Chemical Pollutants Released to the Marine Environment by Degradation of Plastic Debris

Berit Gewert

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Although sampling studies have been conducted all over the world, the concentrations of plastic debris in the Baltic Sea have hardly been investigated. In **Paper I**, the level and distribution of plastic debris in the Stockholm Archipelago were assessed. Plastic concentrations were higher close to suspected point sources compared to remote areas. Fibers accounted for the most common form and the predominant polymer types were polypropylene (PP) and polyethylene (PE).

In **Paper II**, the literature was critically reviewed for the most important degradation pathways for plastic under environmentally relevant conditions. Ultraviolet (UV) radiation, leading to photo-oxidation, is the most important initiating factor for buoyant plastic. Consequently, a UV lamp was used in **Paper III** for an artificial weathering setup in the laboratory to degrade pristine plastics and analyze the chemical leachates by liquid chromatography-mass spectrometry (LC-MS) for degradation products using a nontarget approach. Carboxylic acids and dicarboxylic acids of polymer fragments were the most commonly identified degradation products of the plastic polymers, confirming predictions made in **Paper II**.

To evaluate potential hazards posed by leachates from weathering plastic debris to marine organisms, an acute toxicity screening study with *Nitocra spinipes* was conducted in **Paper IV**. Field-exposed plastic and the corresponding newly purchased plastic were artificially aged with the same weathering setup as in **Paper III**. Poly(vinyl chloride) (PVC) and PP leachates were generally most toxic, while leachates from polystyrene (PS) and poly(ethylene terephthalate) (PET) were least toxic among the tested materials. For plastics, which were supposed to contain only few additives, we observed no difference in toxicity between leachates from the field-exposed and the newly purchased plastic. However, the other plastic products exposed to the marine environment were more toxic than their corresponding newly bought products. This indicates that the toxicity of the leachates not only depends on the polymer type, but also on the weathering condition of the plastic.

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Sammanfattning

Sedan starten av plasters massproduktion under 1940-talet har tillverkningen av plast ökat i snabb takt. Plast ansamlas i miljön och på senare år har nedskräpning av plast i världens hav fått stor uppmärksamhet. Trots den snabba utvecklingen och en numera ständig närvaro av plast i marina miljöer vet vi fortfarande lite om nedbrytningen i havet och potentiella risker. Denna avhandling syftar till att öka kunskapen kring exponering för plaster i haven och riskerna för den marina miljön.

Förekomst av plast i hav har undersökts över hela världen men antalet studier i Östersjön är relativt få. I **Artikel I** undersökte vi förekomst och fördelning av plast i Stockholms skärgård. Koncentrationen av plast var högre nära misstänkta punktkällor jämfört med avlägsna områden. Fibrer var den vanligaste formen och de predominanta polymertyperna var polypropen (PP) och polyeten (PE).

I **Artikel II** gjordes en litteraturundersökning för att identifiera de viktigaste nedbrytningsvägarna för plast under naturliga förhållanden. Ultraviolett (UV) strålning som leder till fotooxidation identifierades som den viktigaste faktorn för att påbörja nedbrytning av flytande plast. Följaktligen användes en UV-lampa i **Artikel III** för att artificiellt åldra plast i laboratoriet. En förutsättningslös analys av nedbrytningsprodukter i lakvattnet utfördes med vätskekromatografi-masspektrometri (LC-MS). Karboxylsyror och dikarboxylsyror av polymerfragment var de vanligaste identifierade nedbrytningsprodukterna av plastpolymererna, vilket stämmer överens med det som framkom i **Artikel II**.

För att bedöma de faror som nedbrytning av plast utgör för marina organismer utfördes en ekotoxikologisk screeningstudie av akuttest med *Nitocra spinipes* i **Artikel IV**. Både plast som samlats in från havet och motsvarande nyinköpt plast åldrades artificiellt med samma metod som i **Artikel III**. Av de material som exponerats med UV-ljus var lakvattnet från polyvinylklorid (PVC) och PP mest giftiga, medan lakvattnet från polystyren (PS) och polyetentereftalat (PET) gav minst effekt. För plaster som bara innehåller lite additiver var det ingen skillnad i effekt mellan plast som samlats in från havet och plast som köpts ny. Däremot var andra plastprodukter som samlats in från havet mer giftiga än deras motsvarande nyinköpta produkter. Detta indikerar att lakvattnets giftighet inte enbart beror på polymertypen utan också på väderförhållandet.

Zusammenfassung

Seit Beginn der Massenproduktion von Plastik in den 1940er Jahren hat die jährliche Produktionsmenge von Plastik schnell zugenommen. Plastik sammelt sich in der Umwelt an und in den letzten Jahren wurde viel Aufmerksamkeit auf die Verschmutzung der Weltmeere gerichtet. Trotz der raschen Entwicklung und der allgegenwärtigen Präsenz von Plastik, sind der Abbau im Meer und die möglichen Risiken nicht vollständig geklärt. Diese Dissertation zielt darauf ab, das Wissen über die Exposition und Gefahren von marinen Plastik zu erweitern.

Obwohl weltweit Probennahmen durchgeführt wurden, sind die Plastik-konzentrationen in der Ostsee kaum untersucht worden. Daher wurden in **Artikel I** die Mengen und Verbreitung von Plastik im Stockholmer Schärengarten untersucht. In der Nähe von vermuteten Punktquellen waren die Plastikkonzentrationen höher als in abgelegenen Gebieten. Die meisten Pastikpartikel waren Fasern und die häufigsten Polymertypen waren Polypropylen (PP) und Polyethylen (PE).

In **Artikel II** wurde die Literatur kritisch auf die wichtigsten Abbauwege von Plastik unter umweltrelevanten Bedingungen untersucht. Ultraviolette (UV) Strahlung ist der wichtigste Initiierungsfaktor für schwimmfähiges Plastik und führt zur Photooxidation. Folglich wurde in **Artikel III** eine UV-Lampe für einen Aufbau im Labor verwendet, um Plastik künstlich zu altern und die chemischen Abbauprodutkte mit nontarget Flüssig-chromatographie-Massenspektrometrie (LC-MS) zu analysieren. Carbon- und Dicarbonsäuren von Polymerfragmenten waren die am häufigsten identifizierten Abbauprodukte von dem Plastikpolymer, welches im Einklang mit den in **Artikel II** vorausgesagten Produkten ist.

Um die Gefahren für Meeresorganismen abzuschätzen, die von der Verwitterung von Plastik ausgehen, wurde in **Artikel IV** eine Studie zur Untersuchung der akuten Toxizität mit *Nitocra spinipes* durchgeführt. Plastik, welches aus dem Meer gesammelt wurde, und die entsprechenden neu erworbenen Plastik wurden künstlich gealtert mit dem gleichen Aufbau wie in **Artikel III**. Nach UV-Belichtung des Plastiks waren von den getesteten Materialien die Leachates von Polyvinylchlorid (PVC) und PP im Allgemeinen am giftigsten, während Polystyrol (PS) und Polyethylenterephthtalat (PET) am wenigsten toxisch waren. Für Plastik, welches nur geringe Mengen an Additiven enthielt, wurde kein Unterschied in der Toxizität zwischen den Leachates von dem Plastik aus dem Meer und dem neu gekauften Plastik beobachtet. Die anderen Plastikprodukte, die aus dem Meer stammten, waren jedoch toxischer als die entsprechenden neu gekauften Produkte. Dies deutet darauf hin, dass die Toxizität der Leachates nicht nur vom Polymertyp, sondern auch vom Witterungszustand des Plastiks abhängt.

List of papers

This doctoral thesis consists of a summary and four papers.

