

**Organic UV stabilizers in the coastal and marine environment -
European North and Baltic Seas compared to Chinese Bohai and Yellow Seas**

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Abstract

Nowadays, the environmental pollution from organic UV stabilizers is of growing scientific and media interest. Organic UV stabilizers are applied worldwide to industrial materials such as plastics and to personal care products, particularly sunscreens. In plastics they prevent photo-induced degradation, while in sunscreens they protect human skin against the effects of UV radiation. UV stabilizers are of emerging concern due to their large production volumes, their widespread uses, their potential persistence or pseudo-persistence, and their potential adverse effects on ecosystems and humans. Information on their behavior and fate in the environment is very limited.

In this thesis, an analytical method is developed for the trace analysis of twenty-two organic UV stabilizers and one hindered amine light stabilizer (HALS) in coastal and marine sediments. For extraction and clean-up, an accelerated solvent extraction (ASE) method is used. For detection, liquid chromatography (LC) coupled to tandem mass spectrometry (MS/MS) is applied. The LC-MS/MS system is operating with both an electrospray ionization (ESI) source and an atmospheric pressure photoionization (APPI) source. In comparison, the APPI source performs better in the sensitive analysis of UV stabilizers in real sediment samples than the ESI source. The method detection limits (MDLs) range from 0.001 to 0.140 ng/g dry weight (dw). The developed method is applied to sediments from the Chinese Bohai and Yellow Seas and the European North and Baltic Seas. In both study areas, the occurrence of UV stabilizers in the sediment is investigated for the first time.

In the Chinese Bohai and Yellow Seas, concentrations were in the low ng/g dw range. The highest concentration of 25 ng/g dw was found for octocrylene (OC) in the Laizhou Bay. In the northern part of the Yellow Sea, region-specific composition profiles could be identified for the Korea Bay and the Shandong Peninsula coastline. In the Korea Bay, the dominating substances were OC and ethylhexyl salicylate (EHS), while all other analytes were below their respective method quantification limits (MQLs). Around the Shandong Peninsula, benzotriazole UV stabilizers were the dominant substance group with octrizole (UV-329) as the predominant compound, reaching concentrations of 6.09 ng/g dw. The distribution pattern of UV-329 and bumetrizole (UV-326) were correlated (Pearson correlation coefficient $r > 0.98$, $p \ll 0.01$ around the Shandong Peninsula), indicating an identical input pathway and similar environmental behavior.

In the European North and Baltic Seas, the concentrations found were in a similar range as in China. OC was the predominant compound with regard to detection frequency (79%) and concentrations (up to 9.7 ng/g dw) and accounted for more than 65% of UV stabilizer contamination in the German Bight. The sparsely studied triazine derivative EHT was quantified in the Rhine-Meuse-Delta and the German Bight in concentrations up to 2.0 ng/g dw. In the Baltic Sea, benzotriazole UV stabilizers accounted for 60% of the contamination, with bisoctrizole (UV-360) as the main substance. Region-specific contamination patterns and riverine influences were revealed. The results suggest that both direct and indirect sources contribute to the UV stabilizer contamination in the North and Baltic Seas.

A preliminary environmental hazard assessment was performed and indicated a most likely negligible impact on benthic and sediment-dwelling organisms in both study areas. A direct comparison between the Bohai and Yellow Seas and the North and Baltic Seas does not reveal statistically significant concentration differences of UV stabilizers. Interestingly, OC accounts for around 50% of the found contamination in both regions, demonstrating the extreme importance of this UV stabilizer in Europe and in China.

Zusammenfassung

Die Belastung der Umwelt durch organische UV-Stabilisatoren ist heutzutage von wachsendem wissenschaftlichem und medialem Interesse. Organische UV-Stabilisatoren werden weltweit in Industriematerialien wie z.B. Kunststoffen sowie in Kosmetikartikeln, hierbei insbesondere in Sonnenschutzmitteln, eingesetzt. In Plastikprodukten verhindern sie den Licht-induzierten Abbau während sie in Sonnenschutzmitteln die menschliche Haut vor den Auswirkungen von UV-Strahlung schützen. UV-Stabilisatoren gelten wegen ihren hohen Produktionsmengen, einem breiten Anwendungsspektrum, einer möglichen Persistenz oder Pseudo-Persistenz und vermuteten negativen Auswirkungen auf Ökosysteme und den Menschen als bedenklich. Informationen zu ihrem Umweltverhalten und Verbleib sind kaum vorhanden.

In dieser Arbeit wurde eine Analysenmethode für die Spurenanalytik von 22 organischen UV-Stabilisatoren und einem sterisch gehinderten Amin in küstennahen und marinen Sedimenten entwickelt. Für die Extraktion und Aufreinigung der Proben wird die beschleunigte Lösungsmittelextraktion verwendet. Die Detektion erfolgt durch Flüssigchromatographie (LC) mit Tandem-Massenspektrometrie (MS/MS)-Kopplung. Das LC-MS/MS-System arbeitet sowohl mit einer Elektronenspray (ESI)-Quelle, als auch mit Photoionisation bei Atmosphärendruck (APPI). Im Vergleich der Quellen hat sich herausgestellt, dass die APPI-Quelle besser für den empfindlichen Nachweis von UV-Stabilisatoren in Realproben geeignet ist. Die Nachweisgrenzen der entwickelten Methoden liegen zwischen 0,001 und 0,140 ng/g Trockenmasse. Mit der entwickelten Methode wurden Sedimente aus China (Golf von Bohai und Gelbes Meer) und Europa (Nord- und Ostsee) analysiert. Das Vorkommen von UV-Stabilisatoren in Sedimenten wurde in beiden Regionen erstmalig untersucht.

Im Golf von Bohai und dem Gelben Meer lagen die Konzentrationen im unteren ng/g Trockengewicht-Bereich. Die höchste gefundene Konzentration war 25 ng/g Trockengewicht von Octocriolen (OC) in der Laizhou-Bucht. Charakteristische Substanzmuster konnten im nördlichen Bereich des Gelben Meeres für die Korea-Bucht und die Küste der Shandong-Halbinsel identifiziert werden: In der Korea-Bucht waren die dominierenden Substanzen OC und Ethylhexylsalicylat (EHS). Alle anderen untersuchten Substanzen lagen in Konzentrationen unterhalb ihrer jeweiligen Quantifizierungsgrenze (MQL) vor. Entlang der Shandong-Halbinsel waren Benzotriazol-UV-Stabilisatoren die dominierende Substanzgruppe mit UV-329 als vorherrschende Substanz und einer Höchstkonzentration von 6,09 ng/g Trockenmasse. Die Verteilungsmuster von UV-329 und UV-326 wiesen eine hohe Korrelation auf (Person Korrelationskoeffizient $r > 0.98$, $p \ll 0.01$ entlang der Shandong-Halbinsel), was auf den selben Eintrittspfad und ein ähnliches Umweltverhalten hindeutet.

In der Nord- und Ostsee lagen die Konzentrationen in einem ähnlichen Bereich wie in China. OC war auch hier die dominierende Substanz in Hinblick auf Detektionsrate (79%) und Konzentrationen (bis zu 9,7 ng/g Trockenmasse) und machte mehr als 65% der UV-Stabilisatoren-Kontamination in der Deutschen Bucht aus. Das kaum untersuchte Triazin-Derivat EHT konnte im Rhein-Maas-Delta und in der Deutschen Bucht in Konzentration bis zu 2,0 ng/g Trockenmasse quantifiziert werden. In der Ostsee machten

Benzotriazol-UV-Stabilisatoren rund 60% der Kontamination aus, mit UV-360 als Hauptsubstanz. Zudem konnten regionale Kontaminationsmuster und der Eintrag von Flüssen gezeigt werden. Die Ergebnisse deuten darauf hin, dass UV-Stabilisatoren sowohl durch direkte, als auch indirekte Quellen in die Nord- und Ostsee gelangen.

In beiden untersuchten Regionen deutet eine vorläufig durchgeführte Gefahrenbeurteilung auf keine zu erwartenden negativen Auswirkungen auf benthische Lebewesen hin. Ein direkter Vergleich zwischen dem chinesischen und dem europäischen Untersuchungsgebiet zeigt keine statistisch signifikant unterschiedlichen Konzentrationsbereiche von UV-Stabilisatoren. Interessanterweise macht OC in beiden Untersuchungsgebieten ca. 50% der gefundenen Kontamination aus, was auf die hohe Bedeutung dieses UV-Stabilisators in Europa und in China hindeutet.

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List of Abbreviations

Abbr.	abbreviation
AhR	aryl hydrocarbon receptor
APCI	atmospheric pressure chemical ionization
APPI	atmospheric pressure photoionization
ASE	accelerated solvent extraction
BfR	German Federal Institute for Risk Assessment
CAS	chemical abstracts service
CAV	cell accelerator voltage
CE	collision energy
Coef.	coefficient
CoRAP	community rolling action plan
CosIng	cosmetic ingredient database
DCM	dichloromethane
d.f.	detection frequency
dw	dry weight
EC _x	effective concentration
ECHA	European Chemicals Agency
e.g.	for example
EPA	Environmental Protection Agency
ESI	electrospray ionization
EU	European Union
GC	gas chromatography
GHS	globally harmonized system of classification and labelling of chemicals
GPC	gel permeation chromatography
HALS	hindered amine light stabilizer
HELCOM	Helsinki Commission
HQ	hazard quotient
HRMS	high resolution mass spectrometry
iLOD	instrumental limit of detection
iLOQ	instrumental limit of quantification
INCI	international nomenclature of cosmetic ingredients
IR	infra-red
IS	internal standard
K _{ow}	octanol/water partition coefficient
K _{oc}	soil organic carbon/water partition coefficient
LC	liquid chromatography
LC _x	lethal concentration
MDL	method detection limit

MEC	measured environmental concentration
MQL	method quantification limit
MS	mass spectrometry
Na ₂ SO ₄	sodium sulfate
N/A	not available
n.a.	not analyzed
n.d.	not detected
NOEC	no observed effect concentration
OECD	organization for economic co-operation and development
PBT	persistent, bioaccumulative, and toxic
PCBs	polychlorinated biphenyls
PCPs	personal care products
PEEK	polyether ether ketone
PFASs	per- and polyfluoroalkyl substances
PFOA	perfluorooctanoic acid
PNEC	predicted no effect concentration
POPs	persistent organic pollutants
PP	polypropylene
psi	pound-force per square inch
PTFE	polytetrafluoroethylene
QSAR	quantitative structure-activity relationship
r	Pearson correlation coefficient
REACH	registration, evaluation, authorization, and restriction of chemicals
SI	supporting information
S/N	signal to noise
SPE	solid phase extraction
SPM	suspended particulate matter
SVHC	substance of very high concern
TiO ₂	titanium dioxide
TOC	total organic carbon
UHPLC	ultra high performance liquid chromatography
U.S.	United States
UVPs	UV protecting compounds
vPvB	very persistent and very bioaccumulative
WHO	World Health Organization
WWTP	wastewater treatment plant
w/w	weight per weight

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1 Introduction

Chemical pollution is a major concern for the coastal and marine environment. Thousands of chemicals are entering the environment through anthropogenic activities (e.g., industrial, agricultural, or recreational activities) and a number of them harmfully affect ecosystems and humans (Dachs and Méjanelle, 2010). At present, more than 18 million organic substances (Theobald, 2011) are known and about 100,000 (BfR, 2018) are used commercially. The identification, assessment, and management of chemical pollutants are key challenges of the “Chemical Anthropocene”, which describes a time period in which the occurrence and distribution of chemicals in the environment reached global dimensions (Quante et al., 2011).

Several international legislative measures and conventions aim at identifying and regulating chemicals of particular environmental concern. Some chemicals and chemical classes have already been identified that cause adverse effects on ecosystems and human health and are listed as persistent organic pollutants (POPs) under the Stockholm Convention. POPs are persistent in the environment, accumulative in organisms, and toxic to humans and wildlife. They can also undergo long-range transport and are detected even in remote regions far from production or usage locations (Stockholm Convention, 2017b). Widely known examples are the pesticide DDT and polychlorinated biphenyls (PCBs) that have been designated on the initial list of POPs when the Stockholm Convention entered into force in 2004 (Stockholm Convention, 2017a). Since then, the list has been regularly updated. It is estimated that approximately 2,000 (Theobald, 2011) substances are environmentally relevant due to these persistent, bioaccumulative, and toxic (PBT) properties. The European chemical regulation REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) approaches this problem by placing responsibility on companies to prove that a chemical can be safely used and how this can be achieved. All chemicals produced and marketed in the EU were required to be registered under REACH by 2018. The European Chemical Agency (ECHA) evaluates the individual registration dossiers and the EU member states evaluate selected substances to clarify initial concerns regarding human health or ecosystems. With this procedure, REACH aims to improve human and environmental protection against chemical risks.

Organic UV protecting compounds (UVPs) are a group of contaminants of emerging concern (EPA, 2018). These are non-regulated or only partially regulated chemical compounds that are increasingly detected in the environment, but information on their behavior, fate, and toxicological impact is very limited (e.g., Combi et al., 2016; EPA, 2018; Hutchinson et al., 2013). UVPs are widely used in personal care products (PCPs), textiles, plastics, paints, adhesives, rubber, and other industrial products (Avagyan et al., 2015; Kim et al., 2011b; Ramos et al., 2015). Depending on their purpose, they can be divided into two categories: i) UV stabilizers that are added to plastics and other industrial products to prevent UV-induced degradation and discoloring of the product and ii) UV filters that are approved ingredients in PCPs such as cosmetics and sunscreens to protect human skin and hair against UV radiation. As most compounds are used for both purposes, a strict differentiation is not possible. For this reason, the term “UV stabilizer” is used for all compounds in this thesis.

UV stabilizers are of environmental concern due to their widespread usages, their large production volumes (chapter 2.2.2), and their potential adverse effects on the environment and humans (chapter 2.1.2). The input pathways to the coastal and marine environment are mainly indirect, through wastewater treatment plant (WWTP) discharges, or direct, through recreational activities such as bathing and swimming (Poiger et al., 2004; Ramos et al., 2016). UV stabilizers have been reported worldwide in water (Balmer et al., 2005; Bratkovics et al., 2015; Kameda et al., 2011; Tsui et al., 2014), suspended particulate matter (SPM) (Wick et al., 2016a), house dust (Kim et al., 2012), sediment (Kameda et al., 2011; Langford et al., 2015; Nakata et al., 2009; Wick et al., 2016a), and biota (Cunha et al., 2015; Gago-Ferrero et al., 2012; Langford et al., 2015; Nakata et al., 2012; Peng et al., 2015; Sang and Leung, 2016; Wick et al., 2016a), underlining their ubiquitous presence in the environment (chapter 2.2.3). Existing regulations are sparse. Presently, four UV stabilizers are classified as substances of very high concern (SVHC) under REACH and numerous others are listed in the European community rolling action plan (CoRAP) to be evaluated in the upcoming years (chapter 2.1.3).

2 General information

2.1 UV stabilizers

2.1.1 Mode of action

Exposure to sunlight results in deterioration of mechanical, physio-chemical, and optical properties of plastics and other polymer materials. This photo-induced degradation or “aging” of materials is mainly ascribed to photo-oxidation of the polymer backbone. UV and light stabilizers show protecting properties against sunlight by preventing or at least retarding this degradation, as a complete inhibition is often not possible. For the human skin, the UV part of sunlight (100 - 400 nm (WHO, 2018)) is the most harmful, as it can cause sunburns and skin cancer.

There are four main protection mechanism of UV stabilizers as described in the following (Zweifel et al., 2009).

- i) UV absorption
- ii) Quenching
- iii) Hydroperoxide decomposition
- iv) Free radical scavenging

UV absorption and its dissipation is an important protection mechanism of UV stabilizers and prevents the starting of the degradation process. In this case, the photons are absorbed before they reach the material and therefore cannot start the degradation reactions. In the cosmetics Regulation (EC) No 1223/2009 of the European Parliament and of the Council, substances approved as “UV filters” have to either absorb, reflect, or scatter the UV part contained in sun or artificial light. This absorption (alternatively reflecting or scattering, but mainly for inorganic UV filters) mechanism is essential, as sunscreens are put on the surface of the human skin to prevent UV radiation from reaching it. In contrast to this, substances approved as “UV absorber” protect the cosmetic product itself and no specific operation principle is requested.

The mechanisms ii, iii, and iv retard a degradation reaction after it started and therefore take place inside the product (Figure 1). Quenching is the deactivation of the excited state by taking over the energy absorbed by the chromophores of the plastic material. The breaking of the polymer chain (initiation reaction) is not taking place. UV stabilizers working after mechanism iii are decomposing the hydroperoxide, which is a decisive part of the degradation reaction. Some UV stabilizers can also act as free radical scavengers (mechanism iv). In this case, the degradation reaction is stopped by free radical terminations. Especially hindered amine light stabilizers (HALS) are an group of excellent alkyl radical scavengers (Zweifel et al., 2009).

It has to be added that the protecting properties of some classes of UV stabilizer are due to more than one single mechanism. For example, cinnamate derivatives absorb energy and transform it into heat on the one hand and quench excited states on the other hand (Zweifel et al., 2009).

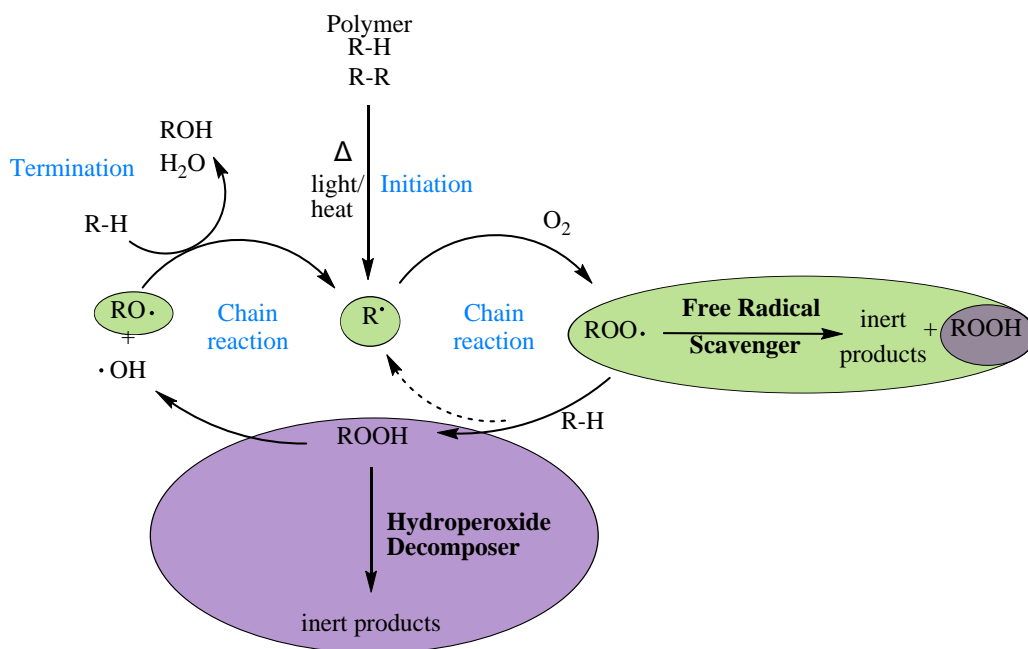


Figure 1: General scheme of polymer degradation after Zweifel et al. (2009).

2.1.2 Adverse effects

The widespread occurrence (chapter 2.2.3) and the resulting potential exposure to UV stabilizers have raised increasing concern about their impact on ecosystems and human health. Many UV stabilizers including benzophenone, camphor, and cinnamate derivatives have been identified as potential endocrine disruptors (Balazs et al., 2016; Kunz and Fent, 2006b; Kunz et al., 2006; Schlumpf et al., 2001; Schlumpf et al., 2004; Wang et al., 2016). For example, several compounds such as benzophenone-3 (BP-3), 4-methylbenzylidene camphor (4-MBC), ethylhexyl methoxycinnamate (EHMC) and homosalate (HMS) showed multiple hormonal activities in *in vitro* human receptor systems (Kunz and Fent, 2006b) and some benzophenone UV stabilizers, including BP-3, showed estrogenic activities in fish both *in vitro* and *in vivo* (Kunz et al., 2006). 4-MBC and octocrylene (OC) interfered with the endocrine system of mollusks (Schmitt et al., 2008) and zebrafish (Zhang et al., 2016), respectively. Moreover, 4-MBC and EHMC negatively affected the development of rat offspring (Axelstad et al., 2011; Schlumpf et al., 2004) and BP-3 caused cytotoxic effects on bacteria and developmental toxicity on zebrafish embryos (Balazs et al., 2016). 4-MBC interfered with the gene transcription in marine copepods and thereby negatively affected their survival, development, and reproduction (Chen et al., 2017). In a sediment toxicity study, EHMC showed toxic effects on the reproduction of snails (Kaiser et al., 2012a). Regarding the toxicity of benzotriazole UV stabilizers, studies showed various adverse effects on aquatic and terrestrial organisms (NTP, 2011). In zebrafish embryos, exposure to drometrizole (UV-P) and bumetrizole (UV-326) led to the activation of the aryl hydrocarbon receptor (AhR) pathway, which may cause metabolic imbalance and developmental toxicity (Fent et al., 2014). In other studies, benzotriazole UV stabilizers interacted with the human serum albumin (Zhuang et al., 2016) and might adversely affect the immune response by interacting with the human AhR

(Nagayoshi et al., 2015). Long-term exposures of UV-320 to rats revealed several adverse effects such as histopathological changes in the liver (Hirata-Koizumi et al., 2008) and toxicity studies showed that direct contact with UV-P might cause acute effects such as dermatitis and skin irritation (Yamano et al., 2001). So far, benzotriazole UV stabilizers showed no estrogenic or androgenic activities *in vitro* and *in vivo* in zebrafish embryos (Fent et al., 2014; Kawamura et al., 2003), but UV-P showed a significant antiandrogenic activity *in vitro* (Fent et al., 2014).

In the environment or within the human body, UV stabilizers can be metabolized, which might result in even higher adverse effects. For example, benzophenone 1 (BP-1) is a metabolite of BP-3 and possessed a higher estrogenic activity than BP-3 in *in vitro* assays (Wang et al., 2016). The UV stabilizer avobenzene (BM-DBM) is photounstable and its photodegradation products arylglyoxals and benzils have been found to be strong skin sensitizers and to be cytotoxic, respectively (Karlsson et al., 2009).

Only few studies investigated the toxicity of UV stabilizers in mixtures, which is an important aspect, as in the environment and in products (e.g., cosmetics) these chemicals are not present as a single chemical but together with numerous other compounds. In mixtures, effects (e.g., toxicity effects) can be additive, synergistic, or antagonistic and therefore might occur at lower concentration levels (Baas et al., 2009; Baas et al., 2010; Kunz and Fent, 2006a). *In vitro* assays showed additive or synergistic estrogenic activities of UV stabilizer mixtures that occurred at no observed effect concentrations (NOEC) of each single compound (Heneweer et al., 2005; Kunz and Fent, 2006a). Synergistic effects of UV stabilizer mixtures were also observed in *Daphnia magna* (Jang et al., 2016). Binary UV stabilizer mixtures of 4-MBC, BP-3, and EHMC showed antagonistic effects on the endocrine system and synergistic effects on the stress response of a midge larvae (Ozaez et al., 2016), showing their complex interactions. In fish, dose-dependent effects were revealed as antagonism was found at low levels (NOEC to a 5% effect concentration [EC₅]) and additivity at higher levels (EC₁₀ to EC₃₀) (Kunz and Fent, 2009).

On the basis of environmental concentrations, it has been demonstrated that UV stabilizers pose a risk to aquatic organisms (Paredes et al., 2014; Sanchez Rodriguez et al., 2015; Tsui et al., 2014). Studies showed that OC could accumulate in fish up to levels that caused transcriptional alterations (Bluthgen et al., 2014). Paredes et al. (2014) investigated the toxicity of four UV stabilizers to marine organisms from three trophic levels and showed a potential environmental risk for BP-3 and 4-MBC in recreational waters. In that study, microalgae were the most affected species. For benzotriazole UV stabilizers, no acute toxicity on freshwater crustaceans was reported at environmental concentrations (Kim et al., 2011a). Beyond that, tropical ecosystems are particularly affected by UV stabilizers as some compounds are a major cause for coral bleaching (Danovaro et al., 2008). Danovaro et al. (2008) revealed mainly 4-MBC, BP-3, and EHMC to cause a complete bleaching of hard corals by promoting viral infections. Developmental effects on coral larvae were observed for two benzophenone UV stabilizers (Downs et al., 2014; Downs et al., 2016).

2.1.3 Regulations

In the EU, substances used in industrial applications have to be registered under the Chemical Regulation REACH. Currently, four benzotriazole UV stabilizers are included on the candidate list of Substances of Very High Concern (SVHC) due to their PBT properties (ECHA, 2018a). These substances are UV-320, UV-327, UV-328, and UV-350. Due to diverse initial concerns for human health or for the environment, numerous others are listed under the European community rolling action plan (CoRAP) (ECHA, 2018b) to be evaluated in the coming years (Table 1). Additionally, EHMC is included in the first European watch list of potential water pollutants under the Environmental Quality Standards Directive 2008/105/EC (European Commission, 2015). While currently EHMC is monitored in water, monitoring of EHMC in sediment in the coming years is recommended (Loos et al., 2018).

Substances allowed in PCPs (especially sunscreens) are differently regulated worldwide. In the EU, sunscreens are regulated as cosmetic products and a list of approved substances to be used as UV filters is provided in Annex VI of the Regulation No. 1223/2009 (European Commission, 2018d). Currently, twenty-seven substances (including two inorganic compounds) are listed and can be added to products in maximum concentrations of 4 to 15% w/w per substance (inorganic up to 25% w/w). In addition, further UV stabilizers are allowed in cosmetic products as so-called “UV absorbers” to stabilize the product itself (European Commission, 2018a). All substances (with the exception of UV-360) approved as UV filters are also approved UV absorbers. The substances BP-12, UV-P, UV-326, and UV-329 are only approved as UV absorbers (see Figure 2). Due to the diverse adverse effects of BP-3 (chapter 2.1.2), products containing BP-3 needs the warning “contains Benzophenone-3” (European Commission, 2018b), unless BP-3 is used in concentrations $\leq 0.5\%$ or as UV absorber (European Commission, 2018c). In China, the same substances are permitted as in the EU (Sanchez-Quiles and Tovar-Sanchez, 2015)¹. In the USA, sunscreens belong to the “over the counter drugs” and therefore UV filters have to be approved the same way as pharmaceuticals (FDA, 2018). Currently, only 16 substances are approved as UV filters (FDA, 2018) and no new sunscreen ingredients have been approved since 1999 (Dennis, 2014). Several “new” UV filters that are used outside the USA for years were declined with the demand for more safety data (Kaskey, 2018). In Australia, sunscreens are regulated by the Therapeutics Goods Administration (Australian Government, 2017). The number of approved substances in Australia is higher than in the EU and USA due to a high risk and fear of skin cancer. As a consequence of these different legislations and authorization procedures, the number of substances and the individual substances approved as UV filters in sunscreens and other PCPs differ between countries. An overview is presented in Sanchez-Quiles and Tovar-Sanchez (2015). For example, the camphor derivative 4-MBC is allowed in sunscreens in the EU and Australia, while it is forbidden in the USA and Japan.

Due the harmful effects of certain UV stabilizers on corals (chapter 2.1.2), the U.S. state Hawaii banned the sale of sunscreens containing BP-3 and EHMC in May 2018 (Moulite, 2018;

¹ in Table 1 of Sanchez-Quiles and Tovar-Sanchez (2015), benzophenone-4 and zinc oxide are only marked as permitted in China, but currently they are also approved in the EU (European Commission, 2018d)

Schuler, 2018). The ban will enter into force as from 2021. Shortly after the ban in Hawaii, the Pacific island Palau banned the use (and not only the sale as in Hawaii) of “reef-toxic” sunscreens (Welt.de, 2018). These are defined as sunscreens containing any one of 10 ingredients, including BP-3 (FoxNews, 2018). The law will be inured in 2020.

Table 1: Analyzed UV stabilizers listed in CoRAP (as from October 2018; 352 entries in total) (ECHA, 2018b).

Substance	Year of Evaluation (planned)	Evaluating Member State	Initial grounds for concern	Substance Evaluation Status
OC	2012	France	<ul style="list-style-type: none"> • Suspected PBT/vPvB • High (aggregated) tonnage • Wide dispersive use 	Information requested
BP-12	2013	Italy	<ul style="list-style-type: none"> • Potential endocrine disruptor • Sensitizer • Consumer use • High (aggregated) tonnage • Wide dispersive use 	Concluded
BP-3	2014	Denmark	<ul style="list-style-type: none"> • Potential endocrine disruptor • Cumulative exposure • Exposure of environment • Exposure of sensitive populations • Exposure of workers • Wide dispersive use 	Ongoing
BM-DBM	2015	Germany	<ul style="list-style-type: none"> • Suspected PBT/vPvB • Consumer use • Exposure of environment • High (aggregated) tonnage • Wide dispersive use 	Information requested
DBT	2015	Germany	<ul style="list-style-type: none"> • Suspected PBT/vPvB • Exposure of environment • Wide dispersive use 	Information requested
EHMC (only trans Isomer; CAS 83834-59-7)	2016	United Kingdom	<ul style="list-style-type: none"> • Potential endocrine disruptor • Suspected PBT/vPvB • Consumer use • Exposure of environment • High (aggregated) tonnage • Other exposure/risk based concern • Wide dispersive use 	Information requested
IAMC	2016	United Kingdom	<ul style="list-style-type: none"> • Potential endocrine disruptor • Consumer use • Wide dispersive use 	Information requested
UV-P	2016	Czech Republic	<ul style="list-style-type: none"> • Sensitizer • Consumer use • Exposure of workers • High RCR • Wide dispersive use 	Concluded
EHS	2020	Germany	<ul style="list-style-type: none"> • Potential endocrine disruptor 	Not started

2.2 UV stabilizers analyzed in this thesis

UV stabilizers to be analyzed in this thesis were selected due to their potential adverse effects (chapter 2.1.2), existing regulations (chapter 2.1.3), production volumes (chapter 2.2.2) and environmental occurrences (chapter 2.2.3). Furthermore, available literature for potential PBT substances or priority chemicals (Howard and Muir, 2010; NORMAN, 2015, 2018; Strempele et al., 2012) was searched.

For the selection of the final analytes, attention was paid to their respective physicochemical properties, as the aim of this thesis was to analyze the selected UV stabilizers in one single sample preparation step and max. two measuring steps. Besides organic UV stabilizers, there are some inorganic compounds (e.g., TiO₂), that were not considered in this thesis.

2.2.1 Properties and structures

Chemically, UV stabilizers are aromatic molecules including, e.g., benzophenones, benzotriazoles, salicylates, cinnamates, and camphor derivatives. This list is not conclusive. 2-Hydroxybenzophenones, 2-hydroxyphenylbenzotriazoles, and sterically hindered amines are belonging to the most important classes of UV stabilizers to be used as plastic additives (Zweifel et al., 2009). A wide range of other chemical classes is also available and approved for the use in PCPs.

Degradation products, which often exhibit more problematic properties than the parent compound (chapter 2.1.2), are not known for most UV stabilizers and were therefore not included in the analysis. Only for some long-used substances such as BM-DBM, EHMC, and BP-3 investigations on the degradation behavior have been performed and the results show the multitude of possible degradation products (e.g., Jentzsch et al., 2016; Semones et al., 2017; Volpe et al., 2017).

An overview of UV stabilizers analyzed in this thesis is given in Figure 2 and Table 2. UV stabilizers marked in **bold** and *italic* are allowed as UV filters and UV absorbers, respectively, in cosmetic products in the EU (see chapter 2.1.3). Further information on the analyzed UV stabilizers is presented in Table 30 (chapter 7.1).

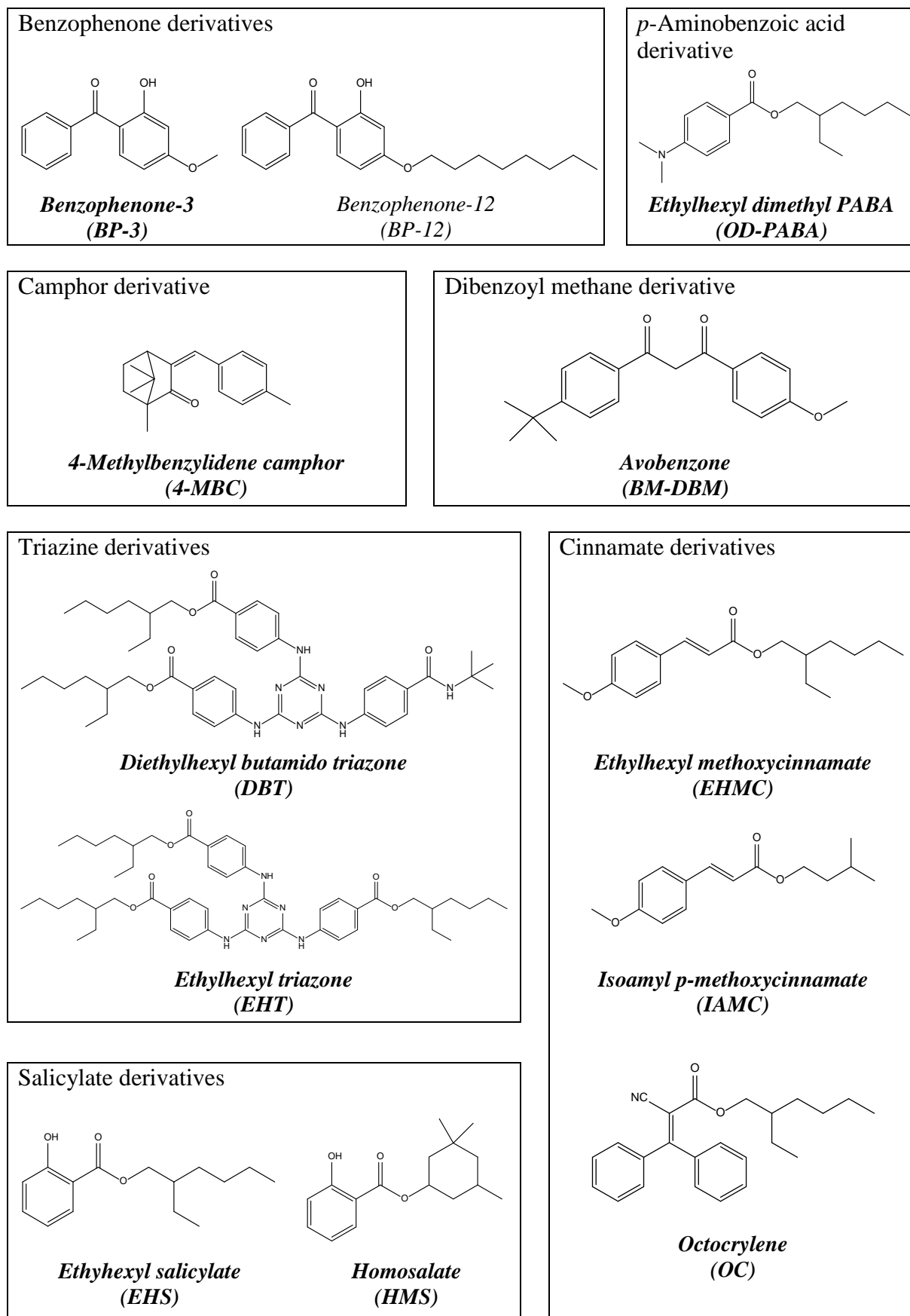


Figure 2: Structures of UV stabilizers analyzed in this thesis.

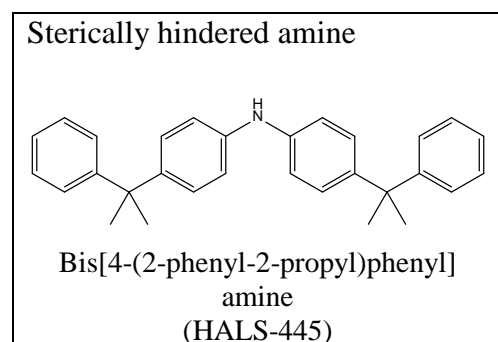
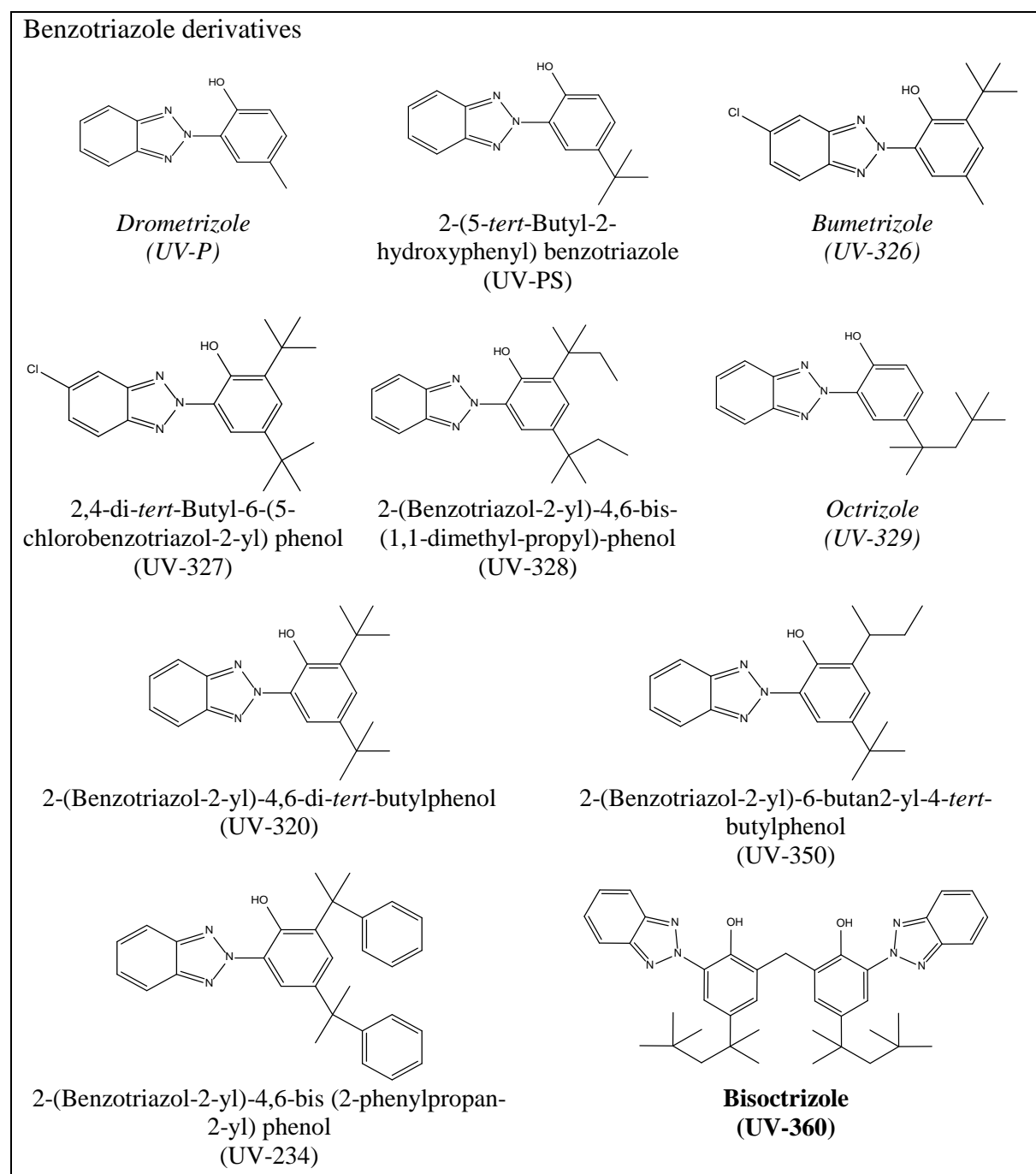


Figure 2 (continued)

Table 2: Overview of UV stabilizers analyzed in this thesis.

Abbr.	CAS	Chemical name/ Common name	INCI name (max. concentration in ready for use preparation)	$\log K_{ow}^2$
4-MBC	36861-47-9	3-(4-Methylbenzylidene)	4-Methylbenzylidene	5.9
	38102-62-4	camphor Enzacamene	camphor (4%)	5.5
BM-DBM	70356-09-1	1-(4- <i>tert</i> -Butylphenyl)-3-(4-methoxyphenyl) propane-1,3-dione Avobenzone	Butylmethoxy dibenzoylmethane (5%)	4.5
BP-3	131-57-7	2-Hydroxy-4-methoxybenzophenone Oxybenzone	Benzophenone-3 (10%/6% (since 2017))	3.5
BP-12	1843-05-6	2-Hydroxy-4- <i>n</i> -octyloxybenzophenone Octabenzone	Benzophenone-12	7.0
DBT	154702-15-5	4,4'-[[6-[[4-[[(1,1-dimethylethyl)amino]carbonyl]phenyl]amino]-1,3,5-triazine-2,4-diyl]diimino]bis-, bis(2-ethylhexyl) benzoate Iscotrizinol	Diethylhexyl butamido triazone (10%)	14
EHMC	5466-77-3	2-Ethylhexyl 4-methoxycinnamate Octinoxate	Ethylhexyl methoxycinnamate (10%)	5.8
EHS	118-60-5	2-Ethylhexyl salicylate Octisalate	Ethylhexyl salicylate (5%)	6.0
EHT	88122-99-0	2,4,6-Trianiino-(<i>p</i> -carbo-2'-ethylhexyl-1'-oxy)-1,3,5-triazine	Ethylhexyl triazone (5%)	17
HALS-445	10081-67-1	Bis[4-(2-phenyl-2-propyl)phenyl] amine	-	8.5
HMS	118-56-9	Benzoic acid, 2-hydroxy-, 3,3,5-trimethylcyclohexyl ester	Homosalate (10%)	6.2
IAMC	71617-10-2	Isopentyl-4-methoxycinnamate Amiloxate	Isopentyl <i>p</i> -methoxycinnamate (10%)	4.3
OC	6197-30-4	2-Cyano-3,3-diphenyl acrylic acid, 2-ethylhexyl ester	Octocrylene (10% (as acid))	6.9
OD-PABA	21245-02-3	2-Ethylhexyl 4-(dimethylamino) benzoate Padimate O	Ethylhexyl dimethyl PABA (8%)	5.8
UV-P	2440-22-4	2-(2H-Benzotriazol-2-yl)- <i>p</i> -cresol	Drometrizole	3.0
UV-PS	3147-76-0	2-(5- <i>tert</i> -Butyl-2-hydroxyphenyl) benzotriazole	-	4.4
UV-326	3896-11-5	2-(5-Chloro-2H-benzotriazol-2-yl)-6-(1,1-dimethylethyl)-4-methyl phenol	Bumetrizole	5.6

² calculated using the KOWWIN v1.68 estimation program from the EPI Suite™ tool (U.S. EPA)

2 General information

Abbr.	CAS	Chemical name/ Common name	INCI name (max. concentration in ready for use preparation)	log K_{ow} ²
UV-327	3864-99-1	2,4-ditert-Butyl-6-(5-chlorobenzotriazol-2-yl) phenol	-	6.9
UV-328	25973-55-1	2-(Benzotriazol-2-yl)-4,6-bis-(1,1-dimethyl-propyl)-phenol	-	7.3
UV-329	3147-75-9	2-(2H-Benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl) phenol	Octrizole	6.2
UV-320	3846-71-7	2-(2H-benzotriazol-2-yl)-4,6-ditert-butylphenol	-	6.3
UV-350	36437-37-3	2-(2H-Benzotriazol-2-yl)-4-(tert-butyl)-6-(sec-butyl) phenol	-	6.3
UV-234	70321-86-7	2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl) phenol	-	7.7
UV-360	103597-45-1	2,2'-Methylene bis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol) Bisoctrizole	Methylene bis-benzotriazolyl tetramethylbutylphenol (10%)	12

2.2.2 Production volumes

The UV stabilizers EHMC, BP-12, UV-P, UV-234, UV-329 and UV-328 are listed as High Production Volume Chemicals by the OECD (OECD, 2018). The annual production/import volumes provided by REACH registrations (ECHA, 2018d) are given in Table 3. The benzotriazole UV stabilizers UV-320, UV-350, and UV-327 are only pre-registered (ECHA, 2018e).

