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**Environmental occurrence and distribution of organic UV  
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1 **Environmental occurrence and distribution of organic UV stabilizers and UV filters in the sediment of**  
2 **Chinese Bohai and Yellow Seas**

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9

10 **Abstract**

11 Organic UV stabilizers and UV filters are applied to industrial materials and cosmetics worldwide. In  
12 plastics they prevent photo-induced degradation, while in cosmetics they protect human skin against  
13 harmful effects of UV radiation. This study reports on the occurrence and distribution of organic  
14 UV stabilizers and UV filters in the surface sediment of the Chinese Bohai and Yellow Seas for the first  
15 time. In total, 16 out of 21 analyzed substances were positively detected. Concentrations ranged from  
16 sub-ng/g dw to low ng/g dw. The highest concentration of 25 ng/g dw was found for octocrylene (OC) in  
17 the Laizhou Bay. In the study area, characteristic composition profiles could be identified. In Korea Bay,  
18 the dominating substances were OC and ethylhexyl salicylate (EHS). All other analytes were below their  
19 method quantification limit (MQL). Around the Shandong Peninsula, highest concentrations of  
20 benzotriazole derivatives were observed in this study with octrizole (UV-329) as the predominant  
21 compound, reaching concentrations of 6.09 ng/g dw. The distribution pattern of UV-329 and bumetrizole  
22 (UV-326) were related (Pearson correlation coefficient  $r > 0.98$ ,  $p \ll 0.01$  around the Shandong  
23 Peninsula), indicating an identical input pathway and similar environmental behavior.

24

25 **Capsule**

26 This study reveals environmental levels of UV stabilizers and UV filters in the Chinese Bohai and Yellow  
27 Seas for the first time.

28

29 **Keywords**

30 UV stabilizers; UV filters; Benzotriazole derivatives; Marine sediments; Bohai Sea; Yellow Sea

31

32 **Highlights**

- 33 • First report on environmental levels of UV stabilizers in the Chinese Bohai and Yellow Seas
- 34 • Triazine derivatives EHT and DBT were identified in marine sediments
- 35 • Regional composition profiles of UV stabilizer contamination were revealed
- 36 • Highest concentrations found for OC with 25 ng/g dw in the outer Laizhou Bay

37

38 **1. Introduction**

39 UV absorbing compounds are widely used in personal care products, textiles, plastics, paints, adhesives,  
40 rubber, and other industrial products (Avagyan et al., 2015; Kim et al., 2011b; Ramos et al., 2015).  
41 Depending on their purpose, they can be divided into two categories as described by Langford et al.  
42 (2015): i) UV stabilizers are added to plastic products (and other materials) to prevent UV-induced  
43 degradation and discoloring of the product and ii) UV filters are used in personal care products (PCPs)  
44 such as sunscreens and cosmetics to protect human skin and hair against UV radiation. Some compounds  
45 are used for both purposes, whereby a strict differentiation is not possible. Therefore, the term  
46 “UV stabilizer” is used for all compounds in the following.

47 UV stabilizers used in PCPs are regulated worldwide. In Europe, Annex VI of the Cosmetic Regulation No.  
48 1223/2009 (European Commission, 2017) provides a positive list of substances allowed in cosmetic  
49 products. In China, the same substances are permitted as in Europe.

50 The input pathways of UV stabilizers to the marine environment are mainly indirect, through wastewater  
51 treatment plant discharges, or direct, through recreational activities such as bathing and swimming  
52 (Poiger et al., 2004; Ramos et al., 2016). Microplastic and plastic debris are also discussed as potential  
53 sources of plastic additives (Cole et al., 2011; Rani et al., 2015; Rani et al., 2017).

54 Some UV stabilizers are currently listed as High Production Volume Chemicals (HPVC) by the OECD  
55 (2017). Due to the widespread usage and high production volumes, UV stabilizers are present in various  
56 environmental matrices. UV stabilizers have been reported worldwide in water (Balmer et al., 2005;  
57 Cunha et al., 2015b; Kameda et al., 2011; Liu et al., 2014; Tsui et al., 2014), suspended particulate matter  
58 (Wick et al., 2016), house dust (Kim et al., 2012), sediment (Kameda et al., 2011; Langford et al., 2015;  
59 Nakata et al., 2009; Wick et al., 2016), and biota (Cunha et al., 2015a; Gago-Ferrero et al., 2012; Langford  
60 et al., 2015; Nakata et al., 2012; Peng et al., 2015; Sang and Leung, 2016; Wick et al., 2016). For example,  
61 Huang et al. (2016) had identified three UV stabilizers in sediment samples from China's Pearl River  
62 estuary with the highest concentrations of ethylhexyl methoxycinnamate (EHMC) and octocrylene (OC)  
63 (around 0.5 µg/g dw) in fishing harbors. Most UV stabilizers are hydrophobic compounds with high  
64 octanol-water partition coefficients ( $\log K_{ow} > 3$ ) and show significant accumulation potentials in  
65 suspended matter, sediments, and biota. Some substances show persistent, bioaccumulative, and toxic  
66 (PBT) properties. For this reason, four benzotriazole UV stabilizers are currently listed as Substances of  
67 Very High Concern (SVHC) under the EU legislation REACH (ECHA, 2017a). Namely, these substances are  
68 2-(Benzotriazol-2-yl)-4,6-di-tert-butylphenol (UV-320), 2,4-di-tert-Butyl-6-(5-chlorobenzotriazol-2-yl)  
69 phenol (UV-327), 2-(Benzotriazol-2-yl)-4,6-bis-(1,1-dimethyl-propyl) phenol (UV-328), and  
70 2-(Benzotriazol-2-yl)-6-butan-2-yl-4-tert-butylphenol (UV-350). In addition, EHMC is included in the  
71 Watch List to be monitored under the Water Framework Directive (European Commission, 2015).

72 The widespread contamination and the resulting potential exposure of UV stabilizers have raised  
73 increasing concern about their impact on ecosystems and human health. There is increasing evidence to  
74 the adverse effects of UV stabilizers. Many UV stabilizers, such as benzophenones, camphor and  
75 cinnamate derivatives, have been identified as potential endocrine disruptors (Balazs et al., 2016; Wang  
76 et al., 2016). Several compounds are a major cause of coral bleaching (Danovaro et al., 2008) and show  
77 hormonal activity and toxicity in *in vivo* rat model systems (Rainieri et al., 2017). So far, for benzotriazole  
78 UV stabilizers no estrogenic and androgenic activities have been observed in zebrafish eleuthero-  
79 embryos (Fent et al., 2014), but exposure to UV-P and UV-326 may lead to metabolic imbalance and  
80 developmental toxicity (Fent et al., 2014). At environmental concentration levels, benzotriazole  
81 UV stabilizers were shown to have no acute toxicity in *Daphnia* (Kim et al., 2011a). Toxicity studies  
82 showed that direct contact with UV-P might cause acute effects such as dermatitis and skin irritation  
83 (Yamano et al., 2001). Benzotriazole UV stabilizers interacted with the human serum albumin (Zhuang et  
84 al., 2016) and showed activity toward the human aryl hydrocarbon receptor (AhR), which could adversely  
85 affect the immune response (Nagayoshi et al., 2015).

86 While the widespread occurrence of UV stabilizers is known, only few studies focused on the marine  
87 environment. The main aim of this study was to assess the significance of UV stabilizers as emerging  
88 contaminants in the sediment of the Chinese Bohai and Yellow Seas.

89 The Bohai Sea is surrounded by the Bohai Economical Rim (BER), which is the largest economic engine in  
90 North China. It includes megacities such as Beijing and Tianjin and comprises parts of the Hebei,  
91 Shandong, and Liaoning provinces. Many chemical pollutants, such as per- and polyfluorinated  
92 substances (Heydebreck et al., 2015; Wang et al., 2014) and organophosphate esters (Wang et al., 2015)  
93 are transported by rivers into the Bohai Sea and pose a great risk for aquatic wildlife (Zhang et al., 2017).  
94 Large volumes of domestic and industrial discharges are entering the Bohai Sea as well as the Yellow Sea,  
95 significantly deteriorating the water quality (Wang et al., 2015; Zhong et al., 2018).

96 In this work, surface sediment samples were collected and analyzed for 20 UV stabilizers and one  
97 hindered amine light stabilizer (HALS) to i) evaluate the current pollution status, ii) characterize regions,  
98 iii) identify potential contamination sources, and iv) give a preliminary risk evaluation of UV stabilizers in  
99 the Bohai and Yellow Seas.

100

## 101 **2. Material and Methods**

### 102 *2.1 Chemicals*

103 Enzacamene (4-MBC), Iscotrizinol (DBT), Ethylhexyl triazone (EHT), Ethylhexyl methoxycinnamate  
104 (EHMC), Octocrylene (OC), Bumetrizole (UV-326), 2,4-di-tert-Butyl-6-(5-chlorobenzotriazol-2-yl) phenol  
105 (UV-327), 2-(Benzotriazol-2-yl)-4,6-bis-(1,1-dimethyl-propyl) phenol (UV-328), Ethylhexyl  
106 methoxycinnamate-d<sub>15</sub> (EHMC-d<sub>15</sub>), Homosalate-d<sub>4</sub> (HMS-d<sub>4</sub>), Octocrylene-d<sub>15</sub> (OC-d<sub>15</sub>), and  
107 Benzophenone-d<sub>10</sub> (BP-d<sub>10</sub>) were purchased from Sigma-Aldrich (Germany). Oxybenzone (BP-3),  
108 Octabenzene (BP-12), Ethylhexyl salicylate (EHS), Bis[4-(2-phenyl-2-propyl)phenyl] amine (HALS-445),  
109 Homosalate (HMS), Amiloxate (IAMC), Padimate O (OD-PABA), Drometrizole (UV-P), 2-(5-tert-butyl-2-  
110 hydroxyphenyl) benzotriazole (UV-PS), Octrizole (UV-329), and 2-(Benzotriazol-2-yl)-4,6-bis-(2-  
111 phenylpropan-2-yl) phenol (UV-234) were obtained from TCI Deutschland GmbH (Germany).  
112 2-(Benzotriazol-2-yl)-6-butan-2-yl-4-tert-butylphenol (UV-350), 2-(Benzotriazol-2-yl)-4,6-di-tert-  
113 butylphenol (UV-320), and 2-(Benzotriazol-2-yl)-4-methyl-6-(2-propenyl) phenol (Allyl-bzt) were supplied  
114 by amchro GmbH (Germany). Enzacamene-d<sub>4</sub> (4-MBC-d<sub>4</sub>) and Oxybenzone-<sup>13</sup>C<sub>6</sub> (BP-3-<sup>13</sup>C<sub>6</sub>) were  
115 distributed by EQ Laboratories GmbH (Germany) and LGC Standards GmbH (Germany), respectively.

