

1 **First assessment of butyltins (BuTs) contamination of the Montenegrin coast**
2 **(Southeast Adriatic): Tributyltin (TBT) poses a threat to the marine ecosystem**

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7 4 Nevenka Mikac^a, Martina Furdek Turk^{a,*}, Dragana Petrović^b, Miljan Bigović^b, Sladjana
8 5 Krivokapić^b

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10
11 6 ^a Division for Marine and Environmental Research, Ruđer Bošković Institute, 10000 Zagreb,
12 7 Croatia

13 8 ^b Faculty of Natural Sciences and Mathematics, University of Montenegro, 81000 Podgorica,
14 9 Montenegro

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21 13 * Corresponding author: mfurdek@irb.hr
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27 16 **Abstract**

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29 17 This study presents the first assessment of butyltins (BuTs) pollution of the Montenegrin coast.
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31 18 The distribution of tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) was
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33 19 investigated in mussels, sediments and water overlying sediment after the sediment
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35 20 resuspension. The results showed that the investigated sites (marinas, ports, shipyards) are
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37 21 contaminated with BuTs (19-402 ng(Sn)/g in mussels; 43-20641 ng(Sn)/g in sediments; 9-566
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39 22 ng(Sn)/L in overlying waters). The measured TBT concentrations indicate that toxic effects on
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41 23 marine organisms are expected at most locations. The simultaneous analysis of BuTs and total
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43 24 Sn in sediment cores allowed the assessment of TBT historical input, and it was demonstrated
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45 25 that resuspension of contaminated sediments leads to the release of all BuTs into the water
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47 26 column. This study shows that, despite the ban of TBT-based antifouling paints more than a
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49 27 decade ago, pollution of the marine environment with TBT is still a problem and regular
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51 28 monitoring remains essential.

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54 30 **Keywords:** tributyltin (TBT), butyltins (BuTs), pollution, Montenegrin Adriatic coast,
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56 31 sediments, mussels

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Tributyltin (TBT), one of the most toxic anthropogenic pollutants intentionally introduced into the aquatic environment, has been used as biocide in antifouling paints since the 1960s (Hoch, 2001). After its high toxicity to various aquatic non-target organisms was established, the use of TBT in antifouling paints was banned in many countries worldwide (Omae, 2003). In 2001, the International Maritime Organization (IMO) established the AFS Convention (International Convention on the Control of Harmful Antifouling Systems on Ships) (IMO, 2008), calling for a global ban on TBT-based paints from 2003. In Europe, the ban was implemented in 2003 by Regulation (EC) No. 782/2003 and 2008 was set as the deadline for the complete ban of their use. Subsequently, a decrease in TBT levels has been observed in European coastal areas (Cacciatore et al., 2018; Guomundsdóttir et al., 2011; Harrison et al., 2020; Langston et al., 2015; Laranjeiro et al., 2018), but TBT levels have still been above concentrations toxic to biota. In the last decade, high levels of TBT have been reported in European seas: Adriatic Sea (Erdelez et al., 2017; Formalewitz et al., 2019; Furdek Turk et al., 2020; Romanelli et al., 2019), North Sea (Eghart et al., 2017), Baltic Sea (Abraham et al., 2017; Filipkowska et al., 2016; Filipkowska and Kowalewska, 2019), Mediterranean and Atlantic coasts (Anastasiou et al., 2016; Concha-Grana et al., 2021; El Ayari et al., 2018) and in the Arctic (Kucklick and Ellisor, 2019; Metelkova et al., 2022). Recently observed TBT pollution was even worse in parts of the world where the use of TBT-based paints is not yet fully regulated (Bandara et al., 2021; Paz-Villarraga et al., 2015; Quintas et al., 2019). The above literature data clearly show that TBT pollution is still a major environmental problem that is far from being solved more than a decade after attempt for its global ban. However, the ban on the use of TBT never became “global” as the restrictions only applied to signatories of the IMO-AFS Convention (91 member states in 2021; Uc-Peraza et al., 2022), EU member states and countries with specific regulation in that sense. To make matters worse, TBT-based antifouling paints were still being manufactured in the United States and available on the market in 2021, even in some countries that are signatories of IMO-AFS Convention (Uc-Peraza et al., 2022).

Once TBT has entered the marine environment, it undergoes various processes such as microbiological and photolytic degradation, bioaccumulation by biota (e.g. gastropods, bivalves, fish) and adsorption to suspended particles (Furdek et al., 2012, 2016). The degradation of TBT occurs both in sediments and in the water column, and consists of a stepwise loss of butyl groups, via dibutyltin (DBT) and monobutyltin (MBT) to the inorganic Sn (Furdek et al., 2016, Furdek Turk et al., 2020). This process in the water column is quite rapid (half-lives of several days to weeks; Rodriguez-Gonzalez et al., 2013), and, therefore,

65 analysis of seawater provides information on the current level of BuTs in the marine
66 environment. On the other hand, butyltins (BuTs) concentrations accumulated in marine
67 organisms, such as mussels, reflect an average pollution of a water column over a longer period
68 of time of about several months (Furdek et al., 2012). Due to its hydrophobic characteristics,
69 TBT has an affinity to adsorb onto the suspended particles in the water column, which settle in
70 the sediments over time. Once in the sediment, TBT degrades slowly, with half-lives of several
71 years to decades (Furdek et al., 2016; Omae, 2003); therefore, TBT content in sediments could
72 provide information on TBT input over a long period of time, from several years to decades.
73 Not only BuTs are highly persistent in sediments, but they can also be released back into bottom
74 waters by diffusion or resuspension of sediments, making sediments a potential source of new
75 pollution to the water column (Furdek Turk et al., 2020; Hoch and Schwesig, 2004; Ruiz et al.,
76 2008). Nevertheless, the field evidence of desorption of BuTs from contaminated sediments
77 are rare (Furdek Turk et al., 2020). Therefore, it is important to determine the status of BuTs
78 pollution of coastal areas not only in the water column but also in sediments, and to assess the
79 risk of BuTs desorption from the contaminated sediments.

80 The level of TBT pollution in the Adriatic Sea (the northernmost arm of the Mediterranean
81 Sea) has been assessed in several studies, covering the coastal waters of Croatia (Erdelez et al.,
82 2017; Furdek et al., 2012; Furdek Turk et al., 2020), Slovenia (Formalewicz et al., 2019;
83 Milivojevič Nemanič et al., 2009) and Italy (Berto et al., 2007; Formalewicz et al., 2019;
84 Romanelli et al., 2019). All these studies showed that TBT pollution is a significant
85 environmental problem in coastal areas. Regular monitoring of the priority pollutants in
86 Croatian coastal waters carried out under the Water Framework Directive (WFD; Directive
87 2000/60/EC, 2000) also revealed that TBT levels in water are frequently above the prescribed
88 maximum annual average concentration (0.2 ng/L) (Furdek Turk et al., 2019). However, the
89 level of TBT pollution in the southern part of the Eastern Adriatic that belongs to Montenegro
90 has never been investigated and there are no data on the status of BuTs in this area. There is
91 only one data set for the port of Bar from 2014, when the total BuTs in sediments ranged from
92 18 to 33 ng(Sn)/g (Romanelli et al., 2019).

93 The Montenegrin coastline has a length of 294 km, of which 105 km belong to the large fjord-
94 like Boka Kotorska Bay, which is naturally divided into several smaller bays (Kotor, Risan,
95 Tivat and Herceg Novi). The entire coast is under high anthropogenic pressure due to
96 urbanisation and discharge of municipal wastewaters, maritime activities (marine traffic,
97 marinas, shipyards), fishing and tourism (Joksimović et al., 2017, 2020). The studies on the

98 distribution of ecotoxic metals in mussels, sediments and seagrass (Jokanović et al., 2021;
99 Joksimović et al., 2011, 2020; Radmirović et al., 2021; Stanković et al., 2015) have shown that
100 most of the investigated sites, especially shipyards and urban areas, are contaminated with
101 metals due to significant anthropogenic pressure.

102 The aims of this work were: i) to assess the level of BuTs pollution along the Montenegrin
103 coast by studying BuTs distribution in mussels and sediments; ii) to assess the extent of BuTs
104 desorption from contaminated sediments into the water column caused by sediment
105 resuspension; and iii) to assess the historical input of BuTs along the Montenegrin Adriatic
106 coast by studying the relationship between total Sn and BuTs in sediments.

107 Sampling locations included various areas along the Montenegrin coast which are affected by
108 intensive shipping and industrial activities, such as marinas, shipyards and municipal and local
109 ports. Samples of mussels *Mytilus galloprovincialis* (Lamarck, 1819) and sediments were
110 collected in July 2015 from 16 sampling sites, covering the areas of Boka Kotorska Bay
111 (namely, Kotor Bay and Tivat Bay) and the towns of Budva and Bar (Fig. 1; Table S1). In the
112 Kotor Bay samples were collected at 5 locations (Kot1, Kot1a, Kot2, Kot3, Kot3a) near the
113 town of Kotor, a tourist town with a marina, cruise port and a number of small ports. In the
114 Tivat Bay, the samples were taken at the marina Porto Montenegro in the town of Tivat (Tiv1,
115 Tiv2, Tiv3) and in front of the Bijela shipyard (TivB). In Budva (tourist town), samples were
116 taken at 4 locations - in the marina (Bud1, Bud3, Bud4) and in the local port (Bud1a). In the
117 town of Bar, one of the largest cargo, passenger and military ports on the Eastern Adriatic,
118 samples were taken at 3 locations, including the cargo (Bar1), military port (Bar4) and the
119 marina (Bar3). A brief description of each sampling site is given in Table S1 in the
120 Supplementary Information. At sites labelled with “a” (which were a short distance from the
121 site labelled with the same number) only mussels were collected. A total of 81 samples,
122 including 14 samples of mussels and 67 samples of sediment obtained by cutting sediment
123 cores (9 cores; 10-20 cm long, cut into 2 cm layers), were analysed for BuTs (i.e. MBT, DBT
124 and TBT). In addition, bottom waters, i.e. water overlying the sediment (9 samples), were
125 collected with a gravity corer to investigate the desorption of BuTs caused by sediment
126 resuspension. The water overlying sediment in the gravity corer was transferred to a dark glass
127 bottle after sediment particles had settled (approximately 15 min after sediment was taken out
128 of the sea with the gravity corer), acidified to pH=2 with nitric acid (HNO₃) and stored in the
129 dark at 4°C until analysis. Mussels (30 specimens per sampling site, with a shell length of 3 to
130 6 cm) were collected from the docks, rocky shores or boat strings. The shells were removed

131 and the soft tissue homogenised in a blender and later freeze-dried and stored at -20°C until
132 analysis. Sediments were collected using a UWITEC gravity corer (Umwelt-und
133 Wissenschaftstechnik, Austria) and frozen immediately after collection. The sediment cores
134 were cut into 2 cm layers, freeze-dried, homogenised by milling and stored at -20 °C until
135 analysis.

136 The analytical methods used for the analysis of BuTs (TBT, DBT and MBT) in seawater and
137 mussels are described in Furdek et al. (2012), while that used for the analysis of sediments is
138 described in Furdek et al. (2016). Briefly, BuTs were extracted from 300 ml of seawater, while
139 simultaneous extraction and derivatisation were performed in a sodium acetate-acetic acid
140 buffer (pH=4.8) by adding sodiumtetraethyl borate (NaBEt₄, 1% (w/v)) and hexane and
141 mechanical shaking for 30 min at 350 rpm. Butyltins from sediments were extracted from 0.5-
142 2 g of sample by acetic acid and ultrasound-assisted agitation (30 min, 55 Hz), while BuTs
143 from mussel were extracted from 0.5-1 g of lyophilised tissue with 0.1 mol/L hydrochloric acid
144 (HCl) in methanol using ultrasound-assisted agitation (30 min, 55 Hz). For both sediments and
145 mussels, the derivatisation of compounds in the extract was performed in sodium acetate-acetic
146 acid buffer (pH=4.8) with NaBEt₄ (1% (w/v)) and transferred into hexane by mechanical
147 shaking at 350 rpm for 30 min. Analyses of BuTs in seawater were carried out on a gas
148 chromatograph (GC Agilent 6890, Agilent Technology) coupled with inductively coupled
149 plasma mass spectrometry (ICP-MS Agilent 7900, Agilent Technology), while detection of
150 BuTs in mussels and sediments was performed using gas chromatograph (GC Varian CP 3800,
151 Varian) with pulsed flame photometric detector (PFPD, Varian). Tripropyltin (TPrT) was used
152 as an internal standard and quantification was performed by applying the standard addition
153 calibration method. Quality control of the analytical procedure for the determination of BuTs
154 in mussels and sediments was performed by analysing the certified reference materials (CRM)
155 for mussels (CE 477, ERM, European Commission, Geel, Belgium) and marine sediment
156 (PACS 2, NRC-CNRC, Canada). In addition, the accuracy of all three methods was further
157 confirmed by successful participation in the proficiency tests. The detection limits for TBT,
158 DBT and MBT were 0.1-0.5 ng(Sn)/L for seawater, 0.9-5.1 ng(Sn)/g for mussels and 0.9-6.1
159 ng(Sn)/g for sediment. Total Sn in sediments was analysed according to the method described
160 in Furdek Turk et al. (2020) using high resolution inductively coupled plasma mass
161 spectrometry (HR-ICPMS; Element 2, Thermo Finnigan). Sediments (0.1 g) were digested in
162 a microwave oven (Multiwave 3000, Anton Paar) by two-step total digestion procedure HNO₃
163 (65% *s.p.*) + HCl (36% *s.p.*) + hydrofluoric acid (HF, 48% *s.p.*), followed by boric acid

164 (H_3BO_3 , 40 g/L). The quality control was performed by simultaneous measurements of
165 certified reference materials for marine sediment (MESS-3, NRC-CNRC, Canada) for which
166 satisfactory results were obtained.

167 The BuTs pollution of the water column was not detected directly, but indirectly by
168 determining the accumulated BuTs in mussels. Indeed, mussels are a reliable biomonitor of
169 TBT pollution as they are sessile and filter-feeding organisms, with a great ability to
170 bioaccumulate TBT from water and a limited ability to metabolise it (Magi et al., 2008). The
171 TBT concentration detected in mussels reflects the ambient TBT level during the last months
172 (2-3 months; Salazar and Salazar, 1996) because during this period an equilibrium is reached
173 between uptake from the water (i.e. accumulation), metabolism of TBT to DBT and MBT, and
174 excretion of these compounds back into the water (Gomez-Ariza et al., 1999; Magi et al., 2008).
175 Therefore, TBT levels measured in mussels are a reliable indicator of recent pollution in the
176 water column over the last few months, in contrast to levels measured in seawater that only
177 indicate the momentary level of pollution. The concentrations of BuTs
178 ($\sum\text{BuTs}=\text{MBT}+\text{DBT}+\text{TBT}$) in mussels varied from 19 to 402 ng(Sn)/g (Table 1, Fig. 2A);
179 concentrations of DBT and TBT were of the same order of magnitude (10-173 ng(Sn)/g for
180 DBT and 6.7-179 ng(Sn)/g for TBT), while MBT was the least abundant compound (<5-50
181 ng(Sn)/g). In all investigated marinas (Kot1a, Tiv1, Tiv2, Tiv3, Bud1 and Bar3), $\sum\text{BuTs}$ were
182 above 100 ng(Sn)/g, while the highest concentration (402 ng(Sn)/g) was found in mussels from
183 the marina Bar3. At all locations, TBT and DBT account for 30-55% and 35-58% of the total
184 BuTs, respectively (Fig. 2B). High concentrations and proportions of TBT in mussels reflect
185 recent inputs of TBT, but may also be a consequence of the limited ability of mussels to
186 metabolise TBT, as bivalves do not have an efficient detoxification system (Chandrinou et al.,
187 2007; Diez et al., 2005; Lee, 1996). However, significant correlations between TBT and DBT
188 ($r=0.912$, $p<0.05$, Spearman) suggest that DBT in mussel tissues may be the product of TBT
189 metabolism, while lower but still significant correlation between TBT and MBT ($r=0.693$,
190 $p<0.05$, Spearman) and DBT and MBT ($r=0.616$, $p<0.05$, Spearman) suggests that DBT could
191 be eliminated from the organism before being degraded to MBT, or that it is metabolised more
192 slowly compared to MBT (Furdek et al., 2012). In conclusion, the measured BuTs
193 concentrations in mussels indicate that TBT pollution in seawater has been present at all
194 investigated sites along the Montenegrin coast in recent months.