Table 3: Annual volumes of UV stabilizers registered under REACH (ECHA, 2018d).

Annual volumes registered under REACH [t/a]	UV Stabilizer
0 - 10	UV-PS
10 - 100	4-MBC, IAMC
100+	UV-360 ³
100 - 1,000	BP-3, DBT ³ , EHT ³ , HALS-445, OD-PABA, UV-328
1,000+	BP-12
1,000 - 10,000	BM-DBM, EHMC (trans-isomer), EHS, HMS, OC, UV-P, UV-234, UV-326, UV-329

³ multiple registrations with different tonnages; highest one was chosen

2.2.3 *UV stabilizers in the environment*

UV stabilizers enter the coastal environment mainly through direct inputs such as rinsing sunscreens from skin during recreational activities or indirect inputs such as discharge of WWTPs (Brausch and Rand, 2011; Poiger et al., 2004; Ramos et al., 2016). UV stabilizers find their way into wastewater during bathing or showering (both from leave-on cosmetic products such as sunscreens and make-up and from rinse-off products such as shampoos), or laundry activities (Avagyan et al., 2015; Wang et al., 2017). Most UV stabilizers are not completely removed in WWTPs (Ramos et al., 2016) and are discharged into the environment. UV stabilizers that might accumulate in the sewage sludge in WWTPs could be applied to agricultural fields, depending on country-specific regulations (Lai et al., 2014; Song et al., 2014; Zhang et al., 2011). Microplastics and plastic debris are also discussed as potential sources of plastic additives (Cole et al., 2011; Rani et al., 2015; Rani et al., 2017). The direct input from sunscreen products into coral reef areas (which are highly impacted by seaside tourism) is estimated to be up to 14,000 t/a (Downs et al., 2016), containing high percentages of UV stabilizers.

UV stabilizers are present in various environmental matrices worldwide, such as in estuarine and coastal waters of Australia (Allinson et al., 2018), China (Sun et al., 2016), the Canary Islands (Garcia-Guerra et al., 2016), Germany (Fisch et al., 2017), and the USA (Bratkovics et al., 2015); in surface water from Korean and Japanese rivers (Ekpeghere et al., 2016; Kameda et al., 2011); in sediment, SPM, and fish from German rivers (Wick et al., 2016a); in sediment, water, and fish in Indian rivers (Vimalkumar et al., 2018); and in mussels from the Portuguese coastline (Castro et al., 2018). They have also been detected in Arctic and Antarctic surface waters (Emnet et al., 2015; Tsui et al., 2014) and in Antarctic sea ice (Emnet et al., 2015).

An overview of UV stabilizers in sediments is given in Tables 4 and 5. It has to be noted that several studies were not published at the beginning of this work in April 2015.

2 General information

Table 4: Overview of selected studies reporting UV stabilizer concentrations in estuarine, riverine, and lake sediments. All data are in ng/g dw.

UV stabilizer	Peng et al. (2017b) , SI	Pintado-Herrera et al. (2017b)	Huang et al. (2016)	Allinson et al. (2018)	Nakata et al. (2009)		Gago-Ferrero et al. (2011)
	Pearl River Estuary, China	Pearl River Estuary, China	Pearl River Estuary, China	Victorian estuaries	Ariake Sea, Japan (estuarine sediments)	Omuta River, Japan	Ebro River Basin, Spain
4-MBC	<MDL	<MDL – 25.4	0.36 – 3.68	<MDL – 1.2	<MDL	<MDL	<MDL
BM-DBM	Severe matrix interferences	-	-	-	-	-	-
BP-3	0.16 – 1.02	<MDL – 4.0	-	<MDL	-	-	<MDL – 27
BP-12	<MDL – 2.67	-	-	-	-	-	-
EHMC	<0.5 – 1.4	<MDL – 30.1	14.4 – 81.6	<MDL – 17.6	-	-	<MDL – 42
EHS	-	<MDL – 13.7	-	<MDL	-	-	-
HMS	-	<MDL – 10.7	-	<MDL	-	-	-
IAMC	-	-	-	-	-	-	-
OC	0.05 – 2.22	<MDL – 105.2	6.26 – 27.8	<MDL	-	-	<MDL – 2400
OD-PABA	<MDL – 0.04	-	-	<MDL	-	-	<MDL – 5.2
UV-P	0.61 – 1.83	-	-	<MDL	-	-	-
UV-PS	-	-	-	-	-	-	-
UV-234	0.12 – 5.19	-	-	<MDL – 21.5	-	-	-
UV-320	-	-	-	-	0.3 – 2.3	2.6 – 14	-
UV-326	0.32 – 9.00	-	-	<MDL	1.5 – 12	23 – 200	-
UV-327	<MDL – 9.3	-	-	0.2 - 1.2	1.6 – 9.9	16 – 190	-
UV-328	<0.5 – 3.2	-	-	<MDL – 18.1	2.6 – 16	18 – 320	-
UV-329	<MDL – 1.02	-	-	<MDL	-	-	-
UV-350	-	-	-	-	-	-	-
UV-360	-	-	-	-	-	-	-

Table 4 (continued)

UV stabilizer	Kaiser et al. (2012b)		Mizukawa et al. (2017)	Wick et al. (2016a)	Zhang et al. (2011)	
	Rhine Main area near Frankfurt am Main, Germany (bathing) Lakes (max. conc.)	Rhine Main area near Frankfurt am Main, Germany Rivers (max. conc.)	Upper Iguaçú Watershed, Brazil (4 rivers)	German Rivers (max. conc.)	Songhua River, China	Saginaw and Detroit Rivers, U. S.
4-MBC	2.0	1.6	<MDL – 49.3	-	-	-
BM-DBM	62.2	22.2	-	-	-	-
BP-3	3.6	<MDL	<MQL – 67.2	-	0.27 – 0.55	0.73 – 4.66
BP-12	-	-	-	-	-	-
EHMC	6.8	3.4	<MDL – 166.8	-	-	-
EHS	-	-	-	-	-	-
HMS	-	-	-	-	-	-
IAMC	-	-	-	-	-	-
OC	642	25.5	<MQL – 322.2	-	-	-
OD-PABA	<MDL	<MDL	<MQL	-	-	-
UV-P	-	-	-	-	-	-
UV-PS	-	-	-	-	<MDL	<MDL
UV-234	-	-	-	10	-	-
UV-320	-	-	-	12	-	-
UV-326	-	-	-	44	1.71 – 2.01	<MDL – 5.88
UV-327	-	-	-	21	<MDL – 0.31	0.22 – 1.90
UV-328	-	-	-	11	2.06 – 7.12	0.72 – 224
UV-329	-	-	-	8	-	-
UV-350	-	-	-	7	-	-
UV-360	-	-	-	62	-	-

Table 5: Overview of selected studies reporting UV stabilizer concentrations in coastal and marine sediments. All data are in ng/g dw.

UV stabilizer	Tsui et al. (2015)		Langford et al. (2015)	Barón et al. (2013)		Pintado-Herrera et al. (2017a)		Combi et al. (2016)	Sanchez-Brunete et al. (2011)
	Hong Kong, China	Tokyo Bay, Japan		Oslofjord, Norway	West Coastal Line, Colombia	Bays in Chile	Cadiz Bay, Atlantic coast of Andalusia (mean conc.)		
4-MBC	<MDL	<MDL	-	<MDL - 7.90	<MDL	1.7	<MDL	-	-
BM-DBM	4.3 - 42.9	2.5 - 64.5	-	-	-	-	-	-	-
BP-3	0.05 - 39.8	<MDL	<MDL	<MDL - 2.52	<MDL - 1.42	0.7	0.9	<MDL - 0.23	<MDL
BP-12	-	-	-	-	-	-	-	-	-
EHMC	0.6 - 447	0.3 - 54.5	8.5 - 16.4	<MDL - 17.8	<MDL	7.3	8.0	0.9 - 10.4	-
EHS	<MDL	<MDL	-	-	-	3.3	5.2	-	13.3
HMS	<MDL	<MDL	-	-	-	4	1.2	-	<MDL
IAMC	<MDL	<MDL	-	-	-	-	-	-	-
OC	0.04 - 15.6	<MDL	<MDL - 82.1	-	-	20.8	15.1	0.8 - 40.7	-
OD-PABA	1.5 - 150	0.8 - 13.9	<MDL	-	-	-	-	-	-
UV-P	-	-	-	-	-	-	-	-	-
UV-PS	-	-	-	-	-	-	-	-	-
UV-234	-	-	<MDL	-	-	-	-	-	-
UV-320	-	-	-	-	-	-	-	-	-
UV-326	-	-	-	-	-	-	-	-	-
UV-327	-	-	<MDL - 8.1	-	-	-	-	-	-
UV-328	-	-	3.2 - 25.1	-	-	-	-	-	-
UV-329	-	-	<MDL	-	-	-	-	-	-
UV-350	-	-	-	-	-	-	-	-	-
UV-360	-	-	-	-	-	-	-	-	-

2.2.4 Sediment

Marine sediments are referred to as the “memory of the ocean”, as they do not react as quickly to pollution changes as other compartments (e.g., air and water). Sediments can act as both a sink for and a source of numerous UV stabilizers in the environment. Due to their chemical properties ($\log K_{ow} > 3$; chapter 2.2.1), the selected UV stabilizers tend to sorb to SPM and sediment. Information on the half-life times of these compounds in the environment is sparse. The estimated half-life of benzotriazole UV stabilizers in sediments is 542 days (Lu et al., 2016), indicating the persistence of these compounds in this environmental compartment. Accumulation in the sediment and a possible remobilization may pose risks to benthic and sediment-dwelling organisms and, because of biomagnification, to the entire marine food web (Peng et al., 2017a).

The probability of organic contaminants to adsorb to SPM and sediment is dependent on diverse properties of the organic compound (e.g., $\log K_{ow}$, $\log K_{oc}$) and the sediment (e.g., total organic carbon (TOC), particle size) (Huang et al., 2016; Tsui et al., 2015). For UV stabilizers, several studies reported a lack of correlation between environmental concentrations and TOC contents (Gago-Ferrero et al., 2011; Huang et al., 2016; Tsui et al., 2015). Only for benzotriazole UV stabilizers was a significant correlation with TOC shown in the Ariake Sea, Japan (Nakata et al., 2009).

3 Research objectives

The objective of this thesis was to investigate the occurrence of organic UV stabilizers in coastal and marine environments of Europe and China and thereby to identify distribution patterns and potential sources. When starting this thesis, few studies had reported data on the occurrence of UV stabilizers in coastal areas and most of these studies focused on water. Only a few studies analyzed the occurrence of UV stabilizers in sediments (see Table 5) and the analytical scope was often limited to a small number of substances.

Coastal and marine environments are characterized by various entry sources such as river discharges, atmospheric deposition, offshore construction and activities (e.g., commercial fisheries) as well as recreational activities (e.g., swimming). The environmental status is subject to short-term and long-term changes due to changing industrial production pathways, environmental awareness and legislation, consumer demands and the development of new chemicals. To assess the relevance of UV stabilizers as micro pollutants, more data about their environmental occurrence and distribution are needed for these ecosystems.

As study areas, the European North and Baltic Seas and the Chinese Bohai and Yellow Seas were chosen. Europe has a long industrial history, which is now highly regulated, while the industry in China is growing extremely rapidly, amplified by industry outsourced from Europe due to regulation changes, such as textile manufacturing (Heydebreck et al., 2015). At the start of this thesis, no environmental data on the occurrence of UV stabilizers in either region were available. Due to the properties of the selected UV stabilizers, sediment was chosen as the environmental compartment of this investigation (see chapters 2.2.1 and 2.2.4).

For these reasons, the specific aims of this thesis were:

- (A) to develop an analytical method for the trace analysis of UV stabilizers in sediments. The method needed to be sensitive enough for coastal regions and should include a large number of compounds, which helps to identify potential sources and to characterize regions.
- (B) to investigate the occurrence, distribution, and input pathways of UV stabilizers in coastal and marine environments of Europe and China. Environmental concentrations in sediments from these areas were revealed for the first time, correlations between single compounds as well as TOC were analyzed, and a preliminary hazard evaluation for sediment-associated organisms was performed.

The results of the method development (A) are presented and discussed in chapter 4. Chapter 4.1 focuses on the instrumental method, chapter 4.2 focuses on the sample preparation method, and chapter 4.3 describes the final method that was used for the investigation of UV stabilizers in environmental sediments.

Chapter 5 presents and discusses the results obtained in (B) and is divided into four parts. The results from the Chinese Bohai and Yellow Seas and from the European North and Baltic Seas are presented in chapter 5.1 and chapter 5.2, respectively. Chapter 5.3 draws a comparison of UV stabilizer contamination between both regions and chapter 5.4 assesses the potential hazard to benthic organisms. Supplementary material for chapter 5 is provided in Appendix A. Portions of chapter 5 have already been published in two peer-reviewed journals (see “List of Publications”). Conclusive remarks and an outlook are provided in chapter 6. Details on used materials and applied methods are provided in chapter 7.

4 Method development

UV stabilizers are present in a variety of laboratory equipment such as gloves, pipetting aids, and seals made of plastic or rubber. To minimize contamination during the collection, storage, and treatment of the samples, the use of rubber and plastic materials, as well as PCPs, was avoided wherever possible. Prior to use, all glassware was cleaned by a laboratory dishwasher, dried at 250 °C, and rinsed with methanol. To minimize background blanks during measurements, plastic parts of the LC-MS/MS system (e.g., the housing of the solvent frits) were replaced by stainless steel or glass parts wherever possible.

4.1 Instrumental analysis

4.1.1 General information

Instrumental analysis was performed on a UHPLC-MS/MS system (1290 Infinity coupled to 6490 triple quadrupole LC/MS; both from Agilent, Germany). For chromatographic separation, a C18 column (Eclipse Plus RRHD 1.8 μm , 2.1 x 150 mm, Agilent, Germany) and a C8 column (Eclipse Plus RRHD 1.8 μm , 2.1 x 150 mm, Agilent, Germany) were used. The separation was achieved by running the solvent gradient described in Table 6. The solvent gradient was adopted from an existing method in the department (Heydebreck, 2013) and was only slightly modified. The solvent flow was 0.2 mL/min for all analyses. For the ionization, three sources were available that are listed in the following.

- (a) **E**lectrospray **I**onization (**ESI**) Jet Stream source
- (b) **A**tmospheric **P**ressure **C**hemical **I**onization (**APCI**) source
- (c) **A**tmospheric **P**ressure **P**hoto**I**onization (**APPI**) source

The ESI source is most commonly used in high sensitivity analysis of organic substances and covers around 80% (Fischer and Perkins, 2005) of all analytes. Substances, which ionize poorly by ESI, can be analyzed by APCI or APPI. These two ionization techniques are especially needed for non-polar compounds (Agilent Technologies, 2012). Recent publications showed that ESI is not the most suited technique for the sensitive analysis of UV stabilizers (Himmelsbach et al., 2009; Rodil et al., 2009b; Wick et al., 2016b). Working with environmental samples, both APCI and APPI sources were less susceptible to ion suppression compared to ESI (Rodil et al., 2009b; Wick et al., 2016b).

The focus of the method development in this thesis was on the APPI source. As the structures of the selected target UV stabilizers differ widely (Figure 2) and only two mass-labeled internal standards (BP-3- $^{13}\text{C}_6$ and 4-MBC-d₄) and one unlabeled internal standard (Allyl-bzt) were available at the beginning of this thesis, minimal matrix effects were essential for a reliable analytical analysis of UV stabilizers. Due to relatively low sensitivities obtained with the APCI source in the negative mode during first optimization steps, the APCI source was not further optimized or used. As more mass-labeled internal standards became available during method

development, the ESI source was optimized additionally to the APPI source to compare the performance of both sources on environmental samples (chapter 4.2.4).

A list of all used solvents, laboratory chemicals, and analytical standards is presented in Tables 29 and 30 of chapter 7.1. For each native and mass-labeled standard, a stock solution of 1 mg/mL was prepared in methanol. From the stock solutions, two dilution levels (10 ng/ μ L and 1 ng/ μ L) were prepared for each standard. In addition, a 0.2 ng/ μ L mixture of all native standards and a mixture of all internal standards (IS; 0.2 to 2 ng/ μ L depending on the substance response) were prepared. All solutions were stored in amber glass vials at $-20\text{ }^{\circ}\text{C}$.

Data acquisition was achieved using the Software MassHunter Data Acquisition LC-MS/MS B.04 (Agilent, Germany). Evaluation of measurements was done either in MassHunter Qualitative Analysis B.06 (Agilent, Germany) or MassHunter Quantitative Analysis B.06 (Agilent, Germany).

Table 6: Solvent gradient modified after Heydebreck (2013).

Time [min]	Water [%]	Methanol [%]
0	30	70
4	30	70
7	10	90
12	10	90
13	0	100
29	0	100
30.5	30	70
32	30	70

4.1.2 Optimization of APPI

The retention times and mass transitions for the APPI acquisition are listed in Table 7. The product ions and the collision energies (CE) were determined using the Agilent Optimizer Software. The respective cell accelerator voltage (CAV) was optimized manually. The benzotriazole derivatives UV-PS and UV-360 were not part of the first optimization but were included in the optimized method later on. For the first optimization only the C18 column was used, on which UV-360 eluted in a very broad peak (retention time ≈ 40 min). For this reason, a C8 column was used in addition to the C18 column later on.

Table 7: Retention times and mass transitions of target and mass-labeled compounds in APPI.

Mode	Substance	Retention time (C18 column) [min]	Precursor ion [m/z]	Product ions (Quantifier Qualifier) [m/z]	CE [V]	CAV [V]
APPI +	4-MBC	10.8	255.2	105.1	32	1
				43.0	48	1
	BM-DBM	13.6	311.2	161.0	28	1
				135.1	20	1
	BP-3	8.2	229.1	151.0	16	2
				76.9	44	2
	BP-12	16.0	327.2	137.0	32	1
				215.0	16	1
	DBT	18.7	766.5	654.3	48	3
				468.1	60	3
	EHMC	(13.2)/13.8	291.2	179.1	4	2
				161.0	12	2
	EHT	17.7 (C8 column)	823.5	711.2	52	2
				308.0/599.1	56	2
	HALS-445	15.8	406.3	196.1	40	1
				91.0	52	1
	IAMC ⁴	10.3	249.2	161.0	12	1
				178.9	4	1
	OC	12.1	362.2	249.9	4	2
				231.8	20	2
OD-PABA	13.2	278.2	151.0	32	1	
			166.1	20	1	
UV-P	10.7	226.1	76.9	48	3	
			107.1	16	3	
UV-PS	13.7	268.2	212.1	20	1	
			57.0	24	1	
UV-234	18.1	448.2	370.2	20	1	
			91.1	64	1	
UV-320	18.1	324.2	268.1	24	1	
			57.1	36	1	
UV-326	18.3	316.1	259.9	16	2	
			57.1	28	2	
UV-327	19.7	328.2	302.1	20	1	
			57.1	32	1	
UV-328	19.4	352.2	282.1	24	1	
			43.1	40	1	
UV-329	16.6	324.2	57.0	32	2	
			65.0	80	2	
UV-350	17.7	324.2	268.1	20	1	
			57.1	32	1	
4-MBC-d ₄	10.7	259.2	216.0	20	2	
			43.1	56	2	

⁴ only one isomer detected

4 Method development

Mode	Substance	Retention time (C18 column) [min]	Precursor ion [m/z]	Product ions (Quantifier Qualifier) [m/z]	CE [V]	CAV [V]
	Allyl-bzt	15.3	266.1	119.1 91.0	16 40	1 1
	BP-d₁₀	4.9 (C8 column) 5.8 (C18 column)	193.2	110.1 81.9	12 36	5 5
	BP-3-¹³C₆	8.2	235.1	150.9 55.0	20 80	1 1
	DBT-d₄	18.7	770.3	658.2 472.2	48 60	2 2
	EHMC-d₁₅	13.5 ⁴	306.3	180.1 161.0	4 12	1 1
	EHT-d₄	17.7 (C8 column)	827.4	715.3 491.1	52 64	2 2
	OC-d₁₅	12.0	377.3	251.0 233.0	4 24	5 2
	UV-P-d₄	10.6	230.1	76.9 107.0	20 52	3 3
	UV-328-d₄	19.4	356.2	286.0 43.1	24 40	1 1
APPI -	EHS	15.2 (C18 column) 11.9 (C8 column)	249.2	137.1 93.0	12 28	3 3
	HMS	14.9/15.4 (C18 column) 11.8/12.1 (C8 column)	261.1	92.9 136.9	28 12	2 2
	UV-360	20.2 (C8 column)	657.4	322.0 249.9	48 80	4 2
	FOSA-¹³C₈	9.2 (C8 column)	506.1	77.9	0	2
	HMS-d₄	14.8/15.3 (C18 column) 11.7/12.1 (C8 column)	265.2	140.9 97.0	20 28	3 3
	UV-360-d₈	20.1 (C8 column)	665.3	326.0 254.1	48 80	2 2

Starting the APPI optimization, the default values for all source parameters were used. Successively, all method parameters were optimized. The results are shown as normalized responses in Figures 3 and 4. The parameter values chosen for the final APPI acquisition method are marked with a box. The results show the enhancement or suppression of the peak area of each UV stabilizer during the variation of each method parameter. The normalization of the peak areas to one value (e.g., “no dopant” in (A) and “150/60” in (B) of Figure 3) was done for an easier comparison between the single UV stabilizers (as some compounds resulted in peak areas with high intensities and some with low intensities) and for a simple graphical presentation. The final optimized APPI acquisition method parameters are listed in Table 8.

In APPI, the sensitivity is enhanced by adding so-called dopants (Raffaelli and Saba, 2003), which are mostly organic solvents that are added in relatively large amounts to the mobile phase. They are ionized in the APPI source and transfer this charge to the target compounds, thus enhancing the number of ionized target molecules. Frequently used dopants are toluene or acetone (Himmelsbach et al., 2009). In Figure 3 (A), both organic solvents were tested and the post-column addition of 5% toluene resulted in the best overall performance. In the negative mode (Figure 4 B) the results for both solvents and both tested concentrations were similar and therefore 5% toluene was chosen as well for a simple handling.

The addition of 0.1% formic acid to the mobile phase (Figure 3 F) resulted in slightly lower intensities (15% in average) of the benzotriazole derivatives and a drastic intensity decrease (> 90%) of DBT. Because of these lower intensities, formic acid was not added to the mobile phase in the beginning of sample analyses. At the same time, the peak widths of the benzophenone derivatives BP-3 and BP-12 got reduced (and as a consequence also the instrumental limits of detection (iLODs) and instrumental limits of quantification (iLOQs)). Figure 5 shows the peak shapes of BP-3 without and with the addition of formic acid. Because of this enhanced peak shape, formic acid was added for the analysis of the North and Baltic Sea samples.

The chosen gas flow and nebulizer pressure for the negative mode are not the best suited for the UV stabilizers EHS and HMS (Figure 4 C and E). The optimization steps of the negative mode also included six phenolic antioxidants (not shown) that are widely used as plastic additives. These chosen gas flow and nebulizer values showed the best overall performance. The phenolic antioxidants gave several problems during the development of the extraction method (high blank values or very low recoveries) and were not analyzed or not found in real environmental samples. Therefore, they are not further mentioned in this thesis. Regarding only the UV stabilizers EHS and HMS, a gas flow of 12 mL/min (instead of 11 mL/min) and a nebulizer pressure of 30 psi (instead of 50 psi) would have been chosen.

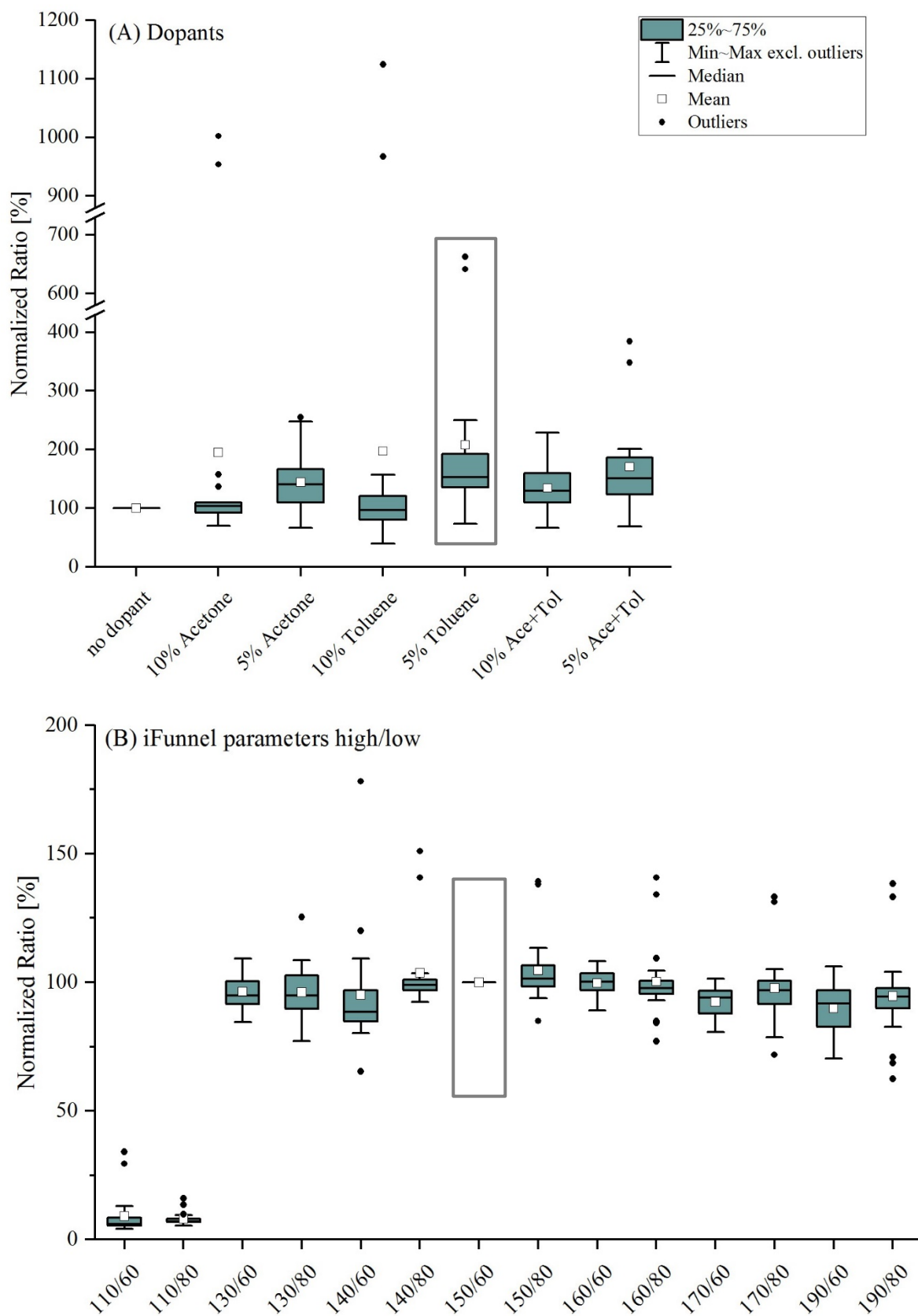


Figure 3: APPI optimization in positive mode. Box diagrams were created in Origin 2018b (OriginLab Corporation, USA).

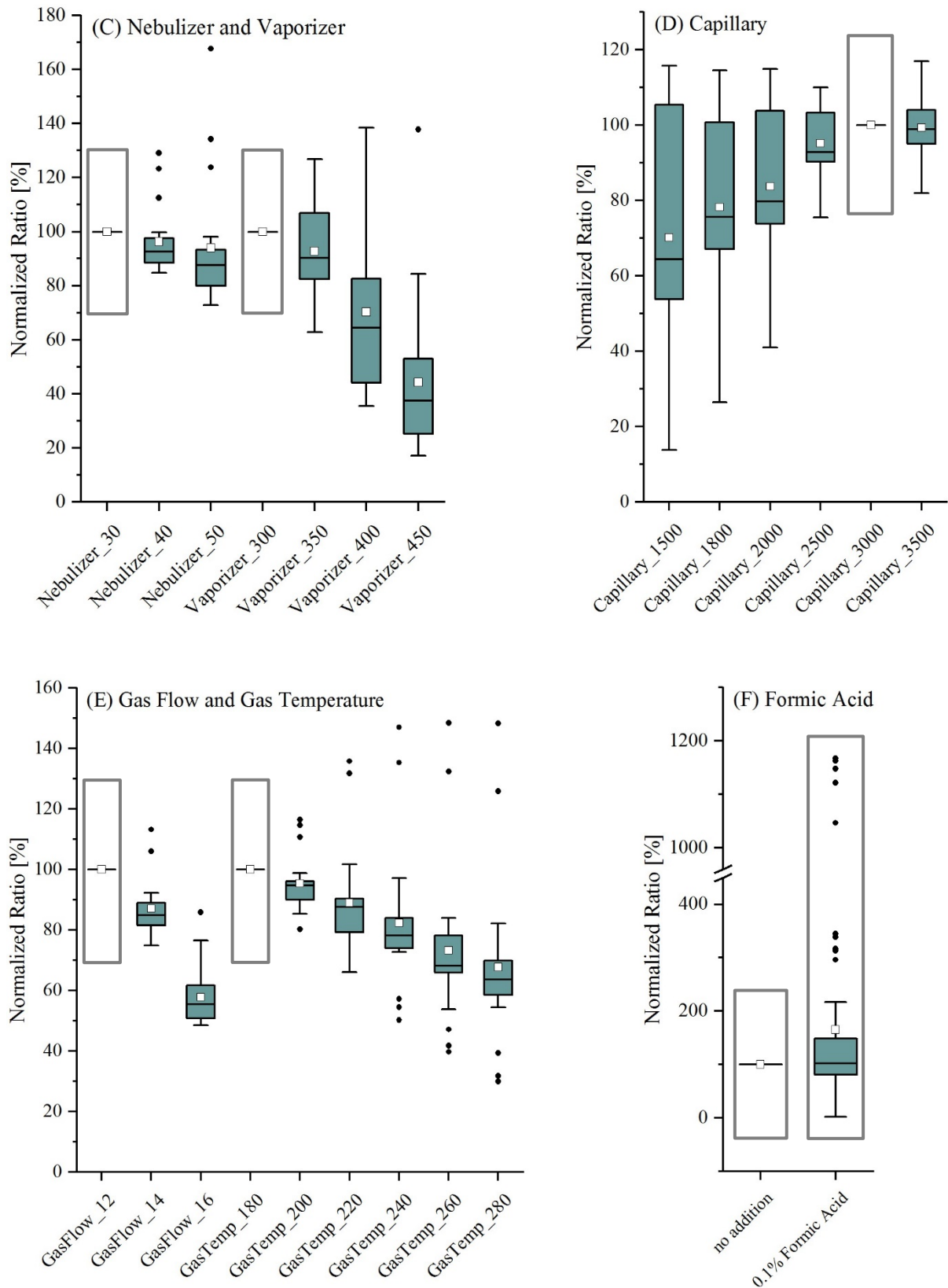


Figure 3 (continued)

4 Method development

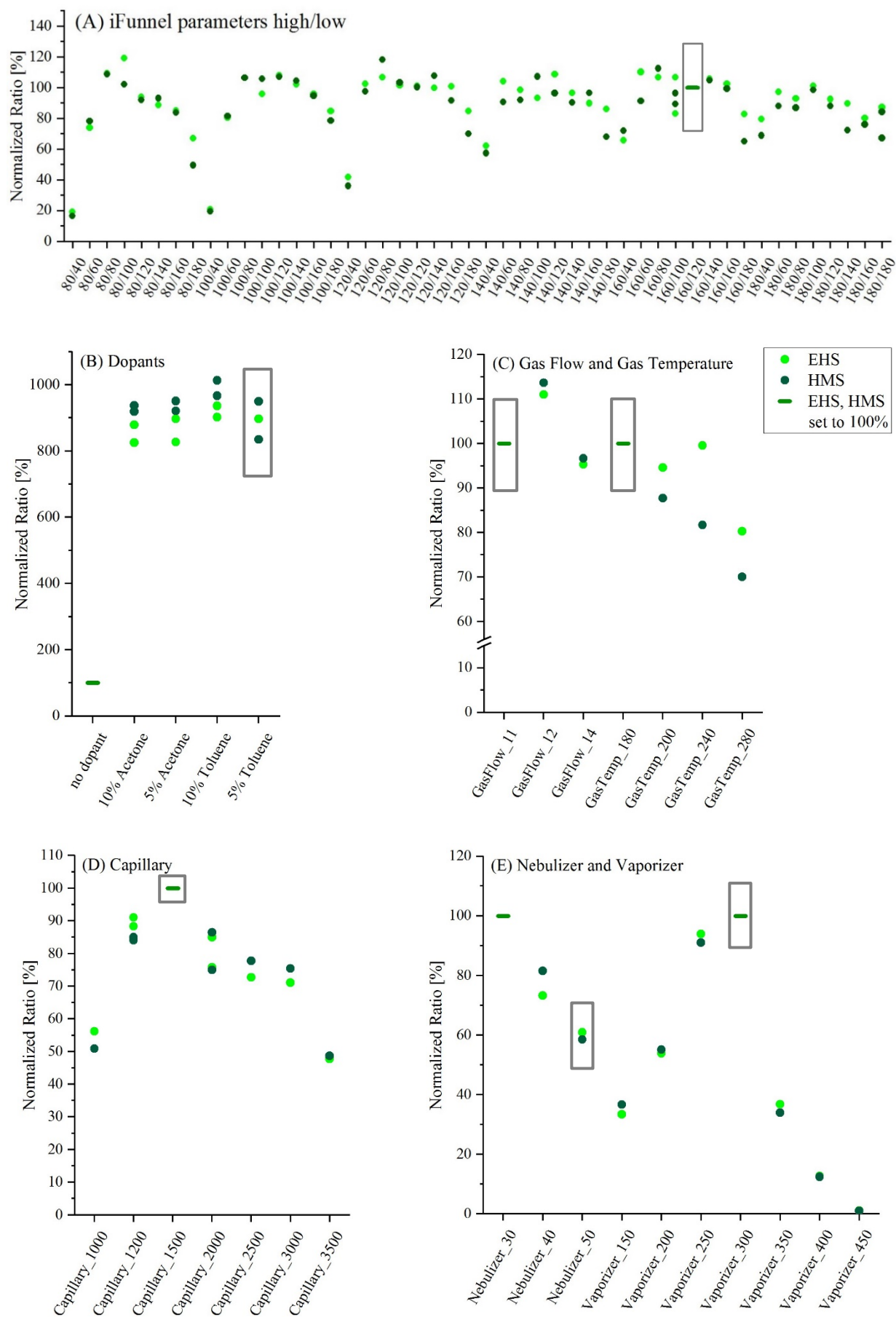


Figure 4: APPI optimization in negative mode.

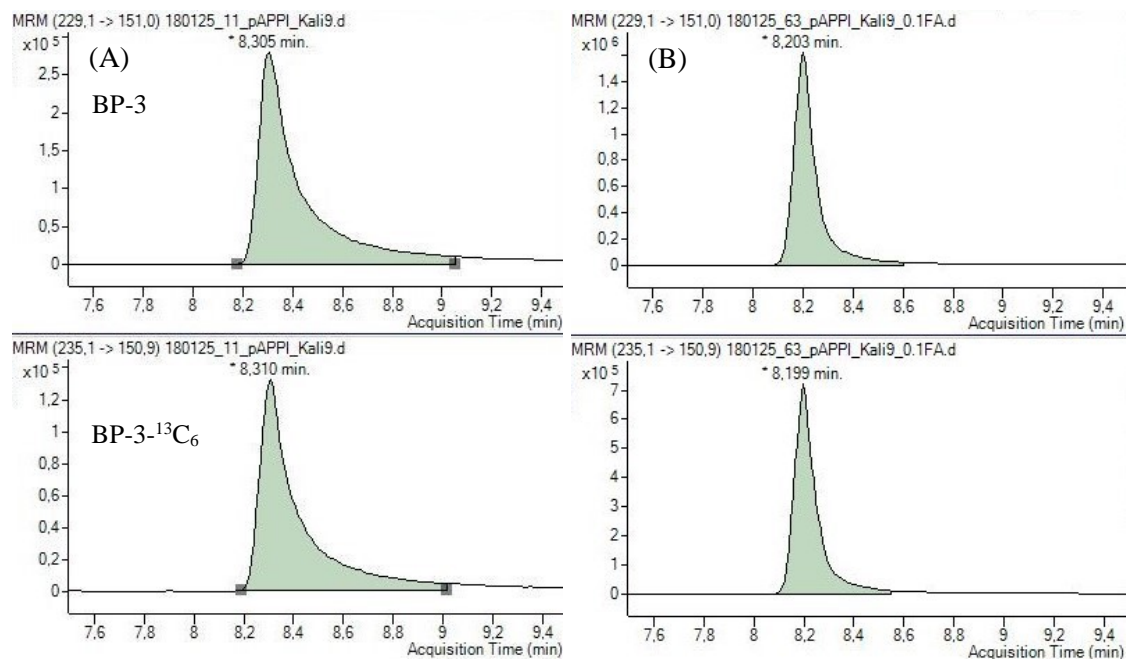


Figure 5: Peak shape of BP-3 and BP-3- $^{13}\text{C}_6$ without (A) and with (B) the addition of 0.1% formic acid.

Table 8: Final APPI parameters.

Parameter	Value for APPI +	Value for APPI -
Gas Temperature	180 °C	180 °C
Gas Flow	12 L/min	11 L/min
Nebulizer	30 psi	50 psi
Vaporizer	300 °C	300 °C
Capillary	3000 V	1500 V
Ion Funnel Parameters		
High Pressure RF	150 V	160 V
Low Pressure RF	60 V	120 V
Mobile Phases	Water (added with 0.1% formic acid for the North and Baltic Sea samples) Methanol (added with 0.1% formic acid for the North and Baltic Sea samples)	Water Methanol
Dopant	5% toluene (added post-column)	5% toluene (added post-column)

4.1.3 Optimization of ESI

The retention times and mass transitions for the ESI acquisition are listed in Table 9. The product ions and the CE values were determined using the Agilent Optimizer Software. The respective CAV value was optimized manually. The native compound UV-PS was not part of the first optimization but was later included in the optimized method. UV-360 was not included as it produces a very broad peak with the C18 column (see chapter 4.1.2) and the C8 column was only used with the APPI source.

Some compounds (most benzotriazole UV stabilizers, both benzophenone UV stabilizers, and OC) could be analyzed in both the positive and negative ESI mode. As comparison measurements showed a higher sensitivity (higher peak intensities and lower iLODs despite a higher noise level in the baseline) in the positive mode, these substances were only measured in the positive mode. The salicylate derivatives EHS and HMS only gave peaks with very low intensities in both the positive and negative ESI mode, even though they were sensitively measurable in the negative ionization mode in the literature (Tsui et al., 2014). Therefore, they were not included in the ESI method. Interestingly, Rodil et al. (2009b) described the same sensitivity problem of EHS and HMS with the ESI source using an API 2000 system.

Table 9: Retention times and mass transitions of target and mass-labeled compounds in ESI.

Mode	Substance	Retention time (C18 column) [min]	Precursor ion [m/z]	Product ions (Quantifier Qualifier) [m/z]	CE [V]	CAV [V]
ESI +	4-MBC	10.7	255.2	105.1	28	1
				43.0	48	1
	BM-DBM	13.6	311.2	160.8	20	4
				134.9	16	4
	BP-3	8.2	229.1	150.9	16	5
				76.8	36	5
	BP-12	16.0	327.2	136.8	28	1
				215.1	16	2
	DBT	18.7	766.5	654.3	48	4
				468.2	60	4
EHMC	(13.2)/13.7	291.2	179.0	4	1	
			161.0	12	5	
EHT	28.4	823.5	711.4	52	4	
			308.1	80	4	
HALS-445	15.8	406.3	195.9	48	3	
			90.9	64	2	
IAMC ⁵	10.3	249.2	161.0	12	4	
			43.0	36	4	
OC	12.0	362.2	249.8	4	5	
			231.9	20	5	

⁵ only one isomer detected

Mode	Substance	Retention time (C18 column) [min]	Precursor ion [m/z]	Product ions (Quantifier Qualifier) [m/z]	CE [V]	CAV [V]
	OD-PABA	13.2	278.2	151.0	32	2
				166.0	20	2
	UV-P	10.7	226.1	119.9	16	1
				76.9	48	3
	UV-PS	13.7	268.2	211.9	16	4
				56.9	28	4
	UV-234	18.0	448.2	370.2	20	2
				90.9	68	2
	UV-320	18.0	324.2	268.1	20	1
				56.9	28	1
	UV-326	18.2	316.1	259.8	20	1
				56.8	28	2
	UV-327	19.7	358.2	57.1	36	1
				301.9	20	1
	UV-328	19.4	352.2	282.0	24	1
				43.0	44	1
	UV-329	16.6	324.2	56.9	28	1
				211.9	24	2
	UV-350	17.7	324.2	268.1	20	1
				56.9	28	1
4-MBC-d₄	10.7	259.2	43.1	40	5	
			41.0	56	5	
Allyl-bzt	15.3	266.2	119.1	24	5	
			90.9	40	5	
BP-d₁₀	5.7	193.2	109.9	16	5	
			81.9	36	5	
BP-3-¹³C₆	8.2	235.1	150.8	16	5	
			111.1	20	5	
DBT-d₄	18.7	770.3	658.2	48	4	
			472.1	60	4	
EHMC-d₁₅	(13.0)/13.5	306.3	180.0	4	4	
			161.0	20	4	
EHT-d₄	28.4	827.4	715.4	48	4	
			491.0	64	4	
OC-d₁₅	11.9	377.2	251.0	10	4	
			233.0	10	4	
UV-P-d₄	10.6	230.1	124.0	16	4	
			77.0	48	4	
UV-328-d₄	19.3	356.4	43.1	40	4	
			286.0	20	4	

4 Method development

The ESI source parameters and the additives of the mobile phases were adopted from an existing method in the department (Heydebreck, 2013) that also included several UV stabilizers. After including all further target substances, the adopted values were tested against the default values and adjusted wherever needed. The final parameters are listed in Table 10.