116 2-(2-Hydroxy-5-methylphenyl)-benzotriazole-d<sub>4</sub> (UV-P-d<sub>4</sub>), 2-(Benzotriazol-2-yl)-4,6-bis-(1,1-dimethyl-  
117 propyl) phenol-d<sub>4</sub> (UV-328-d<sub>4</sub>), and Perfluoro-1-[<sup>13</sup>C<sub>8</sub>]-octanesulfonamide (FOSA-<sup>13</sup>C<sub>8</sub>) were supplied by  
118 CAMPRO Scientific GmbH (Germany). Further information such as structures, CAS-No., chemical names,  
119 and purities can be found in Tables S1 and S2 of the Supplementary Material.

120 Dichloromethane (Picograde) was purchased from LGC Standards (Germany). Both methanol (LiChrosolv,  
121 hypergrade for LC-MS) and toluene (LiChrosolv, for liquid chromatography) were purchased from Merck  
122 (Germany). Deionized water was supplied from a Milli-Q Integral 5 system (Germany).

123

## 124 2.2 *Study area and sample collection*

125 The Bohai and Yellow Seas are semi-enclosed marginal seas in the northwest Pacific Ocean. The Yellow  
126 Sea is surrounded by the west coast of the Korean Peninsula and the east coast of China. It has an area of  
127 approximately 380,000 km<sup>2</sup> (Song, 2010) and an average depth of 44 m (Song, 2010). Its northern  
128 extension is referred to as Korea Bay and in the northwest, the Yellow Sea is connected to the Bohai Sea  
129 through the Bohai Strait. The Bohai Sea has an area of approximately 77,000 km<sup>2</sup> (Song, 2010) and  
130 features three bays, one of them being Laizhou Bay in the south.

131 Surface sediment samples from the Bohai and Yellow Seas were collected in June and July 2016 on the  
132 Chinese research vessel *Dongfanghong 2* sampling campaign. Surface sediment samples from Laizhou  
133 Bay were collected in July 2016 on the *Chuangxin 1* sampling cruise. On both campaigns the samples  
134 were taken using a stainless-steel box corer and the top 10 cm of sediment was collected. Samples were  
135 put afterward into pre-cleaned (cleaned with acetone and baked out at 250 °C) aluminum bowls and  
136 stored at -20 °C until sample preparation. Detailed sampling information can be found in Table S7 of the  
137 Supplementary Material.

138

## 139 2.3 *Sample preparation*

140 The wet sediment samples were freeze-dried (Christ Alpha 1-4 LDplus, Germany) and homogenized using  
141 a laboratory mortar. Large pieces (such as seashells and stones) were removed. Afterwards, extraction  
142 and clean-up were performed simultaneously using an accelerated solvent extraction (DIONEX ASE-350)  
143 method. For this, 22 mL stainless steel ASE cells were filled in layers with 3 g of 10% deactivated silica  
144 and 5 - 8 g of dried sediment. The sediment samples were spiked with the isotopically labeled standards

145 4-MBC-d<sub>4</sub>, BP-3-<sup>13</sup>C<sub>6</sub>, EHMC-d<sub>15</sub>, HMS-d<sub>4</sub>, OC-d<sub>15</sub>, and the non-labeled surrogate standard Allyl-bzt. For  
146 most of the Bohai Sea samples and all Yellow Sea samples Allyl-bzt could be replaced by UV-P-d<sub>4</sub> and  
147 UV-328-d<sub>4</sub>, which became commercially available. Depending on the substance response, internal  
148 standards were added at absolute quantities of 2 - 10 ng. The cells were extracted using  
149 dichloromethane for three 15-min cycles at 100 °C. The ASE extract (~ 40 mL) was solvent-changed to  
150 methanol in a rotary evaporator and reduced in volume to 150 µL under a heated nitrogen stream. The  
151 reduced extract was 0.2 µm-filtered into a LC vial using a Spartan syringe filter (Ø = 13 mm, Whatman,  
152 Germany). Finally, 65 µL water was added (to obtain the needed solvent composition for the following  
153 LC-MS/MS analysis) and the extract was spiked with 2 ng (absolute) of FOSA-<sup>13</sup>C<sub>8</sub> and BP-d<sub>10</sub> as injection  
154 standards, resulting in a sample volume of 225 µL. For every sample, double measurements were  
155 conducted.

156

#### 157 2.4 *LC-MS/MS analysis*

158 The instrumental analysis was performed on a UHPLC-MS/MS system (1290 Infinity coupled to 6490  
159 triple quadrupole LC/MS; both from Agilent, Germany) equipped with an atmospheric pressure  
160 photoionization (APPI) source and both a C18 column (Eclipse Plus RRHD 1.8 µm, 2.1 x 150 mm, Agilent,  
161 Germany) and a C8 column (Eclipse Plus RRHD 1.8 µm, 2.1 x 150 mm, Agilent, Germany). The mobile  
162 phase consisted of A) water and B) methanol. Separation was achieved at a constant flow rate of  
163 0.2 mL/min. The solvent gradient started with an isocratic segment of 70% B (4 min), which was  
164 increased to 90% B over 3 min and held constant for another 5 min. Over 1 min, B was further increased  
165 to 100% and held constant for 13 min. For enhanced ionization, 5% toluene was added as a dopant post-  
166 column. Every sample was measured in positive and in negative ionization mode. Further information on  
167 the instrumental method is presented in the Supplementary Material.

168

#### 169 2.5 *Total organic carbon (TOC) analysis*

170 TOC analysis was carried out with aliquots of the freeze-dried samples using a LECO RC612 multiphase  
171 (Germany). The TOC<sub>400</sub>-values were determined running a temperature program from 150 °C to 400 °C at  
172 70 °C/min in an oxygen flow. The final temperature was held for 2 min. For every sample, a double  
173 measurement was conducted.

174

## 175 2.6 *Statistics and risk evaluation*

176 All statistical analyses were done in OriginPro 9.1 (OriginLab Corporation). Firstly, Shapiro-Wilk and  
177 Kolmogorov-Smirnov normality tests were performed. Whenever the results indicated that the  
178 UV stabilizer concentrations showed no normal distribution ( $p < 0.05$ ), logarithmically transformed  
179 concentrations values were used for subsequent statistical analyses. To test for significant differences in  
180 concentration levels in the Laizhou Bay, other parts of the Bohai Sea, and the Yellow Sea, a test for  
181 homogeneity of variances (Levene's test) was conducted, followed by a one-way ANOVA test coupled  
182 with a Turkey post-hoc test (all at a significance level of 0.05). A Pearson correlation analysis was  
183 performed to evaluate correlations between total UV stabilizer concentrations and TOC contents as well  
184 as among concentrations of single UV stabilizers. For analyses, concentration values  $< \text{MDL}$  were treated  
185 as zero and for concentration values  $< \text{MQL}$ , the obtained concentration value was used.

186 The potential risk was evaluated according to Pintado-Herrera et al. (2017a). Hazard quotients (HQ) were  
187 calculated by dividing measured environmental concentrations (MEC) obtained from this study by  
188 predicted no effect concentrations (PNEC) obtained from the literature. In case no PNEC values were  
189 available, they were calculated from toxicity data by applying an assessment factor of 1000 for acute  
190 toxicity data and 100 for chronic toxicity data. For interpretation, HQ values  $> 1$  indicate to an ecological  
191 risk.

192

## 193 2.7 *Quality Assurance and Quality Control*

194 Because of the widespread presence of UV stabilizers in a variety of laboratory equipment, the use of  
195 rubber and plastic materials was avoided to minimize blank contamination during the transport, storage  
196 and treatment of the samples. Prior to use, all glassware was cleaned by a laboratory dishwasher, baked  
197 at 250 °C, and rinsed with methanol.

198 For blank determination, sea sand (baked at 400 °C) was placed into the freeze-drying system together  
199 with the wet sediment samples and was treated as a sample throughout the entire sample preparation  
200 and measuring steps. Normally, each extraction batch (max. 24 ASE cells) consisted of three procedural  
201 blanks together with 20 samples (10 sediment samples in double measurement). The mean  
202 concentrations of UV stabilizers in the blanks ranged from  $0.6 \pm 0.9 \text{ pg/g}$  (HALS-445) to  $19.6 \pm 6.7 \text{ pg/g}$



203 (EHS). The OC contamination is higher ( $248 \pm 28$  pg/g) and is mainly caused by the freeze drying  
204 procedure.

205 Quantification was performed using the internal standard calibration method. Solvent based calibration  
206 curves were used to obtain the relative response ratio of the target analyte to the amount of an  
207 appropriate mass-labeled standard using a  $1/x$  weighting factor. Substances without isotopically labeled  
208 standards available were corrected with the most fitting (in recovery and retention time) surrogate  
209 standard. For example, EHS was corrected by HMS-d<sub>4</sub>, as recovery tests with matrix resulted in high  
210 accordance of, for example,  $105 \pm 7\%$  (Supplementary Material, Table S5). The reported concentrations  
211 for BP-12 must be considered as semiquantitative, as the resulting concentrations are most likely  
212 overestimated due to different properties of BP-12 and the assigned internal standard (BP-3-<sup>13</sup>C<sub>6</sub>).  
213 However, as BP-12 was only found in low concentrations, the semiquantitative results do not have any  
214 consequences for discussion. Before and after every sample batch, a 10-point calibration curve  
215 (0.0 - 90 pg/ $\mu$ L) was measured and extended whenever needed (130, 220, 440 pg/ $\mu$ L). All calibration  
216 curves were linear with correlation coefficients  $> 0.99$  for all analytes, except for DBT and EHT, which  
217 showed a lower linearity (normally  $> 0.91$ ). Method detection limits (MDLs) were derived from either the  
218 mean blank values plus three times the standard deviation or the signal-to-noise ratio of three ( $S/N = 3$ ),  
219 whichever approach yielded the highest value. Accordingly, method quantification limits (MQLs) were  
220 derived from either the mean blank values plus ten times the standard deviation or the signal-to-noise  
221 ratio of ten ( $S/N = 10$ ). MDLs and MQLs were calculated for every sample batch separately. Based on a  
222 sample volume of 8 g, blank corrected MDLs ranged from 1 (OD-PABA) to 120 pg/g dw (4-MBC). More  
223 information on the method validation is presented in the Supplementary Material.