195 The spatial and depth distributions of BuTs in sediments were highly variable (Fig. 3A, Fig. 4,
196 Table 1), with ranges encompassing 3-4 orders of magnitude (<9-20641 for BuTs; <1-14900

197 for TBT; <2-4279 for DBT; <6-3651 for MBT, expressed in ng(Sn)/g). The highest
198 concentrations of BuTs were found in the sediments sampled in front of the Bijela shipyard
199 (20641 ng(Sn)/g), while at all other sites maximum concentration did not exceed 2000 ng(Sn)/g
200 (Table 1). TBT was the prevailing compound at all sites, accounting for up to 75% of all BuTs
201 (Table 1). The depth profiles of BuTs in 9 sediment cores from different locations were highly
202 variable, both in terms of the level of concentrations and the depth pattern (Fig. 4). Sediments
203 in the city of Kotor (Kot1 and Kot2) may be considered as not polluted with TBT (Fig. 4); the
204 concentrations of Σ BuTs were up to 35 ng(Sn)/g and were mainly in the form of TBT
205 degradation products, i.e. DBT and MBT. In both sediment cores TBT was detected in only
206 one layer (0-2 cm – Kot1 and 10-12 cm – Kot2). The sediment inside the marina in the town
207 of Tivat (Tiv2) was heavily contaminated with BuTs throughout the core (up to 600 ng(Sn)/g),
208 with a high proportion of TBT in each layer (30-40%). In contrast, in the sediment sampled
209 outside the marina (Tiv3), BuTs concentrations were much lower, although the high proportion
210 of TBT (up to 45%) was also detected in the deeper layers. The sediment sampled in front of
211 the Bijela shipyard (TivB) was extremely contaminated; the BuTs concentrations in the upper
212 12 cm did not fall below 6500 ng(Sn)/g, while the maximum concentration of 20641 ng(Sn)/g
213 was detected in the subsurface layer. In all layers, TBT was the prevailing compound and
214 accounted for 50-75% of the total BuTs. The BuTs depth distributions in two sediment cores
215 sampled within the same marina in the city of Budva (Bud1 and Bud3) were different, although
216 these sites are only 100 m apart. While in the sediment core Bud1 only the surface sediment
217 layers were slightly contaminated with BuTs, the sediments sampled closer to the service hoist
218 (Bud3) were heavily contaminated to a depth of 12 cm, with BuTs concentrations up to 1180
219 ng(Sn)/g. In the city of Bar, the sediments of the marina (Bar3) and the military port (Bar4)
220 were significantly contaminated with BuTs (concentrations of up to 1980 ng(Sn)/g), with the
221 highest pollution observed in the deeper layers, where not only the concentrations were high,
222 but also the percentage of undegraded TBT (up to 75%).

223 Based on the depth profiles obtained, several patterns of BuTs behaviour could be observed
224 (Fig. 4). First, BuTs concentration profiles do not follow the same depth pattern; in some
225 sediments BuTs decreased with depth, while in others concentrations were similar or vary
226 throughout the depth of the core. Such different depth distributions may indicate different TBT
227 inputs over time or different BuTs degradation efficiencies in different sediments. Since
228 different BuTs depth distributions were observed in the sediments from marinas of similar size
229 and similar intensity of marine traffic (such as Bud1, Bar3, Kot1 and Tiv2), the most likely

230 explanation is that the observed depth profiles are the result of different persistence of TBT in
231 these sediments. It was demonstrated that sediments characteristics, namely grain size and
232 organic matter, strongly affects the degradation process of TBT and its persistence in sediments
233 (Furdek et al., 2016; Furdek Turk et al., 2020). Organic matter plays a crucial role as a TBT
234 sorbent in sediments and, therefore, influences TBT degradation rate by determining the
235 bioavailable fraction in porewater where TBT degradation occurs (Furdek at al., 2016). This
236 means that, in sediments rich in organic matter, TBT will be less available to degradation and,
237 consequently, more persistent over time (Furdek at al., 2016). Secondly, at most locations TBT
238 degradation products, i.e. MBT and DBT, are the prevailing BuT compounds through the entire
239 depth cores, which could indicate efficient degradation of TBT in these sediments. An
240 exception is the sediments sampled in Bijela shipyard (TivB) and in two layers of cores Tiv2
241 and Bar4, where the percentage of $TBT/\sum BuTs$ was more than 50% (Fig. 4). Although the
242 proportions of DBT and MBT prevail over TBT, their accumulation in the deeper layers was
243 not observed in any sediment core. There are two explanations for this: i) DBT and MBT, being
244 less hydrophobic compounds, are more easily desorbed from sediments than TBT
245 (Poerschmann et al., 1997), and ii) the degradation of DBT and MBT to inorganic Sn is efficient
246 in both oxic and anoxic sediments. Indeed, Furdek et al. (2016) demonstrated that the rate of
247 DBT degradation in sediments is faster than the rate of its formation from TBT, which prevents
248 accumulation of DBT in sediments, and that MBT, after desorption from sediment to anoxic
249 porewater, is almost immediately degraded to inorganic Sn.

250 However, a reliable assessment of the long-term behaviour, persistence and historical input of
251 TBT can only be made by simultaneously determining BuTs and total Sn in sediments (Furdek
252 Turk et al., 2020). First, it should be confirmed that the inorganic Sn contamination originates
253 mainly from TBT-antifouling paints and not from other possible sources such as municipal and
254 industrial wastewater or landfill leachates. Namely, inorganic Sn is used in products such as
255 food cans, welding equipment, electronics, and household products (Pougnnet et al., 2014).
256 Inputs of other organotin compounds such as mono- and disubstituted BuTs (often used as PVC
257 stabilizers) and phenyltins (used as pesticides, while triphenyltin (TPhT) is also used as a
258 biocide in antifouling paints) (Omae, 2003) could also lead to the formation of inorganic Sn.
259 However, in Europe TPhT is used to a much lesser extent than TBT (Lagerstrom et al., 2017),
260 which is confirmed by the data on TPhT contamination of the Croatian Adriatic coast, where
261 only sporadic low levels of TPhT have been detected in mussels (Furdek et al., 2012) and
262 sediments (Furdek et al., 2016).

263 To investigate the source of Sn contamination and confirm that inorganic Sn originates mainly
264 from the degradation of TBT, we examined the relationships between BuTs and inorganic Sn
265 in the sediments by determining the total Sn depth profiles and calculating butyltin degradation
266 index (BDI), following the approach presented in previous studies (Furdek Turk et al., 2020;
267 Pougnet et al., 2014). Total Sn concentrations ranged from 3.8 to 46.5 $\mu\text{g/g}$ (Fig. 4) and were
268 higher than the background levels of Sn, obtained by the analysis of older uncontaminated
269 sediments of the Boka Kotorska Bay (2.8 $\mu\text{g/g}$) and the coastal zone of Montenegro (1.7 $\mu\text{g/g}$)
270 (Mikac et al., 2022). The degree of Sn contamination was assessed by enrichment factors
271 ($\text{EF} = (\text{Sn}/\text{Al})_{\text{sample}} / (\text{Sn}/\text{Al})_{\text{background}}$), according to the scale proposed by Sutherland (2000):
272 $\text{EF} < 2$ indicates no or minimal, $\text{EF} = 2-5$ moderate, $\text{EF} = 5-20$ significant, $\text{EF} = 20-40$ very high,
273 and $\text{EF} > 40$ extreme enrichment or contamination. The calculated EFs showed that all
274 sediments studied were enriched in Sn; the sediments from Kotor Bay (Kot1, Kot2) and Tivat
275 Bay (Tiv1, Tiv2, TivB) were significantly contaminated with Sn (EFs between 5 and 20), while
276 the sediments from Budva (Bud1, Bud3) and Bar (Bar3, Bar4) had EFs between 2 and 12,
277 indicating moderate contamination with Sn.

278 To investigate the source of Sn contamination, we examined the relationship between TBT and
279 its degradation products (DBT, MBT and inorganic Sn) by calculating the BDI index, which is
280 a commonly used tool to study TBT degradation efficiency. We calculated the BDI using two
281 approaches: i) the commonly known approach, which considers only DBT and MBT as TBT
282 degradation products; $\text{BDI} = (\text{MBT} + \text{DBT}) / \text{TBT}$ (Garg et al., 2009), and ii) a modified
283 approach proposed by Pougnet et al. (2014), which considers the inorganic Sn as the final
284 product of total degradation; $\text{BDI}_{\text{mod}} = (\text{Sn}_{\text{inorganic}} + \text{MBT} + \text{DBT}) / \text{TBT}$, while the $\text{Sn}_{\text{inorganic}}$ could
285 be calculated as $\text{Sn}_{\text{total}} - \text{Sn}_{\text{background}} - \sum \text{BuTs}$. A stronger correlation between TBT and BDI_{mod}
286 ($r = 0.961$; $p < 0.01$, Spearman) than between TBT and BDI ($r = 0.722$, $p < 0.05$, Spearman) was
287 observed when combining samples from all sediment cores. This indicates that most of the
288 TBT has been completely degraded to inorganic Sn, while the anthropogenic fraction of
289 inorganic Sn mainly originates from the degradation of TBT released from antifouling paints.

290 Considering the above conclusion that most of the inorganic Sn originates from TBT
291 antifouling paints in the studied environments, we used BuTs and total Sn depth distributions
292 to explain the historical input and behaviour of TBT in the investigated sediments and to clarify
293 whether the observed BuTs depth distributions are the result of different TBT input over time
294 or different TBT persistence in sediments. From the observation of the determined depth
295 profiles (Fig. 4) the following conclusion are drawn. The total Sn depth profiles in the Kotor

296 Bay (Kot1 and Kot2) show high (EF=8-18) and continuous input of Sn over time, while the
297 \sum BuTs accounts for less than 0.5% of the total Sn at all depths, indicating that the low TBT
298 and BuTs levels are a consequence of an efficient TBT degradation rather than low TBT input
299 over time. In the marinas of Budva (Bud1, Bud3) and Tivat (Tiv2, Tiv3) all cores are similarly
300 contaminated with Sn (EF=3-10) (except for a few layers where EF is higher), indicating a
301 comparable input of TBT over time. However, the percentage of \sum BuTs/Sn_{total} in cores Tiv3
302 and Bud1 (<1%) is much lower than in cores Tiv2 and Bud3 (1-18%), indicating less efficient
303 TBT degradation in the later cores. In the sediment cores from Bar (Bar3, Bar4) the total Sn
304 input is generally lower (EF=2-7) compared to the other sites, but \sum BuTs/Sn_{total} was high (4-
305 20%), indicating high persistence of TBT in these sediments, especially in the sediments from
306 marina (Bar3), where the highest level of BuTs in mussels were also found. In the military port
307 (Bar4) the absence of BuTs in the surface sediments suggests that TBT has not been introduced
308 recently; however, the elevated total Sn and the relatively high TBT levels in mussels indicate
309 the opposite, namely that there was a recent input of TBT and its efficient degradation to
310 inorganic Sn in the surface sediments. By contrast, the high level of TBT in the bottom layer
311 of this core indicates poor degradation of TBT in older sediments. After all, the observed depth
312 profiles demonstrated less efficient TBT degradation in cores Tiv2, Bud3 and Bar3 than in the
313 other sediment cores analysed. Finally, the sediment core TivB is clearly different from all the
314 other cores; not only BuTs and total Sn concentrations (EF=15-20) are much higher than in the
315 other sediments, but also the proportions of TBT/ \sum BuTs and \sum BuTs/Sn_{total} are very high (50-
316 75% and 20-65%, respectively). As this core was taken near the shipyard, these results could
317 be explained by the presence of paint particles containing TBT in the form that is not available
318 to degradation (Furdek Turk et al., 2020).

319 It should be emphasized that the proportion of \sum BuTs/Sn_{total} was generally not higher than
320 10% in any of the sediments studied (excluding the sediment from the shipyard), which may
321 be surprising considering that the degradation of TBT in sediments is a slow process ($t_{1/2}$ =
322 several years to decades; Omae, 2003). The same was found by Furdek Turk et al. (2020), who
323 discussed that most of the TBT leached from ships is degraded to inorganic Sn already in the
324 water column ($t_{1/2}$ = several days to weeks; Rodriguez-Gonzalez et al., 2013), so that only a
325 small fraction of TBT (~10%) reaches the sediments. Therefore, a reliable assessment of TBT
326 input in the time period covered by the sediment cores can only be performed by taking into
327 account the total amount of Sn; otherwise, the total TBT input to the certain environment could
328 be underestimated (at least by a factor of ten).

1 TBT pollution of sediments is not only a problem because it poses a threat to the benthic
2 organisms living there; the big problem lies in the fact that contaminated sediments are a
3 potential source of BuTs pollution for the water column. Although it has been experimentally
4 proven many times that BuTs can be desorbed from sediments (Berg et al., 2001; Burton et al.,
5 2004), this has been demonstrated only in a few field studies (Chen et al., 2022; Furdek Turk
6 et al., 2020). However, knowledge about the extent to which contaminated sediments act as a
7 source of BuT pollution is still incomplete. To investigate the behaviour of BuTs during the
8 resuspension of disturbed sediments, we analysed the water overlying the sediment in the
9 gravity corer. It was assumed that the penetration of the gravity corer into the sediment would
10 cause resuspension of fine particles from the sediment surface, which could mimic, to some
11 extent, the resuspension of surface sediments caused by waves or bioturbation. The BuTs
12 concentrations in the water above the sediment (Table 1, Fig. 5A, B) showed a predominance
13 of MBT (8.8-277 ng(Sn)/L) and DBT (0.2-130 ng(Sn)/L) over TBT (<0.1-160 ng(Sn)/L),
14 which was found only at two sites (Tiv2 and TivB) where the surface sediments contained more
15 than 50% of BuTs in the form of TBT (Fig. 3B). As these concentrations are much higher than
16 those normally found in the water column and porewater (<10 ng(Sn)/L; Furdek et al., 2012;
17 Furdek Turk et al., 2020), we assume that most of the detected BuTs are desorbed from the
18 sediments into the overlying water. These data support the results of a similar study conducted
19 with contaminated coastal sediments in Croatia (Furdek Turk al., 2020). Both studies showed
20 that contaminated sediments are a potential source of BuTs to the water column, especially
21 MBT and DBT as less hydrophobic and weakly adsorbed compounds that can be released from
22 the sediments more easily than TBT. However, this study has shown that resuspension of
23 sediments can also lead to the release of TBT, especially from contaminated sediments with
24 high levels of TBT in the surface layers.

25 An assessment of the extent of BuTs contamination in the coastal environment of Montenegro
26 was performed by comparing BuTs and TBT levels determined in different coastal areas of
27 Europe during the last decade (Table 2). The comparison of literature data given in Table 2
28 showed that the Eastern Adriatic coast (Croatian and Montenegrin) is highly contaminated with
29 BuT compounds. However, the level of TBT pollution strongly depends on the type of
30 sampling locations (marina, port, beaches) and is related to the intensity of marine traffic
31 (Briant et al., 2013; Suzdalev et al., 2015), and, therefore, this conclusion should be taken with
32 caution as it may be influenced by different sampling strategies of the presented studies and
33 prevalence of more contaminated sites along the Croatian coast. In the Water Framework

362 Directive (WFD; Directive 2000/60/EC, 2000) TBT is listed as one of the priority substances
363 that should be monitored to assess the chemical status of a water body, but within this Directive
364 TBT presence in the environment is regulated only by the prescribed maximum allowed
365 concentration in seawater (the annual average should be less than 0.2 ng/L). However, several
366 regional conventions, such as OSPAR (Convention for the Protection of the Marine
367 Environment of the North-East Atlantic; OSPAR, 2004) and HELCOM Conventions
368 (Convention on the Protection of the Marine Environment of the Baltic Sea Area; HELCOM,
369 2018), have established Environment Assessment Criteria (EAC) for the assessment and
370 monitoring of the environmental status of regional waters, which could be applied for
371 assessments based on the measurement of TBT in sediments and biota. OSPAR (OSPAR,
372 2004) has established EAC for TBT in mollusks; the lower EAC ($EAC_{low} = 4.9 \text{ ng(Sn)/g}$) is
373 defined as the threshold for protection of all marine species from chronic effects and the upper
374 EAC ($EAC_{high} = 72 \text{ ng(Sn)/g}$) is defined as the highest level at which no acute toxic effects are
375 expected. The TBT concentrations quantified in mussel tissues were above the EAC_{low} at all
376 sites, while they were above the EAC_{high} at site Bar3, indicating that chronic effects for marine
377 organisms sensitive to TBT are to be expected at all locations. The assessment of TBT pollution
378 based on the TBT concentrations quantified in sediments was carried out according to the
379 Norwegian environmental quality classification system defined for management purposes
380 (Bakke et al., 2010); Background: $<0.4 \text{ ng(Sn)/g}$, Good: $0.4\text{-}2.1 \text{ ng(Sn)/g}$, Moderate: $2.1\text{-}8.3$
381 ng(Sn)/g , Poor: $8.3\text{-}41.7 \text{ ng(Sn)/g}$, and Very Poor: $>41.7 \text{ ng(Sn)/g}$. At seven (out of nine) sites
382 investigated surface sediments are contaminated with TBT; Kot1 and Bud1 were moderately
383 contaminated with TBT, while the environmental status of Tiv3 and Bud3, as well as Tiv2,
384 TivB and Bar3, can be evaluated as poor and very poor, respectively, indicating that TBT is
385 expected to have toxic effects on marine organisms and the occurrence of imposex in
386 gastropods is very likely at these locations (Erdelez et al., 2017; Laranjeiro et al., 2018).

387 The presented results show that the investigated areas on the Montenegrin coast are polluted
388 with TBT, which indicates the need for further monitoring of the coastal area. Apparently,
389 TBT-based antifouling paints, despite of its ban, have been used within a few months of
390 sampling (as shown by BuTs levels measured in mussels), but also over a longer period of time
391 (as shown by BuTs levels measured in sediments). The main source of pollution could be small
392 local and leisure boats that are not subject to any control of antifouling paint applied. Therefore,
393 they may be illegally painted with TBT-containing paints, for which is shown that were still
394 present on the global market in 2021 (Uc-Peraza et al., 2022) or can have old layers of TBT-

395 based paint that are not properly removed from the boat (Lagerström et al., 2017, 2019). Indeed,
396 a recent study in the Nordic countries has demonstrated the presence of TBT in the subsurface
397 paint layers of all investigated leisure boats (Lagerström et al., 2017, 2019) and shown that
398 they are source of TBT pollution. The results have also shown that resuspension of
399 contaminated sediments may cause pollution of the water column, especially at the Bijela
400 shipyard (TivB) where remediation measures are strongly recommended. Recently, extreme
401 contamination with ecotoxic metals (Mikac et al., 2022; Radomirović et al., 2021) and
402 significantly altered microbial community have been demonstrated in sediments sampled near
403 this shipyard (Jokanović et al., 2021).