Table 10: Final ESI parameters.

Parameter	Value for ESI +
Gas Temperature	200 °C
Gas Flow	14 L/min
Nebulizer	30 psi
Sheath Gas Heater	395 °C
Sheath Gas Flow	11 L/min
Capillary	3000 V
Nozzle Voltage	1000 V
Ion Funnel Parameters	
High Pressure RF	150 V
Low Pressure RF	60 V
Mobile Phases	Water added with 0.1% formic acid Methanol added with 0.1% formic acid

4.1.4 Instrumental performances

Parameters showing the performance of both optimized acquisition methods are listed in Tables 11 and 12. The linear range was tested from 0.1 to 50 pg/ μ L for ESI and 0.1 to 90 pg/ μ L for APPI. The iLODs were derived from either the mean blank values plus three times the standard deviation or the signal-to-noise ratio of three ($S/N = 3$), whichever approach yielded the highest value. Accordingly, the iLOQs were derived from either the mean blank values plus ten times the standard deviation or the signal-to-noise ratio of ten ($S/N = 10$). All values shown in this chapter were calculated from the peak areas without any correction.

Table 11: Linear range and precision (coefficient of variation) of target UV stabilizers (C18 column).

Analyte	ESI				APPI			
	Linear range [pg/ul]	R ²	Precision (coef. of variation) [%]	Precision (coef. of variation) [%]	Linear range [pg/ul]	R ²	Precision (coef. of variation) [%]	Precision (coef. of variation) [%]
			Intra-day	Inter-day			Intra-day	Inter-day
4-MBC	0.1 - 35	0.997	11	n.a.	0.4 - 90	0.998	8	9
BM-DBM	0.1 - 35	0.996	11	n.a.	0.4 - 70 (quadratic)	0.994	8	19
BP-3	0.1 - 35	0.996	12	n.a.	0.8 - 90	0.992	3	9
BP-12	0.1 - 35	0.996	9	n.a.	0.4 - 90	0.990	3	14
DBT	0.1 - 50	0.998	13	n.a.	2 - 90 (quadratic)	0.993	27 ⁶	32 ⁶
EHMC	0.1 - 35	0.993	12	n.a.	0.4 - 90	0.999	9	14
EHS	-				0.4 - 90	0.998	5	27
EHT	1 - 50	0.995	10	n.a.	2 - 90	0.997	11	57 ⁶
HALS-445	0.1 - 50	0.998	3	n.a.	0.1 - 90	0.997	6	12
HMS	-				0.4 - 90	0.998	6	27
IAMC	0.1 - 35	0.996	12	n.a.	0.4 - 90	0.997	9	16
OC	0.1 - 35	0.997	9	n.a.	0.4 - 90	0.996	6	14
OD-PABA	0.1 - 50	0.998	2	n.a.	0.1 - 90	0.999	7	9
UV-P	0.1 - 50	0.998	5	n.a.	0.4 - 90	0.994	9	11
UV-PS	n.a.				0.4 - 90	0.998	6	13
UV-234	0.1 - 50	0.995	12	n.a.	0.1 - 90	0.997	4	16
UV-326	0.1 - 50	0.997	8	n.a.	0.4 - 90	0.998	10	16
UV-327	0.1 - 50	0.997	8	n.a.	0.1 - 90	0.998	10	14
UV-328	0.1 - 50	0.995	9	n.a.	0.1 - 90	0.999	9	13
UV-329	0.1 - 35	0.996	7	n.a.	0.4 - 90	0.997	5	15
UV-320	0.1 - 20	0.992	9	n.a.	0.1 - 90	0.995	8	16
UV-350	0.1 - 50	0.995	9	n.a.	0.1 - 90	0.998	8	17
UV-360	n.a.				2 - 90	0.996	16	60 ⁶

⁶ without mass-labeled standards to correct for this variation, only qualitative analyses are possible

4 Method development

Table 12: Instrumental limits of detection (iLOD) and quantification (iLOQ) in pg absolute on column.

Analyte	iLOD [pg]			iLOQ [pg]		
	ESI +	APPI +	APPI -	ESI +	APPI +	APPI -
4-MBC	1	3	-	4	10	-
BM-DBM	4	4	-	14	14	-
BP-3	1	4	-	4	14	-
BP-12	1	1	-	4	04	-
DBT	4	20	-	14	70	-
EHMC	0.2	1	-	0.7	4	-
EHS	-	-	4	-	-	14
EHT	8	20	-	27	70	-
HALS-445	0.1	0.4	-	0.4	2	-
HMS	-	-	4	-	-	14
IAMC	1	1	-	4	4	-
OC	4	1	-	14	4	-
OD-PABA	0.1	0.4	-	0.4	1	-
UV-P	0.1	1	-	0.4	4	-
UV-PS	1	1	-	4	4	-
UV-234	1	0.4	-	0.4	1	-
UV-326	1	1	-	4	4	-
UV-327	1	1	-	4	4	-
UV-328	1	1	-	4	4	-
UV-329	1	1	-	4	4	-
UV-320	0.1	0.4	-	0.4	1	-
UV-350	0.1	0.4	-	0.4	1	-
UV-360	-	20 (C8 column)	20 (C8 column)	-	70 (C8 column)	70 (C8 column)

For most substances, the resulting iLODs of the ESI source are lower (factor 3 - 10), but the linear range is shorter. As the retention of UV-360 on the C18 column is too strong and the instrumental limits are the same in both the positive and negative mode, the C8 column is used for measurements in negative mode. The precision of measurements is < 10% (intra-day) and < 20% (inter-day) for most substances and will be improved later on by assigning an appropriate internal standard. For DBT, EHT, and UV-360 the variation coefficients are much higher and without mass-labeled standards to correct for these variations, no reliable quantification is possible.

4.2 Sample preparation

4.2.1 General information

Two major parts in sample preparation are the extraction and the clean-up step. An overview of sample preparation methods for UV stabilizers used in the literature is presented in Table 13. Using an accelerated solvent extraction (ASE) method, both sample extraction and clean-up can be performed simultaneously. For this reason, the sample preparation method development focused on the ASE (chapter 4.2.2). For the optimization a North Sea sediment sample (0.05% TOC; 8.37 °E; 53.67 °N, sampled 2013) was used. The wet sample was dried by grinding it with sodium sulfate (Na_2SO_4). For the evaluation of the sample preparation method (chapter 4.2.3), freeze-dried samples of the Chinese Bohai and Yellow Seas as well as European North and Baltic Seas were used. The tests were performed directly before starting the analysis of the respective samples ensuring available mass-labeled standards and used batches (e.g., silica gel, solvents, syringe filters) were the same. ASE parts (e.g., PEEK washer, PTFE O-rings) were changed whenever needed, which could affect the background contamination.

As UV stabilizers are ubiquitously present in plastic and rubber laboratory equipment as well as in PCPs, great care was taken to avoid any contamination. In preliminary tests, used solvents, gloves, pipetting aids, and parts of the ASE cell end caps (PEEK washer, PTFE O-rings) were tested for blanks. For example, only a transferpettor (using 10 μL capillaries made of glass), Hamilton syringes (10 to 500 μL), and full-glass-syringes (1, 2, 5 mL) were used for sample transfer and the use of PCPs was minimized before and during sample handling. For every sample batch, procedural blanks were measured and used for blank correction as well as for the calculation of method detection limits (MDLs) and method quantification limits (MQLs). All results presented in the following are blank corrected.

Working with an UHPLC system, all solvents and samples have to be 0.2 μm filtrated to avoid plugging of the injection-syringe, in-line filters, or the column. In preliminary tests, three 0.2 μm syringe filters were tested and the SPARTAN syringe filter (Whatman, Germany) turned out to be the most appropriated in regard to blank values and recoveries.

In the final step, all extracts were reduced to a defined volume (150 μL) under a heated nitrogen steam using a Barkey system (Germany) and Milli-Q water was added to obtain the starting gradient for the following LC-MS/MS analysis.

For the calculation of absolute recoveries, the mass-labeled substances benzophenone- d_{10} (BP- d_{10}) and perfluorooctanesulfonamide- $^{13}\text{C}_8$ (FOSA- $^{13}\text{C}_8$) were added as injection standards directly before the instrumental analysis. They compensate for volume variations of sample extracts and for, e.g., sensitivity changes during LC measurements.

Concentration levels used for the optimization were chosen to be close to natural conditions. In general, the concentrations spiked to sea sand (Merck, Germany) or real samples were 4 ng to 20 ng in total, which equals 0.8 to 4 ng/g in a 5 g sample. This is within a concentration range that can be expected in coastal regions (see Table 5).

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Table 13: Overview of sample preparation methods for UV stabilizers in the literature.

Reference	Analytes (among others)	Location and matrix	Sample preparation		Instrumental analysis
			Extraction	Clean-up	
Rodil and Moeder (2008)	4-MBC BP-3 EHMC EHS HMS IAMC OC OD-PABA	Germany, lake sediments	ASE with ethyl acetate/n-hexane (80:20) (160 °C, 4 cycles of 5 min)	Copper powder ⁷ and silica gel packed into the extraction cell below the sample	GC-MS
Rodil et al. (2009c)	4-MBC BM-DBM BP-3 DBT EHMC EHS EHT HMS IAMC OC OD-PABA	Germany, sewage sludge	Pressurized membrane-assisted liquid extraction: a membrane was placed into the ASE cell with a cellulose filter at the bottom; ASE with ethyl acetate/n-hexane (1:3) (70 °C, 4 cycles of 5 min)	Not needed	LC-(APPI)-MS/MS
Zhang et al. (2011)	BP-3	China and USA, sediments and sewage sludge	Extraction in an PP-tube by shaking (3 x 30 min, methanol as extraction solvent)	SPE clean-up (Oasis HLB 0.5 g, Waters Corporation), elution with ethylacetate/methanol (85:15)	LC-(ESI)-MS/MS
	UV-PS UV-326 UV-327 UV-328		Extraction in an PP-tube by shaking (3 x 30 min, ethyl acetate:DCM (1:1) as extraction solvent)	Column packed with silica gel; elution with ethyl ether/n-hexane (1:9)	GC-MS
Heydebreck (2013)	4-MBC BP-3 BP-12 EHMC OC UV-P UV-234 UV-320 UV-326 UV-327 UV-328 UV-329	Germany, sediments and sewage sludge	ASE with methanol (120 bar, 100 °C, 3 cycles of 3 min)	Column packed with silica gel, activated carbon, and Na ₂ SO ₄ ; elution with DCM	LC-(ESI)-MS/MS

⁷ to avoid a sulphur peak in the following GC/MS analysis

Reference	Analytes (among others)	Location and matrix	Sample preparation		Instrumental analysis
			Extraction	Clean-up	
Barón et al. (2013)	4-MBC BP-3 EHMC OC OD-PABA	Colombia and Chile, sediments	ASE with hexane:DCM (1:1) (100 °C)	In-cell purification with alumina	LC-(ESI)- MS/MS
Langford et al. (2015)	BP-3 OD-PABA EHMC OC UV-234 UV-327 UV-328 UV-329	Norway, sediments and sewage sludge	ASE with hexane/DCM (50:50) (100 °C, 3 cycles of 5 min)	Bulk primary secondary amine (<i>PSA</i>) sorbent was added to the ASE cells for clean-up of fatty acids and other matrix interferences; further clean-up by GPC (with two sequential Envirogel clean-up columns and DCM as mobile phase); <i>PSA</i> sorbent was added to the GPC fractions to further remove matrix interferences	GC-HRMS and LC- HRMS
Cantwell et al. (2015)	UV-P UV-PS UV-320 UV-326 UV-327 UV-328	Atlantic Coast of the United States, sediment cores	ASE with acetone/hexane (1:1) (120 °C, 120 bar, 3 cycles of 5 min)	Prepacked solid phase silica cartridges; elution with hexane/diethyl ether (9:1)	GC-MS
Wick et al. (2016a)	UV-234 UV-320 UV-326 UV-327 UV-328 UV-329 UV-350 UV-360	Germany, river sediments and SPM	ASE with n-hexane/acetone (90:10) (3 x 10 min, 100 °C, 100 bar)	Prepacked Chromabond SiOH glass columns (6 mL, 1 g); elution with n-hexane/acetone (90:10)	LC-(APCI)- MS/MS

4.2.2 ASE optimization

The ASE method was developed and optimized as described in the following. The tests were performed on a DIONEX ASE-350. One batch consisted of max. 24 ASE cells that could be analyzed in sequence. Normally, all tests were done in triplicate, but due to instrumental problems (e.g., dropping of an ASE cell or a hydrocarbon vapor error) sometimes only two measurements were evaluable. The volume of the cells was 22 mL and the extracts were collected in 60 mL glass vials. A schematic diagram of an ASE cell is shown in Figure 6. The static time was 15 min in the beginning of the ASE optimization, but was shorted to 10 min later on without any noticeable impact on recoveries. Pre-cleaned sea sand (heated at 450 °C over night) was used for blank determinations, for tests without matrix, and to fill up ASE cells whenever needed.

- (A) To screen for the best extraction solvent, sea sand was spiked with 4 ng of each UV stabilizer (20 μ L of the UV stabilizer mixture, see chapter 4.1.1) and extracted with different solvents (dichloromethane (DCM), DCM/hexane, and acetone/hexane) at 100 °C. (Due to practical reasons, the ESI source was used for the instrumental analysis of this test.)
- (B) To evaluate the matrix effects in the APPI source and the impact of an integrated clean-up, sea sand and aliquots of a North Sea sample were extracted with DCM under three different conditions. Firstly, sea sand was extracted at 100 °C. Secondly, the North Sea sample was extracted at 100 °C. Thirdly, the North Sea sample was extracted at 100 °C again, but 3 g of 10% deactivated silica gel were added to the ASE cell below the sample. In all three cases, the ASE extracts were then spiked with 10 ng of each UV stabilizer before LC measurement. The same was repeated for DCM/methanol (80:20) as extraction solvent.
- (C) The North Sea sample was spiked with 10 ng of each UV stabilizer and extracted at different temperatures (room temperature (\sim 20 °C), 40, 60, 80, 100 °C) using DCM as extraction solvent.

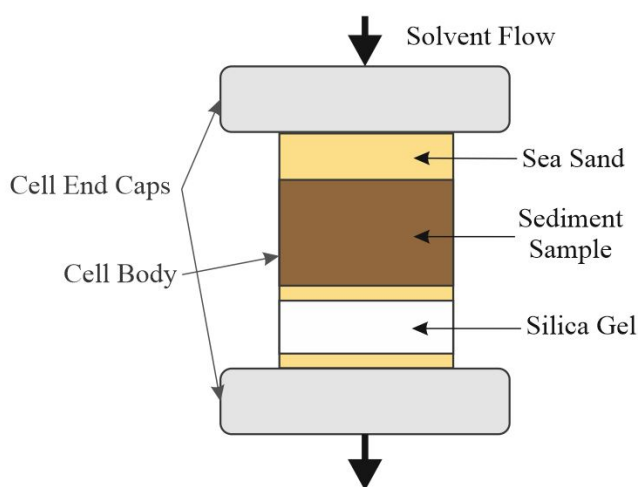


Figure 6: Schematic diagram of an ASE cell.

The results of tests (A), (B), and (C) are shown in Figure 7. In test (A), DCM showed the highest extraction efficiency (highest mean and median). In general, most recoveries were well below 100%, which could indicate a strong sorption of UV stabilizers to the sea sand. Especially the recoveries of OD-PABA and BM-DBM were < 10% for all solvents. In (B), the influence of the sample matrix is clearly seen. In case of DCM as extraction solvent, the recoveries of some UV stabilizers decrease in the presence of matrix, while others increase. This has to be ascribed to ionization enhancement or suppression inside the ionization source. In case of DCM/methanol a strong decrease in recoveries is observed, which also has to be explained by ionization suppression. It has to be taken into account that methanol is a stronger extraction solvent as DCM (elutropic series) and therefore, more unwanted sample matrix is extracted. The addition of silica gel to the ASE cell seems to be suited for clean-up purposes as the addition leads to a reduction of matrix effects. The difference is more distinct with DCM/methanol. In (C), no trend or correlation between extraction temperatures and recoveries can be observed. Therefore, 100 °C was selected for extraction temperature as lower temperatures did not show any advantages. The final sample preparation parameters are listed in Table 14.

Table 14: ASE parameters.

ASE parameter	Value
Temperature	100 °C
Heat	5 min
Static Time	10 min
Cycles	3
Rinse Volume	150%
Purge	100 s
Solvent	DCM
Pressure	1500 psi (\approx 100 bar)

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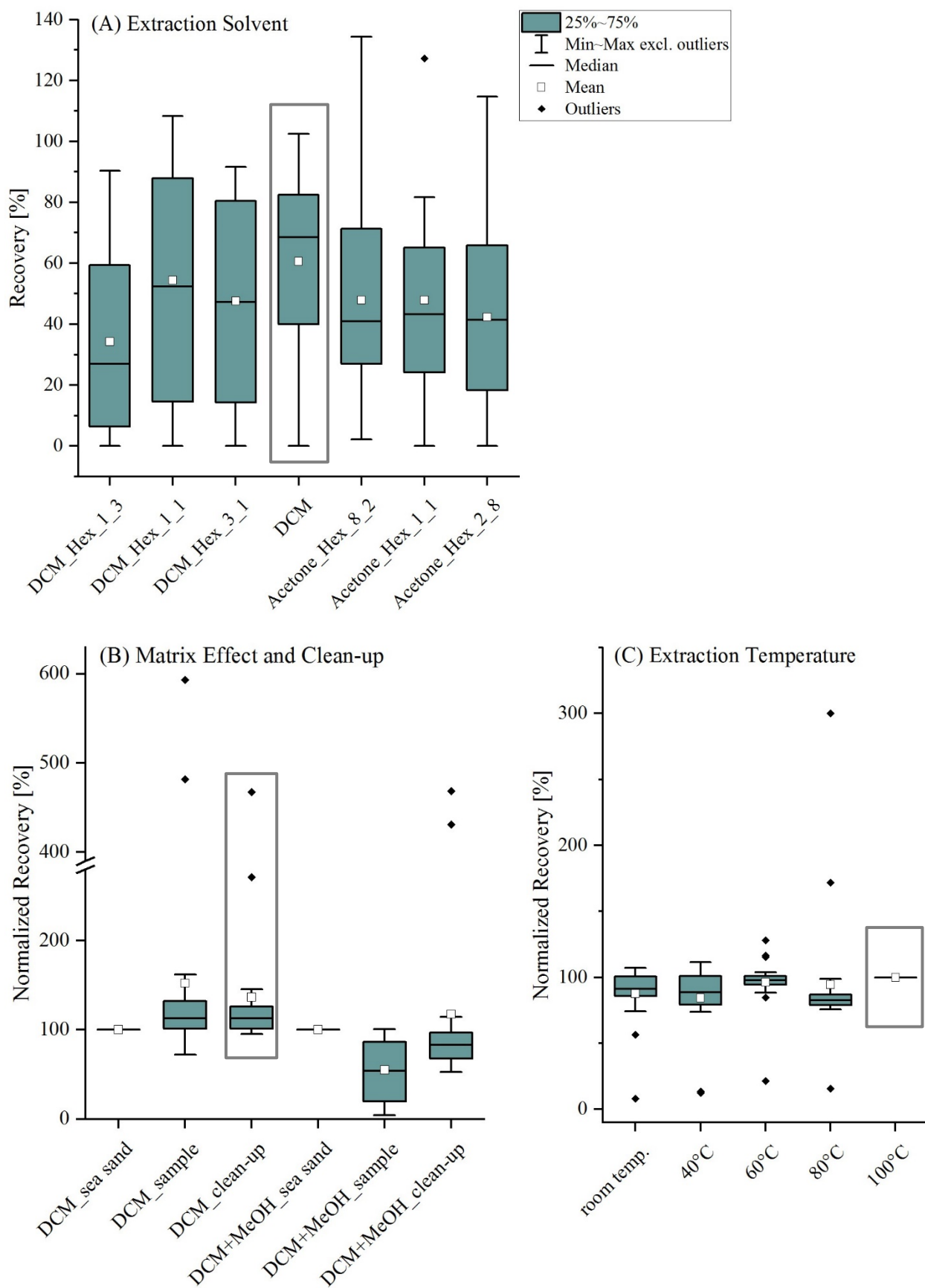


Figure 7: ASE optimization.

4.2.3 Method performance

To assess the performance of the developed method, the following tests were performed.

- (A) Fourfold measurements of spiked sediment samples were done to calculate absolute recoveries and to assign available internal standards to native compounds. The results are presented in Tables 15 and 16.
- (B) Two samples from China were analyzed by the developed method and, additionally, by a standard addition method (or spiking method) to compare the quantification results of both methods. The results are presented in Figure 8 and Table 17.
- (C) To determine MDLs and MQLs, blank cells (ASE cells filled with pre-cleaned sea sand) were analyzed. For substances without any blank values, MDLs and MQLs were calculated from the spiked samples of test (B). MDL and MQL values are presented in Table 18.

Tables 15 and 16 summarize absolute and method (corrected by internal standards) recovery rates obtained from test (A). Samples were spiked with absolute quantities of 10 to 20 ng of each native compound and 10 μ L internal standard mix (which equals 2 to 10 ng of each mass-labeled compound). The Laizhou Bay sample had to be filtrated twice (all other samples only once). The first filtration was done after the volume reduction of the extract to 150 μ L and the second filtration was done after water addition. The second filtration was necessary to avoid blocking of the LC column due to precipitated matrix components. Both absolute and method recoveries were calculated according to equation 1. In both cases the concentration of each compound quantified in the spiked sample (c_{Sample}) was corrected by the originally present concentration in the (not spiked) sample (c_0) and then divided by the added concentration (c_{Spike}). The quantification conducted for the **absolute recovery** is based on the relative response ratio of the target analyte to the amount of the **injection standard** (for volume correction of the sample extract and to compensate for, e.g., sensitivity changes during LC measurement). The quantification for the **method recovery** is based on the ratio of the target analyte to the amount of the assigned **internal standard**. This corrects for any losses or effects during sample preparation and measurement.

$$(Eq. 1) \quad Recovery [\%] = \frac{c_{Sample} - c_0}{c_{Spike}} * 100$$

The method recoveries are in the range of 80 - 120% resulting in a reliable quantification. Only BM-DBM and BP-12 sometimes show higher or lower recoveries. Therefore, the calculated concentrations for BM-DBM and BP-12 have to be considered as semiquantitative. Even though the absolute recoveries for some substances (e.g., BP-3, EHS, and HMS in Recovery Tests 1-3) are only 40 to 60%, the method recoveries are within an acceptable range and therefore, the quantification is still reliable.

The UV stabilizers DBT, EHT, and UV-360 are not included in Table 15. These substances show high variations in recoveries and for a reliable quantification mass-labeled standards are needed (as described in chapter 4.1.4). For all three substances, mass-labeled substances became available after method optimization and could be used for the analysis of North and

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Baltic Sea samples (Table 16 and chapter 4.3). Unfortunately, the developed method is not suited for the analysis of DBT, as DBT-d₄ showed very low recoveries in the analyzed samples from the North and Baltic Seas, which further decreased by the addition of formic acid to the mobile phase (see chapter 4.1.2). Therefore, DBT was excluded from the results.

Table 15: Recoveries of UV stabilizers in spiked sediments from the Bohai and Yellow Seas.

Analyte	Internal Standard	Recovery Test 1 Yellow Sea sediment (YS30; n = 4)		Recovery Test 2 Bohai Sea sediment (BS08; n = 4)		Recovery Test 3 Laizhou Bay sediment (LzB05; n = 3)	
		Absolute Recovery [%]	Method Recovery [%]	Absolute Recovery [%]	Method Recovery [%]	Absolute Recovery [%]	Method Recovery [%]
4-MBC	4-MBC-d ₄	73 ± 6	100 ± 4	83 ± 5	97 ± 2	84 ± 3	100 ± 7
BP-3	BP-3- ¹³ C ₆	35 ± 3	92 ± 4	60 ± 15	106 ± 5	59 ± 13	99 ± 11
BP-12	BP-3- ¹³ C ₆	62 ± 14	158 ± 13	90 ± 12	183 ± 23	51 ± 19	87 ± 32
EHMC	EHMC-d ₁₅	91 ± 6	101 ± 2	93 ± 6	100 ± 3	83 ± 6	101 ± 2
EHS	HMS-d ₄	61 ± 6	105 ± 7	60 ± 2	88 ± 2	41 ± 2	93 ± 5
HALS-445	Allyl-bzt; UV-328-d ₄	82 ± 7	92 ± 4	89 ± 8	95 ± 8	39 ± 15	108 ± 17
HMS	HMS-d ₄	54 ± 6	94 ± 2	52 ± 2	83 ± 5	37 ± 5	83 ± 3
IAMC	EHMC-d ₁₅	89 ± 8	99 ± 3	89 ± 7	98 ± 3	89 ± 3	108 ± 5
OC	OC-d ₁₅	99 ± 10	108 ± 6	106 ± 11	103 ± 3	94 ± 3	104 ± 4
OD-PABA	EHMC-d ₁₅	80 ± 7	90 ± 3	89 ± 6	97 ± 2	81 ± 4	99 ± 3
UV-P	Allyl-bzt; UV-P-d ₄	85 ± 8	97 ± 1	82 ± 6	96 ± 2	85 ± 4	101 ± 2
UV-PS	Allyl-bzt; UV-P-d ₄	85 ± 8	99 ± 4	94 ± 5	110 ± 6	85 ± 4	101 ± 7
UV-234	Allyl-bzt; UV-328-d ₄	94 ± 6	105 ± 10	96 ± 13	104 ± 2	39 ± 16	104 ± 19
UV-320	Allyl-bzt; UV-328-d ₄	83 ± 5	96 ± 7	91 ± 10	99 ± 5	46 ± 19	125 ± 16
UV-326	Allyl-bzt; UV-328-d ₄	87 ± 6	102 ± 2	88 ± 13	96 ± 5	41 ± 18	111 ± 19
UV-327	Allyl-bzt; UV-328-d ₄	92 ± 8	105 ± 4	96 ± 14	104 ± 4	34 ± 9	95 ± 9
UV-328	Allyl-bzt; UV-328-d ₄	82 ± 7	99 ± 2	94 ± 13	99 ± 2	35 ± 16	96 ± 15
UV-329	Allyl-bzt	91 ± 10	102 ± 2	97 ± 8	108 ± 2	69 ± 14	96 ± 11
UV-350	Allyl-bzt; UV-328-d ₄	85 ± 6	100 ± 5	94 ± 11	101 ± 6	49 ± 17	136 ± 16
4-MBC-d ₄	-	71 ± 4	-	86 ± 4	-	84 ± 5	-
Allyl-bzt	-	90 ± 5	-	92 ± 7	-	72 ± 7	-
BP-3- ¹³ C ₆	-	40 ± 11	-	54 ± 20	-	61 ± 19	-
EHMC-d ₁₅	-	88 ± 5	-	92 ± 1	-	83 ± 5	-
HMS-d ₄	-	55 ± 7	-	64 ± 2	-	45 ± 4	-
OC-d ₁₅	-	95 ± 8	-	101 ± 6	-	91 ± 6	-
UV-P-d ₄	-	87 ± 10	-	89 ± 11	-	84 ± 5	-
UV-328-d ₄	-	85 ± 5	-	93 ± 15	-	36 ± 11	-

Table 16: Recoveries of UV stabilizers in spiked sediments from the North and Baltic Seas.

Analyte	Assigned Internal standard	Recovery Test 4 North Sea sediment (MSM50/04; n = 4)		Recovery Test 5 Baltic Sea sediment (LP1709/05; n = 4)	
		Absolute Recovery [%]	Method Recovery [%]	Absolute Recovery [%]	Method Recovery [%]
4-MBC	4-MBC-d ₄	78 ± 8	92 ± 1	82 ± 8	97 ± 2
BP-3	BP-3- ¹³ C ₆	82 ± 10	96 ± 5	85 ± 7	98 ± 1
BP-12	BP-3- ¹³ C ₆	92 ± 20	107 ± 10	103 ± 11	118 ± 14
BM-DBM	BP-3- ¹³ C ₆	49 ± 8	56 ± 3	59 ± 13	69 ± 13
EHMC	EHMC-d ₁₅	84 ± 9	89 ± 2	82 ± 8	94 ± 2
EHS	HMS-d ₄	65 ± 16	85 ± 4	77 ± 7	88 ± 5
EHT	EHT-d ₄	73 ± 10	93 ± 2	n.a.	n.a.
HALS-445	UV-P-d ₄	73 ± 19	87 ± 7	81 ± 23	92 ± 28
HMS	HMS-d ₄	65 ± 16	86 ± 3	76 ± 5	87 ± 1
IAMC	EHMC-d ₁₅	80 ± 8	87 ± 4	78 ± 9	91 ± 2
OC	OC-d ₁₅	87 ± 6	95 ± 6	82 ± 8	95 ± 4
OD-PABA	EHMC-d ₁₅	80 ± 10	86 ± 2	77 ± 7	88 ± 4
UV-P	UV-P-d ₄	79 ± 10	92 ± 2	82 ± 7	96 ± 3
UV-PS	UV-P-d ₄	81 ± 9	93 ± 2	82 ± 6	95 ± 3
UV-234	UV-328-d ₄	85 ± 17	88 ± 3	110 ± 33	105 ± 10
UV-320	UV-328-d ₄	86 ± 13	91 ± 4	93 ± 21	92 ± 6
UV-326	UV-328-d ₄	72 ± 16	92 ± 2	94 ± 28	94 ± 4
UV-327	UV-328-d ₄	83 ± 17	89 ± 3	99 ± 34	95 ± 13
UV-328	UV-328-d ₄	86 ± 15	91 ± 2	100 ± 34	96 ± 4
UV-329	Allyl-bzt	89 ± 13	96 ± 4	94 ± 11	100 ± 7
UV-350	UV-328-d ₄	83 ± 12	88 ± 4	91 ± 19	90 ± 8
UV-360	UV-360-d ₈	73 ± 41	94 ± 3	143 ± 11	102 ± 2
4-MBC-d ₄	-	86 ± 8	-	85 ± 8	-
Allyl-bzt	-	92 ± 12	-	93 ± 7	-
BP-3- ¹³ C ₆	-	87 ± 11	-	88 ± 8	-
EHT-d ₄	-	77 ± 12	-	n.a.	-
EHMC-d ₁₅	-	94 ± 11	-	87 ± 9	-
HMS-d ₄	-	76 ± 15	-	87 ± 6	-
OC-d ₁₅	-	96 ± 11	-	90 ± 10	-
UV-P-d ₄	-	87 ± 9	-	87 ± 9	-
UV-328-d ₄	-	98 ± 17	-	106 ± 30	-
UV-360-d ₈	-	84 ± 41	-	138 ± 6	-

As mass-labeled standards are not available for all target UV stabilizers, a standard addition method (or spiking method) was performed for two samples from China (B). The samples were first analyzed with the internal standard method (quantification based on the peak area ratio of the target compound and an assigned internal standard in an external solvent calibration curve) developed in this thesis to get information about substances above their MQs and about the concentration ranges. Afterwards, the samples were spiked at three levels (0.4, 1.0, 2.0 ng/g) and handled in the same way as before. This time, quantification was based on the peak area (corrected by injection standard to compensate for volume differences or sensitivity changes

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during LC measurements) of the non-spiked sample and the three spiking points (4 point matrix calibration). Due to the limited amount of freeze-dried sediment sample available, duplicates or triplicates at all addition levels were not possible.

The results are shown in Figure 8 and Table 17. The quantification results of both methods only differ slightly (< 10%) for all four UV stabilizers underlining the reliable quantification of the developed method.

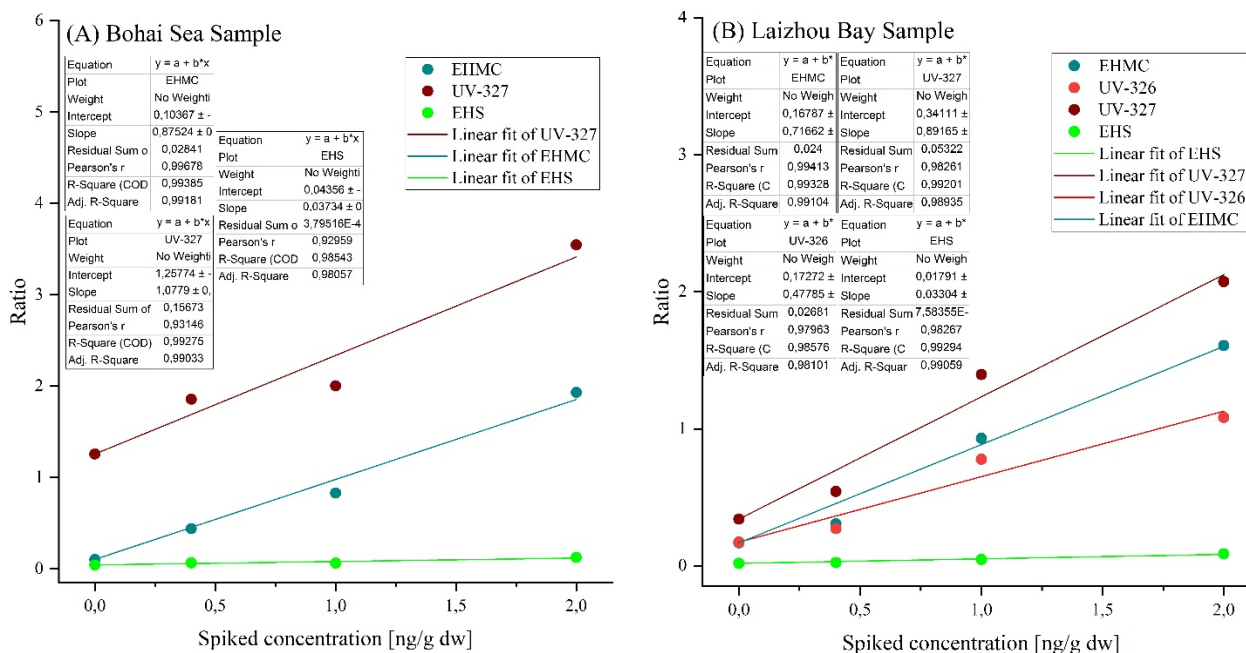


Figure 8: Calculation of UV stabilizer concentrations from the spiking method. Origin 2018b (OriginLab Corporation, USA) was used for fitting analysis.

Table 17: UV stabilizer concentrations obtained from the internal standard (IS) method and spiking method.

Sample	UV stabilizer	Concentrations [ng/g dw]		Deviation [%]	Assigned IS for IS method
		Spiking method	IS method		
Bohai Sea Sample	EHMC	0.11	0.11	6	EHMC-d ₁₅
	EHS	1.12	1.14	-1	HMS-d ₄
	UV-327	1.17	1.24	-6	Allyl-bzt
Laizhou Bay Sample	EHMC	0.23	0.22	7	EHMC-d ₁₅
	EHS	0.54	0.56	-4	HMS-d ₄
	UV-326	0.36	0.34	6	Allyl-bzt
	UV-327	0.38	0.39	-3	Allyl-bzt

In (C), MDLs were derived from either the mean blank values plus three times the standard deviation or the signal-to-noise ratio of three (S/N = 3), whichever approach yielded the highest value. Accordingly, MQLs were derived from either the mean blank values plus ten times the standard deviation or the signal-to-noise ratio of ten (S/N = 10). For MDL and MQL calculation from blank values, cleaned sea sand was put into the ASE-cells (completely filling it, approx.

30 g) and was handled as a sample in all following steps. MDLs and MQLs of all other substances were calculated from spiked samples (spiking method test; Figure 8). The S/N ratio of the peaks obtained at a spiking level of 0.4 ng/g were calculated for a ratio of 3 or 10, respectively.

Table 18: MDL and MQL values calculated for a sample volume of 5 g.

Analyte	Blank value	MDL [pg/g]	MQL [pg/g]
4-MBC	No	30	100
BM-DBM	Yes	140	450
BP-3	Yes	40	140
BP-12 ⁸	Yes	-	-
DBT ⁹	No	-	-
EHMC	Yes	80	250
EHS	Yes	20	70
EHT	Yes	80	270
IAMC	No	14	45
HALS-445	Yes	14	45
HMS	Yes	7	24
OC	Yes	135	450
OD-PABA	No	1	4
UV-P	Yes	19	60
UV-PS	No	27	90
UV-234	Yes	19	60
UV-320	No	7	23
UV-326	Yes	11	36
UV-327	Yes	4	14
UV-328	Yes	3	9
UV-329	No	40	135
UV-350	No	16	54
UV-360	No	27	90

The results presented in this chapter show the suitability of the developed method for analyzing UV stabilizers in sediments. The detection and quantification limits are sufficient for measurements in coastal and marine regions (compare to Table 5). Due to the ubiquitous presence of UV stabilizers in laboratory equipment etc., procedural blanks are essential to minimize the risk of false-detects. Therefore, each sample batch (max. 24 ASE cells) includes three blanks to monitor the background contamination and calculate the detection and quantification limits individually.

⁸ high blank value occurred, MDL in this test was around 5 ng/g dw, but normally much lower

⁹ not found in spiking experiments, therefore no calculation of MDL and MQL values possible

4.2.4 Matrix effects of ESI compared to APPI

This sub-chapter compares the performance of both ionization sources on environmental samples and gives a recommendation for future work. The results presented here were obtained in between and after analyzing the samples from the Chinese Bohai and Yellow Seas and the European North and Baltic Seas. Additionally, the used injection standards were checked for suitability.

The performance of the APPI source was already discussed in chapter 4.2.3. To compare the performance of the ESI source, the same sample extracts were measured as with the APPI source. In this way, any differences can be ascribed to the distinct matrix effects inside the sources. Additionally, the absolute recoveries of the internal standards in sample extracts from the North and Baltic Seas and the matrix effects of the injection standards in sample extracts from all four seas were calculated (Tests B and D).

- (A) Absolute and method recoveries were calculated for the ESI source exactly as done for the APPI source (Table 19 compared to Table 16).
- (B) Absolute recoveries of the internal standards were calculated in 49 samples (all in double measurements) from the North and Baltic Seas for both sources (Table 20).
- (C) MDL and MQL values of ESI were calculated for the North and Baltic Sea sediment batches and compared to APPI (Table 21 compared to Table 39 in Appendix A.2.2).
- (D) For both sources, matrix effects of the injection standards BP-d₁₀ and FOSA-¹³C₈ (only APPI) were calculated for samples from the Bohai, Yellow, North and Baltic Seas (Table 22).

Comparing absolute recoveries acquired with ESI and APPI (Test (A); Table 19 compared to Table 16), lower recoveries were obtained with ESI. This higher matrix suppression is in agreement with other studies (Himmelsbach et al., 2009; Rodil et al., 2009b). One exception was EHT and the corresponding mass-labeled standard EHT-d₄. There, the recoveries and standard deviations between measurements were similar. As the ESI source is more sensitive at the same recovery rate, the ESI source might be more suitable for analyzing low environmental concentrations in this case. The recovery of DBT-d₄ was very low (for most samples < 5%) for both sources which could either indicate a very strong matrix suppression or a sorption of DBT-d₄ to the silica gel inside the ASE cells. As DBT was found with higher recoveries (30 - 180%) in spiked matrix extracts (chapter 4.2.2 (B)), a sorption to silica-gel is quite likely.

The same effect can be observed for the internal standards (Test (B), Table 20). The recovery loss in ESI is 16 to 51% in average (except for EHT-d₄), which can be attributed to more distinct matrix effects. Especially benzotriazole derivatives are affected greatly (51% more ion suppression compared to APPI for UV-328-d₄, Table 20). This is also graphically shown in Figure 9 and noticeable in the results, e.g., in the non-detection of UV-326 in any sample extracts measured with the ESI source. Additionally, more interfering substances (peaks) occurred in ESI.

Looking at the method recoveries of ESI (Table 19), a reliable quantification is still possible for all UV stabilizers with a mass-labeled standard (e.g., EHMC and UV-P) and UV stabilizers

that are structurally similar (e.g., IAMC and UV-PS). For all other substances, the results are only semi-quantitative.

The MDLs and MQLs of ESI are similar or higher compared to APPI (Test (C), Table 21). For the benzotriazole UV stabilizers, the values are slightly higher, which can be easily explained by the lower absolute recoveries obtained in tests (A) and (B). Interestingly, EHT cannot be measured more sensitively with the ESI source, as the peak height dropped drastically at low concentrations. For several substances, e.g., BM-DBM, BP-3, and OD-PABA, the MDLs are the same.

In test (D), the matrix effect was calculated according to equation 2 as the recovery loss of the area of the injection standard in a sample ($Area_{Sample}$) compared to the mean area obtained in the calibration curve ($Area_{Calibr.}$). The average matrix effects are quite low (between -11 and +10%, Table 22) for both sources. The standard deviations on the other hand are rather high (up to 35%). The high variation can be explained by two main reasons. For APPI, the standard deviation for the calibration curves (one before and one after each sample batch) was up to 20%, which could be explained by a sensitivity loss over acquisition time. Apart from matrix effects and sensitivity changes, the area size can also be influenced by the sample extract volume. Volume losses during extract transfer or filtration are possible. Overall, the two substances are quite suited to be used as injection standards for volume and sensitivity correction.

(Eq. 2)

$$Matrix\ effect\ [\%] = \left(\frac{Area_{Sample}}{Area_{Calibr.}} - 1 \right) * 100$$

To conclude, for a reliable quantification of UV stabilizers without an appropriate IS available, the APPI source is needed, or a separate clean-up step to further remove matrix components has to be performed before ESI analysis.

4 Method development

Table 19: Recoveries of UV stabilizers in spiked sediments from the North and Baltic Seas (ESI source).

Analyte	Assigned Internal standard	Recovery Test North Sea sediment (MSM50/04; n = 4)		Recovery Test Baltic Sea sediment (LP1709/05; n = 4)	
		Absolute Recovery [%]	Method Recovery [%]	Absolute Recovery [%]	Method Recovery [%]
4-MBC	4-MBC-d ₄	71 ± 11	92 ± 4	68 ± 4	95 ± 2
BM-DBM	BP-3- ¹³ C ₆	40 ± 18	57 ± 32	47 ± 5	75 ± 15
BP-3	BP-3- ¹³ C ₆	74 ± 8	93 ± 5	78 ± 4	98 ± 1
BP-12	BP-3- ¹³ C ₆	36 ± 19	48 ± 30	18 ± 3	23 ± 4
EHMC	EHMC-d ₁₅	63 ± 17	89 ± 5	57 ± 5	96 ± 3
EHT	EHT-d ₄	69 ± 40	98 ± 5	n.a.	n.a.
HALS-445	UV-P-d ₄	54 ± 17	63 ± 18	36 ± 16	45 ± 25
IAMC	EHMC-d ₁₅	58 ± 14	82 ± 3	54 ± 6	90 ± 2
OC	OC-d ₁₅	90 ± 17	107 ± 13	90 ± 4	111 ± 4
OD-PABA	EHMC-d ₁₅	86 ± 10	108 ± 22	96 ± 7	154 ± 26
UV-P	UV-P-d ₄	67 ± 11	88 ± 8	71 ± 3	99 ± 4
UV-PS	UV-P-d ₄	71 ± 12	94 ± 10	71 ± 3	100 ± 6
UV-234	UV-328-d ₄	45 ± 13	76 ± 5	31 ± 10	97 ± 14
UV-320	UV-328-d ₄	58 ± 18	101 ± 10	35 ± 7	113 ± 8
UV-326	UV-328-d ₄	52 ± 14	85 ± 5	35 ± 10	107 ± 10
UV-327	UV-328-d ₄	53 ± 15	86 ± 12	36 ± 9	106 ± 13
UV-328	UV-328-d ₄	52 ± 15	88 ± 9	29 ± 5	90 ± 5
UV-329	Allyl-bzt	59 ± 23	104 ± 35	29 ± 9	88 ± 23
UV-350	UV-328-d ₄	58 ± 22	98 ± 18	32 ± 6	103 ± 16
4-MBC-d₄	-	79 ± 9	-	72 ± 5	-
Allyl-bzt	-	74 ± 18	-	43 ± 9	-
BP-3-¹³C₆	-	82 ± 7	-	81 ± 6	-
EHMC-d₁₅	-	70 ± 15	-	60 ± 7	-
EHT-d₄	-	97 ± 56	-	n.a.	-
OC-d₁₅	-	87 ± 11	-	85 ± 4	-
UV-P-d₄	-	81 ± 7	-	77 ± 5	-
UV-328-d₄	-	75 ± 19	-	41 ± 8	-

Table 20: Absolute recoveries of internal standards in samples from the North and Baltic Seas.