224 The mean absolute recoveries of the mass-labeled standards for all Bohai and Yellow Seas samples were  
225  $74 \pm 27\%$  (4-MBC-d<sub>4</sub>),  $56 \pm 28\%$  (BP-3-<sup>13</sup>C<sub>6</sub>),  $70 \pm 31\%$  (EHMC-d<sub>15</sub>),  $58 \pm 29\%$  (HMS-d<sub>4</sub>),  $72 \pm 31\%$  (OC-d<sub>15</sub>),  
226  $81 \pm 22\%$  (UV-P-d<sub>4</sub>),  $87 \pm 61\%$  (UV-328-d<sub>4</sub>), and  $71 \pm 39\%$  (Allyl-bzt).

227 All presented concentrations are corrected for recovery and blank.

228

### 229 **3. Results and Discussion**

#### 230 *3.1 Environmental concentrations of UV stabilizers in the Bohai and Yellow Seas*

231 Organic UV stabilizers could be detected in all surface sediment samples of the Bohai and Yellow Seas.  
232 Concentrations are shown in Figure 1 and Table 1. In 16% of the analyzed samples, all UV stabilizer  
233 concentrations were < MQL. The concentrations of total UV stabilizers ( $\Sigma$  UV stabilizers) ranged from  
234 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  
235 of the Bohai Sea, and 2.1 ng/g dw for the Yellow Sea. No statistically different contamination levels were  
236 observed for these regions. The levels of the UV stabilizers UV-PS, UV-350, BP-3, IAMC, and 4-MBC were  
237 below their MDLs in all analyzed samples.

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

241 A comparison with the concentrations among different regions may be better for understanding the  
242 pollution situation in China. Concentrations of UV stabilizers in coastal and marine sediments worldwide  
243 were summarized in Table 2.

244 The UV stabilizer found in highest concentration in this study is OC. It was identified in 46% of samples  
245 with highest concentrations up to 25 ng/g dw at the central and outer Laizhou Bay (Figure 1). In the  
246 other parts of the Bohai Sea, OC occurred in remarkably lower concentrations (up to 0.3 ng/g dw). These  
247 OC concentrations are similar to lower compared to reported coastal concentrations in other studies  
248 (Table 2). In the Bohai Sea, all other UV stabilizers occurred in lower concentrations than OC. EHS  
249 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  
250 Laizhou Bay; other substance concentrations were  $\leq$  0.2 ng/g dw.

251 In the North Yellow Sea, both OC and EHS could be quantified in all Korea Bay samples in concentrations  
252 of  $1.39 \pm 0.71$  ng/g dw and  $0.76 \pm 0.36$  ng/g dw, respectively. All other substance concentrations were  
253 < MQL. EHS was found in slightly higher concentrations at the Atlantic Coast, but was not detected in  
254 Hong Kong and Tokyo Bay sediments (Table 2). In Korea, EHS (in addition to EHMC and BP-3) was a main  
255 contaminant in different environmental matrices (Ekpeghere et al., 2016; Kim et al., 2017). In the South  
256 Yellow Sea, OC and EHS were found in highest concentrations of 4.25 ng/g dw, and 0.95 ng/g dw,  
257 respectively.

258 Around the Shandong Peninsula, benzotriazole UV stabilizers were the most prominent substance group.  
259 The highest benzotriazole concentrations occurred at the northern tip of the peninsula.  $\Sigma$  UV stabilizers  
260 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.

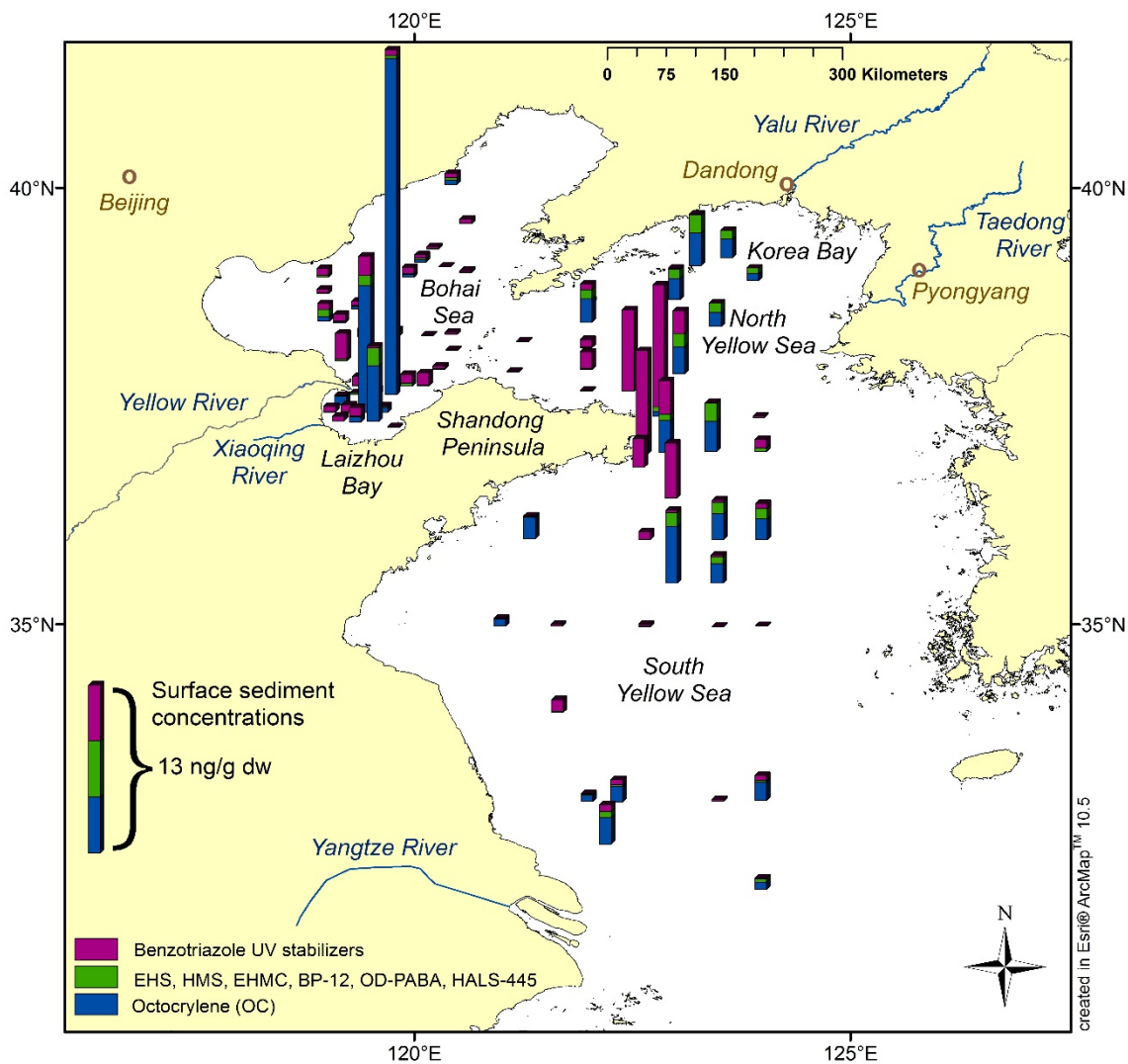
261 These concentrations were slightly lower than in sediments of the Ariake Sea and the Oslofjord, where  
262 highest concentrations of 16 ng/g dw and 25 ng/g dw, respectively were observed for UV-328 (Table 2).  
263 In the Pearl River Estuary, UV-326 was the dominating benzotriazole UV stabilizer, followed by UV-328,  
264 UV-234, UV-P, UV-329, and UV-327 (Peng et al., 2017). In German river sediments, the dominating  
265 substances were UV-360 (bisotrizole, not analyzed in this study) and UV-326, while UV-329 was found in  
266 a median concentration of 2.2 ng/dw (Wick et al., 2016). In contrast to these reports, UV-329 was the  
267 dominating substance attributing to 42% of benzotriazole UV stabilizer contamination in this study,  
268 followed by UV-326 (23%) and UV-327 (19%). It can be concluded that, while benzotriazole UV stabilizers  
269 are applied worldwide, the main compounds seem to be region specific.

270 In recent studies, EHMC was often one of the dominant UV stabilizers in sediments, reaching  
271 concentrations of several hundred ng/g dw (Table 2). Interestingly, the concentrations found in this  
272 study are much lower even though EHMC is used in > 95% of cosmetics and sunscreens currently  
273 marketed in China (Peng et al., 2017).

274 While 4-MBC was one dominant contaminant in Switzerland (Balmer et al., 2005; Poiger et al., 2004), it  
275 was not detected in Japan (Table 2), where the use of 4-MBC as sunscreen ingredients is not allowed  
276 (Kameda et al., 2011). Its non-detection in this study could also be ascribed to the infrequent use of  
277 4-MBC in currently marketed PCPs in China (Peng et al., 2017). A similar observation was made for  
278 OD-PABA. While OD-PABA was identified as one of the predominant compounds in Hong Kong and Tokyo  
279 Bay sediments (Table 2), it was only a minor contaminant in the Korean environment (Ekpeghere et al.,  
280 2016; Kim et al., 2017), where OD-PABA is not permitted in personal care products (Ekpeghere et al.,  
281 2016). In Hong Kong, Tsui et al. (2014) connected the presence of 4-MBC, IAMC and OD-PABA with  
282 recreational activities. Consequently, their absence or infrequent detection in this study indicates other  
283 sources of UV stabilizers into the Bohai and Yellow Seas.

284 The infrequent detection of UV-P and the non-detection of BP-3 could possibly be explained by their  
285 relatively higher water solubility ( $\log K_{ow}$ -values are 3.00 and 3.52, respectively) compared to the other  
286 UV stabilizers analyzed in this study ( $4 < \log K_{ow} \leq 17$ , Table S1 of the Supplementary Material).  
287 Furthermore, BP-3 is not a major UV stabilizer in sunscreens in China (Liao and Kannan, 2014).