Paper I
Gewert, Berit; Ogonowski, Martin; Barth, Andreas; MacLeod, Matthew. Abundance and composition of near surface microplastics and plastic debris in the Stockholm Archipelago, Baltic Sea. Marine Pollution Bulletin 2017, 120, 1-2, 292-302.

Paper II
Gewert, Berit; Plassmann, Merle M.; MacLeod, Matthew. Pathways for degradation of plastic polymers floating in the marine environment. Environmental Science: Processes & Impacts 2015, 17, 1513-152.1.

Paper III
Gewert, Berit; Plassmann, Merle M.; Sandblom, Oskar; MacLeod, Matthew. Identification of Chain Scission Products Released to Water by Plastic Exposed to Ultraviolet Light. Accepted in Environmental Science and Technology Letters 2018.

Paper IV
Gewert, Berit; MacLeod, Matthew; Breitholtz, Magnus. Variability in toxicity of plastic leachates as a function of weathering and polymer type: A screening study with *Nitocra spinipes*. Manuscript.

Author contributions

I made the following contributions to the papers included in this thesis:

Paper I
I organized the sampling campaign, collected the samples with help and did the laboratory work including the separation and counting of the plastic particles. After instrumental advice, the FTIR measurements were done by me and I took the lead in writing the paper.

Paper II
I took the lead in conducting the literature research and writing the paper. I generated the figures showing the chemical pathways.

Paper III
I generated the idea for the initial design of the weathering wheel. I carried out most of the artificial aging and the LC-MS analysis. After receiving advice, I also took the lead in the subsequent evaluation of the data and writing the paper.

Paper IV
I designed the study. I gathered the plastic materials and conducted the laboratory work, which included the artificial weathering, extraction of the plastics and the acute toxicity tests. I took the lead in writing the paper.

Paper not included in this thesis:

Jahnke, Annika.; Arp, Hans Peter H.; Escher, Beate I.; Gewert, Berit; Gorokhova, Elena; Kühnel, Dana; Ogonowski, Martin; Potthoff, Annegret; Rummel, Christoph; Schmitt-Jansen, Mechthild; Toorman, Erik; MacLeod, Matthew. Reducing Uncertainty and Confronting Ignorance about the Possible Impacts of Weathering Plastic in the Marine Environment. Environmental Science & Technology Letters 2017, 4 (3) 85-90.

Abbreviations

Acronym	Definition
B	bioaccumulation
FTIR	Fourier-transform infrared spectroscopy
HRMS	high-resolution mass spectrometry
LC	liquid chromatography
L/S	liquid-to-solid ratio
MS	mass spectrometry
MS/MS	tandem mass spectrometry
m/z	mass-to-charge ratio
N. spinipes	*Nitocra spinipes*
P	persistence
PE	polyethylene
PET	poly(ethylene terephthalate)
POPs	persistent organic pollutants
PP	polypropylene
PS	polystyrene
PU	polyurethane
PVC	poly(vinyl chloride)
rpm	revolutions per minute
SPE	solid phase extraction
UV	ultraviolet
UHPLC	ultra-high performance liquid chromatography
WWTP	wastewater treatment plant

Contents

1. Introduction

Around 8% of global oil production is used to produce plastic (Thompson et al., 2009), whereof half is used as raw material and the other half for processing the plastic (Andrady and Neal, 2009). Plastic is lightweight, durable, persistent, and has low production prices and has become a ubiquitous material used for many applications (Bodni and Klotz, 2009). The main plastic types are polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET), poly(vinyl chloride) (PVC), and polyurethane (PU). Together they account for more than 80% of the European demand (PlasticsEurope, 2015).

Since the beginning of the plastic mass production in the 1940s (Roy and Visakh, 2015), the production volume has increased steadily and rapidly resulting in high quantities of plastics (Bodni and Klotz, 2009). In 2015 the global plastic production reached a level of 322 Mt of plastic and continues to rise (PlasticsEurope, 2016). Packaging made out of plastic is more and more replacing conventional materials like glass or metal (Andrady, 2003). About 40% of the produced plastic is used for packaging, of which PE, PP, and PET account for the largest proportion of common packaging materials (Andrady and Neal, 2009; PlasticsEurope, 2012). Plastic contributes about 10% by mass of municipal waste generated worldwide (Barnes et al., 2009).

Since the beginning of plastic production, additives have been used with basic polymer resins to make them processable (Murphy, 2001; Pritchard, 1998). Additives enhance certain properties of the plastic, eliminate or mitigate undesired properties, and the durability of the plastic product can be increased (Murphy, 2001; Tolinski, 2009). Therefore, a wide range of additives are used in the production of plastic (Murphy, 2001).

1.1 Marine plastic pollution

GESAMP defined marine pollution as "the introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of sea water, and reduction of amenities" (GESAMP, 1993). Marine pollution includes marine debris, especially plastic (GESAMP, 2015). Either through direct input or via transportation from land sources, plastic can enter the marine environment (Sheavly, 2007). The main sources contributing to the plastic debris in the marine environment are land based, including beach litter (Andrady, 2011). Especially densely populated or industrialized areas close to the shorelines are major input sources (Gregory, 1991; Pruter, 1987). Wastewater treatment plants (WWTPs) also contribute to plastic pollution by releasing plastic, like synthetic fibers and primary plastics from cosmetics, with the outlet water (Browne et al., 2011; Magnusson and Norén, 2014). Direct input from ships is also possible, for example through fragments of synthetic ropes (Dubaish and Liebezeit, 2013; Norén, 2007). About 18% of the marine plastics are estimated to originate from the fishing industry (Andrady, 2011), which mainly uses PE, PP, and nylon (Klust, 1982; Timmers et al., 2005).

In the early 1970s, plastic pollution was first described in scientific literature (Carpenter and Smith, 1972; Jambeck et al., 2015). Due to its high durability, plastic persists for a long time and tends to accumulate in the world's oceans (Sivan, 2011). Most plastic materials are buoyant and can be distributed via currents, resulting in ubiquitous plastic pollution (Barnes et al., 2009; Derraik, 2002; Gregory, 1996). Plastic has been observed even in areas as remote as the Antarctic (Barnes et al., 2010, 2009).

Many sampling studies have been conducted worldwide and computer models have been used to estimate the quantity of plastic debris entering the marine environment. According to estimates, between 60 and 80% of all marine litter today consists of plastics (Derraik, 2002). Furthermore, the level of plastics floating in the oceans has increased by approximately one order of magnitude since the early 1980s (Ryan et al., 2009; Thompson, 2004). Although the estimates vary significantly, there is likely to be between 7,000 and 35,000 tons of plastic on the open ocean surface (Cozar et al., 2014).

1.2 Effects of plastic in the marine environment

Lately attention has been drawn to the marine plastic pollution, including potential negative effects in the marine environment. Thus, as the prevalence of plastic in oceans increases, environmental concerns are also growing (Andrady, 2003).

Small plastics with a diameter less than 5 mm are defined as microplastics (Cole et al., 2011). Whereas macroplastic (larger than 5 mm in diameter) effects are more commonly described, the ecological hazards of microplastics are poorly characterized and remain largely speculative (Gregory and Andrady, 2003). Marine plastic, especially macroplastic, is aesthetically unappealing and has the potential to cause direct physical harm to marine species (Collard et al., 2015; Law and Thompson, 2014). Many studies have reported entanglement (Bodni and Klotz, 2009; Derraik, 2002; Gregory, 2009; Votier et al., 2011) and ingestion of plastic particles by for example turtles, seabirds, fish, and marine mammals (Boerger et al., 2010; Bravo Rebolledo et al., 2013; Bugoni et al., 2001; Denuncio et al., 2011; Moser and Lee, 1992; Rummel et al., 2016; van Franeker et al., 2011). When these materials are ingested they can block the digestive system, damage stomach linings, or reduce feeding instincts (Laist, 1987; Possatto et al., 2011; Teuten et al., 2009).

