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Chemical additives in weathered microplastic in the marine environment



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This publication is also available online in a web-accessible version at <https://pub.norden.org/temanord2022-520>.

Summary

This Nordic project identified and measured residues of chemical additives in microplastic particles of polyurethane (PUR) and polyvinyl chloride (PVC). Measurements were performed in new plastic, and in plastic exposed to weathering in the marine environment for four months. The particles had a size fraction of 250 µm – 710 µm, and the weathering experiments were conducted in Samnangerfjorden near Bergen from June to October 2020.

A suspect list of chemical additives in PUR and PVC was constructed, consisting of 48 possible chemicals of which 20 were included in a suspect screening based on gas chromatography-high resolution mass spectrometry (GC-HRMS)

Four plasticizers were detected in PUR, and three in PVC, before and after weathering: Dibutyl adipate, N-butylbenzenesulphonamide, dibutyl phthalate, and di-2-ethylhexyl phthalate (DEHP). Two additives were detected, but not quantified, these were a heat stabilizer (triphenyl phosphite) and an antioxidant (octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), identified both in PUR and PVC before and after weathering. Using conventional GC-low resolution MS methods, maximum concentrations were determined to be 1587 ng/g plastic before weathering, and 946 ng/g plastic after weathering for N-butylbenzenesulphonamide. For N-butylbenzenesulphonamide and dibutyl phthalate, a loss by approximately a factor of 2 was observed during the weathering process.

Measured concentrations were used to calculate Predicted Environmental Concentrations (PECs) values for the marine water, representing exposure to zooplankton and fish, and for food intake for seabirds and fish. Low and high exposure estimates were made to account for the variations in the measured concentrations, ingestion rates, and bio-available fractions on the particles. A hazard screening was done to derive Predicted No-Effect Concentrations (PNECs) and to calculate risk characterisation ratios ($RCR = PEC/PNEC$) for the marine organisms.

RCRs larger than one, indicating potential risk, were not observed for any individual additive, nor for the sum of RCRs for all quantified additives. For zooplankton and fish combined with plastic particle ingestion via seawater, the sum RCR was $1E-09$ and $3E-06$ for the low and high exposure scenarios, respectively. For fish and birds combined with ingestion via food, the sum RCR varied between $3E-11$ and $1E-05$, for the low and high exposure scenarios. The highest individual RCR was $1E-05$ was found for dibutyl phthalate and exposure via food intake for birds. Overall, there was a minimum safety margin of approx. 100,000 ($1E05$) across all chemicals and exposure scenarios, indicating a low added risk towards the marine environment.

Additionally, non-target screening with GC-HRMS tentatively identified 16 chemicals, including 2,6-diisopropyl-naphthalene, used as plant growth retardant and agrochemical, and tris(chloroisopropyl)phosphate (TCIPP), a known flame retardant. Both compounds are classified in ECHA by notifiers as toxic, and with respect to aquatic toxicity the former as *H410: Very toxic to aquatic life with long lasting effects*, and TCIPP as *H412: Harmful to aquatic life with long lasting effects*, and

H413: May cause long lasting harmful effects to aquatic life. The compounds were tentatively identified by using NIST library and MassBank database and filters for certain chemical structures.

The results have been disseminated in the Nordic NordMar Plastic network. They will further be included in educational material and as information for decision-makers, the plastics industry, industry organisations and distributors. The results will also be presented and discussed with the Danish Environmental Protection Agency, at conferences and in the scientific literature, as well as on the project partners' and social media's websites.

Sammenfatning

I dette nordiske projekt blev rester af kemiske additiver i mikroplastik partikler af polyurethan (PUR) og polyvinyl chlorid (PVC) identificeret og målt. Plastik blev indledningsvis granuleret til partikler i størrelsen 250 – 710 µm, og derefter eksponeret i det marine miljø i fire måneder i Samnangerfjorden nær Bergen, fra juni til oktober 2020. Der blev målt på både nyt plastik og plastik efter eksponeringen i det marine miljø.

Der blev opstillet en liste med mulige kemiske additiver (suspect liste) i PUR og PVC. Ud af i alt 48 mulige kemikalier blev 20 inkluderet i suspect screening med gas chromatografi-høj opløselig masse spektroskopi (GC-HRMS).

Fire blødgørere blev detekteret i PUR, og tre af disse blev også detekteret i PVC, både før og efter eksponering: Dibutyl adipate, N-butylbenzenesulphonamide, dibutyl phthalate, og di-2-ethylhexyl phthalate (DEHP). To detekterede, men ikke kvantificerede, additiver var en varmestabilisator (triphenyl phosphite) og en antioxidant (octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate). De blev detekteret i både PUR og PVC før og efter nedbrydning. Ved analyse med konventionelle GC-lav opløselig MS metoder blev der fundet maksimum koncentration af N-butylbenzenesulphonamide på 1587 ng/g plastik før nedbrydning, og 946 ng/g plastik efter nedbrydning. For N-butylbenzenesulphonamide og dibutyl phthalate var reduktionen i koncentrationerne efter nedbrydning ca. en faktor 2 i forhold til før nedbrydning.

De målte koncentrationer blev brugt til at beregne Predicted Environmental Concentrations (PECs) værdier dels for vandfasen, hvilket repræsenterer eksponering for zooplankton og fisk, og dels for fødeindtag for havfugle og fisk. Lave og høje eksponeringsscenarier blev opstillet for at tage højde for variationer i målte koncentrationer, samt fraktion af kemikalier, der blev indtaget og optaget i organismerne. En farevurdering blev udført for at fastlægge Predicted No-Effect Concentrations (PNECs) og til at beregne risikokoefficienter ($RCR = PEC/PNEC$) for de marine organismer.

RCR større end én, der indikerer potentiel risiko, blev ikke fundet for hverken individuelle kemikalier eller for summen af risici for de fire kvantificerede kemikalier. For zooplankton og fisk i kombination med plastik optag via vandfasen varierede sum RCR mellem $1E-09$ og $3E-06$ for hhv. det lave og det høje eksponeringsscenarie. For fisk og fugle i kombination med eksponering via fødeoptag varierede sum RCR mellem $3E-11$ og $1E-05$, for hhv. det lave og det høje eksponeringsscenarie. Den højeste individuelle RCR var $1E-05$ for dibutyl phthalate i kombination med eksponering via fødeoptag for fugle. Overordnet set var der en minimum sikkerhedsmargin på ca. $1E05$ på tværs af alle kemikalier og eksponeringsscenarier, hvilket indikerer en lav risiko overfor de undersøgte marine organismer.

Non-target screening med GC-HRMS identificerede tentativt 16 kemikalier, bl.a. 2,6-diisopropylnaphthalene, der anvendes som plantevækst hæmmer, og tris(chloroisopropyl)phosphate (TCIPP), som er en kendt flammehæmmer. Begge kemikalier er indberettet som toksiske i ECHA og med hensyn til akvatisk toksicitet er førstnævnte klassificeret som *H410: Meget giftig med langvarige virkninger for*

vandlevende organismer, og TCIPP som H412: Skadelig for vandlevende organismer, med langvarige virkninger, og H413: Kan forårsage langvarige skadelige virkninger for vandlevende organismer. Kemikalierne blev tentativt identificeret via NIST biblioteket og MassBank databasen samt filtre for visse kemiske strukturer.

Resultaterne er blevet formidlet i det nordiske NordMar Plastic netværk. De vil desuden inkluderes i uddannelsesmateriale og som information til plastikindustrien, brancheorganisationer og distributører. Resultaterne vil endvidere præsenteres og diskuteres med Miljøstyrelsen, til videnskabelige konferencer og i artikler, samt på projektpartnerenes og sociale mediers hjemmesider.

Preface

This work was funded by the Nordic Working Group for Oceans and Coastal Areas (Nordisk Arbejdsgruppe for Hav og Kyst, NHK) and the Nordic Working Group for Chemicals, Environment, and Health (Nordisk Arbejdsgruppe for Kemikalier, Miljø og Sundhed, NKE), under the auspices of the Nordic Council of Ministers.

The project was initiated March 2020 and finalized December 2021.

The project group was:

Senior scientist Patrik Fauser, Aarhus University, Department of Environmental Science: Project leader, data acquisition, preparation of plastic particles, development of suspect list of additives, data interpretation, exposure and risk screening, dissemination.

Professor Katrin Vorkamp, Aarhus University, Department of Environmental Science: Conceptualisation, establishment of the project group, design of chemical analysis, data interpretation, dissemination.

Post doc Linyan Zhu, Aarhus University, Department of Environmental Science: Development of suspect list of additives, sample preparation for analysis, design and performance of chemical analysis, data interpretation.

Senior scientist Hans Sanderson, Aarhus University, Department of Environmental Science: Hazard and risk screening.

Laboratory technicians Birgit Groth and Annegrete Ljungqvist, Aarhus University, Department of Environmental Science: General practical assistance, sample preparation of weathered plastic samples, assistance in chemical analysis and data interpretation.

Scientist André Borgevik, Nofima, Norway: Sampling design and setting up of sampling equipment and plastic samples in Samnangerfjorden, dissemination.

Project manager Sophie Jensen, Matis, Iceland: Dissemination of project and results in Nordic networks such as NordMar Plastic (<https://nordmarplastic.com/>), dissemination.

Peer assessment of the report has been conducted by senior scientist Pia Lassen, Aarhus University, Department of Environmental Science and quality assurance by Chief consultant Susanne Boutrup, Aarhus University, DCE.

1. Introduction

Plastic pollution is recognized as a serious threat to the marine environment, both at the global and regional level. For example, the United Nations Environment Assembly has adopted four resolutions on marine litter since 2014 (<https://www.unep.org/>; <http://unea.marinelitter.no>); and the European Union has developed the Marine Strategy Framework Directive (MSFD), with marine litter as one of the descriptors (Direktive 2008/56/EC; Galgani et al., 2013). In 2020, the Nordic Council of Ministers issued a declaration describing the need for a global agreement to reduce and prevent marine plastic pollution (<https://www.norden.org/en/declaration/nordic-ministerial-declaration-need-new-global-agreement-prevent-marine-plastic-litter>). A Nordic Programme has been developed to reduce the impact of plastics (NCM, 2017). The new 2019-2024 Nordic environment and climate collaboration plan (<https://nordiccitynetwork.com/news/new-2019-2024-nordic-environment-and-climate-collaboration-plan/>); Islands Formandsskabsprogram 2019; the Oslo-Paris Commission (OSPAR) and the Baltic Marine Environment Protection Commission (HELCOM) issued Regional Action Plans for Marine Litter in 2014 and 2015, respectively. In the Arctic area, the Arctic Council Working Group for the Protection of the Arctic Marine Environment (PAME) has developed a Regional Action Plan that is currently being implemented (PAME, 2021), and the Arctic Monitoring & Assessment Program (AMAP) has prepared Monitoring Guidelines for Litter and Microplastics in the Arctic (AMAP, 2021). A key aspect in these programs is to reduce the negative environmental effect of plastic and to identify means to reduce the inflow into the marine environment. It is prioritized to enhance the knowledge of sources and occurrence of plastic, and to develop common methodologies to measure the extent of plastic in the marine environment.

This Nordic project addresses Agenda 2030 and the Sustainable Development Goals (SDGs), in particular Goals 12 and 14:

- Goal 12 Ensure sustainable consumption and production patterns:
Bullet 12.4 By 2020, achieve the environmentally sound management of chemicals and all wastes throughout their life cycle, in accordance with agreed international frameworks, and significantly reduce their release to air, water and soil in order to minimize their adverse impacts on human health and the environment.
Bullet 12.8 By 2030, ensure that people everywhere have the relevant information and awareness for sustainable development and lifestyles in harmony with nature.
- Goal 14. Conserve and sustainably use the oceans, seas and marine resources for sustainable development:
Bullet 14.1 By 2025, prevent and significantly reduce marine pollution of all kinds, in particular from Land based activities, including marine debris and nutrient pollution.

This project builds on the previous study "Mikroplast i havmiljøet – viden om skadevirkninger, detektionsmetoder og skæbne", funded by the VELUX foundation, where Danish universities compiled and assessed information and data on the state and effects of microplastics in the marine environment (Fauser et al., 2019; 2020). In

dialog with the plastic industry a number of cases were defined in the previous project with polymer types, product groups and chemical additives with highest potential for hazardous effects towards the marine environment. The results of the previous projects were presented and discussed with Danish national authorities, municipalities, with relevant industry and trade organisations, non-governmental organisations and consultancy companies: ▫ The Danish EPA ▫ The Danish ministry for environment and food ▫ Kommunernes Internationale Miljøorganisation (KIMO) ▫ PVC information council ▫ Cosmetic og Hygiene trade organisation ▫ Trade organisation (VKH) Vask Kosmetik Husholdningsindustri ▫ Plastic industry (SABIC) ▫ Environmental organization Plastic Change ▫ Ecological Council ▫ Greenpeace ▫ Consultancy companies (NIRAS, COWI, Krüger, Ramböll) ▫ ATV-foundation for soil and groundwater ▫ IWA/DANVA ▫ Trade organisation "Genanvend biomasse" ▫ WWF ▫ Danmarks Fiskeriforening Producent Organisation. The results obtained in this project will be made available for these interested parties.

The current project also builds on the experience from PlastiCod, a project for the Norwegian Research Council that aimed at investigating potential sources to pollution with microplastic along the coast of Norway (Vorkamp et al., 2019). PlastiCod considered, e.g. the affinity of microplastic towards chemical pollutants by exposing plastic particles in coastal waters and their effect on Atlantic cod (*Gadus morhua*) food webs. Participants of the present project group also participated in PlastiCod and used similar methodological approaches. The project also has a link to NordMar Plastic (2019–2021), lead by Mátis (Iceland), a Nordic network, funded by the Nordic Council of Ministers, to develop harmonized methods for analysing microplastic. The network also produces educational material, hosts work-shops and informs the general public on the problems and solutions of pollution.