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412 **References**

- 413 Abraham M, Westphal L, Hand I, Lerz A, Jeschek J, Bunke D, Leipe T, Schulz-Bull D (2017)
414 TBT and its metabolites in sediments: Survey at a German coastal site and the central Baltic
415 Sea. *Mar. Pollut. Bull.* 121, 404-410.
- 416 Anastasiou TI, Chatzinikolaou E, Mandalakis M, Arvanitidis C (2016) Imposex and organotin
417 compounds in ports of the Mediterranean and the Atlantic: Is the story over? *Sci. Total.*
418 *Environ.* 569-570, 1315-1329.
- 419 Bandara KRV, Chinthaka SDM, Yasawardene SG, Manage PM (2021) Modified, optimized
420 method of determination of Tributyltin (TBT) contamination in coastal water, sediment and
421 biota in Sri Lanka. *Mar. Pollut. Bull.* 166, 112202.
- 422 Bakke T, Källqvist T, Ruus A, Breedveld GD, Hylland K (2010) Development of sediment
423 quality criteria in Norway. *J. Soil Sed.* 10, 172-178.

- 1 424 Berg M, Arnold CG, Müller RS, Mühlemann J, Schwarzenbach RP (2001) Sorption and
2 425 desorption behaviour of organotin compounds in sediment-pore water systems. Environ. Sci.
3 426 Technol. 35, 3151-3157.
- 4
5
6 427 Berto D, Giani M, Boscolo R, Covelli S, Giovanardi O, Massironi M, Grassia L (2007)
7 428 Organotins (TBT and DBT) in water, sediments, and gastropods of the southern Venice lagoon
8 429 (Italy). Mar. Pollut. Bull. 55, 425-435.
- 9
10
11
12 430 Briant N, Bancon-Montigny C, Elbaz-Poulichet F, Freydier R, Delpoux S, Cossa D (2013)
13 431 Trace elements in the sediments of a large Mediterranean marina (Port Camargue, France):
14 432 Levels and contamination history. Mar. Pollut. Bull. 73, 78-85.
- 15
16
17
18 433 Briant N, Bancon-Montigny C, Freydier R, Delpoux S, Elbaz-Poulichet F (2016) Behaviour of
19 434 butyltin compounds in the sediment pore waters of a contaminated marina (Port Camargue,
20 435 South of France). Chemosphere 150, 123-129.
- 21
22
23
24 436 Burton ED, Phillips IR, Hawker DW (2004) Sorption and desorption behavior of tributyltin
25 437 with natural sediments. Environ. Sci. Technol. 38, 6694-6700.
- 26
27
28 438 Cacciatore F, Brusà RB, Noventa S, Antonini C, Moschino V, Formalewicz M, Gion C, Berto
29 439 D, Gabellini M, Marin MG (2018) Imposex levels and butyltin compounds (BTs) in *Hexaplex*
30 440 *trunculus* (Linnaeus, 1758) from the northern Adriatic Sea (Italy): Ecological risk assessment
31 441 before and after the ban. Ecotoxicol. Environ. Safety 147, 688-698.
- 32
33
34
35
36 442 Chandrinou S, Stasinakis AS, Thomaidis NS, Nikolaou A, Wegener JW (2007) Distribution of
37 443 organotin compounds in the bivalves of the Aegean Sea, Greece. Environ. Inter. 33, 226-232.
- 38
39
40 444 Chen C, Chen L, Huang Q, Zhang W, Leung KM (2022) Pulsed distribution of organotins in
41 445 the turbidity maximum zone of the Yangtze Estuary throughout a tidal cycle. Mar. Pollut. Bull.
42 446 178, 113600.
- 43
44
45
46 447 Concha-Graña E, Moscoso-Pérez C, Fernández-González V, López-Mahía P, Gago J, León
47 448 VM, Muniategui-Lorenzo S (2021) Phthalates, organotin compounds and per-polyfluoroalkyl
48 449 substances in semiconfined areas of the Spanish coast: Occurrence, sources and risk
49 450 assessment. Sci. Total. Environ. 780, 146450.
- 50
51
52
53
54 451 Diez S, Lacorte S, Viana P, Barcelo D, Bayona J (2005) Survey of organotin compounds in
55 452 rivers and coastal environments in Portugal 1999-2000. Environ. Pollut. 136, 525-536.
- 56
57
58
59
60
61
62
63
64
65

1
2 454 Directive 2000/60/EC (2000) Directive of the European Parliament and of the Council
3 establishing a framework for the Community action in the field of water policy (EU Water
4 Framework Directive - WFD), Official Journal L 327.
5
6 456 Egardt J, Nilsson P, Dahllöf I (2017) Sediments indicates the continued use of banned
7 antifouling compounds. *Mar. Pollut. Bull.* 125, 282-288.
8
9
10 458 El Ayari T, Bierne N, El Menifa NT (2018) ImPOSEX incidence in *Stramonita haemastoma*
11 (Gastropoda: Muricidae) from the Mediterranean and Atlantic coast after Tributyltin global
12 ban. *J. Sea Res.* 134, 10-15.
13
14 460
15
16 461 Erdelez A, Furdek Turk M, Štambuk A, Župan I, Peharda M (2017) Ecological quality status
17 of the Adriatic coastal waters evaluated by the organotin pollution biomonitoring. *Mar. Pollut.*
18 *Bull.* 123, 313-323.
19
20 463
21
22 464 Filipkowska A, Lubecki L (2016) Endocrine disruptors in blue mussels and sediments from the
23 Gulf of Gdańsk (Southern Baltic). *Environ. Sci. Pollut. Res.* 23, 13864–13876.
24 465
25
26 466 Filipkowska A, Złoch I, Wawrzyniak-Wydrowska B, Kowalewska G (2016) Organotins in fish
27 muscle and liver from the Polish coast of the Baltic Sea: Is the total ban successful? *Mar. Pollut.*
28 *Bull.* 111, 493-499.
29
30 468
31
32 469 Filipkowska A, Kowalewska G (2019) Butyltins in sediments from the Southern Baltic coastal
33 zone: Is it still a matter of concern, 10 years after implementation of the total ban? *Mar. Pollut.*
34 *Bull.* 146, 343-348.
35
36 471
37
38 472 Formalewicz MM, Rampazzo F, Noventa S, Gion C, Petranich E, Crosera M, Covelli S,
39 Faganeli J, Berto D. (2019) Organotin compounds in touristic marinas of the northern Adriatic
40 Sea: occurrence, speciation and potential recycling at the sediment-water interface. *Environ.*
41 *Sci. Pollut. Res.* 26, 31142–31157.
42 474
43
44 475
45
46 476 Furdek Turk M, Ivanić M, Zuliani T, Milačić R, Mikac N (2019) State of pollution of Croatian
47 Adriatic coast with tributyltin compounds, Proceeding of the 7th Croatian water conference with
48 international participation, Opatija, Croatia, June 2019, pp. 555-563 (in Croatian)
49
50 478
51
52 479 Furdek M, Mikac N, Bueno M, Tessier E, Cavalheiro J, Monperrus M (2016) Organotin
53 persistence in contaminated marine sediments and porewaters: In situ degradation study using
54 species-specific stable isotopic tracers. *J. Hazard. Mater.* 307, 263-273.
55
56 481
57
58
59
60
61
62
63
64
65

- 1
2 482 Furdek M, Vahčić M, Ščančar J, Milačić R, Kniewald G, Mikac N (2012) Organotin
3 483 compounds in seawater and mussels *Mytilus galloprovincialis* along the Croatian Adriatic
4 484 coast. *Mar. Pollut. Bull.* 64, 189-199.
- 5
6 485 Furdek Turk M, Ivanić M, Dautović J, Bačić N, Mikac N (2020) Simultaneous analysis of
7 486 butyltins and total tin in sediments as a tool for the assessment of tributyltin behaviour, long-
8 487 term persistence and historical contamination in the coastal environment, *Chemosphere* 258,
9 488 127303.
- 10
11
12
13
14 489 Garg A, Antón-Martín R, García-Luque E, Riba I, DelValls T (2009) Distribution of butyltins
15 490 (TBT, DBT, MBT) in sediments of Gulf of Cádiz (Spain) and its bioaccumulation in the clam
16 491 *Ruditapes philippinarum*. *Ecotoxicology* 18,1029–1035.
- 17
18
19
20 492 Gomez-Ariza JL, Morales E, Giraldez I (1999) Uptake and elimination of tributyltin in clams,
21 493 *Venerupis decussata*. *Mar. Environ. Res.* 47, 399-413.
- 22
23
24 494 Guomundsdóttir LO, Ho KKY, Lam JCW, Svavarsson J, Leung KMY (2011) Long-term
25 495 temporal trend (1992-2008) of imposex status associated with organotin contamination in the
26 496 dogwhelk *Nucella lapillus* along the Icelandic coast. *Mar. Pollut. Bull.* 63, 500-507.
- 27
28
29
30 497 Harrison TD, Gilmour G, McNeill MT, Armour N, McIlroy L (2020) Survey of imposex in
31 498 *Nucella lapillus* as an indicator of tributyltin pollution in Northern Irish coastal waters, 2004
32 499 to 2017. *Mar. Pollut. Bull.* 159, 111474.
- 33
34
35
36 500 HELCOM (2018) TBT and imposex. HELCOM core indicator report. Online. [October 2022],
37 501 [[https://www.helcom.fi/wp-content/uploads/2019/08/Tributyltin-TBT-and-imposex-](https://www.helcom.fi/wp-content/uploads/2019/08/Tributyltin-TBT-and-imposex-HELCOM-core-indicator-2018.pdf)
38 502 [HELCOM-core-indicator-2018.pdf](https://www.helcom.fi/wp-content/uploads/2019/08/Tributyltin-TBT-and-imposex-HELCOM-core-indicator-2018.pdf)]
- 39
40
41
42 503 Hoch M (2001) Organotin compounds in the environment. *Appl. Geochem.* 16, 719-743.
- 43
44 504 Hoch M and Schwesig D (2004) Parameters controlling the partitioning of tributyltin (TBT) in
45 505 aquatic systems. *Appl. Geochem.* 19, 323–334.
- 46
47
48
49 506 IMO, 2008. Summary of the status of conventions as at 31 May 2007. Available in:
50 507 International Maritime Organization, United Kingdom. <http://www.imo.org>.
- 51
52
53 508 Jokanović S, Kajan S, Perović S, Ivanić M, Mačić V, Orlić S (2021) Anthropogenic influence
54 509 on the environmental health along Montenegro coast based on the bacterial and chemical
55 510 characterization. *Environ. Pollut.* 271, 116383.

- 511 Joksimović A, Djurović M, Semenov AV, Zonn IS, Kostianoy AG (Eds) (2017) The Boka
512 Kotorska Bay Environment. The Handbook of Environmental Chemistry 54 (Series Eds: D.
513 Barceló, A. G. Kostianoy). Springer.
- 514 Joksimović D, Perošević A, Castelli A, Pestorić B, Šušković D, Đurović D (2020) Assessment
515 of heavy metal pollution in surface sediments of the Montenegrin coasts: a 10-years review. J.
516 Soil Sed. 20, 2598-2607.
- 517 Joksimović D, Tomić I, Stanković AR, Jović M, Stanković S (2011) Trace metal concentrations
518 in Mediterranean blue mussel and surface sediments and evaluation of the mussels quality and
519 possible risks of high human consumption. Food Chem. 127, 632–637.
- 520 Kucklick JR, Ellisor MD (2019) A review of organotin contamination in arctic and subarctic
521 regions. Emerging Contaminants 5, 150-156.
- 522 Lagerström M, Yngsell D, Eklund B, Ytreberg E (2019) Identification of commercial and
523 recreational vessels coated with banned organotin paint through screening of tin by portable
524 XRF. J. Hazard. Mater. 362, 107-114.
- 525 Lagerström M, Strand J, Eklund B, Ytreberg E (2017) Total tin and organotin speciation in
526 historic layers of antifouling paint on leisure boat hulls. Environ. Pollut. 220, 1333-1341.
- 527 Langston WJ, Pope ND, Davey M, Langston KM, O' Hara SCM, Gibbs PE, Pascoe PL (2015)
528 Recovery from TBT pollution in English Channel environments: a problem solved? Mar.
529 Pollut. Bull. 95, 551-564.
- 530 Laranjeiro F, Sanchez-Marin P, Oliveira IB, Galante-Oliveira S, Barroso C (2018) Fifteen
531 years of imposex and tributyltin monitoring along the Portuguese coast. Environ. Pollut. 232,
532 411-421.
- 533 Lee RF (1996) Metabolism of tributyltin by aquatic organisms, in: Champ, M.A. and Selignam,
534 P.F., Organotin - environmental fate and effects. Chapman and Hall, London, pp. 369-382.
- 535 Magi E, Liscio C, Pistarino E, Santamaria B, Di Carro M, Tiso M, Scaloni A, Renzone G,
536 Cosulich ME (2008) Interdisciplinary study for the evaluation of biochemical alternations on
537 mussel *Mytilus galloprovincialis* exposed to a tributyltin-polluted area. Anal. Bioanal. Chem.
538 391, 671-678.
- 539 Metelkova L, Zhakovskaya Z, Kukhareva G, Voskoboynikov G, Zimina O (2022) Organotin
540 compounds (OTs) in surface sediments, bivalves and algae from the Russian coast of the

541 Barents Sea (Kola Peninsula) and the Fram Strait (Svalbard Archipelago) Environ. Sci Pollut.
1 29(23), 34659-34669.
2
3
4 543 Mikac N, Sondi I, Vdović N, Pikelj K, Ivanić M, Lučić M, Bačić N, Furdek Turk M, Škapin
5 DS, Krivokapić S (2022) Origin and history of trace elements accumulation in recent
6 544 Mediterranean sediments under heavy human impact. A case study of the Boka Kotorska Bay
7 545 (Southeast Adriatic Sea) Mar. Pollut. Bull. 179, 113702.
8
9 546
10
11 547 Milivojević Nemanič T, Milačić R, Ščančar J (2009) A survey of organotin compounds in the
12 Northern Adriatic Sea. Water Air Soil Pollut. 196, 211-224.
13
14 548
15
16 549 Omae I (2003) Organotin antifouling paints and their alternatives. Appl. Organomet. Chem.
17 17, 81-105.
18
19 550
20 551 OSPAR (2004) OSPAR/ICES Workshop on the evaluation and update of background reference
21 concentrations (B/RCS) and ecotoxicological assessment criteria (EACs) and how these
22 552 assessment tools should be used in assessing contaminants in water, sediment and biota, Final
23 report, OSPAR Commission.
24
25 553
26 554
27
28 555 Paz-Villarraga CA, Castro ÍB, Miloslavich P, Fillmann G (2015) Venezuelan Caribbean Sea
29 under the threat of TBT. Chemosphere 119, 704–710.
30
31 556
32 557 Pougnet F, Schäfer J, Dutruch L, Garnier C, Tessier E, Dang DU, Lancelleur M, Mullot JU,
33 Lenoble V, Blanc G (2014) Sources and historical record of tin and butyl-tin species in a
34 558 Mediterranean bay (Toulon Bay, France). Environ. Sci. Pollut. Res. 21, 6640-6651.
35
36 559
37
38 560 Poerschmann J, Kopinke, FD, Pawliszyn J (1997) Solid phase microextraction to study the
39 sorption of organotin compounds onto particulate and dissolved humic organic matter.
40 561 Environ. Sci. Technol. 31(12), 3629-3636.
41
42 562
43
44 563 Quintas PY, Alvarez MB, Arias AH, Garrido M, Marcovecchio JE (2019) Spatiotemporal
45 distribution of organotin compounds in the coastal water of the Bahía Blanca estuary
46 564 (Argentina). Environ. Sci. Pollut. Res. 26, 7601-7613.
47
48 565
49
50 566 Radomirović M, Mijatović N, Vasić M, Tanaskovski B, Mandić M, Pezo L, Onjia A (2021)
51 The characterization and pollution status of the surface sediment in the Boka Kotorska Bay,
52 567 Montenegro. Environ. Sci. Pollut. Res. 28, 42496-42515.
53
54 568
55
56 569 Regulation (EC) No 782/2003 (2003) of the European Parliament and of the Council of 14
57 April 2003 on the prohibition of organotin compounds on ships, Official Journal L 115.
58
59 570
60
61
62
63
64
65

1 571 Rodriguez-Gonzalez P, Bouchet S, Monperrus M, Tessier T, Amouroux D (2013) In situ
2 572 experiments for element species-specific environmental reactivity of tin and mercury
3
4 573 compounds using isotopic tracers and multiple linear regression. Environ. Sci. Pollut. R. 20,
5 574 1269-1280.

6
7
8 575 Romanelli G, Berto D, Calace N, Amici M, Maltese S, Formalewicz M, Campanelli A, Marini
9
10 576 M, Magaletti E, Scarpato A (2019) Ballast water management system: Assessment of chemical
11 577 quality status of several ports in Adriatic Sea. Mar. Pollut. Bull. 147, 86-97.

12
13
14 578 Ruiz JM, Barreiro R, Couceiro L, Quintela M (2008) Decreased TBT pollution and changing
15 579 bioaccumulation pattern in gastropods imply butyltin desorption from sediments. Chemosphere
16 580 73, 1253-1257.

17
18
19
20 581 Salazar MH, Salazar SM (1996) Mussels as bioindicators: Effects of TBT on survival,
21 582 bioaccumulation, and growth under natural conditions, in: Champ MA, Selignam PF,
22 583 Organotin - environmental fate and effects. Chapman and Hall, London, pp. 306-330.