Furthermore, plastics are known to sorb persistent organic pollutants (POPs), resulting in concentrations that can be orders of magnitude greater than in surrounding waters (Ziccardi et al., 2016). Plastic can function as a vector of transport for these chemicals, increasing the exposure of an organism to these contaminants due to plastic ingestion. In contrast, ingested plastic can act as a sink for pollutants leading to a decreased bioaccumulation, and this is actively debated (Bakir et al., 2016, 2014; Koelmans et al., 2014, 2013; Teuten et al., 2009; Ziccardi et al., 2016). A laboratory study did not observe an effect for ingested plastics to act as a sink for pollutants (Rummel et al., 2016). Two recent critical reviews concluded that ingestion of plastic was not likely to significantly influence the exposure of organisms in the marine environment to hydrophobic organic chemicals (Koelmans et al., 2016; Ziccardi et al., 2016). Thus, more research is needed to clarify the potential effects of ingested plastics in marine life.

Additives used in plastic products are not chemically bound to the plastic and can consequently leach out (OECD, 2009). This can pose a potential threat to marine organisms since many additives have been recognized as hazardous (Lithner et al., 2011). Transfer of additives

from ingested plastic to marine organisms has been shown in laboratory experiments and field studies (Hermabessiere et al., 2017).

Sunlight, oxidants, and physical stress cause weathering of plastic (Bergmann, 2015; Hakkarainen and Albertsson, 2004; Pritchard, 1998). This can lead to changes of the surface and thereby to changes in the physical and chemical characteristics of the material (Andrady, 2011; Vasile, 2000). When plastic degrades slowly, a broad number of chemicals can be released, presenting new potential hazards to marine environments (Teuten et al., 2009, 2007). Released chemicals can include additives, POPs, residuals from production, and degradation products that are formed during chain scission of the polymer backbone. In particular, leachates from degrading plastics and their ecotoxicological effects have not been well-characterized.

1.3 Plastic identification

By identifying plastic debris, information about degradation products and potentially even sources can be gained. Fourier-transform infrared (FTIR) spectroscopy is by far the most widely used and accepted method for plastics identification (Shah, 2007). It is a nondestructive method to analyze the composition and state of a material (ASM International, 2003). The physical property that is measured is the ability of matter to absorb, transmit, or reflect infrared radiation (Alpert et al., 1970). Infrared energy produces vibrations within the molecular bonds, these molecular vibrations occur at characteristic frequencies (ASM International, 2003; Larkin, 2011). Because of the unique molecular structure, the obtained spectrum resembles a unique fingerprint of a particular plastic polymer (Shah, 2007). Identification of an unknown sample can be achieved by comparing its spectrum with reference spectra.

However, there is a great need for new identification methods, since available methods are rather tedious and have limitations especially for small-size particles of a few µm and less (Hidalgo-Ruz et al., 2012; Shim et al., 2017).

2. Thesis aim and objectives

A few decades ago, Carpenter and Smith speculated that the problem of plastic in the marine environment will get worse and that toxic, non-polymeric plasticizers could be delivered to marine organisms (Carpenter and Smith, 1972). Since then, the scientific interest in plastic and associated hazards has increased steadily.

The main aim of this thesis was to assess the risks posed by chemicals liberated from plastic debris to the marine environment. The focus was on chemicals that are degradation products of the plastic polymer and are released into the surrounding waters during weathering processes. These chemicals might contribute to the total chemical exposure of marine organisms. Figure 1 gives an overview of the four major objectives and papers included in this thesis.
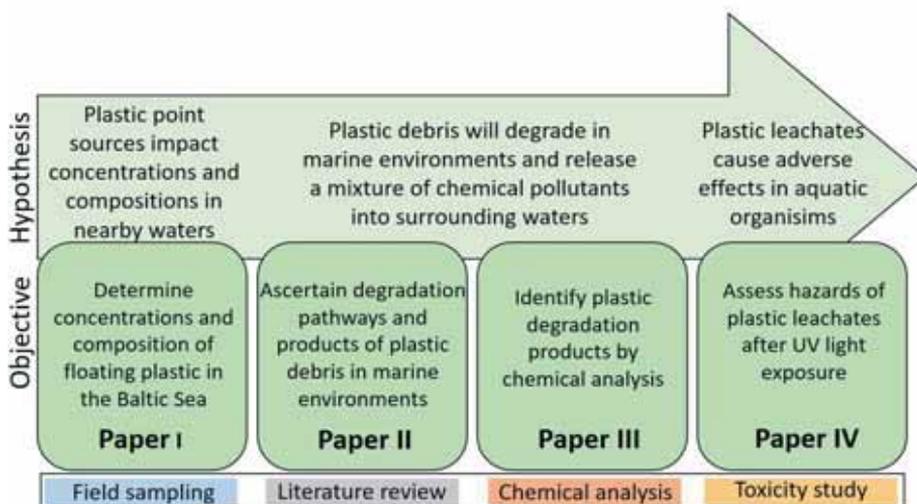

Figure 1: Hypotheses and objectives for each of the papers included in this thesis.

Even though many studies have shown that plastic can be found in the world's oceans, there have not been many studies analyzing the plastic concentration in the Baltic Sea. Stockholm is one of the largest urban areas at the Baltic Sea and the outer Archipelago is a known recreation

area with many inhabited islands. These conditions provide a large gradient between areas with a high and low anthropogenic impact. In **Paper I**, we sampled surface water in the Stockholm Archipelago for the determination of the abundance of floating plastic debris and we studied the spatial distribution between urban sites and remote areas.

Even though many studies show that plastic is ubiquitous in the world's oceans, the weathering processes of plastic in these environments are barely studied. To understand exposure and potential hazards it is necessary to know what free chemicals, which are chain scission products, might be present in the ocean due to plastic degradation. In **Paper II**, we reviewed the literature and extrapolated findings to gain information about the most important initiating factors for degradation and potential degradation products in the marine environment.

While additives and POPs sorbed to plastic are widely studied due to their known adverse effects, degradation products of the plastic polymers have received less attention. In **Paper III**, we built an artificial weathering set-up to degrade plastic in the laboratory. Subsequently, we conducted a nontarget ultra-high performance liquid chromatography-high-resolution mass spectrometry (UHPLC-HRMS) analysis to identify plastic polymer degradation products that leached into water.

Some chemicals associated with plastics are directly tested in acute toxicity studies. The hazards of plastic are often assessed by studying the effects in organisms after they have been exposed to plastic particles. Often these plastics are newly purchased spherical beads. We included more ecologically relevant conditions by using plastics collected from the marine environment and weathering plastic under environmentally relevant conditions in the laboratory. We conducted a screening study with the crustacean *Nitocra spinipes* in **Paper IV** to assess the toxic potential of compounds leached from plastic into the surrounding water.

3. Methods

The methods described in this thesis were often adapted from the literature. However, the experimental set-up for the artificial weathering was newly developed and the chemical analysis of plastic degradation products by LC-MS was a novel method.