2. Background

Up to 8 million tons of plastic waste are emitted to the oceans annually on a global scale, and emissions are expected to increase in the coming years (Smith et al., 2018; Gourmelon, 2015). According to the European Chemicals Agency ECHA (2020) microplastics are defined as particles with a size between 100 nm and 5 mm or fibers with a length between 300 nm and 15 mm; however, other definitions exist as well. In the environment, microplastic particles can be defined as primary and secondary according to GESAMP (2016): Primary particles were originally manufactured to be this size (e.g. used in cosmetics, cleaning products, industrial abrasives). Secondary particles are breakdown fractions from larger items, due to weathering processes on land and at sea, such as fragmentation and degradation by mechanical processes and UV radiation.

Many chemicals (additives) are added to the plastic material, to achieve the desired plastic properties (Hahladakis et al., 2018). Plastic products that end up in the ocean decompose into smaller particles, as a result of physical, chemical and biological processes. This weathering process will most likely also change the structure and chemical composition of the plastic particles. Chemical additives can be released from the plastic and lead to unwanted effects in the marine environment. It is not known whether there may also be effects on humans, as a result of eating seafood containing microplastic and/or additives. However, knowledge of which chemicals are added to the plastic products, how much is released into the sea and their risk to the marine environment is limited.

During the fragmentation and weathering processes, the surface area of the particle relative to its volume increases, which may also increase the leaching rates of chemical additives (Kwon et al., 2017). In this project it is therefore relevant to consider the leaching potential from micro size plastic particles.

This project focusses on polyurethane (PUR) and polyvinylchloride (PVC) polymer materials as they are used in many products, e.g. PUR rigid foam is used in building insulation and materials, and PVC is used in cables and linoleum floors but also on ships and buoys. PUR and PVC fragments are frequently found in the Nordic marine environment (Feld et al., 2019), and chemical additives leaching from PUR and PVC can therefore also be significant in terms of occurrence, related exposures and risks.

Plastic materials can contain many different types of additives (Hahladakis et al., 2018). Polymerisation additives become part of the polymer (e.g. cross linking agents, curing agents, inhibitors, initiators), or are necessary to preserve the stability of the polymer. Other additives typically form a mixture with the polymer, to achieve particular properties needed for the manufacture of articles. These latter "inherent" additives are numerous and include among others stabilizers, plasticizers, flame retardants, antioxidants and photostabilizers (EC, 2012). Some of these chemicals may be found at high proportions (10–15 wt-%) in the plastic material, and they are potentially bioavailable after ingestion by organisms (Andrady, 2017).

Measurements of residual additives in weathered plastic particles are limited. There is even less knowledge and data on the comparison between the amounts in the original plastic products and the weathered plastics, which would give an

understanding of the leaching potential as a part of the weathering processes. Typically, existing studies do not distinguish between chemicals added to the polymer or those that are sorbed from the environment. However, a general conclusion is that measured concentrations in plastic particles of, e.g., brominated flame retardants, phthalate softeners and some metals, that have often been associated with marine plastic debris, are likely to be much higher than what can be achieved through sorption from seawater (Hermabessiere et al., 2017; Al-Odaini et al., 2015).

Traditional measurement methods in analytical chemistry usually target specific, pre-defined compounds. The analytical methods are optimized for these compounds, with regard to specificity, sensitivity, precision and accuracy, and aim at producing high-quality data as needed in e.g. time series and compliance checking. However, they only consider a very small window of the chemical universe and disregard, or even remove, compounds that are present in the sample as well, but not pre-defined for analysis. New developments in analytical chemistry, called non-target screening, take advantage of the selectivity of high-resolution mass spectroscopy (HRMS) and advanced algorithms to approach large groups of chemicals, including unknown compounds. In these approaches, sample-preparation steps are kept as non-selective as possible, and the selectivity of the HRMS instrument is used to identify unknown compounds (Hajeb et al., 2022). These techniques are usually limited to compound identification, as quantification requires certified analytical standards.

Suspect screening is a sub-category of non-target screening, which is closer to conventional target analyses (Schymanski et al., 2015). In these approaches, the analyses do not screen for completely unknown, but for "suspected" compounds in a sample. These suspect lists can be extensive and diverse, often combining chemicals from different use categories and with different physical-chemical properties, which would not be combined in traditional analyses. In some cases, standards may be available, but suspect screening usually operates from a defined molecular structure (Schymanski et al., 2015).

3. Objectives

The purpose of this project was to identify new, and quantify suspected, chemical additives present in PUR and PVC plastic, respectively, that are potentially hazardous to the marine environment. An important aspect was to investigate the effect of weathering, by placing micro-size plastic particles in marine water and assess the occurrence of chemical additives before and after weathering. This was done both qualitatively, on an indication basis with non-target screening, and quantitatively for selected compounds.

To reach the project goals the following three targets were set up:

Target 1 (section 4.1): Data compilation and establishment of a suspect list of plastic additives and monomers that are potentially present in PUR and PVC plastics. Data comprise types and amounts of chemicals in PUR and PVC, respectively, as well as marine environmental health effect values.

Target 2 (section 4.2, 4.3, 4.4): Preparation of plastic in micro-size particles, performance of weathering experiment and chemical analysis. PUR and PVC samples in micro-size particles (250 μm – 710 μm), placed in water permeable nylon bags, expose to weathering in the coastal marine environment and subsequently analyze with suspect and non-target screening methods.

Target 3 (section 4.5, 4.6, 4.7): Risk screening and dissemination. Exposure and hazard assessments of the identified and quantified chemical additives are used to calculate their risk towards selected marine species. Dissemination of results.

This project will contribute to the identification and risk screening of known and emerging chemical additives in common plastic types. It aims to improve our understanding of the presence of additives in plastic materials and their leaching to the marine environment. New knowledge in this field can enter a risk management procedure and be considered in potential regulations of chemical additives, plastic types and products.

4. Method

4.1 Suspect and total list of plastic additives

The suspect list of chemical additives was built based on ECHA's list of plastic additives from the plastic additives initiative (PLASI) project:

<https://echa.europa.eu/mapping-exercise-plastic-additives-initiative>. The additives represent softeners, flame retardants, light-, heat- and other stabilizers, antioxidants, pigments and other functions.

Criteria for being on the suspect list were:

- i. Chemical additive is applied (before weathering) in PUR and/or PVC
- ii. Relatively high use, i.e. mass concentration in plastic is higher than 1%
- iii. Relevant with respect to aquatic toxicity
- iv. All additive groups on the ECHA list should be represented
- v. Certified analytical standards are available.

The screening for toxicological relevance (iii) used the Globally Harmonized System (GHS) via ECHA's C&L Inventory database (<https://echa.europa.eu/information-on-chemicals/cl-inventory-database>) that contains classification and labelling information on notified and registered substances received from manufacturers and importers as well as harmonized classifications.

Additionally, some phthalates were also included in the suspect list as standards were available in-house.

4.2 Preparation of plastic samples in the laboratory

The PVC and PUR materials were retrieved from plastic manufacturers in Denmark. The PVC was from a buoy and the PUR was from a block used as building material. PVC and PUR samples were prepared separately at Aarhus University. A coffee grinder was used to grind the plastic material. Subsequently, the particles were sieved into defined size classes before the weathering experiments at sea.

In details, the production of plastic particles followed this procedure:

- i. Only plastic pieces from the same product, and that appear to be similar in structure and color were used.
- ii. Plastic material was cut with scissors into approx. 5x5 cm pieces.
- iii. The pieces were ground in a coffee grinder for approx. 1 minute. To enable grinding of the PVC pieces, they were placed in liquid nitrogen (approx. minus 200 °C) for approx. 30 seconds prior to grinding. To avoid contamination the coffee grinder was cleaned in ethanol and air dried between the PVC and PUR sample preparations.
- iv. Ground plastic material was sieved using > 710, 500, 250 µm filters in succession.
- v. Four bags were prepared for each of PUR and PVC, as safeguard against loss of bags during the weathering experiment.
PUR: Three bags each consisted of approx. 15 g of size fraction 500–710 µm mixed with approx. 70 g of size fraction 250–500 µm. One bag consisted of

approx. 90 g of size fraction $>710\ \mu\text{m}$.

PVC: Three bags each consisted of 45 g of size fraction $500\text{--}710\ \mu\text{m}$ mixed with approx. 75 g of size fraction $250\text{--}500\ \mu\text{m}$. One bag consisted of approx. 290 g of size fraction $>710\ \mu\text{m}$.

- vi. One sample was prepared with approx. 100 g of size fraction $<250\ \mu\text{m}$ of PUR and PVC, respectively, for analysis of the pure plastic material (not included in the weathering experiment).
- vii. The eight samples of plastic particles were placed in water permeable nylon draw string bags with mesh size $200\ \mu\text{m}$, see Figure 4.2.1. The bags were placed into separate Rilsan® Polyamide 11 Resin bags and packed in cardboard boxes before transport.
- viii. The bags were deployed at sea for 4 months.
- ix. The eight nylon bags were at termination of the weathering experiment put into separate Rilsan® Polyamide 11 Resin bags and sealed for transport back to Denmark.

FILTERBAG.COM
A DIVISION OF MIDWEST FILTER, LLC

Size: 12x18

Material: Nylon Monofilament Mesh

Micron Rating: 200

Style: Drawstring

Ring Material: Drawstring



Figure 4.2.1 Water permeable nylon drawstring bags with mesh size $200\ \mu\text{m}$ for plastic particle containment.

When the nylon bags with plastic particles were shaken prior to shipment, dust was released from the bags. Considering the $200\ \mu\text{m}$ mesh size of the nylon bags and the smallest sieved particle sizes of $250\ \mu\text{m}$, it was assumed that the released material was dust of a smaller size than $200\ \mu\text{m}$. Similar observations had been made in the PlastiCod project. Possibly, the electrical charge between the smallest plastic particles hampered separation and complete sieving of these. They could be released when the bags were shaken and when the bags were submerged in water. However, the loss was insignificant with regard to the material required for chemical analysis. Furthermore, the bag with particles $>710\ \mu\text{m}$ was included to ensure that sufficient plastic material would remain for chemical analysis, in case there was considerable loss of the smallest particles from the bags.

4.3 Weathering of plastic particles in the fjord

Four sample bags of PVC and four bags of PUR, sealed tightly with strips, were submerged to 3 meter in the coastal water in Samnangerfjorden near Bergen, Norway. See Figure 4.3.1 for experimental set-up. The location was chosen as the general pollution/contamination in the area is low with low-density housing, limited industry and boat traffic, and no significant point sources of the considered chemicals, see Figures 4.3.2a and b. A fish farming facility (Bolaks) was not considered as a point source for these chemicals according to a survey from Godal (2018), see Figure 4.3.2b.

The weathering experiment ran for four months from mid-June to mid-October 2020, after which the weathered plastic samples in nylon bags were packed in Rilsan bags and shipped to Aarhus University for chemical analysis.

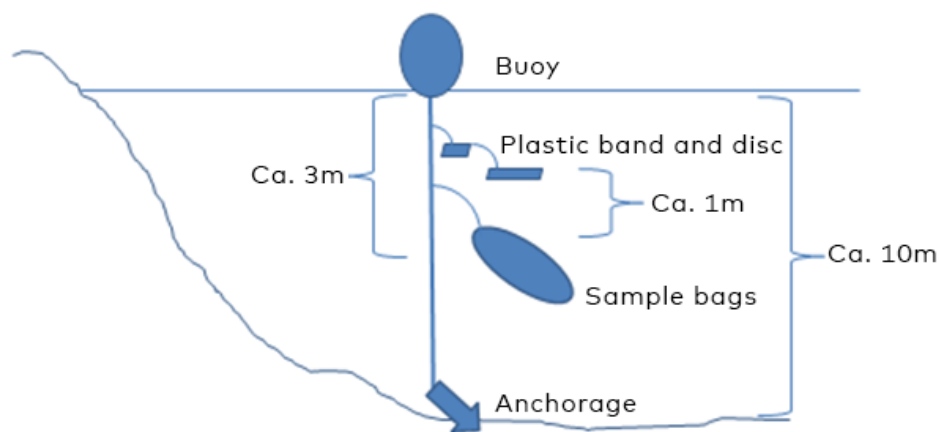


Figure 4.3.1 Experimental set-up in Samnangerfjorden.

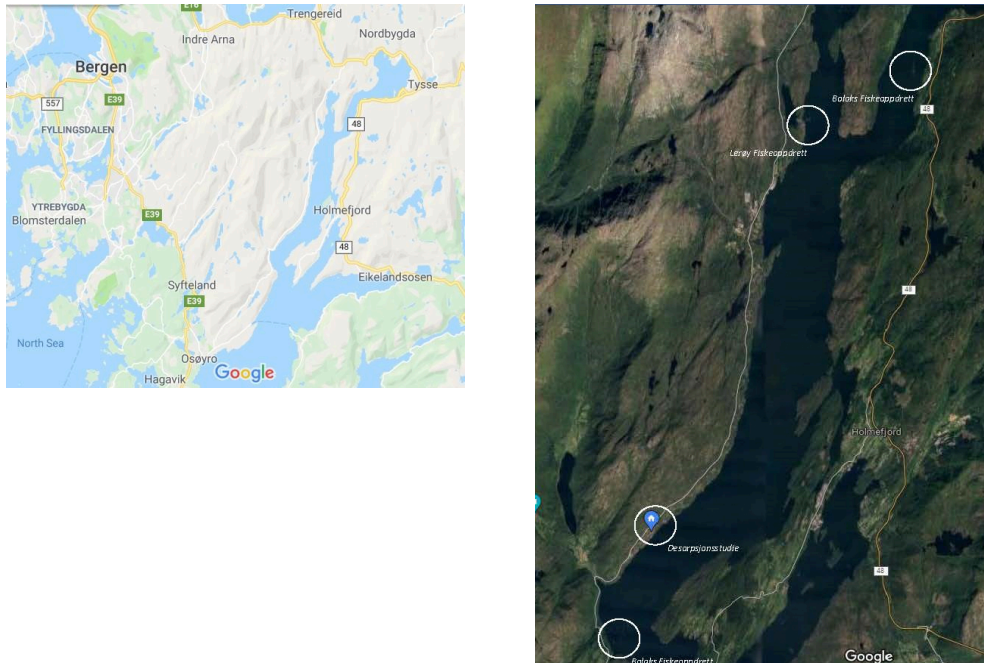


Figure 4.3.2a and b Samnangerfjorden, Norway. Location for weathering experiment.