23
24
25
26 584 Stanković S, Jović M, Tanasovski B, Mihajlović ML, Joksimović D, Pezo L (2015) Can the
27 585 origin of some metals in the seagrass *Posidonia oceanica* be determined by the index of metals
28 586 pollutions? Environ. Sci. Pollut. Res. 22, 8253-8263.

29
30
31
32 587 Sutherland R A (2000) Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii.
33 588 Environ. Geol. 39, 611-627.

34
35
36 589 Suzdalev S, Gulbinskas S, Blažauskas N (2015) Distribution of tributyltin in surface sediments
37 590 from transitional marine-lagoon system of the south-eastern Baltic Sea, Lithuania. Environ.
38 591 Sci. Pollut. Res. 22, 2634–2642.

39
40
41
42 592 Uc-Peraza RG, Castro IB, Fillmann G (2022) An absurd scenario in 2021: Banned TBT-based
43 593 antifouling products still available on the market. Sci. Total. Environ. 805, 150377.

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46 594

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599 **Figures caption**

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4 601 Figure 1. Sampling locations along the Montenegrin Adriatic coast.

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6 602 Figure 2. Distribution of BuTs in mussel tissue: (a) MBT, DBT and TBT concentrations, and
7 603 (b) percentage of each chemical species ($\text{BuT}/\sum\text{BuTs}$).

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9 604 Figure 3. Distribution of BuTs and total Sn in surface sediments: (a) MBT, DBT, TBT and Sn
10 605 concentrations, and (b) percentage of each BuT species ($\text{BuT}/\sum\text{BuTs}$) along with
11 606 proportion of $\sum\text{BuTs}/\text{Sn}_{\text{total}}$. The absence of bars for BuTs means that they were
12 607 not detected – concentrations <LOD.

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15 608 Figure 4. Depth distributions of butyltins (MBT, DBT, TBT and $\sum\text{BuTs}$) and total Sn in
16 609 sediment cores along with proportions of $\sum\text{BuTs}/\text{Sn}_{\text{total}}$. The absence of bars for
17 610 BuTs means that they were not detected – concentrations <LOD.

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20 611 Figure 5. Distribution of BuTs in water overlying sediment: (a) MBT, DBT and TBT
21 612 concentrations, and (b) percentage of each BuT species ($\text{BuT}/\sum\text{BuTs}$).

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614 Table 1. Summarizing statistic for butyltins (MBT, DBT, TBT, Σ BuTs) concentrations and
 1 615 proportions of TBT/ Σ BuTs and Σ BuTs/ Sn_{total} in different types of samples collected along the
 2 616 Montenegrin Adriatic coast.

	Concentration (ng(Sn)/g; ng(Sn)/L)				Proportion (%)	
	MBT	DBT	TBT	Σ BuTs	TBT/ Σ BuTs	Σ BuTs/ Sn_{total}
Mussels						
min	<5	10.4	6.7	19.7	28.2	-
max	50.7	173	179	402	55.5	-
average	15.1	43.0	40.6	98.6	39.1	-
median	11.1	30.6	25.9	67.8	39.3	-
Sediment cores (all depths)						
min	<6	<2	<1	<9	-	0.01
max	3651	4279	14900	20641	75.4	62.0
average	248	288	829	1365	25.9	6.09
median	20.8	14.1	12.4	43.1	17.2	0.43
max*	650	445	1304	1979	74.8	26.5
average *	62	41	85	188	22.0	2.37
median*	11.1	3.9	0.5	31.2	11.1	0.10
Water overlaying sediment						
min	8.8	0.2	<0.1	9.1	<0.2	-
max	277	130	160	566	28.2	-
average	91.3	52.4	24.4	168	6.0	-
median	38.2	58.9	0.3	80.4	0.4	-
max*	219	114	58	333	22.9	-
average *	68.1	42.7	7.5	118	3.2	-
median*	29.0	40.9	0.3	70.9	0.4	-

36 617 *without samples from Bijela shipyard

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629 Table 2. Literature data on butyltins (BuTs=TBT+DBT+MBT) and tributyltin (TBT) concentration in
 630 seawater, sediment and biota from the coastal areas of Europe reported in the last decade.

Area and year of sampling	Seawater (ng(Sn)/L)	Sediment (ng(Sn)/g)	Biota (ng(Sn)/g)	Reference
Southeast Adriatic coast (Montenegro); 2015	-	BuTs: <9-2000 (20641)* TBT: <1-1300 (14900)*	BuTs: 20-400 TBT: 7-179	This study
East Adriatic coast (Croatia); 2010-2012	BuTs: 0.5-28 TBT: <0.2-15	BuTs: 3-1362 (66345)** TBT: 1-790 (32317)**	Mussels BuTs: <10-1676 TBT: <10-1045	Furdek et al. (2012); Furdek Turk et al. (2020)
East Adriatic coast (Croatia), 2015-2017	TBT: <0.2-6.3	TBT: <1-92	Gastropoda BuTs: 1.9-155 TBT: 0.5-59	Furdek Turk et al. (2019) ; Erdelez et al. (2017)
East Adriatic coast (Slovenia, Croatia, Montenegro, Albania); 2014	TBT: <2	BuTs: 7-731 TBT: 3-566	Mussels BuTs: 25-220 TBT: 20-170	Romanelli et al. (2019)
West Adriatic coast (Italy); 2014	TBT: <2	BuTs: 7-240 TBT: 2-186	Mussels BuTs: 25-100 TBT: 60-75	Romanelli et al. (2019)
North Adriatic coast (Italy, Slovenia); 2016	-	BuTs: 121-352 TBT: 53-174	-	Formalewicz et al. (2019)
North Sea (Sweden); 2014	-	BuTs: 10-500 TBT: 10-300	-	Egardt et al. (2017)
Baltic sea (Lithuania); 2010-2012	-	TBT: 1-5200	-	Suzdalev et al. (2015)
Baltic Sea (Poland); 2014-2015 (fish), 2018 (sediment)	-	BuTs: 5.7-3321 TBT: 3.7-1942	Fish muscle BuTs: nd-715 TBT: nd-503	Filipkowska et al. (2016); Filipkowska and Kowalewska (2019)
Baltic Sea (Poland); 2012-2013	-	BuTs: nd-22	Mussels BuTs: 41-164 TBT: 11-103	Filipkowska and Lubecki (2016)
Baltic Sea (Germany); 2015	-	BuTs: 100-1426 TBT: 2.5-380	-	Abraham et al. (2017)
Mediterranean (France); 2009, 2011, 2013	Porewater BuTs: 40-600 TBT: 0.1-70	BuTs: 8-16000 TBT: nd-10700	-	Briant et al. (2013, 2016)
Mediterranean and Atlantic coast (Portugal, Italy, Turkey); 2012	-	BuTs: 8-200 TBT: 3-75	Gastropoda BuTs: 30-720 TBT: 12-172	Anastasiu et al. (2016)
Mediterranean and Atlantic coast (Spain); 2015	BuTs: nd-20 TBT: nd-17	BuTs: nd-100 TBT: nd-75	-	Concha-Grana et al. (2021)
Barents Sea (Russia); 2019	-	BuTs: 28-83 TBT: 2-24	Bivalves BuTs: nd-50 TBT: nd-38	Metelkova et al. (2022)

631 *including samples from shipyard Bijela; ** including samples from shipyard and service hoists

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Figure 1. Sampling locations along the Montenegrin Adriatic coast.

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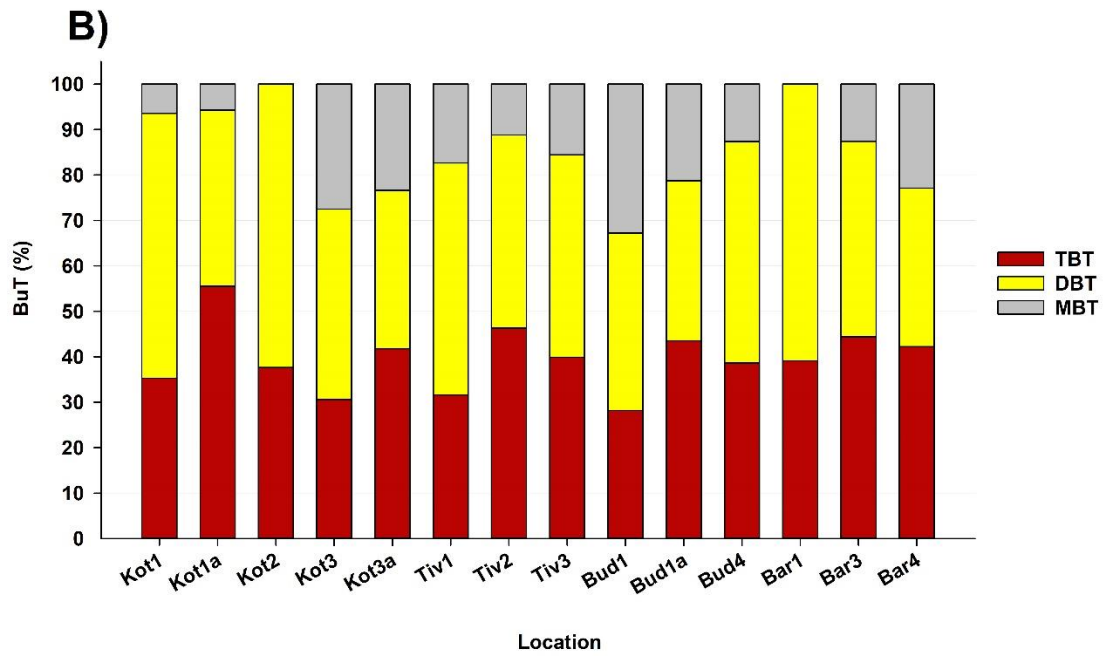
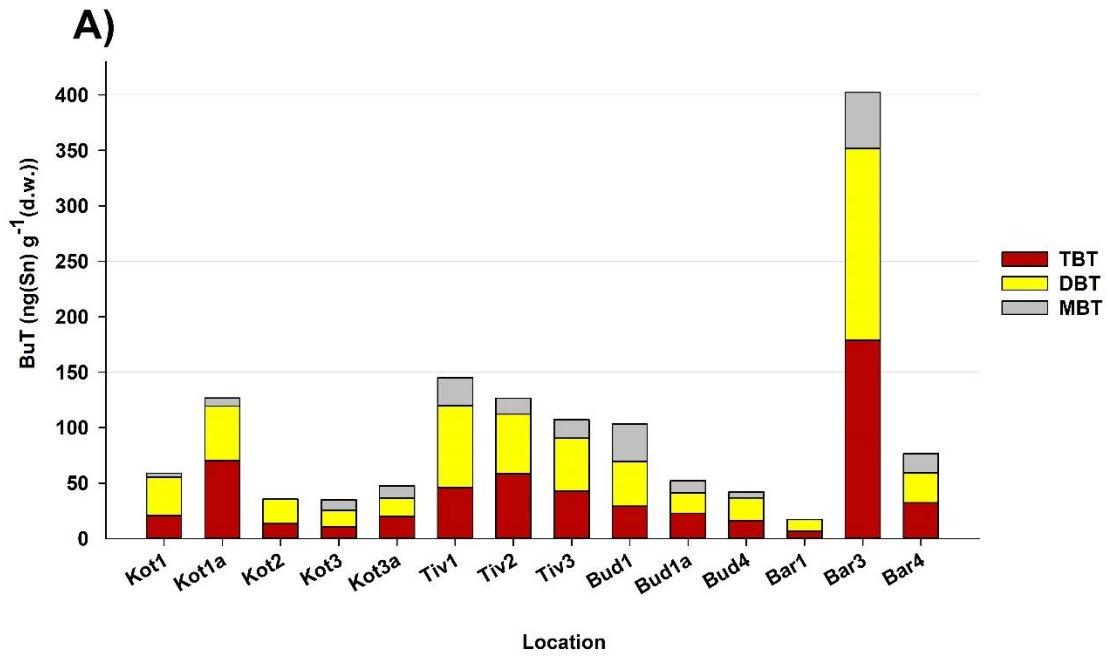
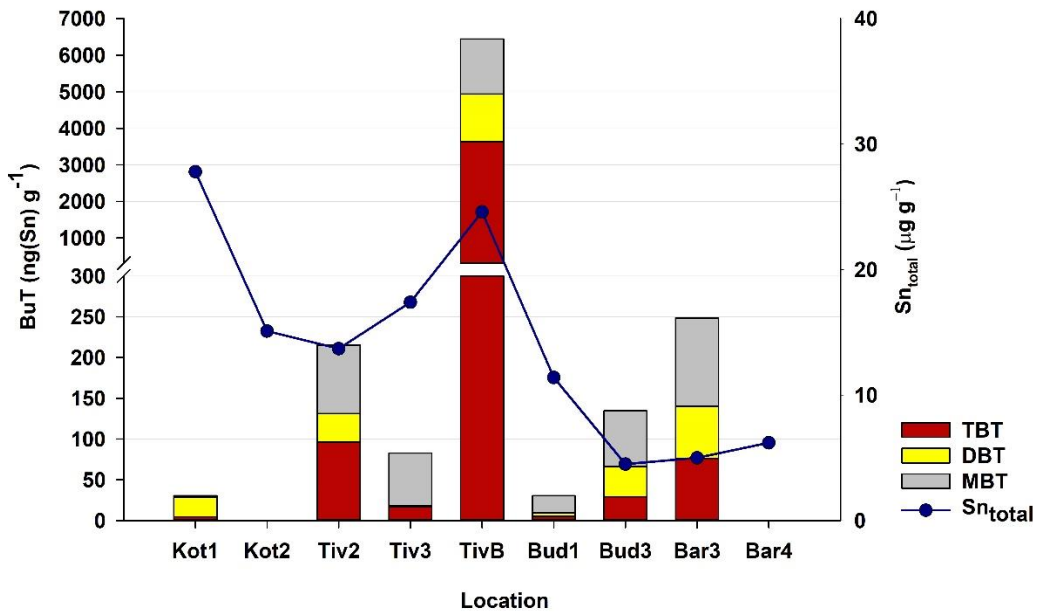


Figure 2. Distribution of BuTs mussel tissue: (a) MBT, DBT and TBT concentrations, and (b) percentage of each species ($BuT/\sum BuTs$).

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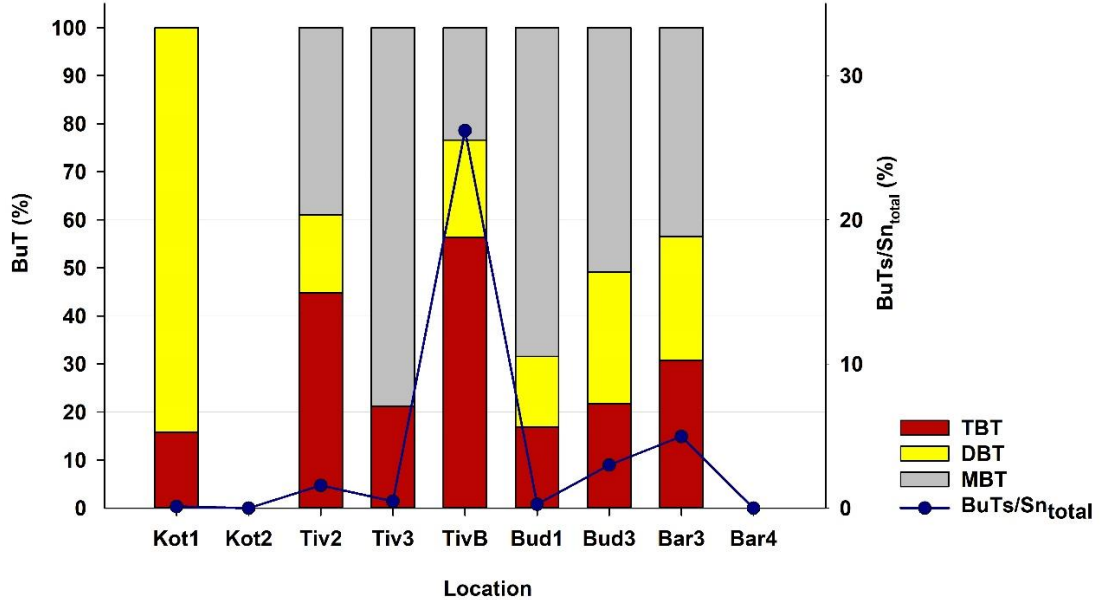


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658 **Figure 3.** Distribution of BuTs and total Sn in surface sediments: (a) MBT, DBT, TBT and Sn

659 concentrations, and (b) percentage of each BuT species (BuT/∑BuTs) along with

660 proportion of ∑BuTs/Sn_{total}. The absence of bars for BuTs means that they were not

661 detected – concentrations <LOD.