3.1 Quantification of floating plastic debris

In **Paper I**, we identified and quantified plastic debris in the Stockholm Archipelago. The procedures of this study are shown in Figure 2.
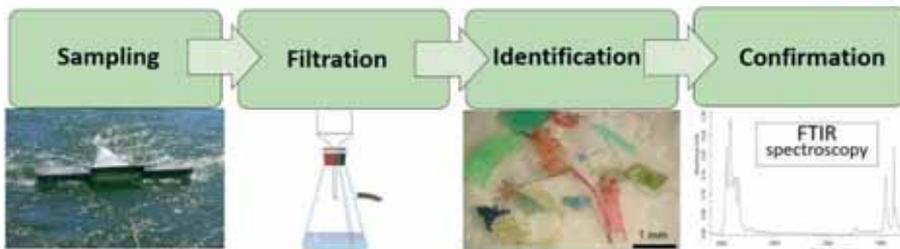
Figure 2: Flowchart for quantification of floating plastic debris.

Sampling: In summer 2014 the surface of the Baltic Sea in the Stockholm Archipelago was sampled with a 335 μm manta trawl (obtained from Marcus Eriksen from 5Gyres). The trawl was towed about 35 m behind the sampling vessel, which was traveling with a speed of 2-3 knots. After a maximal sampling time of 60 minutes, the net and the collecting bag were rinsed with about 6-10 L of seawater. In order to reduce the water volume, the samples were then filtered through a 110 μm mesh and material was collected by rinsing the net with about 0.5 L of tap water. Afterwards the samples were stored in darkness at 4°C until further analysis.

Filtration: In the laboratory, we separated the plastic from the water and biological matrix via further filtration based on a method described by Mason et al. (2016). First larger biological material was picked out

by tweezers and rinsed with water to avoid the loss of small plastic material stuck to the biological material. After allowing the sample settle, the supernatant was carefully decanted onto a glass fiber filter (GF/F; 0.75 μm; 47 mm Ø; Whatman, Maidstone, Kent, U.K.) aided with a vacuum pump. The remaining organic rich water was oxidized with a 33% hydrogen peroxide and water mixture of a 1:1 ratio by volume, similar to the methods used by Imhof et al. (2012) and Nuelle et al. (2014) to remove and/or bleach biological debris. After the organic material was oxidized or after a maximum period of 24 hours the sample was poured onto a filter until a thin layer of biological material and plastic debris was formed. New filters were used until the whole sample was filtered.

Identification: Visual identification and separation were based on several other publications (Hidalgo-Ruz et al., 2012; Norén, 2007). The selection criteria included unnatural and vivid colors, which expanded over the whole length of the plastic, no organic structure, and texture. Additionally, fibers should have the same diameter over the whole length. Suspected plastic pieces that matched these criteria were carefully picked out by very fine and pointy tweezers, counted, and collected in a separate dish.

Confirmation: First plastics of known identity were measured with the FTIR spectrometer in order to achieve a database of reference spectra. Then, 59 selected pieces that were representative and large enough to be seen with the naked eye were analyzed. The spectra of the samples were then compared with the reference spectra.

3.2 Critical review of plastic degradation pathways

Within **Paper II** we reviewed the literature about pathways for degradation of plastic polymers. We focused on the most common plastic types in use: PE, PP, PS, PET, PVC, and PU. Most of the published literature about plastic degradation is authored by polymer engineers, which include many studies with degradation experiments conducted under conditions that are not environmentally relevant. Hence, we explicitly evaluated their relevance under marine conditions. Most plastics are buoyant and therefore concentrate at the water surface (Gregory, 2009, 1996). Thus, we made extrapolations for plastic debris floating in the marine environment. Furthermore, likely degradation products were reviewed.

3.3 Artificial weathering of plastic

UV light was selected as the initiating factor to degrade plastic artificially in the laboratory. Three UV lamps of different wavelengths were chosen: 254 nm (UVP Pen-Ray (11SC-3.95-PO-16G Hg), purchased at Ultra-Violet Products Ltd), 220-450 nm (UV Lamp LIH 5/3/1, purchased at Light Impex Henze GmbH), and 275-450 nm (HTC 400-241 SUPRATEC HTC/HTT, purchased at OSRAM GmbH). A custom-designed weathering wheel was built at Stockholm University (Figure 3), which could hold up to six 350 ml quartz glass tubes horizontally placed around the centered UV lamp, which was exchangeable.
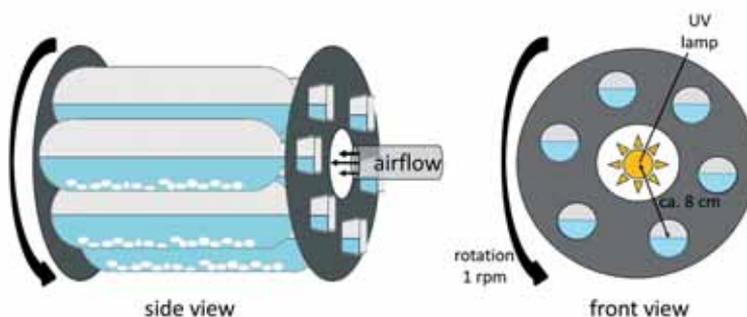

Figure 3: Weathering wheel scheme (adapted from Gewert et al., 2018).

Each sample tube contained plastic and water, while the blank only contained water. During exposure the wheel rotated at a speed of one rpm around the lamp for five days. A strong airflow maintained an air temperature of about 37°C.

3.4 Identification of plastic polymer degradation products

In **Paper III**, the leachates generated during accelerated artificial aging were analyzed with a nontarget approach using UHPLC-HRMS to identify degradation products of the polymer itself. Pristine PE, PP, PS, and PET plastic pellets were chosen, because they contained only few additives according to the distributer (Goodfellow GmbH, Germany). For each sample 5 g of plastic and 250 ml of Milli-Q water were used. In addition, dark controls of each plastic type were conducted, using the same experimental setup, but the samples were kept in darkness. After exposure, the leachates were concentrated on solid phase extraction

(SPE) columns (Waters, Oasis HLB Plus Short Cartridge, 225 mg Sorbent per Cartridge, 60 µm Particle Size).

The concentrated leachates were analyzed with an UltiMate 3000 Rapid Separation Liquid Chromatography system (Dionex, Germering, Germany) coupled to a Q Exactive HF Hybrid Quadrupole-Orbitrap mass spectrometer (Thermo Scientific, Bremen, Germany). We used a Hypersil GOLD aQ C18 column (2.1 mm x 100 mm, 1.9 µm I.D. from Thermo Fisher Scientific) and a solvent gradient, changing from 100% water in the beginning to 100% acetonitrile over time. For the nontarget analysis, the MS was run in full scan (100-1000 Da) at a resolution of 120,000 (at 200 m/z) with a data-dependent MS/MS scan of the five highest peaks present in the full scan. Every sample was analyzed three times.

The data processing was done using Compound Discoverer 2.0 (Thermo Fisher Scientific). An average of the peak areas of the three measurements was calculated and then the potential degradation products were determined according to the workflow shown in Figure 4.
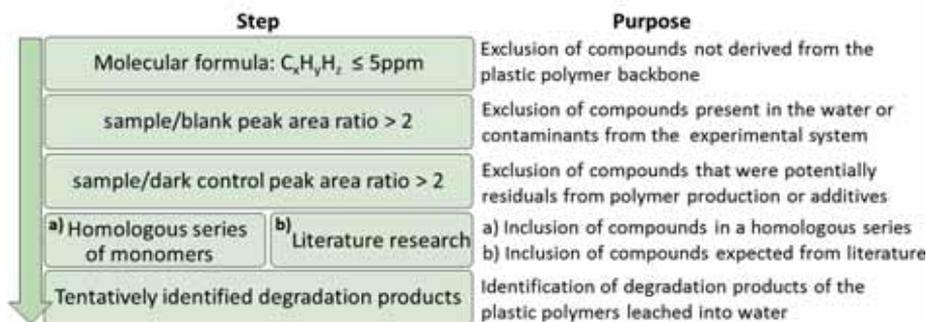

Step	Purpose
Molecular formula: $C_xH_yH_z \leq 5ppm$	Exclusion of compounds not derived from the plastic polymer backbone
sample/blank peak area ratio > 2	Exclusion of compounds present in the water or contaminants from the experimental system
sample/dark control peak area ratio > 2	Exclusion of compounds that were potentially residuals from polymer production or additives
a) Homologous series of monomers / b) Literature research	a) Inclusion of compounds in a homologous series / b) Inclusion of compounds expected from literature
Tentatively identified degradation products	Identification of degradation products of the plastic polymers leached into water

Figure 4: Workflow for identification of polymer degradation products.