After two weeks of exposure in the water the bags were checked for loss of plastic particles. Some reduction, especially in the PVC amount, was observed, but no further significant loss was observed at the end of the experiment. Biofouling was observed on the ropes near the surface but less at 3 meter depth on the nylon bags themselves, after two weeks.

Biofouling was expected at the time of year, and in Figure 4.3.3 it is illustrated that the sampling bags had some biofouling at the end of the four months experiment. This potentially reduces the water flow through the bags. Furthermore, the solar radiation at 3 meters depth is reduced compared to the surface, and is further reduced by biofouling so weathering due to sunlight was expected to be limited. However, to counteract potential reductions in weathering, compared to natural condition, the sample bags remained in the sea as long as practically possible in the project period, i.e. for four months. This will be further discussed in section 5.

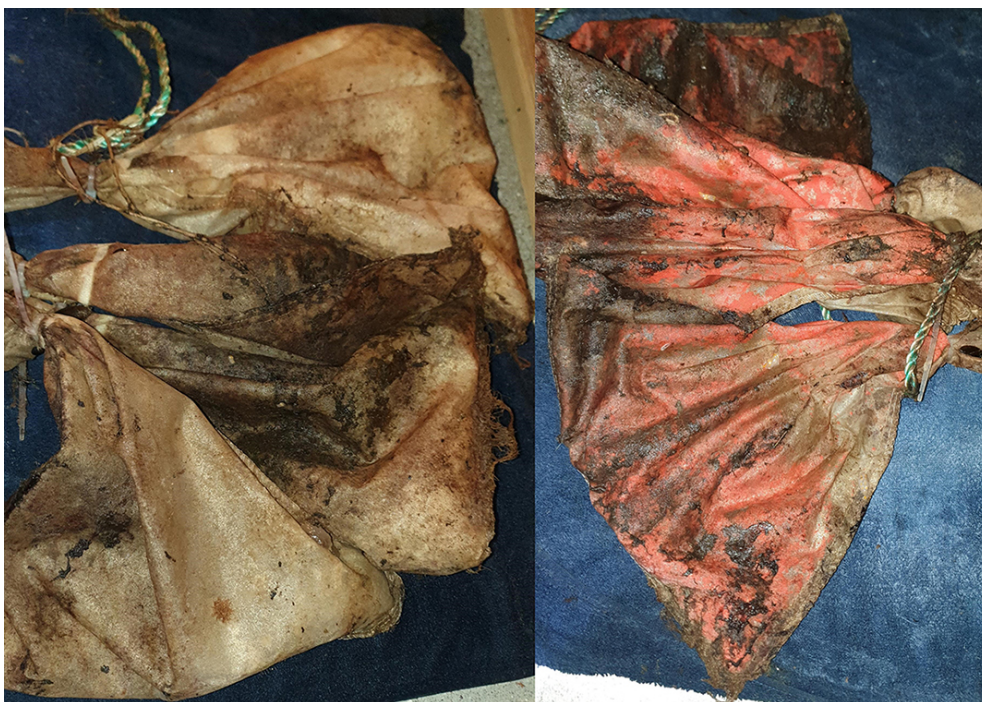


Figure 4.3.3 Sampling bags with PUR (left) and PVC (right) particles after four months of weathering in the fjord.

After shipment of the samples to Denmark, for chemical analysis, the samples were stored at -20°C until analysis.

4.4 Chemical analysis using suspect and non-target screening

Prior to analysis, the samples were air-dried in a fume hood, covered by aluminium foil. This procedure followed the guidelines from the PlastiCod project as wet plastic samples cause non-reproducible and difficult analyses.

The procedure for chemical analysis of the applied and the weathered plastic samples consisted of the following task:

1. Extraction of the chemical additives in the laboratory.

- The plastic samples were extracted using 10 mL DCM:Hexane (1:1) 10 min at 40 °C ultrasonication three times. The extracts were combined and evaporated.

2. Construction of a library with mass spectra, based on analytical standards for the compounds on the suspect list.

3. Instrumental analysis using gas chromatography (GC) with HRMS (GC-Orbitrap, Thermo Fisher) in full scan mode.

The GC-HRMS-method was used for identification of the following:

- Chemicals from the suspect list (suspect screening)

- Chemicals with certain structures found in the NIST library¹ and MassBank² high quality mass spectral database. Proper datafiltration were applied to the HRMS data to identify four groups of chemicals with certain clustering, i.e. phthalates, polyaromatic hydrocarbons (PAHs), chlorinated or brominated compounds, and aromatic nitro compounds, according to the method developed by Hilton et al. (2010). These chemical groups can be considered as representatives of plasticizers, impurities in PVC, flame retardants, and biocides, respectively.

4. Target analysis used for quantification of selected compounds, using GC with low resolution MS (GC-LRMS).

The GC-LRMS-method was used to:

- Quantify chemicals from the suspect list that were identified with suspect screening
- Check and validate the negative results from the GC-HRMS-method, i.e. those cases where chemicals from the suspect list could not be identified with the GC-HRMS-method.

5. Data analysis.

The high-resolution mass spectra were first deconvoluted using TraceFinder 4.0. The peaks from the mass spectrum were picked up based on several criteria: mass error < 5 ppm, signal noise ratio (S/N) > 10, TIC intensity > 1000, ion overlap window > 95% and sample/blank ration > 10. Non-target screening was performed to identify unknown compounds detected in the samples by matching the NIST library and MassBank library.

4.5 Hazard assessment and Predicted No-Effect Concentrations (PNECs)

A hazard assessment was performed for identified and quantified chemicals on the suspect list to compile and assess toxicity data for zooplankton (copepod, *copepoda*), fish (cod, *Gadus morhua*), and seabirds (fulmar, *Fulmarus glacialis*). These three species were selected as representatives of three trophic levels of marine organisms and followed the approach in the previous risk assessment project of chemicals in plastic (Fauser et al., 2019, 2020). Copepods and cod are exposed to plastic particles in the pelagic marine water. In addition, cods are also exposed via ingestion of plastic particles in food, e.g. zooplankton, and fulmars are exposed by ingesting plastic fragments from the sea surface and via exposure of plastic particles through the food chain, in e.g. fish, as a top predator.

When an ECHA REACH registration, according to EC (2006), was available for a compound, hazard data were used from this as it was considered the most

1. The NIST mass spectral library is the product of an ongoing comprehensive evaluation and expansion of the world's most widely used mass spectral reference library. It contains EI MS library, tandem (MS/MS) library and GC method/retention index library (<https://chemdata.nist.gov/>)

2. MassBank is an ecosystem of databases and tools for mass spectrometry reference spectra. It is provided as open source (<https://massbank.eu/MassBank/>)

comprehensive and applicable. When no REACH registration was available, risk assessments by other OECD jurisdictions were retrieved via OECD's e-chem portal. For chemicals included in the Water Framework Directive (https://ec.europa.eu/environment/water/water-framework/index_en.html) PNECs were set to European Environmental Quality Standards (EQS) for "prioritized substances and certain other pollutants" in "other surface waters" for the pelagic community (copepods and cod), or, in the absence of European EQS values, national Scandinavian environmental quality values, in the same way as described by Fauser et al. (2020). EQS values for food intake were used as PNEC for birds and fish, which have been set at EU level. Finally, a toxicity data review and extraction was done in regulatory databases, or in recent scientific literature.

Where no EQS values were available, PNECs were determined following the conservative EQS guidelines (EC, 2018). In principle, PNECs were calculated by dividing the lowest short-term LC50/EC50 or long-term No Observed Effect Concentrations (NOEC) value by an appropriate conservative assessment factor. The assessment factors are technical but also a reflection of national priority and level of conservatism. They reflect the degree of uncertainty in extrapolation from laboratory toxicity test data for a limited number of species to the "real" environment, and thus compensate for the missing knowledge and representativeness of the data towards the effects on the ecosystem (EC, 2003).

When no data were available for a species, toxicity values for other representative species, such as daphnia, were used. There is generally no data on food intake of birds, hence as a precautionary measure the general human population oral derived no-effect level (DNEL) was used as a surrogate for a PNEC for birds. DNEL is defined as the level of exposure to a substance above which humans should not be exposed.

The chemicals tentatively identified with non-target screening (GC-Orbitrap) were subjected to a qualitative hazard screening with respect to the marine environment, if the following conditions were met: They have assigned a CAS no., and no GHS classification was found by screening in ECHAs C&L Inventory database. The same procedure as described for the identified suspect list chemicals was followed apart from establishing PNEC values. Furthermore, chemicals with no registrations, e.g. REACH, were investigated in the Danish QSAR database. This was done to estimate oral absorption, bioaccumulation and aquatic toxicity. The QSAR results were assessed in a weight-of-evidence analysis if the following criteria were met: 1) the effects must be within the domain of the model; 2) they must have a positive result; 3) there must be agreement between the model estimates. If these criteria were met it was assumed that the compound caused the investigated effect, and there was reason for a more thorough experimental assessment of the hypothesis. This is however beyond the scope of this project.

Further details of the hazard assessment are shown in Appendix 2.

4.6 Risk screening

The chemical risk screening procedure of the quantified chemical additives in weathered PUR and PVC particles, respectively, for the three marine species, was based on the Technical Guidance Document from the European Chemicals Agency (ECHA) (ECHA, 2008; 2016a; 2016b). The guidance is a framework consisting of an initial information gathering (hazard identification) followed by an exposure assessment and a hazard assessment (see section 4.5), leading up to the risk characterization. The outcome is Predicted Environmental Concentrations (PECs) for additives in plastic particles, PNECs, and Risk Characterisation ratio (RCRs).

RCR was calculated as the ratio between PEC and PNEC:

$$RCR = \frac{PEC}{PNEC} \quad (Eq. 1)$$

If the RCR was below one (1), there was no risk as the PEC was below PNEC, while $RCR \geq 1$ indicated there was a risk. RCR was determined for each chemical. If more than one chemical was comprised, additivity of risk was assumed and the RCRs of the individual chemicals were summed. In this initial risk screening the RCR will be used to assess the need for further analysis to determine the environmental or even ecosystem risk in support of ecosystem based management options. If the RCR was orders of magnitude below 1 the suggestion would be not to prioritize further risk evaluation – but if the RCR was above or close to one for hazardous chemicals the recommendation would be to further investigate the risk.

PEC is the concentration of additive present in the plastic particles that the organism is exposed to, i.e. particles that are ingested. PEC was derived from the measured chemical concentrations in the weathered particles, as found in this study, multiplied with the ingested plastic particle mass.

The directly ingested plastic particle mass from the water, for zooplankton and fish, is set to 0.42 – 42 µg plastic particles (PP)/L, which represent the abundance of microplastic particles in Nordic and UK marine waters (Tamminga et al., 2018; Everaert et al., 2018). In addition to direct uptake the plastic can be taken up by fish and birds via ingested food. The mass of ingested plastic particles via food is estimated from studies on ingestion rates for cod (Bråte et al., 2016; Daan, 1973; Ursin et al., 1985) and fulmar (van Franeker et al., 2011; Herzke et al., 2016; Barrett et al., 2002), respectively. The ranges 70 – 700 µg PP/kg food are set as food intake plastic particle exposure levels for cod, and 13 – 48,000 µg PP/kg food for fulmar (Fauser et al., 2020), respectively. For fulmar no distinction is made between uptake from sea surface and from food.

Assumptions for bio-uptake were taken from Fauser et al. (2020) and were used to estimate the fraction of the chemical PECs values that are bio-available. An estimated 1–10% of the chemical additives in the weathered plastic particles were assumed to leach and to be taken up in the bloodstream of the organisms following ingestion via water or food intake.

The risk screening delivered RCRs for a low and a high exposure scenario, which reflects to variations and uncertainties in measured and estimated values in the calculation of PEC and PNEC.

4.7 Dissemination

The dissemination of project outcomes and results were divided into the following milestones:

- Dissemination of results in the NordMar Plastic network, conferences and to the plastic industry trade organisations and the Danish EPA.
- Aim to include the results in the teaching material and other information material developed in the NordMar Plastic project.
- The results will be delivered in the project report.
- The results will be published in a peer reviewed scientific article after completion of the project.

Table 4.7.1: Key messages to different stakeholders

Stakeholder	Key message
Environmental agencies, municipalities, decision-makers, Nordic Council of Ministers	Risk to marine organisms from plastic particle pollution. Plastic types and products with the highest risk. Type of chemicals that pose the greatest risk. Critical shortcomings in knowledge and data to make the risk screening more accurate.
Plastic industries and trade associations	Plastics and chemical additives that can be critical to the marine environment.
Scientific communities	Effect of degradation of plastic particles in the marine environment with respect to occurrence and leaching of additives. Additives found in the two selected plastic types. Methods of degradation testing and analytical chemistry.
NGOs, general population	Risk to the aquatic environment as a result of plastic pollution. Plastics and products that should be avoided. Update on what is happening in research and consulting in the field.

5. Results and discussion

5.1 Suspect list

Table 5.1.1 Final suspect list of plastic additives, from ECHA's list of plastic additives (PLASI) and toxicity screening via the ECHAs C&L Inventory database, applying the selection criteria shown in section 4.1. Hazard statements for the aquatic toxicity, from the GHS (Globally Harmonized System) Classification, are marked in red.