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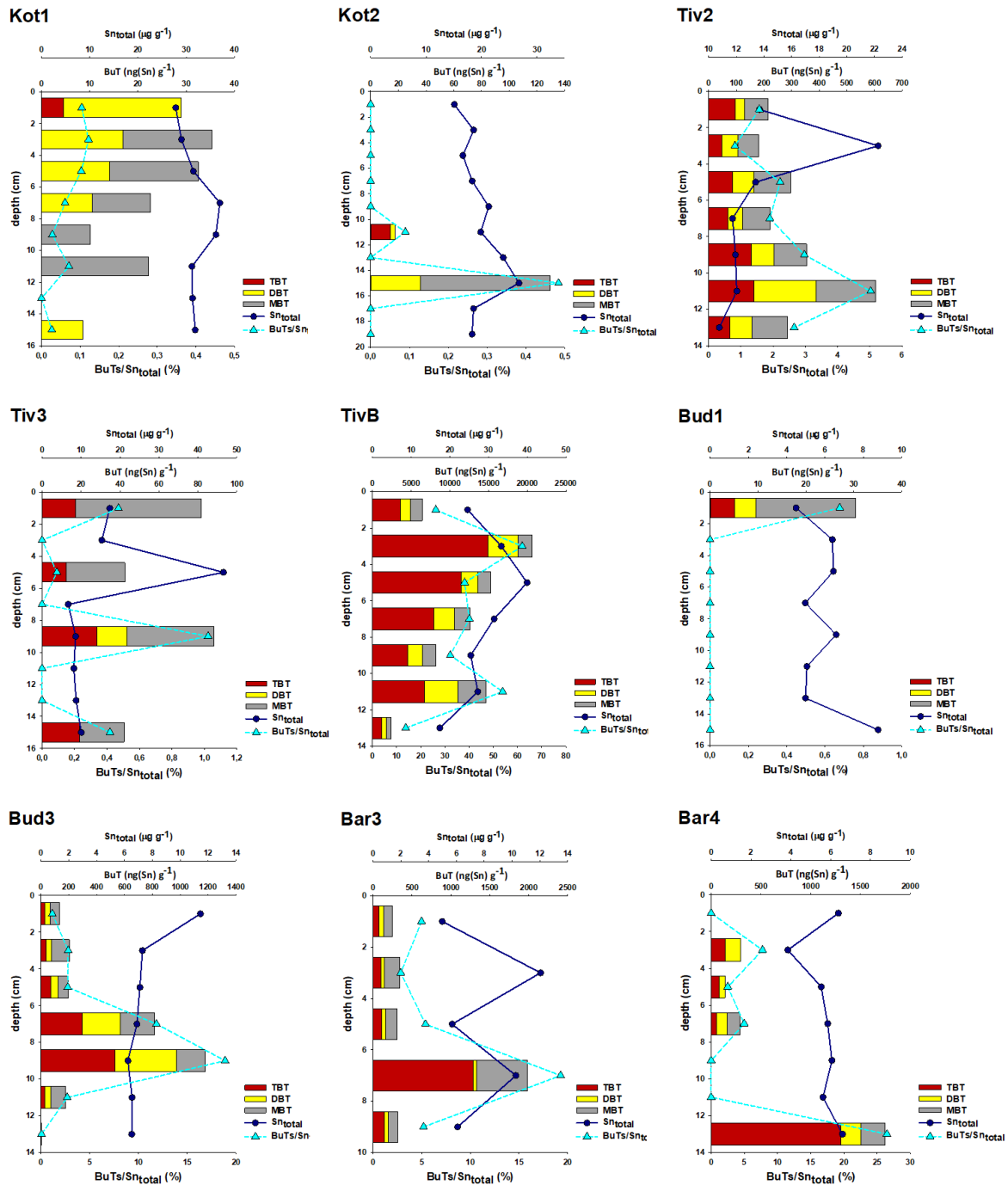
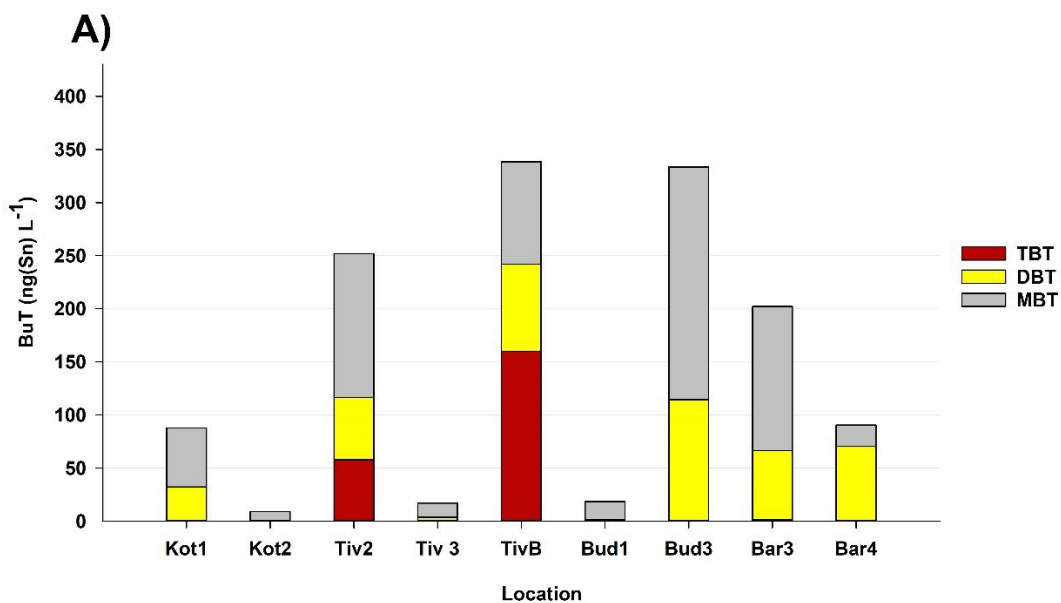


Figure 4. Depth distributions of butyltins (MBT, DBT, TBT and $\Sigma BuTs$) and total Sn in sediment cores along with proportions of $\Sigma BuTs/Sn_{total}$. The absence of bars for BuTs means that they were not detected – concentrations $< LOD$.

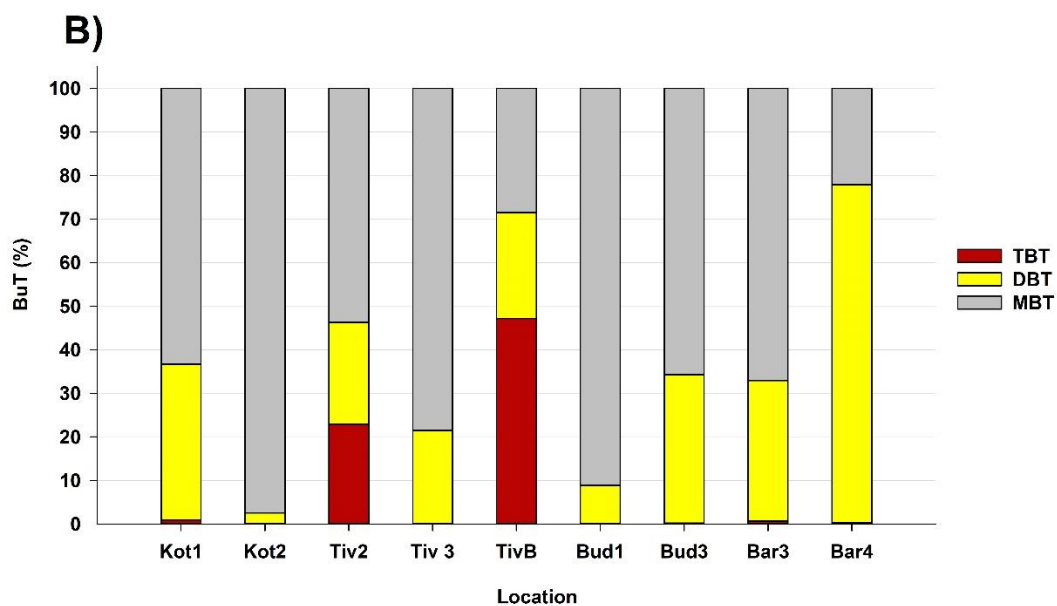
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Figure 5. Distribution of BuTs in waters overlying sediment: (a) MBT, DBT and TBT concentrations, and (b) percentage of each BuT species ($BuT/\sum BuTs$).

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7 1 **First assessment of butyltins (BuTs) contamination of the Montenegrin coast**
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9 2 **(Southeast Adriatic): Tributyltin (TBT) poses a threat to the marine ecosystem**

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12 4 Nevenka Mikac^a, Martina Furdek Turk^{a,*}, Dragana Petrović^b, Miljan Bigović^b, Sladjana
13 5 Krivokapić^b

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16 6 ^a Division for Marine and Environmental Research, Ruđer Bošković Institute, 10000 Zagreb,
17 7 Croatia

18 8 ^b Faculty of Natural Sciences and Mathematics, University of Montenegro, 81000 Podgorica,
19 9 Montenegro

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23 13 * Corresponding author: mfurdek@irb.hr
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28 16 **Abstract**

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30 17 This study presents the first assessment of butyltins (BuTs) pollution of the Montenegrin coast
31 18 ~~(Southeast Adriatic)~~. The distribution of tributyltin (TBT), dibutyltin (DBT) and monobutyltin
32 19 (MBT) was investigated in mussels, sediment ~~s-cores~~ and ~~in~~-water overlying sediment after the
33 20 sediment resuspension. The results showed that the investigated sites (marinas, ports,
34 21 shipyard~~s~~) are ~~significantly~~ contaminated with BuTs (19-402 ng(Sn)/g in mussels; 43-20641
35 22 ng(Sn)/g in sediments; 9-566 ng(Sn)/L in ~~water~~-overlying ~~waters~~sediment) ~~despite the ban of~~
36 23 ~~TBT-based paints more than a decade ago. The measured~~ TBT concentrations ~~were above the~~
37 24 ~~proposed ecotoxicological criteria at most locations,~~ indicating that toxic effects on marine
38 25 organisms are expected at most locations. The simultaneous analysis of BuTs and total Sn in
39 26 sediment cores allowed the assessment of TBT historical input ~~and its long-term behaviour at~~
40 27 ~~the investigated sites. Finally, and~~ it was demonstrated that resuspension of contaminated
41 28 sediments leads to the release of all BuTs into the water column, ~~especially MBT and DBT.~~
42 29 This study shows that, despite the ban of TBT-based antifouling paints more than a decade ago,
43 30 pollution of the marine environment with TBT is still a problem and regular monitoring
44 31 remains essential.
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Keywords: tributyltin (TBT), butyltins (BuTs), pollution, Montenegrin Adriatic coast, sediments, mussels

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7 36 Tributyltin (TBT), one of the most toxic anthropogenic pollutants intentionally introduced into
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9 37 the aquatic environment, has been used as biocide in antifouling paints since the 1960s (Hoch,
10 38 2001). After its high toxicity to various aquatic non-target organisms was established, the use
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12 39 of TBT in antifouling paints was banned in many countries worldwide (Omae, 2003). ~~The~~
13 40 ~~regulation on the use of TBT based paints in Europe was enacted as early as 1989, but was~~
14 41 ~~fully implemented in 2008 (Furdek et al., 2012). In 2001, the International Maritime~~
15 42 ~~Organization (IMO) established the AFS Convention (International Convention on the Control~~
16 43 ~~of Harmful Antifouling Systems on Ships) (IMO, 2008), calling for a global ban on TBT-based~~
17 44 ~~paints from 2003. In Europe, the ban was implemented in 2003 by Regulation (EC) No.~~
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19 45 782/2003 and 2008 was set as the deadline for the complete ban of their use. Subsequently, a
20 46 decrease in TBT levels has been observed in European coastal areas (Cacciatore et al., 2018;
21 47 ~~Cuevas et al., 2014~~; Guomundsdóttir et al., 2011; Harrison et al., 2020; Langston et al., 2015;
22 48 ~~Laranjeiro et al., 2018, Nicolaus and Barry, 2015~~), but TBT levels have still been above
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24 49 concentrations toxic to biota. In the last decade, high levels of TBT have been reported in
25 50 European seas: Adriatic Sea (Erdelez et al., 2017; Formalewitz et al., 2019; Furdek Turk et al.,
26 51 2020; Romanelli et al., 2019), North Sea (Eghart et al., 2017), Baltic Sea (Abraham et al., 2017;
27 52 Filipkowska et al., 2016; Filipkowska and Kowalewska, 2019), Mediterranean and Atlantic
28 53 coasts (Anastasiou et al., 2016; Concha-Grana et al., 2021; El Ayari et al., 2018) and in the
29 54 Arctic (Kucklick and Ellisor, 2019; Metelkova et al., 2022). Recently observed TBT pollution
30 55 was even worse in parts of the world where the use of TBT-based paints is not yet fully
31 56 regulated (Bandara et al., 2021; Batista et al., 2016; Paz-Villarraga et al., 2015; Quintas et al.,
32 57 2019). The above literature data clearly show that TBT pollution is still a major environmental
33 58 problem that is far from being solved more than a decade after attempt for its global ban.
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35 59 ~~However, the ban on the use of TBT never became “global” as the restrictions only applied to~~
36 60 ~~signatories of the IMO-AFS Convention (91 member states in 2021; Uc-Peraza et al., 2022),~~
37 61 ~~EU member states and countries with specific regulation in that sense. To make matters worse,~~
38 62 ~~TBT-based antifouling paints were still being manufactured in the Unites States and available~~
39 63 ~~on the market in 2021, even in some countries that are signatories of IMO-AFS Convention~~
40 64 ~~(Uc-Peraza et al., 2022).~~

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42 65 Once TBT has entered the marine environment, it undergoes various processes such as
43 66 microbiological and photolytic degradation, bioaccumulation by biota (e.g. gastropods,
44 67 bivalves, fish) and adsorption to suspended particles (Furdek et al., 2012, 2016). The
45 68 degradation of TBT occurs both in sediments and in the water column, and consists of a

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7 69 stepwise loss of butyl groups, via dibutyltin (DBT) and monobutyltin (MBT) to the inorganic
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9 70 Sn (Furdek et al., 2016, Furdek Turk et al., 2020). This process in the water column is quite
10 71 rapid (half-lives of several days to weeks; Rodriguez-Gonzalez et al., 2013), and, therefore,
11 72 analysis of seawater provides information on the current level of [butyltins \(BuTs\)](#) in the marine
12 73 environment. On the other hand, BuTs concentrations accumulated in marine organisms, such
13 74 as mussels, reflect an average pollution of a water column over a longer period of time of about
14 75 several months (Furdek et al., 2012). Due to its hydrophobic characteristics, TBT has an
15 76 affinity to adsorb onto the suspended particles in the water column, which settle in the
16 77 sediments over time. Once in the sediment, TBT degrades slowly, with half-lives of several
17 78 years to decades (Furdek et al., 2016; Omae, 2003); therefore, TBT content in sediments could
18 79 provide information on TBT input over a long period of time, from several years to decades.
19 80 Not only BuTs are highly persistent in sediments, but they can also be released back into bottom
20 81 waters by diffusion or resuspension of sediments, making sediments a potential source of new
21 82 pollution to the water column (Furdek Turk et al., 2020; Hoch and Schwesig, 2004; Ruiz et al.,
22 83 2008). Nevertheless, the field evidence of desorption of BuTs from contaminated sediments
23 84 are rare (Furdek Turk et al., 2020). Therefore, it is important to determine the status of BuTs
24 85 pollution of coastal areas not only in the water column but also in sediments, and to assess the
25 86 risk of BuTs desorption from the contaminated sediments.

26 87 The level of TBT pollution in the Adriatic Sea (the northernmost arm of the Mediterranean
27 88 Sea) has been assessed in several studies, covering the coastal waters of Croatia (Erdelez et al.,
28 89 2017; Furdek et al., 2012; Furdek Turk et al., 2020), Slovenia (Milivojević Nemanič et al.,
29 90 2009; Formalewicz et al., 2019) and Italy (Romanelli et al., 2019; Formalewicz et al., 2019;
30 91 Berto et al., 2007). All these studies showed that TBT pollution is a significant environmental
31 92 problem in coastal areas. Regular monitoring of the priority pollutants in Croatian coastal
32 93 waters carried out under the Water Framework Directive (WFD; [DirectiveEC_2000/60/EC_2000](#))
33 94 also revealed that TBT levels in water are frequently above the prescribed maximum
34 95 annual average concentration (0.2 ng/L) (Furdek Turk et al., 2019). However, the level of TBT
35 96 pollution in the southern part of the Eastern Adriatic that belongs to Montenegro has never
36 97 been investigated and there are no data on the status of BuTs in this area. There is only one
37 98 data [set](#) for the port of Bar from 2014, when the total BuTs in sediments ranged from 18 to 33
38 99 ng(Sn)/g (Romanelli et al., 2019).

39 100 The Montenegrin coastline has a length of 294 km, of which 105 km belong to the large fjord-
40 101 like Boka Kotorska Bay, which is naturally divided into several smaller bays (Kotor, Risan,
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Tivat and Herceg Novi). The entire coast is under high anthropogenic pressure due to urbanisation and discharge of municipal wastewaters, maritime activities (marine traffic, marinas, shipyards), fishing and tourism (Joksimović et al., 2017, 2020). The studies on the distribution of ecotoxic metals in mussels, sediments and seagrass (Jokanović et al., 2021; Joksimović et al., 2011, 2020; Radmirović et al., 2021; Stanković et al., ~~2014~~2015) have shown that most of the investigated sites, especially shipyards and urban areas, are contaminated with metals due to significant anthropogenic pressure.

The aims of this work were: i) to assess the level of BuTs pollution along the Montenegrin coast by studying BuTs distribution in mussels and sediments; ii) to assess the extent of BuTs desorption from contaminated sediments into the water column caused by sediment resuspension; and iii) to assess the historical input of BuTs along the Montenegrin Adriatic coast by studying the relationship between total Sn and BuTs in sediments.