3.5 Time series of degradation

To observe changes over time in relative concentrations of the plastic degradation products, plastic was exposed to UV light for different time periods. The four pristine plastic pellets from Goodfellow were selected to study after exposure times of 1, 2, 4, and 7 days. For this study, a different artificial aging set-up was used, which consisted of twelve 20 ml quartz glass tubes, which were placed around a UV lamp with an approximate distance of 3.5 cm. The lamp was cooled with a strong airflow and the whole construction was placed on a shaking table. Each

tube contained 2 g of plastic pellets suspended in 10 ml Milli-Q water and there were three replicates per time point. In this experimental set-up, only the 254 nm lamp was used, but not the 220-450 nm lamp and the 275-450 nm lamp. After exposure, the samples were analyzed without SPE concentration using our LC-MS method. An average peak area of the three replicates was calculated and relative peak areas were compared to each other.

3.6 Hazard assessment of plastic leachates

In **Paper IV**, we conducted a screening study to assess the toxicity of plastic leachates. We gathered plastic materials of different categories and weathered conditions, which are explained in Table 1.

Table 1: Materials used in Paper IV (* = is not weathered in the marine environment).

Condition Category	NEW newly purchased	OLD naturally weathered
Negative control	Glass beads	
Positive control	new keyboard (PS-blend)	e-waste* (mainly PVC)
Pristine plastic pellet	4 plastic pellets purchased from Goodfellow (PE, PP, PS, PET)	3 plastic pellets purchased from Goodfellow exposed in Oslo Fjord (PE, PP, PS)
Consumer product	5 newly purchased plastic products (PE, 2 x PP, PET, PVC)	5 plastics collected from the Swedish west coast (PE, 2 x PP, PET, PVC)

As a negative control, we used glass beads of a similar size fraction as the pristine plastic pellets (3 mm; purchased from Sigma Aldrich). Two positive controls were a newly purchased computer keyboard, which was ground up, and old cable coating (e-waste). The e-waste was aged, but not in the marine environment. We used the pristine plastic pellets from Goodfellow as described in **Paper III**. Some of these pellets were exposed to environmental conditions in the Oslo Fjord for seven months during summer 2017. Old plastic was collected from a remote shore on the Swedish west coast. The corresponding new products were purchased. A blank, not containing any plastic, was also included in this study.

Bigger plastic pieces were cut into smaller fragments of about 1 cm^2. A subsample of each material was extracted twice with an acetone:hexane

(1:1) mixture in a sonication bath for 15 minutes, which was described by Van et al. (2012) to remove contaminants from the surface of the plastic. Then the plastic was rinsed with tap water and dried for seven days.

We used a liquid-to-solid ratio (L/S) of 10 of artificial brackish water to plastic. The plastic material was artificially weathered under UV light with the weathering wheel as described in **Paper III**. A dark control was conducted using the same setup but the samples were exposed in darkness. After five days of exposure, the solid fraction of the plastic material was filtered out with a 40 µm metal filter. The water containing the leachates was stored at 4°C until analysis.

About 20 individuals of three-to-four-week-old *N. spinipes* without egg sacks were exposed to 10 ml of the plastic leachates at different concentrations. The raw leachate had an L/S of 10 and dilutions of this raw leachate were done at 1/3, 1/5, and 1/10 with brackish water. Three replicates per dilution were analyzed and after 96 hours of exposure at 20°C (±1) in darkness the final percentage of dead *N. spinipes* was calculated.

4. Results and discussion

4.1 Plastic debris in the Stockholm Archipelago

We detected plastic in all of our samples in **Paper I.** The level and composition of plastic debris in the Stockholm Archipelago are area dependent (Figure 5). A relationship between the anthropogenic impact index, which is based on the density of current or historical hazardous activities, and plastic concentration was observed. However, this relationship was strongly driven by the Stockholm samples (samples10-12) and no correlation remained once those three samples were excluded. The concentration rather depended on the distance of the sampling location to suspected point sources of plastic debris. This was specifically evident when taking samples at three different distances from Nynäshamn harbor, where the highest plastic concentrations were found closest to the harbor. Overall, a high gradient of plastic levels was found with highest concentrations in Stockholm ($6.18 \cdot 10^5$ plastic pieces km^{-2}), which is an urban site, and lowest concentrations in remote areas of the outer Stockholm Archipelago ($1.56 \cdot 10^4$ plastic pieces km^{-2}). Elevated concentrations were found close to the outlet of a WWTP (sample 17) and harbor areas (samples 13, 18, and 21).

Most of the observed plastics were in the form of fibers, which accounted for 82% of all the detected plastic material. A subsample of 248 fibers was measured and revealed that their length varied widely between 290 μm and 27 mm, with an average length of 2.9 mm.

In the three Stockholm samples (samples 10-12) the proportions of fibers were lower with a share between ~40-60%. More than 90% of all the retrieved macroplastic and paint flakes were found in these three samples.
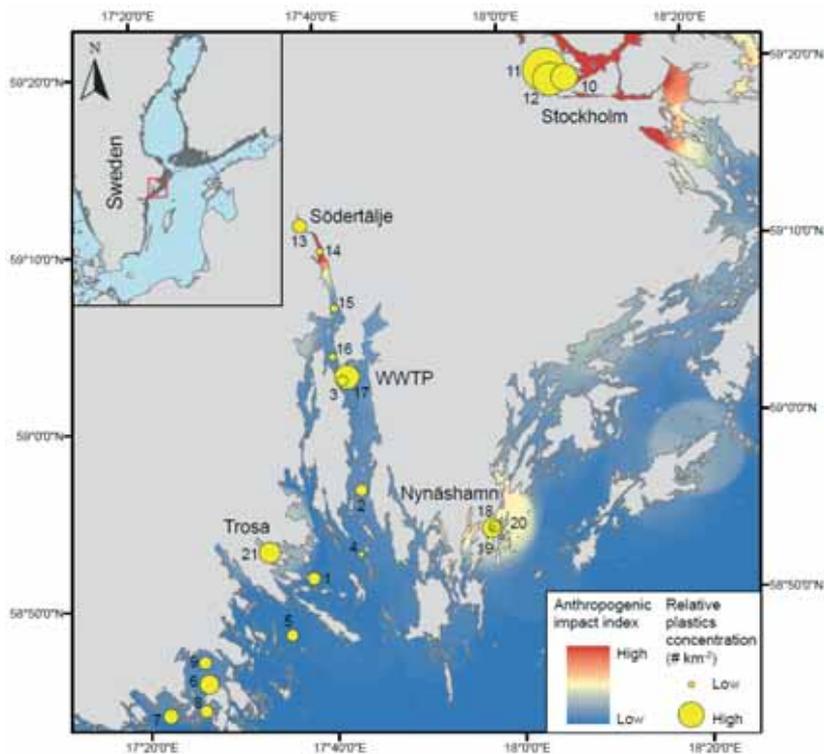
Figure 5: Relative abundance of plastic debris found in the Stockholm Archipelago (Gewert et al., 2017).