IS	absolute recovery	absolute recovery	Recovery loss ¹⁰
	APPI [%]	ESI [%]	ESI compared to APPI [%]
4-MBC-d ₄ ¹¹	80 ± 27	41 ± 27	-39
Allyl-bzt	71 ± 22	24 ± 26	-48
BP-3- ¹³ C ₆	53 ± 30	37 ± 23	-16
EHMC-d ₁₅	67 ± 22	28 ± 19	-39
EHT-d ₄ ¹²	52 ± 57	54 ± 53	+3
OC-d ₁₅	66 ± 21	32 ± 21	-35
UV-P-d ₄	71 ± 17	34 ± 20	-37
UV-328-d ₄	74 ± 33	26 ± 41	-51

Table 21: ESI source MDLs and MQLs of samples from the North and Baltic Seas.

Analyte	Blank	MDL [ng/g dw]	MQL [ng/g dw]
4-MBC ¹³	No	0.05	0.15
BM-DBM	Yes	0.03	0.11
BP-3	Yes	0.01	0.04
BP-12	Yes	0.16	0.55
EHMC	Yes	0.03	0.11
EHT	Yes	0.13	0.43
HALS-445	Yes	0.02	0.06
IAMC ¹³	No	0.02	0.06
OC	Yes	0.07	0.24
OD-PABA	Yes	0.002	0.007
UV-P	Yes	0.08	0.25
UV-PS ¹³	No	0.002	0.007
UV-234	Yes	0.03	0.10
UV-320	No	0.02	0.05
UV-326	No	0.07	0.23
UV-327	No	0.07	0.23
UV-328	Yes	0.05	0.18
UV-329	Yes	0.02	0.06
UV-350	No	0.02	0.05

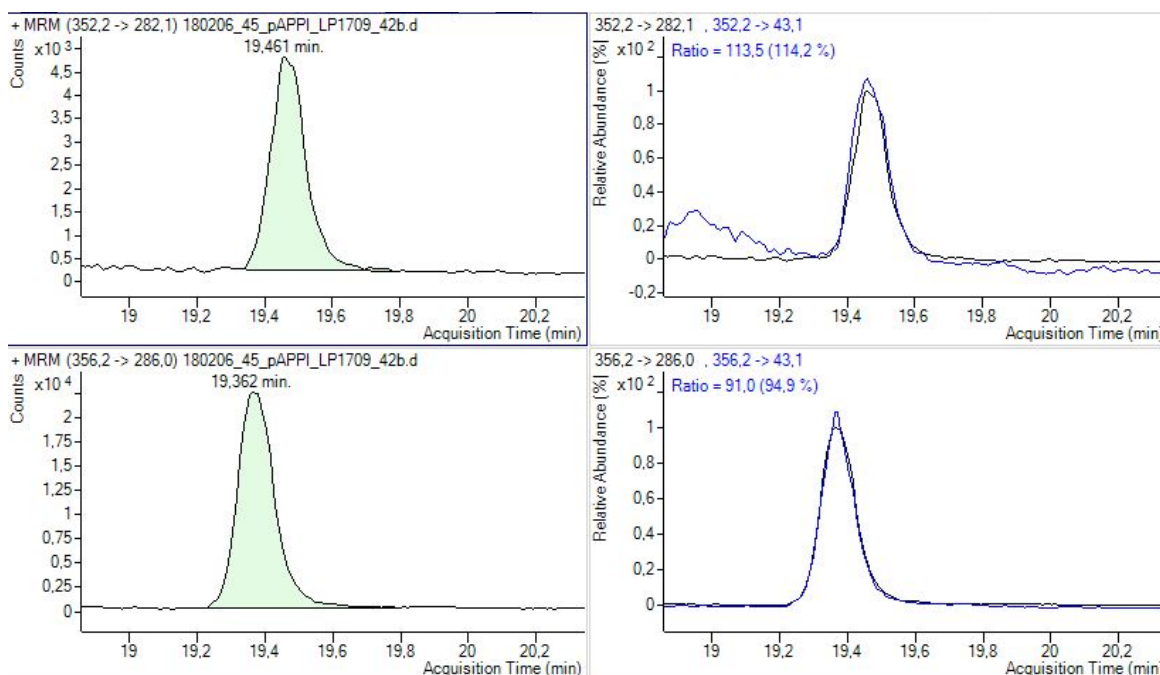
Table 22: Matrix effects of injection standards.

Samples	Matrix effect [%]		
	FOSA- ¹³ C ₈ (APPI-)	BP-d ₁₀ (APPI+)	BP-d ₁₀ (ESI+)
Bohai and Yellow Seas	+3 ± 28	+1 ± 35	n.a.
North and Baltic Seas	+10 ± 35	-6 ± 14	-11 ± 35

¹⁰ calculated for every measurement and the mean value is presented¹¹ sample number is 42 due to some matrix interferences in 7 samples¹² not analyzed in samples from the Baltic Sea¹³ calculated over S/N from spiked matrix samples

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(i) UV-328 (upper picture) and UV-328-d₄ (bottom picture) in sample LP1709/16 measured with APPI



(ii) UV-328 (upper picture) and UV-328-d₄ (bottom picture) in sample LP1709/16 measured with ESI

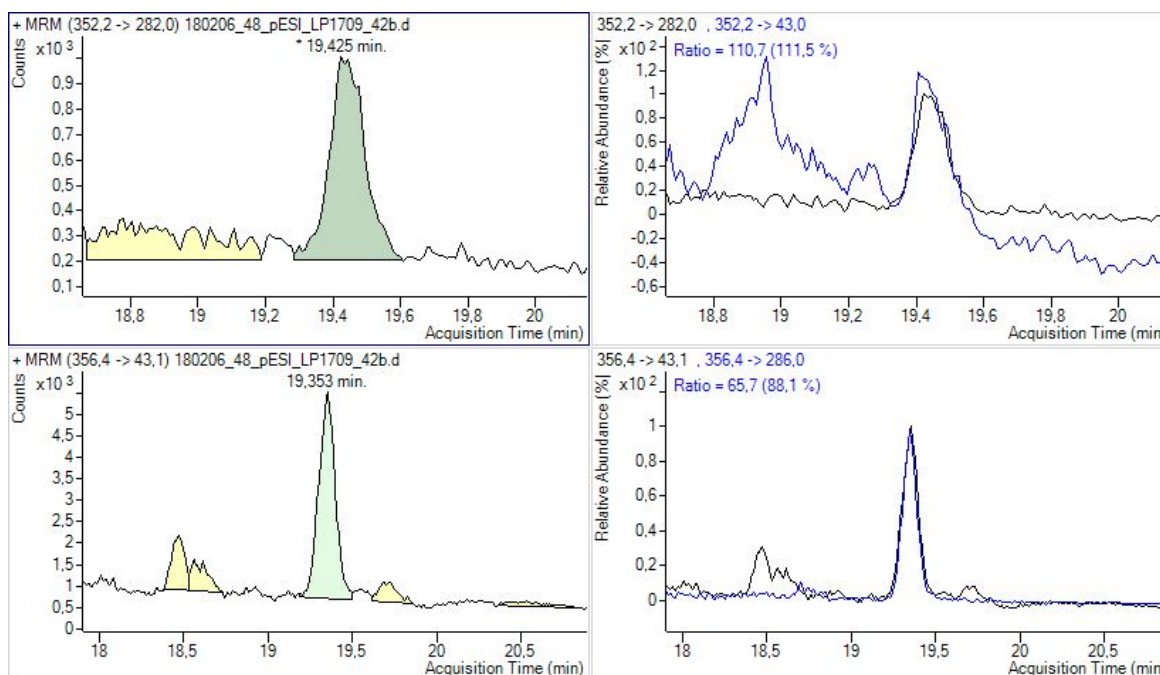


Figure 9: Peaks of UV-328 and UV-328-d₄ in sample LP1709/16.

4.3 Final method used for real samples

For blank determination, each extraction batch was accompanied by three procedural blanks (pre-cleaned sea sand) that were added to the freeze-drying system and treated as samples throughout all sample preparation and measuring steps.

The freeze-dried sediment samples were homogenized using a laboratory mortar. Large pieces (such as seashells and stones) were removed. Afterwards, extraction and clean-up were performed simultaneously using an ASE method. For this, 22 mL stainless steel ASE cells were filled in layers with 3 g of 10% deactivated silica and approximately 5 g of dried sediment (Figure 6). The sediment samples were spiked with 10 μL of the IS mixture, which equals absolute quantities of 2 to 20 ng. The cells were extracted using DCM (added with 0.3% methanol for the North and Baltic Sea samples) for three 10-min cycles at 100 °C and 1500 psi. All ASE parameters are presented in Table 14. The ASE extract (~ 40 mL) was solvent-changed to methanol in a rotary evaporator and reduced in volume to 150 μL under a heated nitrogen stream. The reduced extract was 0.2 μm -filtered into an LC vial (Spartan syringe filter, regenerated cellulose membrane, $\text{Ø} = 13 \text{ mm}$). The extract was spiked with 2 ng (absolute) of FOSA- $^{13}\text{C}_8$ and BP- d_{10} as injection standards. Finally, 65 μL Milli-Q water was added to obtain the needed solvent composition for the following LC-MS/MS analysis, resulting in a total sample volume of 225 μL . For every sediment sample, double measurements were conducted.

The instrumental analysis was performed on a UHPLC-MS/MS system equipped with an APPI source and both a C18 column and a C8 column. Every sample was measured in positive ionization mode using the C18 column and in negative ionization mode using the C8 column. Before and after every sample batch, a solvent-based calibration curve (10-points, 0.0 - 90 $\text{pg}/\mu\text{L}$; extended to 220 $\text{pg}/\mu\text{L}$ whenever needed) was measured. The mobile phase consisted of A) water and B) methanol. For the North and Baltic Sea samples, both were added with 0.1% formic acid in the positive ionization mode for an improved chromatographic peak shape of the benzophenone derivatives. Separation was achieved at a constant flow rate of 0.2 mL/min . The solvent gradient (Table 6) started with an isocratic segment of 70% B (4 min), which was increased to 90% B over 3 min and held constant for another 5 min. Over 1 min, B was further increased to 100% and held constant for 13 min. For enhanced ionization, 5% toluene was added as a dopant post-column.

5 Environmental occurrence, distribution, and hazard of organic UV stabilizers in coastal and marine sediments

5.1 Chinese Bohai and Yellow Seas¹⁴

5.1.1 Study area and sample collection

The Bohai and Yellow Seas are semi-enclosed marginal seas in the northwest Pacific Ocean (Figure 10). The Yellow Sea is surrounded by the west coast of the Korean Peninsula and the east coast of China. It has an area of approximately 380,000 km² (Song, 2010) and an average depth of 44 m (Song, 2010). Its northern extension is referred to as Korea Bay and in the northwest, the Yellow Sea is connected to the Bohai Sea through the Bohai Strait. The Bohai Sea has an area of approximately 77,000 km² (Song, 2010) and features three bays, one of them being Laizhou Bay in the south. The Bohai Sea is surrounded by the Bohai Economical Rim, which is the largest economic engine in North China. It includes megacities such as Beijing and Tianjin and comprises parts of the Hebei, Shandong, and Liaoning provinces. Many chemical pollutants, such as per- and polyfluoroalkyl substances (PFASs) (Heydebreck et al., 2015; Wang et al., 2014) and organophosphate esters (Wang et al., 2015) are transported by rivers into the Bohai Sea and pose a great risk for aquatic wildlife (Zhang et al., 2017). Large volumes of domestic and industrial discharges are entering the Bohai Sea as well as the Yellow Sea, significantly deteriorating the water quality (Wang et al., 2015; Zhong et al., 2018).

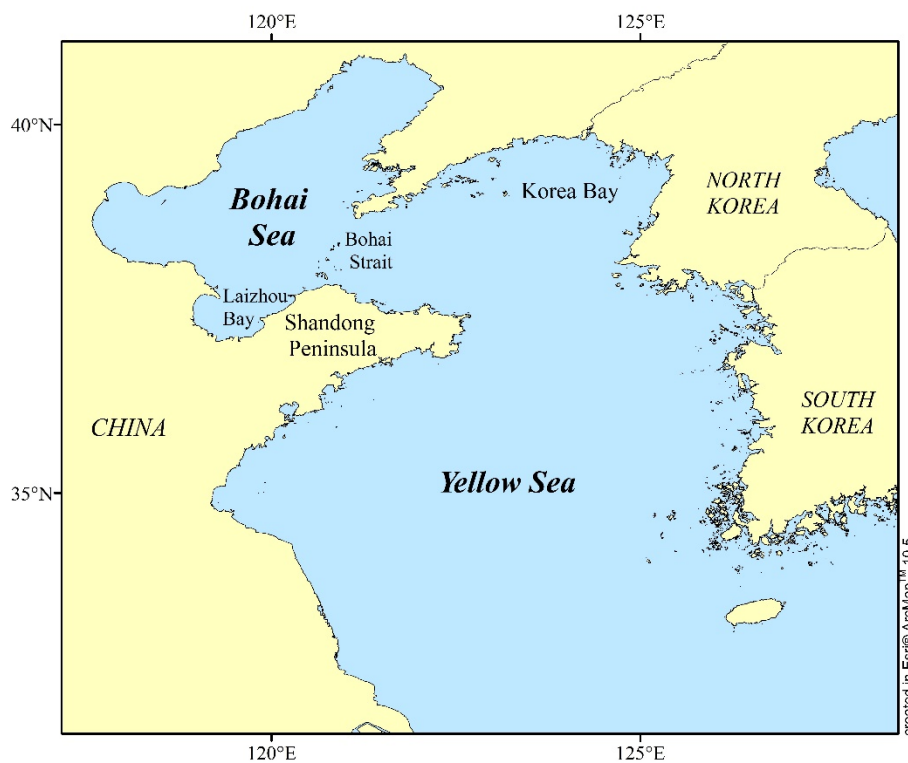


Figure 10: Map of Chinese study area.

¹⁴ published in: Apel, C.; Tang, J. and R. Ebinghaus (2018). *Environmental Pollution* **235**: 85-94.

Surface sediment samples from the Bohai and Yellow Seas were collected in June and July 2016 on the Chinese research vessel *Dongfanghong 2* sampling campaign. Surface sediment samples from Laizhou Bay were collected in July 2016 on the *Chuangxin 1* sampling cruise. On both campaigns the samples were taken using a stainless-steel box corer and the top 10 cm of sediment was collected. Detailed sampling information can be found in Table 31 (Appendix A.1.1). All samples were put into pre-cleaned aluminum bowls (cleaned with acetone and dried at 250 °C), and stored at -20 °C until freeze-drying (Christ Alpha 1-4 LDplus, Germany). Afterwards, sample preparation and analysis was done as described in chapter 4.3.

5.1.2 Environmental concentrations of UV stabilizers in the Bohai and Yellow Seas

Organic UV stabilizers could be detected in all surface sediment samples of the Bohai and Yellow Seas. Concentrations are shown in Table 23 and Figure 11. In 16% of the analyzed samples, all UV stabilizer concentrations were < MQL. The concentrations of total UV stabilizers (Σ UV stabilizers) ranged from 0.06 to 25.7 ng/g dw with average values of 3.9 ng/g dw for Laizhou Bay, 0.6 ng/g dw for the other parts of the Bohai Sea, and 2.1 ng/g dw for the Yellow Sea. No statistically significantly different contamination levels were observed for these regions. The concentrations of the UV stabilizers UV-PS, UV-350, BP-3, IAMC, and 4-MBC were below their MDLs in all analyzed samples.

The predominant contaminants were OC and UV-329, accounting for 52% and 15% of total UV stabilizer contamination in the sediment. The highest detection frequency was found for UV-234 (69%) followed by UV-326, UV-329, UV-328, and HALS-445 (all > 60%).

The UV stabilizer found in highest concentration in this study is OC. It was identified in 46% of samples with highest concentrations up to 25 ng/g dw at the central and outer Laizhou Bay (Figure 11). In the other parts of the Bohai Sea, OC occurred in remarkably lower concentrations (up to 0.3 ng/g dw). These OC concentrations are similar compared to reported coastal concentrations in other studies (Table 5). In the Bohai Sea, all other UV stabilizers occurred in lower concentrations than OC. EHS reached concentrations up to 1.2 ng/g dw, UV-326 up to 0.8 ng/g dw, and UV-327 up to 0.5 ng/g dw in Laizhou Bay; other substance concentrations were \leq 0.2 ng/g dw.

In the North Yellow Sea, both OC and EHS could be quantified in all Korea Bay samples in concentrations of 1.39 ± 0.71 ng/g dw and 0.76 ± 0.36 ng/g dw, respectively. All other substance concentrations were < MQL. EHS was found in higher concentrations at the Atlantic coast of Andalusia and at the Mediterranean coast of Spain, but was not detected in Hong Kong and Tokyo Bay sediments (Table 5). In Korea, EHS (in addition to EHMC and BP-3) was a main contaminant in different environmental matrices (Ekpeghere et al., 2016; Kim et al., 2017). In the South Yellow Sea, OC and EHS were found in highest concentrations of 4.25 ng/g dw and 0.95 ng/g dw, respectively.

Around the Shandong Peninsula, benzotriazole UV stabilizers were the most prominent substance group. The highest benzotriazole concentrations occurred at the northern tip of the peninsula. Σ UV stabilizers was 9.82 ng/g dw with UV-329 (6.09 ng/g dw) and UV-326

(1.96 ng/g dw) as the main contributors. These concentrations were slightly lower than in sediments of the Ariake Sea and the Oslofjord, where highest concentrations of 16 ng/g dw and 25 ng/g dw, respectively, were observed for UV-328 (Tables 4 and 5). In the Pearl River Estuary, UV-326 was the dominating benzotriazole UV stabilizer, followed by UV-328, UV-234, UV-P, UV-329, and UV-327 (Peng et al., 2017b). In German river sediments, the dominating substances were UV-360 (not analyzed in the Bohai and Yellow Seas) and UV-326, while UV-329 was found in a median concentration of 2.2 ng/dw (Wick et al., 2016a). In contrast to these reports, UV-329 was the dominating substance attributing to 42% of benzotriazole UV stabilizer contamination in this study, followed by UV-326 (23%) and UV-327 (19%). It can be concluded that, while benzotriazole UV stabilizers are applied worldwide, the main compounds seem to be region-specific.

In recent studies, EHMC was often one of the dominant UV stabilizers in sediments, reaching concentrations of several hundred ng/g dw (Tables 4 and 5). Interestingly, the concentrations found in this study are much lower even though EHMC is used in > 95% of cosmetics and sunscreens currently marketed in China (Peng et al., 2017b).

While 4-MBC was one dominant contaminant in Switzerland (Balmer et al., 2005; Poiger et al., 2004), it was not detected in Japan (Tables 4 and 5), where the use of 4-MBC as sunscreen ingredients is not allowed (Kameda et al., 2011). Its non-detection in this study could also be ascribed to the infrequent use of 4-MBC in currently marketed PCPs in China (Peng et al., 2017b). A similar observation was made for OD-PABA. While OD-PABA was identified as one of the predominant compounds in Hong Kong and Tokyo Bay sediments (Table 5), it was only a minor contaminant in the Korean environment (Ekpeghere et al., 2016; Kim et al., 2017), where OD-PABA is not permitted in PCPs (Ekpeghere et al., 2016). Furthermore, OD-PABA is known to be photodegradable in water (Rodil et al., 2009a) and therefore, it might depend on the input pathway if OD-PABA is degraded before it reaches the sediment. In Hong Kong, Tsui et al. (2014) connected the presence of 4-MBC, IAMC, and OD-PABA with recreational activities. Consequently, their absence or infrequent detection in this study indicates other sources of UV stabilizers into the Bohai and Yellow Seas.

The infrequent detection of UV-P and the non-detection of BP-3 could possibly be explained by their relatively higher water solubility and lower hydrophobicity ($\log K_{OW}$ values are 3.0 and 3.5, respectively) compared to the other UV stabilizers analyzed in this study ($4 < \log K_{OW} \leq 17$, Table 2). Furthermore, BP-3 is not a major UV stabilizer in sunscreens in China (Liao and Kannan, 2014).

5 Environmental occurrence, distribution, and hazard of organic UV stabilizers in coastal and marine sediments

Table 23: Concentration ranges [ng/g dw], mean concentrations [ng/g dw], and detection frequencies [%] of UV stabilizers in the surface sediment of the Bohai and Yellow Seas.

UV stabilizer	Laizhou Bay (n = 12)			Bohai Sea (excluding Laizhou Bay) (n = 22)			Yellow Sea (n = 40)		
	Range [ng/g dw]	Mean ¹⁵ [ng/g dw]	d.f. [%]	Range [ng/g dw]	Mean ¹⁵ [ng/g dw]	d.f. [%]	Range [ng/g dw]	Mean ¹⁵ [ng/g dw]	d.f. [%]
BP-12 ¹⁶	<MQL	<MQL	60	<MDL – 0.25	<MQL	57	<MDL – 0.16	<MQL	36
EHMC	<MDL – 0.22	<MQL	33	<MDL – 0.24	<MQL	27	<MDL – 0.08	<MDL	15
EHS	<MDL – 1.28	0.16	33	<MQL	<MDL	18	<MDL – 1.35	0.26	63
HALS-445	<MQL	<MQL	58	<MDL – 0.21	0.022	86	<MDL – 0.18	0.010	50
HMS	<MQL	<MDL	8	<MDL – 0.06	<MQL	59	<MDL – 0.94	0.03	25
OC	<MDL – 25	3.34	50	<MDL – 0.36	<MDL	27	<MDL – 4.25	0.83	55
OD-PABA	<MDL	-	0	<MDL	-	0	<MDL – 0.004	<MDL	8
UV-P	<MDL – 0.02	<MQL	50	<MDL – 0.06	<MQL	45	<MDL – 0.06	0.02	58
UV-234	<MDL – 0.05	0.02	67	<MDL – 0.25	0.03	86	<MDL – 0.39	0.07	60
UV-320	<MQL	<MDL	8	<MDL	-	0	<MDL – 0.20	<MQL	15
UV-326	<MDL – 0.75	0.11	67	<MDL – 0.65	0.12	82	<MDL – 1.96	0.20	58
UV-327	<MDL – 0.50	0.17	67	<MDL – 1.22	0.17	82	<MDL – 1.23	0.10	35
UV-328	<MDL – 0.16	0.04	58	<MDL – 0.12	0.04	91	<MDL – 0.41	0.06	50
UV-329	<MDL – 0.04	<MQL	50	<MDL – 0.09	<MQL	73	<MDL – 6.09	0.53	65

¹⁵ The mean value was calculated as following: The sum of concentrations in all samples was divided by the total number of samples (including samples < MDL). For calculation, concentration values < MDL were treated as zero and for concentration values < MQL, the calculated concentration value was used.

¹⁶ The benzophenone derivative BP-12 could only be analyzed in 52 of 74 sediment samples. For some sample batches, a high bank value occurred during sample preparation whereby an investigation of BP-12 for these samples was not possible.

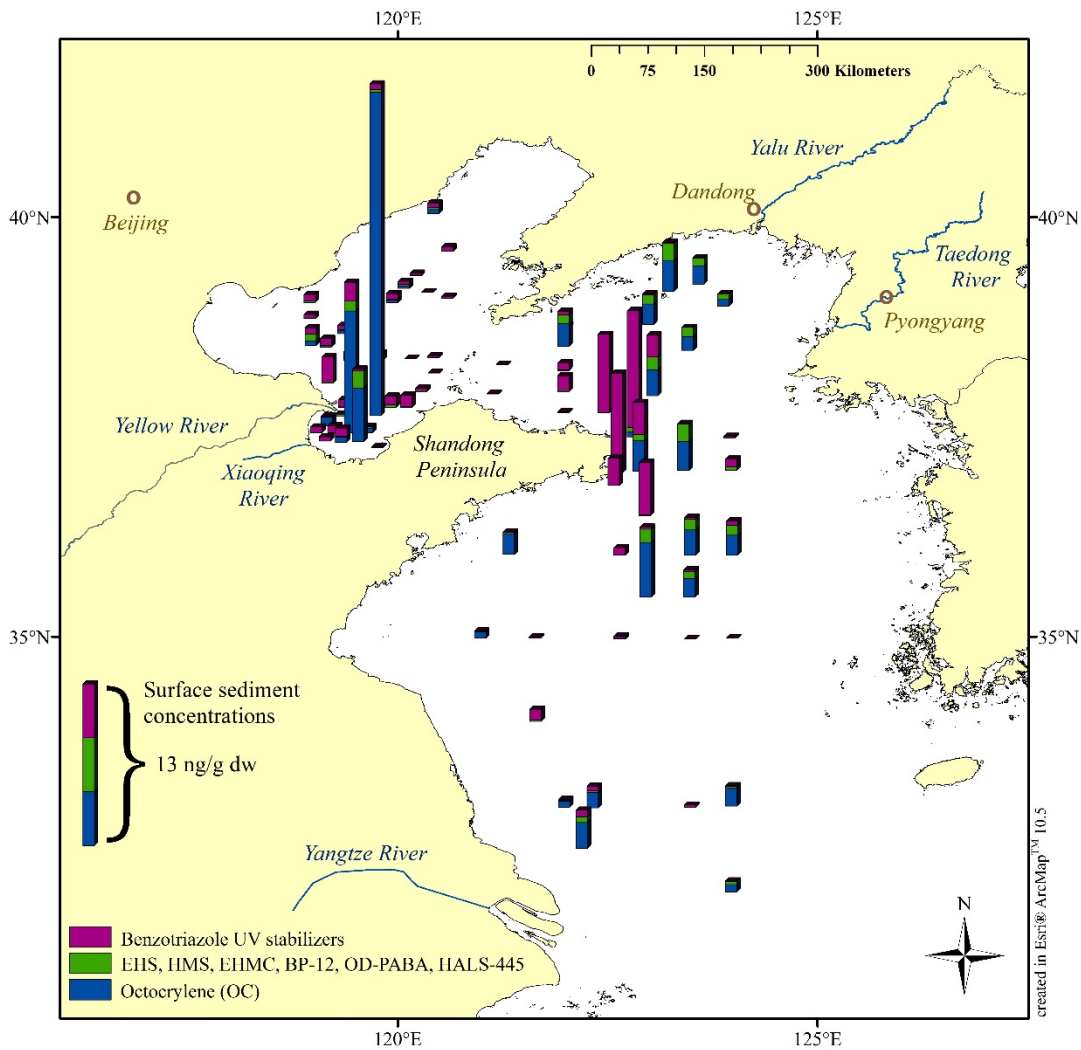


Figure 11: UV stabilizer concentrations in surface sediments [ng/g dw] of the Chinese Bohai and Yellow Seas.

5 Environmental occurrence, distribution, and hazard of organic UV stabilizers in coastal and marine sediments

5.1.3 Distribution pattern of UV stabilizers

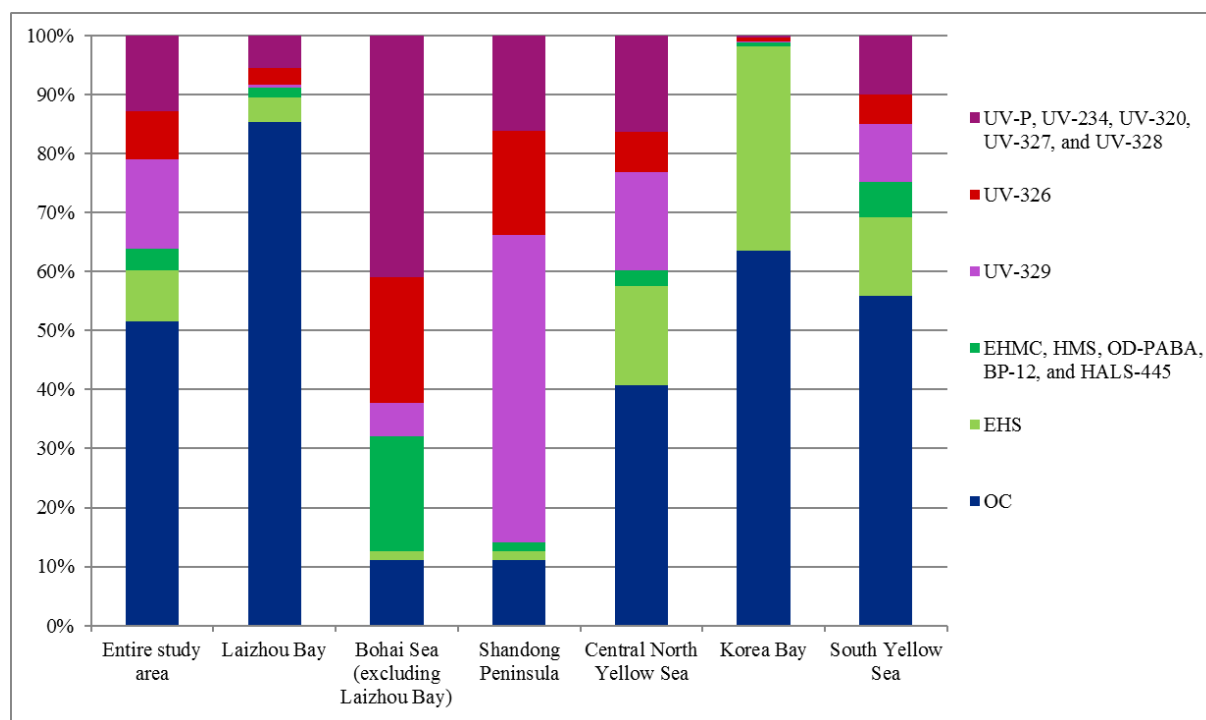


Figure 12: Composition profiles of UV stabilizers in different regions of the Bohai and Yellow Seas.

While most UV stabilizers are distributed quite homogeneously over the Bohai Sea sampling area, there is an entry of OC into Laizhou Bay. OC has wide dispersive uses in PCPs and other industrial products (ECHA, 2017). While recreational activities such as swimming (Poiger et al., 2004; Sanchez Rodriguez et al., 2015) are the major input pathway of OC into the environment in other regions, Laizhou Bay is strongly affected by land-based pollutants imported from rivers. Among the rivers leading into the Laizhou Bay, both the Yellow River and the Xiaoqing River are the most important regarding contamination discharges (Heydebreck et al., 2015; Yu et al., 2017). The OC distribution with elevated levels in the Laizhou Bay could possibly be explained by riverine inputs followed by a deposition in the central and outer Laizhou Bay. This agrees with the water-current patterns (Qiao et al., 2010) in this area.

In the North Yellow Sea, the distribution of UV stabilizers is very interesting. In Korea Bay, OC and EHS are the dominant substances. In contrast to this, benzotriazole UV stabilizers are the most prominent substance group around the Shandong Peninsula. This change in regional contamination composition is graphically shown in Figure 12. The different composition profiles of UV stabilizers in Korea Bay and around the Shandong Peninsula are mixing together in the central North Yellow Sea. This distribution pattern indicates different sources of UV stabilizers deposited into the North Yellow Sea.

Like OC, EHS is used in sunscreens worldwide and environmental contaminations are therefore often connected to recreational activities (Sankoda et al., 2015; Tashiro and Kameda, 2013). In Korea Bay however, a direct input through recreational activities seems unlikely, especially as all other compounds approved in sunscreens were < MQL. A moderate correlation of OC and

EHS in North Yellow Sea sediments ($r = 0.83$, $p < 0.01$) indicates identical sources for both compounds in this region. Apart from recreational activities, the incomplete removal of UV stabilizers in wastewater and sewage treatment plants is a major contributor to their occurrence in the environment (Ekpeghere et al., 2016; Tsui et al., 2014). In South Korea, EHS (in addition to EHMC) was the most dominant contaminant in rivers receiving sewage treatment plant discharges, mainly from domestic origins (Ekpeghere et al., 2016; Kim et al., 2017). Riverine inputs (e.g., the Yalu River forming the border between China and North Korea or the North Korean Taedong River, Figure 11) derived from domestic or industrial discharges might also be the most likely contamination source in Korea Bay.

Around the Shandong Peninsula, the concentrations of the benzotriazole derivatives UV-326 and UV-329 showed a strong correlation ($r > 0.98$, $p \ll 0.01$; Table 36). In addition, a moderate correlation could be observed between UV-234 and UV-327 ($r > 0.82$, $p = 0.01$). The correlation between the other benzotriazole derivatives UV-326, UV-327, UV-328, UV-329, and UV-234 was poor ($r \approx 0.7$; $p > 0.02$). In conclusion, these substances, especially UV-326 and UV-329, seemed to derive from the same sources and to behave similarly in the environment. A correlation between concentrations of benzotriazole UV stabilizers was also reported by Wick et al. (2016a) in German river sediments and by Nakata et al. (2009) in sediments of the Japanese Ariake Sea even though other substances correlated most. Kameda et al. (2011) investigated the occurrence of UV stabilizers in rivers in Japan and noticed that benzotriazole UV stabilizers accumulated particularly in sediment receiving chemical plant effluent, residential wastewaters, sewage treatment plant effluent, and surface runoff. Similar sources seem likely to be responsible for the detected benzotriazole contamination at the Shandong Peninsula. In China, benzotriazole UV stabilizers were shown to be present in sewage sludge collected from wastewater treatment plants, with UV-234, UV-326, UV-329, and UV-328 being the dominant compounds (Ruan et al., 2012; Song et al., 2014). Since most benzotriazole UV stabilizers (except UV-P) are almost completely removed from the final effluent (Liu et al., 2012; Song et al., 2014), the direct effluent discharge of wastewater treatment plants only seems to be of minor importance as a contamination source in this case. In sewage sludge however, benzotriazole UV stabilizers are present in the final stage (Liu et al., 2012) and could reach the environment due to biosolid applications in agriculture. This was demonstrated by Lai et al. (2014) who investigated the occurrence of benzotriazole UV stabilizers in biosolid-amended soils. They detected several compounds in soils, with UV-329 being the dominant substance and with the highest concentrations in Shandong (up to 33.3 ± 7.3 ng/g). The results by Lai et al. (2014) underline the importance of UV-329 as a characteristic contaminant in this region and also indicate surface runoff as an important contamination source of UV stabilizers introduced into the environment. Benzotriazole UV stabilizers could then be transported into the Yellow Sea via rivers.

Going south from Korea Bay into the South Yellow Sea, the pollution characteristics of Shandong Peninsula and Korea Bay are mixing together as they do in the central North Yellow Sea (Figure 12). The highest UV stabilizer concentrations were found in the northern central part of the South Yellow Sea, where a mud area is located (Yang et al., 2003). Going further to the south or to coastal regions (with the exception of the Shandong Peninsula), UV stabilizer

concentrations decrease. Two possible sources of South Yellow Sea contaminations are the Yangtze and Yellow Rivers (Figure 11). Lan et al. (2007) recognized Yangtze River-specific sediment compositions in South Yellow Sea sediments. Yang and Liu (2007) showed that Yellow River-derived sediment is transported from the Bohai Sea along the Shandong Peninsula coast into the South Yellow Sea. The contaminations found in this study are more likely to originate from the Yangtze River and to be transported by ocean currents (Zhong et al., 2018) into the South Yellow Sea. Yellow River-derived contamination seems unlikely, as the found contamination pattern changes drastically over the described sediment transportation pathway.

5.1.4 Correlation with TOC

The TOC content in the analyzed sediment samples ranged from 0.03 to 0.87% (Table 31 of Appendix A.1.1). In Figure 13, UV stabilizer concentrations are plotted against the TOC content of each sample. No correlation could be observed. This is consistent with recent studies (Gago-Ferrero et al., 2011; Huang et al., 2016; Tsui et al., 2015). So far, only Nakata et al. (2009) revealed a positive correlation between benzotriazole UV stabilizer concentrations and TOC contents in samples from the Ariake Sea, Japan. The TOC contents in the Ariake Sea samples ranged from 2 to 15%, which are much higher values compared to those in this study. The lacking correlation in this study could be due to several reasons, such as an inhomogeneous distribution over the sampling area or the ability of UV stabilizers to partition to other phases in dynamic aquatic environments (Tsui et al., 2015). Low UV stabilizer concentrations (in most samples) or the narrow TOC range could also result in an indiscernible correlation.

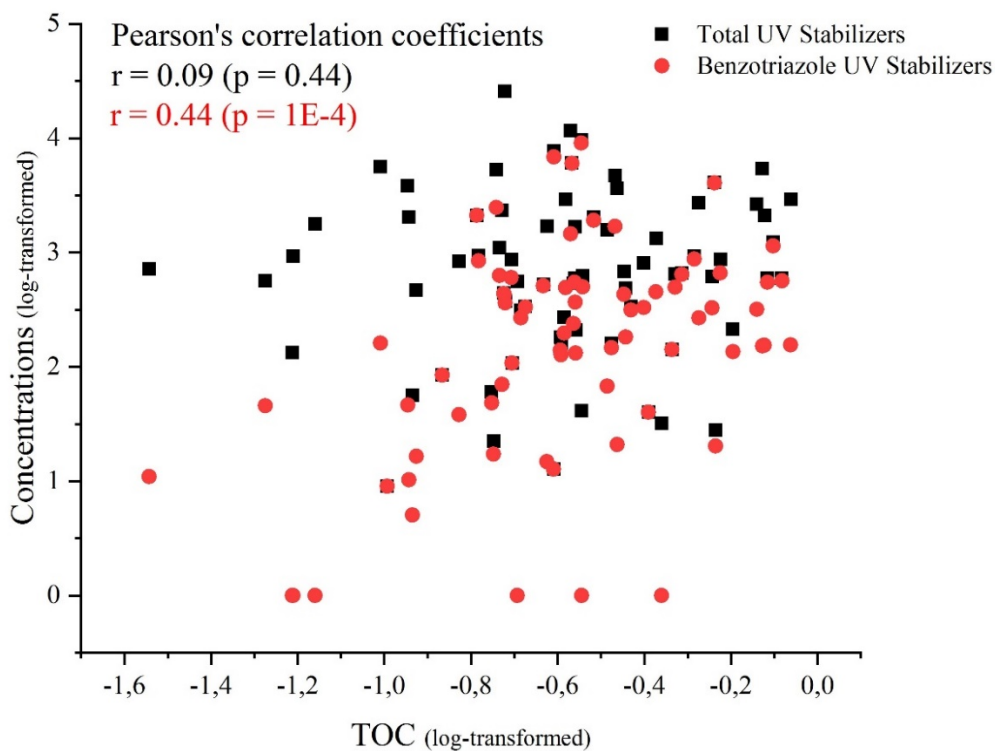


Figure 13: Logarithmically transformed values of total UV stabilizer concentrations plotted against the TOC content of each sample. The Pearson correlation coefficient was calculated using OriginPro 9.1 (OriginLab Corporation).

5.1.5 *Qualitative information on DBT and EHT in marine sediments*

In addition to the findings presented in Figure 11 and Table 23, the UV stabilizers DBT and EHT could be identified in several samples of the Bohai and Yellow Seas (Table 34). Because of low recoveries, low reproducibility, and lack of appropriate mass-labeled standards, the applied method is not suitable for quantifying these compounds. Estimated concentrations of the triazine derivatives DBT and EHT in some samples are in the high ng/g dw range. As an example, disregarding possible matrix effects and assuming a theoretical recovery rate of 5%, the concentrations are 750 ng/g dw for DBT and 150 ng/g dw for EHT at the tip of the Shandong Peninsula. Even assuming a recovery rate of 100%, the concentrations are 40 ng/g dw and 8 ng/g dw, respectively, and are therefore comparable to or even higher than those of other UV stabilizers in this study. In addition to their use in industrial materials, these substances are approved as ingredients in cosmetic products in Europe (European Commission, 2018d), China (following the European Cosmetic Directive), and Australia (only EHT) (Australian Government, 2017). DBT and EHT are highly hydrophobic compounds with calculated $\log K_{ow}$ values > 14 (Table 2), resulting in a high accumulation potential in sediment. So far, environmental data on these compounds are sparse. They have been measured in sewage sludge at concentration levels of several hundred ng/g dw (Kupper et al., 2006; Plagellat et al., 2006; Rodil et al., 2009c) and in wastewater (Kupper et al., 2006). This is the first time these substances have been found in marine sediments. Further investigations of environmental levels and behavior should be conducted.

5.2 European North and Baltic Seas¹⁷

5.2.1 Study area and sample collection

The North Sea is an Atlantic Ocean shelf sea that connects to the Baltic Sea via the Skagerrak and Kattegat (Figure 14). The Baltic Sea is an intra-continental sea and has limited water exchange with the North Sea through the Danish Straits. With a turnover time of approximately thirty to fifty years, the water of the Baltic Sea is brackish (Fisch et al., 2017). Due to its geographical structure, the Baltic Sea is sensitive to pollution and the environmental state is deteriorating at an alarming pace (Tynkkynen, 2017). The catchment areas of the North and Baltic Seas are inhabited by approximately 184 (OSPAR, 2010) and 84 (HELCOM, 2015) million people, respectively, causing high anthropogenic input into both areas. Major activities in the North and Baltic Seas constitute fishing and diverse offshore activities, such as the exploitation of gas and oil deposits as well as offshore wind energy farms. Furthermore, the rivers discharging into the North and Baltic Seas pass through heavily industrialized areas and the coastal zones are intensively used for agriculture and recreational activities.

Surface sediment samples of the North Sea, the Skagerrak and Kattegat regions, and the Baltic Sea were taken on the *Maria S. Merian* sampling cruise in January 2016. In addition, surface sediment samples of the German Bight and the German Baltic Sea coastline were collected on two sampling campaigns with the research vessel *Ludwig Prandtl* in June and September 2017. All samples were taken using a stainless-steel box corer. The Rhine-Meuse-Delta and the Oder Lagoon were sampled from land in October 2015 and September 2017, respectively, using either a Van Veen Grab sampler or a shovel. Table 37 (Appendix A.2.1) provides a detailed list of sampling stations. All samples were homogenized, put into pre-cleaned aluminum bowls (cleaned with acetone and dried at 250 °C), and stored at -20 °C until freeze-drying (Christ Gamma 1-16 LSCplus, Germany).

