606–618.

López-Carrillo, L., Hernández-Ramírez, R. U., Calafat, A. M., Torres-Sánchez, L., Galván-Portillo, M., Needham, L. L., Ruiz-Ramos, R., and Cebrián, M. E. (2010). Exposure to phthalates and breast cancer risk in northern mexico. *Environmental health perspectives*, 118(4):539–544.

Luo, H., Xiang, Y., He, D., Li, Y., Zhao, Y., Wang, S., and Pan, X. (2019a). Leaching behavior of fluorescent additives from microplastics and the toxicity of leachate to chlorella vulgaris. *Science of The Total Environment*, 678:1–9.

Luo, W., Su, L., Craig, N. J., Du, F., Wu, C., and Shi, H. (2019b). Comparison of microplastic pollution in different water bodies from urban creeks to coastal waters. *Environmental Pollution*, 246:174–182.

Mani, T., Hauk, A., Walter, U., and Burkhardt-Holm, P. (2015). Microplastics profile along the rhine river. *Scientific reports*, 5(1):1–7.

Mason, S. A., Garneau, D., Sutton, R., Chu, Y., Ehmann, K., Barnes, J., Fink, P., Papazissimos, D., and Rogers, D. L. (2016). Microplastic pollution is widely detected in us municipal wastewater treatment plant effluent. *Environmental Pollution*, 218:1045–1054.

Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., and Kaminuma, T. (2001). Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. *Environmental science & technology*, 35(2):318–324.

Mayer, P., Tolls, J., Hermens, J. L., and Mackay, D. (2003). Peer reviewed: equilibrium sampling devices.

Mehrer, H. (2007). *Diffusion in solids: fundamentals, methods, materials, diffusion-controlled processes*, volume 155. Springer Science & Business Media.

MoE (2015). Ministry Of Environment Denmark - Microplastics: Occurrence, effects and sources of releases to the environment in Denmark. *Journal of Environmental projects*.

Moore, C. J. (2008). Synthetic polymers in the marine environment: a rapidly increasing, long-term threat. *Environmental research*, 108(2):131–139.

Moore, C. J., Moore, S. L., Leecaster, M. K., and Weisberg, S. B. (2001). A comparison of plastic and plankton in the North Pacific central gyre. *Marine pollution bulletin*, 42(12):1297–1300.

Namieśnik, J., Zabiegała, B., Kot-Wasik, A., Partyka, M., and Wasik, A. (2005). Passive sampling and/or extraction techniques in environmental analysis: a review. *Analytical and bioanalytical chemistry*, 381(2):279–301.

National Geographic, . (2020). 10 erschreckende Fakten über Plastik. `https://www.nationalgeographic.de/10-erschreckende-fakten-uber-plastik`. Viewed on 12.11.2020.

Peijnenburg, W. J. and Struijs, J. (2006). Occurrence of phthalate esters in the environment of the netherlands. *Ecotoxicology and environmental safety*, 63(2):204–215.

Plasticseurope, . (2019). Plastics, the Facts 2019. An analysis of European plastics production, demand and waste data. `https://www.plasticseurope.org/application/files/9715/7129/9584/FINAL_web_version_Plastics_the_facts2019_14102019.pdf`.

R Core Team (2013). R: A language and environment for statistical computing.

Rakowska, M. I., Smit, M. P., Kupryianchyk, D., Qin, J., Koelmans, A. A., Rijnaarts, H. H., and Grotenhuis, T. (2017). Turbulent mixing accelerates pah desorption due to fragmentation of sediment particle aggregates. *Journal of Soils and Sediments*, 17(1):277–285.

Richardson, J., Harker, J., and Backhurst, J. (2002). Chapter 10 - leaching. In *Chemical Engineering (Fifth Edition)*, Chemical Engineering Series. Butterworth-Heinemann, Oxford, fifth edition edition.

Rochman, C., Browne, M., van Franeker, J., Thompson, R., and Amaral-Zettler, L. (2015a). Perceived and demonstrated ecological impacts of marine debris. *Ecology, in review*.