Sampling locations included various areas along the Montenegrin coast which are affected by intensive shipping and industrial activities, such as marinas, shipyards and municipal and local ports. Samples of mussels *Mytilus galloprovincialis* (Lamarck, 1819) and sediments were collected in July 2015 from 16 sampling sites, covering the areas of Boka Kotorska Bay (namely, Kotor Bay and Tivat Bay) and the towns of Budva and Bar (Fig. 1; Table S1). In the Kotor Bay samples were collected at 5 locations (Kot1, Kot1a, Kot2, Kot3, Kot3a) near the town of Kotor, a tourist town with a marina, cruise port and a number of small ports. In the Tivat Bay, the samples were taken at the marina Porto Montenegro in the town of Tivat (Tiv1, Tiv2, Tiv3) and in front of the Bijela shipyard (TivB). In Budva (tourist town), samples were taken at 4 locations - in the marina (Bud1, Bud3, Bud4) and in the local port (Bud1a). In the town of Bar, one of the largest cargo, passenger and military ports on the Eastern Adriatic, samples were taken at 3 locations, including the cargo (Bar1), military port (Bar4) and the marina (Bar3). A brief description of each sampling site is given in Table S1 in the Supplementary Information. At sites labelled with “a” (which were a short distance from the site labelled with the same number) only mussels were collected. A total of 81 samples, including 14 samples of mussels and 67 samples of sediment obtained by cutting sediment cores (9 cores; 10-20 cm long, cut into 2 cm layers), were analysed for BuTs (i.e. MBT, DBT and TBT). In addition, bottom waters, i.e. water overlying the sediment (9 samples), were collected with a gravity corer to investigate the desorption of BuTs caused by sediment resuspension. The water overlying sediment in the gravity corer was transferred to a dark glass bottle after sediment particles had settled (approximately 15 min after sediment was taken out

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of the sea with the gravity corer), acidified to pH=2 with [nitric acid \(HNO₃\)](#)-and stored in the dark at 4°C until analysis. Mussels (30 specimens per sampling site, [with a shell length of 3 to 6 cm](#)) were collected from the docks, rocky shores or boat strings. The shells were removed and the soft tissue homogenised in a blender and later freeze-dried and stored at -20°C until analysis. Sediments were collected using a UWITEC gravity corer ([Umwelt-und Wissenschaftstechnik, Austria](#)) and frozen immediately after collection. The sediment cores were cut into 2 cm layers, freeze-dried, homogenised by milling and stored at -20 °C until analysis.

The analytical methods used for the analysis of BuTs (TBT, DBT and MBT) in seawater and mussels are described in Furdek et al. (2012), while that used for the analysis of sediments is described in Furdek et al. (2016). Briefly, BuTs were extracted from 300 ml of seawater, while simultaneous extraction and derivatisation were performed in a sodium acetate-acetic acid buffer (pH=4.8) by adding [sodiumtetraethyl borate \(NaBEt₄\)](#) (1% (w/v)) and hexane and mechanical shaking for 30 min at 350 rpm. Butyltins from sediments were extracted from 0.5-2 g of sample by acetic acid and ultrasound-assisted agitation (30 min, 55 Hz), while BuTs from mussel were extracted from 0.5-1 g of lyophilised tissue with 0.1 mol/L [hydrochloric acid \(HCl\)](#) in methanol using ultrasound-assisted agitation (30 min, 55 Hz). For both sediments and mussels, the derivatisation of compounds in the extract was performed in sodium acetate-acetic acid buffer (pH=4.8) with NaBEt₄ (1% (w/v)) and transferred into hexane by mechanical shaking at 350 rpm for 30 min. Analyses of BuTs in seawater were carried out on a gas chromatograph (GC; Agilent 6890, [Agilent Technology](#)) coupled with inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7900, [Agilent Technology](#)), while detection of BuTs in mussels and sediments was performed using gas chromatograph (GC; Varian CP 3800, [Varian](#)) with pulsed flame photometric detector (PFPD, Varian). Tripropyltin (TPPrT) was used as an internal standard and quantification was performed by applying the standard addition calibration method. Quality control of the analytical procedure for the determination of BuTs in mussels and sediments was performed by analysing the certified reference materials (CRM) for mussels (CE 477, ERM, European Commission, Geel, Belgium) and marine sediment (PACS 2, [OttawaNRC-CNRC](#), Canada). In addition, the accuracy of all three methods was further confirmed by successful participation in the proficiency tests. The detection limits for TBT, DBT and MBT were 0.1-0.5 ng(Sn)/L for seawater, 0.9-5.1 ng(Sn)/g for mussels and 0.9-6.1 ng(Sn)/g for sediment. Total Sn in sediments was analysed according to the method described in Furdek Turk et al. (2020) using high resolution inductively coupled plasma mass

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7 168 spectrometry (HR-ICPMS; Element 2, Thermo Finnigan). Sediments (0.1 g) were digested in
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9 169 a microwave oven (Multiwave 3000, Anton Paar) by two-step total digestion procedure (HNO₃
10 170 (65% *s.p.*) + HCl (36% *s.p.*) + hydrofluoric acid (HF, (48% *s.p.*)), followed by boric acid (
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12 171 H₃BO₃ ~~(40 g/L)~~. The quality control was performed by simultaneous measurements of
13 172 certified reference materials for marine sediment (MESS-3, NRC-CNRC, Canada) for which
14 173 satisfactory results were obtained.
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16 174 The BuTs pollution of the water column was not detected directly, but indirectly by
17 175 determining the accumulated BuTs in mussels. Indeed, mussels are a reliable biomonitor of
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19 176 TBT pollution as they are sessile and filter-feeding organisms, with a great ability to
20 177 bioaccumulate TBT from water and a limited ability to metabolise it (Magi et al., 2008). The
21 178 TBT concentration detected in mussels reflects the ambient TBT level during the last months
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23 179 (2-3 months; Salazar and Salazar, 1996) because during this period an equilibrium is reached
24 180 between uptake from the water (i.e. accumulation), metabolism of TBT to DBT and MBT, and
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26 181 excretion of these compounds back into the water (Gomez-Ariza et al., 1999; Magi et al., 2008).
27 182 Therefore, TBT levels measured in mussels are a reliable indicator of recent pollution in the
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29 183 water column over the last few months, in contrast to levels measured in seawater that only
30 184 indicate the momentary level of pollution. The concentrations of BuTs
31 185 (Σ BuTs=MBT+DBT+TBT) in mussels varied from 19 to 402 ng(Sn)/g (Table 1, Fig. 2a2A);
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33 186 concentrations of DBT and TBT were of the same order of magnitudes similar (10-173 ng(Sn)/g
34 187 for DBT and 6.7-179 ng(Sn)/g for TBT), while MBT was the least abundant compound (<5-
35 188 50 ng(Sn)/g). In all investigated marinas (Kot1a, Tiv1, Tiv2 and Tiv3, ~~and Bud1 and Bar3~~),
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37 189 Σ BuTs were above 100 ng(Sn)/g, while the highest concentration (402 ng(Sn)/g) was found in
38 190 mussels from the marina Bar3. At all locations, TBT and DBT account for 30-55% and 35-
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40 191 58% of the total BuTs, respectively (Fig. 2b2B). High concentrations and proportions of TBT
41 192 in mussels reflect ~~a~~ recent inputs of TBT, but may also be a consequence of the limited ability
42 193 of mussels to metabolise TBT, as bivalves do not have an efficient detoxification system (Lee,
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44 194 1996; Chandrinou et al., 2007; Diez et al., 2005). However, significant correlations between
45 195 TBT and DBT ($r=0.912$, $p<0.05$, Spearman) suggest that DBT in mussel tissues may be the
46 196 product of TBT metabolism, while lower but still significant correlation between TBT and
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48 197 MBT ($r=0.693$, $p<0.05$, Spearman) and DBT and MBT ($r=0.616$, $p<0.05$, Spearman) suggests
49 198 that DBT could be eliminated from the organism before being degraded to MBT, or that it is
50 199 metabolised more slowly compared to MBT (Furdek et al., 2012). In conclusion, the measured
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BuTs concentrations in mussels indicate that TBT pollution ~~with TBT~~ in seawater has been present at all investigated sites along the Montenegrin coast in recent months.

The spatial and depth distributions of BuTs in sediments were highly variable (Fig. ~~3a3A~~, Fig. 4, Table 1), with ranges encompassing 3-4 orders of magnitude (<9-20641 for BuTs; <1-14900 for TBT; <2-4279 for DBT; <6-3651 for MBT, expressed in ng(Sn)/g). The highest concentrations of BuTs were found in the sediments sampled in front of the Bijela shipyard (20641 ng(Sn)/g), while at all other sites maximum concentration did not exceed 2000 ng(Sn)/g (Table 1). TBT was the prevailing compound at all sites, accounting for up to 75% of all BuTs (Table 1). The depth profiles of BuTs in 9 sediment cores from different locations were highly variable, both in terms of the level of concentrations and the depth pattern (Fig. 4). Sediments in the city of Kotor (Kot1 and Kot2) may be considered as not polluted with TBT (Fig. 4); the concentrations of Σ BuTs were up to 35 ng(Sn)/g and were mainly in the form of TBT degradation products, i.e. DBT and MBT. In both sediment cores TBT was detected in only one layer (0-2 cm – Kot1 and 10-12 cm – Kot2). ~~In marina in the town of Tivat, the~~ The sediment inside the marina in the town of Tivat at location (Tiv2) (inside the marina) was heavily contaminated with BuTs throughout the core (up to 600 ng(Sn)/g), with a high proportion of TBT in each layer (30-40%). In contrast, in the sediment sampled outside the marina (Tiv3), BuTs concentrations were much lower, although the high proportion of TBT (up to 45%) was also detected in the deeper layers. The sediment sampled in front of the Bijela shipyard (TivB) was extremely contaminated; the BuTs concentrations in the upper 12 cm did not fall below 6500 ng(Sn)/g, while the maximum concentration of 20641 ng(Sn)/g was detected in the subsurface layer. In all layers, TBT was the prevailing compound and accounted for 50-75% of the total BuTs. The BuTs depth distributions in two sediment cores sampled within the same marina in the city of Budva (Bud1 and Bud3) were different, although these sites are only 100 m apart. While in the sediment core Bud1 only the surface sediment layers were slightly contaminated with BuTs, the sediments sampled closer to the service hoist (Bud3) were heavily contaminated to a depth of 12 cm, with BuTs concentrations up to 1180 ng(Sn)/g. In the city of Bar, the sediments of the marina (Bar3) and the military port (Bar4) were significantly contaminated with BuTs (concentrations of up to 1980 ng(Sn)/g), with the highest pollution observed in the deeper layers, where not only the concentrations were high, but also the percentage of undegraded TBT (up to 75%).

Based on the depth profiles obtained, several patterns of BuTs behaviour could be observed (Fig. 4). First, ~~the~~ BuTs concentration profiles do not follow the same depth pattern; in some

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sediments BuTs decreased with depth, while in others ~~their~~ concentrations were similar or vary throughout the depth of the core. Such different depth distributions may indicate different TBT inputs over time or different BuTs degradation efficiencies in different sediments. Since different BuTs depth distributions were observed in the sediments from marinas of similar size and similar intensity of marine traffic (such as Bud1, Bar3, Kot1 and Tiv2), the most likely explanation is that the observed depth profiles are the result of different persistence of TBT in these sediments. It was demonstrated that sediments characteristics, namely grain size and organic matter, strongly affects the degradation process of TBT and its persistence in sediments (Furdek et al., 2016; Furdek Turk et al., 2020). Organic matter plays a crucial role as a TBT sorbent in sediments and, therefore, influences TBT degradation rate by determining the bioavailable fraction in porewater where TBT degradation occurs (Furdek et al., 2016). This means that, in sediments rich in organic matter, TBT will be less available to degradation and, consequently, more persistent over time (Furdek et al., 2016). Secondly, at most locations TBT degradation products, i.e. MBT and DBT, are the prevailing BuT compounds through the entire depth cores, which could indicate efficient degradation of TBT in these sediments. An exception is the sediments sampled in Bijela shipyard (TivB) and in two layers of cores Tiv2 and Bar4, where the percentage of TBT/ Σ BuTs was more than 50% (Fig. 4). Although the proportions of DBT and MBT prevail over TBT, their accumulation in the deeper layers was not observed in any sediment core. There are two explanations for this: i) DBT and MBT, being less hydrophobic compounds, are more easily desorbed from sediments than TBT (Poerschmann et al., 1997), and ii) the degradation of DBT and MBT to inorganic Sn is efficient in both oxic and anoxic sediments. Indeed, Furdek et al. (2016) demonstrated that the rate of DBT degradation in sediments is faster than the rate of its formation from TBT, which prevents accumulation of DBT in sediments, and that MBT, after desorption from sediment to anoxic porewater, is almost immediately degraded to inorganic Sn.

However, a reliable assessment of the long-term behaviour, persistence and historical input of TBT can only be made by simultaneously determining BuTs and total Sn in sediments (Furdek Turk et al., 2020). First, it should be confirmed that the inorganic Sn contamination originates mainly from TBT-antifouling paints and not from other possible sources such as municipal and industrial wastewater (Pougnnet et al., 2014), or landfill leachates. Namely, inorganic Sn is used in products such as food cans, welding equipment, electronics, and household products (Pougnnet et al., 2014). Inputs of other organotin compounds such as mono- and disubstituted BuTs (often used as PVC stabilizers) and phenyltins (used as pesticides, while triphenyltin

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(TPhT) is also used as a biocide in antifouling paints) (Omae, 2003) could also lead to the formation of inorganic Sn. However, in Europe TPhT is used to a much lesser extent than TBT (Lagerstrom et al., 2017), which is confirmed by the data on TPhT contamination of the Croatian Adriatic coast, where only sporadic low levels of TPhT have been detected in mussels (Furdek et al., 2012) and sediments (Furdek et al., 2016).

To investigate the source of Sn contamination and confirm that inorganic Sn originates mainly from the degradation of TBT, we examined the relationships between BuTs and inorganic Sn in the sediments by determining the total Sn depth profiles and calculating butyltin degradation index (BDI), following the approach presented in previous studies (Furdek Turk et al., 2020; Pougnet et al., 2014). Total Sn concentrations ranged from 3.8 to 46.5 µg/g (Fig. 4) and were higher than the background levels of Sn, obtained by the analysis of older uncontaminated recently determined for the sediments of the Boka Kotorska Bay (2.8 µg/g) and the coastal zone of Montenegro (1.7 µg/g) (Mikac et al., 2022). The degree of Sn contamination was assessed by enrichment factors ($EF = (Sn/Al)_{sample} / (Sn/Al)_{background}$), according to the scale proposed by Sutherland (2000): $EF < 2$ indicates no or minimal, $EF = 2-5$ moderate, $EF = 5-20$ significant, $EF = 20-40$ very high, and $EF > 40$ extreme enrichment or contamination. The calculated EFs showed that all sediments studied were enriched in Sn; the sediments from Kotor Bay (Kot1, Kot2) and Tivat Bay (Tiv1, Tiv2, TivB) were significantly contaminated with Sn (EFs between 5 and 20), while the sediments from Budva (Bud1, Bud3) and Bar (Bar3, Bar4) had EFs between 2 and 12, indicating moderate contamination with Sn.

To investigate the source of Sn contamination, we examined the relationship between TBT and its degradation products (DBT, MBT and inorganic Sn) by calculating the BDI index, which is a commonly used tool to study TBT degradation efficiency. We calculated the BDI using two approaches: i) the commonly known approach, which considers only DBT and MBT as TBT degradation products; $BDI = (MBT+DBT)/TBT$ (Garg et al., 2009), and ii) a modified approach proposed by Pougnet et al. (2014), which considers the inorganic Sn as the final product of total degradation; $BDI_{mod} = (Sn_{inorganic}+MBT+DBT)/TBT$, while the $Sn_{inorganic}$ could be calculated as $Sn_{total}-Sn_{background}-\sum BuTs$. A stronger correlation between TBT and BDI_{mod} ($r=0.961$; $p<0.01$, Spearman) than between TBT and BDI ($r=0.722$, $p<0.05$, Spearman) was observed when combining samples from all sediment cores. This indicates that most of the TBT has been completely degraded to inorganic Sn, while the anthropogenic fraction of inorganic Sn mainly originates from the degradation of TBT released from antifouling paints.

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Considering the above conclusion that most of the inorganic Sn originates from TBT antifouling paints in the studied environments, we used BuTs and total Sn depth distributions to explain the historical input and behaviour of TBT in the investigated sediments and to clarify whether the observed BuTs depth distributions are the result of different TBT input over time or different TBT persistence in sediments. From the observation of the determined depth profiles (Fig. 4) the following conclusion are drawn. The total Sn depth profiles in the Kotor Bay (Kot1 and Kot2) show high (EF=8-18) and continuous input of Sn over time, while the \sum BuTs accounts for less than 0.5% of the total Sn at all depths, indicating that the low TBT and BuTs levels are a consequence of an efficient TBT degradation rather than low TBT input over time. In the marinas of Budva (Bud1, Bud3) and Tivat (Tiv2, Tiv3) all cores are similarly contaminated with Sn (EF=3-10) (except for a few layers where EF is higher), indicating a comparable input of TBT over time. However, the percentage of \sum BuTs/Sn_{total} in cores Tiv3 and Bud1 (<1%) is much lower than in cores Tiv2 and Bud3 (1-18%), indicating less efficient TBT degradation in the later cores. In the sediment cores from Bar (Bar3, Bar4) the total Sn input is generally lower (EF=2-7) compared to the other sites, but \sum BuTs/Sn_{total} was high (4-20%), indicating high persistence of TBT in these sediments, especially in the sediments from marina (Bar3), where the highest level of BuTs in mussels were also found. In the military port (Bar4) the absence of BuTs in the surface sediments suggests that TBT has not been introduced recently; however, the elevated total Sn and the relatively high TBT levels in mussels indicate the opposite, namely that there was a recent input of TBT and its efficient degradation to inorganic Sn in the surface sediments. By contrast, the high level of TBT in the bottom layer of this core indicates poor degradation of TBT in older sediments. After all, the observed depth profiles demonstrated less efficient TBT degradation in cores Tiv2, Bud3 and Bar3 than in the other sediment cores analysed. Finally, the sediment core TivB is clearly different from all the other cores; not only BuTs and total Sn concentrations (EF=15-20) are much higher than in the other sediments, but also the proportions of TBT/ \sum BuTs and \sum BuTs/ Sn_{total} are very high (50-75% and 20-65%, respectively). As this core was taken near the shipyard, these results could be explained by the presence of paint particles containing TBT in the form that is not available to degradation (Furdek Turk et al., 2020).