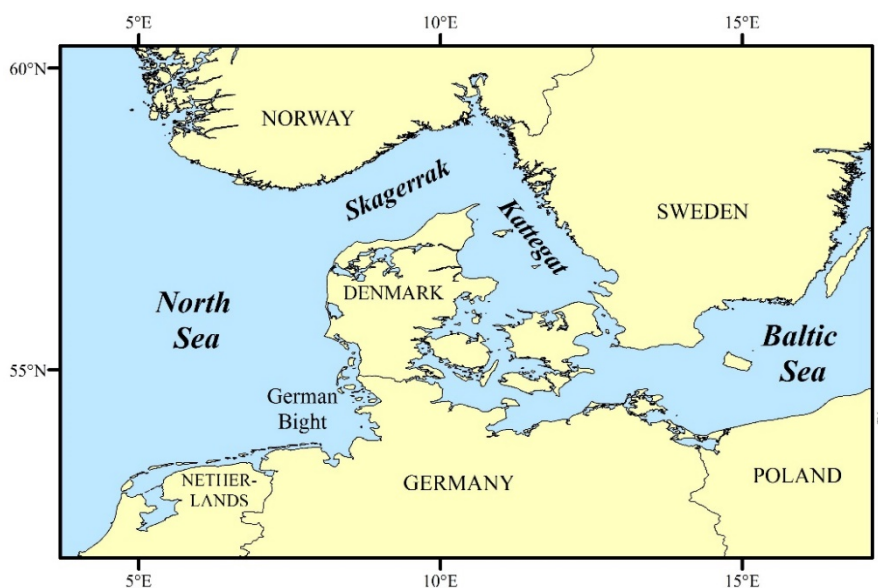


Figure 14: Map of European study area.

¹⁷ published in: Apel, C.; Joerss, H. and R. Ebinghaus (2018). *Chemosphere* **212**: 254-261.

5.2.2 Environmental concentrations of UV stabilizers in the North and Baltic Seas

Organic UV stabilizers could be detected in nearly all analyzed sediment samples from the North and Baltic Seas and from the inflows. Concentrations are presented in Tables 24 and 25. The concentrations of total UV stabilizers ranged from 0.12 to 11.2 ng/g dw. In four samples, all concentrations were <MQL and in one sample from the western Skagerrak, all concentrations were <MDL. No statistically different contamination levels were observed for the German Bight (2.0 ng/g dw on average, excluding EHT, as it was not analyzed in the Baltic Sea), the Skagerrak and Kattegat (0.5 ng/g dw), and the German Baltic Sea (1.7 ng/g dw).

In the German Bight, OC is the dominating UV stabilizer found in highest concentrations (9.7 ng/g dw) south of Heligoland, close to the harbor (Figure 15). The concentration at this station was higher than in the Rhine-Meuse-Delta (max. 2.5 ng/g dw) and in the Elbe estuary (max. 2.7 ng/g dw). These OC concentrations lie in a similar range as reported concentrations for other coastal regions such as Hong Kong (Table 5) and the Bohai and Yellow (this thesis, Table 23); the concentrations are, however, lower compared to the Oslofjord with a maximum of 82.1 ng/g dw (Table 5). The UV stabilizer BM-DBM was found in the Elbe estuary, the German Bight and in one sample from the German Baltic Sea with highest concentrations of 0.70 ng/g dw. These concentrations are much lower than in sediments from Hong Kong and Tokyo Bay, with a maximum of 43 and 65 ng/g dw, respectively, and in German riverine and (bathing) lake sediments from the Rhine Main area, with a maximum of 22 and 62 ng/g dw, respectively (Tables 4 and 5). OC and BM-DBM are currently listed under CoRAP due to suspected PBT/vPvB properties (among others, see Table 1). The estimated half-lives in sediment are 135 d and 542 d, respectively (calculated with the U.S. EPA EPI Suite™ tool). Studies showed that OC could accumulate in fish up to levels that caused transcriptional alterations (Bluthgen et al., 2014) and adverse effects on the endocrine system (Zhang et al., 2016). In the Rhine-Meuse-Delta and in the German Bight, the triazine derivative EHT was found in concentrations up to 2.0 and 0.31 ng/g dw, respectively. This is the first study presenting concentration data of EHT in coastal sediments. So far, EHT was found in sewage sludge and wastewater (Kupper et al., 2006; Plagellat et al., 2006; Rodil et al., 2009c) and was identified in the sediment of the Chinese Bohai and Yellow Seas (this thesis; chapter 5.1.5). Another compound that has been reported in the environment only recently is the benzotriazole derivative UV-360. It was present on beaches of Gran Canaria Island (Garcia-Guerra et al., 2016) and in four German rivers (Wick et al., 2016a). In German rivers, the highest concentrations (up to 62 ng/g dw) were found in the Rhine, which is heavily influenced by industry. In this study, UV-360 was present over the entire study area with highest concentrations in the Baltic Sea and in the Rhine-Meuse-Delta (4.0 ng/g dw and 2.7 ng/g dw, respectively). Benzotriazole UV stabilizers can cause various adverse effects on aquatic and terrestrial organisms (NTP, 2011). For example, in zebrafish eleuthero-embryos, exposure led to activation of the aryl hydrocarbon receptor pathway, which might cause metabolic imbalance and developmental toxicity (Fent et al., 2014). The salicylate derivative HMS was also present over the entire sampling area, reaching concentrations up to 2.1 ng/g dw in the Baltic Sea. HMS was found in similar concentrations in the Chinese Bohai and Yellow seas (this thesis, Table 23)

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and in slightly higher concentrations at the Atlantic coast of Andalusia (Table 5), in the Chinese Pearl River estuary (Table 4), and in Japanese rivers and lakes (Kameda et al., 2011).

4-MBC was one of the most frequently used UV stabilizers in PCPs some years ago (Kerr, 2011; Poiger et al., 2004). In this study, 4-MBC, IAMC, and UV-PS were not detected in any sample. While 4-MBC and IAMC are approved in PCPs in Europe (European Commission, 2018d), they are barely used nowadays (Kerr, 2011; Manova et al., 2013). In other countries such as Japan, the use of 4-MBC is forbidden (Kameda et al., 2011). In the environment, 4-MBC was predominantly present at recreational beaches and lakes (Poiger et al., 2004; Sanchez Rodriguez et al., 2015; Tsui et al., 2014), but beyond this, it was not detected in coastal and marine regions of China and Japan (Tables 5 and 23).

Table 24: Concentration ranges [ng/g dw] of two river mouths and one lagoon discharging into the North and Baltic Seas.

UV stabilizer	Range [ng/g dw]		
	Rhine-Meuse Delta (n = 3)	Elbe Estuary (n = 2)	Oder Lagoon (n = 3)
BM-DBM	<MDL	<MQL	<MDL
BP-3	<MDL - 0.03	<MDL	<MDL - 0.09
BP-12	<MDL - 1.8	<MDL	<MDL
EHMC	<MQL	<MDL - 0.07	<MDL
EHS	0.28 - 0.31	<MQL - 0.24	<MDL
EHT	<MDL - 2.0	<MDL	n.a.
HALS-445	<MDL - 0.06	<MDL - 0.05	<MDL
HMS	0.21 - 0.23	<MDL	<MDL
OC	0.27 - 2.5	0.54 - 2.7	0.09 - 0.76
OD-PABA	<MQL	<MDL - 0.015	<MDL
UV-P	<MDL - 0.25	<MDL	<MQL
UV-234	<MDL - 0.33	<MQL	0.02 - 0.07
UV-320	<MDL - 0.07	<MQL	<MDL
UV-326	<MDL - 0.52	<MDL	<MQL
UV-327	<MDL - 0.40	<MDL	<MQL
UV-328	<MDL - 0.15	<MDL	<MQL
UV-329	<MDL - 0.17	<MQL	<MDL
UV-350	<MDL - 0.07	<MQL	<MDL
UV-360	<MDL - 2.7	<MQL	<MDL - 0.21

Table 25: Concentration ranges [ng/g dw], mean concentrations [ng/g dw], and detection frequencies [%] of UV stabilizers in surface sediments of the German Bight, the Skagerrak and Kattegat areas, and the German Baltic Sea.

UV stabilizer	German Bight (n = 13)			Skagerrak and Kattegat (n = 11)			German Baltic Sea (n = 24)		
	Range [ng/g dw]	Mean [ng/g dw]	d.f. [%]	Range [ng/g dw]	Mean [ng/g dw]	d.f. [%]	Range [ng/g dw]	Mean [ng/g dw]	d.f. [%]
BM-DBM	<MDL – 0.70	0.16	46	<MDL	-	-	<MDL – 0.17	<MDL	4
BP-3	<MQL	<MDL	23	<MDL	-	-	<MDL	-	-
BP-12	<MDL – 0.13	<MQL	15	<MDL	-	-	<MDL – 0.06	<MDL	4
EHMC	<MDL – 0.32	<MQL	31	<MDL	-	-	<MQL	<MDL	33
EHS	<MDL – 0.20	<MQL	38	<MDL – 0.19	<MQL	36	<MDL – 0.42	0.08	42
EHT	<MDL – 0.31	<MQL	31	<MDL	-	-	n.a.	-	-
HALS-445	<MDL	<MDL	-	<MDL – 0.09	0.02	55	<MDL – 0.56	0.04	38
HMS	<MDL – 0.64	0.11	62	<MDL – 0.16	0.08	73	<MDL – 2.1	0.25	58
OC	<MDL – 9.7	1.3	92	<MDL – 0.10	<MQL	36	<MDL – 1.7	0.25	83
OD-PABA	<MDL	-	-	<MDL – 0.008	<MDL	9	<MDL – 0.014	<MDL	8
UV-P	<MDL – 0.24	0.03	23	<MDL – 0.10	0.03	73	<MDL – 0.19	0.03	38
UV-234	<MDL – 0.25	0.05	46	<MDL – 0.24	0.10	82	<MDL – 0.62	0.10	63
UV-320	<MQL	<MDL	15	<MDL	-	-	<MDL	-	-
UV-326	<MQL	<MDL	23	<MDL – 0.13	<MDL	9	<MDL – 0.97	<MQL	29
UV-327	<MDL – 0.24	<MQL	23	<MDL – 0.20	<MDL	27	<MDL – 0.16	<MDL	17
UV-328	<MDL – 0.07	<MQL	31	<MDL – 0.15	0.06	82	<MDL – 0.88	0.12	50
UV-329	<MQL	<MDL	8	<MDL – 0.23	<MQL	9	<MDL	-	-
UV-350	<MQL	<MDL	8	<MDL	-	-	<MDL	-	-
UV-360	<MDL – 0.77	0.13	54	<MDL – 0.21	<MQL	55	<MDL – 4.0	0.63	75

5 Environmental occurrence, distribution, and hazard of organic UV stabilizers in coastal and marine sediments

5.2.3 Distribution pattern of UV stabilizers in the North and Baltic Seas

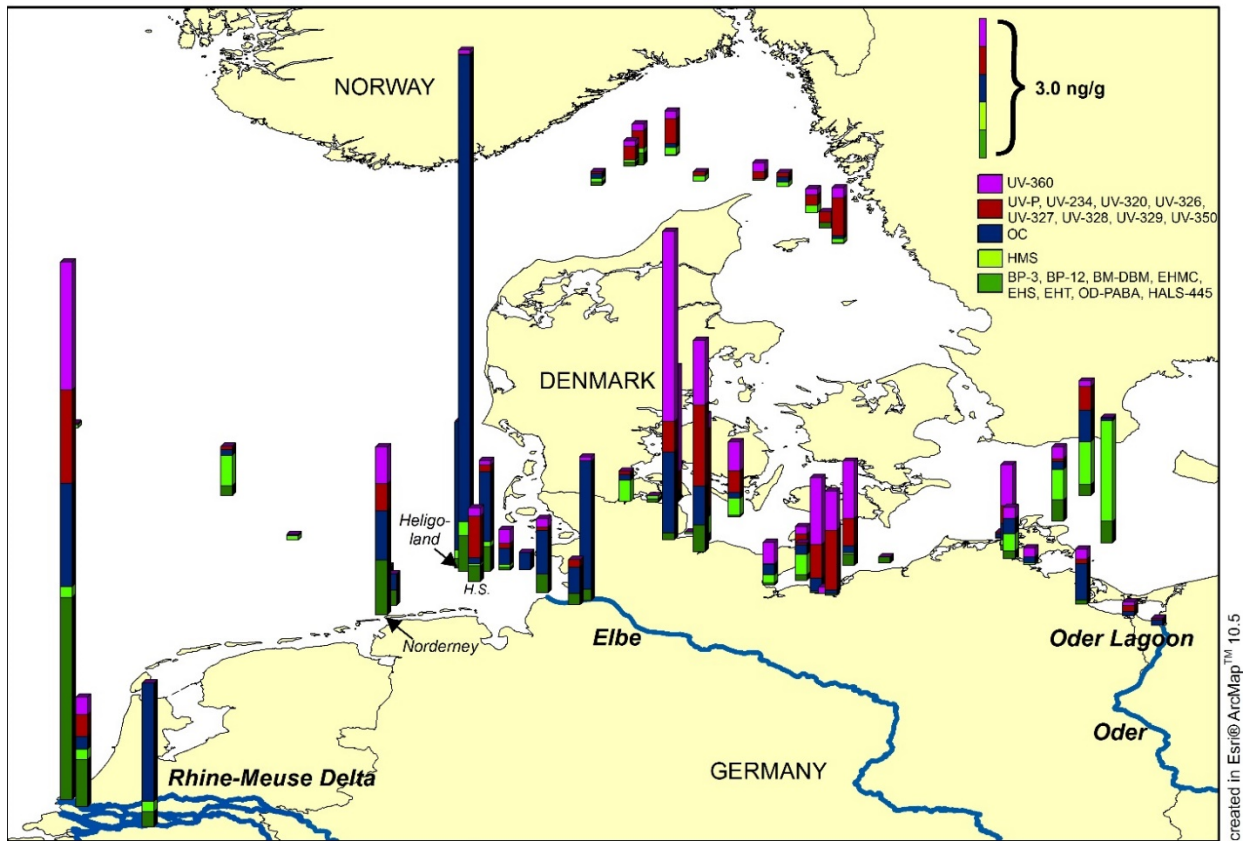


Figure 15: Concentrations of UV stabilizers in surface sediments [ng/g dw] over the entire study area. The sample labeled "H.S." was taken at the "Helgoländer Schlickloch".

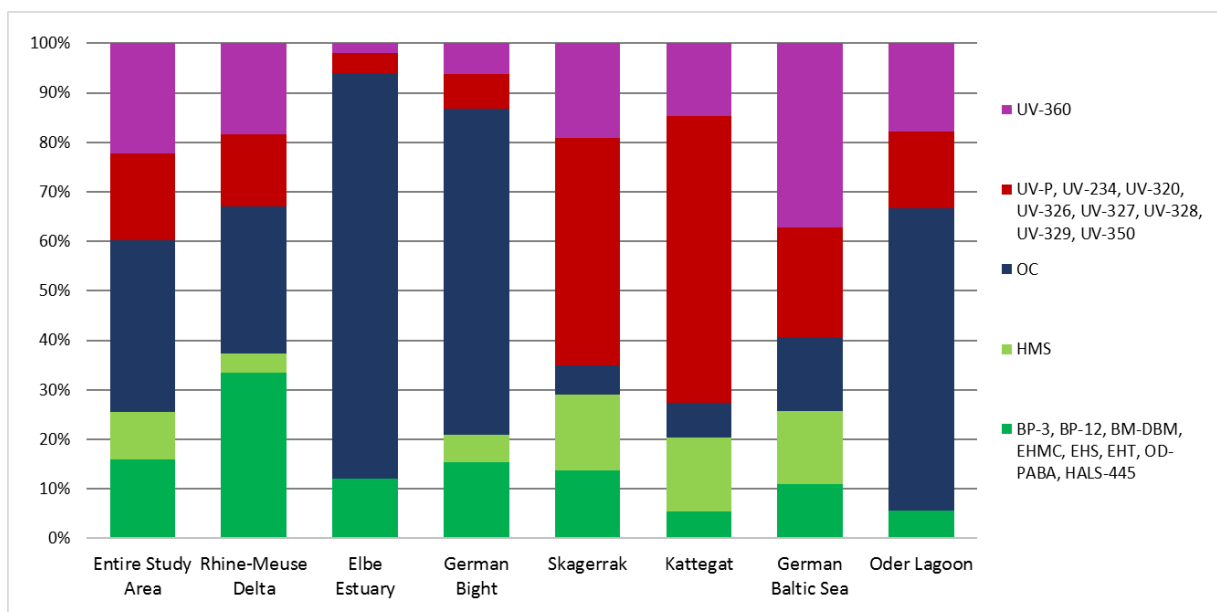


Figure 16: Composition profiles of UV stabilizers in different regions of the North and Baltic Seas.

The distribution pattern and composition profiles of UV stabilizers in the study area are graphically shown in Figures 15 and 16 and reveal region-specific contamination differences.

The Rhine and Elbe Rivers are two important dischargers into the southern North Sea in terms of nutrients, organic and inorganic pollutants (BSH, 2013; Möller et al., 2010; Neumann et al., 2017; OSPAR, 2010; Wolschke et al., 2011). The river influences can be directly seen in Figure 15. Due to residual coastal currents, which flow counter clock-wise along the Danish and German Frisian Islands (OSPAR, 2010), the composition profile of UV stabilizers found north of Norderney is similar to those in the Rhine-Meuse-Delta. The influence of the Elbe River can be followed up to Heligoland. The sample labeled “H.S.” was taken at the “Helgoländer Schlickloch”, a muddy area close to the dumping site Tonne E3, where dredged material from the Hamburg portion of the Elbe River (especially from the harbor) is dumped. This might explain the higher benzotriazole proportion at this station in comparison to adjacent stations. With the exception of OD-PABA, all substances present in the river mouths could also be identified in the German Bight. The predominant compound in the German Bight is OC, which accounted for > 65% of the total UV stabilizer contamination (Figure 16). At or close to the port of Heligoland, there seems to be a point source of OC into the environment resulting in the highest observed concentration in this study area. The TOC of this sample (LP1706/05, 0.23%, see Table 37) is similar to the TOC of adjacent stations (0.26 to 0.65%) and therefore this observation cannot be explained by different TOC levels. To ascertain the origin of this point source is difficult, as OC has widely diverse uses as an ingredient in PCPs and in other industrial products. OC is used in PCPs since the late 1990s (de Groot and Roberts, 2014) and shows a high prevalence in PCPs worldwide (de Groot and Roberts, 2014; Kerr, 2011; Manova et al., 2013). It is further used in automotive care products, paints, coating products, and, generally, in products made of plastic and paper (ECHA, 2017). In literature, the presence of OC in the environment is connected to recreational activities (Langford and Thomas, 2008; Poiger et al., 2004) and wastewater discharges (Kameda et al., 2011; Langford et al., 2015). BM-DBM mainly occurred near the islands Norderney and Heligoland. Its presence most likely originates from recreational activities, as both regions are popular beach resorts and BM-DBM is one of the most applied UV stabilizers in sunscreens (Kerr, 2011; Manova et al., 2013; Wahie et al., 2007).

The Skagerrak and northern Kattegat regions are well known as accumulation sites of SPM from the North Sea (Kuijpers et al., 1993). Sediments can be transported into the Skagerrak and Kattegat by the Jutland Current (originating from the southern North Sea), by local rivers (e.g., sediments discharged from the Swedish mainland and transported into the Kattegat by the Göta Älv River), and the Baltic Sea (Kristiansen and Aas, 2015; Kuijpers et al., 1993). UV-234, UV-360, and HMS each contributed $\geq 15\%$ to the total contamination. OC was found in significantly lower concentrations and frequency than in the North Sea, only accounting for < 10% of the contamination. The benzotriazole UV stabilizers UV-P, UV-328, UV-234, and UV-360 showed a positive correlation ($r \geq 0.68$, $p \leq 0.02$, Table 42) with UV-328 and UV-234 showing the strongest correlation ($r = 0.97$, $p = 7E-07$). These results suggest that benzotriazole UV stabilizers enter the Skagerrak and Kattegat from the same sources and show a similar environmental behavior.

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In the Baltic Sea, the most prevalent substance is UV-360, which accounted for ~ 40% of the total UV stabilizer contamination, followed by OC and HMS, both accounting for 15%. In the Skagerrak and Kattegat as well as in the Baltic Sea, benzotriazole derivatives are the prevalent substance class ($\geq 60\%$), while their contribution is only ~ 10% in the North Sea.

The Oder River is one of the seven major rivers entering the Baltic Sea. In parts, it is the border river between Germany and Poland and discharges into the Baltic Sea through the Oder Lagoon. Interestingly, many substances identified in the Baltic Sea are not detected in the Oder Lagoon, indicating that the Oder River might not be a major source of UV stabilizers in the Baltic Sea. UV-360 and OC are present all along the coast, with highest concentrations (4.0 ng/g dw and 1.7 ng/g dw, respectively) close to the beach resort Eckernförde. In Europe, both substances are allowed in cosmetic products (European Commission, 2018d). As these samples were taken in September, the presence of both substances could be explained by a direct input via recreational activities over the summer. This is consistent with the study conducted by Fisch et al. (2017), which identified recreational activities as the major source of OC in coastal waters from the Baltic Sea. HMS is found in highest concentrations east of Rügen. In Europe, HMS is also allowed in PCPs, but shows only a low prevalence in analyzed products (Manova et al., 2013; Wahie et al., 2007). Therefore, recreational activities seem an unlikely contamination source. A potential source could be the direct input from offshore activities, as the Baltic Sea is intensively used, e.g., as a site for offshore wind energy farms. Alternatively, HMS could be discharged into the Baltic Sea somewhere outside of the sampling area and be transported (e.g., adsorbed to SPM) to that region.

In comparison, the described region-specific contamination differences over the study area can be explained by different sources and input pathways. The results suggest river discharges as major sources of UV stabilizers into the German Bight and reveal only a smaller impact of bathing sites. In the Baltic Sea, mainly recreational activities were identified as sources along the coastline. For the Skagerrak and Kattegat, the contamination source could not be identified and it must be noted that the sediments were sampled during winter, while all other sampling campaigns took place during summer. Different sediment properties over the study areas (e.g., more sandy sediments in the German Bight) might have an influence, but there is no indication in the results.

5.2.4 Correlation with TOC

The TOC contents ranged from 0.03 to 6.13% (Table 37). A Pearson correlation analysis showed no correlation between concentrations of UV stabilizers and the TOC content in the analyzed sediments (Figure 17). This agrees with the results from the Chinese Bohai and Yellow Seas and can be explained similarly (chapter 5.1.4).

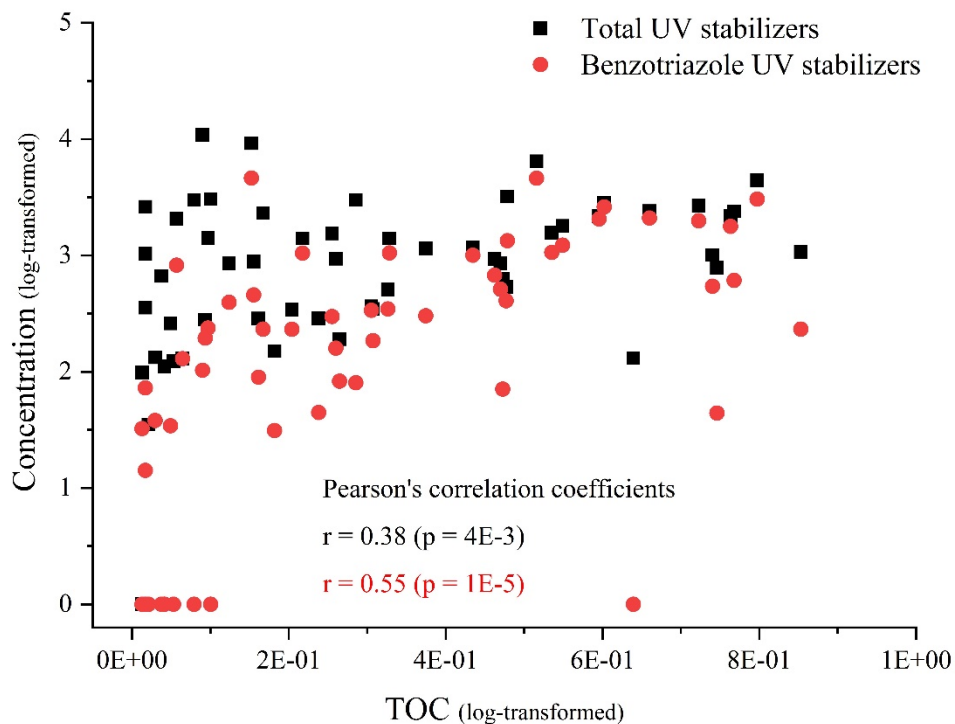


Figure 17: Logarithmically transformed values of total UV stabilizer concentrations plotted against the TOC content of each sample. The Pearson correlation coefficient was calculated using OriginPro 9.1 (OriginLab Corporation).

5.3 Comparison between China and Europe

The geographical structures of the Bohai and Yellow Seas are similar to the ones of the Baltic and North Seas, allowing a direct and meaningful comparison of both study areas (see chapters 5.1.1 and 5.2.1).

As EHT, UV-360, and BM-DBM were not analyzed (or quantified) in the Chinese sediments, these three substances were excluded for the comparison. As no river mouths were sampled in China, the samples from the Rhine-Meuse-Delta, the Elbe estuary, and the Oder Lagoon were also excluded for the comparison.

Table 26: Marine concentration comparison between China and Europe.

	China	Europe
Mean Σ UV stabilizer concentrations	2.0 ng/g dw	1.1 ng/g dw
Highest Σ UV stabilizer concentrations	26 ng/g dw	10.2 ng/d dw
Highest single substance concentration	25 ng/g dw for OC	9.7 ng/g dw for OC

Table 26 gives a comparison of UV stabilizer concentrations in the coastal and marine environment of China and Europe. The concentrations found in these two study areas are in the same order of magnitude and are statistically not significantly different. For other compound classes such as PFASs the observation is another. For example, the concentrations of perfluorooctanoic acid (PFOA) in surface waters of the North Sea were one order of magnitude lower than in the Yellow Sea and two orders of magnitude lower than in the Bohai Sea (Zhao et al., 2017; Zhao et al., 2015a). These observations can be attributed to stricter regulations of PFASs in Europe than in China and the consequential outsourcing of a large part of the fluoropolymer industry to Asian countries (e.g., Heydebreck et al., 2015). For UV stabilizers, the existing regulations in China and Europe are similar (chapter 2.1.3) and it can be concluded that the amount of UV stabilizers released into the environment is alike in both regions.

Figure 18 shows the composition profiles of the found UV stabilizer contamination in China and in Europe. Regarding the whole study areas (Figure 18; upper part), the most noteworthy point is that OC contributes to around 50% of the found contamination in both areas. This result shows again the ubiquitous presence of OC in the marine environment due to its widely disperse and frequent uses in PCPs and industrial materials. OC seems to be an equally important UV stabilizer for both the European and the Chinese industry. Regarding the other half of the found contamination, there are differences between China and Europe. In China, benzotriazole UV stabilizers contribute to 35% with UV-329 as single substance contributing to 14%. EHS contributes to 8%, while all other detected substances (HMS, BP-3, BP-12, EHMC, HALS-445, and OD-PABA) contribute only to 4% in total. In Europe, benzotriazole UV stabilizers contribute to 25%, without a single dominating substance (as UV-360 was excluded for the comparison). HMS contributes to 14%, while all other compounds only contribute to 9%.

Splitting the composition profiles of the whole sampling areas into the different regions (Figure 18; lower part), the characteristic composition profiles that are described in chapters 5.1.3 and 5.2.3 are recognizable.

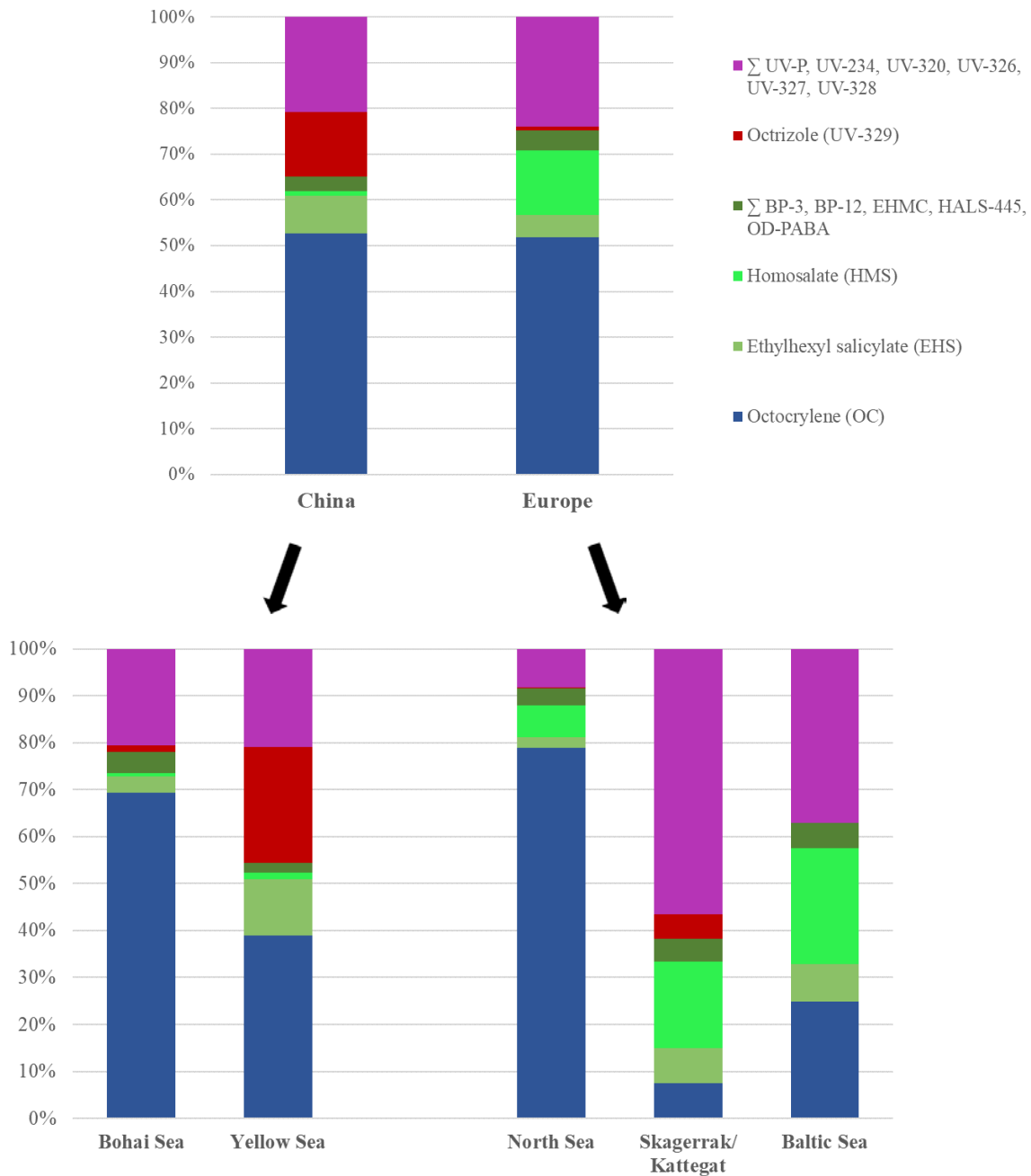


Figure 18: Composition profiles of UV stabilizers in China and Europe.

5.4 Potential environmental hazard¹⁸

While it has been demonstrated that UV stabilizers pose a risk to aquatic organisms (Sanchez Rodriguez et al., 2015; Tsui et al., 2014), only few studies reported sediment toxicity data and investigated the ecotoxicological impact on benthic organisms, which are especially affected by hydrophobic substances.

Tsui et al. (2015) evaluated the probabilistic risk of EHMC (up to 447 ng/g dw, Table 5) for sediment associated organisms. They found it to be > 30% and > 80% in both Hong Kong and Tokyo Bay for the different species. The calculated risk to fish was lower than 20%, but due to their high lipophilicity, UV stabilizers may still pose a threat to aquatic organisms at higher trophic levels by entering the food chain. Using both *in vivo* and predicted toxicity data, preliminary hazard estimations were carried out for six UV stabilizers (OC, EHS, HMS, BP-3, 4-MBC, and EHMC) that were present in the sediment from the Atlantic Coast of Andalusia (Pintado-Herrera et al., 2017a) and of the Pearl River estuary (Pintado-Herrera et al., 2017b). At both sites, two substances (EHMC and 4-MBC) were found to possibly pose a risk to benthic species.

In the present study, a hazard assessment was carried out for those UV stabilizers that were detected in the present study and for which sediment toxicity data were available (Table 28). Due to limited information, the potential hazard could only be estimated for twelve of nineteen identified substances (BM-DBM, BP-3, BP-12, EHMC, EHS, EHT, HMS, OC, OD-PABA, UV-P, UV-328, and UV-360). It must be stressed that *in vivo* toxicity data for benthic organisms were sparse. Information on the hazard assessment procedure and the ranking criteria is given in chapter 7.4.

Table 27: Highest found concentration and calculated hazard quotient (HQ) of each UV stabilizer.

UV stabilizer	BM-DBM	BP-3	BP-12	EHMC	EHS	EHT
Highest found concentration [ng/g dw]	0.70	0.09	1.8	0.32	1.35	2.0
Study Area	German Bight	Oder Lagoon	Rhine-Meuse-Delta	German Bight	Yellow Sea	Rhine-Meuse-Delta
HQ value	< 0.001	0.014	< 0.001	0.400	0.023	< 0.001

UV stabilizer	HMS	OC	OD-PABA	UV-P	UV-328	UV-360
Highest found concentration [ng/g dw]	0.94	25	0.015	0.25	0.88	4.0
Study Area	Yellow Sea	Laizhou Bay	Elbe Estuary	Rhine-Meuse-Delta	German Baltic Sea	German Baltic Sea
HQ value	0.043	0.139	0.004	0.018	< 0.001	< 0.001

¹⁸ published in Apel, C.; Tang, J. and R. Ebinghaus (2018). *Environmental Pollution* **235**: 85-94 and Apel, C; Joerss, H. and R. Ebinghaus (2018). *Chemosphere* **212**: 254-261.

The highest calculated hazard quotients (HQs) of each UV stabilizer are summarized in Table 27. The HQ values for UV stabilizers in the Bohai and Yellow Seas and in the North and Baltic Seas were < 1 in all cases, indicating that UV stabilizers most likely do not negatively affect benthic organisms in both regions. Highest HQ values were found for EHMC and OC with 0.40 and 0.14, respectively. The calculated HQ values of all other UV stabilizers were < 0.1 . Due to potential bioaccumulation and biomagnification in the marine food web (Peng et al., 2017a), the reported environmental concentrations could still pose a hazard to benthic species and species at a higher trophic level. Moreover, information on the potential synergistic toxicity of UV stabilizers in mixtures is sparse. Effects of a mixture might occur at lower concentrations levels (chapter 2.1.2). More *in vivo* sediment toxicity data for sediment-associated species are needed to fill this gap in knowledge.

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Table 28: Sediment toxicity data of analyzed UV stabilizers.

UV stabilizer	Organism	Toxicity data [ng/g]	Assessment Factor	PNEC _{sed} [ng/g]	Reference
4-MBC	Worm (<i>Lumbriculus variegatus</i>)	PNEC = 51.5	-	51.5	ECHA (2018c)
BM-DBM	Two snail species and zebrafish	No effects (10 - 1000 µg/g)	-	-	Kaiser et al. (2012a)
BM-DBM	N/A	PNEC = 11,960	-	11,960	ECHA (2018c)
BP-3	QSAR	PNEC = 370	-	370	Pintado-Herrera et al. (2017a)
BP-3	N/A	PNEC = 6.6	-	6.6	ECHA (2018c)
BP-12	midge larvae (<i>Chironomus riparius</i>)	PNEC = 10,000	-	10,000	ECHA (2018c)
DBT	N/A	PNEC = 1,750	-	1,750	ECHA (2018c)
EHMC	Snail (<i>Potamopyrus antipodarum</i>)	NOEC = 80	100	0.8	Kaiser et al. (2012a)
EHS	QSAR	PNEC = 60	-	60	Pintado-Herrera et al. (2017a)
EHT	N/A	PNEC = 2,300	-	2,300	ECHA (2018c)
HMS	QSAR	PNEC = 22	-	22	Pintado-Herrera et al. (2017a)
IAMC	N/A	PNEC = 8.75	-	8.75	ECHA (2018c)
OC	Two snail species and zebrafish	No effects (10 - 1000 µg/g)	-	-	Kaiser et al. (2012a)
OC	QSAR	PNEC = 180	-	180	Pintado-Herrera et al. (2017a)
OD-PABA	N/A	PNEC = 4.21	-	4.21	ECHA (2018c)
UV-P	N/A	PNEC = 13.6	-	13.6	ECHA (2018c)
UV-328	N/A	PNEC = 45,100	-	45,100	ECHA (2018c)
UV-360	N/A	PNEC = 8,500	-	8,500	ECHA (2018c)

6 Conclusions and outlook

In this thesis, an analytical method was developed for the trace analysis of twenty-two organic UV stabilizers and one HALS in coastal and marine sediments. The developed analytical method consists of an ASE method for sample extraction with in-cell clean-up and a target LC-MS/MS detection method. Two ionization sources (ESI and APPI) were tested and the APPI source performed better in the sensitive analysis of UV stabilizers in real sediment samples than the ESI source. Due to limited matching mass-labeled internal standards, the APPI source is needed for a reliable quantification of the selected UV stabilizers in real sediments. For ESI analysis, a separate clean-up to remove further matrix components would be needed. The developed ASE and LC-APPI-MS/MS methods show detection and quantification limits suited for low concentrations that are expected in coastal and marine environments. The MDLs range from 0.001 to 0.140 ng/g (dw).

The developed method was successfully applied to provide quantitative environmental data on the spatial distribution of UV stabilizers in the Chinese Bohai and Yellow Seas and in the European North and Baltic Seas for the first time. In total, nineteen out of twenty-two analyzed UV stabilizers and one analyzed HALS were identified in coastal and marine sediments pointing out their presence not only in limnic, riverine, and estuarine systems but also in coastal and marine environments. They occurred ubiquitously over the entire sampling areas in the low ng/g range. The compounds found in highest concentrations in the Bohai and Yellow Seas were OC (25 ng/g dw in the Laizhou Bay) and UV-329 (6.1 ng/g dw around the Shandong Peninsula). The compounds found in highest concentrations in the North and Baltic Seas were again OC (9.7 ng/g dw in the German Bight, close to Heligoland) and the sparsely studied benzotriazole derivative UV-360 (4.0 ng/g dw in the Baltic Sea, close to the beach resort of Eckernförde). The triazine derivative EHT was present in the Rhine-Meuse-Delta and in the German Bight and was quantified in a coastal environment for the first time. No significant differences in concentration ranges were found between China and Europe. OC accounted for around 50% of the contamination in both study areas underlining its widely dispersed and frequent uses as well as its importance for the Chinese and European industries.

Region-specific pollution profiles and distribution pattern were identified, which indicate different sources of UV stabilizers introduced into the study areas. The results suggest that the Chinese Bohai and Yellow Seas were contaminated mainly by indirect sources via riverine input. The same observation was made for the North Sea, while the Baltic Sea seemed to be contaminated mainly through direct inputs (e.g., bathing and swimming).

The ubiquitous presence of UV stabilizers in the investigated coastal and marine sediments underlines the importance of further investigations regarding their impact on these ecosystems. Because of limited environmental toxicity data available, an environmental risk assessment of UV stabilizers in the investigated areas is not yet possible even though a preliminary hazard estimation does not indicate any likely adverse effects for sediment-associated organisms in both study areas.

Overall, it can be concluded that UV stabilizers are a relevant group of ubiquitously present contaminants in the coastal and marine environments of China and Europe. For most compounds, little is known about their environmental behavior. The occurrence of certain UV stabilizers (e.g., OC and HMS) even in off-shore locations suggests long half-life times in the marine environment, especially in marine sediments. More attention should also be given to highly hydrophobic UV stabilizers such as triazine derivatives, which could be an important but so far overlooked group of emerging contaminants. Due to potential bioaccumulation and biomagnification in the marine food web, especially highly hydrophobic substances could pose a hazard to benthic species and species at a higher trophic level. As environmental toxicity data for UV stabilizers are sparse, more sediment toxicity data, especially for benthic organisms, are urgently needed to better understand the impact on the environment and to identify the most impaired organisms and ecosystems.

The obtained information may act as support for ongoing substance evaluations (e.g., under CoRAP) or as basis level if environmental conventions or legislation for UV stabilizers go into effect in the future (e.g., Stockholm Convention; Environmental Quality Standards Directive).

For a better understanding of input pathways and the distribution of UV stabilizers between different environmental compartments, more than one matrix should be analyzed. The sampling of water, SPM, and sediment from the same locations would provide information about the partitioning of UV stabilizers in the environment and would improve the understanding of the input, transport, and possible sinks of UV stabilizers.

Regarding the applied methodology, LC-MS/MS is suitable to analyze pre-selected UV stabilizers in coastal and marine sediments. This target approach is useful and is able to cover typically used UV stabilizers, but it is also limited to a relatively small number of known substances with analytical standards available. The application of non-target methods would be a promising approach to either identify new substances of potential environmental concern or to undertake retrospective screenings in the future. Using non-target methods, possible metabolites and degradation products could also be identified. So far, degradation products or metabolites have been scarcely assessed and, in addition to laboratory experiments, their occurrence should be investigated in the environment.

7 Materials and Methods

7.1 Chemicals

Information on used solvents, gases, laboratory chemicals, native and mass-labeled standards is listed in Tables 29 and 30. For mass-labeled standards without Globally Harmonized System of Classification and Labelling of Chemicals (GHS) information available, the data of the non-labeled substance was adopted.

Table 29: Solvents, gases, and laboratory chemicals used, including safety data information according to the Globally Harmonized System of Classification and Labeling of Chemicals (GHS).