Rochman, C. M., Browne, M. A., Halpern, B. S., Hentschel, B. T., Hoh, E., Karapanagioti, H. K., Rios-Mendoza, L. M., Takada, H., Teh, S., and Thompson, R. C. (2013a). Policy: Classify plastic waste as hazardous. *Nature*, 494(7436):169–171.

Rochman, C. M., Hoh, E., Hentschel, B. T., and Kaye, S. (2013b). Long-term field measurement of sorption of organic contaminants to five types of plastic pellets: implications for plastic marine debris. *Environmental Science & Technology*, 47(3):1646–1654.

Rochman, C. M., Tahir, A., Williams, S. L., Baxa, D. V., Lam, R., Miller, J. T., Teh, F.-C., Werorilangi, S., and Teh, S. J. (2015b). Anthropogenic debris in seafood: Plastic debris and fibers from textiles in fish and bivalves sold for human consumption. *Scientific reports*, 5.

Rönnefahrt, I., Amato, R., Ebert, I., and Schönfeld, J. (2012). Arzneimittel in der Umwelt–Ein Risiko? *UMID*, page 36.

Rose, R., Priston, M., Rigby-Jones, A., and Sneyd, J. (2012). The effect of temperature on di (2-ethylhexyl) phthalate leaching from pvc infusion sets exposed to lipid emulsions. *Anaesthesia*, 67(5):514–520.

Sajiki, J. and Yonekubo, J. (2003). Leaching of bisphenol a (bpa) to seawater from polycarbonate plastic and its degradation by reactive oxygen species. *Chemosphere*, 51(1):55–62.

Schwarzenbach, R. P., Gschwend, P. M., and Imboden, D. M. (2002). *Environmental Organic Chemistry*. Wiley-Interscience.

Schwedt, G. (2007). *Taschenatlas der Analytik, Dritte, überarbeitete und erweiterte Auflage*. Wiley-VCH Verlag GmbH Co. KGaA, Weinheim.

Seidensticker, S., Grathwohl, P., Lamprecht, J., and Zarfl, C. (2018). A combined experimental and modeling study to evaluate ph-dependent sorption of polar and non-polar compounds to polyethylene and polystyrene microplastics. *Environmental Sciences Europe*, 30(1):30.

Seidensticker, S., Zarfl, C., Cirpka, O. A., Fellenberg, G., and Grathwohl, P. (2017). Shift in mass transfer of wastewater contaminants from microplastics in the presence of dissolved substances. *Environmental Science & Technology*, 51(21):12254–12263.

Shea, K. M., on Environmental Health, C., et al. (2003). Pediatric exposure and potential toxicity of phthalate plasticizers. *Pediatrics*, 111(6):1467–1474.

Smith, K. E., Thullner, M., Wick, L. Y., and Harms, H. (2011). Dissolved organic carbon enhances the mass transfer of hydrophobic organic compounds from nonaqueous phase liquids (napls) into the aqueous phase. *Environmental science & technology*, 45(20):8741–8747.

SpecialChem (2017). The material selection platform, Selecting plasticizers for polymers. `https://polymer-additives.specialchem.com/selection-guide/plasticizers`. Viewed on 26.11.2020.

Staples, C. A., Peterson, D. R., Parkerton, T. F., and Adams, W. J. (1997). The environmental fate of phthalate esters: a literature review. *Chemosphere*, 35(4):667–749.

Stark, T., Choi, H., and Diebel, P. (2005). Influence of plasticizer molecular weight on plasticizer retention in pvc geomembranes. *Geosynthetics International*, 12(2):99–110.

Suhrhoff, T. J. and Scholz-Böttcher, B. M. (2016). Qualitative impact of salinity, uv radiation and turbulence on leaching of organic plastic additives from four common plastics—a lab experiment. *Marine pollution bulletin*, 102(1):84–94.

Talsness, C. E., Andrade, A. J., Kuriyama, S. N., Taylor, J. A., and Vom Saal, F. S. (2009). Components of plastic: experimental studies in animals and relevance for human health. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 364(1526):2079–2096.