CAS No/ EC/ List no.	Name	Polymer type	Typical concentration (mass-%)	Tox screening (ECHA C&L Inventory database) Hazard statements from notifications or from harmonized classification (Aquatic toxicity in red)
Light Stabilizers				
2440-22-4/ 219-470-5	2-(2H-Benzotriazol-2-yl)-p-cresol	Polyolefin-I; Polyolefin-II; PVC (soft); ABS; PVC (rigid); PMMA; (E)PS	0.0015 – 0.5	Notified: H317: May cause an allergic skin reaction H410: Very toxic to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
3896-11-5/ 223-445-4	Bumetrizole	Polyolefin-I; PUR; Polyolefin-II; PVC (soft); ABS; PVC (rigid); PC; (E)PS	0.3 – 1.0	Notified: H312: Harmful in contact with skin H315: Causes skin irritation H319: Causes serious eye irritation H332: Harmful if inhaled H335: May cause respiratory irritation H400: Very toxic to aquatic life H411: Toxic to aquatic life with long lasting effects H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
70321-86-7/ 274-570-6	2-(2H-Benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol	Polyolefin-I; PUR; Polyolefin-II; PVC (soft); ABS; PVC (rigid); PET; PMMA; PA; PC; (E)PS	0.2 – 5.0	Notified: H315: Causes skin irritation H319: Causes serious eye irritation. H335: May cause respiratory irritation H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
1843-05-6/ 217-421-2	Octabenzene	Polyolefin-I; PUR; Polyolefin-II; PVC (soft); ABS; PVC (rigid); PMMA; PC; (E)PS	0.2 – 5.0	Notified: H315: Causes skin irritation H317: May cause an allergic skin reaction H319: Causes serious eye irritation H400: Very toxic to aquatic life H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
25973-55-1/ 247-384-8	2-(2H-Benzotriazol-2-yl)-4,6-ditertpentyl	Styrene homopolymers and copolymers, acrylic polymers, unsaturated Polyesters, PVC, Polyolefins, PUR	0.1 – 1.0	Notified: H315: Causes skin irritation H319: Causes serious eye irritation H335: May cause respiratory irritation H372: Causes damage to organs through prolonged or repeated exposure H411: Toxic to aquatic life with long lasting effects

H412: Harmful to aquatic life with long lasting effects
H413: May cause long lasting harmful effects to aquatic life

Heat stabilizers				
77-58-7/ 682-479-1	Dibutyltin dilaurate	Polyolefin-I; PVC (soft); PVC (rigid)	3	Notified: H314: Causes severe skin burns and eye damage H318: Causes serious eye damage H317: May cause an allergic skin reaction H341: Suspected of causing genetic defects H360: May damage fertility or the unborn child H370: Causes damage to organs H372: Causes damage to organs through prolonged or repeated exposure H400: Very toxic to aquatic life H410: Very toxic to aquatic life with long lasting effects
101-02-0/ 202-908-4	Triphenyl phosphite	PVC (soft); PVC (rigid)	3	Harmonized: H315: Causes skin H319: Causes serious eye irritation H400: Very toxic to aquatic life H410: Very toxic to aquatic life with long lasting effects
Antioxidants				
2082-79-3/ 218-216-0	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate	Polyolefin-I; Polyolefin-II; PVC (soft); ABS; PVC (rigid); PMMA; PC; (E)PS	0.002 – 0.4	Notified: H315 Causes skin irritation H317: May cause an allergic skin reaction H319: Causes serious eye irritation H335: May cause respiratory irritation H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
32687-78-8/ 251-156-3	2',3-Bis[[3-[3,5-di-tert-butyl-4-hydroxyphenyl] propionyl]] propionohydrazide	Polyolefin-I; PUR; Polyolefin-II; PVC (soft); PA; PC	0.002 – 3.0	Notified: H300: Fatal if swallowed H302: Harmful if swallowed H312: Harmful in contact with skin H315: Causes skin irritation H319: Causes serious eye irritation H332: Harmful if inhaled H335: May cause respiratory irritation H400: Very toxic to aquatic life H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
6683-19-8/ 229-722-6	Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)	Polyolefin-I; PUR; Polyolefin-II; PVC (soft); PVC (rigid); PET; PA; PC; (E)PS	0.002 – 0.5	Notified: H302: Harmful if swallowed H312: Harmful in contact with skin H315: Causes skin irritation H331: Toxic if inhaled H332: Harmful if inhaled H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
36443-68-2/ 253-039-2	Ethylenebis (oxyethylene) bis [3-(5-tert-butyl-4-hydroxy-m-tolyl)propionate]	PUR; PVC (soft); ABS; PVC (rigid); PMMA; PA; (E)PS	0.005 – 3.0	Notified:

				H400: Very toxic to aquatic life H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
85-60-9/ 201-618-5	6,6'-Di-tert-butyl-4,4'-butylidenedi-m-cresol	PVC (rigid); PA	0.5	Notified: H315: Causes skin irritation H319: Causes serious eye irritation H335: May cause respiratory irritation H373: Causes damage to organs through prolonged or repeated exposure H400: Very toxic to aquatic life H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
Pigments agents				
81-77-6/ 201-375-5	6,15-dihydroanthra-zine-5,9,14,18-tetrone	Polyolefin-I; PUR; Polyolefin-II; PVC (soft); ABS; PVC (rigid); PET; PMMA; PA; PC; (E)PS	2	Notified: H302: Harmful if swallowed H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
Other functions				
23128-74-7/ 245-442-7	N,N'-Hexane-1,6-diylbis [3-(3,5-di-tert-butyl-4-hydroxyphenyl-propionamide)]	PUR; PA	0.5	Notified: H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
Plasticizers				
84-74-2/ 201-557-4	Dibutyl phthalate	PUR; PVC (soft)	10.0 – 35.0	Harmonized: H360: May damage fertility or the unborn child H400: Very toxic to aquatic life
105-99-7/ 203-350-4	Dibutyl adipate	PUR; PVC (soft)	10.0 – 35.0	Notified: H361: Suspected of damaging fertility or the unborn child H411: Toxic to aquatic life with long lasting effects H412: Harmful to aquatic life with long lasting effects
117-81-7/ 204-211-0	Di-2-ethylhexyl phthalate	PUR; PVC (soft); ABS; (E)PS	2.0 – 35.0	Harmonized: H360FD: May damage fertility. Suspected of damaging the unborn child Notified: H400: Very toxic to aquatic life H410: Very toxic to aquatic life with long lasting effects H411: Toxic to aquatic life with long lasting effects H412: Harmful to aquatic life with long lasting effects
3622-84-2/ 222-823-6	N-butylbenzene-sulphonamide	PUR; PA	10.0 – 15.0	Notified: H302: Harmful if swallowed H312: Harmful in contact with skin H315: Causes skin irritation H319: Causes serious eye irritation H331: Toxic if inhaled

				H332: Harmful if inhaled H335: May cause respiratory irritation H373: Causes damage to organs through prolonged or repeated exposure H412: Harmful to aquatic life with long lasting effects
77-94-1/ 201-071-2	Tributyl citrate	PUR; PVC (soft)	10.0 – 35.0	Notified: H318: Causes serious eye damage H400: Very toxic to aquatic life
131-17-9/ 205-016-3	Di-allyl phthalate	PUR; PVC (soft)	10.0 – 35.0	Harmonized: H302: Harmful if swallowed H400: Very toxic to aquatic life H410: Very toxic to aquatic life with long lasting effects Notified: H301: Toxic if swallowed H317: May cause an allergic skin reaction H332: Harmful if inhaled H413: May cause long lasting harmful effects to aquatic life

5.2 Suspect list identification and quantification

Twenty chemicals on the suspect list (Table 5.1.1) were screened for by the suspect screening HRMS-method, which resulted in the detection of six chemicals, see Tables 5.2.1 and 5.2.2. In general, it was difficult to work with the PVC samples as they contained high amounts of phthalates, resulting in broad chromatographic peaks that interfered strongly with other compounds in the chromatogram. Attempts were made to dilute the samples and to subtract the phthalate-specific ions, but it cannot be ruled out that the dominating phthalate peak masked other compounds in the chromatogram.

The six compounds were subsequently subjected to quantitative analysis with GC-MS in the PUR samples. Quantification of additives in PVC samples was not possible due to the pronounced phthalate signal that inhibited separation and integration of specific signals. The quantification of chemicals in the PUR was based on an external calibration since the internal standard could not be integrated due to interferences in the chromatogram. Two chemicals in PUR, i.e. triphenyl phosphite, and octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, could not be quantified due to missing match with the reference standards in the GC-MS analysis. In case of findings with <LOQ the mean concentrations were calculated by setting <LOQ = 0.5*LOQ (Table 5.2.1).

Table 5.2.1 Mean and (min-max) concentrations in PUR (ng/g plastic) for suspect list additives that were identified with suspect screening (GC-Orbitrap), and subsequently quantified with GC-MS. LOQ in ng/g plastic was calculated based on a sample amount of 0.5 g plastic/ml. The potential presence/use in PUR, PVC and nylon (PA) was based on information in ECHA (2021).

Name	LOQ ng/g plastic	PUR ng/g plastic		Potential presence/use (mass- %)
		Before weathering	After weathering	
Dibutyl adipate	296	1481	1481	Plasticizer in PUR, PVC (10–35)
N-butylbenzenesulphonamide	216	1394 (1201–1587)	743 (452–946)	Plasticizer in PUR, PA (10–15)
Dibutyl phthalate	68.5	67.4 (34.31–101)	34.31	Plasticizer in PUR, PVC (10–35)
Di-2-ethylhexyl phthalate (DEHP)	101	78.0 (50.61–105)	253 (128–423)	Plasticizer in PUR, PVC (2–35)
Triphenyl phosphite	-	n.q.	n.q.	Heat stabilizer in PVC (3)
Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	-	n.q.	n.q.	Antioxidant in PVC (0.002–0.4)

1 <LOQ = 0.5*LOQ

n.q. not quantified because of missing match with the reference standard in the GC-MS analysis

- not relevant

To qualitatively evaluate the presence of the identified chemicals in PUR and PVC and to assess the potential contamination from the nylon (PA) bags that were used for containing the plastic samples in the water, information on additive uses were compiled from ECHA (2021) and included in Table 5.2.1.

Table 5.2.2 Identification and quantification of chemicals in samples and replicates. The first number is the total number of replicates, i.e. two before and eight after the weathering experiments, for both PUR and PVC. The second number is replicates with identification of the compound, and the last number is replicates with measured values above LOQ. The last number is relevant only for PUR as explained previously.

Name	PUR		PVC	
	Before weathering	After weathering	Before weathering	After weathering
	(no. of replicates, no. of identifications, no. of replicates>LOQ)	(no. of replicates, no. of identifications, no. of replicates>LOQ)	(no. of replicates, no. of identifications)	(no. of replicates, no. of identifications)
Dibutyl adipate	2,2,0	8,8,0	2,2	8,7
N-butylbenzenesulphonamide	2,2,2	8,8,8	n.d.	n.d.
Dibutyl phthalate	2,2,1	8,8,0	2,2	8,8
Di-2-ethylhexyl phthalate (DEHP)	2,2,1	8,8,8	2,2	8,8
Triphenyl phosphite	2,2,n.q.	8,2,n.q.	2,1	8,2
Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	2,2,n.q.	8,8,n.q.	2,2	8,8

n.d. not detected

n.q. not quantified, see above

Information on identification and quantification of the six chemicals in the four PUR and PVC samples after weathering, each with two replicates, and the two PUR and PVC samples before weathering, are outlined in Table 5.2.2. The four quantified chemicals were detected in all PUR samples and in replicates. All measurements of dibutyl adipate were below LOQ, and all N-butylbenzenesulphonamide were above LOQ. All measurements of dibutyl phthalate after weathering were below LOQ, and one was above LOQ before weathering. For DEHP, all measurements after and one before weathering, were above LOQ. This means that all replicates after weathering had quantification of N-butylbenzenesulphonamide and DEHP, and one sample before weathering had quantification of three chemicals, i.e. except dibutyl adipate.

The four additives detected in PUR before and after weathering, were measured in concentrations ranging from <LOQ (68.5 ng/g plastic) to 1587 ng/g plastic before weathering, and from <LOQ (68.5 ng/g plastic) to 946 ng/g plastic after weathering. The four detected and quantified additives were plasticizers in PUR, and three of them in PVC and one in PA. The two detected, but not quantified, additives were a heat stabilizer and an antioxidant, respectively, both in PVC according to ECHA. However, both compounds were detected also in the non-weathered PUR material.

The measured concentrations before and after weathering were a factor of $> 10^5$ lower than the typical concentration ranges in "plastic materials", confirmed by the industry, as stated in the last column in Table 5.2.1 from ECHA (2021). As an example DEHP is found in a concentration of 8E-06% before weathering, compared to 2-35% as stated in ECHA (2021). The large difference between the measured concentrations in applied and weathered PUR compared to the numbers in ECHA (2021) is difficult to explain. Losses can occur during the manufacture process of articles and products. However, it cannot be ruled out either that the ultrasonic extraction method applied in this project preferably extracted additives from the surface and not from deeper layers of the plastic material. The analysis of plastic materials as a matrix for chemicals is not as well-established as that of classical environmental matrices, such as air or water, and might benefit from more method development and stringent quality assurance and quality control. In general, the distribution of additives within the different plastic polymer types, their migration under varying environmental conditions and potential effects on extraction efficiencies are largely unknown.

No data from the literature was found for the same or similar plasticizers in applied or weathered PUR samples. However, for other additive groups such as benzotriazole UV-stabilizers, similar concentration ranges, i.e. from <LOD and up to approx. 80000 ng/g plastic, were found in new and weathered polyethylene (PE), polypropylene (PP), and polyethylene terephthalate (PET) debris from beaches (Rani et al., 2017).

N-butylbenzenesulphonamide was only present in PUR, and was detected both before and after weathering. The concentration decreased with approximately a factor of two after weathering. Potential contamination from the nylon (PA) bags, according to their probable use in PA (ECHA, 2021), does not seem likely. The same decrease was observed for dibutyl phthalate, however, the concentration after weathering was below LOQ, i.e. for concentration comparison after weathering the value was set to 0.5*LOQ. The elevated concentration of DEHP in PUR after weathering compared to before, could indicate a contamination from the surroundings, most likely from the PVC particles that were contained in separate

bags, but attached to the same rope, see Figure 4.3.1. Dibutyl phthalate was present both in PUR and PVC before weathering, but a similar increase in concentrations in PUR after weathering, as seen for DEHP, was not found, which does not confirm such a cross contamination. In fact a comparable decrease was seen as for N-butylbenzenesulphonamide, that was only present in PUR and not in PVC before weathering.