Chemical	Abbreviation/ Acronym	CAS	Producer/Supplier (purity)	Sum formula	H and P statements	Hazard pictograms
Solvents						
Acetone Picograde®	-	67-64-1	LGC Standards (≥ 99.0%)	C ₃ H ₆ O	H225; H319; H336 P210; P241 P303+P361+P353 P305+P351+P338 P405; P501	 Danger
Acetonitrile LiChrosolv®	ACN	75-05-08	Merck (≥ 99.9%)	C ₂ H ₃ N	H225; H319 H302+H312+H332 P210; P240 P302+P352 P305+P351+P338 P403+P233	 Danger
Dichloromethane Picograde®	DCM	75-09-2	LGC Standards (≥ 99.5%)	CH ₂ Cl ₂	H351 P280; P201; P202 P308+P313 P405 P501	 Warning
n-Hexane LiChrosolv®	-	110-54-3	Merck (≥ 99.9%)	C ₆ H ₁₄	H225; H304; H315 H336; H361fd; H373 H411 P210; P240; P273 P301+P330+P331 P302+P352 P314 P403+P233	 Danger

Table 29 (continued)





Chemical	Abbreviation/ Acronym	CAS	Producer/Supplier (purity)	Sum formula	H and P statements	Hazard pictograms
n-Hexane Picograde®	-	110-54-3	LGC Standards (≥ 99.0%)	C ₆ H ₁₄	H225; H304; H315 H336; H361fd; H373 H411 P210; P240; P273 P301+P330+P331 P302+P352 P314 P403+P233	 Danger
Methanol LiChrosolv®	MeOH	67-56-1	Merck (≥ 99.9%)	CH ₄ O	H225; H370 H301+H311+H331 P210; P240; P280 P302+P352 P304+P340 P308+P310 P403+P233	 Danger
Methanol Picograde®	MeOH	67-56-1	LGC Standards (≥ 99.0%)	CH ₄ O	H225; H370 H301+H311+H331 P210; P240; P280 P302+P352 P304+P340 P308+P310 P403+P233	 Danger
2-Propanol LiChrosolv®	IPA	67-63-0	Merck (≥ 99.9%)	C ₃ H ₈ O	H225; H319; H336 P210; P240 P305+P351+P338 P403+P233	 Danger

Table 29 (continued)


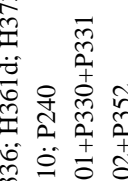


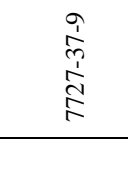
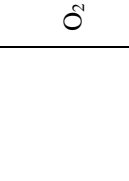
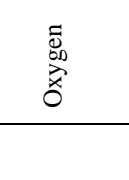
Chemical	Abbreviation/ Acronym	CAS	Producer/Supplier (purity)	Sum formula	H and P statements	Hazard pictograms
Toluene LiChrosolv®	-	108-88-3	Merck (≥ 99.9%)	C ₇ H ₈	H225; H304; H315 H336; H361d; H373 P210; P240 P301+P330+P331 P302+P352 P314 P403+P233	   Danger
Millipore Water supplied by Milli-Q Integral 5	H ₂ O	7732-18-5	Merck (N/A)	H ₂ O	-	-
Gases						
Liquid nitrogen for LC-MS/MS	LN ₂	7727-37-9	Air Liquide (99.99%)	N ₂	H281 P282; P403 P336+P315	 Warning
Nitrogen ALPHAGAZ™ 1	N ₂	7727-37-9	Air Liquide (99.999%)	N ₂	H280 P403	 Warning
Oxygen	O ₂	7782-44-7	Air Liquide (≥ 99.5%)	O ₂	H270; H280 P244; P220; P403 P370+P376	  Danger

Table 29 (continued)


Chemical	Abbreviation/ Acronym	CAS	Producer/Supplier (purity)	Sum formula	H and P statements	Hazard pictograms
Laboratory Chemicals						
Ammonium acetate LC-MS ultra	NH ₄ Ac	631-61-8	Fluka/Sigma- Aldrich (≥ 99.0%)	C ₂ H ₇ NO ₂	-	-
Formic Acid for mass spectrometry	FA	64-18-6	Fluka/Sigma- Aldrich (~98%)	CH ₂ O ₂	H226; H302; H314 H331; EUH071 P210; P280; P284 P301+P330+P331 P302+P352 P304+P340 P305+P351+P338 P308+P313	 Danger
Sea sand	-	14808-60-7	Merck (N/A)	SiO ₂	P260	-
Silica Gel 60 (140 – 70 mesh)	-	N/A	Macherey-Nagel (N/A)	SiO ₂	P260	-
Sodium sulfate Emsure®	Na ₂ SO ₄	7757-82-6	Merck (≥ 99.0%)	Na ₂ SO ₄	-	-

Table 30: Native and mass-labeled standards used, including safety data information according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).





Chemical name	Abbr.	Common names	CAS	Producer/Supplier (purity)	Sum formula	H and P statements	Hazard pictograms
3-(4-Methylbenzylidene) camphor	4-MBC	Enzacamene	36861-47-9 (EU) 38102-62-4 (US)	Sigma-Aldrich (99.9%)	C ₁₈ H ₂₂ O	H361 P281	 Warning
1-(4-(tert-Butylphenyl)-3-(4-methoxyphenyl) propane-1,3-dione	BM-DBM	Avobenzone	70356-09-1	TCI Deutschland GmbH (98.7%)	C ₂₀ H ₂₂ O ₃	H410 P273; P501	 Warning
2-Hydroxy-4-methoxybenzophenone	BP-3	Oxybenzone; Benzophenone 3	131-57-7	TCI Deutschland GmbH (99.9%)	C ₁₄ H ₁₂ O ₃	H315; H319; H400 H410 P273; P264; P280 P305+P351+P338 P337+P313 P302+P352 P332+P313 P362; P391; P501	 Warning
2-Hydroxy-4- <i>n</i> -octyloxybenzophenone	BP-12	Octabenzone	1843-05-6	TCI Deutschland GmbH (99.9%)	C ₂₁ H ₂₆ O ₃	H315; H319 P264; P280 P305+P351+P338 P337+P313 P302+P352 P332+P313 P362	 Warning

Table 30 (continued).


Chemical name	Abbr.	Common names	CAS	Producer/ Supplier (purity)	Sum formula	H and P statements	Hazard pictograms
4,4'-[[6-[[4-[[[(1,1-dimethylethyl)amino]carbon yl]phenyl]amino]-1,3,5- triazine-2,4- diyl]diimino]bis-, bis(2- ethylhexyl) benzoate	DBT	Iscotrizinol	154702-15-5	Sigma-Aldrich (99,5%)	C ₄₄ H ₅₉ N ₇ O ₅	-	-
Ethylhexyl methoxycinnamate	EHMC	Octinoxat	5466-77-3	Sigma-Aldrich (98,4%)	C ₁₈ H ₂₆ O ₃	-	-
Benzoic acid, 2-hydroxy-, 2- ethylhexyl ester	EHS	Ethylhexyl salicylate/ Octisalate	118-60-5	TCI Deutschland GmbH (98,5%)	C ₁₅ H ₂₂ O ₃	H319 P280 P305+P351+P338 P337+P313 P264	 Warning
2,4,6-Trianiilino-(p-carbo-2'- ethylhexyl-1'-oxy)-1,3,5- triazine	EHT	-	88122-99-0	Sigma-Aldrich (98,8%)	C ₄₈ H ₆₆ N ₆ O ₆	H413	-
Bis[4-(2-phenyl-2- propyl)phenyl] amine	HALS-445	-	10081-67-1	TCI Deutschland GmbH (98,9%)	C ₃₀ H ₃₁ N	-	-
Benzoic acid, 2-hydroxy-, 3,3,5-trimethylcyclohexyl ester	HMS	Homosalate	118-56-9	TCI Deutschland GmbH (99,6%)	C ₁₆ H ₂₂ O ₃	-	-
Isoamyl methoxycinnamate	IAMC	Amiloxate	71617-10-2	TCI Deutschland GmbH (99,2%)	C ₁₅ H ₂₀ O ₃	-	-

Table 30 (continued).




Chemical name	Abbr.	Common names	CAS	Producer/ Supplier (purity)	Sum formula	H and P statements	Hazard pictograms
2-Ethylhexyl-2-cyano-3,3-diphenyl-2-propenoate	OC	Octocrylene	6197-30-4	Sigma-Aldrich (99.2%)	$C_{24}H_{27}NO_2$	H413	-
2-Ethylhexyl 4-(dimethylamino) benzoate	OD-PABA	Padimate O	21245-02-3	TCI Deutschland GmbH (99.1%)	$C_{17}H_{27}NO_2$	H315; H319 P264; P280 P305+P351+P338 P337+P313 P302+P352 P332+P313 P362	 Warning
2-(Benzotriazol-2-yl)-4-methylphenol	UV-P	Drometrizole	2440-22-4	TCI Deutschland GmbH (99.9%)	$C_{13}H_{11}N_3O$	H320; H317 P261; P272; P280 P305+P351+P338 P337+P313 P302+P352 P333+P313 P264; P363	 Warning
2-(5-tert-Butyl-2-hydroxyphenyl) benzotriazole	UV-PS	-	3147-76-0	TCI Deutschland GmbH (99.6%)	$C_{16}H_{17}N_3O$	H315; H319 P264; P280 P302+P352 P332+P313 P362+P364 P305+P351+P338 P337+P313	 Warning

Table 30 (continued).







Chemical name	Abbr.	Common names	CAS	Producer/ Supplier (purity)	Sum formula	H and P statements	Hazard pictograms
2-(Benzotriazol-2-yl)-4,6-bis(2-phenylpropan-2-yl)phenol	UV-234	-	70321-86-7	TCI Deutschland GmbH (99.9%)	$C_{30}H_{29}N_3O$	H315; H319 P264; P280 P305+P351+P338 P337+P313 P302+P352 P332+P313 P362	 Warning
2-(Benzotriazol-2-yl)-4,6-di-tert-butylphenol	UV-320	-	3846-71-7	amchro GmbH (100%)	$C_{20}H_{25}N_3O$	H302; H313 H333; H335 P202; P235; P262 P264; P284; P338 P360; P404	  Warning
2-tert-Butyl-6-(5-chlorobenzotriazol-2-yl)-4-methylphenol	UV-326	Bumetrizole	3896-11-5	Sigma-Aldrich (99.6%)	$C_{17}H_{18}ClN_3O$	H315; H319 P264; P280 P302+P352 P332+P313+P362 P305+P351+P338 P337+P313	 Warning
2,4-ditert-Butyl-6-(5-chlorobenzotriazol-2-yl)phenol	UV-327	-	3864-99-1	Sigma-Aldrich (99.9%)	$C_{20}H_{24}ClN_3O$	H315; H319; H335 P261 P305+P351+P338	 Warning
2-(Benzotriazol-2-yl)-4,6-bis-(1,1-dimethylpropyl)phenol	UV-328	-	25973-55-1	Sigma-Aldrich (99.9%)	$C_{22}H_{29}N_3O$	H315; H319 H335; H413 P261 P305+P351+P338	 Warning

Table 30 (continued).



Chemical name	Abbr.	Common names	CAS	Producer/ Supplier (purity)	Sum formula	H and P statements	Hazard pictograms
2-(Benzotriazol-2-yl)-4-(2,4,4-trimethylpentan-2-yl)phenol	UV-329	Octrizole	3147-75-9	TCI Deutschland GmbH (99.9%)	$C_{20}H_{25}N_3O$	H315; H319 P264; P280 P305+P351+P338 P337+P313 P302+P352 P332+P313 P362	 Warning
2-(Benzotriazol-2-yl)-6-butan-2-yl-4-tert-butylphenol	UV-350	-	36437-37-3	amchro GmbH (99.3%)	$C_{20}H_{25}N_3O$	H303; H313 H333; H335 P202; P235; P262 P264; P284; P338 P360; P404	- Warning
2,2'-Methylene bis[4-(1,1,3,3-tetramethylbutyl)-6-2H-benzotriazole-2-yl]phenol]	UV-360	Bisoctrizole	103597-45-1	Sigma Aldrich (99.0%)	$C_{41}H_{50}N_6O_2$	H413 P273; P501	-
2-(Benzotriazol-2-yl)-4-methyl-6-(2-propenyl)phenol	Allyl-bzt	-	2170-39-0	amchro GmbH (100%)	$C_{16}H_{15}N_3O$	-	-
3-(4-Methylbenzylidene-d ₄)camphor	4-MBC-d₄	Enzacamene-d ₄	1219806-41-3	CDN Isotopes (>98%)	$C_{18}D_4H_{18}O$	H361 P281	 Warning

Table 30 (continued).





Chemical name	Abbr.	Common names	CAS	Producer/Supplier (purity)	Sum formula	H and P statements	Hazard pictograms
Benzophenone-d ₁₀	BP-d₁₀	Benzophenone-d ₁₀	22583-75-1	Sigma Aldrich (99.1%)	C ₁₃ D ₁₀ O	H410	 Warning
2-Hydroxy-4-methoxybenzophenone- ¹³ C ₆ (in acetonitrile)	BP-3-¹³C₆	Oxybenzone- ¹³ C ₆ ; Benzophenone 3- ¹³ C ₆	N/A	Cambridge Isotope Laboratories (>98%)	¹³ C ₆ H ₈ O ₃	See information on acetonitrile (Table 29)	
Diethylhexyl butamido triazone-d ₄	DBT-d₄	Iscotrizinol-d ₄	N/A	ASCA GmbH (98.7%)	C ₄₄ D ₄ H ₅₅ N ₇ O ₅	-	-
2-Ethyl-d ₅ -hexyl-2,3,4,4,5,5,6,6-d ₁₀ 4-methoxycinnamate	EHMC-d₁₅	-	N/A	Sigma-Aldrich (98.2%)	C ₁₈ D ₁₅ H ₁₁ O ₃	-	-
Ethylhexyl triazone-d ₄	EHT-d₄	-	N/A	ASCA GmbH (99.7%)	C ₄₈ D ₄ H ₆₂ N ₆ O ₆	H413	-
Perfluoro-1-[¹³ C ₈]-octanesulfonamide (in methanol)	FOSA-¹³C₈	-	N/A	CAMPRO Scientific GmbH (>99%)	¹³ C ₈ F ₁₇ H ₂ NSO ₂	See information on methanol (Table 29)	
2-Hydroxybenzoic-d ₄ acid 3,3,5-trimethylcyclohexyl ester	HMS-d₄	Homosalate-d ₄	N/A	Sigma-Aldrich (98.2%)	C ₁₆ D ₄ H ₁₈ O ₃	H315, H319;H336 P280 P304+P340+P312 P305+P351+P338 P337+P313	 Warning
[2-(Ethyl-d ₅)-hexyl-2,3,3,4,4,5,5,6,6,6-d ₁₀] 2-cyano-3,3-diphenylacrylate	OC-d₁₅	Octocrylene-d ₁₅	N/A	Sigma-Aldrich (99.7%)	C ₂₄ D ₁₅ H ₁₂ NO ₂	H413	-

Table 30 (continued).

Chemical name	Abbr.	Common names	CAS	Producer/Supplier (purity)	Sum formula	H and P statements	Hazard pictograms
2-(2-Hydroxy-5-methylphenyl)benzotriazole-d ₄	UV-P-d₄	Drometrizole-d ₄	N/A	CAMPRO Scientific GmbH (99.0%)	C ₁₃ D ₄ H ₇ N ₃ O	H320; H317 P261; P272; P280 P305+P351+P338 P337+P313 P302+P352 P333+P313 P264; P363	 Warning
2-Benzotriazol-2-yl-4,6-bis-(1,1-dimethyl-propyl)-phenol-d ₄	UV-328-d₄	-	N/A	CAMPRO Scientific GmbH (99.0%)	C ₂₂ D ₄ H ₂₅ N ₃ O	H315; H319 H335; H413 P261 P305+P351+P338	 Warning
2,2'-Methylene bis[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol-d ₄]	UV-360-d₈	Bisoctrizole-d ₈	N/A	CAMPRO Scientific GmbH (99.2%)	C ₄₁ D ₈ H ₄₂ N ₆ O ₂	H413 P273; P501	-

7.2 Total organic carbon (TOC) analysis

TOC is the amount of organic carbon present in a solid sample such as sediment. Depending on their physicochemical properties, many organic contaminants preferably adsorb to the organic part of a sample resulting in a positive correlation of TOC amounts and substance concentrations (e.g., shown for some perfluoroalkyl acids (Zhao et al., 2015b) and synthetic musks (Huang et al., 2016)).

TOC analysis of sediment samples was performed using a LECO RC612 multiphase carbon/hydrogen/moisture determinator (Germany). For this, aliquots of freeze-dried sediment samples from the Bohai and Yellow Seas, and aliquots of North and Baltic Seas samples (dried at 40 °C until reaching constant weight) were used. For quantitative determination, the organic carbon is oxidized by running a temperature program from 150 °C to 400 °C at 70 °C/min in an oxygen flow and the formed carbon dioxide (CO₂) is IR-detected. The final temperature was held for 2 minutes. The quantification limit is 0.03 mg carbon (absolute), which equals a TOC amount of 0.006% in a 500 mg sample. All measurements were done in duplicate. Mean TOC values of the analyzed samples are listed in Tables 31 and 37.

7.3 Statistics

Statistical methods were used to test for significant differences of UV stabilizer concentrations between regions and to test for correlations between single UV stabilizers and TOC. All statistical analyses were done using OriginPro 9.1 (OriginLab Corporation). Concentration values < MDL were treated as zero and for concentration values < MQL the calculated concentration value was used.

First, the Kolmogorov-Smirnov normality test was performed and UV stabilizer concentrations and TOC contents were log₁₀-transformed whenever they were not normally distributed ($p < 0.05$). To test for significant differences in concentration levels in different parts of the study areas, the Levene test for homogeneity of variances was conducted, followed by a one-way ANOVA test coupled with a Turkey post-hoc test (all at a significance level of 0.05). A Pearson correlation analysis was performed to test for correlations among UV stabilizer concentrations and TOC contents.

7.4 Hazard assessment

A sediment effects assessment is only reasonable for substances with $\log K_{oc}$ or $\log K_{ow} \geq 3$, as they are likely sorbed to sediment (European Commission, 2003). This is complied by all tested substances (see Table 2).

The performed hazard assessment is based on estimated hazard quotients (HQs), as described in the literature (e.g., Combi et al., 2016; Molins-Delgado et al., 2016; Pintado-Herrera et al., 2017a; Pintado-Herrera et al., 2017b). For this, HQ values were calculated as the ratio of measured environmental concentrations (MECs) obtained from this study and predicted no effect concentrations (PNECs) obtained from the literature (Eq. 3). PNEC values were calculated from toxicity data whenever needed by using an assessment factor approach (European Commission, 2003; Liu et al., 2015). PNEC values were derived from EC_{50}/LC_{50} divided by an assessment factor of 1000 in case of acute toxicity data or from no observed effects concentrations (NOECs) divided by an assessment factor of 100.

(Eq. 3)
$$HQ = \frac{MEC}{PNEC}$$

The sediment toxicity data used for HQ calculation are listed in Table 28. The individual MECs in the study areas are listed in Tables 34 and 40. The evaluation followed common ranking criteria (e.g., Sanchez Rodriguez et al., 2015 and Pintado-Herrera et al., 2017b), in which $HQ < 1$ means no potential adverse effects are expected and $HQ \geq 1$ indicates that potential adverse effects might occur and a risk evaluation is recommended.

Appendix A: Supplementary material for chapter 5

A.1 Chinese Bohai and Yellow Seas

The appendix A.1 provides additional information to chapter 5.1. Appendix A.1.1 summarizes the sampling information and the TOC content of each sediment sample and gives an overview of the entire sampling area. Appendix A.1.2 provides MDLs, MQLs, and UV stabilizer concentrations in procedural blanks. Appendix A.1.3 presents single UV stabilizer concentrations in all analyzed samples, as well as means, medians, and detection frequencies (d.f.). Appendix A.1.4 shows the Person Correlation results for benzotriazole UV stabilizers around the Shandong Peninsula.

A.1.1 Study area and sampling information

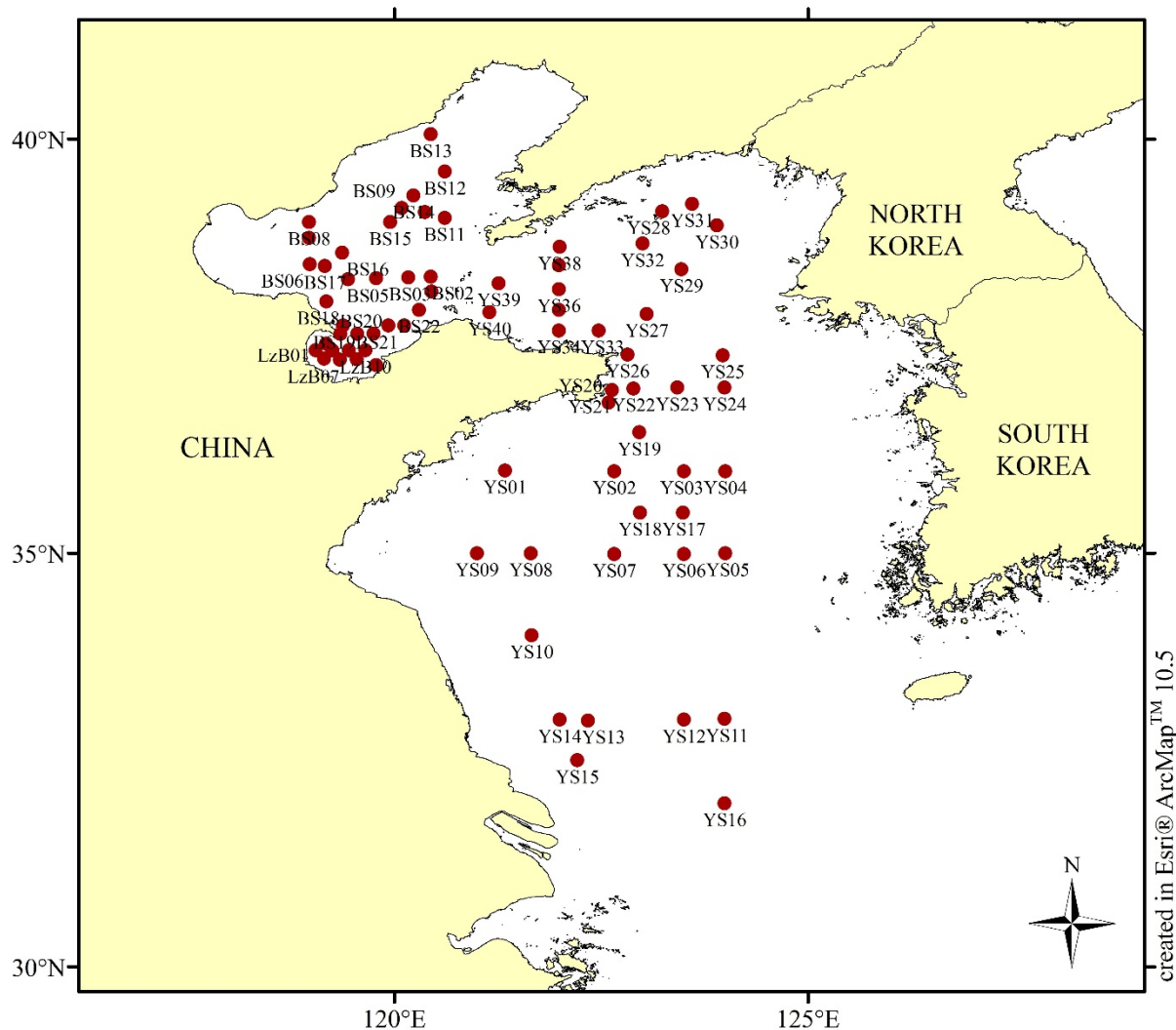


Figure 19: Overview of sampling locations in the Bohai and Yellow Seas.

Table 31: Detailed sampling information and Total Organic Carbon (TOC) contents.

Sampling Area	Station	Sampling date	Latitude °N	Longitude °E	Water depth [m]	TOC [%]
Laizhou Bay	LzB01	02.07.2016	37.45	119.05	5.5	0.19
	LzB02	02.07.2016	37.35	119.15	6.5	0.21
	LzB03	02.07.2016	37.45	119.25	8.5	0.23
	LzB04	02.07.2016	37.53	119.18	4	0.03
	LzB05	02.07.2016	37.65	119.35	8	0.06
	LzB06	02.07.2016	37.45	119.45	11.5	0.27
	LzB07	02.07.2016	37.34	119.34	8.5	0.18
	LzB08	03.07.2016	37.34	119.55	10.5	0.10
	LzB09	03.07.2016	37.27	119.78	8	0.12
	LzB10	03.07.2016	37.45	119.65	13	0.12
	LzB11	03.07.2016	37.65	119.55	14	0.19
	LzB12	03.07.2016	37.65	119.75	15	0.19
Yellow Sea	YS01	29.06.2016	36.00	121.34	37	0.24
	YS02	29.06.2016	35.99	122.66	65	0.83
	YS03	29.06.2016	35.99	123.50	75	0.87
	YS04	30.06.2016	35.99	124.00	77	0.72
	YS05	30.06.2016	35.00	124.00	81	0.44
	YS06	30.06.2016	34.99	123.50	72	0.58
	YS07	30.06.2016	34.99	122.66	70	0.64
	YS08	01.07.2016	35.00	121.65	45	0.20
	YS09	01.07.2016	35.00	121.00	35	0.20
	YS10	01.07.2016	34.01	121.66	20	0.16
	YS11	02.07.2016	33.00	123.99	49	0.33
	YS12	03.07.2016	32.99	123.50	37	0.46
	YS13	03.07.2016	32.98	122.34	26	0.28
	YS14	03.07.2016	32.99	122.00	17	0.05
	YS15	03.07.2016	32.50	122.21	23	0.26
	YS16	04.07.2016	31.98	123.99	40	0.15
	YS17	05.07.2016	35.49	123.49	75	0.75
	YS18	05.07.2016	35.49	122.97	71	0.75
	YS19	08.07.2016	36.46	122.96	71	0.58
	YS20	08.07.2016	36.82	122.59	37	0.16
	YS21	08.07.2016	36.97	122.63	30	0.25
	YS22	08.07.2016	36.99	122.89	29	0.18
	YS23	08.07.2016	37.00	123.42	73	0.34
	YS24	08.07.2016	37.00	123.99	75	0.20
	YS25	09.07.2016	37.39	123.97	70	0.14
	YS26	09.07.2016	37.40	122.82	29	0.29
	YS27	09.07.2016	37.89	123.05	61	0.34
	YS28	09.07.2016	39.13	123.24	64	0.11
	YS29	09.07.2016	38.43	123.47	65	0.07
	YS30	10.07.2016	38.96	123.90	54	0.06
	YS31	10.07.2016	39.22	123.60	36	0.11
	YS32	10.07.2016	38.74	123.00	54	0.19
	YS33	10.07.2016	37.69	122.47	27	0.27
	YS34	10.07.2016	37.69	121.99	22	0.18

Sampling Area	Station	Sampling date	Latitude °N	Longitude °E	Water depth [m]	TOC [%]
	YS35	11.07.2016	37.94	121.99	44	0.79
	YS36	11.07.2016	38.19	121.99	54	0.77
	YS37	11.07.2016	38.48	121.99	50	0.53
	YS38	11.07.2016	38.70	122.00	51	0.28
	YS39	11.07.2016	38.26	121.26	40	0.18
	YS40	11.07.2016	37.91	121.15	20	0.29
Bohai Sea	BS01	12.07.2016	38.16	120.45	22	0.41
	BS02	12.07.2016	38.34	120.44	29	0.33
	BS03	12.07.2016	38.33	120.17	28	0.25
	BS04	12.07.2016	38.32	119.78	25	0.36
	BS05	12.07.2016	38.31	119.44	24	0.49
	BS06	12.07.2016	38.49	118.98	23	0.42
	BS07	12.07.2016	38.81	118.97	30	0.21
	BS08	13.07.2016	39.00	118.97	20	0.29
	BS09	13.07.2016	39.17	120.09	22	0.27
	BS10	13.07.2016	39.12	120.37	21	0.10
	BS11	13.07.2016	39.05	120.61	36	0.26
	BS12	13.07.2016	39.61	120.61	29	0.37
	BS13	13.07.2016	40.06	120.44	26	0.40
	BS14	13.07.2016	39.32	120.23	23	0.25
	BS15	13.07.2016	39.00	119.95	22	0.36
	BS16	14.07.2016	38.63	119.37	26	0.57
	BS17	14.07.2016	38.47	119.16	24	0.47
	BS18	14.07.2016	38.04	119.18	14	0.30
	BS19	14.07.2016	37.75	119.38	13	0.27
	BS20	14.07.2016	37.75	119.93	16	0.60
	BS21	14.07.2016	37.75	120.12	16	0.52
	BS22	14.07.2016	37.94	120.30	17	0.26

A.1.2 MDLs, MQLs, and procedural blank concentrations

For blank determination, pre-cleaned sea sand was put into the freeze-drying system together with the wet sediment samples and was treated as sample throughout all following steps. Three procedural blanks were included in every ASE batch. UV stabilizer concentrations in the procedural blanks are given in Table 32. For batches 4, 5, and 6 freshly pre-cleaned sea sand (that has not been in the freeze-drying system) was used as not to use up all of the available sea sand from the freeze-drying (e.g., for a later analysis of the samples for other contaminants).

Table 32: Procedural blank concentrations of UV stabilizers.

UV Stabilizer	Blank values [pg/g]					
	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6
4-MBC	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BP-3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BP-12	1 ± 1	1 ± 1	High blank	17 ± 14	12 ± 11	High blank
EHMC	20 ± 14	29 ± 16	5 ± 1	10 ± 10	11 ± 12	2 ± 0.5
EHS	50 ± 9	31 ± 7	11 ± 2	17 ± 10	24 ± 4	16 ± 6
HALS-445	1 ± 1	< 1	< 1	< 1	< 1	1 ± 2
HMS	4 ± 2	9 ± 2	n.d.	2 ± 2	4 ± 3	n.d.
IAMC	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OC	211 ± 66	150 ± 70	93 ± 40	28 ± 20	56 ± 40	21 ± 6
OD-PABA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
UV-P	4 ± 2	5 ± 1	3 ± 0.4	4 ± 1	6 ± 2	5 ± 1
UV-PS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
UV-234	< 1	1 ± 0.2	< 1	3 ± 3	3 ± 6	< 1
UV-320	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
UV-326	2 ± 2	4 ± 1	< 1	n.d.	n.d.	n.d.
UV-327	6 ± 9	8 ± 5	< 1	12 ± 10	12 ± 15	n.d.
UV-328	4 ± 6	6 ± 2	4 ± 1	4 ± 4	4 ± 5	2 ± 1
UV-329	n.d.	n.d.	4 ± 2	n.d.	1 ± 2	n.d.
UV-350	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

For every sample batch, the MDL and MQL values were calculated from the procedural blanks and analyzed samples separately. The approach is described in chapter 4.2.3. Table 33 presents average MDL and MQL values that were blank corrected and calculated for a sample volume of 8 g dw. For some batches, the MDL and MQL values of some substances are slightly higher due to changes in blank values (e.g., after changing o-rings in the ASE caps). As OC is present in increased concentrations in the sea sand from the freeze-drying (Batch 1, 2, and 3 in Table 32), the MDL and MQL were calculated from the four highest blank values and applied to all six batches. The substances 4-MBC, BP-3, IAMC, UV-PS and UV-350 were not detected in real samples and were not present in blanks, therefore the MDLs and MQLs were calculated over S/N from spiked matrix samples.

Table 33: MDLs and MQLs of UV stabilizers in the Bohai and Yellow Seas.

UV Stabilizer	MDL [ng/g dw]	MQL [ng/g dw]
4-MBC	0.12	0.38
BP-3	0.03	0.10
BP-12	0.01 (batch 1,2) 0.03 (batch 4,5)	0.02 (batch 1,2) 0.10 (batch 4,5)
EHMC	0.02	0.07
EHS	0.02	0.07
HALS-445	0.003	0.010
HMS	0.01	0.03
IAMC	0.02	0.07
OC	0.08	0.28
OD-PABA	0.001	0.004
UV-P	0.004	0.014
UV-PS	0.02	0.07
UV-234	0.01	0.03
UV-320	0.004	0.014
UV-326	0.02	0.06
UV-327	0.02	0.06
UV-328	0.01	0.03
UV-329	0.01	0.04
UV-350	0.01	0.02

A.1.3 UV stabilizer concentrations in the Chinese Bohai and Yellow Seas

Table 34 lists single UV stabilizer concentrations in all analyzed samples and Table 35 shows mean, median, and detection frequency (d.f.) of each UV stabilizer. Concentrations between MDL and MQL are presented in brackets. The concentrations of 4-MBC, BP-3, IAMC, UV-PS and UV-350 were below their respective MDLs in all samples. BP-12 could not be analyzed in all samples due to high blank values in two ASE batches.

Table 34: UV stabilizer concentrations in the Chinese Bohai and Yellow Seas. All reported concentrations are mean values of double determinations.

Sample	Concentrations [ng/g dw]								
	BP-12	EHMC	EHS	HMS	HALS-445	OC	OD-PABA	DBT ¹⁹	EHT ¹⁹
LzB01	<MDL	<MDL	<MDL	<MDL	(0.01)	<MDL	<MDL	yes	yes
LzB02	<MDL	<MDL	<MDL	<MDL	(0.01)	<MDL	<MDL	yes	yes
LzB03	n.a.	<MDL	<MDL	<MDL	(0.01)	<MDL	<MDL	yes	yes
LzB04	<MDL	(0.07)	<MDL	<MDL	<MDL	0.64	<MDL	yes	yes
LzB05	<MDL	(0.13)	<MDL	<MDL	<MDL	<MDL	<MDL	no	no
LzB06	(0.03)	0.22	0.49	<MDL	(0.01)	9.4	<MDL	yes	yes
LzB07	(0.02)	(0.04)	<MDL	<MDL	(0.01)	0.40	<MDL	yes	yes
LzB08	(0.02)	<MDL	1.28	<MDL	<MDL	4.16	<MDL	no	no
LzB09	(0.05)	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	no	yes
LzB10	(0.03)	<MDL	(0.06)	<MDL	<MDL	(0.36)	<MDL	no	no
LzB11	n.a.	<MDL	<MDL	<MDL	(0.01)	<MDL	<MDL	yes	yes
LzB12	(0.07)	<MDL	(0.12)	(0.03)	(0.02)	25.1	<MDL	no	no
BS01	n.a.	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	yes	yes
BS02	n.a.	<MDL	<MDL	<MDL	(0.01)	<MDL	<MDL	yes	yes
BS03	n.a.	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	no	no
BS04	n.a.	0.24	<MDL	0.06	0.02	<MDL	<MDL	no	yes
BS05	n.a.	<MDL	<MDL	<MDL	0.02	<MDL	<MDL	no	no
BS06	0.25	<MDL	(0.07)	(0.05)	0.21	(0.36)	<MDL	yes	yes
BS07	<MDL	<MDL	<MDL	(0.02)	(0.01)	<MDL	<MDL	yes	no
BS08	(0.04)	<MDL	<MDL	(0.03)	0.06	<MDL	<MDL	yes	no
BS09	(0.06)	<MDL	<MDL	(0.02)	0.01	(0.20)	<MDL	no	no
BS10	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	no	no
BS11	<MDL	<MDL	<MDL	<MDL	(0.01)	<MDL	<MDL	no	no
BS12	n.a.	(0.02)	<MDL	<MDL	0.01	<MDL	<MDL	no	no
BS13	<MDL	0.08	(0.03)	0.04	0.01	0.30	<MDL	no	no
BS14	n.a.	(0.02)	<MDL	(0.02)	(0.01)	<MDL	<MDL	no	yes
BS15	(0.03)	<MDL	<MDL	(0.03)	0.02	(0.18)	<MDL	no	yes
BS16	(0.03)	<MDL	(0.04)	<MDL	0.02	(0.20)	<MDL	no	yes
BS17	<MDL	<MDL	<MDL	(0.01)	0.01	(0.11)	<MDL	no	no
BS18	<MDL	<MDL	(0.04)	(0.04)	(0.01)	<MDL	<MDL	yes	yes
BS19	(0.03)	<MDL	<MDL	<MDL	0.02	<MDL	<MDL	yes	yes
BS20	0.17	<MDL	<MDL	(0.02)	0.03	<MDL	<MDL	yes	no

¹⁹ only qualitative; no = not detected or S/N < 3; yes = S/N > 3

Sample	Concentrations [ng/g dw]								
	BP-12	EHMC	EHS	HMS	HALS-445	OC	OD-PABA	DBT ¹⁹	EHT ¹⁹
BS21	n.a.	(0.02)	<MDL	(0.02)	0.02	<MDL	<MDL	yes	yes
BS22	(0.04)	(0.02)	<MDL	(0.01)	(0.01)	<MDL	<MDL	no	yes
YS39	n.a.	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	yes	yes
YS40	n.a.	(0.04)	<MDL	<MDL	<MDL	<MDL	<MDL	no	yes
YS26	0.16	<MDL	<MDL	(0.04)	(0.01)	0.38	<MDL	yes	yes
YS27	<MDL	<MDL	0.91	0.07	(0.01)	2.02	<MDL	no	no
YS33	<MDL	<MDL	<MDL	<MDL	(0.01)	<MDL	<MDL	yes	yes
YS34	<MDL	<MDL	<MDL	(0.01)	(0.01)	<MDL	<MDL	no	yes
YS35	n.a.	(0.04)	<MDL	<MDL	0.04	<MDL	<MDL	yes	yes
YS36	n.a.	<MDL	<MDL	<MDL	0.05	<MDL	<MDL	no	no
YS37	n.a.	(0.03)	0.65	(0.01)	(0.01)	1.74	<MDL	yes	yes
YS38	(0.04)	<MDL	(0.03)	<MDL	(0.01)	<MDL	<MDL	yes	yes
YS28	<MDL	<MDL	1.35	<MDL	<MDL	2.42	<MDL	yes	yes
YS29	<MDL	<MDL	0.71	<MDL	<MDL	1.06	<MDL	no	no
YS30	(0.05)	<MDL	0.38	(0.02)	<MDL	0.49	<MDL	yes	yes
YS31	n.a.	<MDL	0.65	<MDL	<MDL	1.38	<MDL	no	yes
YS32	<MDL	<MDL	0.70	<MDL	(0.01)	1.58	<MDL	no	no
YS19	n.a.	(0.03)	<MDL	<MDL	0.02	<MDL	<MDL	no	yes
YS20	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	no	no
YS21	<MDL	<MDL	0.13	<MDL	0.01	0.70	<MDL	yes	yes
YS22	n.a.	0.08	0.30	0.05	0.18	2.36	0.004	no	no
YS23	n.a.	<MDL	0.44	0.94	<MDL	2.23	<MDL	no	no
YS24	(0.09)	<MDL	(0.04)	0.04	0.09	<MDL	(0.003)	no	yes
YS25	n.a.	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	no	no
YS18	(0.06)	<MDL	0.95	<MDL	<MDL	4.25	<MDL	no	yes
YS01	n.a.	<MDL	(0.08)	<MDL	<MDL	1.60	<MDL	no	yes
YS02	n.a.	(0.02)	<MDL	<MDL	0.02	<MDL	<MDL	no	no
YS03	(0.06)	<MDL	0.76	<MDL	(0.01)	1.95	<MDL	no	yes
YS04	(0.06)	<MDL	0.73	<MDL	<MDL	1.54	<MDL	yes	yes
YS05	<MDL	<MDL	(0.03)	<MDL	<MDL	<MDL	<MDL	no	yes
YS06	<MDL	<MDL	<MDL	<MDL	(0.01)	<MDL	<MDL	no	yes
YS07	<MDL	<MDL	(0.06)	(0.01)	0.05	<MDL	(0.002)	no	yes
YS08	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	no	yes
YS09	<MDL	<MDL	(0.04)	(0.01)	<MDL	0.51	<MDL	no	yes
YS10	(0.09)	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	no	yes
YS11	<MDL	<MDL	0.14	<MDL	<MDL	1.37	<MDL	no	no
YS12	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	no	no
YS13	(0.07)	<MDL	(0.05)	<MDL	(0.01)	1.19	<MDL	no	yes
YS14	<MDL	<MDL	0.08	<MDL	<MDL	0.44	<MDL	no	no
YS15	(0.05)	<MDL	0.40	<MDL	(0.01)	1.98	<MDL	yes	yes
YS16	<MDL	<MDL	0.25	<MDL	<MDL	0.55	<MDL	no	yes
YS17	<MDL	<MDL	0.48	<MDL	0.03	1.47	<MDL	yes	no

Table 34 (continued)

Sample	Concentrations [ng/g dw]						
	UV-P	UV-320	UV-326	UV-327	UV-328	UV-329	UV-234
LzB01	(0.01)	<MDL	0.08	0.25	(0.03)	(0.03)	0.02
LzB02	(0.01)	<MDL	0.06	0.18	(0.03)	0.04	(0.02)
LzB03	(0.01)	<MDL	0.08	0.31	0.04	(0.02)	0.05
LzB04	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
LzB05	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
LzB06	<MDL	<MDL	0.75	0.50	0.16	<MDL	0.05
LzB07	(0.01)	<MDL	0.15	0.33	(0.06)	(0.03)	0.05
LzB08	<MDL	<MDL	0.07	(0.08)	<MDL	<MDL	(0.01)
LzB09	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
LzB10	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
LzB11	0.02	<MDL	(0.06)	0.18	0.04	(0.03)	0.04
LzB12	(0.02)	(0.01)	0.05	(0.15)	0.13	0.04	0.04
BS01	<MDL	<MDL	<MDL	<MDL	(0.01)	(0.02)	(0.01)
BS02	(0.01)	<MDL	<MDL	(0.03)	0.02	0.04	0.04
BS03	<MDL	<MDL	<MDL	<MDL	(0.01)	<MDL	<MDL
BS04	(0.01)	<MDL	(0.05)	(0.04)	0.03	0.03	(0.02)
BS05	0.02	<MDL	0.25	0.23	0.03	0.06	0.04
BS06	<MDL	<MDL	0.15	0.21	0.06	<MDL	0.02
BS07	<MDL	<MDL	0.18	(0.04)	0.04	<MDL	(0.01)
BS08	<MDL	<MDL	0.21	0.18	0.05	0.05	(0.02)
BS09	<MDL	<MDL	0.05	(0.06)	0.06	0.05	0.02
BS10	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	(0.01)
BS11	<MDL	<MDL	(0.02)	<MDL	0.05	(0.03)	0.03
BS12	(0.01)	<MDL	0.11	0.14	(0.02)	(0.03)	(0.02)
BS13	<MDL	<MDL	0.09	0.13	0.05	(0.03)	0.03
BS14	<MDL	<MDL	(0.04)	(0.05)	(0.02)	(0.02)	0.02
BS15	<MDL	<MDL	0.08	0.15	0.12	0.05	0.04
BS16	(0.01)	<MDL	0.09	0.09	0.06	0.04	0.04
BS17	(0.01)	<MDL	0.16	0.24	0.08	<MDL	0.02
BS18	(0.03)	<MDL	0.65	1.22	<MDL	(0.02)	<MDL
BS19	<MDL	<MDL	0.10	0.30	0.06	0.04	0.04
BS20	0.06	<MDL	0.09	0.27	0.11	0.09	0.05
BS21	0.05	<MDL	0.20	0.25	0.06	0.07	0.25
BS22	(0.01)	<MDL	(0.05)	(0.12)	(0.02)	<MDL	<MDL
YS39	<MDL	<MDL	<MDL	<MDL	(0.01)	<MDL	(0.01)
YS40	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
YS26	0.04	0.20	1.96	0.31	0.23	6.1	0.25
YS27	<MDL	<MDL	0.34	0.23	0.11	0.95	(0.08)
YS33	(0.02)	<MDL	1.08	0.66	0.41	3.53	0.33
YS34	<MDL	<MDL	(0.01)	<MDL	<MDL	(0.03)	<MDL
YS35	0.03	<MDL	0.17	0.09	0.30	0.39	0.16
YS36	0.02	<MDL	0.10	0.09	0.12	0.12	0.10
YS37	(0.01)	<MDL	(0.03)	(0.02)	0.11	0.06	0.04
YS38	(0.01)	<MDL	(0.09)	<MDL	<MDL	0.04	<MDL
YS28	<MDL	<MDL	(0.04)	<MDL	<MDL	<MDL	<MDL

Sample	Concentrations [ng/g dw]						
	UV-P	UV-320	UV-326	UV-327	UV-328	UV-329	UV-234
YS29	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
YS30	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
YS31	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
YS32	<MDL	<MDL	(0.04)	<MDL	<MDL	<MDL	(0.03)
YS19	0.03	(0.01)	0.95	0.50	0.32	2.02	0.25
YS20	<MDL	<MDL	0.56	(0.12)	(0.04)	1.40	<MDL
YS21	0.05	<MDL	1.28	1.23	0.10	3.87	0.34
YS22	(0.01)	(0.01)	0.57	0.46	0.12	1.22	0.11
YS23	<MDL	<MDL	<MDL	<MDL	<MDL	(0.02)	<MDL
YS24	0.03	<MDL	0.17	0.20	0.08	0.07	(0.05)
YS25	<MDL	<MDL	<MDL	(0.04)	(0.02)	(0.02)	(0.02)
YS18	0.03	<MDL	<MDL	<MDL	0.07	<MDL	(0.05)
YS01	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
YS02	0.02	<MDL	0.07	(0.05)	0.06	0.08	0.28
YS03	0.02	<MDL	(0.04)	<MDL	0.04	<MDL	0.05
YS04	(0.01)	<MDL	0.15	<MDL	<MDL	0.15	(0.02)
YS05	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
YS06	(0.01)	<MDL	<MDL	<MDL	<MDL	<MDL	(0.01)
YS07	0.02	<MDL	<MDL	<MDL	0.01	(0.06)	0.04
YS08	<MDL	<MDL	0.09	<MDL	<MDL	(0.02)	<MDL
YS09	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
YS10	(0.02)	(0.01)	0.07	<MDL	<MDL	0.36	0.39
YS11	(0.03)	<MDL	<MDL	<MDL	<MDL	(0.04)	<MDL
YS12	0.05	<MDL	<MDL	<MDL	<MDL	(0.08)	(0.02)
YS13	0.06	(0.01)	(0.03)	<MDL	0.02	0.14	0.12
YS14	<MDL	<MDL	<MDL	<MDL	<MDL	0.05	<MDL
YS15	0.06	(0.01)	(0.04)	<MDL	0.02	0.23	0.13
YS16	(0.02)	<MDL	<MDL	<MDL	<MDL	(0.02)	<MDL
YS17	(0.02)	<MDL	(0.05)	(0.02)	0.03	<MDL	0.04

Table 35: Mean, median, and detection frequencies of UV stabilizers in the Chinese Bohai and Yellow Seas.