288



289

290 **Figure 1: UV stabilizer concentrations in surface sediments [ng/g dw] over the entire study area.**

291

292 **3.2 Distribution pattern of UV stabilizers**

293 While most UV stabilizers are distributed quite homogeneously over the Bohai Sea sampling area, there  
 294 is an entry of OC into Laizhou Bay. OC has wide dispersive uses in PCPs and other industrial products  
 295 (ECHA, 2017b). While recreational activities such as swimming (Poiger et al., 2004; Sanchez Rodriguez et  
 296 al., 2015) are the major input pathway of OC into the environment in other regions, Laizhou Bay is  
 297 strongly affected by land-based pollutants imported from rivers. Among the rivers leading into the

298 Laizhou Bay, both the Yellow River and the Xiaoqing River are the most important regarding  
299 contamination discharges (Heydebreck et al., 2015; Yu et al., 2017). The OC distribution with elevated  
300 levels in the Laizhou Bay could possibly be explained by riverine inputs followed by a deposition in the  
301 central and outer Laizhou Bay. This agrees with the flow-current patterns (Qiao et al., 2010) in this area.

302 In the North Yellow Sea, the distribution of UV stabilizers is very interesting. In Korea Bay, OC and EHS  
303 are the dominant substances. In contrast to this, benzotriazole UV stabilizers are the most prominent  
304 substance group around the Shandong Peninsula. This change in regional contamination composition is  
305 graphically shown in Figure 2. The different composition profiles of UV stabilizers in Korea Bay and  
306 around the Shandong Peninsula are mixing together in the central North Yellow Sea. This distribution  
307 pattern indicates different sources of UV stabilizers deposited into the North Yellow Sea.

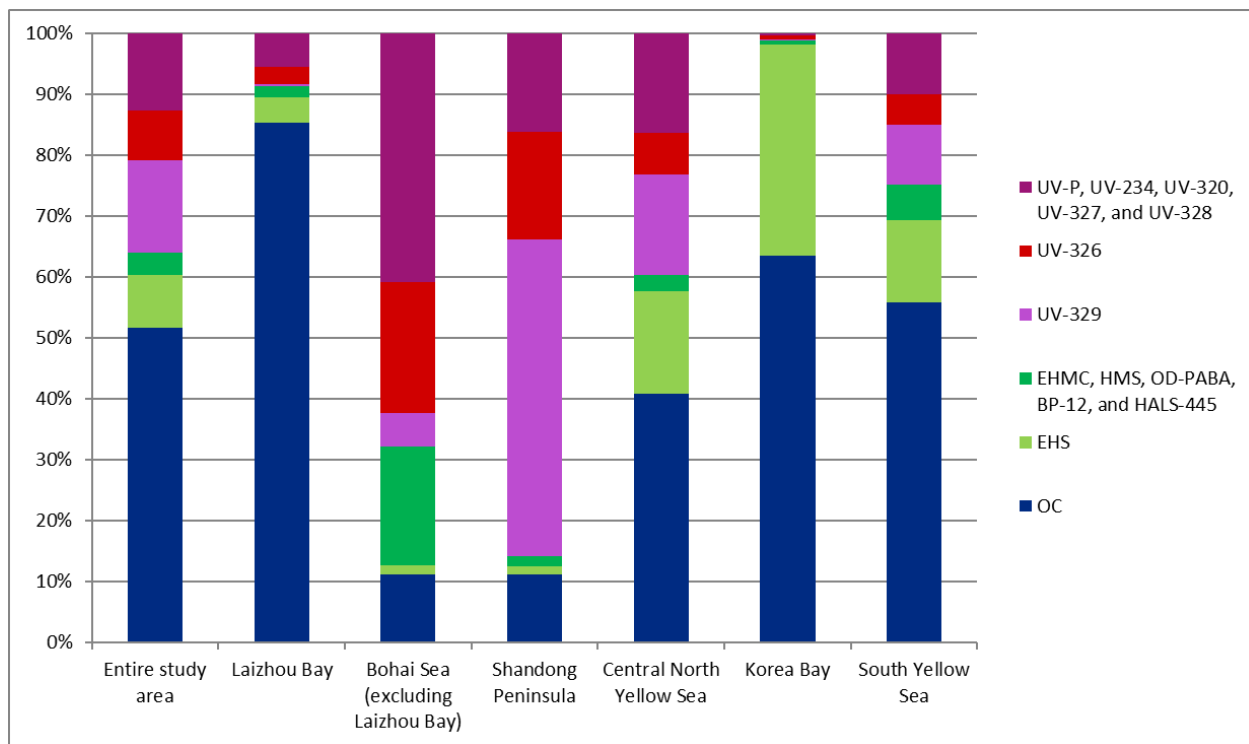
308 Like OC, EHS is used in sunscreens worldwide and environmental contaminations are therefore often  
309 connected to recreational activities (Sankoda et al., 2015; Tashiro and Kameda, 2013). In Korea Bay  
310 however, a direct input through recreational activities seems unlikely, especially as all other compounds  
311 approved in sunscreens were < MQL. A moderate correlation of OC and EHS in North Yellow Sea  
312 sediments ( $r = 0.83$ ,  $p < 0.01$ ) indicates identical sources for both compounds in this region. Apart from  
313 recreational activities, the incomplete removal of UV stabilizers in wastewater and sewage treatment  
314 plants is a major contributor to their occurrence in the environment (Ekpeghere et al., 2016; Tsui et al.,  
315 2014). In South Korea, EHS (in addition to EHMC) was the most dominant contaminant in rivers receiving  
316 sewage treatment plant discharges, mainly from domestic origins (Ekpeghere et al., 2016; Kim et al.,  
317 2017). Riverine inputs (e.g., the Yalu River forming the border between China and North Korea or the  
318 North Korean Taedong River, Figure 1) derived from domestic or industrial discharges might also be the  
319 most likely contamination source in Korea Bay.

320 Around the Shandong Peninsula the concentrations of the benzotriazole derivatives UV-326 and UV-329  
321 showed a strong correlation ( $r > 0.98$ ,  $p << 0.01$ ). In addition, a moderate correlation could be observed  
322 between UV-234 and UV-327 ( $r > 0.82$ ,  $p = 0.01$ ). The correlation between the other benzotriazole  
323 derivatives UV-326, UV-327, UV-328, UV-329, and UV-234 was poor ( $r < 0.7$ ;  $p > 0.02$ ). In conclusion,  
324 these substances, especially UV-326 and UV-329, seemed to derive from the same sources and to  
325 behave similarly in the environment. A correlation between concentrations of benzotriazole  
326 UV stabilizers was also reported by Wick et al. (2016) in German river sediments and Nakata et al. (2009)  
327 in sediments of the Japanese Ariake Sea even though other substances correlated most. Kameda et al.  
328 (2011) investigated the occurrence of UV stabilizers in rivers in Japan and noticed that benzotriazole

329 UV stabilizers accumulated particularly in sediment receiving chemical plant effluent, residential  
330 wastewaters, sewage treatment plant effluent, and surface runoff. Similar sources seem likely to be  
331 responsible for the detected benzotriazole contamination at the Shandong Peninsula. In China,  
332 benzotriazole UV stabilizers are present in sewage sludge collected from wastewater treatment plants,  
333 with UV-234, UV-326, UV-329, and UV-328 being the dominant compounds (Ruan et al., 2012; Song et  
334 al., 2014). Since most benzotriazole UV stabilizers (except UV-P) are almost completely removed from  
335 the final effluent (Liu et al., 2012; Song et al., 2014), the direct effluent discharge of wastewater  
336 treatment plants only seems to be of minor importance as a contamination source in this case. In sewage  
337 sludge however, benzotriazole UV stabilizers are present in the final stage (Liu et al., 2012) and could  
338 reach the environment due to biosolid applications in agriculture. This was demonstrated by Lai et al.  
339 (2014) who investigated the occurrence of benzotriazole UV stabilizers in biosolid-amended soils. They  
340 positively detected several compounds in soils, with UV-329 being the dominant substance and with the  
341 highest concentrations in Shandong (up to  $33.3 \pm 7.3$  ng/g). The results by Lai et al. (2014) underline the  
342 importance of UV-329 as a characteristic contaminant in this region and also indicate surface runoff as  
343 an important contamination source of UV stabilizers introduced into the environment. Benzotriazole  
344 UV stabilizers could then be transported into the Yellow Sea via rivers.

345 Going south from Korea Bay into the South Yellow Sea, the pollution characteristics of Shandong  
346 Peninsula and Korea Bay are mixing together as they do in the central North Yellow Sea (Figure 2). The  
347 highest UV stabilizer concentrations were found in the northern central part of the South Yellow Sea,  
348 where a mud area is located (Yang et al., 2003). Going further to the south or to coastal regions (with the  
349 exception of the Shandong Peninsula), UV stabilizer concentrations decrease. Two possible sources of  
350 South Yellow Sea contaminations are the Yangtze and Yellow Rivers (Figure 1). Lan et al. (2007)  
351 recognized Yangtze River-specific sediment compositions in South Yellow Sea sediments. Yang and Liu  
352 (2007) showed that Yellow River-derived sediment is transported from the Bohai Sea along the  
353 Shandong Peninsula coast into the South Yellow Sea. The contaminations found in this study are more  
354 likely to originate from the Yangtze River and to be transported by ocean currents (Zhong et al., 2018)  
355 into the South Yellow Sea. Yellow River-derived contamination seems unlikely, as the contamination  
356 pattern changes drastically over the described sediment transportation pathway.

357



358

359 **Figure 2: Composition profiles of UV stabilizers in different regions of the Bohai and Yellow Seas.**

360

### 361 3.3 Correlation with TOC

362 The TOC content in the analyzed sediment samples ranged from 0.03 to 0.87% (Table S7, Supplementary  
 363 Material). In Figure S3 of the Supplementary Material, UV stabilizer concentrations are plotted against  
 364 the TOC content of each sample. No correlation could be observed ( $r = 0.09$ ,  $p = 0.44$ ). This is consistent  
 365 with recent studies (Gago-Ferrero et al., 2011; Huang et al., 2016; Tsui et al., 2015). So far, only Nakata et  
 366 al. (2009) revealed a positive correlation between benzotriazole UV stabilizer concentrations and the  
 367 TOC content in samples from the Ariake Sea, Japan. The TOC content in the Ariake Sea samples ranged  
 368 from 2 to 15%, which are much higher values compared to those in this study. The lacking correlation in  
 369 this study could be due to several reasons, such as an inhomogeneous distribution over the sampling  
 370 area or the ability of UV stabilizers to partition to other phases in dynamic aquatic environments (Tsui et  
 371 al., 2015). Too low UV stabilizer concentrations (in most samples) or a too narrow TOC range could also  
 372 result in an indiscernible correlation.