It should be emphasized that the proportion of \sum BuTs/Sn_{total} was generally not higher than 10% in any of the sediments studied (excluding the sediment from the shipyard), which may be surprising considering that the degradation of TBT in sediments is a slow process ($t_{1/2}$ = several years to decades; Omae, 2003). The same was found by Furdek Turk et al. (2020), who

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discussed that most of the TBT leached from ships is degraded to inorganic Sn already in the water column ($t_{1/2}$ = several days to weeks; Rodriguez-Gonzalez et al., 2013), so that only a small fraction of TBT (~10%) reaches the sediments. Therefore, a reliable assessment of TBT input in the time period covered by the sediment cores can only be performed by taking into account the total amount of Sn; otherwise, the total TBT input to the certain environment could be underestimated (at least by a factor of ten).

TBT pollution of sediments is not only a problem because it poses a threat to the benthic organisms living there; the big problem lies in the fact that contaminated sediments are a potential source of BuTs pollution for the water column. Although it has been experimentally proven many times that BuTs can be desorbed from sediments (Berg et al., 2001; Burton et al., 2004), this has been demonstrated only in a few field studies (Furdek Turk et al., 2020; Chen et al., 2022). However, knowledge about the extent to which contaminated sediments act as a source of BuT pollution is still incomplete. To investigate the behaviour of BuTs during the resuspension of disturbed sediments, we analysed the water overlying the sediment in the gravity corer. It was assumed that the penetration of the gravity corer into the sediment would cause resuspension of fine particles from the sediment surface, which could mimic, to some extent, the resuspension of surface sediments caused by waves or bioturbation. The BuTs concentrations in the water above the sediment (Table 1, Fig. 5a5A,bB) showed a predominance of MBT (8.8-277 ng(Sn)/L) and DBT (0.2-130 ng(Sn)/L) over TBT (<0.1-160 ng(Sn)/L), which was found only at two sites (Tiv2 and TivB) where the surface sediments contained more than 50% of BuTs in the form of TBT (Fig. 3b3B). As these concentrations are much higher than those normally found in the water column and porewater (<10 ng(Sn)/L; Furdek et al., 2012; Furdek Turk et al., 2020), we assume that most of the detected BuTs are desorbed from the sediments into the overlying water. These data support the results of a similar study conducted with contaminated coastal sediments in Croatia (Furdek Turk al., 2020). Both studies showed that contaminated sediments are a potential source of BuTs to the water column, especially MBT and DBT as less hydrophobic and weakly adsorbed compounds that can be released from the sediments more easily than TBT. However, this study has shown that resuspension of sediments can also lead to the release of TBT, especially from contaminated sediments with high levels of TBT in the surface layers.

An assessment of the extent of BuTs contamination in the coastal environment of Montenegro was performed by comparing BuTs and TBT levels determined in different coastal areas of Europe during the last decade (Table 2). The comparison of literature data given in Table 2

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showed that the Eastern Adriatic coast (Croatian and Montenegrin) is highly contaminated with BuT compounds. However, the level of TBT pollution strongly depends on the type of sampling locations (marina, port, beaches) and is related to the intensity of marine traffic (Briant et al., 2013; Suzdalev et al., 2015), and therefore, this conclusion should be taken with caution as it may be influenced by different sampling strategies of the presented studies and prevalence of more contaminated sites along the Croatian coast. In the Water Framework Directive (WFD; [Directive 2000/60/EC, 2000](#)) TBT is listed as one of the priority substances that should be monitored to assess the chemical status of a water body, but within this Directive TBT presence in the environment is regulated only by the prescribed maximum allowed concentration in seawater (the annual average should be less than 0.2 ng/L). However, several regional conventions, ~~such as (i.e.)~~ [OSPAR \(Convention for the Protection of the Marine Environment of the North-East Atlantic; OSPAR, 2004\)](#) and [HELCOM Conventions \(Convention on the Protection of the Marine Environment of the Baltic Sea Area; HELCOM, 2018\)](#), ~~Barcelona Convention~~ have established Environment Assessment Criteria (EAC) for the assessment and monitoring of the environmental status of regional waters, which could be applied for assessments based on the measurement of TBT in sediments and biota. OSPAR (OSPAR, 2004) has established EAC for TBT in mollusks; the lower EAC ($EAC_{low} = 4.9$ ng(Sn)/g) is defined as the threshold for protection of all marine species from chronic effects and the upper EAC ($EAC_{high} = 72$ ng(Sn)/g) is defined as the highest level at which no acute toxic effects are expected. ~~The measured~~ TBT concentrations quantified in mussels tissue were above the EAC_{low} at all sites, while they were above the EAC_{high} at site Bar3, indicating that chronic effects for marine organisms sensitive to TBT are to be expected at all locations. The assessment of TBT pollution based on the TBT concentrations ~~measured-quantified in the~~ sediments was carried out according to the Norwegian environmental quality classification system defined for management purposes (Bakke et al., 2010); Background: <0.4 ng(Sn)/g, Good: 0.4-2.1 ng(Sn)/g, Moderate: 2.1-8.3 ng(Sn)/g, Poor: 8.3-41.7 ng(Sn)/g, and Very Poor: >41.7 ng(Sn)/g. At seven (out of nine) sites investigated surface sediments are contaminated with TBT; Kot1 and Bud1 were moderately contaminated with TBT, while the environmental status of Tiv3 and Bud3, as well as Tiv2, TivB and Bar3, can be evaluated as poor and very poor, respectively, indicating that TBT is expected to have toxic effects on marine organisms and the occurrence of imposex in gastropods is very likely at these locations (Erdelez et al., 2017; Laranjeiro et al., 2018).

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The presented results show that the investigated areas on the Montenegrin coast are polluted with TBT, which indicates the need for further monitoring of the coastal area. Apparently, TBT-based antifouling paints, despite of its ban, have been used within a few months of sampling (as shown by BuTs levels measured in mussels), but also over a longer period of time (as shown by BuTs levels measured in sediments). The main source of pollution could be small local and leisure boats that are not subject to any control of antifouling paint applied. Therefore, they may be illegally painted with TBT-containing paints, for which is shown that were still present on the global market in 2021 (Uc-Peraza et al., 2022) or can have old layers of TBT-based paint that are not properly removed from the boat (Lagerstrom et al., 2017, 2019). Indeed, a recent study in the Nordic countries has demonstrated the presence of TBT in the subsurface paint layers of all investigated leisure boats (Lagerström et al., 2017, 2019) and shown that they are source of TBT pollution. The results have also shown that resuspension of contaminated sediments may cause pollution of the water column, especially at the Bijela shipyard (TivB) where remediation measures are strongly recommended. Recently, extreme contamination with ecotoxic metals (Mikac et al., 2022; Radomirović et al., 2021) and significantly altered microbial community have been demonstrated in sediments sampled near this shipyard (Jokanović et al., 2021).

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References

Abraham M, Westphal L, Hand I, Lerz A, Jeschek J, Bunke D, Leipe T, Schulz-Bull D (2017) TBT and its metabolites in sediments: Survey at a German coastal site and the central Baltic Sea. *Mar. Pollut. Bull.* 121, 404-410.

Anastasiou TI, Chatzinikolaou E, Mandalakis M, Arvanitidis C (2016) Imposex and organotin compounds in ports of the Mediterranean and the Atlantic: Is the story over? *Sci. Total. Environ.* 569-570, 1315-1329.

1
2
3
4
5
6
7 428 Bandara KRV, Chinthaka SDM, Yasawardene SG, Manage PM (2021) Modified, optimized
8 method of determination of Tributyltin (TBT) contamination in coastal water, sediment and
9 429 biota in Sri Lanka. Mar. Pollut. Bull. 166, 112202.
10 430
11
12 431 Bakke T, Källqvist T, Ruus A, Breedveld GD, Hylland K (2010) Development of sediment
13 432 quality criteria in Norway. J. Soil Sed. 10, 172-178.
14
15 433 Batista RM, Castro IB, Fillmann G (2016) ImPOSEX and butyltin contamination still evident in
16 434 Chile after global ban. Sci. Total Environ. 566-567, 446-453.
17
18 435 Berg M, Arnold CG, Müller RS, Mühlemann J, Schwarzenbach RP (2001) Sorption and
19 436 desorption behaviour of organotin compounds in sediment-pore water systems. Environ. Sci.
20 Technol. 35, 3151-3157.
21 437
22
23 438 Berto D, Giani M, Boscolo R, Covelli S, Giovanardi O, Massironi M, Grassia L (2007)
24 439 Organotins (TBT and DBT) in water, sediments, and gastropods of the southern Venice lagoon
25 440 (Italy). Mar. Pollut. Bull. 55, 425-435.
26
27 441 Briant N, Bancon-Montigny C, Elbaz-Poulichet F, Freyrier R, Delpoux S, Cossa D (2013)
28 Trace elements in the sediments of a large Mediterranean marina (Port Camargue, France):
29 442 Levels and contamination history. Mar. Pollut. Bull. 73, 78-85.
30 443
31
32 444 Briant N, Bancon-Montigny C, Freyrier R, Delpoux S, Elbaz-Poulichet F (2016) Behaviour of
33 445 butyltin compounds in the sediment pore waters of a contaminated marina (Port Camargue,
34 446 South of France). Chemosphere 150, 123-129.
35
36 447 Burton ED, Phillips IR, Hawker DW (2004) Sorption and desorption behavior of tributyltin
37 with natural sediments. Environ. Sci. Technol. 38, 6694-6700.
38 448
39 449 Cacciatore F, Brusaa RB, Noventa S, Antonini C, Moschino V, Formalewicz M, Gion C,
40 Berto D, Gabellini M, Marin MG (2018) ImPOSEX levels and butyltin compounds (BTs) in
41 450 *Hexaplex trunculus* (Linnaeus, 1758) from the northern Adriatic Sea (Italy): Ecological risk
42 451 assessment before and after the ban. Ecotoxicol. Environ. Safety 147, 688-698.
43 452
44
45 453 Chandrinou S, Stasinakis AS, Thomaidis NS, Nikolaou A, Wegener JW (2007) Distribution of
46 organotin compounds in the bivalves of the Aegean Sea, Greece. Environ. Inter. 33, 226-232.
47 454
48 455 Chen C, Chen L, Huang Q, Zhang W, Leung KM (2022) Pulsed distribution of organotins in
49 the turbidity maximum zone of the Yangtze Estuary throughout a tidal cycle. Mar. Pollut. Bull.
50 456 178, 113600.
51 457
52
53
54
55
56
57
58
59
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6
7 458 ~~Commission Directive 2000/62/EC (2000) EU Water Framework Directive. Official Journal~~
8 ~~of the European Communities, 327.~~
9 459
10 460 Directive 2000/60/EC (2000) Directive of the European Parliament and of the Council
11 establishing a framework for the Community action in the field of water policy (EU Water
12 Framework Directive - WFD), Official Journal L 327
13 462
14
15 463 Concha-Graña E, Moscoso-Pérez C, Fernández-González V, López-Mahía P, Gago J, León
16 464 VM, Muniategui-Lorenzo S (2021) Phthalates, organotin compounds and per-polyfluoroalkyl
17 465 substances in semiconfined areas of the Spanish coast: Occurrence, sources and risk
18 466 assessment. Sci. Total. Environ. 780, 146450.
19
20
21 467 Díez S, Lacorte S, Viana P, Barcelo D, Bayona J (2005) Survey of organotin compounds in
22 468 rivers and coastal environments in Portugal 1999-2000. Environ. Pollut. 136, 525-536.
23
24 469 Egardt J, Nilsson P, Dahllöf I (2017) Sediments indicates the continued use of banned
25 470 antifouling compounds. Mar. Pollut. Bull. 125, 282-288.
26
27 471 El Ayaria T, Bierne N, El Menifa NT (2018) ImPOSEX incidence in *Stramonita haemastoma*
28 472 (Gastropoda: Muricidae) from the Mediterranean and Atlantic coast after Tributyltin global
29 473 ban. J. Sea Res. 134, 10-15.
30
31
32 474 Erdelez A, Furdek Turk M, Štambuk A, Župan I, Peharda M (2017) Ecological quality status
33 475 of the Adriatic coastal waters evaluated by the organotin pollution biomonitoring. Mar. Pollut.
34 476 Bull. 123, 313-323.
35
36 477 Filipkowska A, ~~and~~ Lubecki L (2016) Endocrine disruptors in blue mussels and sediments
37 478 from the Gulf of Gdańsk (Southern Baltic). Environ. Sci. Pollut. Res. 23, 13864–13876.
38
39 479 Filipkowska A, Zloch I, Wawrzyniak-Wydrowska B, Kowalewska G (2016) Organotins in fish
40 480 muscle and liver from the Polish coast of the Baltic Sea: Is the total ban successful? Mar. Pollut.
41 481 Bull. 111, 493-499.
42
43
44 482 Filipkowska A, Kowalewska G (2019) Butyltins in sediments from the Southern Baltic coastal
45 483 zone: Is it still a matter of concern, 10 years after implementation of the total ban? Mar. Pollut.
46 484 Bull, 146, 343-348.
47
48 485 Formalewicz MM, Rampazzo F, Noventa S, Gion C, Petranich E, Crosera M, Covelli S,
49 486 Faganeli J, Berto D. (2019) Organotin compounds in touristic marinas of the northern Adriatic
50 487 Sea: occurrence, speciation and potential recycling at the sediment-water interface. Environ.
51 488 Sci. Pollut. Res. 26, 31142–31157.
52
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7 489 Furdek Turk M, Ivanić M, Zuliani T, Milačić R, Mikac N (2019) State of pollution of Croatian
8
9 490 Adriatic coast with tributyltin compounds, Proceeding of the 7th Croatian water conference with
10 491 international participation, Opatija, Croatia, June 2019, pp. 555-563 (in Croatian)
11
12 492 Furdek M, Mikac N, Bueno M, Tessier E, Cavalheiro J, Monperrus M (2016) Organotin
13 493 persistence in contaminated marine sediments and porewaters: In situ degradation study using
14
15 494 species-specific stable isotopic tracers. *J. Hazard. Mater.* 307, 263-273.
16
17 495 Furdek M, Vahčić M, Ščančar J, Milačić R, Kniewald G, Mikac N (2012) Organotin
18 496 compounds in seawater and mussels *Mytilus galloprovincialis* along the Croatian Adriatic
19 497 coast. *Mar. Pollut. Bull.* 64, 189-199.
20
21 498 Furdek Turk M, Ivanić M, Dautović J, Bačić N, Mikac N (2020) Simultaneous analysis
22 499 of tributyltins and total tin in sediments as a tool for the assessment of tributyltin behaviour,
23
24 500 long-term persistence and historical contamination in the coastal environment, *Chemosphere*
25 501 258, 127303.
26
27 502 [Garg A, Antón-Martín R, García-Luque E, Riba I, DelValls T \(2009\) Distribution of butyltins](#)
28 503 [\(TBT, DBT, MBT\) in sediments of Gulf of Cádiz \(Spain\) and its bioaccumulation in the clam](#)
29
30 504 [Ruditapes philippinarum. Ecotoxicology 18, 1029–1035.](#)
31
32 505 Gomez-Ariza JL, Morales E, Giraldez I (1999) Uptake and elimination of tributyltin in clams,
33 506 *Venerupis decussata*. *Mar. Environ. Res.* 47, 399-413.
34
35 507 Guomundsdóttir LO, Ho KKY, Lam JCW, Svavarsson J, Leung KMY (2011) Long-term
36 508 temporal trend (1992-2008) of imposex status associated with organotin contamination in the
37 509 dogwhelk *Nucella lapillus* along the Icelandic coast. *Mar. Pollut. Bull.* 63, 500-507.
38
39 510 Harrison TD, Gilmour G, McNeill MT, Armour N, McIlroy L (2020) Survey of imposex in
40 511 *Nucella lapillus* as an indicator of tributyltin pollution in Northern Irish coastal waters, 2004 to
41
42 512 2017. *Mar. Pollut. Bull.* 159, 111474.
43
44 513 Hoch M (2001) Organotin compounds in the environment. *Appl. Geochem.* 16, 719-743.
45 514 Hoch M and Schwesig D (2004) Parameters controlling the partitioning of tributyltin (TBT) in
46
47 515 aquatic systems. *Appl. Geochem.* 19, 323–334.
48
49 516 Jokanović S, Kajan S, Perović S, Ivanić M, Mačić V, Orlić S (2021) Anthropogenic influence
50 517 on the environmental health along Montenegro coast based on the bacterial and chemical
51 518 characterization. *Environ. Pollut.* 271, 116383.
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7⁵¹⁹ Joksimović A, Djurović M, Semenov AV, Zonn IS, Kostianoy AG (Eds) (2017) The Boka
8
9⁵²⁰ Kotorska Bay Environment. The Handbook of Environmental Chemistry 54 (Series Eds: D.
10⁵²¹ Barceló, A. G. Kostianoy). Springer.
11
12⁵²² Joksimović D, Perošević A, Castelli A, Pestorić B, Šušković D, Đurović D (2020) Assessment
13⁵²³ of heavy metal pollution in surface sediments of the Montenegrin coasts: a 10-years review. J.
14
15⁵²⁴ Soil Sed. 20, 2598-2607.
16
17⁵²⁵ Joksimović D, Tomić I, Stanković AR, Jović M, Stanković S (2011) Trace metal concentrations
18⁵²⁶ in Mediterranean blue mussel and surface sediments and evaluation of the mussels quality and
19⁵²⁷ possible risks of high human consumption. Food Chem. 127, 632–637.
20
21⁵²⁸ Kucklick JR, Ellisor MD (2019) A review of organotin contamination in arctic and subarctic
22⁵²⁹ regions. Emerging Contaminants 5, 150-156.
23
24⁵³⁰ Lagerström M, Yngsell D, Eklund B, Ytreberg E (2019) Identification of commercial and
25⁵³¹ recreational vessels coated with banned organotin paint through screening of tin by portable
26
27⁵³² XRF. J. Hazard. Mater. 362, 107-114.
28
29⁵³³ Lagerström M, Strand J, Eklund B, Ytreberg E (2017) Total tin and organotin speciation in
30⁵³⁴ historic layers of antifouling paint on leisure boat hulls. Environ. Pollut. 220, 1333-1341.
31
32⁵³⁵ Langston WJ, Pope ND, Davey M, Langston KM, O' Hara SCM, Gibbs PE, Pascoe PL (2015)
33⁵³⁶ Recovery from TBT pollution in English Channel environments: a problem solved? Mar.
34
35⁵³⁷ Pollut. Bull. 95, 551-564.
36
37⁵³⁸ Laranjeiro F, Sanchez-Marin P, Oliveira IB, Galante-Oliveira S, Barroso C (2018) Fifteen
38⁵³⁹ years of imposex and tributyltin monitoring along the Portuguese coast. Environ. Pollut. 232,
39⁵⁴⁰ 411-421.
40
41⁵⁴¹ Lee RF (1996) Metabolism of tributyltin by aquatic organisms, in: Champ, M.A. and Selignam,
42⁵⁴² P.F., Organotin - environmental fate and effects. Chapman and Hall, London, pp. 369-382.
43
44⁵⁴³ Magi E, Liscio C, Pistarino E, Santamaria B, Di Carro M, Tiso M, Scaloni A, Renzone G,
45⁵⁴⁴ Cosulich ME (2008) Interdisciplinary study for the evaluation of biochemical alternations on
46
47⁵⁴⁵ mussel *Mytilus galloprovincialis* exposed to a tributyltin-polluted area. Anal. Bioanal. Chem.
48⁵⁴⁶ 391, 671-678.
49
50⁵⁴⁷ Metelkova L, Zhakovskaya Z, Kukhareva G, Voskoboinikov G, Zimina O (2022) Organotin
51⁵⁴⁸ compounds (OTs) in surface sediments, bivalves and algae from the Russian coast of the
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7⁵⁴⁹ Barents Sea (Kola Peninsula) and the Fram Strait (Svalbard Archipelago) Environ. Sci Pollut.
8
9⁵⁵⁰ 29(23), 34659-34669.