UV stabilizer	Whole study area (n = 74)				Laizhou Bay (n = 12)				Bohai Sea (excl. Laizhou Bay) (n = 22)				Yellow Sea (n = 40)			
	Mean [ng/g dw]	Median [ng/g dw]	D.f. [%]		Mean [ng/g dw]	Median [ng/g dw]	D.f. [%]		Mean [ng/g dw]	Median [ng/g dw]	D.f. [%]		Mean [ng/g dw]	Median [ng/g dw]	D.f. [%]	
BP-12	0.03 (0.03)	<MDL	46		0.02 (0.02)	0.02 (0.02)	60		0.05 (0.05)	0.03 (0.03)	57		0.03 (0.03)	<MDL	36	
EHMC	0.02 (0.02)	<MDL	22		0.04 (0.04)	<MDL	33		0.02 (0.02)	<MDL	27		<MDL	<MDL	15	
EHS	0.17 (0.17)	<MDL	45		0.16 (0.16)	<MDL	33		<MDL	<MDL	18		0.26 (0.05)	0.05 (0.05)	63	
HALS-445	0.02 (0.02)	0.01 (0.01)	62		0.01 (0.01)	0.01 (0.01)	58		0.02 (0.02)	0.01 (0.01)	86		0.01 (0.01)	<MDL	50	
HMS	0.02 (0.02)	<MDL	32		<MDL	<MDL	8		0.02 (0.02)	0.02 (0.02)	59		0.03 (0.03)	<MDL	25	
OC	1.01 (1.01)	<MDL	46		3.34 (3.34)	0.18 (0.18)	50		<MDL	<MDL	27		0.83 (0.83)	0.46 (0.46)	55	
OD-PABA	<MDL	<MDL	4		-	-	0		-	-	0		<MDL	<MDL	8	
UV-P	0.01 (0.01)	0.01 (0.01)	53		0.01 (0.01)	<MDL	50		0.01 (0.01)	<MDL	45		0.02 (0.02)	0.01 (0.01)	58	
UV-234	0.05 (0.05)	0.02 (0.02)	69		0.02 (0.02)	0.02 (0.02)	67		0.03 (0.03)	0.02 (0.02)	86		0.07 (0.07)	0.02 (0.02)	60	
UV-320	<MDL	<MDL	9		<MDL	<MDL	8		-	-	0		0.006 (0.006)	<MDL	15	
UV-326	0.16 (0.16)	0.05 (0.05)	66		0.11 (0.11)	0.06 (0.06)	67		0.12 (0.12)	0.09 (0.09)	82		0.20 (0.20)	0.04 (0.04)	58	
UV-327	0.13 (0.13)	0.03 (0.03)	54		0.17 (0.17)	0.16 (0.16)	67		0.17 (0.17)	0.13 (0.13)	82		0.10 (0.10)	<MDL	35	
UV-328	0.05 (0.05)	0.02 (0.02)	64		0.04 (0.04)	0.03 (0.03)	58		0.04 (0.04)	0.04 (0.04)	91		0.06 (0.06)	0.01 (0.01)	50	
UV-329	0.30 (0.30)	0.03 (0.03)	65		0.02 (0.02)	0.01 (0.01)	50		0.03 (0.03)	0.03 (0.03)	73		0.53 (0.53)	0.04 (0.04)	65	

A.1.4 Pearson Correlation

Pearson correlations were conducted using OriginPro 9.1 (OriginLab Corporation). Only (\log_{10} -transformed) concentrations showing a normal distribution were used for analyses (Kolmogorov-Smirnov normality test, $p > 0.05$; see chapter 7.3).

Table 36: Pearson correlation among UV stabilizer concentrations around the Shandong Peninsula ($n = 8$).

		UV-326	UV-327	UV-328	UV-329	UV-234
UV-326	Pearson Corr.	1	0.494	0.546	0.983	0.775
	Sig.	--	0.213	0.162	0.000	0.024
UV-327	Pearson Corr.	0.494	1	0.333	0.480	0.823
	Sig.	0.213	--	0.420	0.229	0.012
UV-328	Pearson Corr.	0.546	0.333	1	0.518	0.745
	Sig.	0.162	0.420	--	0.189	0.034
UV-329	Pearson Corr.	0.983	0.480	0.518	1	0.763
	Sig.	0.000	0.229	0.189	--	0.028
UV-234	Pearson Corr.	0.775	0.823	0.745	0.763	1
	Sig.	0.024	0.012	0.034	0.028	--

A.2 European North and Baltic Seas

The appendix A.2 provides additional information to chapter 5.2. Appendix A.2.1 summarizes the sampling information and the TOC content of each sediment sample and gives an overview of the entire sampling area. Appendix A.2.2 provides MDLs, MQLs, and UV stabilizer concentrations in procedural blanks. Appendix A.2.3 presents single UV stabilizer concentrations in all analyzed samples, as well as means, medians, and detection frequencies (d.f.). Appendix A.2.4 shows the Person Correlation results for UV stabilizers in the Skagerrak and Kattegat area.

A.2.1 Study area and sampling information

Table 37: Detailed sampling information and Total Organic Carbon (TOC) contents.

Sampling Area	Station	Sampling date	Latitude [°N]	Longitude [°E]	Water depth [m]	TOC [%]
Rhine-Meuse-Delta	R1	02.10.2015	51.980	4.111	low tide	0.42
	R2	02.10.2015	51.912	4.258	low tide	0.14
	R3	02.10.2015	51.720	4.893	low tide	0.20
North Sea, Skagerrak, Kattegat, Baltic Sea	MSM50/01	06.01.2016	54.063	8.015	23	0.65
	MSM50/02	07.01.2016	54.462	6.275	34	0.10
	MSM50/03	08.01.2016	54.885	5.644	37	0.04
	MSM50/04	09.01.2016	55.532	4.166	33	0.03
	MSM50/05	10.01.2016	57.418	8.452	54	0.03
	MSM50/06	10.01.2016	57.850	9.182	172	0.73
	MSM50/07	10.01.2016	58.034	9.500	427	2.00
	MSM50/08	12.01.2016	58.048	9.581	387	1.95
	MSM50/09	12.01.2016	58.133	9.892	336	1.90
	MSM50/10	13.01.2016	57.892	10.166	79	0.84
	MSM50/11	13.01.2016	57.900	10.733	145	1.02
	MSM50/12	14.01.2016	57.839	10.965	64	0.45
	MSM50/13	14.01.2016	57.586	11.240	51	1.12
	MSM50/14	14.01.2016	57.444	11.369	70	0.60
	MSM50/15	15.01.2016	57.293	11.491	78	1.72
	MSM50/16	16.01.2016	54.128	11.139	24	4.50
	MSM50/17	18.01.2016	54.215	11.593	28	4.80
	MSM50/18	21.01.2016	54.242	11.937	19	0.13
	MSM50/19	23.01.2016	54.885	13.855	48	4.86
	MSM50/20	25.01.2016	54.433	14.063	16	0.04
	MSM50/21	26.01.2016	54.641	13.593	30	0.80
German Bight and Elbe Estuary	E1	06.06.2017	53.882	9.077	-	0.93
	LP1706/01	09.06.2017	53.745	7.126	12	2.01
	LP1706/02	10.06.2017	53.833	7.213	22	0.09
	LP1706/03	10.06.2017	54.053	7.151	34	0.12
	LP1706/04	10.06.2017	54.194	7.882	10	0.26
	LP1706/05	11.06.2017	54.159	7.918	15	0.23
	LP1706/06	11.06.2017	54.162	8.115	20	0.47
	LP1706/07	11.06.2017	54.173	8.303	16	0.33

Sampling Area	Station	Sampling date	Latitude [°N]	Longitude [°E]	Water depth [m]	TOC [%]
	LP1706/08	11.06.2017	54.179	8.497	9	0.04
	LP1706/09	12.06.2017	53.956	8.663	7	0.25
	E2	12.06.2017	53.844	8.970	7	0.82
Baltic Sea	LP1709/01	04.09.2017	54.226	13.322	4	1.03
	LP1709/02	04.09.2017	54.282	13.129	5	6.13
	LP1709/03	05.09.2017	54.364	13.106	6	2.54
	LP1709/04	05.09.2017	54.478	13.057	4	0.07
	LP1709/05	06.09.2017	53.950	11.363	4	0.16
	LP1709/06	06.09.2017	53.929	11.425	4	2.94
	LP1709/07	06.09.2017	53.958	11.430	4	1.13
	LP1709/08	06.09.2017	53.956	11.283	10	3.57
	LP1709/09	07.09.2017	54.075	11.140	21	4.57
	LP1709/10	07.09.2017	54.030	10.829	17	0.43
	LP1709/11	08.09.2017	54.346	10.163	12	5.27
	LP1709/12	09.09.2017	54.435	10.187	17	4.28
	LP1709/13	09.09.2017	54.682	10.501	25	2.43
	LP1709/14	09.09.2017	54.519	10.082	15	0.05
	LP1709/15	09.09.2017	54.465	9.871	21	2.28
	LP1709/16	10.09.2017	54.830	9.909	25	3.00
	LP1709/17	10.09.2017	54.823	9.720	21	3.36
	LP1709/18	10.09.2017	54.831	9.452	16	1.97
Oder Lagoon	SH1	05.09.2017	53.847	13.819	2	1.37
	SH2	05.09.2017	53.738	14.272	3	0.24
	SH3	05.09.2017	53.643	14.544	1	0.52

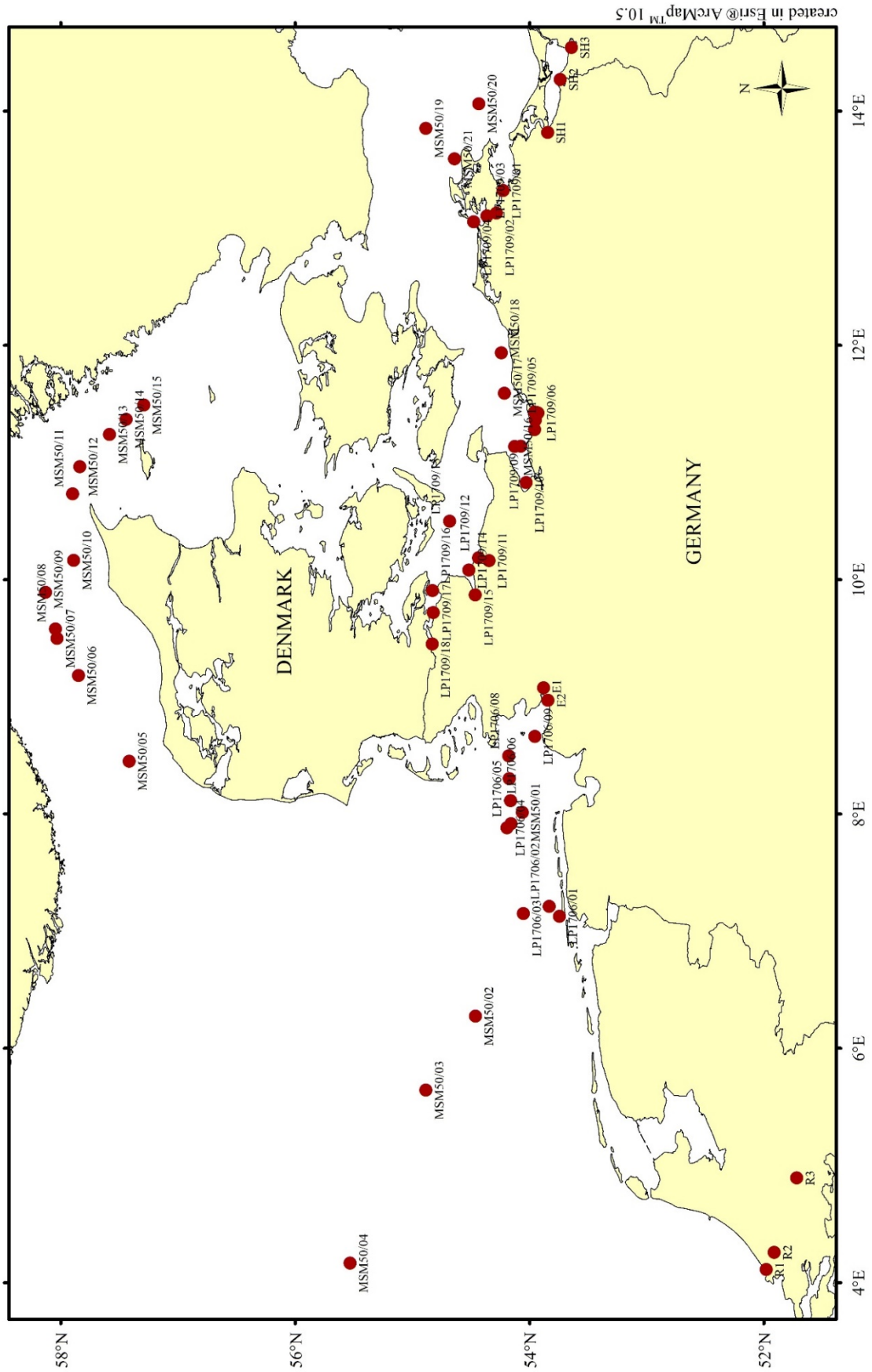


Figure 20: Overview of sampling locations in the North and Baltic Seas.

A.2.2 MDLs, MQLs, and procedural blank concentrations

For blank determination, pre-cleaned sea sand was put into the freeze-drying system together with the wet sediment samples and was treated as sample throughout all following steps. Three procedural blanks were included in every ASE batch. UV stabilizer concentrations in the procedural blanks are given in Table 38.

Table 38: Procedural blank concentrations of UV stabilizers.

UV Stabilizer	Blank values [pg/g]				
	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
4-MBC	n.d.	n.d.	n.d.	n.d.	n.d.
BM-DBM	n.d.	n.d.	n.d.	14 ± 9	5 ± 1
BP-3	n.d.	n.d.	n.d.	5 ± 2	n.d.
BP-12	24 ± 26	9 ± 16 ²⁰	n.d.	n.d.	1 ± 1
EHMC	4 ± 0.5	n.d.	12 ± 2	11 ± 6	3 ± 0.5
EHS	116 ± 11	39 ± 7	69 ± 8	58 ± 8	25 ± 10
EHT	n.a.	n.a.	n.a.	13 ± 4	n.d.
HALS-445	1 ± 1 ²⁰	n.d.	n.d.	5 ± 2	5 ± 3
HMS	68 ± 6	61 ± 10	61 ± 10	38 ± 10	46 ± 11
IAMC	n.d.	n.d.	n.d.	n.d.	n.d.
OC	54 ± 4	36 ± 8	75 ± 7	70 ± 2	27 ± 6
OD-PABA	< 1	n.d.	n.d.	< 1 ²⁰	< 1
UV-P	28 ± 2	33 ± 7	27 ± 7	27 ± 1	18 ± 1
UV-PS	n.d.	n.d.	n.d.	n.d.	n.d.
UV-234	< 1	< 1	2 ± 1	15 ± 7	10 ± 6
UV-320	n.d.	n.d.	n.d.	5 ± 2	9 ± 6
UV-326	n.d.	n.d.	n.d.	17 ± 6	20 ± 8
UV-327	5 ± 0.3	n.d.	n.d.	17 ± 12	13 ± 8
UV-328	5 ± 1	5 ± 2	5 ± 1	14 ± 6	12 ± 6
UV-329	n.d.	n.d.	n.d.	n.d.	5 ± 5
UV-350	n.d.	n.d.	n.d.	4 ± 2	10 ± 6
UV-360	n.d.	9 ± 16 ²⁰	n.d.	12 ± 4	n.d.

For every sample batch, the MDL and MQL values were calculated from the procedural blanks and analyzed samples separately. The approach is described in chapter 4.2.3. Table 39 presents average MDL and MQL values that were blank corrected and calculated for a sample volume of 5 g dw. For some batches, the MDL and MQL values of some substances are slightly higher due to changes in blank values (e.g., after changing o-rings in the ASE caps). The substances 4-MBC, IAMC, and UV-PS were not detected in real samples and were not present in blanks, therefore the MDLs and MQLs were calculated over S/N from spiked matrix samples.

²⁰ a blank value was only detected in one of three procedural blanks

Table 39: MDLs and MQLs of UV stabilizers in the North and Baltic Seas.

UV Stabilizer	MDL [ng/g dw]	MQL [ng/g dw]
4-MBC	0.03	0.10
BM-DBM	0.03	0.09
BP-3	0.01	0.03
BP-12	0.08 (batch 1,2) 0.01 (batch 3-5)	0.26 (batch 1,2) 0.04 (batch 3-5)
EHMC	0.02	0.07
EHS	0.03	0.10
EHT	0.02	0.08
HALS-445	0.01	0.03
HMS	0.03	0.10
IAMC	0.02	0.07
OC	0.03	0.10
OD-PABA	0.002	0.007
UV-P	0.02	0.07
UV-PS	0.02	0.07
UV-234	0.02	0.07
UV-320	0.01	0.03
UV-326	0.04	0.13
UV-327	0.03	0.10
UV-328	0.02	0.07
UV-329	0.02	0.07
UV-350	0.01	0.03
UV-360	0.03	0.11

A.2.3 UV stabilizer concentrations in the European North and Baltic Seas

Table 40 lists single UV stabilizer concentrations in all analyzed samples and Table 41 shows mean, median, and detection frequency (d.f.) of each UV stabilizer. Concentrations between MDL and MQL are presented in brackets. The concentrations of 4-MBC, IAMC, and UV-PS were below their respective MDLs in all samples. EHT was not analyzed (n.a.) in the Baltic Sea.

Table 40: UV stabilizer concentrations in the European North and Baltic Seas. All reported concentrations are mean values of double determinations.

Sample	Concentrations [ng/g dw]												
	BP-3	BP-12	BM-DBM	EHMC	EHS	EHT	HMS	HALS-445	OC	OD-PABA			
R1	0.03	1.78	<MDL	(0.04)	0.28	2.02	0.23	0.06	2.15	<MDL			
R2	<MDL	0.42	<MDL	(0.03)	0.31	0.22	0.21	<MDL	0.27	(0.002)			
R3	<MDL	<MDL	<MDL	<MDL	0.31	<MDL	0.21	<MDL	2.47	<MDL			
E1	<MDL	<MDL	<MDL	<MDL	0.24	<MDL	<MDL	<MDL	2.67	<MDL			
E2	<MDL	<MDL	(0.05)	0.07	(0.06)	<MDL	<MDL	0.05	0.54	0.015			
LP1706/01	(0.01)	0.13	0.69	<MDL	<MDL	0.31	<MDL	<MDL	1.03	<MDL			
LP1706/02	<MDL	<MDL	<MDL	0.32	<MDL	<MDL	<MDL	<MDL	0.34	<MDL			
LP1706/03	<MDL	<MDL	(0.06)	<MDL	<MDL	0.09	<MDL	<MDL	0.19	<MDL			
LP1706/04	<MDL	<MDL	(0.08)	0.12	<MDL	<MDL	0.18	<MDL	2.68	<MDL			
LP1706/05	<MDL	<MDL	0.60	(0.04)	0.11	<MDL	0.29	<MDL	9.7	<MDL			
LP1706/06	<MDL	<MDL	0.46	<MDL	(0.05)	<MDL	0.11	<MDL	1.46	<MDL			
LP1706/07	<MDL	<MDL	<MDL	<MDL	(0.05)	<MDL	0.07	<MDL	0.34	<MDL			
LP1706/08	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.35	<MDL			
LP1706/09	(0.01)	<MDL	0.18	0.07	<MDL	0.13	<MDL	<MDL	0.92	<MDL			
MSM50/01	(0.02)	0.09	<MDL	<MDL	(0.08)	0.14	(0.04)	<MDL	0.13	<MDL			
MSM50/02	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	(0.08)	<MDL	(0.03)	<MDL			
MSM50/03	<MDL	<MDL	<MDL	<MDL	0.20	<MDL	0.64	<MDL	(0.12)	<MDL			
MSM50/04	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	(0.07)	<MDL	<MDL	<MDL			
MSM50/05	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL			
MSM50/06	<MDL	<MDL	<MDL	<MDL	(0.07)	<MDL	0.08	<MDL	0.10	<MDL			
MSM50/07	<MDL	<MDL	<MDL	<MDL	(0.05)	<MDL	0.05	0.02	<MDL	<MDL			
MSM50/08	<MDL	<MDL	<MDL	<MDL	0.19	<MDL	0.11	0.04	<MDL	(0.008)			
MSM50/09	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.14	0.03	0.09	<MDL			
MSM50/10	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.11	<MDL	<MDL	<MDL			
MSM50/11	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.03	<MDL	<MDL			
MSM50/12	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	(0.09)	<MDL	0.10	<MDL			
MSM50/13	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.16	<MDL	<MDL	<MDL			
MSM50/14	<MDL	<MDL	<MDL	<MDL	(0.02)	<MDL	<MDL	0.09	<MDL	<MDL			

Table 40 (continued)

Sample	Concentrations [ng/g dw]										
	BP-3	BP-12	BM-DBM	EHMC	EHS	EHT	HMS	HALS-445	OC	OD-PABA	
MSM50/15	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.09	0.01	(0.06)	<MDL	
MSM50/16	<MDL	<MDL	<MDL	<MDL	0.25	n.a.	<MDL	<MDL	0.21	<MDL	
MSM50/17	<MDL	<MDL	<MDL	(0.04)	0.16	n.a.	(0.03)	0.03	0.14	0.008	
MSM50/18	<MDL	<MDL	<MDL	<MDL	0.12	n.a.	<MDL	<MDL	<MDL	<MDL	
MSM50/19	<MDL	<MDL	<MDL	<MDL	0.22	n.a.	0.89	<MDL	0.66	0.014	
MSM50/20	<MDL	<MDL	<MDL	(0.03)	0.42	n.a.	2.10	<MDL	0.06	<MDL	
MSM50/21	<MDL	<MDL	<MDL	(0.05)	0.38	n.a.	0.64	<MDL	0.17	<MDL	
LP1709/01	<MDL	<MDL	<MDL	<MDL	<MDL	n.a.	(0.03)	<MDL	0.13	<MDL	
LP1709/02	<MDL	<MDL	<MDL	<MDL	0.16	n.a.	0.36	<MDL	0.32	<MDL	
LP1709/03	<MDL	<MDL	<MDL	<MDL	0.09	n.a.	0.10	0.02	0.35	<MDL	
LP1709/04	<MDL	<MDL	<MDL	(0.01)	<MDL	n.a.	<MDL	<MDL	0.08	<MDL	
LP1709/05	<MDL	<MDL	<MDL	<MDL	<MDL	n.a.	<MDL	<MDL	<MDL	<MDL	
LP1709/06	<MDL	<MDL	<MDL	<MDL	<MDL	n.a.	<MDL	0.03	0.08	<MDL	
LP1709/07	<MDL	0.06	0.17	<MDL	<MDL	n.a.	<MDL	<MDL	0.12	<MDL	
LP1709/08	<MDL	<MDL	<MDL	<MDL	<MDL	n.a.	<MDL	0.03	0.28	<MDL	
LP1709/09	<MDL	<MDL	<MDL	<MDL	0.11	n.a.	0.42	<MDL	0.20	<MDL	
LP1709/10	<MDL	<MDL	<MDL	<MDL	(0.04)	n.a.	0.17	<MDL	0.21	<MDL	
LP1709/11	<MDL	<MDL	<MDL	<MDL	<MDL	n.a.	<MDL	0.56	0.81	<MDL	
LP1709/12	<MDL	<MDL	<MDL	(0.06)	<MDL	n.a.	0.36	0.10	0.17	<MDL	
LP1709/13	<MDL	<MDL	<MDL	<MDL	<MDL	n.a.	0.36	0.03	0.12	<MDL	
LP1709/14	<MDL	<MDL	<MDL	<MDL	<MDL	n.a.	(0.04)	<MDL	<MDL	<MDL	
LP1709/15	<MDL	<MDL	<MDL	(0.05)	<MDL	n.a.	<MDL	0.09	1.68	<MDL	
LP1709/16	<MDL	<MDL	<MDL	(0.04)	<MDL	n.a.	<MDL	0.02	0.15	<MDL	
LP1709/17	<MDL	<MDL	<MDL	(0.07)	<MDL	n.a.	(0.06)	<MDL	<MDL	<MDL	
LP1709/18	<MDL	<MDL	<MDL	<MDL	<MDL	n.a.	0.44	<MDL	0.12	<MDL	
SH1	0.09	<MDL	<MDL	<MDL	<MDL	n.a.	<MDL	<MDL	0.76	<MDL	
SH2	<MDL	<MDL	<MDL	<MDL	<MDL	n.a.	<MDL	<MDL	0.09	<MDL	
SH3	<MDL	<MDL	<MDL	<MDL	<MDL	n.a.	<MDL	<MDL	0.12	<MDL	

Table 40 (continued)

Sample	Concentrations [ng/g dw]													
	UV-P	UV-234	UV-320	UV-326	UV-327	UV-328	UV-329	UV-350	UV-360					
R1	0.25	0.33 (0.03)	0.07 (0.01)	0.52 (0.12)	0.40 (0.10)	0.15 (0.02)	0.17 (0.03)	0.07 (0.02)	2.67 (0.37)					
R2	0.13	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL					
R3	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL					
E1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL					
E2	<MDL	0.25 (0.02)	0.03 (0.01)	<MDL	<MDL	<MDL	0.04 (0.04)	0.03 (0.03)	<MDL					
LPI706/01	0.05	0.25 (0.01)	0.01	<MDL	0.17	0.07	<MDL	0.02	0.77					
LPI706/02	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL					
LPI706/03	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.03					
LPI706/04	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL					
LPI706/05	<MDL	0.02	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.08					
LPI706/06	<MDL	0.07	<MDL	0.05	<MDL	0.03	<MDL	<MDL	0.09					
LPI706/07	<MDL	0.04	<MDL	0.02	0.04	<MDL	<MDL	<MDL	0.30					
LPI706/08	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL					
LPI706/09	<MDL	0.05	<MDL	<MDL	<MDL	0.01	<MDL	<MDL	0.17					
MSM50/01	0.24	0.15	0.02	0.15	0.24	0.06	<MDL	<MDL	0.18					
MSM50/02	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL					
MSM50/03	0.07	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL					
MSM50/04	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.03	<MDL	<MDL					
MSM50/05	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL					
MSM50/06	<MDL	0.02	<MDL	<MDL	<MDL	0.02	<MDL	<MDL	<MDL					
MSM50/07	0.03	0.14	<MDL	<MDL	<MDL	0.12	<MDL	<MDL	0.12					
MSM50/08	0.04	0.19	<MDL	<MDL	<MDL	0.15	<MDL	<MDL	0.14					
MSM50/09	0.04	0.24	<MDL	<MDL	0.08	0.15	<MDL	<MDL	0.16					
MSM50/10	0.02	0.05	<MDL	<MDL	<MDL	0.01	<MDL	<MDL	<MDL					
MSM50/11	0.04	0.07	<MDL	<MDL	<MDL	0.04	<MDL	<MDL	0.19					
MSM50/12	0.03	0.04	<MDL	<MDL	<MDL	0.03	<MDL	<MDL	<MDL					
MSM50/13	0.05	0.08	<MDL	<MDL	0.04	0.05	<MDL	<MDL	0.13					
MSM50/14	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.23	<MDL	<MDL					

Table 40 (continued)

Sample	Concentrations [ng/g dw]										
	UV-P	UV-234	UV-320	UV-326	UV-327	UV-328	UV-329	UV-350	UV-360		
MSM50/15	0.10	0.23	<MDL	0.13	0.20	0.14	<MDL	<MDL	0.21		
MSM50/16	(0.04)	0.18	<MDL	<MDL	<MDL	0.16	<MDL	<MDL	0.16		
MSM50/17	<MDL	0.10	<MDL	(0.13)	(0.16)	0.18	<MDL	<MDL	1.20		
MSM50/18	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL		
MSM50/19	0.07	0.11	<MDL	<MDL	(0.16)	0.16	<MDL	<MDL	0.11		
MSM50/20	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	(0.01)		
MSM50/21	(0.01)	0.02	<MDL	<MDL	<MDL	(0.03)	<MDL	<MDL	0.24		
LPI709/01	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.18		
LPI709/02	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.23		
LPI709/03	0.03	0.08	<MDL	0.15	0.11	<MDL	<MDL	<MDL	0.86		
LPI709/04	0.04	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL		
LPI709/05	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.13		
LPI709/06	<MDL	0.11	<MDL	0.97	<MDL	0.17	<MDL	<MDL	0.82		
LPI709/07	<MDL	(0.05)	<MDL	(0.09)	(0.04)	(0.03)	<MDL	<MDL	0.84		
LPI709/08	0.10	0.12	<MDL	(0.30)	<MDL	0.18	<MDL	<MDL	1.39		
LPI709/09	<MDL	0.04	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL		
LPI709/10	<MDL	0.01	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.44		
LPI709/11	0.19	0.62	<MDL	<MDL	<MDL	0.88	<MDL	<MDL	1.35		
LPI709/12	(0.07)	0.44	<MDL	0.72	<MDL	0.43	<MDL	<MDL	0.32		
LPI709/13	<MDL	0.18	<MDL	<MDL	<MDL	0.27	<MDL	<MDL	0.61		
LPI709/14	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL		
LPI709/15	<MDL	0.15	<MDL	(0.30)	<MDL	0.20	<MDL	<MDL	3.97		
LPI709/16	<MDL	0.16	<MDL	<MDL	<MDL	0.23	<MDL	<MDL	2.21		
LPI709/17	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL		
LPI709/18	(0.07)	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL		
SH1	(0.03)	0.07	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.21		
SH2	<MDL	0.02	<MDL	(0.07)	(0.04)	<MDL	<MDL	<MDL	(0.07)		
SH3	<MDL	0.02	<MDL	<MDL	<MDL	(0.01)	<MDL	<MDL	<MDL		

Table 41.: Mean, median, and detection frequencies of UV stabilizers in the European North and Baltic Seas.

UV stabilizer	Whole study area (incl. inflows) (n = 56)				North Sea (n = 13)				Skagerrak and Kattegat (n = 11)				Baltic Sea (n = 24)			
	Mean [ng/g dw]	Median [ng/g dw]	D.f. [%]		Mean [ng/g dw]	Median [ng/g dw]	D.f. [%]		Mean [ng/g dw]	Median [ng/g dw]	D.f. [%]		Mean [ng/g dw]	Median [ng/g dw]	D.f. [%]	
BM-DBM	<MDL	<MDL	14		0.16	<MDL	46		-	-	0		<MDL	<MDL	4	
BP-3	<MDL	<MDL	9		<MDL	<MDL	23		-	-	0		-	-	0	
BP-12	0.04	<MDL	9		(0.02)	<MDL	15		-	-	0		<MDL	<MDL	4	
EHMC	<MDL	<MDL	27		(0.04)	<MDL	31		-	-	0		<MDL	<MDL	33	
EHS	0.07	<MDL	43		(0.04)	<MDL	38		(0.03)	<MDL	36		0.08	<MDL	42	
EHT	-	-	-		(0.05)	<MDL	31		-	-	0		-	-	-	
HALS-445	0.02	<MDL	30		-	-	0		0.02	0.01	55		0.04	<MDL	38	
HMS	0.16	(0.05)	59		0.11	(0.07)	62		(0.08)	(0.09)	73		0.25	(0.03)	58	
OC	0.59	0.14	79		1.33	0.34	92		0.10	<MDL	31		0.25	0.15	83	
OD-PABA	<MDL	<MDL	9		-	-	0		<MDL	<MDL	9		<MDL	<MDL	8	
UV-P	0.03	<MDL	41		0.03	<MDL	23		0.03	0.03	73		(0.03)	<MDL	38	
UV-234	0.08	0.03	64		0.05	<MDL	46		(0.01)	0.07	82		0.10	0.05	63	
UV-320	<MDL	<MDL	9		<MDL	<MDL	15		-	-	0		-	-	0	
UV-326	(0.07)	<MDL	25		<MDL	<MDL	23		<MDL	<MDL	9		(0.11)	<MDL	29	
UV-327	0.03	<MDL	23		0.04	<MDL	23		0.03	<MDL	27		<MDL	<MDL	17	
UV-328	0.07	<MDL	50		(0.01)	<MDL	31		0.06	0.04	82		0.12	(0.01)	50	
UV-329	<MDL	<MDL	9		<MDL	<MDL	8		(0.02)	<MDL	9		-	-	0	
UV-350	<MDL	<MDL	7		<MDL	<MDL	8		-	-	0		-	-	0	
UV-360	0.38	0.12	64		0.13	(0.03)	54		(0.09)	0.12	55		0.63	0.24	75	

A.2.4 Pearson Correlation

Pearson correlations were conducted using OriginPro 9.1 (OriginLab Corporation). Only (\log_{10} -transformed) concentrations showing a normal distribution were used for analyses (Kolmogorov-Smirnov normality test, $p > 0.05$; see chapter 7.3).

Table 42: Pearson correlation among UV stabilizer concentrations in the Skagerrak and Kattegat area ($n = 11$).

		EHS	HMS	UV-P	UV-328	UV-234	UV-360
EHS	Pearson Corr.	1	0.077	-0.115	0.389	0.237	0.086
	Sig.	--	0.822	0.736	0.237	0.484	0.801
HMS	Pearson Corr.	0.077	1	0.461	0.439	0.509	0.250
	Sig.	0.822	--	0.154	0.177	0.110	0.458
UV-P	Pearson Corr.	-0.115	0.461	1	0.680	0.768	0.825
	Sig.	0.736	0.154	--	0.021	0.006	0.002
UV-328	Pearson Corr.	0.389	0.439	0.680	1	0.971	0.794
	Sig.	0.237	0.177	0.021	--	6.55E-07	0.004
UV-234	Pearson Corr.	0.237	0.509	0.768	0.971	1	0.808
	Sig.	0.484	0.110	0.006	6.55E-07	--	0.003
UV-360	Pearson Corr.	0.086	0.250	0.825	0.794	0.808	1
	Sig.	0.801	0.458	0.002	0.004	0.003	--

References

- Agilent Technologies, **2012**. *Agilent 6400 Series Triple Quadrupole LC/MS System Concepts Guide*, Revision A, November 2012 ed. Agilent Technologies.
- Allinson, M., Kameda, Y., Kimura, K., Allinson, G., **2018**. *Occurrence and assessment of the risk of ultraviolet filters and light stabilizers in Victorian estuaries*. *Environ Sci Pollut Res Int* **25**, 12022-12033. doi: 10.1007/s11356-018-1386-7
- Australian Government, **2017**. *Australian regulatory guidelines for sunscreens (ARGS)*, <https://www.tga.gov.au/book/9-permitted-ingredients#s91> (accessed **05/2017**)
- Avagyan, R., Luongo, G., Thorsen, G., Ostman, C., **2015**. *Benzothiazole, benzotriazole, and their derivatives in clothing textiles-a potential source of environmental pollutants and human exposure*. *Environ Sci Pollut Res Int* **22**, 5842-5849. doi: 10.1007/s11356-014-3691-0
- Axelstad, M., Boberg, J., Hougaard, K.S., Christiansen, S., Jacobsen, P.R., Mandrup, K.R., Nellemann, C., Lund, S.P., Hass, U., **2011**. *Effects of pre- and postnatal exposure to the UV-filter octyl methoxycinnamate (OMC) on the reproductive, auditory and neurological development of rat offspring*. *Toxicol Appl Pharmacol* **250**, 278-290. doi: 10.1016/j.taap.2010.10.031
- Baas, J., Jager, T., Kooijman, S.A., **2009**. *A model to analyze effects of complex mixtures on survival*. *Ecotoxicol Environ Saf* **72**, 669-676. doi: 10.1016/j.ecoenv.2008.09.003
- Baas, J., Stefanowicz, A.M., Klimek, B., Laskowski, R., Kooijman, S.A., **2010**. *Model-based experimental design for assessing effects of mixtures of chemicals*. *Environ Pollut* **158**, 115-120. doi: 10.1016/j.envpol.2009.07.030
- Balazs, A., Krifaton, C., Orosz, I., Szoboszlai, S., Kovacs, R., Csenki, Z., Urbanyi, B., Kriszt, B., **2016**. *Hormonal activity, cytotoxicity and developmental toxicity of UV filters*. *Ecotoxicol Environ Saf* **131**, 45-53. doi: 10.1016/j.ecoenv.2016.04.037
- Balmer, M.E., Buser, H.R., Muller, M.D., Poiger, T., **2005**. *Occurrence of some organic UV filters in wastewater, in surface waters, and in fish from Swiss lakes*. *Environ Sci Technol* **39**, 953-962. doi: 10.1021/es040055r
- Barón, E., Gago-Ferrero, P., Gorga, M., Rudolph, I., Mendoza, G., Zapata, A.M., Diaz-Cruz, S., Barra, R., Ocampo-Duque, W., Paez, M., Darbra, R.M., Eljarrat, E., Barcelo, D., **2013**. *Occurrence of hydrophobic organic pollutants (BFRs and UV-filters) in sediments from South America*. *Chemosphere* **92**, 309-316. doi: 10.1016/j.chemosphere.2013.03.032
- BfR, **2018**. *OECD-Programm zur Bewertung von Chemikalien mit hohem Produktionsvolumen*, http://www.bfr.bund.de/de/oecd_programm_zur_bewertung_von_chemikalien_mit_hohem_produktionsvolumen-61590.html (accessed **05/2018**)
- Bluthgen, N., Meili, N., Chew, G., Odermatt, A., Fent, K., **2014**. *Accumulation and effects of the UV-filter octocrylene in adult and embryonic zebrafish (Danio rerio)*. *Sci Total Environ* **476-477**, 207-217. doi: 10.1016/j.scitotenv.2014.01.015
- Bratkovics, S., Wirth, E., Sapozhnikova, Y., Pennington, P., Sanger, D., **2015**. *Baseline monitoring of organic sunscreen compounds along South Carolina's coastal marine environment*. *Mar Pollut Bull* **101**, 370-377. doi: 10.1016/j.marpolbul.2015.10.015
- Brausch, J.M., Rand, G.M., **2011**. *A review of personal care products in the aquatic environment: environmental concentrations and toxicity*. *Chemosphere* **82**, 1518-1532. doi: 10.1016/j.chemosphere.2010.11.018
- BSH, **2013**. *System Nordsee - 2006 & 2007: Zustand und Entwicklungen*, in: Loewe, P., Klein, H., Weigelt-Krenz, S. (Eds.), *Berichte des BSH, Nr. 49*. Bundesamtes für Seeschifffahrt und Hydrographie, Hamburg und Rostock.