Teitelbaum, S. L., Mervish, N., Moshier, E. L., Vangeepuram, N., Galvez, M. P., Calafat, A. M., Silva, M. J., Brenner, B. L., and Wolff, M. S. (2012). Associations between

phthalate metabolite urinary concentrations and body size measures in new york city children. *Environmental research*, 112:186–193.

Ter Laak, T. L., Van Eijkeren, J. C., Busser, F. J., Van Leeuwen, H. P., and Hermens, J. L. (2009). Facilitated transport of polychlorinated biphenyls and polybrominated diphenyl ethers by dissolved organic matter. *Environmental science & technology*, 43(5):1379–1385.

Teuten, E. L., Rowland, S. J., Galloway, T. S., and Thompson, R. C. (2007). Potential for plastics to transport hydrophobic contaminants. *Environmental science & technology*, 41(22):7759–7764.

Teuten, E. L., Saquing, J. M., Knappe, D. R., Barlaz, M. A., Jonsson, S., Björn, A., Rowland, S. J., Thompson, R. C., Galloway, T. S., Yamashita, R., et al. (2009). Transport and release of chemicals from plastics to the environment and to wildlife. *Philosophical Transactions of the Royal Society of London B: Biological Sciences*, 364(1526):2027–2045.

Thompson, R. C. (2006). Plastic debris in the marine environment: consequences and solutions. *Marine Nature Conservation in Europe*.

Thompson, R. C., Swan, S. H., Moore, C. J., and Vom Saal, F. S. (2009). Our plastic age.

Tickner, J. A., Schettler, T., Guidotti, T., McCally, M., and Rossi, M. (2001). Health risks posed by use of di-2-ethylhexyl phthalate (dehp) in pvc medical devices: A critical review. *American journal of industrial medicine*, 39(1):100–111.

UBA (2017). Das Umweltbundesamt, Stoffe im Boden, Grundwasser und Oberflächengewässern. `http://www.umweltbundesamt.de/themen/boden-landwirtschaft/bodenbelastungen/stoffe-in-boeden`. Viewed on 21.11.2020.

Ventrice, P., Ventrice, D., Russo, E., and De Sarro, G. (2013). Phthalates: European regulation, chemistry, pharmacokinetic and related toxicity. *Environmental toxicology and pharmacology*, 36(1):88–96.

Ward, J. E. and Shumway, S. E. (2004). Separating the grain from the chaff: particle selection in suspension-and deposit-feeding bivalves. *Journal of Experimental Marine Biology and Ecology*, 300(1):83–130.

Wickham, H. (2011). ggplot2. *Wiley Interdisciplinary Reviews: Computational Statistics*, 3(2):180–185.

Wilkes, C. E., Summers, J. W., Daniels, C. A., and Berard, M. T. (2005). *PVC handbook*, volume 184. Hanser Munich.

Wu, F.-C., Tseng, R.-L., and Juang, R.-S. (2009). Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics. *Chemical engineering journal*, 153(1-3):1–8.

Xie, W.-H., Shiu, W.-Y., and Mackay, D. (1997). A review of the effect of salts on the solubility of organic compounds in seawater. *Marine Environmental Research*, 44(4):429–444.

Yuan, H., Hao, Q., Su, R., Qi, W., and He, Z. (2020). Migration of phthalates from polyvinyl chloride film to fatty food simulants: experimental studies and model application. *Journal of Consumer Protection and Food Safety*, 15(2):135–143.

Zarfl, C. and Matthies, M. (2010). Are marine plastic particles transport vectors for organic pollutants to the Arctic? *Marine Pollution Bulletin*, 60(10):1810–1814.

Zhang, Z.-M., Zhang, H.-H., Zhang, J., Wang, Q.-W., and Yang, G.-P. (2018). Occurrence, distribution, and ecological risks of phthalate esters in the seawater and sediment of changjiang river estuary and its adjacent area. *Science of the Total Environment*, 619:93–102.