373

### 374 3.4 Qualitative information on DBT and EHT in marine sediments

375 In addition to the findings presented in Figure 1 and Table 1, the UV stabilizers DBT and EHT could be  
376 identified in several samples of the Bohai Sea and the Yellow Sea. Because of low recoveries, low  
377 reproducibility, and lack of appropriate mass-labeled standards, the applied method is not suitable for  
378 quantifying these compounds. Estimated concentrations of the triazine derivatives DBT and EHT in some  
379 samples are in the high ng/g dw range. As an example, disregarding possible matrix effects and assuming  
380 a theoretical recovery rate of 5%, the concentrations are 750 ng/g dw for DBT and 150 ng/g dw for EHT  
381 at the tip of the Shandong Peninsula. Even assuming a recovery rate of 100%, the concentrations are  
382 40 ng/g dw and 8 ng/g dw, respectively, and are therefore comparable to or even higher than those of  
383 other UV stabilizers in this study. In addition to their use in industrial materials, these substances are  
384 approved as ingredients in sunscreen products in Europe (European Commission, 2017), China (following  
385 the European Cosmetic Directive), and Australia (only EHT) (Australian Government, 2017). DBT and EHT  
386 are highly hydrophobic compounds with calculated  $\log K_{ow}$  values  $> 14$  (Table S1, Supplementary  
387 Material), resulting in a high accumulation potential in sediment. So far, environmental data on these  
388 compounds are sparse. They have been measured in sewage sludge at concentration levels of several  
389 hundred ng/g dw (Kupper et al., 2006; Plagellat et al., 2006; Rodil et al., 2009) and in wastewater (Kupper  
390 et al., 2006). To the best of the authors' knowledge, this is the first time these substances have been  
391 found in marine sediments. Further investigations of environmental levels and behavior should be  
392 conducted.

393

### 394 3.5 Potential Environmental Risk

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

398 *In vivo* toxicity values are available only for EHMC and 4-MBC (Kaiser et al., 2012; Schmitt et al., 2008) for  
399 invertebrates. Using these data, Tsui et al. (2015) evaluated the probabilistic risk of sediment associated  
400 with EHMC (up to 447 ng/g dw, Table 2). They found it to be  $> 30\%$  and  $> 80\%$  in both Hong Kong and  
401 Tokyo Bay for the different species. The calculated risk to fish was lower than 20%, but due to their high  
402 lipophilicity, UV stabilizers may still pose a threat to aquatic organisms at higher trophic levels by  
403 entering the food chain. Using both *in vivo* and predicted toxicity data, preliminary risk assessments were  
404 carried out for six UV stabilizers (OC, EHS, HMS, BP-3, 4-MBC, and EHMC) that were present in the  
405 sediment from the Atlantic Coast (Pintado-Herrera et al., 2017a) and of the Pearl River Estuary (Pintado-



406 Herrera et al., 2017b). At both sites, the HQs for two substances (EHMC and 4-MBC) were > 1 and  
407 therefore pose a risk to benthic species.

408 In the present study, the environmental concentrations were lower than in the regions described above.  
409 As 4-MBC and BP-3 levels were <MDL in all samples, a potential risk evaluation was only carried out for  
410 OC, EHMC, EHS, and HMS. The PNEC values used for calculation are listed in Table S8 (Supplementary  
411 Material). The HQ values were < 1 for all substances in all samples, which means that according to  
412 present knowledge, no adverse effects of UV stabilizers for benthic species are expected in the Bohai and  
413 Yellow Seas.

414

#### 415 **4. Conclusions**

416 This study provides environmental levels of UV stabilizers in the Chinese Bohai and Yellow Seas for the  
417 first time. 16 out of 21 analyzed UV stabilizers have been identified in marine sediments pointing out the  
418 presence of UV stabilizer not only in limnic, riverine, estuarine, and coastal systems but also in the  
419 marine environment. They occur ubiquitously over the entire sampling area, underlying the importance  
420 for further investigations on their occurrence and impact on these ecosystems. Characteristic pollution  
421 profiles and distribution pattern have been identified, which indicate different sources of UV stabilizers  
422 introduced into the study area. The results suggest that the Chinese Bohai and Yellow Seas are  
423 contaminated mainly by indirect sources via riverine input. More focus should be given to highly  
424 hydrophobic UV stabilizers such as triazine derivatives, which could be an important but so far  
425 overlooked group of emerging contaminants. Because of limited information available, an environmental  
426 risk assessment of UV stabilizers in the investigated area is not yet possible even though a preliminary  
427 risk evaluation does not indicate any risk for sediment-associated organisms in the Bohai and Yellow  
428 Seas. More sediment toxicity data for benthic organisms are urgently needed to fill this gap in  
429 knowledge.

430

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435

436

437 **Table 1: Concentration ranges [ng/g dw], mean concentrations [ng/g dw], and detection frequencies**  
 438 **[%] of UV stabilizers in the surface sediment of Laizhou Bay (n = 12), the other parts of the Bohai Sea**  
 439 **(n = 22), and the Yellow Sea (n = 40).**

Substance	Laizhou Bay (n = 12)			Bohai Sea (excluding Laizhou Bay) (n = 22)			Yellow Sea (n = 40)		
	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. [%]
UV-P	<MDL – 0.02	<MQL	50	<MDL – 0.06	<MQL	45	<MDL – 0.06	0.02	58
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
UV-234	<MDL – 0.05	0.02	67	<MDL – 0.25	0.03	86	<MDL – 0.39	0.07	60
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
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
BP-12**	<MQL	<MQL	60	<MDL – 0.25	<MQL	57	<MDL – 0.16	<MQL	36
HALS-445	<MQL	<MQL	58	<MDL – 0.21	0.022	86	<MDL – 0.18	0.010	50

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

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

446

447 **Table 2: Overview of selected studies reporting UV stabilizer concentrations in coastal and marine**  
 448 **sediments. All data are in ng/g dw.**

UV stabilizer	This study	Tsui et al. (2015)		Nakata et al. (2009)	Langford et al. (2015)	Barón et al. (2013)	
	Bohai and Yellow Seas, China	Hong Kong, China	Tokyo Bay, Japan	Ariake Sea, Japan	Oslofjord, Norway	West Coastal Line, Colombia	Bays in Chile
4-MBC	<MDL	<MDL	<MDL	<MDL	-	<MDL – 7.90	<MDL
EHMC	<MDL – 0.24	0.6 – 447	0.3 – 54.5	-	8.5 – 16.4	<MDL – 17.8	<MDL
EHS	<MDL – 1.35	<MDL	<MDL	-	-	-	-
HMS	<MDL – 0.94	<MDL	<MDL	-	-	-	-
IAMC	<MDL	<MDL	<MDL	-	-	-	-
BP-3	<MDL	0.05 – 39.8	<MDL	-	<MDL	<MDL – 2.52	<MDL – 1.42
OC	<MDL – 25	0.04 – 15.6	<MDL	-	<MDL – 82.1	-	-
OD-PABA	<MDL – 0.004	1.5 – 150	0.8 – 13.9	-	<MDL	-	-
UV-234	<MDL – 0.39	-	-	-	<MDL	-	-
UV-320	<MDL – 0.20	-	-	0.3 – 2.3	-	-	-
UV-326	<MDL – 1.96	-	-	1.5 – 12	-	-	-
UV-327	<MDL – 1.23	-	-	1.6 – 9.9	<MDL – 8.1	-	-
UV-328	<MDL – 0.41	-	-	2.6 - 16	3.2 – 25.1	-	-
UV-329	<MDL – 6.09	-	-	-	<MDL	-	-

449

450 **Table 2 (continued)**

UV stabilizer	Pintado-Herrera et al. (2017a)		Combi et al. (2016)	Amine et al. (2012)	Sanchez-Brunete et al. (2011)
	Cadiz Bay, Atlantic coast of Andalusia (SW Spain) (mean concentrations)	Huelva Estuary, Atlantic coast of Andalusia (SW Spain) (mean concentrations)	Adriatic Sea	Lebanon	Spain (one sediment)
4-MBC	1.7	<MDL	-	-	-
EHMC	7.3	8.0	0.9 – 10.4	up to 9	-
EHS	3.3	5.2	-	-	13.3
HMS	4	1.2	-	-	<MDL

IAMC	-	-	-	-	-
BP-3	0.7	0.9	<MDL – 0.23	-	<MDL
OC	20.8	15.1	0.8 – 40.7	up to 79	-
OD-PABA	-	-	-	up to 9	-
UV-234	-	-	-	-	-
UV-320	-	-	-	-	-
UV-326	-	-	-	-	-
UV-327	-	-	-	-	-
UV-328	-	-	-	-	-
UV-329	-	-	-	-	-

451

452

453 **Appendix A. Supplementary Material**

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455

456

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457

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1           **Environmental occurrence and distribution of organic**  
2           **UV stabilizers and UV filters in the sediment of Chinese Bohai**  
3           **and Yellow Seas**