The results from Rani et al. (2017) were also consistent regarding higher concentrations in new compared to weathered plastics of the investigated additives. Additive levels varied widely, both among plastics and among chemicals, probably reflecting different weathering behavior, binding efficiencies in the plastic matrix of the different additive types, and uneven addition of chemicals in plastic products. Typical decreases were a factor of five. The higher loss from weathering in Rani et al. (2017) were probably due to longer weathering times, as the plastics were collected from beaches. Moreover, the new plastic materials were assessed to be similar with respect to brand and product to the sampled plastic debris; however, there could still be significant differences between them. In this project, a controlled approach was taken so the material was the exact same before and after weathering. Nevertheless, uncontrolled variables such as high releases of phthalates, both during extraction and possibly also the weathering phase, increased the uncertainty of our findings.

The leaching potential and possible origin of a chemical could tentatively be prioritized according to: Chemicals that occur only before weathering have the highest leaching potential; Chemicals that occur before and after weathering have some degree of mobility and leaching potential; Chemicals that only occur after leaching will probably originate from sorption from the surrounding marine environment.

5.3 Non-target screening

Table 5.3.1 lists the chemicals that were tentatively identified with non-target screening, and that were not on the suspect list. Spectral data were found in the NIST or Massbank libraries, and use of data screening filters, as described by Hilton et al. (2010). These were applied to identify selected groups of chemicals. Table 5.3.1 also includes the potential use of these compounds in plastics, or if this could not be established; the possible cause of association with plastic. Results from a GHS classification screening are noted. It should be noted that this identification remains uncertain as long as it cannot be verified with an analytical standard (Schymanski et al., 2015).

A hazard assessment has high priority for chemicals found with non-target screening as they potentially fulfil the criteria for being new or unknown in the marine environment, and they could therefore be relevant to consider in a quantitative risk screening. The three chemicals marked in bold in Table 5.3.1 have CAS numbers and no GHS classification according to the hazard initial screening in ECHA C&L, and were therefore subjected to a more in-depth hazard assessment. None of them has a REACH registration. Only tris(3-chloropropyl) phosphate has a registration with the Australian EPA NICNAS from a 2001 category assessment, but with no data registered specifically for this compound. This structure corresponds to

two CAS numbers, i.e. 1067-98-7 and 26248-87-3. This structure was the only one that was assessable in the Danish QSAR Database out of the three. There are no hazard data publicly available for the remaining two compounds in any of the assessed databases, such as eChemPortal, SciFinder, Google Scholar, Google, or Web of Science. In Appendix 2 a summary of the QSAR derived toxicity information for tris(3-chloropropyl) phosphate is shown.

Table 5.3.1 Chemical additives tentatively identified with the non-target screening HRMS-method (GC-Orbitrap) that are not on the suspect list of chemical additives. Their potential presence in PUR, PVC and PA, and the potential additive use or cause of association with plastic is indicated. The GHS hazard classification towards the environment and humans, based on a screening in ECHAs C&L Inventory database, is stated. The three chemicals marked in bold, with no GHS classification were hazard assessed, with respect to humans and the marine environment.

CAS No/ EC/List no.	Name	Identified in	Potential additive use	Hazards towards humans and marine environment
24157-81-1/ 246-045-1	2,6-Diisopropylnaphthalene ²⁾	PVC (before) PVC (after)	PAH impurity in plasticizers. Plant growth retardant and agrochemical	ECHA (notified): H302 Harmful if swallowed. H410: Very toxic to aquatic life with long lasting effects
13674-84-5/ 237-158-7	Tris(chloroisopropyl)phosphate (TCIPP) ³⁾	PUR (before) PUR (after)	Adhesive, sealant, finishing agents, flame retardants, paint and coating additive	ECHA (notified): H302 Harmful if swallowed H315: Causes skin irritation H319: Causes serious eye irritation H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
1067-98-7	Tris(3-chloropropyl) phosphate³⁾	PUR (before) PUR (after)	Flame retardant	No REACH registration Registration with the Australian EPA NICNAS QSAR predictions: Daphnids: Average acute LC50 = 0.03 (±0.02SD) mg/L Fish models were outside the domain and thus less reliable: Average acute LC50 = 1.96 (±0.21SD) mg/L
62990-21-0	5,5,10,10-Tetrachlorotricyclo[7.1.0.0-(4,6)]decane³⁾	PVC (before) PVC (after)		No REACH registration No hazard data publicly available
62434-98-4	5,5,10,10-Tetrachlorotricyclo[7.1.0.0-(4,6)]decane³⁾	PVC (before) PVC (after)		No REACH registration No hazard data publicly available
607-99-8/ 627-908-5	Benzene, 1,3,5-tribromo-2-methoxy- ³⁾	PVC (after)	Flame retardant	ECHA (notified): H413: May cause long lasting harmful effects to aquatic life
-	Terephthalic acid, nonyl octyl ester ¹⁾	PUR (before)PUR (after) PVC (before) VC (after)	Resin composition for golf ball cover	
-	Phthalic acid, 6-methylhept-2-yl	PUR		

	nonyl ester ¹⁾	(before) PUR (after)	
-	1H-Indene, 2,3-dihydro-1,1,3-trimethyl-3-- phenyl- ²⁾	PVC (before) PVC (after)	PAH impurity in plasticizers.
-	Phthalic acid, 2-ethylbutyl nonyl ester ¹⁾	PUR (before)	Plasticizer
-	Phthalic acid, cycloheptyl nonyl ester ¹⁾	PUR (before)	
-	Phthalic acid, 6-ethyl-3-octyl butyl ester ¹⁾	PVC (after)	
-	6-Bromohexanoic acid, 4-nitrophenyl ester ³⁾	PVC (after)	
-	4-Ethylbenzoic acid, 2-chlorophenyl ester ³⁾	PVC (after)	
-	Methyl-3-[(2-nitrobenzoyl)amino]- benzoate ⁴⁾	PUR (after)	
-	Oxalamide, N- (isochroman-1-yl)methyl-N'- phenyl- ⁴⁾	PVC (after)	

¹⁾ Phthalates

²⁾ Polyaromatic hydrocarbons (PAHs)

³⁾ Chlorinated or brominated compounds

⁴⁾ Aromatic nitro compounds.

Chemicals identified in PUR before and after weathering:

Of the sixteen chemicals identified with non-target screening in Table 5.3.1, four were identified in PUR both before and after weathering. Two were chlorinated with potential uses as e.g. flame retardants. These were tris(chloroisopropyl)phosphate (TCIPP), which is notified in ECHA as *H412: Harmful to aquatic life with long lasting effects*, and tris(3-chloropropyl) phosphate, which is mentioned above. TCIPP is furthermore suspected to be carcinogenic and not allowed for use in children's toys in the EU (Reemtsma et al., 2008; EU, 2014). Two phthalates found in PUR before and after weathering did not have CAS numbers and could not be further hazard assessed.

Chemicals identified in PVC before and after weathering:

Four chemicals were tentatively identified in PVC both before and after weathering. Two were PAHs and as such possible impurities in plasticizers, e.g. mineral oil and coal based extender oils (Hansen et al., 2013; 2014). One of these, i.e. 2,6-diisopropyl-naphthalene is furthermore used as a plant growth retardant and agrochemical and has a registration in REACH as *H410: Very toxic to aquatic life with long lasting effects*. The other PAH (1H-Indene, 2,3-dihydro-1,1,3-trimethyl-3-phenyl-) did not have a CAS no. nor a hazard classification. The chlorinated compound 5,5,10,10-tetrachlorotricyclo[7.1.0.0(4,6)]decane was hazard assessed but no data was available. Finally, the identified phthalate, which also was identified before and after weathering in PUR, did not have a CAS no. nor a hazard classification. As discussed in section 5.1, the analysis of the PVC chromatograms was affected by large phthalate peaks potentially masking other compounds in the chromatogram. Thus, the tentative identifications of compounds in PVC might be limited due to the chromatographic challenges.

Chemicals identified either before or after weathering:

One chlorinated chemical (1,4-pentadiene, 1,1-dichloro-4-methyl-) (CAS no 62434-98-4) was detected only in PVC before weathering but no hazard information was available. Two phthalates were identified in PUR only before weathering, with no CAS numbers or hazard classification. One aromatic nitro compound was found in PUR only after weathering and five chemicals were found in PVC only after weathering. Only one of these has a CAS no, i.e. the flame retardant benzene, 1,3,5-tribromo-2-methoxy- (CAS no 607-99-8). It has an ECHA notification as *H413: May cause long lasting harmful effects to aquatic life*. It appears questionable that a compound is detected after, but not before weathering. As was the case for some of the suspect additives in Table 5.2.1, cross contamination of the weathered samples, between the bags placed in the sea, could explain some of the detections after weathering in Table 5.3.1.

Rani et al. (2015) performed a qualitative screening of plastic debris collected from coastal beaches along with new similar plastics, and reported the presence of a range of additives. Of the 231 chemicals found in new plastic items and marine debris, UV stabilizers, e.g. UV-328, antioxidants, plasticizers, e.g. DEHP, di-n-octylisophthalate, diisooctyl phthalate, and hydrocarbons were most frequently

detected. The chemical analysis in this study detected 63 of the detected chemicals in both new and debris plastic. For 83 of the detected chemicals there were only findings in debris plastic, possibly indicating adsorption of additional chemicals in the environment. Thus, this corresponds to the detection of some compounds only after weathering in the present project.

Of the 20 analyzed chemical additives in the suspect list (Table 5.1.1), the suspect screening HRMS-method identified six. Comparing with the conventional target screening, the suspect and non-target screening have higher uncertainty in the identification, but a higher capacity to identify suspected and unknown chemicals. Non-target screening based on HRMS is able to detect tens or hundreds of chemicals in the mass spectrum. However, the data analysis method to identify and confirm the chemicals is still limited for many reasons, e.g. HRMS databases can be incomplete. Further, the compound identification can only be considered valid if the compound identity can be confirmed with an analytical standard. However, these are not available for all chemicals that might be relevant, in particular the large number of chemical additives in plastic materials. Furthermore, conventional GC-LRMS is in general more sensitive for the specific chemicals, as they only detect specific ions of the targeted chemicals compared to the GC-Orbitrap that screens for the entire chemical spectra operating in full scan which reduces the sensitivity.

Five of the suspect chemicals that had not been identified in the PUR samples with GC-Orbitrap, i.e. HRMS, were selected for screening by GC-LRMS. These were:

2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol (light stabilizer in PUR, PVC and PA, probable amount according to ECHA (2021): 0.2--5.0 mass-%)

2-(2H-benzotriazol-2-yl)-p-cresol (light stabilizer in PVC, 0.0015–0.5 mass-%)

Bumetrizole (light stabilizer in PUR and PVC, 0.3–1.0 mass-%)

6,6'-di-tert-butyl-4,4'-butylidenedi-m-cresol (antioxidant in PVC and PA, 0.5 mass-%)

UV-328 (2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol) (light stabilizer in PUR and PVC, 0.1–1 mass-%).

None of these additives were identified with GC-LRMS in analytical methods that targeted these compounds specifically. This confirmed the HRMS-results and indicated that their absence in the HRMS-chromatograms obtained with non-target method was not primarily an issue of lower sensitivity compared to conventional GC-LRMS.

5.4 Hazard, exposure and risk screening of quantified suspect additives

For the four quantified chemicals on the suspect list in Table 5.2.1, a set of toxicity data, assessment factors and PNECs were compiled, see Appendix 2. This was done for three trophic levels of marine organisms: zooplankton, fish and seabirds, according to the method outlined in section 4.5.

Table 5.4.1 PNECs for the four identified and quantified suspect additives.

Additive name	CAS no.	PNEC marine (zooplankton, fish) (mg/L)	PNEC food intake (birds, fish) (mg/kg food)
Dibutyl adipate	105-99-7	0.003 (fish acute)	No data
N-butylbenzenesulphonamide	3622-84-2	0.004 (fish acute)	Fish: 52 ³⁾ Birds: 0.87 ³⁾
Dibutyl phthalate	84-74-2	0.001 (fish chronic)	Fish: 1,4 ³⁾ Birds: 0.023 ³⁾
Di-2-ethylhexyl phthalate (DEHP)	117-81-7	0.0013 ¹⁾	Fish: 16 ¹⁾ Birds: 1700 ²⁾

1) Directive 2013/39/EU

2) DEHP summary risk assessment report 2008

3) Derived from human DNEL

In the absence of toxicity data for food intake for fish and birds, human oral DNELs are used as PNECs, see Appendix 2. This approach does not consider the differences between intake via water or food. However, in this risk screening using human values adds an extra conservatism in the estimate. Human DNELs are converted to PNECs for food intake for cod and fulmar by using food ingestion rates of 0.005 kg food/kg bw/day and 0.3 kg food/kg bw/day, for cod and fulmar, respectively (Bråte et al., 2016; Daan, 1973; Ursin et al., 1985; Barrett et al., 2002).

PECs for the water (zooplankton and fish) and food intake (fish and birds) were calculated as follows: The concentrations of chemicals in the weathered plastic particles (Table 5.2.1) were multiplied with the ingested plastic particle mass from the water and via food intake (section 4.6) and the fraction of bio-available chemicals. Uncertainties were associated with these parameters, i.e. measured additive concentrations varied between the four samples and the two replicates, abundance of plastic particles varies between the studies used in this calculation (see section 4.6), and amounts of plastic found in cod and fulmar stomachs varied between samples. Furthermore, the bioavailable fraction of chemicals in the ingested plastic particles were estimated to vary from 1 to 10%. To illustrate the influence of these variations in the calculation of PECs, a low and a high exposure scenario was defined, as shown in Table 5.4.2.

As an example, the high PECs for the chemical N-butylbenzenesulphonamide in PUR after weathering, were:

$$PEC(\text{water, zooplankton, fish}) = 946 \times 10^{-9} \frac{\mu g}{\mu g PP} \times 0.1 \times 42 \frac{\mu g PP}{L} = 0.000004 \frac{\mu g}{L}$$

$$PEC(\text{food intake, fish}) = 946 \times 10^{-9} \frac{\mu g}{\mu g PP} \times 0.1 \times 700 \frac{\mu g PP}{kg food} = 0.000066 \frac{\mu g}{kg food}$$

$$PEC(\text{food intake, birds}) = 946 \times 10^{-9} \frac{\mu g}{\mu g PP} \times 0.1 \times 48,000 \frac{\mu g PP}{kg food} = 0.000004 \frac{\mu g}{kg food}$$

Table 5.4.2 Low and high exposure scenarios for calculation of PECs.