FTIR spectroscopy was used to confirm the identity of pieces visually identified as plastic (Figure 6). We confirmed 48 out of 59 analyzed pieces as plastic of a certain polymer type, with PP (53%) and PE (24%) predominating. Eight further spectra showed bands that indicate the polymer character of the sample without being matched to any of our reference spectra. One spectrum did not contain bands typical for non-biological polymers, while the identity of the two last materials remained unclear. The high percentage of PP and PE is most likely due to their natural buoyancy and high production volume and is in line with other sampling studies (Hidalgo-Ruz et al., 2012; PlasticsEurope, 2015). Furthermore, PP is often used in ropes that have a high exposure to marine environments and therefore fragments and degradations products are likely to be found in areas with high boat traffic (MacKown, 1992).

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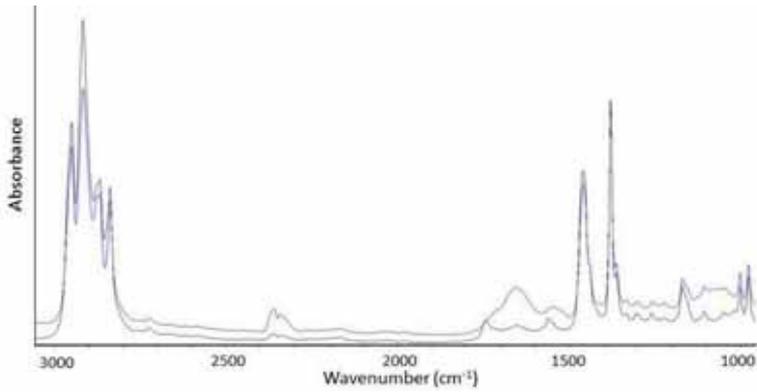
Figure 6: A PP reference spectrum (black line) compared with an unknown sample collected from the surface of the Baltic Sea in the Stockholm Archipelago, which we identified as PP (blue line).

4.2 Degradation pathways of plastic polymers

Most of the literature we reviewed describes degradation of plastic under extreme laboratory conditions. These imply high temperatures above 100°C and intense UV light at short wavelengths. As these harsh conditions do not occur in the marine environment, in **Paper II** we extrapolated these findings to conditions found in the marine environment. Figure 7 shows the most important initiating factors for degradation of floating plastics for the six most widely used polymers.
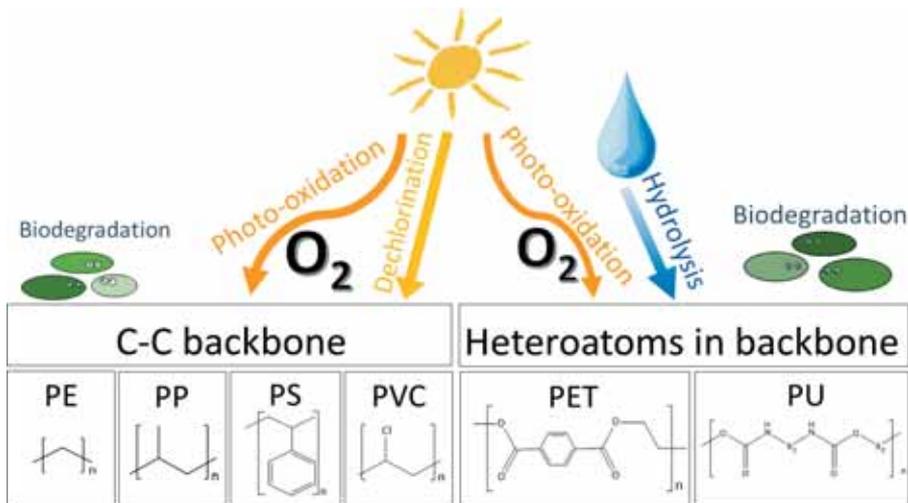
Figure 7: Initiating factors for plastic degradation in the marine environment of the six most widely used polymers (adapted from Gewert et al., 2015).

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The initiating step during the abiotic degradation mechanism is also the limiting step. A certain energy is required to break a bond within the polymer. UV light initiates the dechlorination of PVC. Photo-oxidation is the most important degradation pathway for PE, PP, and PS. First radicals are formed, followed by autoxidation, and chain scission (Figure 8). The formation of new end groups, shorter chain lengths, and degradation products are the main results.
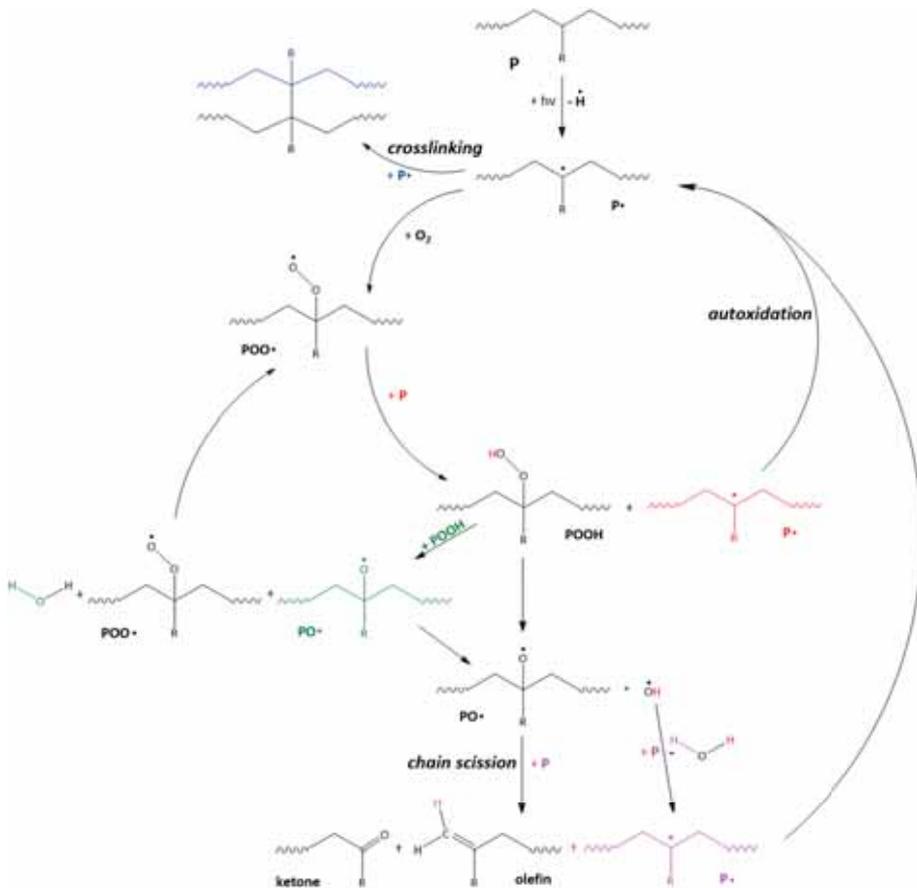

Figure 8: Abiotic degradation pathways for PE (R=H), PP (R=CH3) and PS (R=aromatic ring) after initiation by photolytic cleavage of a C-H bond of the polymer backbone (P=polymer backbone) (adapted from Gewert et al., 2015).

Relevant degradation pathways for PET and PUR, which contain heteroatoms in the main chain, are hydrolysis, photo-oxidation, and biodegradation. This will lead to smaller polymer fragments and formation of carboxylic end groups.