7 Appendix

7.1 Used Materials and Methods

Table A1: Characteristics of the infinite sink materials

	trade name	manufacturer	characteristic
activated carbon	Norit1 SAE SUPER	Cabot Norit Nederland B.V., Klazienaveen, Netherlands	absorbs DEHP from aqueous phase
filter paper	Grade 50 filter paper	Whatman GE Heathcare, Dassel, Germany	permeable for DEHP, holds activated carbon together
stainless steel wire	Nr 317L (0.35 mm thickness)	manufacturer unknown, shop: zivipf.com	inert, stabilizes infinite sink

Table A2: Used salts for the three saline solutions (1 mM KCl, EPA moderate hard water, artificial sea saltwater)

salt	molecular formula	producer
potassium chloride	KCl	VWR, BDH Prolabo, Leuven, Belgium
calcium sulphate	$CaSO_4$*2 H_2O	VWR, BDH Prolabo, Leuven, Belgium
magnesium sulfate	$MgSO_4$	Sigma Aldrich, St. Louis, USA
sodium hydrogen carbonate	$NaHCO_3$	Merck KGaA, Damstadt, Germany
sea salt	mixture of several salts (mainly NaCl)	Sigma Aldrich, St. Louis, USA

Table A3: GC-MS Settings with the used system and the associated measuring program

System	
Gas chromatograph	7980A, Agilent Technologies,
Injector	OPTIC-4, GL Sciences B.V.
Mass spectrometer	5975C, Agilent Technologies
Methode	PNTTT / SIM
Column	HP- 5MS, Agilent J&W film thickness: 0.25 μm , dimensions: 30 m x 0.25 mm
Carrier gas	Helium 5.0, Linde Gas GmbH
Programme	
Column flow	1 mL/min
Injection	pulsed splitless
Temperature programme	80°C (0.5 min stable) 20 °C/min to 300 °C (10 min)

Table A4: TOC contents, el. conductivity and pH values for the used solutions (1 mM potassium chloride, moderate hard water, sea salt water)

Solution	Solution number	pH value	el. conductivity [μS/cm]	ϕ TOC [mg/L]
sea salt	1	8.53	51 100	0.390
	2	8.49	49 900	0.530
mod. hard	1	8.25	308	0.090
	2	8.21	298	0.240
1 mM KCl	1	5.69	172	0.130
	2	5.90	179	0.090
	3	6.01	192	0.370
	4	5.78	157	0.260
	5	6.04	158	0.240

7.2 R-scripts for Model Calculations

```
#Define ABLD model (x=t)
ABLD <- function(x,delta=0.000038,Dw=3.9e-10,r=0.0025,K=1*10^(8.37))
  {(1-exp(-(3*Dw*x*86400)/(r*delta*K)))*29925}
#Model is multiplied by total mass of DEHP in pellets (29925 mg) to
#obtain total mass of DEHP leached (mg)
#Call function for e.g. t = 80 days
ABLD(80)

#Define IPD model (x=t)
IPD <- function(t,D=10e-14,r=0.0025,n=1:1000000)
  {(1-(6/pi^2)*sum((1/n^2)*exp(-(n^2*pi^2*t*D*86400)/r^2)))*29925}
#Model is multiplied by total mass of DEHP in pellets (29925 mg) to
#obtain total mass of DEHP leached (mg)
#n=1:1000000 defines the bounds of the summation
#Call function for e.g. t = 80 days
IPD(80)

#Plot both models (ggplot package required)
library(ggplot2)
ggplot()+
  stat_function(fun = Vectorize(IPD), args = list(D=8.2*10^(-14)),
                xlim = c(0,1600000),aes(linetype = "solid"))+
  stat_function(fun = ABLD, args = list(delta=0.000038),
                xlim = c(0,1600000),aes(linetype = "dotted"))+
  ylab("Total mass leached")+xlab("Time [d]")
```

7.3 Measurement Data

In the following, measured values for all five experiments are listed in Tables A5 to A9.

Table A5: Measured DEHP masses [μg] with the GC-MS of the 125 rpm/1 mM KCl experiment. Missing values due to broken infinite sinks are indicated with a hyphen.