	Low exposure scenario	High exposure scenario
Measured additive concentration after weathering	Lowest of 4 samples and 2 replicates	Highest of 4 samples and 2 replicates
Plastic particle abundance in water (µg/L)	0.42	42
Plastic ingestion fish (µg/kg food)	70	700
Plastic ingestion birds (µg/kg food)	13	48,000
Bioavailable fraction of chemical on plastic particles (%)	1	10

Subsequent division of PEC by PNEC, from Table 5.4.1 resulted in the risk characterisation ratios (RCR) in Table 5.4.4.

Table 5.4.3 Calculated PECs of suspect list additives in weathered PUR (from Table 5.2.1) that were identified with suspect screening (GC-Orbitrap), and subsequently quantified with GC/LRMS. Low and high exposure scenarios are used.

Name	Low			High		
	PEC marine (zooplankton, fish) (mg/L)	PEC food intake (birds) (mg/kg food)	PEC food intake (fish) (mg/kg food)	PEC marine (zooplankton, fish) (mg/L)	PEC food intake (birds) (mg/kg food)	PEC food intake (fish) (mg/kg food)
Dibutyl adipate	6.2E-13	1.9E-11	1.0E-10	6.2E-10	7.1E-07	1.0E-08
N-butylbenzenesulphonamide	1.9E-12	5.9E-11	3.2E-10	4.0E-09	4.5E-06	6.6E-08
Dibutyl phthalate	1.4E-13	4.5E-12	2.4E-11	1.4E-10	1.6E-07	2.4E-09
Di-2-ethylhexyl phthalate (DEHP)	5.4E-13	1.7E-11	9.0E-11	1.8E-09	2.0E-06	3.0E-08

Table 5.4.4 Calculated RCRs (= PEC/PNEC) for low and high exposure scenarios. PNECs are from Table 5.4.1.

Name	Low			High		
	RCR marine (zooplankton, fish)	RCR food intake (birds)	RCR food intake (fish)	RCR marine (zooplankton, fish)	RCR food intake (birds)	RCR food intake (fish)
Dibutyl adipate	2.1E-10	n.a.	n.a.	2.1E-07	n.a.	n.a.
N-butylbenzenesulphonamide	4.7E-10	6.8E-11	6.1E-12	9.9E-07	5.2E-06	1.3E-09
Dibutyl phthalate	1.4E-10	1.9E-10	1.7E-11	1.4E-07	7.0E-06	1.7E-09
Di-2-ethylhexyl phthalate (DEHP)	4.1E-10	9.8E-15	5.6E-12	1.4E-06	1.2E-09	1.9E-09
Sum RCRs	1.2E-09	2.6E-10	2.9E-11	2.7E-06	1.2E-05	4.8E-09

n.a. not assessable

RCRs larger than one, indicating a potential risk, were not observed for any of the additives, nor for the sum of RCRs for all investigated chemicals. For zooplankton and fish combined with plastic particle ingestion via seawater, the sum RCR was 1E-09 and 3E-06 for the low and high exposure scenarios, respectively. For fish and birds combined with ingestion via food, the sum RCR varied between 3E-11 and 1E-05, for the two exposure scenarios. The highest individual RCR was 1E-05 found for dibutyl phthalate and exposure via food uptake for birds. Overall there was a minimum safety margin of approx. 100,000 (1E05) across all chemicals and exposure scenarios.

In a recent theoretical study of the marine environment, RCR > 1 were found for copepods and cods and the flame-retardant PBDE used in PUR, the biocide tributyltin (TBT) present as impurity in PVC and PUR, and the flame-retardant HBCDD used in expanded polystyrene (EPS) (Fauser et al., 2020). A potential risk was found for fulmar and PBDE used in PUR. This theoretical study had a similar set-up as the present project, but it was not based on measurements. For other additives than softeners and metals, and for plastics such as EPS, PUR, PVC, cellulose nitrate (cigarette butts), polyethylene (PE), acrylics, styrene butadiene rubber (SBR) and polycarbonate (PC), the calculated PECs and RCRs were lower or similar to the values in this study. For phthalate softeners, such as DEHP and BBP in PVC the theoretically determined PECs and RCRs were high, i.e. RCR approx. 0.1. For this reason, PVC was selected as a priority material for the present study. However, the high concentrations of phthalates in PCV caused substantial challenges in the chromatographic analyses due to the dominant phthalate peaks in the chromatograms.

Only few other studies exist that have conducted a risk assessment of chemical additives in plastic particles in the marine environment. Risk characterisation ratios for seawater showed a moderate risk ($0.1 \leq \text{RCR} < 1$) for nonylphenol in seawaters and sediments from two coastal areas in Spain (Salgueiro-Gonzalez et al., 2019). Tato et al. (2018) calculated very low or low risks for BPA and triclosan, and low to high risks for 4-nonylphenol 4-NP in coastal ecosystems. Two UV filters, ethylhexyl dimethyl p-aminobenzoic acid (OD-PABA) and octocrylene (OC), showed toxicity to marine species, but the calculated risk characterisation ratios were < 1 (Giraldo et al., 2017).

The above studies found RCRs that vary between low, moderate and high risks of specific microplastic-associated compounds and were not necessarily consistent for the same compound, e.g. both low and moderate risks were identified for BPA.

The results from the present study show that it is possible to identify and quantify plastic related additives after four months of weathering, despite working with a complex matrix. Rani et al. (2017) found a slightly higher fraction of leached additives in weathered plastic collected from beaches compared to the weathered plastic in this project, but there are large differences in study design. It is also a possibility, that other additives are present in the plastic which could not be determined due to challenges with the analytical determination and the limitations of non-target screening as mentioned above.

5.5 Dissemination

The project has been disseminated through several different channels.

The initiation of the project was announced on NordMar Plastic's home page ([Nordic project on plastic additives in the sea – NordMar Plastic](#)), Twitter account and Instagram account as well as in Icelandic on the Matís homepage ([Norrænt verkefni um aukaefni úr plasti í sjó - Matís \(matis.is\)](#)), EPA Iceland (see below) and in Danish on the Aarhus University homepage ([Nordisk projekt om plast additiver i havet \(au.dk\)](#))

The outcomes of the project will be presented through these same channels, in addition to others.

Results of the project were presented to the NordMar Plastic network at the annual NordMar Plastic meeting in November 2021.

The project was introduced at the conference "International Symposium on Plastics in the Arctic and Sub-Arctic Region" hosted by The Government of Iceland in collaboration with the Nordic Council of Ministers, online March 2021.

Due to late onset of the project the development and release of the NordMar Plastic educational material had already been finalized and the results from this project could not be included in that material. However, results will be included in lectures at the international Winter School "POPs and Chemicals of Emerging Arctic Concern in an Arctic under Climate Change", organized by Harbin Institute of Technology, China, in January 2022. The course includes two lectures on chemicals of emerging concern and plastics where results from this project will be a relevant contribution.

In addition, measures have been taken to exploit the research findings:

The project outcomes along with some infographics will be forwarded to Landvernd (NGO; www.landvernd.is) who will further distribute it to their network of NGOs that are working on the topic in the Nordic countries, such as Hold Norge rent, Hold Sverige rent etc. They will also disseminate the results on their website and social media and send them to schools that are working with the "Clean seas" teaching material.

The results will be used for public awareness raising at several different events:

"Hope about the Ocean" exhibition will be launched and opened for public in Húsavík from 1st of May 2022. The exhibition will include sections on "Plastic pollution" as well as "Microplastics in the ocean" and the results on chemical additives leaching into the ocean will be part of the information in those sections.

Landvernd and the Environment Agency of Iceland will use the results as a source for an informative event connected to the Day of the Ocean in the beginning of June 2022.

The project will furthermore be disseminated for public awareness raising and possibly for producing material for social media and outreach, by NordMar plastic via a new project in 2022 with Landvernd.

EPA Iceland (umhverfisstofnun) will assist in disseminating the project results through their channels:

<https://samangegnsoun.is/plast/>

www.ust.is

<https://www.ust.is/haf-og-vatn/plastmengun/>

<https://www.ust.is/graent-samfelag/graenn-lifstill/plast/>

The findings will also be disseminated via meetings and correspondence with the Danish EPA, Danish plastic trade organisations, and industry.

In addition to delivering this project report, a scientific paper will be published (manuscript in preparation), and an abstract has been submitted for presentation at SETAC 2022 in May in Copenhagen.

6. Conclusions and outlook

Four hazardous chemical additives used as softeners, were identified with suspect screening using GC-HRMS (GC-Orbitrap) and quantified with conventional chemical methods, i.e. GC-LRMS, in weathered micro-size polyurethane (PUR) particles. A risk screening towards zooplankton, fish and sea birds did not demonstrate that there were significant risks, and that the minimum margin of safety was 100,000 (1E05) for the sum of risk characterisation ratios (RCRs). The concentrations determined in plastics before and after weathering were lower than those given for pure plastic polymers in a guidance by ECHA (2020). The reasons are unclear. Given the complexity of the matrix, underestimations cannot be completely ruled out. However, the concentration ranges in another study on leaching of additives (Rani et al., 2017) were in the same order of magnitude as the findings in this project, even though the chemical groups and the plastic polymers were different.

The few existing studies (Salgueiro-Gonzalez et al., 2019; Tato et al., 2018; Giraldo et al., 2017; Fauser et al., 2020) on risks of plastic additives in the marine environment found that RCRs varied between low ($RCR < 0.1$), moderate ($0.1 \leq RCR < 1$) and high ($RCR \geq 1$) risks of specific microplastic-associated compounds, and that the results were not necessarily consistent for the same compound.

Non-target screening with GC-Orbitrap tentatively identified 16 not suspected chemicals. A hazard screening showed that one PAH and possible impurity in plasticizers, i.e. 2,6-Diisopropylnaphthalene (CAS no 24157-81-1), were identified in PVC both before and after weathering. The PAH has an ECHA classification by notifiers as *H410: very toxic to aquatic life with long lasting effects*. One chlorinated compound with use as flame retardant, i.e. tris(chloroisopropyl)phosphate (TCIPP) (CAS no 13674-84-5), was identified in PUR both before and after weathering. It is a suspected carcinogenic (EU, 2014) and has an ECHA notification as *H412: Harmful to aquatic life with long lasting effects*.

The results showed a decrease in concentrations between applied and weathered PUR which was approx. a factor two for N-butylbenzenesulphonamide and dibutyl phthalate. However for the latter the concentration was below LOQ after weathering. There is very limited information available on additive concentrations in applied and weathered plastic in the literature. There are a few studies (e.g. Rani et al., 2017) that in general did not show consistent results regarding higher concentrations in new compared to weathered plastics, and which found widely varying amounts (mass-%) of remaining additives in different weathered plastic types collected at beaches. Some chemicals were detected in weathered samples but not in the new plastic. This could be explained by cross contamination from the PVC particles and the surrounding water, or increased accessibility of the chemicals in the extraction of weathered plastic, due to breakdown of the material.

The suspect and non-target screening techniques hold a great potential of approaching a large number of compounds at the same time. However, the technique is not yet fully developed for routine applications, and still includes many uncertainties that are subject to ongoing research. One challenge is the extent of sample preparation as was recently discussed for a variety of environmental, food and human matrices (Hajeb et al., 2022). While matrix components that could

interfere with the chromatographic analysis, should be removed during sample processing, all other chemicals should ideally remain in the sample. The present project also shows that besides matrix components, that can impact sensitivity and selectivity, individual high-concentration compounds can affect the chromatographic analysis to the extent that the identification of other compounds becomes difficult or even impossible, despite technical possibilities of selecting specific ions.

Furthermore, currently available databases and workflows within peak identification undergo rapid developments (Hollender et al., 2017). Datafilters based on Hilton et al. (2010) was the approach chosen in this project, but it is not an exhaustive identification of all potential compounds in the sample. It should also be noted that the data analysis in non-target screening is highly time-consuming and only allows the thorough analysis of a few samples within a reasonable timeframe.

This project has shown a way how non-target screening, suspect screening and conventional target analysis (using GC-LRMS) can be combined for maximum information gain. Ongoing research will optimize approaches within each of these types of analyses as well as for their interactions. The plastic matrix is not monitored in the same way as other environmental matrices, and its analysis will also benefit from more method development applying stringent QA/QC measures.

Recommendations for further work:

- Measure amounts of known high-concentration additives in weathered plastic particles, such as banned and currently used softeners and flame retardants, and perform a risk screening
- Develop suspect and non-targeted screening methods, combined with conventional analysis where meaningful, to identify other potentially hazardous additives groups, e.g. light and heat stabilizers, such as benzotriazoles, antioxidants, pigments incl. metal compounds, non-halogenated flame retardants, such as organophosphate flame retardants
- Further develop sample preparation and data treatment methods in suspect and non-target screening, which increase sensitivity, accuracy and comparability
- Investigate extraction efficiencies for various compounds, solvents and plastic materials, including the influence from weathering
- Investigate the relationship between the extractable fraction and the bio-available fraction
- Better describe and quantify the bio-availability of chemicals in plastic additives after uptake by an organism, i.e. in the stomach and gut of organisms with leaching experiments and modelling
- Compare exposure to plastic additives from ingestion of plastics to other exposure sources, e.g. from the food chain
- Quantify and reduce uncertainties in calculations of PECs and PNECs
- Develop PNECs for identified not expected potentially hazardous additives
- Perform targeted, quantitative investigation, of identified chemicals with relatively high hazard, for more precise risk assessment
- Perform source identification of high-risk chemicals, polymers and products for risk management
- Disseminate the result to industry, decision makers and the public and continue dialogues for mutual knowledge gain.

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Appendix 1 Projektopslag (dansk)

Nordisk projekt om kemiske additiver i plastik og deres frigivelse i havet.

Udføres af Aarhus Universitet (Danmark), Nofima (Norge) og Matis (Island) finansieret af Nordisk Ministerråds Hav- og Kystgruppe, og Kemikaliegruppe.