4                           **Supplementary Material**  
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7           Christina Apel<sup>1,3\*</sup>, Jianhui Tang<sup>2\*</sup>, Ralf Ebinghaus<sup>1</sup>  
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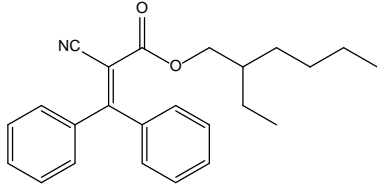
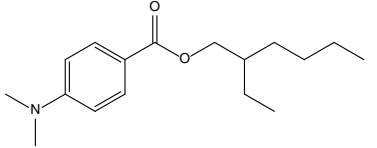
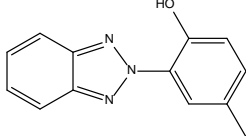
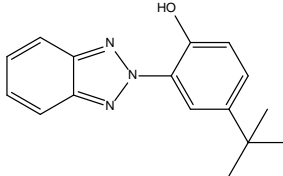
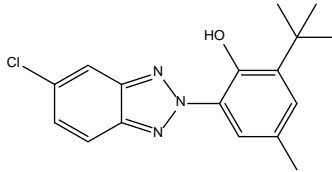
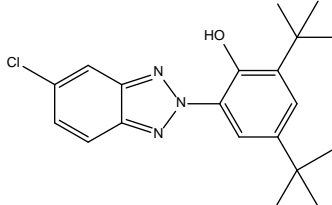
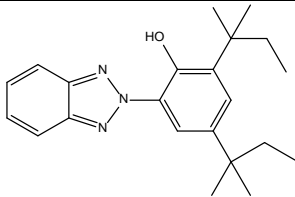
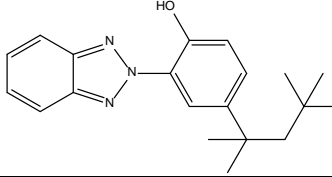
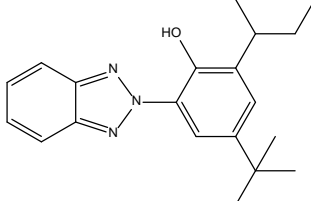
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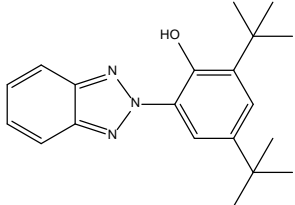
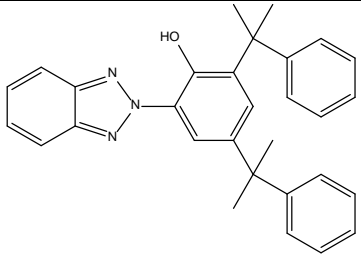
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15 **1** Chemical properties

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17 **Table S1: Overview of examined UV stabilizers. The reported logK<sub>ow</sub> values are calculated using KOWWIN v1.68.**

Abbreviation	logK <sub>ow</sub>	Sum formula	Structure
4-MBC	5.92	C <sub>18</sub> H <sub>22</sub> O	
BP-3	3.52	C <sub>14</sub> H <sub>12</sub> O <sub>3</sub>	
BP-12/ UV-531	6.96	C <sub>21</sub> H <sub>26</sub> O <sub>3</sub>	
DBT	14	C <sub>44</sub> H <sub>59</sub> N <sub>7</sub> O <sub>5</sub>	
EHMC/OMC	5.80	C <sub>18</sub> H <sub>26</sub> O <sub>3</sub>	
EHS	5.97	C <sub>15</sub> H <sub>22</sub> O <sub>3</sub>	
EHT	17	C <sub>48</sub> H <sub>66</sub> N <sub>6</sub> O <sub>6</sub>	
HALS-445	8.51	C <sub>30</sub> H <sub>31</sub> N	
HMS	6.16	C <sub>16</sub> H <sub>22</sub> O <sub>3</sub>	
IAMC	4.33	C <sub>15</sub> H <sub>20</sub> O <sub>3</sub>	

OC	6.88	C <sub>24</sub> H <sub>27</sub> NO <sub>2</sub>	
OD-PABA	5.77	C <sub>17</sub> H <sub>27</sub> NO <sub>2</sub>	
UV-P	3.00	C <sub>13</sub> H <sub>11</sub> N <sub>3</sub> O	
UV-PS	4.36	C <sub>16</sub> H <sub>17</sub> N <sub>3</sub> O	
UV-326	5.55	C <sub>17</sub> H <sub>18</sub> ClN <sub>3</sub> O	
UV-327	6.91	C <sub>20</sub> H <sub>24</sub> ClN <sub>3</sub> O	
UV-328	7.25	C <sub>22</sub> H <sub>29</sub> N <sub>3</sub> O	
UV-329	6.21	C <sub>20</sub> H <sub>25</sub> N <sub>3</sub> O	
UV-350	6.31	C <sub>20</sub> H <sub>25</sub> N <sub>3</sub> O	

UV-320	6.27	C <sub>20</sub> H <sub>25</sub> N <sub>3</sub> O	
UV-234	7.67	C <sub>30</sub> H <sub>29</sub> N <sub>3</sub> O	

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**Table S2: Analyte abbreviations, chemical names, CAS-No., purities, and producers of the used native and mass-labeled standards.**

	<b>Abbreviation</b>	<b>CAS-No.</b>	<b>Chemical name</b>	<b>Purity [%]</b>	<b>Producer/Supplier</b>
<b>Target analytes</b>	4-MBC	36861-47-9 (EU) 38102-62-4 (US)	3-(4-Methylbenzylidene)camphor	99.9	Sigma-Aldrich
	BP-3	131-57-7	2-Hydroxy-4-methoxybenzophenone	99.9	TCI Deutschland GmbH
	BP-12/ UV-531	1843-05-6	2-Hydroxy-4-n-octyloxybenzophenone	99.9	TCI Deutschland GmbH
	DBT	154702-15-5	Diethylhexyl butamido triazone	99.5	Sigma-Aldrich
	EHMC/ OMC	5466-77-3	Ethylhexyl methoxycinnamate	98.4	Fluka/ Sigma-Aldrich
	EHS	118-60-5	Benzoic acid, 2-hydroxy-, 2-ethylhexyl ester	98.5	TCI Deutschland GmbH
	EHT	88122-99-0	Ethylhexyl triazone	98.8	Sigma-Aldrich
	HALS-445	10081-67-1	Bis[4-(2-phenyl-2-propyl)phenyl] amine	98.9	TCI Deutschland GmbH
	HMS	118-56-9	3,3,5-Trimethylcyclohexyl salicylate (cis- and trans- mixture)	99.6	TCI Deutschland GmbH
	IAMC	71617-10-2	Isoamyl methoxycinnamate	99.2	TCI Deutschland GmbH
	OC	6197-30-4	2-Ethylhexyl-2-cyano-3,3-diphenyl-2-propenoate	99.2	Sigma-Aldrich
	OD-PABA	21245-02-3	2-Ethylhexyl 4-(dimethylamino) benzoate	99.1	TCI Deutschland GmbH
	UV-P	2440-22-4	2-(Benzotriazol-2-yl)-4-methylphenol	99.9	TCI Deutschland GmbH
	UV-PS	3147-76-0	2-(5-tert-butyl-2-hydroxyphenyl) benzotriazole	99.6	TCI Deutschland GmbH
	UV-326	3896-11-5	2-tert-butyl-6-(5-chlorobenzotriazol-2-yl)-4-methylphenol	99.6	Sigma-Aldrich
	UV-327	3864-99-1	2,4-ditert-butyl-6-(5-chlorobenzotriazol-2-yl) phenol	99.9	Sigma-Aldrich

	UV-328	25973-55-1	2-(Benzotriazol-2-yl)-4,6-bis-(1,1-dimethyl-propyl)-phenol	99.9	Sigma-Aldrich
	UV-329	3147-75-9	2-(benzotriazol-2-yl)-4-(2,4,4trimethylpentan-2-yl) phenol	99.9	TCI Deutschland GmbH
	UV-350	36437-37-3	2-(benzotriazol-2-yl)-6-butan-2-yl-4-tert-butylphenol	99.3	AccuStandard/ amchro GmbH
	UV-320	3846-71-7	2-(benzotriazol-2-yl)-4,6-di-tert-butylphenol	100	AccuStandard/ amchro GmbH
	UV-234	70321-86-7	2-(benzotriazol-2-yl)-4,6-bis(2-phenylpropan-2-yl) phenol	99.9	TCI Deutschland GmbH
<b>Internal standards</b>	4-MBC-d <sub>4</sub>	N/A	3-(4-Methylbenzylidene-d <sub>4</sub> ) camphor	98.3	CDN Isotopes/ EQ Laboratories GmbH
	BP-3- <sup>13</sup> C <sub>6</sub>	N/A	2-Hydroxy-4-methoxy benzophenone-(phenyl- <sup>13</sup> C <sub>6</sub> )	99	Cambridge Isotope Laboratories/ LGC Standards GmbH
	EHMC-d <sub>15</sub>	N/A	4-Methoxycinnamate-(2-ethyl-d <sub>5</sub> -hexyl-2,3,3,4,4,5,5,6,6,6-d <sub>10</sub> )	99.3	Sigma-Aldrich
	HMS-d <sub>4</sub>	N/A	2-Hydroxybenzoic-d <sub>4</sub> acid 3,3,5-trimethylcyclohexyl ester	98.2	Sigma-Aldrich
	OC-d <sub>15</sub>	N/A	Octocrylene-(2-ethyl-d <sub>5</sub> -hexyl-2,3,3,4,4,5,5,6,6,6-d <sub>10</sub> )	99.7	Sigma-Aldrich
	Allyl-bzt	2170-39-0	2-(2H-Benzotriazol-2-yl)-4-methyl,-6-(2-propenyl) phenol	100	AccuStandard/ amchro GmbH
	UV-P-d <sub>4</sub>	N/A	2-(2-Hydroxy-5-methylphenyl)-benzotriazole-d <sub>4</sub>	99.4	CAMPRO Scientific GmbH
	UV-328-d <sub>4</sub>	N/A	2-(Benzotriazol-2-yl)-4,6-bis-(1,1-dimethyl-propyl)-phenol-d <sub>4</sub>	99.0	CAMPRO Scientific GmbH
<b>Injection standards</b>	BP-d <sub>10</sub>	22583-75-1	Benzophenone-d <sub>10</sub>	99.1	Sigma-Aldrich
	FOSA- <sup>13</sup> C <sub>8</sub>	N/A	Perfluoro-1-[ <sup>13</sup> C <sub>8</sub> ]-octanesulfonamide	> 97	Wellington Laboratories/ CAMPRO Scientific GmbH

24 **2 Instrumental Method**

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**Table S3: Optimized APPI source parameters in positive and negative operation mode.**

	Positive mode	Negative mode
iFunnel parameters: High/Low Pressure RF [V]	150/60	160/120
Gas Flow [L/min]	12	11
Gas Temperature [°C]	180	180
Nebulizer [psi]	30	50
Vaporizer [°C]	300	300
Capillary [V]	3000	1500
Dopant	5% toluene	5% toluene

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**Table S4: LC-MS/MS mass transitions and retention times for target analytes and mass-labeled standards. The upper product ion was used as quantifier and the one below as qualifier.**