References

- Cantwell, M.G., Sullivan, J.C., Katz, D.R., Burgess, R.M., Bradford Hubeny, J., King, J., **2015**. *Source determination of benzotriazoles in sediment cores from two urban estuaries on the Atlantic Coast of the United States*. Mar Pollut Bull **101**, 208-218. doi: 10.1016/j.marpolbul.2015.10.075
- Castro, M., Fernandes, J.O., Pena, A., Cunha, S.C., **2018**. *Occurrence, profile and spatial distribution of UV-filters and musk fragrances in mussels from Portuguese coastline*. Mar Environ Res **138**, 110-118. doi: 10.1016/j.marenvres.2018.04.005
- Chen, L., Li, X., Hong, H., Shi, D., **2017**. *Multigenerational effects of 4-methylbenzylidene camphor (4-MBC) on the survival, development and reproduction of the marine copepod Tigriopus japonicus*. Aquat Toxicol **194**, 94-102. doi: 10.1016/j.aquatox.2017.11.008
- Cole, M., Lindeque, P., Halsband, C., Galloway, T.S., **2011**. *Microplastics as contaminants in the marine environment: a review*. Mar Pollut Bull **62**, 2588-2597. doi: 10.1016/j.marpolbul.2011.09.025
- Combi, T., Pintado-Herrera, M.G., Lara-Martin, P.A., Miserocchi, S., Langone, L., Guerra, R., **2016**. *Distribution and fate of legacy and emerging contaminants along the Adriatic Sea: A comparative study*. Environ Pollut **218**, 1055-1064. doi: 10.1016/j.envpol.2016.08.057
- Cunha, S.C., Fernandes, J.O., Vallecillos, L., Cano-Sancho, G., Domingo, J.L., Pocurull, E., Borrull, F., Maulvault, A.L., Ferrari, F., Fernandez-Tejedor, M., Van den Heuvel, F., Kotterman, M., **2015**. *Co-occurrence of musk fragrances and UV-filters in seafood and macroalgae collected in European hotspots*. Environ Res **143**, 65-71. doi: 10.1016/j.envres.2015.05.003
- Dachs, J., Méjanelle, L., **2010**. *Organic Pollutants in Coastal Waters, Sediments, and Biota: A Relevant Driver for Ecosystems During the Anthropocene?* Estuaries and Coasts **33**, 1-14. doi: 10.1007/s12237-009-9255-8
- Danovaro, R., Bongiorno, L., Corinaldesi, C., Giovannelli, D., Damiani, E., Astolfi, P., Greci, L., Pusceddu, A., **2008**. *Sunscreens cause coral bleaching by promoting viral infections*. Environ Health Perspect **116**, 441-447. doi: 10.1289/ehp.10966
- de Groot, A.C., Roberts, D.W., **2014**. *Contact and photocontact allergy to octocrylene: a review*. Contact Dermatitis **70**, 193-204. doi: 10.1111/cod.12205
- Dennis, B., **2014**. *FDA review of new sunscreen ingredients languishes, frustrating advocates*, https://www.washingtonpost.com/gdpr-consent/?destination=%2fnational%2fhealth-science%2f2014%2f03%2f20%2f85a288-a9fc-11e3-9e82-8064fcd31b5b_story.html%3f (accessed **10/2016**)
- Downs, C.A., Kramarsky-Winter, E., Fauth, J.E., Segal, R., Bronstein, O., Jeger, R., Lichtenfeld, Y., Woodley, C.M., Pennington, P., Kushmaro, A., Loya, Y., **2014**. *Toxicological effects of the sunscreen UV filter, benzophenone-2, on planulae and in vitro cells of the coral, Stylophora pistillata*. Ecotoxicology **23**, 175-191. doi: 10.1007/s10646-013-1161-y
- Downs, C.A., Kramarsky-Winter, E., Segal, R., Fauth, J., Knutson, S., Bronstein, O., Ciner, F.R., Jeger, R., Lichtenfeld, Y., Woodley, C.M., Pennington, P., Cadenas, K., Kushmaro, A., Loya, Y., **2016**. *Toxicopathological Effects of the Sunscreen UV Filter, Oxybenzone (Benzophenone-3), on Coral Planulae and Cultured Primary Cells and Its Environmental Contamination in Hawaii and the U.S. Virgin Islands*. Arch Environ Contam Toxicol **70**, 265-288. doi: 10.1007/s00244-015-0227-7
- ECHA, **2017**. *Substance information on Octocrylene*, <https://echa.europa.eu/de/substance-information/-/substanceinfo/100.025.683> (accessed **11/2017**)
- ECHA, **2018a**. *Candidate List of substances of very high concern for Authorisation*, <https://echa.europa.eu/web/guest/candidate-list-table> (accessed **03/2018**)
- ECHA, **2018b**. *Community Rolling Action Plan (CoRAP): List of Substances*, <https://echa.europa.eu/de/information-on-chemicals/evaluation/community-rolling-action-plan/corap-table> (accessed **03/2018**)

-
- ECHA, **2018c**. *European Chemicals Agency*, www.echa.europa.eu (accessed **04/2018**)
- ECHA, **2018d**. *Registrierte Stoffe*, <https://echa.europa.eu/de/information-on-chemicals/registered-substances> (accessed **10/2018**)
- ECHA, **2018e**. *Vorregistrierte Stoffe*, <https://echa.europa.eu/de/information-on-chemicals/pre-registered-substances> (accessed **10/2018**)
- Ekpeghere, K.I., Kim, U.J., O, S.H., Kim, H.Y., Oh, J.E., **2016**. *Distribution and seasonal occurrence of UV filters in rivers and wastewater treatment plants in Korea*. *Sci Total Environ* **542**, 121-128. doi: 10.1016/j.scitotenv.2015.10.033
- Emnet, P., Gaw, S., Northcott, G., Storey, B., Graham, L., **2015**. *Personal care products and steroid hormones in the Antarctic coastal environment associated with two Antarctic research stations, McMurdo Station and Scott Base*. *Environ Res* **136**, 331-342. doi: 10.1016/j.envres.2014.10.019
- EPA, **2018**. *Contaminants of Emerging Concern including Pharmaceuticals and Personal Care Products*, <https://www.epa.gov/wqc/contaminants-emerging-concern-including-pharmaceuticals-and-personal-care-products> (accessed **11/2018**)
- European Commission, **2003**. *Technical Guidance Document on Risk Assessment in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances, and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market. Part II*.
- European Commission, **2015**. *COMMISSION IMPLEMENTING DECISION (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council*, Official Journal of the European Union.
- European Commission, **2018a**. *CosIng: List of functions*, http://ec.europa.eu/growth/tools-databases/cosing/index.cfm?fuseaction=ref_data.functions (accessed **10/2018**)
- European Commission, **2018b**. *CosIng: Substance information on 2-Hydroxy-4-methoxybenzophenone / Oxybenzone from the EU Regulation*, http://ec.europa.eu/growth/tools-databases/cosing/index.cfm?fuseaction=search.details_v2&id=28809 (accessed **10/2018**)
- European Commission, **2018c**. *CosIng: Substance information on Oxybenzone (INN) from the Cosmetic Directive*, <http://ec.europa.eu/growth/tools-databases/cosing/index.cfm?fuseaction=search.details&id=28809> (accessed **10/2018**)
- European Commission, **2018d**. *Cosmetic ingredient database*, https://ec.europa.eu/growth/sectors/cosmetics/cosing_de (accessed **03/2018**)
- FDA, **2018**. *U.S. Food & Drug Administration. Sunscreen: How to Help Protect Your Skin from the Sun*, <https://www.fda.gov/Drugs/ResourcesForYou/Consumers/BuyingUsingMedicineSafely/Understanding-Over-the-CounterMedicines/ucm239463.htm#ingredients> (accessed **04/2018**)
- Fent, K., Chew, G., Li, J., Gomez, E., **2014**. *Benzotriazole UV-stabilizers and benzotriazole: Antiandrogenic activity in vitro and activation of aryl hydrocarbon receptor pathway in zebrafish eleuthero-embryos*. *Sci Total Environ* **482-483**, 125-136. doi: 10.1016/j.scitotenv.2014.02.109
- Fisch, K., Waniek, J.J., Schulz-Bull, D.E., **2017**. *Occurrence of pharmaceuticals and UV-filters in riverine run-offs and waters of the German Baltic Sea*. *Mar Pollut Bull* **124**, 388-399. doi: 10.1016/j.marpolbul.2017.07.057
- Fischer, S.M., Perkins, P.D., **2005**. *Simultaneous Electrospray and Atmospheric Pressure Chemical Ionization: The Science Behind the Agilent Multimode Ion Source - Technical Overview*, Agilent Technologies.

References

- FoxNews, **2018**. *Pacific island Palau bans sunscreen*, <https://www.foxnews.com/travel/pacific-island-palau-bans-sunscreen> (accessed **11/2018**)
- Gago-Ferrero, P., Diaz-Cruz, M.S., Barcelo, D., **2011**. *Fast pressurized liquid extraction with in-cell purification and analysis by liquid chromatography tandem mass spectrometry for the determination of UV filters and their degradation products in sediments*. *Anal Bioanal Chem* **400**, 2195-2204. doi: 10.1007/s00216-011-4951-1
- Gago-Ferrero, P., Diaz-Cruz, M.S., Barcelo, D., **2012**. *An overview of UV-absorbing compounds (organic UV filters) in aquatic biota*. *Anal Bioanal Chem* **404**, 2597-2610. doi: 10.1007/s00216-012-6067-7
- Garcia-Guerra, R.B., Montesdeoca-Esponda, S., Sosa-Ferrera, Z., Kabir, A., Furton, K.G., Santana-Rodriguez, J.J., **2016**. *Rapid monitoring of residual UV-stabilizers in seawater samples from beaches using fabric phase sorptive extraction and UHPLC-MS/MS*. *Chemosphere* **164**, 201-207. doi: 10.1016/j.chemosphere.2016.08.102
- HELCOM, **2015**. *Updated Fifth Baltic Sea pollution load compilation (PLC-5.5)*. *Baltic Sea Environment Proceedings No. 145*.
- Heneweer, M., Muusse, M., van den Berg, M., Sanderson, J.T., **2005**. *Additive estrogenic effects of mixtures of frequently used UV filters on pS2-gene transcription in MCF-7 cells*. *Toxicol Appl Pharmacol* **208**, 170-177. doi: 10.1016/j.taap.2005.02.006
- Heydebreck, F., **2013**. *Entwicklung einer Methode zur Bestimmung von Plastikadditiven in Sedimenten mittels LC-MS/MS*. Technische Universität Braunschweig.
- Heydebreck, F., Tang, J., Xie, Z., Ebinghaus, R., **2015**. *Alternative and Legacy Perfluoroalkyl Substances: Differences between European and Chinese River/Estuary Systems*. *Environ Sci Technol* **49**, 8386-8395. doi: 10.1021/acs.est.5b01648
- Himmelsbach, M., Buchberger, W., Reingruber, E., **2009**. *Determination of polymer additives by liquid chromatography coupled with mass spectrometry. A comparison of atmospheric pressure photoionization (APPI), atmospheric pressure chemical ionization (APCI), and electrospray ionization (ESI)*. *Polymer Degradation and Stability* **94**, 1213-1219. doi: 10.1016/j.polymdegradstab.2009.04.021
- Hirata-Koizumi, M., Ogata, H., Imai, T., Hirose, A., Kamata, E., Ema, M., **2008**. *A 52-week repeated dose toxicity study of ultraviolet absorber 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)benzotriazole in rats*. *Drug Chem Toxicol* **31**, 81-96. doi: 10.1080/01480540701688758
- Howard, P.H., Muir, D.C.G., **2010**. *Identifying New Persistent and Bioaccumulative Organics Among Chemicals in Commerce*. *Environ Sci Technol* **44**, 2277-2285. doi: 10.1021/es903383a
- Huang, W., Xie, Z., Yan, W., Mi, W., Xu, W., **2016**. *Occurrence and distribution of synthetic musks and organic UV filters from riverine and coastal sediments in the Pearl River estuary of China*. *Mar Pollut Bull* **111**, 153-159. doi: 10.1016/j.marpolbul.2016.07.018
- Hutchinson, T.H., Lyons, B.P., Thain, J.E., Law, R.J., **2013**. *Evaluating legacy contaminants and emerging chemicals in marine environments using adverse outcome pathways and biological effects-directed analysis*. *Marine Pollution Bulletin* **74**, 517-525. doi: 10.1016/j.marpolbul.2013.06.012
- Jang, G.H., Park, C.B., Kang, B.J., Kim, Y.J., Lee, K.H., **2016**. *Sequential assessment via daphnia and zebrafish for systematic toxicity screening of heterogeneous substances*. *Environ Pollut* **216**, 292-303. doi: 10.1016/j.envpol.2016.06.001
- Jentsch, F., Olsson, O., Westphal, J., Reich, M., Leder, C., Kummerer, K., **2016**. *Photodegradation of the UV filter ethylhexyl methoxycinnamate under ultraviolet light: Identification and in silico assessment of photo-transformation products in the context of grey water reuse*. *Sci Total Environ* **572**, 1092-1100. doi: 10.1016/j.scitotenv.2016.08.017

-
- Kaiser, D., Sieratowicz, A., Zielke, H., Oetken, M., Hollert, H., Oehlmann, J., **2012a**. *Ecotoxicological effect characterisation of widely used organic UV filters*. Environ Pollut **163**, 84–90. doi: 10.1016/j.envpol.2011.12.014
- Kaiser, D., Wappelhorst, O., Oetken, M., Oehlmann, J., **2012b**. *Occurrence of widely used organic UV filters in lake and river sediments*. Environmental Chemistry **9**, 139-147. doi: 10.1071/En11076
- Kameda, Y., Kimura, K., Miyazaki, M., **2011**. *Occurrence and profiles of organic sun-blocking agents in surface waters and sediments in Japanese rivers and lakes*. Environ Pollut **159**, 1570-1576. doi: 10.1016/j.envpol.2011.02.055
- Karlsson, I., Hillerstrom, L., Stenfeldt, A.L., Martensson, J., Borje, A., **2009**. *Photodegradation of dibenzoylmethanes: potential cause of photocontact allergy to sunscreens*. Chem Res Toxicol **22**, 1881-1892. doi: 10.1021/tx900284e
- Kaskey, J., **2018**. *Your Outdated U.S. Sunscreen Exposes You to Needless Cancer Risk*, <https://www.bloomberg.com/news/articles/2018-05-25/america-is-losing-race-to-develop-the-sunscreens-of-the-future> (accessed 11/2018)
- Kawamura, Y., Ogawa, Y., Nishimura, T., Kikuchi, Y., Nishikawa, J., Nishihara, T., Tanamoto, K., **2003**. *Estrogenic activities of UV stabilizers used in food contact plastics and benzophenone derivatives tested by the yeast two-hybrid assay*. Journal of Health Science **49**, 205-212. doi: 10.1248/jhs.49.205
- Kerr, A.C., **2011**. *A survey of the availability of sunscreen filters in the UK*. Clin Exp Dermatol **36**, 541-543. doi: 10.1111/j.1365-2230.2010.04007.x
- Kim, J.W., Chang, K.H., Isobe, T., Tanabe, S., **2011a**. *Acute toxicity of benzotriazole ultraviolet stabilizers on freshwater crustacean (*Daphnia pulex*)*. J Toxicol Sci **36**, 247-251. doi: 10.2131/jts.36.247
- Kim, J.W., Isobe, T., Malarvannan, G., Sudaryanto, A., Chang, K.H., Prudente, M., Tanabe, S., **2012**. *Contamination of benzotriazole ultraviolet stabilizers in house dust from the Philippines: implications on human exposure*. Sci Total Environ **424**, 174-181. doi: 10.1016/j.scitotenv.2012.02.040
- Kim, J.W., Isobe, T., Ramaswamy, B.R., Chang, K.H., Amano, A., Miller, T.M., Siringan, F.P., Tanabe, S., **2011b**. *Contamination and bioaccumulation of benzotriazole ultraviolet stabilizers in fish from Manila Bay, the Philippines using an ultra-fast liquid chromatography-tandem mass spectrometry*. Chemosphere **85**, 751-758. doi: 10.1016/j.chemosphere.2011.06.054
- Kim, K.Y., Ekpeghere, K.I., Jeong, H.J., Oh, J.E., **2017**. *Effects of the summer holiday season on UV filter and illicit drug concentrations in the Korean wastewater system and aquatic environment*. Environ Pollut **227**, 587-595. doi: 10.1016/j.envpol.2017.04.055
- Kristiansen, T., Aas, E., **2015**. *Water type quantification in the Skagerrak, the Kattegat and off the Jutland west coast*. Oceanologia **57**, 177-195. doi: 10.1016/j.oceano.2014.11.002
- Kuijpers, A., Dennegard, B., Albinsson, Y., Jensen, A., **1993**. *Sediment Transport Pathways in the Skagerrak and Kattegat as Indicated by Sediment Chernobyl Radioactivity and Heavy-Metal Concentrations*. Marine Geology **111**, 231-244. doi: 10.1016/0025-3227(93)90133-G
- Kunz, P.Y., Fent, K., **2006a**. *Estrogenic activity of UV filter mixtures*. Toxicol Appl Pharmacol **217**, 86-99. doi: 10.1016/j.taap.2006.07.014
- Kunz, P.Y., Fent, K., **2006b**. *Multiple hormonal activities of UV filters and comparison of in vivo and in vitro estrogenic activity of ethyl-4-aminobenzoate in fish*. Aquatic Toxicology **79**, 305-324. doi: 10.1016/j.aquatox.2006.06.016
- Kunz, P.Y., Fent, K., **2009**. *Estrogenic activity of ternary UV filter mixtures in fish (*Pimephales promelas*) - an analysis with nonlinear isobolograms*. Toxicol Appl Pharmacol **234**, 77-88. doi: 10.1016/j.taap.2008.09.032

References

- Kunz, P.Y., Galicia, H.F., Fent, K., **2006**. *Comparison of in vitro and in vivo estrogenic activity of UV filters in fish*. Toxicol Sci **90**, 349-361. doi: 10.1093/toxsci/kfj082
- Kupper, T., Plagellat, C., Brandli, R.C., de Alencastro, L.F., Grandjean, D., Tarradellas, J., **2006**. *Fate and removal of polycyclic musks, UV filters and biocides during wastewater treatment*. Water Res **40**, 2603-2612. doi: 10.1016/j.watres.2006.04.012
- Lai, H.J., Ying, G.G., Ma, Y.B., Chen, Z.F., Chen, F., Liu, Y.S., **2014**. *Occurrence and dissipation of benzotriazoles and benzotriazole ultraviolet stabilizers in biosolid-amended soils*. Environ Toxicol Chem **33**, 761-767. doi: 10.1002/etc.2498
- Lan, X., Wang, H., Li, R., Lin, Z., Zhang, Z., **2007**. *Major Elements Composition and Provenance Analysis in the Sediments of the South Yellow Sea*. Earth Science Frontiers **14**, 197-203. doi: 10.1016/s1872-5791(07)60033-5
- Langford, K.H., Reid, M.J., Fjeld, E., Oxnevad, S., Thomas, K.V., **2015**. *Environmental occurrence and risk of organic UV filters and stabilizers in multiple matrices in Norway*. Environ Int **80**, 1-7. doi: 10.1016/j.envint.2015.03.012
- Langford, K.H., Thomas, K.V., **2008**. *Inputs of chemicals from recreational activities into the Norwegian coastal zone*. J Environ Monit **10**, 894-898. doi: 10.1039/b806198j
- Liao, C., Kannan, K., **2014**. *Widespread occurrence of benzophenone-type UV light filters in personal care products from China and the United States: an assessment of human exposure*. Environ Sci Technol **48**, 4103-4109. doi: 10.1021/es405450n
- Liu, W.R., Zhao, J.L., Liu, Y.S., Chen, Z.F., Yang, Y.Y., Zhang, Q.Q., Ying, G.G., **2015**. *Biocides in the Yangtze River of China: spatiotemporal distribution, mass load and risk assessment*. Environ Pollut **200**, 53-63. doi: 10.1016/j.envpol.2015.02.013
- Liu, Y.S., Ying, G.G., Shareef, A., Kookana, R.S., **2012**. *Occurrence and removal of benzotriazoles and ultraviolet filters in a municipal wastewater treatment plant*. Environ Pollut **165**, 225-232. doi: 10.1016/j.envpol.2011.10.009
- Loos, R., Marinov, D., Sanseverino, I., Napierska, D., Lettieri, T., **2018**. *Review of the 1st Watch List under the Water Framework Directive and recommendations for the 2nd Watch List*, JRC Technical Reports, Luxembourg.
- Lu, Z., De Silva, A.O., Peart, T.E., Cook, C.J., Tetreault, G.R., Servos, M.R., Muir, D.C., **2016**. *Distribution, Partitioning and Bioaccumulation of Substituted Diphenylamine Antioxidants and Benzotriazole UV Stabilizers in an Urban Creek in Canada*. Environ Sci Technol **50**, 9089-9097. doi: 10.1021/acs.est.6b01796
- Manova, E., von Goetz, N., Hauri, U., Bogdal, C., Hungerbuhler, K., **2013**. *Organic UV filters in personal care products in Switzerland: a survey of occurrence and concentrations*. Int J Hyg Environ Health **216**, 508-514. doi: 10.1016/j.ijheh.2012.08.003
- Mizukawa, A., Molins-Delgado, D., de Azevedo, J.C.R., Fernandes, C.V.S., Diaz-Cruz, S., Barcelo, D., **2017**. *Sediments as a sink for UV filters and benzotriazoles: the case study of Upper Iguacu watershed, Curitiba (Brazil)*. Environ Sci Pollut Res Int **24**, 18284-18294. doi: 10.1007/s11356-017-9472-9
- Molins-Delgado, D., Gago-Ferrero, P., Diaz-Cruz, M.S., Barcelo, D., **2016**. *Single and joint ecotoxicity data estimation of organic UV filters and nanomaterials toward selected aquatic organisms. Urban groundwater risk assessment*. Environ Res **145**, 126-134. doi: 10.1016/j.envres.2015.11.026
- Möller, A., Ahrens, L., Surm, R., Westerveld, J., van der Wielen, F., Ebinghaus, R., de Voogt, P., **2010**. *Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed*. Environ Pollut **158**, 3243-3250. doi: 10.1016/j.envpol.2010.07.019
- Moulite, M., **2018**. *Is your sunscreen killing coral reefs?*, <https://edition.cnn.com/2018/07/09/health/hawaii-sunscreen-ban-questions/index.html> (accessed 10/2018)

-
- Nagayoshi, H., Kakimoto, K., Takagi, S., Konishi, Y., Kajimura, K., Matsuda, T., **2015**. *Benzotriazole ultraviolet stabilizers show potent activities as human aryl hydrocarbon receptor ligands*. Environ Sci Technol **49**, 578-587. doi: 10.1021/es503926w
- Nakata, H., Murata, S., Filatreau, J., **2009**. *Occurrence and Concentrations of Benzotriazole UV Stabilizers in Marine Organisms and Sediments from the Ariake Sea, Japan*. Environ. Sci. Technol. **43**, 6920–6926. doi: 10.1021/es900939j
- Nakata, H., Shinohara, R., Nakazawa, Y., Isobe, T., Sudaryanto, A., Subramanian, A., Tanabe, S., Zakaria, M.P., Zheng, G.J., Lam, P.K., Kim, E.Y., Min, B.Y., We, S.U., Viet, P.H., Tana, T.S., Prudente, M., Frank, D., Lauenstein, G., Kannan, K., **2012**. *Asia-Pacific mussel watch for emerging pollutants: Distribution of synthetic musks and benzotriazole UV stabilizers in Asian and US coastal waters*. Mar Pollut Bull **64**, 2211-2218. doi: 10.1016/j.marpolbul.2012.07.049
- Neumann, A., van Beusekom, J.E.E., Holtappels, M., Emeis, K.-C., **2017**. *Nitrate consumption in sediments of the German Bight (North Sea)*. Journal of Sea Research **127**, 26-35. doi: 10.1016/j.seares.2017.06.012
- NORMAN, **2015**. *NORMAN Prioritisation framework for emerging substances*, <http://www.norman-network.net/?q=node/19> (accessed **05/2015**)
- NORMAN, **2018**. *NORMAN List of Emerging Substances*, <https://www.norman-network.net/?q=node/81#sub19> (accessed **10/2018**)
- NTP, **2011**. *U.S. Department for Health and Human Services: National Toxicology Program, Chemical Information Review Document for Phenolic Benzotriazoles*.
- OECD, **2018**. *HPV database*, <http://webnet.oecd.org/HPV/UI/Search.aspx> (accessed **03/2018**)
- OSPAR, **2010**. *Quality Status Report 2010: Region II Greater North Sea*, London.
- Ozaez, I., Morcillo, G., Martinez-Guitarte, J.L., **2016**. *The effects of binary UV filter mixtures on the midge Chironomus riparius*. Sci Total Environ **556**, 154-162. doi: 10.1016/j.scitotenv.2016.02.210
- Paredes, E., Perez, S., Rodil, R., Quintana, J.B., Beiras, R., **2014**. *Ecotoxicological evaluation of four UV filters using marine organisms from different trophic levels Isochrysis galbana, Mytilus galloprovincialis, Paracentrotus lividus, and Siriella armata*. Chemosphere **104**, 44-50. doi: 10.1016/j.chemosphere.2013.10.053
- Peng, X., Fan, Y., Jin, J., Xiong, S., Liu, J., Tang, C., **2017a**. *Bioaccumulation and biomagnification of ultraviolet absorbents in marine wildlife of the Pearl River Estuarine, South China Sea*. Environ Pollut **225**, 55-65. doi: 10.1016/j.envpol.2017.03.035
- Peng, X., Jin, J., Wang, C., Ou, W., Tang, C., **2015**. *Multi-target determination of organic ultraviolet absorbents in organism tissues by ultrasonic assisted extraction and ultra-high performance liquid chromatography-tandem mass spectrometry*. J Chromatogr A **1384**, 97-106. doi: 10.1016/j.chroma.2015.01.051
- Peng, X., Xiong, S., Ou, W., Wang, Z., Tan, J., Jin, J., Tang, C., Liu, J., Fan, Y., **2017b**. *Persistence, temporal and spatial profiles of ultraviolet absorbents and phenolic personal care products in riverine and estuarine sediment of the Pearl River catchment, China*. J Hazard Mater **323**, 139-146. doi: 10.1016/j.jhazmat.2016.05.020
- Pintado-Herrera, M.G., Combi, T., Corada-Fernandez, C., Gonzalez-Mazo, E., Lara-Martin, P.A., **2017a**. *Occurrence and spatial distribution of legacy and emerging organic pollutants in marine sediments from the Atlantic coast (Andalusia, SW Spain)*. Sci Total Environ **605-606**, 980-994. doi: 10.1016/j.scitotenv.2017.06.055
- Pintado-Herrera, M.G., Wang, C., Lu, J., Chang, Y.P., Chen, W., Li, X., Lara-Martin, P.A., **2017b**. *Distribution, mass inventories, and ecological risk assessment of legacy and emerging contaminants in sediments from the Pearl River Estuary in China*. J Hazard Mater **323**, 128-138. doi: 10.1016/j.jhazmat.2016.02.046

References

- Plagellat, C., Kupper, T., Furrer, R., de Alencastro, L.F., Grandjean, D., Tarradellas, J., **2006**. *Concentrations and specific loads of UV filters in sewage sludge originating from a monitoring network in Switzerland*. Chemosphere **62**, 915-925. doi: 10.1016/j.chemosphere.2005.05.024
- Poiger, T., Buser, H.-R., Balmer, M.E., Bergqvist, P.-A., Müller, M.D., **2004**. *Occurrence of UV filter compounds from sunscreens in surface waters: regional mass balance in two Swiss lakes*. Chemosphere **55**, 951-963. doi: 10.1016/j.chemosphere.2004.01.012
- Qiao, S.Q., Shi, X.F., Zhu, A.M., Liu, Y.G., Bi, N.S., Fang, X.S., Yang, G., **2010**. *Distribution and transport of suspended sediments off the Yellow River (Huanghe) mouth and the nearby Bohai Sea*. Estuarine Coastal and Shelf Science **86**, 337-344. doi: 10.1016/j.ecss.2009.07.019
- Quante, M., Ebinghaus, R., Flöser, G., **2011**. *Persistent Pollution – Past, Present and Future*. Springer-Verlag, Berlin Heidelberg.
- Raffaelli, A., Saba, A., **2003**. *Atmospheric pressure photoionization mass spectrometry*. Mass Spectrometry Reviews **22**, 318–331. doi: 10.1002/mas.10060
- Ramos, S., Homem, V., Alves, A., Santos, L., **2015**. *Advances in analytical methods and occurrence of organic UV-filters in the environment - A review*. Sci Total Environ **526**, 278-311. doi: 10.1016/j.scitotenv.2015.04.055
- Ramos, S., Homem, V., Alves, A., Santos, L., **2016**. *A review of organic UV-filters in wastewater treatment plants*. Environ Int **86**, 24-44. doi: 10.1016/j.envint.2015.10.004
- Rani, M., Shim, W.J., Han, G.M., Jang, M., Al-Odaini, N.A., Song, Y.K., Hong, S.H., **2015**. *Qualitative Analysis of Additives in Plastic Marine Debris and Its New Products*. Arch Environ Contam Toxicol **69**, 352-366. doi: 10.1007/s00244-015-0224-x
- Rani, M., Shim, W.J., Han, G.M., Jang, M., Song, Y.K., Hong, S.H., **2017**. *Benzotriazole-type ultraviolet stabilizers and antioxidants in plastic marine debris and their new products*. Sci Total Environ **579**, 745-754. doi: 10.1016/j.scitotenv.2016.11.033
- Rodil, R., Moeder, M., **2008**. *Development of a simultaneous pressurised-liquid extraction and clean-up procedure for the determination of UV filters in sediments*. Anal Chim Acta **612**, 152-159. doi: 10.1016/j.aca.2008.02.030
- Rodil, R., Moeder, M., Altenburger, R., Schmitt-Jansen, M., **2009a**. *Photostability and phytotoxicity of selected sunscreen agents and their degradation mixtures in water*. Anal Bioanal Chem **395**, 1513-1524. doi: 10.1007/s00216-009-3113-1
- Rodil, R., Schrader, S., Moeder, M., **2009b**. *Comparison of atmospheric pressure photoionization and electrospray ionization mass spectrometry for the analysis of UV filters*. Rapid Commun Mass Spectrom **23**, 580-588. doi: 10.1002/rcm.3910
- Rodil, R., Schrader, S., Moeder, M., **2009c**. *Pressurised membrane-assisted liquid extraction of UV filters from sludge*. J Chromatogr A **1216**, 8851-8858. doi: 10.1016/j.chroma.2009.10.058
- Ruan, T., Liu, R., Fu, Q., Wang, T., Wang, Y., Song, S., Wang, P., Teng, M., Jiang, G., **2012**. *Concentrations and composition profiles of benzotriazole UV stabilizers in municipal sewage sludge in China*. Environ Sci Technol **46**, 2071-2079. doi: 10.1021/es203376x
- Sanchez-Brunete, C., Miguel, E., Albero, B., Tadeo, J.L., **2011**. *Analysis of salicylate and benzophenone-type UV filters in soils and sediments by simultaneous extraction cleanup and gas chromatography–mass spectrometry*. Journal of Chromatography A **1218**, 4291–4298. doi: 10.1016/j.chroma.2011.05.030
- Sanchez-Quiles, D., Tovar-Sanchez, A., **2015**. *Are sunscreens a new environmental risk associated with coastal tourism?* Environ Int **83**, 158-170. doi: 10.1016/j.envint.2015.06.007

-
- Sanchez Rodriguez, A., Rodrigo Sanz, M., Betancort Rodriguez, J.R., **2015**. *Occurrence of eight UV filters in beaches of Gran Canaria (Canary Islands). An approach to environmental risk assessment*. Chemosphere **131**, 85-90. doi: 10.1016/j.chemosphere.2015.02.054
- Sang, Z., Leung, K.S., **2016**. *Environmental occurrence and ecological risk assessment of organic UV filters in marine organisms from Hong Kong coastal waters*. Sci Total Environ **566-567**, 489-498. doi: 10.1016/j.scitotenv.2016.05.120
- Sankoda, K., Murata, K., Tanihata, M., Suzuki, K., Nomiya, K., Shinohara, R., **2015**. *Seasonal and diurnal variation of organic ultraviolet filters from personal care products used along the Japanese coast*. Arch Environ Contam Toxicol **68**, 217-224. doi: 10.1007/s00244-014-0106-7
- Schlumpf, M., Cotton, B., Conscience, M., Haller, V., Steinmann, B., Lichtensteiger, W., **2001**. *In vitro and in vivo estrogenicity of UV screens*. Environ Health Perspect **109**, 239-244. doi: 10.1289/ehp.01109239
- Schlumpf, M., Schmid, P., Durrer, S., Conscience, M., Maerkel, K., Henseler, M., Gruetter, M., Herzog, I., Reolon, S., Ceccatelli, R., Faass, O., Stutz, E., Jarry, H., Wuttke, W., Lichtensteiger, W., **2004**. *Endocrine activity and developmental toxicity of cosmetic UV filters—an update*. Toxicology **205**, 113-122. doi: 10.1016/j.tox.2004.06.043
- Schmitt, C., Oetken, M., Dittberner, O., Wagner, M., Oehlmann, J., **2008**. *Endocrine modulation and toxic effects of two commonly used UV screens on the aquatic invertebrates *Potamopyrgus antipodarum* and *Lumbriculus variegatus**. Environ Pollut **152**, 322-329. doi: 10.1016/j.envpol.2007.06.031
- Schuler, M., **2018**. *Zum Schutz der Korallen - Hawaii verbietet bestimmte Sonnencremes*, https://www.deutschlandfunk.de/zum-schutz-der-korallen-hawaii-verbietet-bestimmte.1773.de.html?dram:article_id=422093 (accessed **07/2018**)
- Semones, M.C., Sharpless, C.M., MacKay, A.A., Chin, Y.-P., **2017**. *Photodegradation of UV filters oxybenzone and sulisobenzene in wastewater effluent and by dissolved organic matter*. Applied Geochemistry **83**, 150-157. doi: 10.1016/j.apgeochem.2017.02.008
- Song, J., **2010**. *Biogeochemical Processes of Biogenic Elements in China Marginal Seas*. Springer-Verlag Berlin Heidelberg.
- Song, S., Ruan, T., Wang, T., Liu, R., Jiang, G., **2014**. *Occurrence and removal of benzotriazole ultraviolet stabilizers in a wastewater treatment plant in China*. Environ Sci Process Impacts **16**, 1076-1082. doi: 10.1039/c3em00483j
- Stockholm Convention, **2017a**. *The 12 initial POPs under the Stockholm Convention*, <http://chm.pops.int/TheConvention/ThePOPs/The12InitialPOPs/tabid/296/Default.aspx> (accessed **12/2017**)
- Stockholm Convention, **2017b**. *What are POPs?*, <http://chm.pops.int/TheConvention/ThePOPs/tabid/673/Default.aspx> (accessed **12/2017**)
- Strepel, S., Scheringer, M., Ng, C.A., Hungerbühler, K., **2012**. *Screening for PBT chemicals among the "existing" and "new" chemicals of the EU*. Environ Sci Technol **46**, 5680-5687. doi: 10.1021/es3002713
- Sun, Q., Li, Y., Li, M., Ashfaq, M., Lv, M., Wang, H., Hu, A., Yu, C.P., **2016**. *PPCPs in Jiulong River estuary (China): Spatiotemporal distributions, fate, and their use as chemical markers of wastewater*. Chemosphere **150**, 596-604. doi: 10.1016/j.chemosphere.2016.02.036
- Tashiro, Y., Kameda, Y., **2013**. *Concentration of organic sun-blocking agents in seawater of beaches and coral reefs of Okinawa Island, Japan*. Mar Pollut Bull **77**, 333-340. doi: 10.1016/j.marpolbul.2013.09.013
- Theobald, N., **2011**. *Emerging Persistent Organic Pollutants in the Marine Environment*, in: Quante, M., Ebinghaus, R., Flöser, G. (Eds.), *Persistent Pollution - Past, Present and Future*. Springer-Verlag.

References

- Tsui, M.M., Leung, H.W., Kwan, B.K., Ng, K.Y., Yamashita, N., Taniyasu, S., Lam, P.K., Murphy, M.B., **2015**. *Occurrence, distribution and ecological risk assessment of multiple classes of UV filters in marine sediments in Hong Kong and Japan*. J Hazard Mater **292**, 180-187. doi: 10.1016/j.jhazmat.2015.03.025
- Tsui, M.M., Leung, H.W., Wai, T.C., Yamashita, N., Taniyasu, S., Liu, W., Lam, P.K., Murphy, M.B., **2014**. *Occurrence, distribution and ecological risk assessment of multiple classes of UV filters in surface waters from different countries*. Water Res **67**, 55-65. doi: 10.1016/j.watres.2014.09.013
- Tynkkynen, N., **2017**. *The Baltic Sea environment and the European Union: Analysis of governance barriers*. Marine Policy **81**, 124-131. doi: 10.1016/j.marpol.2017.01.027
- Vimalkumar, K., Arun, E., Krishna-Kumar, S., Poopal, R.K., Nikhil, N.P., Subramanian, A., Babu-Rajendran, R., **2018**. *Occurrence of triclocarban and benzotriazole ultraviolet stabilizers in water, sediment, and fish from Indian rivers*. Science of The Total Environment **625**, 1351-1360. doi: 10.1016/j.scitotenv.2018.01.042
- Volpe, A., Pagano, M., Mascolo, G., Grenni, P., Rossetti, S., **2017**. *Biodegradation of UV-filters in marine sediments*. Sci Total Environ **575**, 448-457. doi: 10.1016/j.scitotenv.2016.10.001
- Wahie, S., Lloyd, J.J., Farr, P.M., **2007**. *Sunscreen ingredients and labelling: a survey of products available in the UK*. Clin Exp Dermatol **32**, 359-364. doi: 10.1111/j.1365-2230.2007.02404.x
- Wang, C., Xie, T., Xu, R., Lin, J., Li, L., **2017**. *Simultaneous Determination of Ultraviolet Absorbers and Antibacterial Agents in Textiles by Ultra-High Performance Liquid Chromatography/Orbitrap High Resolution Mass Spectrometry*. World Journal of Engineering and Technology **05**, 1-18. doi: 10.4236/wjet.2017.51B001
- Wang, J., Pan, L., Wu, S., Lu, L., Xu, Y., Zhu, Y., Guo, M., Zhuang, S., **2016**. *Recent Advances on Endocrine Disrupting Effects of UV Filters*. Int J Environ Res Public Health **13**. doi: 10.3390/ijerph13080782
- Wang, P., Lu, Y., Wang, T., Fu, Y., Zhu, Z., Liu, S., Xie, S., Xiao, Y., Giesy, J.P., **2014**. *Occurrence and transport of 17 perfluoroalkyl acids in 12 coastal rivers in south Bohai coastal region of China with concentrated fluoropolymer facilities*. Environ Pollut **190**, 115-122. doi: 10.1016/j.envpol.2014.03.030
- Wang, R., Tang, J., Xie, Z., Mi, W., Chen, Y., Wolschke, H., Tian, C., Pan, X., Luo, Y., Ebinghaus, R., **2015**. *Occurrence and spatial distribution of organophosphate ester flame retardants and plasticizers in 40 rivers draining into the Bohai Sea, north China*. Environ Pollut **198**, 172-178. doi: 10.1016/j.envpol.2014.12.037
- Welt.de, **2018**. *Palau verbietet als erstes Land der Welt Sonnencremes*, <https://www.welt.de/reise/Fern/article183155918/Pazifikstaat-Palau-verbietet-als-erstes-Land-der-Welt-Sonnencremes.html> (accessed **11/2018**)
- WHO, **2018**. *World Health Organization. Ultraviolet radiation and health*, http://www.who.int/uv/uv_and_health/en/ (accessed **05/2018**)
- Wick, A., Jacobs, B., Kunkel, U., Heininger, P., Ternes, T.A., **2016a**. *Benzotriazole UV stabilizers in sediments, suspended particulate matter and fish of German rivers: New insights into occurrence, time trends and persistency*. Environ Pollut **212**, 401-412. doi: 10.1016/j.envpol.2016.01.024
- Wick, A., Jacobs, B., Ternes, T.A., **2016b**. *Phenol-Benzotriazole in Proben der Umweltprobenbank – Screening und Zeitreihen*. Bundesanstalt für Gewässerkunde, Koblenz.
- Wolschke, H., Xie, Z., Möller, A., Sturm, R., Ebinghaus, R., **2011**. *Occurrence, distribution and fluxes of benzotriazoles along the German large river basins into the North Sea*. Water Research **45**, 6259-6266. doi: 10.1016/j.watres.2011.09.028
- Yamano, T., Shimizu, M., Noda, T., **2001**. *Relative elicitation potencies of seven chemical allergens in the guinea pig maximization test*. Journal of Health Science **47**, 123-128. doi: 10.1248/jhs.47.123

-
- Yang, S.Y., Jung, H.S., Lim, D.I., Li, C.X., **2003**. *A review on the provenance discrimination of sediments in the Yellow Sea*. Earth-Science Reviews **63**, 93-120. doi: 10.1016/S0012-8252(03)00033-3
- Yang, Z.S., Liu, J.P., **2007**. *A unique Yellow River-derived distal subaqueous delta in the Yellow Sea*. Marine Geology **240**, 169-176. doi: 10.1016/j.margeo.2007.02.008
- Yu, S.X., Pang, Y.L., Wang, Y.C., Li, J.L., Qin, S., **2017**. *Spatial variation of microbial communities in sediments along the environmental gradients from Xiaoqing River to Laizhou Bay*. Mar Pollut Bull **120**, 90-98. doi: 10.1016/j.marpolbul.2017.04.059
- Zhang, Q.Y., Ma, X.Y., Wang, X.C., Ngo, H.H., **2016**. *Assessment of multiple hormone activities of a UV-filter (octocrylene) in zebrafish (Danio rerio)*. Chemosphere **159**, 433-441. doi: 10.1016/j.chemosphere.2016.06.037
- Zhang, Y., Johnson, A.C., Su, C., Zhang, M., Jurgens, M.D., Shi, Y., Lu, Y., **2017**. *Which persistent organic pollutants in the rivers of the Bohai Region of China represent the greatest risk to the local ecosystem?* Chemosphere **178**, 11-18. doi: 10.1016/j.chemosphere.2017.02.137
- Zhang, Z., Ren, N., Li, Y.F., Kunisue, T., Gao, D., Kannan, K., **2011**. *Determination of benzotriazole and benzophenone UV filters in sediment and sewage sludge*. Environ Sci Technol **45**, 3909-3916. doi: 10.1021/es2004057
- Zhao, Z., Tang, J., Mi, L., Tian, C., Zhong, G., Zhang, G., Wang, S., Li, Q., Ebinghaus, R., Xie, Z., Sun, H., **2017**. *Perfluoroalkyl and polyfluoroalkyl substances in the lower atmosphere and surface waters of the Chinese Bohai Sea, Yellow Sea, and Yangtze River estuary*. Sci Total Environ **599-600**, 114-123. doi: 10.1016/j.scitotenv.2017.04.147
- Zhao, Z., Xie, Z., Tang, J., Sturm, R., Chen, Y., Zhang, G., Ebinghaus, R., **2015a**. *Seasonal variations and spatial distributions of perfluoroalkyl substances in the rivers Elbe and lower Weser and the North Sea*. Chemosphere **129**, 118-125. doi: 10.1016/j.chemosphere.2014.03.050
- Zhao, Z., Xie, Z., Tang, J., Zhang, G., Ebinghaus, R., **2015b**. *Spatial distribution of perfluoroalkyl acids in surface sediments of the German Bight, North Sea*. Sci Total Environ **511**, 145-152. doi: 10.1016/j.scitotenv.2014.12.063
- Zhong, M., Wu, H., Mi, W., Li, F., Ji, C., Ebinghaus, R., Tang, J., Xie, Z., **2018**. *Occurrences and distribution characteristics of organophosphate ester flame retardants and plasticizers in the sediments of the Bohai and Yellow Seas, China*. Science of The Total Environment **615**, 1305-1311. doi: 10.1016/j.scitotenv.2017.09.272
- Zhuang, S., Wang, H., Ding, K., Wang, J., Pan, L., Lu, Y., Liu, Q., Zhang, C., **2016**. *Interactions of benzotriazole UV stabilizers with human serum albumin: Atomic insights revealed by biosensors, spectroscopies and molecular dynamics simulations*. Chemosphere **144**, 1050-1059. doi: 10.1016/j.chemosphere.2015.09.085
- Zweifel, H., Maier, R.D., Schiller, M., **2009**. *Plastics Additives Handbook*, 6th edition ed. Hanser Publishers, Munich.

Eidesstattliche Versicherung

Hiermit versichere ich an Eides statt, die vorliegende Dissertation selbst verfasst und keine anderen als die angegebenen Hilfsmittel benutzt zu haben. Die eingereichte schriftliche Fassung entspricht der auf dem elektronischen Speichermedium. Ich versichere, dass diese Dissertation nicht in einem früheren Promotionsverfahren eingereicht wurde.

Hamburg, den 20. März 2019