Baggrund: Op imod 8 millioner tons plastaffald antages at blive tilført til havene årligt på global skala, og udledningerne antages at stige i de kommende år. Plast findes i et utal af produkter og der tilsættes mange kemikalier (additiver) for at plasten skal opnå de ønskede egenskaber. Plastprodukter, der ender i havet, nedbrydes til mindre partikler og vil også ændre deres struktur og kemiske sammensætning som følge af nedbrydning. Kemiske additiver kan frigives fra plasten og føre til uønskede effekter på havmiljøet, hvis de har sundhedsskadelige virkninger. Det vides ikke, om der muligvis også kan være effekter på mennesker som følge af indtag af fisk og skaldyr. Viden om hvilke kemikalier der tilsættes, hvor meget der frigives til havet og deres risiko for havmiljøet, er imidlertid begrænset.

Om projektet: Dette Nordiske projekt vil identificere og måle rester af kemiske additiver i to produkter lavet af de almindeligt anvendte plasttyper polyvinylchlorid (PVC) og polyurethan (PUR). Plasten bliver granuleret til partikler i mikro-meter størrelse (mikroplast) og udsat i vandgennemtrængelige poser i Samnangerfjorden nær Bergen fra juni til oktober 2020. Efter nedbrydning i vandet vil typer og mængder af kemiske additiver i plastpartiklerne bestemmes og sammenlignes med typer og mængder i det oprindelige plastmateriale. Dette vil give en viden om hvilke kemiske additiver der er tilstede i plasten, samt deres potentiale til frigivelse til havmiljøet. Baseret på de kemiske additivs potentielle effekter på havmiljøet og mennesker vil projektet lave en liste af målte additiver, der prioriteres ud fra deres risiko overfor havmiljøet og mennesker.

Formidling: Resultaterne bliver formidlet i en projektrapport, samt i det Nordiske NordMar Plastic netværk, hvor resultaterne tilstræbes at indgå i undervisningsmateriale og som informationer til beslutningstagere, plastindustrien, brancheorganisationer og distributører. Resultaterne vil ligeledes blive præsenteret og diskuteret med den danske Miljøstyrelse og i den videnskabelige litteratur, samt på projektpartneres og sociale mediers hjemmesider.

Kontaktperson:

Patrik Fauser, Institut for Miljøvidenskab, Aarhus Universitet

Appendix 2 Hazard assessment

There are four chemicals from the suspect list that have been identified and quantified in the project. Below is a review of the associated environmental hazards of these compounds.

There is a REACH registration for dibutyl adipate (<https://echa.europa.eu/da/registration-dossier/-/registered-dossier/5939/6/1>) in accordance to the EC (2006) legislation. There are no marine toxicity data reported. The predicted no effect concentration (PNEC) for marine organisms for the compound is determined to be 0.003 mg/L. The compound triggers the GHS H401 and 411. There are no data on secondary poisoning nor toxicity data towards birds. The registration concludes that; as the substance is not toxic to mammals (not classified for toxicity) and not bioaccumulative - no further toxicity testing on birds is proposed.

As for the dibutyl adipate there is a REACH registration for N-butylbenzenesulphamide (<https://echa.europa.eu/da/registration-dossier/-/registered-dossier/13402/6/1>). There are no marine toxicity data reported. The predicted no effect concentration (PNEC) for marine organisms for the compound is determined to be 0.004 mg/L. The compound triggers the GHS H412. There are no data on secondary poisoning nor toxicity data towards birds. The registration concludes that; as the substance is not toxic to mammals (not classified for toxicity) and not bioaccumulative - no further toxicity testing on birds is proposed. The human oral DNEL is determined to be 0.26 mg/kg bw/day.

There three REACH registrations for dibutyl phthalate (<https://echa.europa.eu/da/registration-dossier/-/registered-dossier/1805/6/7>; <https://echa.europa.eu/da/registration-dossier/-/registered-dossier/14862>; <https://echa.europa.eu/da/registration-dossier/-/registered-dossier/1805/1/1>). As for the other compounds there are no marine data. The lowest measured chronic NOEC toxicity value was 0.1 mg/L over 99 days study with rainbow trout. With an assessment factor of 10^3 the freshwater PNEC becomes 0.01 mg/L with an additional assessment factor to move from fresh to saltwater of 10 the saltwater PNEC become 0.001 mg/L. The compound triggers H361 (may damage the fertility of the unborn child) and H400. There are no data on secondary poisoning nor toxicity data towards birds. There is a study on egg-shell thickness as a surrogate for bird toxicity 9.19 mg (no further units provided). The registration concludes that; as the substance is not toxic to mammals (not classified for toxicity) and not bioaccumulative - no further toxicity testing on birds is proposed. The human oral DNEL is determined to be 0.007 mg/kg bw/day.

There are two REACH registrations for DEHP (<https://echa.europa.eu/da/registration-dossier/-/registered-dossier/15358>; and <https://echa.europa.eu/da/registration-dossier/-/registered-dossier/8568>). The first one has no data, while the latter does contain data. The compound has a very high Log Kow of 7.1 and a very low water solubility of 0.003 mg/L. This strongly impairs the accurate assessment of aquatic toxicity. It is concluded in the registration - that due to low water solubility DEHP does not cause systemic toxicity to aquatic organisms due to lacking exposure. Springborn Bionomics determined and reported Chronic Toxicity of Fourteen Phthalate Esters to *Daphnia magna* toxicity test report submitted to Chemical Manufacturers Association, Washington, DC, Report No. BW-84-5-1567

3. EU TGD, for deriving EQS, Doc #27, 2018.

(1984), a NOEC concentration of 0.077 mg/L. It triggers H361, GHS08 (health hazard) and H413. The human oral DNEL is determined to be 0.036 mg/kg bw/day. The toxicity towards birds has been determined to be 1700 mg/kg feed.

Additive name	CAS no.	Toxicity values (mg/L)	Assessment factors	PNEC marine (zooplankton, fish) (mg/L)	PNEC food intake (birds) (mg/kg food)
Dibutyl adipate	105-99-7	3.64 acute fish measured value	500	0.003 (fish acute)	No data
N-butylbenzenesulphonamide	3622-84-2	36.7 acute fish measured value	10000	0.004 (fish acute)	Human DNEL = 0.26 mg/kg bw/day
Dibutyl phthalate	84-74-2	0,1 (chronic fish measured)	100*10	0.001 (fish chronic)	Human DNEL = 0.007 mg/kg bw/day (ED50 = 9.19 mg (egg thickness))
Di-2-ethylhexyl phthalate (DEHP)	117-81-7	NA due to solubility issues (0.077 mg/L chronic Daphnia magna)	Not assessable	0.0013 ¹⁾	Human DNEL = 0.036 mg/kg bw/d Fish: 161) mg/kg food Birds: 17002) mg/kg food

1) Directive 2013/39/EU; 2) DEHP summary risk assessment report 2008

In addition to the above-mentioned compounds, three compounds were identified in the assessment. None of these have a REACH registration. Only CAS# 1067-98-7 has a registration with the Australian EPA NICNAS from 2001 category assessment but with no data specifically for this compound. This structure corresponds to two CAS#'s; 1067-98-7 and CAS# 26248-87-3. This was the only compound that was assessable in the Danish QSAR Database out of the three. There are no hazard data publically available for the remaining two compounds in any of normal databases such as e-chem portal; SciFinder, Google Scholar, Google, or Web of Science – rendering them non-assessable.

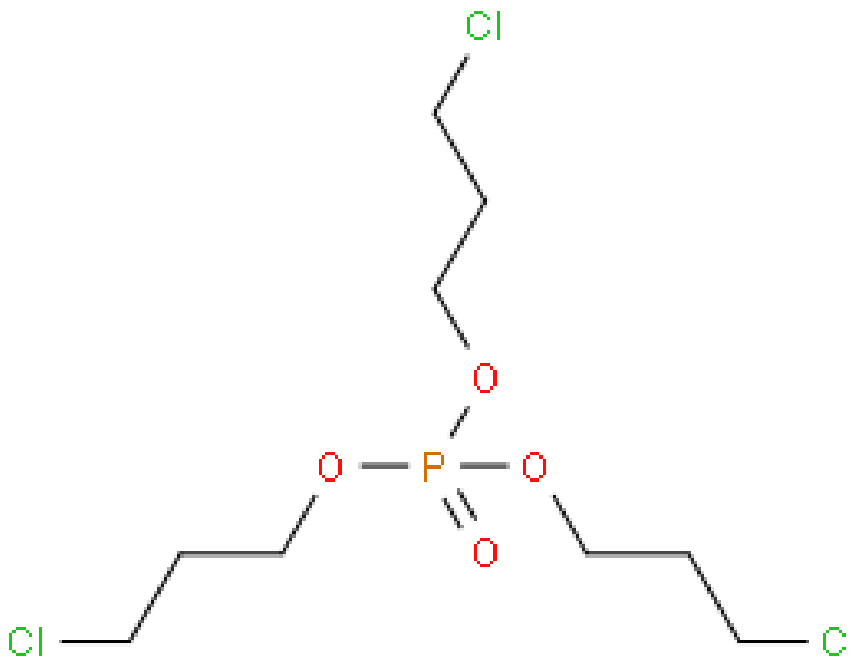
There is no reported aquatic toxicity for the compound CAS# 1067-98-7, but there are data for other compounds from the same chemical category of Trisphosphates from the NICNAS report (2001)⁴. The lowest determined acute NOEC for the category was determined to be 1.8 mg/L for *D. magna*, and 0.56 mg/L for Rainbow Trout for the compound tris (1,3-dichloro-2-propyl) phosphate. Below is a summary of the QSAR derived toxicity information for tris(3-chloropropyl) phosphate. The QSAR predictions were inside the domain of the models for the daphnids and the average predicted acute LC50 was 0.03 (±0.02SD) mg/L. The fish models were outside the domain and thus less reliable with an average predicted acute LC50 of 1.96 (±0.21SD) mg/L.

Danish (Q)SAR Database, <http://qsar.food.dtu.dk>

4. Trisphosphates, 2001. Priority Existing Chemicals Assessment Report, No 17, 2001. NICNAS Australia.

(Q)SAR predicted profile

Structure (as used for QSAR prediction):



SMILES (used for QSAR prediction): C(Cl)CCOP(=O)(OCCCl)OCCCl

ID

REACH EC Number (pre-registration, by 2013)		REACH EC Number (registration, by Dec. 2019)	
Registry Number	1067-98-7 & 26248-87-3	PubChem CID	
EU CLP Harmonized Classification*		DK-EPA / DTU QSAR-based CLP Advisory Classification	
REACH registration cumulated minimum annual tonnage		US TSCA (Oct. 2021)	
Tox21 (2019)		ToxCast (Oct. 2021)	
Molecular Formula	C9 H18 Cl3 O4 P1	Molecular weight (g/mole)	327.57
Chemical Name	C9 H18 Cl3 O4 P1	Molecular weight (g/mole)	327.57

(Annex VI to CLP up to and including the 9th ATP, and including Nordic Council of Minister SPIN list for group entries)

Log Kow	3.11		
Log Kow Exp		Log Kow Exp Ref	327.57
EPI WSKOW model LogKow: log octanol-water partition coefficient			
Koc from MCI (L/kg)	2350	Log Koc from MCI	3.3711
Koc from Kow (L/kg)	560.6	Log Koc from Kow	2.7487
EPI KOCWIN models Koc: soil adsorption coefficient of organic compounds. Kow: octanol-water partition coefficient. MCI: first order Molecular Connectivity Index DTU developed models			

Oral absorption

Lipinski's Rule-of-five score (bioavailability)	0
Absorption from gastrointestinal tract for 1 mg dose (%)	100
Absorption from gastrointestinal tract for 1000 mg dose (%)	50
Leadscope model on Lipinski's Rule-of-five. Equation from literature on GI abs. Lipinski scores of 0 or 1: The substance may be bioavailable. Lipinski scores of 2, 3 or 4: The substance may not be bioavailable.	

Bioaccumulation

BCF (L/kg wet-wt)	7.8
Log BCF (L/kg wet-wt)	0.892
Whole Body Primary Biotransformation Fish Half-Life (days)	0.1882
BCF Arnot-Gobas (upper trophic) Including Biotransformation (L/kg wet-wt)	49.14
BCF Arnot-Gobas (upper trophic) Zero Biotransformation (L/kg wet-wt)	137.1
BAF Arnot-Gobas (upper trophic) Including Biotransformation (L/kg wet-wt)	49.14
BAF Arnot-Gobas (upper trophic) Zero Biotransformation (L/kg wet-wt)	161
EPI BCFBAF models BCF: Bioconcentration factor, BAF: Bioaccumulation factor	

Aquatic toxicity

	Exp	Battery	Leadscope	SciQSAR
Fathead minnow 96h LC50 (mg/L)			1.332886	1.637134
Domain		OUT	OUT	OUT
Daphnia magna 48h EC50 (mg/L)		0.03924967	0.02046511	0.05803422
Domain		IN	IN	IN
Pseudokirchneriella s. 72h EC50 (mg/L)			13.52397	0.4910256
Domain		OUT	OUT	OUT

DTU developed models

	Fish 96h	Daphnid 48h	Green Algae 96h
LC50 (Fish) or EC50 (Daphnid and Algae) for Most Toxic Class (mg/L)	2.912	0.005	6.518
Max. Log Kow for Most Toxic Class	5	5	6.4
Most Toxic Class	Esters (phosphate)	Esters (phosphate)	Esters
Note		IN	IN

EPI ECOSAR models
ECOSAR Classes: Esters;Esters (phosphate)