Sample	DEHP mass, sink [μg]	DEHP mass, solution [μg]	$\sum$ of sink and solution means [μg]
1 day	1.53E-01 1.31E-01 1.47E-01	2.43E-01 2.16E-01 2.72E-01	3.88E-01 ± 4.01E-02
ϕ	1.44E-01 ± 1.18E-02	2.44E-01 ± 2.83E-02	
3 days	1.46E-01 3.32E-01 2.94E-01	1.42E-01 1.52E-01 3.71E-01	4.79E-01 ± 2.28E-01
ϕ	2.57E-01 ± 9.83E-02	2.22E-01 ± 1.30E-01	
5 days	6.37E-01 5.12E-01 4.17E-01	2.62E-01 4.97E-01 2.94E-01	8.73E-01 ± 2.38E-01
ϕ	5.22E-01 ± 1.10E-01	3.51E-01 ± 1.28E-01	
9 days	8.28E-01 7.69E-01 7.18E-01	3.20E-01 2.65E-01 4.59E-01	1.12E+00± 1.55E-01
ϕ	7.72E-01 ± 5.47E-02	3.48E-01 ± 1.00E-01	
15 days	1.14E+00 1.17E+00	5.80E-01 3.92E-01	1.64E+00 ± 1.56E-01
ϕ	1.15E+00 ± 2.26E-02	4.86E-01 ± 1.33E-01	
30 days	2.44E+00 2.42E+00 1.48E+00	7.07E-01 1.25E+00 8.64E-01	3.06E+00 ± 8.29E-01
ϕ	2.11E+00 ± 5.47E-01	9.41E-01 ± 2.82E-01	
50 days	4.91E+00 4.48E+00 3.77E+00	5.28E-01 8.02E-01 6.29E-01	5.04E+00 ± 7.15E-01
ϕ	4.39E+00 ± 5.77E-01	6.53E-01 ± 1.38E-01	
80 days	1.36E+01 1.15E+01 6.34E+00	2.82E+00 1.42E+00 1.19E+00	1.16E+01 ± 3.88E+00
ϕ	1.05E+01 ± 3.72E+00	1.19E+00 ± 1.65E-01	
ϕ Blanks	5.80E-02 ± 5.95E-02	2.05E-02 ± 1.18E-02	7.85E-02 ± 7.13E-02

Table A6: Measured DEHP masses [μg] with the GC-MS of the 25 rpm experiment. Missing values due to broken infinite sinks are indicated with a hyphen.

Sample	DEHP mass, sink [μg]	DEHP mass, solution [μg]	$\sum$ of sink and solution means [μg]
1 day	1.34E-03 1.81E-02	0.00E+00 0.00E+00	6.49E-03 ± 1.01E-02
ϕ	6.49E-03 ± 1.01E-02	0.00E+00 ± 2.93E-02	
3 days	4.59E-0 3.17E-02 6.18E-02	1.37E-02 - 1.40E-02	4.81E-02 ± 1.53E-02
ϕ	3.88E-02 ± 3.25E-02	9.24E-03 ± 2.29E-04	
5 days	1.18E-01 6.66E-02 7.96E-02	2.83E-02 2.80E-03 1.44E-02	1.03E-01 ± 3.96E-02
ϕ	8.81E-02 ± 2.69E-02	1.52E-02 ± 1.28E-02	
9 days	2.20E-01 1.38E-01 8.36E-02	- 1.48E-01 1.56E-01	2.63E-01 ± 4.42E-02
ϕ	1.11E-01 ± 3.85E-02	1.52E-01 ± 5.68E-03	
15 days	1.56E-01 6.93E-02 1.01E-01	1.82E-01 1.93E-01 1.43E-01	2.81E-01 ± 6.98E-02
ϕ	1.08E-01 ± 4.37E-02	1.73E-01 ± 2.62E-02	
30 days	- - 8.57E-04	4.30E-01 4.32E-01 2.48E-01	3.71E-01 ± 1.13E-01
ϕ	8.57E-04 ± 0.00E-00	3.70E-01 ± 1.05E-01	
49 days	6.93E-02 1.12E-01	1.12E+00 4.35E-01	8.71E-01 ± 5.18E-01
ϕ	9.08E-02 ± 3.04E-02	7.80E-01 ± 1.69E-01	
80 days	1.54E-01 1.13E-01	1.11E+00 7.62E-01	1.07E+00 ± 2.72E-01
ϕ	1.33E-01 ± 2.92E-02	9.34E-01 ± 2.43E-01	
ϕ Blanks	2.74E-02 ± 3.14E-02	8.19E-02 ± 1.90E-02	1.09E-01 ± 5.04E-02