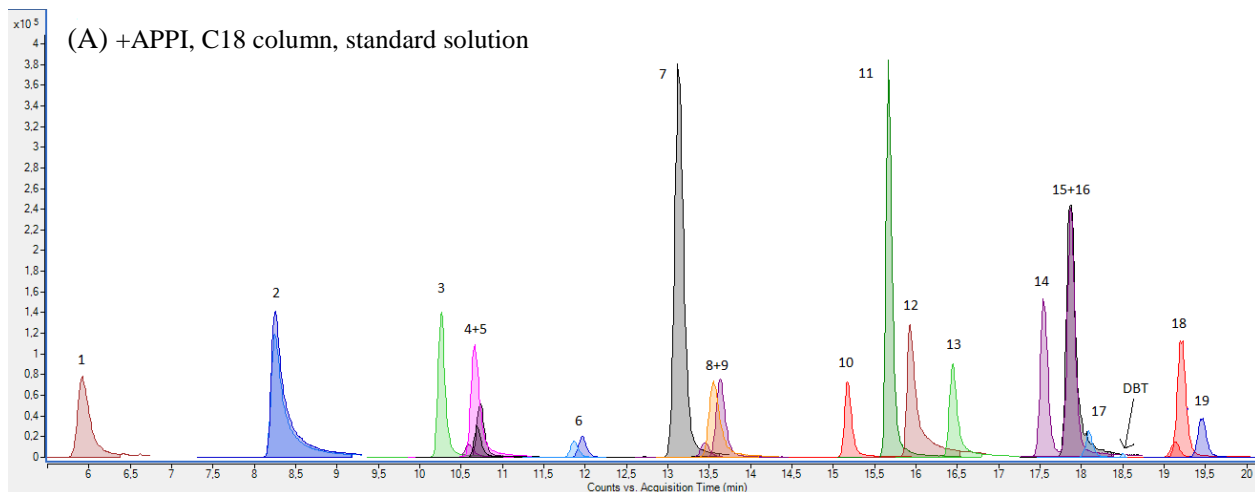
	Analyte	Retention time (C18 column) [min]	Precursor ion (m/z)	Product ions (m/z)	Collision Energy (V)	CAV (V)
APPI +	4-MBC	10.8	255.2	105.1	32	1
				43.0	48	1
	BP-3	8.2	229.1	151.0	16	2
				76.9	44	2
	BP-12	15.9	327.2	137.0	32	1
				215.0	16	1
	DBT	18.5	766.5	468.1	60	3
				654.3	48	3
	EHMC	13.1/13.6	291.2	179.1	4	2
				161.0	12	2
	EHT	17.8 (C8 column)	823.5	711.2	52	2
				599.1	56	2
	HALS-445	15.7	406.26	196.1	40	1
				91.0	52	1
	IAMC	10.2*	249.2	161.0	12	1
				178.9	4	1
	OC	12.0	362.2	249.9	4	2
				231.8	20	2
	OD-PABA	13.1	278.2	151.0	32	1
				166.1	20	1
	UV-P	10.6	226.1	76.9	48	3
				107.1	16	3
	UV-PS	13.6	268.2	212.1	20	1
				57.0	24	1
	UV-326	18.0	316.1	259.9	16	2
				57.1	28	2
	UV-327	19.5	328.2	57.1	32	1
				302.1	20	1
	UV-328	19.2	352.2	282.1	24	1
				43.1	40	1
	UV-329	16.4	324.2	56.9	32	2
				65.0	80	2
	UV-350	17.5	324.2	268.1	20	1

				57.1	32	1
	UV-320	17.9	324.2	268.1 57.1	24 36	1 1
	UV-234	17.9	448.2	370.2 91.1	20 64	1 1
	4-MBC-d <sub>4</sub>	10.7	259.2	216.0 43.1	20 56	2 2
	BP-d <sub>10</sub>	4.9 (C8 column) 5.9 (C18 column)	193.2	110.1 81.9	12 36	5 5
	BP-3- <sup>13</sup> C <sub>6</sub>	8.2	235.1	150.9 55.0	20 80	1 1
	EHMC-d <sub>15</sub>	13.5*	306.3	180.1 161.0	4 12	1 1
	OC-d <sub>15</sub>	11.9	377.3	251.0 233.0	4 24	5 2
	Allyl-bzt	15.2	266.1	119.1 91.0	16 40	1 1
	UV-P-d <sub>4</sub>	10.6	230.1	76.9 107.0	20 52	3 3
	UV-328-d <sub>4</sub>	19.1	356.2	286.0 43.1	24 40	1 1
<b>APPI -</b>	EHS	12.0 (C8 column)	249.2	137.1 93.0	12 28	3 3
	HMS	11.9/12.2 (C8 column)	261.1	92.9 136.9	28 12	2 2
	HMS-d <sub>4</sub>	11.8/12.1 (C8 column)	265.2	140.9 97.0	20 28	3 3
	FOSA- <sup>13</sup> C <sub>8</sub>	9.2 (C8 column)	506.1	77.9	0	2

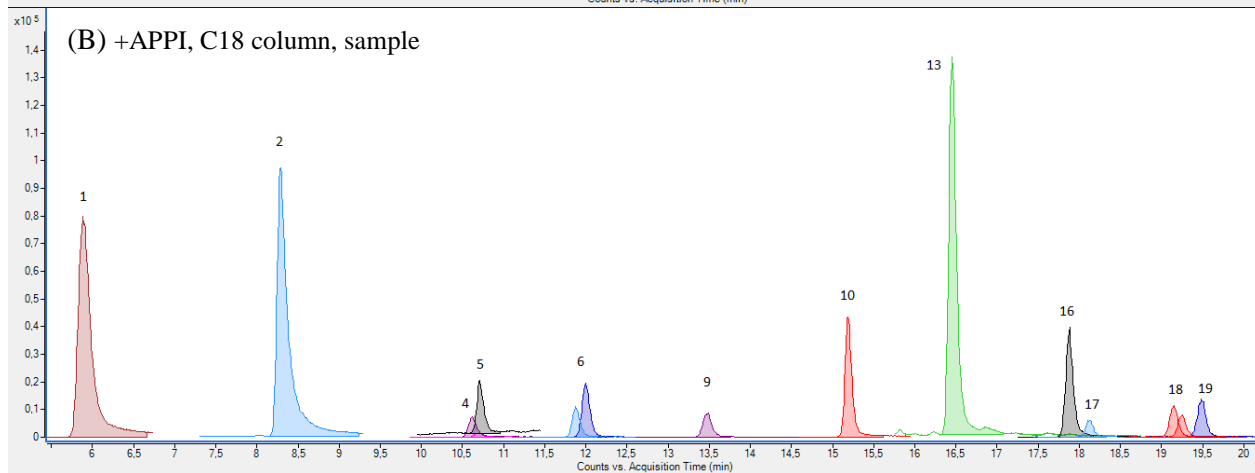
\* Only one isomer present in standards

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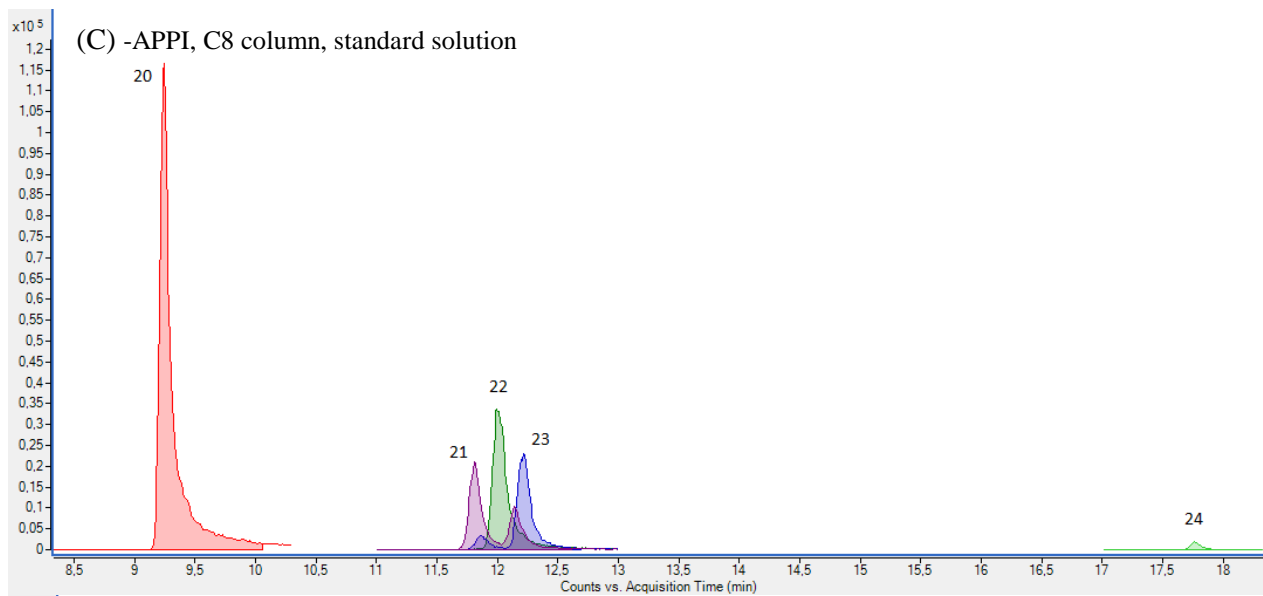
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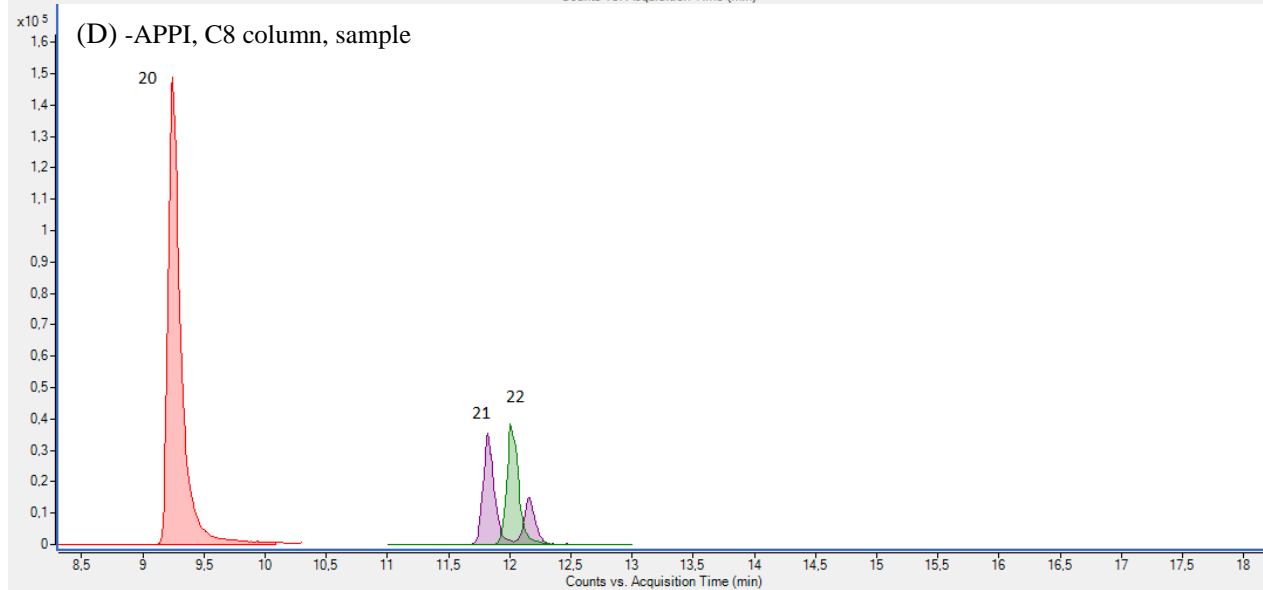
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**Figure S1: Exemplary LC-MS/MS chromatograms of (A) a 1 ng/ $\mu$ L standard solution of UV stabilizers and mass-labeled standards and (B) a sample. 1) BP-d<sub>10</sub>, 2) BP-3 (dark blue) and BP-3-<sup>13</sup>C<sub>6</sub> (light blue), 3) IAMC, 4) UV-P (pink) and UV-P-d<sub>4</sub> (violet), 5) 4-MBC and 4-MBC-d<sub>4</sub> (both black), 6) OC (dark blue) and OC-d<sub>15</sub> (light blue), 7) OD-PABA, 8) UV-PS (orange), 9) EHMC and EHMC-d<sub>15</sub> (both violet), 10) Allyl-bzt, 11) HALS-445, 12) BP-12, 13) UV-329, 14) UV-350, 15) UV-320 (violet), 16) UV-234 (black), 17) UV-326 (blue), 18) UV-328 and UV-328-d<sub>4</sub> (both red), and 19) UV-327. Only quantifiers are displayed.**