Appendix 3 Total list of suspect plastic additives

CAS No/EC/ List no.	Name	Polymer type	Typical concentration (mass-%)	Tox screening (ECHA C&L Inventory database) Hazard statements from notifications or from harmonized classification
Light Stabilizers				
2440-22-4/ 219-470-5	2-(2H-Benzotriazol-2-yl)-p-cresol	Polyolefin-I; Polyolefin-II; PVC (soft); ABS; PVC (rigid); PMMA; (E)PS	0.0015 – 0.5	Notified: H317: May cause an allergic skin reaction H410: Very toxic to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
3896-11-5/ 223-445-4	Bumetrizole	Polyolefin-I; PUR; Polyolefin-II; PVC (soft); ABS; PVC (rigid); PC; (E)PS	0.3 – 1.0	Notified: H312: Harmful in contact with skin H315: Causes skin irritation H319: Causes serious eye irritation H332: Harmful if inhaled H335: May cause respiratory irritation H400: Very toxic to aquatic life H411: Toxic to aquatic life with long lasting effects H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
70321-86-7/ 274-570-6	2-(2H-Benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol	Polyolefin-I; PUR; Polyolefin-II; PVC (soft); ABS; PVC (rigid); PET; PMMA; PA; PC; (E)PS	0.2 – 5.0	Notified: H315: Causes skin irritation H319: Causes serious eye irritation. H335: May cause respiratory irritation H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
1843-05-6/ 217-421-2	Dibutyltin dilaurate	Polyolefin-I; PUR; Polyolefin-II; PVC (soft); ABS; PVC (rigid); PMMA; PC; (E)PS	0.2 – 5.0	Notified: H315: Causes skin irritation H317: May cause an allergic skin reaction H319: Causes serious eye irritation H400: Very toxic to aquatic life H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
23949-66-8	N-(2-Ethoxyphenyl)-N'-(2-ethylphenyl) oxamide	PVC (soft); ABS; PVC (rigid); PA; PC; (E)PS	0.7	Notified: H413: May cause long lasting harmful effects to aquatic life
25973-55-1/ 247-384-8	2-(2H-Benzotriazol-2-yl)-4,6-ditertpentylphenol (UV-328)	Styrene homopolymers and copolymers, acrylic polymers, unsaturated Polyesters, PVC, Polyolefins, PUR	0.1 – 1.0	Notified: H315: Causes skin irritation H319: Causes serious eye irritation H335: May cause respiratory irritation H372: Causes damage to organs through prolonged or repeated exposure H411: Toxic to aquatic life with long lasting effects H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
Heat stabilizers				
77-58-7/ 682-479-1	Dibutyltin dilaurate	Polyolefin-I; PVC (soft); PVC (rigid)	3	Notified: H314: Causes severe skin burns and eye damage H318: Causes serious eye damage

				H317: May cause an allergic skin reaction H341: Suspected of causing genetic defects H360: May damage fertility or the unborn child H370: Causes damage to organs H372: Causes damage to organs through prolonged or repeated exposure H400: Very toxic to aquatic life H410: Very toxic to aquatic life with long lasting effects
101-02-0/ 202-908-4	Triphenyl phosphite	PVC (soft); PVC (rigid)	3	Harmonized: H315: Causes skin H319: Causes serious eye irritation H400: Very toxic to aquatic life H410: Very toxic to aquatic life with long lasting effects
15647-08-2	2-Ethylhexyl diphenyl phosphite	PVC (soft); PVC (rigid)	2	Notified: H302: Harmful if swallowed H315: Causes skin irritation H319: Causes serious eye irritation H332: Harmful if inhaled H373: May cause damage to organs through prolonged or repeated exposure H411: Toxic to aquatic life with long lasting effects
Other stabilizers				
120-46-7	1,3-Diphenylpropane-1,3-dione	PVC (soft); PVC (rigid); PET	n.a.	Notified: H302: Harmful if swallowed H312: Harmful in contact with skin H315 Causes skin irritation H317: May cause an allergic skin reaction H319: Causes serious eye irritation H335: May cause respiratory irritation H400: Very toxic to aquatic life H410: Very toxic to aquatic life with long lasting effects
Antioxidants				
2082-79-3/ 218-216-0	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	Polyolefin-I; Polyolefin-II; PVC (soft); ABS; PVC (rigid); PMMA; PC; (E)PS	0.002 – 0.4	Notified: H315 Causes skin irritation H317: May cause an allergic skin reaction H319: Causes serious eye irritation H335: May cause respiratory irritation H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
31570-04-4	Tris(2,4-ditert-butylphenyl) phosphite	Polyolefin-I; PUR; Polyolefin-II; ABS; PET; PMMA; PA; PC; (E)PS	0.004 – 0.5	Notified: H312: Harmful in contact with skin H315 Causes skin irritation H317: May cause an allergic skin reaction H319: Causes serious eye irritation H411: Toxic to aquatic life with long lasting effects H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
32687-78-8/ 251-156-3	2',3-Bis[[3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionyl]propionohydrazide]	Polyolefin-I; PUR; Polyolefin-II; PVC (soft); PA; PC	0.002 – 3.0	Notified: H300: Fatal if swallowed H302: Harmful if swallowed H312: Harmful in contact with skin H315: Causes skin irritation H319: Causes serious eye irritation H332: Harmful if inhaled H335: May cause respiratory irritation H400: Very toxic to aquatic life H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life

6683-19-8/ 229-722-6	Pentaerythritol tetrakis(3-(3,5-di- tert- butyl-4-hydroxy phenyl)propionate)	Polyolefin-I; PUR; Polyolefin-II; PVC (soft); PVC (rigid); PET; PA; PC; (E)PS	0.002 – 0.5	Notified: H302: Harmful if swallowed H312: Harmful in contact with skin H315: Causes skin irritation H331: Toxic if inhaled H332: Harmful if inhaled H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
36443-68-2/ 253-039-2	Ethylenebis(oxye thylene) bis[3-(5-tert- butyl-4-hydroxy- m- tolyl)propionate]	PUR; PVC (soft); ABS; PVC (rigid); PMMA; PA; (E)PS	0.005 – 3.0	Notified: H400: Very toxic to aquatic life H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
1843-03-4	4,4',4''- (1-Methylpropanyl-3- ylidene)tris[6-tert- butyl-m-cresol]	Polyolefin-I; Polyolefin-II; PVC (soft); ABS; PVC (rigid); (E)PS	0.5 – 1.0	Notified: H317: May cause an allergic skin reaction H413: May cause long lasting harmful effects to aquatic life
85-60-9/ 201-618-5	6,6'-Di-tert- butyl-4,4'- butylidenedi-m- cresol	PVC (rigid); PA	0.5	Notified:H315: Causes skin irritation H319: Causes serious eye irritation H335: May cause respiratory irritation H373: Causes damage to organs through prolonged or repeated exposure H400: Very toxic to aquatic life H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
Pigments agents				
6358-31-2	2-[(2-Methoxy-4-nit rophenyl)azo]-N- (2-methoxyphenyl)-3- -oxobutyramide	Polyolefin-I; Polyolefin-II; PVC (soft); ABS; PVC (rigid); PET; PC; (E)PS	2	Notified: H303: May be harmful if swallowed H315: Causes skin irritation H319: Causes serious eye irritation H362: May cause harm to breast-fed children
81-33-4	Perylene-3,4:9,10- tetracarboxydiimide	Polyolefin-I; PUR; Polyolefin-II; ABS; PVC (rigid); PET; PMMA; PA; PC; (E)PS	2	No information
81-77-6/ 201-375-5	6,15-dihydroantra zine-5,9,14,18-tetron	Polyolefin-I; PUR; Polyolefin-II; PVC (soft); ABS; PVC (rigid); PET; PMMA; PA; PC; (E)PS	2	Notified: H302: Harmful if swallowed H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
574-93-6	29H,31H- Phthalocyanine	Polyolefin-I; PUR; Polyolefin-II; PVC (soft); ABS; PVC (rigid); PET; PMMA; PA; PC; (E)PS	2	Notified: H315: Causes skin irritation H319: Causes serious eye irritation H335: May cause respiratory irritation
1047-16-1	5,12-Dihydroquino [2,3-b]acridine-7,14 -dione	Polyolefin-I; PUR; Polyolefin-II; PVC (soft); ABS; PVC (rigid); PET; PMMA; PA; PC; (E)PS	2	No information
6041-94-7	4-[(2,5-Dichloro	Polyolefin-I; PUR;	2	Notified:

	phenyl)azo]-3-hydroxy-N-phenyl naphthalene-2-carboxamide	Polyolefin-II; PVC (soft); ABS; PVC (rigid); PET; PMMA; PA; PC; (E)PS		H341: Suspected of causing genetic defects
5521-31-3	2,9-Dimethylanthra [2,1,9-def:6,5,10-d'e' f']diisoquinoline-1,3,8,10(2H,9H)-tetrone	Polyolefin-I; PUR; Polyolefin-II; PVC (rigid); PET; PMMA; PA; PC; (E)PS	2	No information
Flame retardants				
78-40-0	Triethyl phosphate	PUR	10	Harmonized: H302: Harmful if swallowed
108-78-1	Melamine	PUR	25	Notified: H314: Causes severe skin burns and eye damage H315: Causes skin irritation H319: Causes serious eye irritation H335: May cause respiratory irritation H361: Suspected of damaging fertility or the unborn child H361f: Suspected of damaging fertility H373: Causes damage to organs through prolonged or repeated exposure H400: Very toxic to aquatic life H410: Very toxic to aquatic life with long lasting effects
18755-43-6	Dimethyl propylphosphonate	PUR	15	Notified: H319: Causes serious eye irritation H360: May damage fertility or the unborn child
84852-53-9	1,1'-(Ethane-1,2-diyl)bis [pentabromobenzene]	PUR; PVC (soft)	15.0 – 35.0	Notified: H413: May cause long lasting harmful effects to aquatic life
5436-43-1, 60348-60-9, 41318-75-6, 189084-64-8, 68631-49-2, 207122-15-4	Pentabromodiphenyl ethers (PBDE). The PolyBDEs EQS dossier 2011, relates to the commercial PBDE mixture, i.e. BDE-47 + BDE-99 + BDE-28 + BDE-100 + BDE-153 + BDE-154.	PUR	3–25 wt-% (PBDEs, not specific) (Hahladakis et al., 2018)	The specific congeners are not classified
Other functions				
123-77-3	Azodicarbonamide	Polyolefin-I; PVC (rigid)	0.1	Harmonized: H334: May cause allergy or asthma symptoms or breathing difficulties if inhaled
23128-74-7/ 245-442-7	N,N'-Hexane-1,6-diylbis [3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionamide]	PUR; PA	0.5	Notified: H412: Harmful to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
624-03-3	Ethane-1,2-diyl palmitate	PVC (rigid)	n.a.	Notified: Not classified
Plasticizers				

77-90-7	Tributyl-O-Acetyl citrate	PUR; PVC (soft)	10.0 – 35.0	Notified: H315 Causes skin irritation H319: Causes serious eye irritation H340: May cause genetic defects H350: May cause cancer H411: Toxic to aquatic life with long lasting effects H412: Harmful to aquatic life with long lasting effects
84-74-2/ 201-557-4	Dibutyl phthalate	PUR; PVC (soft)	10.0 – 35.0	Harmonized: H360: May damage fertility or the unborn child H400: Very toxic to aquatic life
103-23-1	Bis(2-ethylhexyl) adipate	PUR; PVC (soft)	10.0 – 35.0	Notified: Not classified
105-99-7/ 203-350-4	Dibutyl adipate	PUR; PVC (soft)	10.0 – 35.0	Notified: H361: Suspected of damaging fertility or the unborn child H411: Toxic to aquatic life with long lasting effects H412: Harmful to aquatic life with long lasting effects
122-62-3	Decanedioic acid, 1,10-bis (2-ethylhexyl) ester	PUR; PVC (soft)	10.0 – 35.0	Notified: H302: Harmful if swallowed
33703-08-1	Diisononyladipate	PUR; PVC (soft)	10.0 – 35.0	Notified Not classified
117-81-7/ 204-211-0	Di-2-ethylhexyl phthalate	PUR; PVC (soft); ABS; (E)PS	2.0 – 35.0	Harmonized: H360FD: May damage fertility. Suspected of damaging the unborn child Notified: H400: Very toxic to aquatic life H410: Very toxic to aquatic life with long lasting effects H411: Toxic to aquatic life with long lasting effects H412: Harmful to aquatic life with long lasting effects
3319-31-1	Tris(2-ethylhexyl) benzene-1,2,4-tricarboxylate	PVC (soft)	35	No information
29761-21-5	Isodecyl diphenyl phosphate	PUR	10	Notified: H400: Very toxic to aquatic life H410: Very toxic to aquatic life with long lasting effects H413: May cause long lasting harmful effects to aquatic life
3622-84-2/ 222-823-6	N-butylbenzenesulphonamide	PUR; PA	10.0 – 15.0	Notified: H302: Harmful if swallowed H312: Harmful in contact with skin H315: Causes skin irritation H319: Causes serious eye irritation H331: Toxic if inhaled H332: Harmful if inhaled H335: May cause respiratory irritation H373: Causes damage to organs through prolonged or repeated exposure H412: Harmful to aquatic life with long lasting effects
77-94-1/ 201-071-2	Tributyl citrate	PUR; PVC (soft)	10.0 – 35.0	Notified: H318: Causes serious eye damage H400: Very toxic to aquatic life
109-43-3	Dibutyl sebacate	PUR; PVC (soft)	10.0 – 35.0	Notified: H315: Causes skin irritation H317: May cause an allergic skin reaction H319: Causes serious eye irritation

				H335: May cause respiratory irritation
110-33-8	Dihexyl adipate	PUR; PVC (soft)	10.0 – 35.0	Notified: Not classified
131-17-9/ 205-016-3	Di-allyl phthalate	PUR; PVC (soft)	10.0 – 35.0	Harmonized: H302: Harmful if swallowed H400: Very toxic to aquatic life H410: Very toxic to aquatic life with long lasting effects Notified: H301: Toxic if swallowed H317: May cause an allergic skin reaction H332: Harmful if inhaled H413: May cause long lasting harmful effects to aquatic life
28553-12-0; 68515-48-0	Diisononylphthalate	PUR; PVC (soft)	10.0 – 35.0	Notified: H332: Harmful if inhaled H334: May cause allergy or asthma symptoms or breathing difficulties if inhaled H361: Suspected of damaging fertility or the unborn child H400: Very toxic to aquatic life
3622-84-2	N-butylbenzenesulphonamide	PUR; PA	10.0 – 15.0	Notified: H302: Harmful if swallowed H312: Harmful in contact with skin H315: Causes skin irritation H319: Causes serious eye irritation H373: Causes damage to organs through prolonged or repeated exposure H412: Harmful to aquatic life with long lasting effects

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