Table A7: Measured DEHP masses [μg] with the GC-MS of the 0 rpm experiment. Missing values due to broken infinite sinks are indicated with a hyphen.

Sample	DEHP mass, sink [μg]	DEHP mass, solution [μg]	$\sum$ of sink and solution means [μg]
1 day	2.56E-02 1.75E-02 3.97E-02	2.06E-02 2.35E-02 7.27E-02	6.65E-02 ± 4.05E-02
ϕ	2.76E-02 ± 1.12E-02	3.89E-02 ± 2.93E-02	
3 days	1.87E-02 4.09E-02	6.78E-02 -	9.76E-02 ± 1.57E-02
ϕ	2.98E-02 ± 1.57E-02	6.78E-02 ± 0E+00	
5 days	9.41E-02 3.69E-02 9.22E-02	- 7.44E-02 7.58E-02	1.41E-01 ± 3.34E-02
ϕ	6.55E-02 ± 3.25E-02	7.51E-02 ± 9.36E-0	
9 days	1.53E-01 7.62E-02 2.46E-02	- 2.41E-02 7.71E-02	1.35E-01 ± 1.02E-01
ϕ	8.45E-02 ± 6.45E-02	5.06E-02 ± 3.75E-02	
15 days	3.72E-02 3.72E-02	5.55E-02 6.38E-02	9.68E-02 ± 5.93E-03
ϕ	3.72E-02 ± 3.08E-05	5.97E-02 ± 5.90E-03	
30 days	5.67E-02 4.59E-02 5.01E-02	4.79E-02 1.05E-01 7.48E-02	1.27E-01 ± 3.42E-02
ϕ	5.09E-02 ± 5.47E-03	7.60E-02 ± 2.87E-02	
50 days	6.34E-02 7.31E-02 8.06E-02	1.44E-01 1.27E-01 1.11E-01	2.00E-01 ± 2.49E-02
ϕ	7.24E-02 ± 8.59E-03	1.27E-01 ± 1.63E-02	
80 days	1.28E-01 4.19E-02 8.59E-02	3.11E-01 3.52E-01 4.00E-01	4.40E-01 ± 6.53E-02
ϕ	6.39E-02 ± 3.11E-02	3.76E-01 ± 3.41E-02	
ϕ Blanks	1.35E-02 ± 1.65E-02	7.94E-03 ± 6.36E-03	2.14E-02 ± 2.29E-02

Table A8: Measured DEHP masses [μg] with the GC-MS of the moderate hard water experiment. Missing values due to broken infinite sinks are indicated with a hyphen.