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**Figure S2: Exemplary LC-MS/MS chromatograms of (C) a 1 ng/ $\mu$ L standard solution of UV stabilizers and mass-labeled standards and (D) a sample. 20) FOSA-<sup>13</sup>C<sub>8</sub>, 21) HMS-d<sub>4</sub> (violet, two peaks), 22) EHS (green), 23) HMS (blue, two peaks), and 24) EHT. EHT was measured in positive ion monitoring mode. Only quantifiers are displayed.**

## 53 3 Method validation

### 54 3.1 Recovery rates

55 Table S5 summarizes absolute and corrected (by internal standard) recovery rates obtained during method  
56 validation. For both “Recovery Test 1” and “Recovery Test 2” fourfold measurements were conducted (n = 4).  
57 Samples were spiked with an absolute quantity of 10 ng of each native compound and 10 µL internal standard mix  
58 (which equals 2 - 10 ng of each mass-labeled compound). Both absolute and corrected recoveries were calculated  
59 according to equation 1. In both cases the concentration of each compound quantified in spiked samples ( $c_{Sample}$ )  
60 was divided by the concentration added ( $c_{Spike}$ ). The quantification conducted for the **absolute recovery** is based on  
61 the relative response ratio of the target analyte to the amount of the **injection standard** (for volume correction of  
62 the sample extract and to compensate for e.g. sensitivity changes during LC measurement). The quantification for  
63 the **corrected recovery** is based on the ratio of the target analyte to the amount of the assigned **internal standard**.  
64 This corrects for any losses or effects during sample preparation and measurement.

65

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

67

68 The corrected recoveries for both “Recovery Test 1” and “Recovery Test 2” are in the range of 80 - 120% resulting  
69 in a reliable quantification. The only exception is BP-12, as higher corrected recoveries ( $158 \pm 13$  and  $183 \pm 23$ ) are  
70 obtained. Therefore, the calculated concentrations for BP-12 have to be considered as semiquantitative, as the  
71 resulting concentrations are overestimated.

72

73 In this study, 74 sediment samples have been analyzed in double measurements. For all samples, the absolute  
74 recoveries of the internal (mass-labeled) standards have been calculated. As presented in the main manuscript, the  
75 mean absolute recoveries were  $74 \pm 27\%$  (4-MBC-d<sub>4</sub>),  $56 \pm 28\%$  (BP-3-<sup>13</sup>C<sub>6</sub>),  $70 \pm 31\%$  (EHMC-d<sub>15</sub>),  $58 \pm 29\%$   
76 (HMS-d<sub>4</sub>),  $72 \pm 31\%$  (OC-d<sub>15</sub>),  $81 \pm 22\%$  (UV-P-d<sub>4</sub>),  $87 \pm 61\%$  (UV-328-d<sub>4</sub>), and  $71 \pm 39\%$  (Allyl-bzt). In some samples,  
77 the absolute recovery of some internal standards was low (~ 30%), wherefore a further spiking experiment was  
78 conducted. The sample LzB05 was spiked with 20 ng of each native compound and 10 µL internal standard mix. In  
79 contrast to the samples YS30 and BS08 used in Recovery tests 1 and 2, this sample had to be filtrated twice. The  
80 first filtration was done after the volume reduction of the extract to 150 µL (see main manuscript) and a second  
81 filtration was done after water addition. The second filtration was necessary to avoid blocking of the LC column due  
82 to precipitated matrix components. In “Recovery Test 3” of Table S5 the recovery results are presented. Even  
83 though the absolute recovery for most benzotriazoles, EHS, and HMS are low (30-40%) the corrected recoveries are  
84 within an acceptable range.

85

86 **Table S5: Absolute and corrected (by internal standard) recoveries obtained from spiking experiments during**  
 87 **method validation.**

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

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90 **3.2 MDLs and MQLs**

91 Method detection limits (MDLs) were derived from either the mean blank values plus three times the standard  
92 deviation or the signal-to-noise ratio of three (S/N = 3), whichever approach yielded the highest value. Accordingly,  
93 method quantification limits (MQLs) were derived from either the mean blank values plus ten times the standard  
94 deviation or the signal-to-noise ratio of ten (S/N = 10). The MDL and MQL values were calculated for every sample  
95 batch separately. Blank corrected MDLs and MQLs, calculated for a sample volume of 8 g dw, are presented in  
96 Table S6. For some batches, the MDL and MQL values of some substances are slightly higher due to changes in  
97 blank values (e.g. after changing o-rings in the ASE caps).

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99 **Table S6: Method detection limits (MDLs), method quantification limits (MQLs) based on a sample volume of**  
100 **8 g dw. All values are blank corrected.**

Analyte	MDL [pg/g dw]	MQL [pg/g dw]
UV-P	4	14
UV-PS	20*	70*
UV-320	4	14
UV-350	5*	17*
UV-326	14	46
UV-327	17	57
UV-328	7	24
UV-329	11	37
UV-234	6	21
BP-3	30*	100*
BP-12	22	74
4-MBC	120*	380*
OC	84	280
EHMC	16	60
IAMC	20*	70*
HALS-445	3	10
OD-PABA	1	4
EHS	20	70
HMS	7	24

\* calculated over S/N from spiked matrix sample

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#### 4 Sampling and sample information

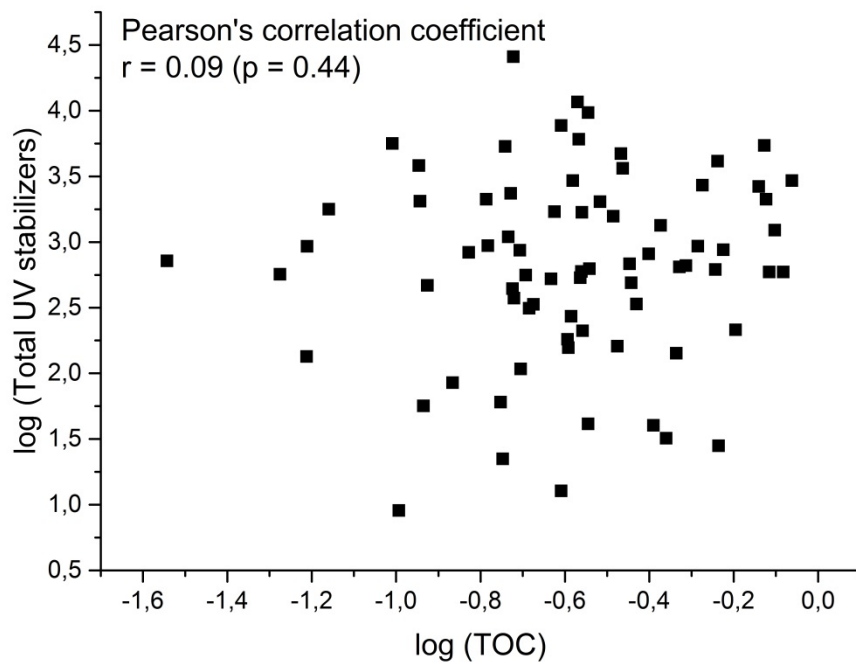
Table S7: Detailed sampling information and TOC values of each sample.

Station	Sampling date	Latitude °N	Longitude °E	Water depth [m]	TOC [%]
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
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

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
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

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110 **Figure S3: Logarithmically transformed values of total UV stabilizer concentrations plotted against the TOC**  
111 **content of each sample. The Pearson correlation coefficient was calculated using OriginPro 9.1 (OriginLab**  
112 **Corporation).**  
113  
114



115 **6 Potential Environmental Risk**

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117 **Table S8: Data used for HQ calculation.**

UV stabilizer	Organism	Toxicity data [ng/g]	Assessment Factor	PNEC [ng/g]	Reference
EHMC	Potamopyrus antipodarum (snail)	NOEC = 80	100	0.8	Kaiser et al. (2012)
OC	QSAR	PNEC = 180	-	180	Pintado-Herrera et al. (2017)
EHS	QSAR	PNEC = 60	-	60	Pintado-Herrera et al. (2017)
HMS	QSAR	PNEC = 22	-	22	Pintado-Herrera et al. (2017)

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120 **References**

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