When the molecular weight is lower and more hydrophilic end groups are formed, biodegradation takes place at faster rates. Thus, abiotic degradation usually precedes biodegradation. Smaller polymer fragments formed during abiotic degradation can pass through cellular membranes and can then be biodegraded within microbial cells by enzymatic action. Certain microbes are also known to excrete extracellular enzymes that can act on specific plastic polymers (Shah et al., 2008). The chemical structure generally has an influence on the biodegradation rate. Generally, chain branching and halogens increase resistance towards biodegradation (Shah et al., 2008).

Since most plastic products contain additives, a general estimation of degradation rates for the different polymer types is not possible. Some of these additives can be stabilizers, increasing the resistance towards degradation. Since the additives are not covalently bound to the polymer backbone, they will eventually be released into the water. Biofilm formation, shielding by water, and the degree of aging of the plastic also modulate plastic degradation rates, in addition to the presence of additives. Thus, we were not able to estimate degradation rates and times for plastic debris in the ocean more precisely.
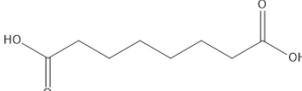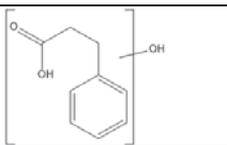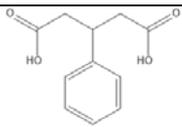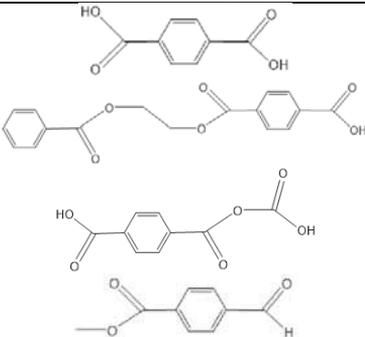
4.3 Plastic polymer degradation products

For the identification of plastic polymer degradation products, three different lamps were tested. The detected compounds varied for PS and PET between the three lamps, while it resulted in the same degradation products for PE. With the 254 nm lamp PS and PET degradation products of higher molecular weight, greater than 166 g/mol and 358 g/mol respectively, were not detected. The absorption peak of benzene, which is around 255 nm and can be shifted by functional groups, corresponds to the emission spectrum of this lamp. PS and PET have an aromatic ring structure and therefore some degradation products might have been broken down further and were not detected by LC-MS.

These findings point out that lamps with short wavelengths around 255 nm might not be suited for artificial weathering of plastics, because they interfere with aromatic ring structures and potentially destroy degradation products. Furthermore, solar radiation reaching the earth's surface has wavelengths between 290 nm and 320 nm, which is mimicked most closely by the 275–450 nm lamp and results can be more easily extrapolated to environmental conditions. Thus, the results

included in **Paper III** come from the data gained by using the high intensity UV lamp with a spectral radiation distribution from 275–450 nm and an exposure time of five days, which corresponds to about 510 days of European mean solar irradiance.

We were able to experimentally confirm that free chemicals, which are likely chain scission products of the polymer backbone, are released into water under artificial weathering conditions by detecting and identifying them with UHPLC-HRMS. In total, we identified 22 degradation products of the plastic polymers for PE, PS, and PET after being exposed to intense UV radiation, which are listed in Table 2.

Table 2: Number of compounds found during the evaluation for all four polymer types.

Polymer type	Total peaks	Tentatively identified degradation products	Smallest member of homologous series, identified as degradation product	Identified degradation product due to literature research
PE	965	6		
PP	1097	0		
PS	1242	4		
PET	1590	12		

For all four polymer types, we detected homologous series. We were able to confirm some of these compounds as degradation products of the polymer backbone for PE, PS, and PET. For PP, however, we were not able to confirm the identity of the detected compounds being members of the homologous series of dicarboxylic acids. This homologous series includes five compounds, which have the same molecular mass and molecular formula as the members of the

homologous series of PE. Even though the chemical structure should be different, the MS/MS fragmentation pattern and the RT were the same for PP and PE. Furthermore, the peak intensities for PP were low compared to PE and these compounds were also detected at low intensities in the blank. Thus, we did not include these five compounds in the list of tentatively identified degradation products. Additionally to the compounds of the homologous series, we were able to identify one more degradation product for PS, which is a dicarboxylic acid and also an expected degradation product based on our literature review in **Paper II**.

While studying time series of degradation, we detected an increase of the peak areas for PE and PS with the 254 nm lamp, which indicates that more degradation products are formed than are destroyed over the tested time period. However, for PET the peak areas of the detected degradation products decreased with longer exposure time with this lamp. These results indicate that the 254 nm lamp might destroy some of the degradation products. Thus, this lamp is unsuitable for degradation studies of plastics that could be readily applicable to environmental conditions.

4.4 Acute toxicity of leachates from degrading plastic

In **Paper IV**, we conducted a screening study to assess the acute toxicity of plastic leachates. We observed no mortality in our blanks and negative control in any of the treatments, thus we exclude background contamination and sample handling as a source of toxicity. Of the materials that were exposed in darkness only the e-waste, the glove (old and new), and the keyboard affected *N. spinipes* survival. PVC is the main component of the e-waste and the glove. This polymer type is generally known to contain a high percentage of additives, many of them being toxic (International Life Sciences Institute, 2003; Navarro et al., 2010; Stringer and Johnston, 2001). Since additives are not covalently bound to the polymer, they can leach out from the plastic material independent of the degradation of the plastic polymer (OECD, 2009).
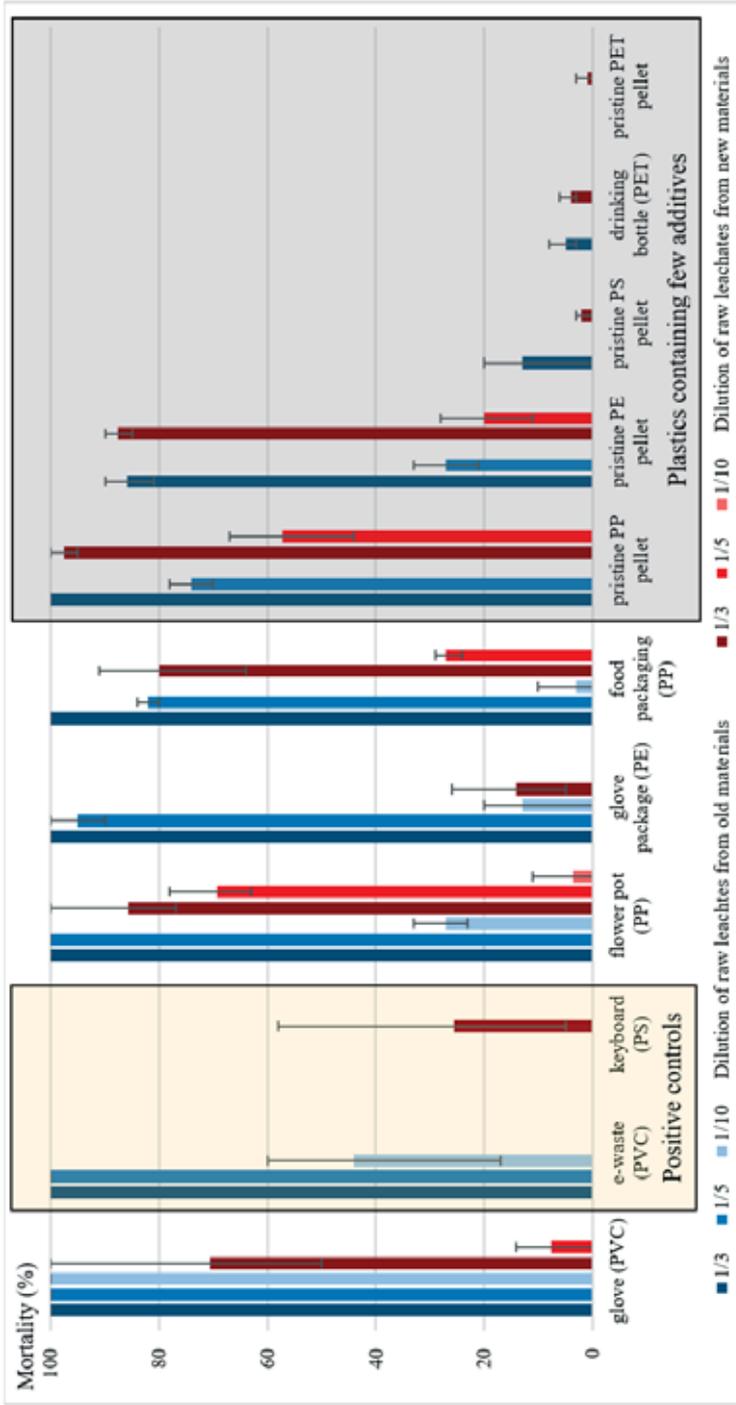
Figure 9: Average mortality of N. spinipes after being exposed to leachates from UV exposure; error bars show the maximum and minimum observed mortality