Sample	DEHP mass, sink [μg]	DEHP mass, solution [μg]	$\sum$ of sink and solution means [μg]
1 day	4.54E-02 2.01E-01 2.07E-01	1.79E-01 2.48E-01 1.49E-01	3.43E-01 ± 1.43E-01
ϕ	1.51E-01 ± 9.17E-02	1.92E-01 ± 5.08E-02	
3 days	2.70E-01 4.97E-01	2.15E-01 2.28E-01	6.05E-01 ± 1.70E-01
ϕ	3.83E-01 ± 1.60E-01	2.22E-01 ± 9.72E-03	
5 days	4.23E-01 5.07E-01 4.63E-01	4.24E-01 3.09E-01 3.99E-01	8.41E-01 ± 1.02E-01
ϕ	4.64E-01 ± 4.20E-02	3.77E-01 ± 6.05E-02	
9 days	6.76E-01 6.56E-01 7.15E-01	4.38E-01 3.56E-01 3.93E-01	1.08E+00 ± 7.10E-02
ϕ	6.82E-01 ± 3.00E-02	3.96E-01 ± 4.10E-02	
15 days	5.49E-01 5.18E-01	8.01E-01 3.62E-01	1.11E+00 ± 3.32E-01
ϕ	5.33E-01 ± 2.13E-02	5.81E-01 ± 3.10E-01	
30 days	2.41E+00 1.57E+00 2.04E+00	1.30E+00 1.17E+00 1.39E+00	3.30E+00 ± 5.27E-01
ϕ	2.01E+00 ± 4.18E-01	1.29E+00 ± 1.09E-01	
50 days	3.38E+00 3.46E+00 4.46E+00	2.02E+00 2.09E+00 4.13E+00	6.51E+00 ± 1.80E+00
ϕ	3.77E+00 ± 6.03E-01	2.74E+00 ± 1.20E+00	
80 days	7.92E+00 8.97E+00 9.03E+00	3.74E+00 1.59E+00 1.23E+00	1.08E+01 ± 1.99E+00
ϕ	8.64E+00 ± 6.28E-01	2.19E+00 ± 1.36E+00	
ϕ Blanks	6.80E-02 ± 3.14E-02	9.62E-03 ± 7.69E-03	7.77E-02 ± 3.91E-02

Table A9: Measured DEHP masses [μg] with the GC-MS of the sea saltwater experiment. Missing values due to broken infinite sinks are indicated with a hyphen.

Sample	DEHP mass, sink [μg]	DEHP mass, solution [μg]	$\sum$ of sink and solution means [μg]
1 day	2.59E-01 2.45E-01 1.16E-01	2.24E-01 3.82E-01 1.81E-01	4.69E-01 ± 1.85E-01
ϕ	2.07E-01 ± 7.86E-02	2.63E-01 ± 1.06E-01	
3 days	3.24E-01 6.59E-01 4.47E-01	2.38E-01 5.05E-01 2.16E-01	7.96E-01 ± 3.31E-01
ϕ	4.77E-01 ± 1.70E-01	3.20E-01 ± 1.61E-01	
5 days	6.44E-01 5.05E-01 6.99E-01	2.52E-01 2.64E-01 4.92E-01	9.52E-01 ± 2.35E-01
ϕ	6.16E-01 ± 1.00E-01	3.36E-01 ± 1.35E-01	
9 days	9.17E-01 7.11E-01	5.74E-01 3.29E-01	1.27E+00 ± 3.19E-01
ϕ	8.14E-01 ± 1.46E-01	4.51E-01 ± 1.73E-01	
15 days	1.03E+00 1.23E+00 1.10E+00	4.13E-01 6.42E-01 4.34E-01	1.62E+00 ± 2.31E-01
ϕ	1.12E+00 ± 1.04E-01	4.97E-01 ± 1.27E-01	
30 days	2.79E+00 2.96E+00 2.59E+00 2.38E+00	1.13E+00 1.03E+00 9.17E-01 8.95E-01	3.67E+00 ± 3.60E-01
ϕ	2.68E+00 ± 2.53E-01	9.91E-01 ± 1.08E-01	
50 days	4.47E+00 2.48E+00 3.27E+00	8.75E-01 6.45E-01 4.94E-01	4.08E+00 ± 1.19E+00
ϕ	3.41E+00 ± 1.00E+00	6.72E-01 ± 1.92E-01	
80 days	4.95E+00 4.28E+00	1.57E+00 7.04E-01	5.76E+00 ± 1.09E+00
ϕ	4.62E+00 ± 4.74E-01	1.14E+00 ± 6.14E-01	
ϕ Blanks	2.37E-01 ± 2.29E-01	3.55E-02 ± 1.65E-02	2.72E-01 ± 2.45E-01