The raw leachates of all of the tested plastics showed 100% mortality of *N. spinipes* after being exposed to UV light, thus only the three dilutions of the raw leachates are presented in Figure 9. The polymer type affected the toxicity. PS and PET leachates caused the lowest observed mortality, while PVC and PP were most toxic. PVC has been identified in other studies as the most toxic polymer type (Li et al., 2016; Lithner et al., 2011, 2009), while PS was the least toxic one (Li et al., 2016).

The new pristine plastic pellets are supposed to contain only few additives, but these materials were generally as toxic as compared to new plastics of the same polymer type. However, the keyboard is not solely made up by PS, but it is a copolymer with PS as the main component and it was expected to contain many additives like flame retardants. Thus, the keyboard and the PS pellet are not directly comparable. The new pellets of PE and PP caused a relatively high toxicity, indicating that either more additives are present in the pellets than assumed or that other leachates, e.g. degradation products of the polymer, led to the observed toxicity.

When comparing the new with the old material, we observed no significant difference for the three pristine pellets (PE, PP, and PS) and the PET drinking bottle (Figure 9). All of those plastics are supposed to contain a low amount of additives (Bach et al., 2012; ILSI Europe et al., 2017, 2000; Welle, 2011). However, the four other tested plastics, which were the glove package, glove, food packaging, and flowerpot, showed a higher toxicity in the old material as compared to the new material. This might be explained by a reduction in the protective additives after marine exposure, and thus more rapid degradation in the laboratory and release of toxic compounds into the water. POPs sorbed to the plastic have probably a lower toxic effect in *N. spinipes* than compounds from the plastic itself, since not all old materials showed a higher toxicity. Additionally, even after an extensive surface cleaning of the old plastic, the leachates did not become less toxic. In contrast, leachates from some new plastics became more toxic after extraction of compounds from the materials, while no decrease in toxicity was observed. This indicates that additives could also be removed during the extraction, which might lead to disintegration of the polymer and thus more toxic chemicals could leach into the water.

5. Conclusions and future perspectives

The overall focus of this thesis was on chemical pollutants released to the marine environment by degrading plastics debris. We hypothesized that plastic in the oceans will weather and release chemicals into the surrounding water. These chemicals contribute to the total chemical exposure of marine organisms and can cause adverse effects. Understanding the level of exposure to a hazard can help to better estimate the risk associated with this hazard. Thus, within this thesis, information were gained about potential hazards of chemical leachates from degrading plastics and exposure of aquatic organisms.

Even though plastic was observed in all of the samples in **Paper I**, the concentrations varied widely. High plastic concentrations indicate point sources of plastic. Knowing input pathways of plastics into the oceans can help to introduce new regulations to decrease plastic pollution. One important point that is addressed in many publications, and we noticed while carrying out the research for **Paper I**, is that even though many scientific articles describe the quantity of plastic debris in the world's oceans, concentrations described in these studies are hard to compare. Therefore, there is a great need for uniform sampling, separation, and identification methods.

In **Paper II**, we reviewed that degradation of plastic debris floating in the marine environment is generally possible by UV light exposure. Since a diversity of factors influence degradation, it difficult to specify degradation rates and times for plastics. These factors could be the use and amount of additives, shielding by water or biofilm, size, and condition of the plastic particle. However, information about degradation rates is of great importance to be able to estimate the fate and longevity of plastic. The closer the conditions in laboratory experiments are to real marine conditions, the more precise conclusions can be drawn from laboratory work.

In **Paper III**, we demonstrated that degradation products, which are mostly dicarboxylic acids, are detectable in water after UV light exposure of the plastic. Thus, degradation products of weathering plastics in the marine environment will contribute to the chemical exposure in the oceans. The degradations products, which were identified in **Paper III**, can serve as a fingerprint to potentially identify sources of plastic pollution.

Previous studies have focused on additives and POPs leaching from plastic into water. We hypothesize that the amount of plastic polymer degradation products released from weathering plastics can be higher compared to leaching additives and POPs. This is because the amount of the polymer in a plastic product is generally higher compared to the additives and sorbed POPs. Furthermore, plastic is produced and used in high amounts globally. Thus, degrading plastic represents a constant source of organic carbon into the oceans, which might have an impact on microbes and ocean systems.

The ecological hazards of plastics, especially of microplastics and chemicals associated with degrading plastic, are also mostly unknown. We did not find any hazard assessments conducted with aquatic organisms for the degradation products we identified in **Paper III**.

In order to evaluate potential hazards of leachates from degrading plastics, we conducted a screening study, assessing acute toxicity in *N. spinipes* in **Paper IV**. From the tested materials, PVC and PP were the most toxic polymer types. PP is one of the most produced polymer types and was also the predominant polymer type in the Stockholm Archipelago. The major application of PP is food packaging, which is often discarded after short time. There is a potential risk of PP, given the high exposure and hazards observed in **Paper IV**. Further toxicity studies are therefore recommended.

The acute toxicity screening study also indicates that leachates from some plastics get more toxic the longer plastic has weathered. Therefore, it would be of interest to conduct a study with material that has been exposed for different lengths of time. A chemical analysis would be helpful to understand the cause of the negative effects and detect changes in concentrations of leached chemicals. Leachates could be analyzed by LC-MS. Many additives are known, due to their wide application, and can be used as a starting point for a suspect screening. Furthermore, known POPs and the degradation products we identified in **Paper III**, can be included in the suspect list.

Studying the concentration of compounds in the water after different exposure times might also provide information to gain a better understanding of degradation times and rates. Since there are even standards available for some of the plastic degradation products, POPs, and additives, these compounds could be quantified.

Besides toxicity, also persistence (P) and bioaccumulation (B) of the mixture of leached chemicals from plastics are interesting factors to test. A P and B hazard assessment of the mixture of chemicals liberated from plastic debris would be required to evaluate the hazards of weathering plastics in a broader perspective.

Over all, there are remarkably few plastic studies conducted under conditions that can be readily extrapolated to environmentally relevant conditions. Thus, exposure studies and weathering experiments in the laboratory simulating environmental relevant conditions are needed to reduce uncertainties in environmental hazard and risk assessment of plastic.

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