10⁵⁵¹ Mikac N, Sondi I, Vdović N, Pikelj K, Ivanić M, Lučić M, Bačić N, Furdek Turk M, Škapin
11
12⁵⁵² DS, Krivokapić S (2022) Origin and history of trace elements accumulation in recent
13⁵⁵³ Mediterranean sediments under heavy human impact. A case study of the Boka Kotorska Bay
14
15⁵⁵⁴ (Southeast Adriatic Sea) Mar. Pollut. Bull. 179, 113702.

16⁵⁵⁵ Milivojević Nemanich T, Milačić R, Ščančar J (2009) A survey of organotin compounds in the
17
18⁵⁵⁶ Northern Adriatic Sea. Water Air Soil Pollut. 196, 211-224.

19⁵⁵⁷ Nicolaus EEM, Barry J (2015) Imposex in the dogwhelk (*Nucella lapillus*): 22-year monitoring
20
21⁵⁵⁸ around England and Wales. Environ. Monit. Assess. 187, 736.

22
23⁵⁵⁹ Omae I (2003) Organotin antifouling paints and their alternatives. Appl. Organomet. Chem.
24
25⁵⁶⁰ 17, 81-105.

26⁵⁶¹ OSPAR (2004) OSPAR/ICES Workshop on the evaluation and update of background reference
27
28⁵⁶² concentrations (B/RCS) and ecotoxicological assessment criteria (EACs) and how these
29
30⁵⁶³ assessment tools should be used in assessing contaminants in water, sediment and biota, Final
31
32⁵⁶⁴ report, OSPAR Commission.

33⁵⁶⁵ Paz-Villarraga CA, Castro ÍB, Miloslavich P, Fillmann G (2015) Venezuelan Caribbean Sea
34
35⁵⁶⁶ under the threat of TBT. Chemosphere 119, 704–710.

36⁵⁶⁷ Pougnet F, Schäfer J, Dutruch L, Garnier C, Tessier E, Dang DU, Lanceleur M, Mullot JU,
37
38⁵⁶⁸ Lenoble V, Blanc G (2014) Sources and historical record of tin and butyl-tin species in a
39
40⁵⁶⁹ Mediterranean bay (Toulon Bay, France). Environ. Sci. Pollut. Res. 21, 6640-6651.

41⁵⁷⁰ Poerschmann J, Kopinke, FD, Pawliszyn J (1997) Solid phase microextraction to study the
42
43⁵⁷¹ sorption of organotin compounds onto particulate and dissolved humic organic matter.
44
45⁵⁷² Environ. Sci. Technol. 31(12), 3629-3636.

46
47⁵⁷³ Quintas PY, Alvarez MB, Arias AH, Garrido M, Marcovecchio JE (2019) Spatiotemporal
48
49⁵⁷⁴ distribution of organotin compounds in the coastal water of the Bahía Blanca estuary
50
51⁵⁷⁵ (Argentina). Environ. Sci. Pollut. Res. 26, 7601-7613.

52
53⁵⁷⁶ Radomirović M, Mijatović N, Vasić M, Tanaskovski B, Mandić M, Pezo L, Onjia A (2021)
54
55⁵⁷⁷ The characterization and pollution status of the surface sediment in the Boka Kotorska Bay,
56
57⁵⁷⁸ Montenegro. Environ. Sci. Pollut. Res. 28, 42496-42515.

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7 579 Rodriguez-Gonzalez P, Bouchet S, Monperrus M, Tessier T, Amouroux D (2013) In situ
8
9 580 experiments for element species-specific environmental reactivity of tin and mercury
10 581 compounds using isotopic tracers and multiple linear regression. Environ. Sci. Pollut. R. 20,
11 582 1269-1280.
12
13 583 Romanelli G, Berto D, Calace N, Amici M, Maltese S, Formalewicz M, Campanelli A, Marini
14
15 584 M, Magaletti E, Scarpato A (2019) Ballast water management system: Assessment of chemical
16 585 quality status of several ports in Adriatic Sea. Mar. Pollut. Bull. 147, 86-97.
17
18 586 Ruiz JM, Barreiro R, Couceiro L, Quintela M (2008) Decreased TBT pollution and changing
19 587 bioaccumulation pattern in gastropods imply butyltin desorption from sediments. Chemosphere
20
21 588 73, 1253-1257.
22 589 Salazar MH, Salazar SM (1996) Mussels as bioindicators: Effects of TBT on survival,
23
24 590 bioaccumulation, and growth under natural conditions, in: Champ MA, Selignam PF,
25 591 Organotin - environmental fate and effects. Chapman and Hall, London, pp. 306-330.
26
27 592 Stanković S, Jović M, Tanasovski B, Mihajlović ML, Joksimović D, Pezo L (2015) Can the
28 593 origin of some metals in the seagrass *Posidonia oceanica* be determined by the index of metals
29
30 594 pollutions? Environ. Sci. Pollut. Res. 22, 8253-8263.
31 595 Sutherland R A (2000) Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii.
32
33 596 Environ. Geol. 39, 611-627.
34
35 597 Suzdalev S, Gulbinskas S, Blažauskas N (2015) Distribution of tributyltin in surface sediments
36 598 from transitional marine-lagoon system of the south-eastern Baltic Sea, Lithuania. Environ.
37 599 Sci. Pollut. Res. 22, 2634–2642.
38
39 600 ~~Tang CH, Hsu CH, Wang WH (2010) Butyltin accumulation in marine bivalves under field
40 601 conditions in Taiwan. Mar. Environ. Res. 70, 125-132.~~
41
42 602 Uc-Peraza R-G, Castro I-B, Fillmann G (2022) An absurd scenario in 2021: Banned TBT-
43 603 based antifouling products still available on the market. Sci. Total. Environ. 805, 150377.
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Figures caption

- Figure 1. ~~The~~ sampling locations along the Montenegrin Adriatic coast.
- Figure 2. ~~The~~ distribution of BuTs ~~in~~ mussels ~~tissue~~: (a) MBT, DBT and TBT concentrations, and (b) percentage of each ~~chemical~~ species ($BuT/\sum BuTs$).
- Figure 3. ~~The~~ distribution of BuTs and total Sn in surface sediments: (a) MBT, DBT, TBT and Sn concentrations, and (b) percentage of each BuT species ($BuT/\sum BuTs$) along with proportion of $\sum BuTs/Sn_{total}$. ~~(The absence of bars for BuTs means that they were not detected – the concentrations are <LOD.)~~
- Figure 4. ~~The~~ depth distributions of butyltins (MBT, DBT, TBT and $\sum BuTs$) and total Sn in sediment cores along with proportions of $\sum BuTs/Sn_{total}$. ~~(The absence of bars for BuTs means that they were not detected – the concentrations are <LOD.)~~
- Figure 5. ~~The~~ distribution of BuTs in waters overlying sediment: (a) MBT, DBT and TBT concentrations, and (b) percentage of each BuT species ($BuT/\sum BuTs$).

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Table 1. Summarizing statistic for butyltins (MBT, DBT, TBT, Σ BuTs) concentrations and proportions of TBT/ Σ BuTs and Σ BuTs/ Sn_{total} in different types of samples collected along the Montenegrin Adriatic coast.

	Concentration (ng(Sn)/g; ng(Sn)/L)				Proportion (%)	
	MBT	DBT	TBT	Σ BuTs	TBT/ Σ BuTs	Σ BuTs/ Sn_{total}
Mussels						
min	<5	10.4	6.7	19.7	28.2	-
max	50.7	173	179	402	55.5	-
average	15.1	43.0	40.6	98.6	39.1	-
median	11.1	30.6	25.9	67.8	39.3	-
Sediment cores (all depths)						
min	<6	<2	<1	<9	-	0.01
max	3651	4279	14900	20641	75.4	62.0
average	248	288	829	1365	25.9	6.09
median	20.8	14.1	12.4	43.1	17.2	0.43
max*	650	445	1304	1979	74.8	26.5
average *	62	41	85	188	22.0	2.37
median*	11.1	3.9	0.5	31.2	11.1	0.10
Water overlaying sediment						
min	8.8	0.2	<0.1	9.1	<0.2	-
max	277	130	160	566	28.2	-
average	91.3	52.4	24.4	168	6.0	-
median	38.2	58.9	0.3	80.4	0.4	-
max*	219	114	58	333	22.9	-
average *	68.1	42.7	7.5	118	3.2	-
median*	29.0	40.9	0.3	70.9	0.4	-

*without samples from Bijela shipyard

Table 2. Literature data on butyltins (BuTs=TBT+DBT+MBT) and tributyltin (TBT) concentration in seawater, sediment and biota from the coastal areas of Europe reported in the last decade.

Area and year of sampling	Seawater (ng(Sn)/L)	Sediment (ng(Sn)/g)	Biota (ng(Sn)/g)	Reference
Southeast Adriatic coast (Montenegro); 2015	-	BuTs: <9-2000 (20641)* TBT: <1-1300 (14900)*	BuTs: 20-400 TBT: 7-179	This study
East Adriatic coast (Croatia); 2010-2012	BuTs: 0.5-28 TBT: <0.2-15	BuTs: 3-1362 (66345)** TBT: 1-790 (32317)**	Mussels BuTs: <10-1676 TBT: <10-1045	Furdek et al. (2012); Furdek Turk et al. (2020)
East Adriatic coast (Croatia), 2015-2017	TBT: <0.2-6.3	TBT: <1-92	Gastropoda BuTs: 1.9-155 TBT: 0.5-59	Furdek Turk et al. (2019); Erdelez et al. (2017)
East Adriatic coast (Slovenia, Croatia, Montenegro, Albania); 2014	TBT: <2	BuTs: 7-731 TBT: 3-566	Mussels BuTs: 25-220 TBT: 20-170	Romanelli et al. (2019)
West Adriatic coast (Italy); 2014	TBT: <2	BuTs: 7-240 TBT: 2-186	Mussels BuTs: 25-100 TBT: 60-75	Romanelli et al. (2019)
North Adriatic coast (Italy, Slovenia); 2016	-	BuTs: 121-352 TBT: 53-174	-	Formalewicz et al. (2019)
North Sea (Sweden); 2014	-	BuTs: 10-500 TBT: 10-300	-	Egardt et al. (2017)
Baltic sea (Lithuania); 2010-2012	-	TBT: 1-5200	-	Suzdalev et al. (2015)
Baltic Sea (Poland); 2014-2015 (fish), 2018 (sediment)	-	BuTs: 5.7-3321 TBT: 3.7-1942	Fish muscle BuTs: nd-715 TBT: nd-503	Filipkowska et al. (2016); Filipkowska and Kowalewska (2019)
Baltic Sea (Poland); 2012-2013	-	BuTs: nd-22	Mussels BuTs: 41-164 TBT: 11-103	Filipkowska and Lubecki (2016)
Baltic Sea (Germany); 2015	-	BuTs: 100-1426 TBT: 2.5-380	-	Abraham et al. (2017)
Mediterranean (France); 2009, 2011, 2013	Porewater BuTs: 40-600 TBT: 0.1-70	BuTs: 8-16000 TBT: nd-10700	-	Briant et al. (2013, 2016)
Mediterranean and Atlantic coast (Portugal, Italy, Turkey); 2012	-	BuTs: 8-200 TBT: 3-75	Gastropoda BuTs: 30-720 TBT: 12-172	Anastasiu et al. (2016)
Mediterranean and Atlantic coast (Spain); 2015	BuTs: nd-20 TBT: nd-17	BuTs: nd-100 TBT: nd-75	-	Concha-Grana et al. (2021)
Barents Sea (Russia); 2019	-	BuTs: 28-83 TBT: 2-24	Bivalves BuTs: nd-50 TBT: nd-38	Metelkova et al. (2022)

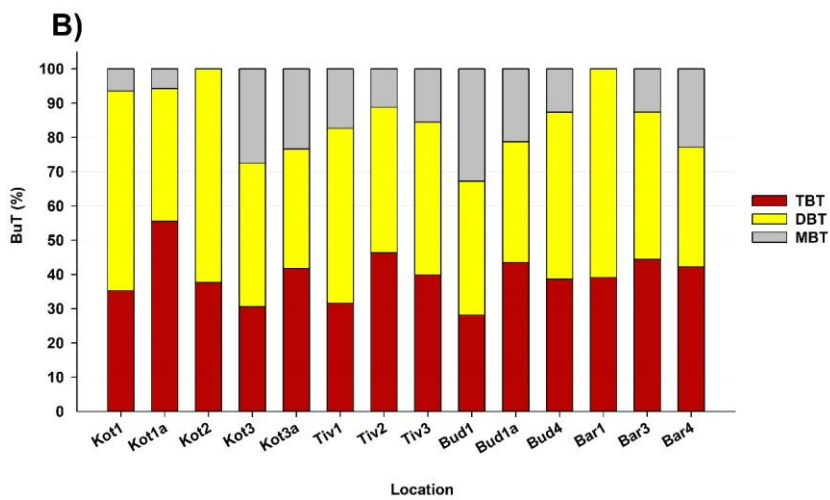
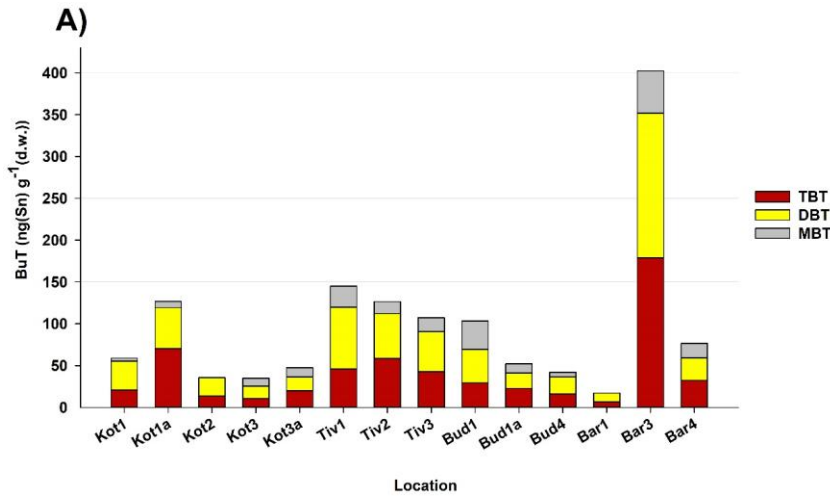
*including samples from shipyard Bijela; ** including samples from shipyard and service hoists

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Figure 1. The sampling locations along the Montenegrin Adriatic coast.

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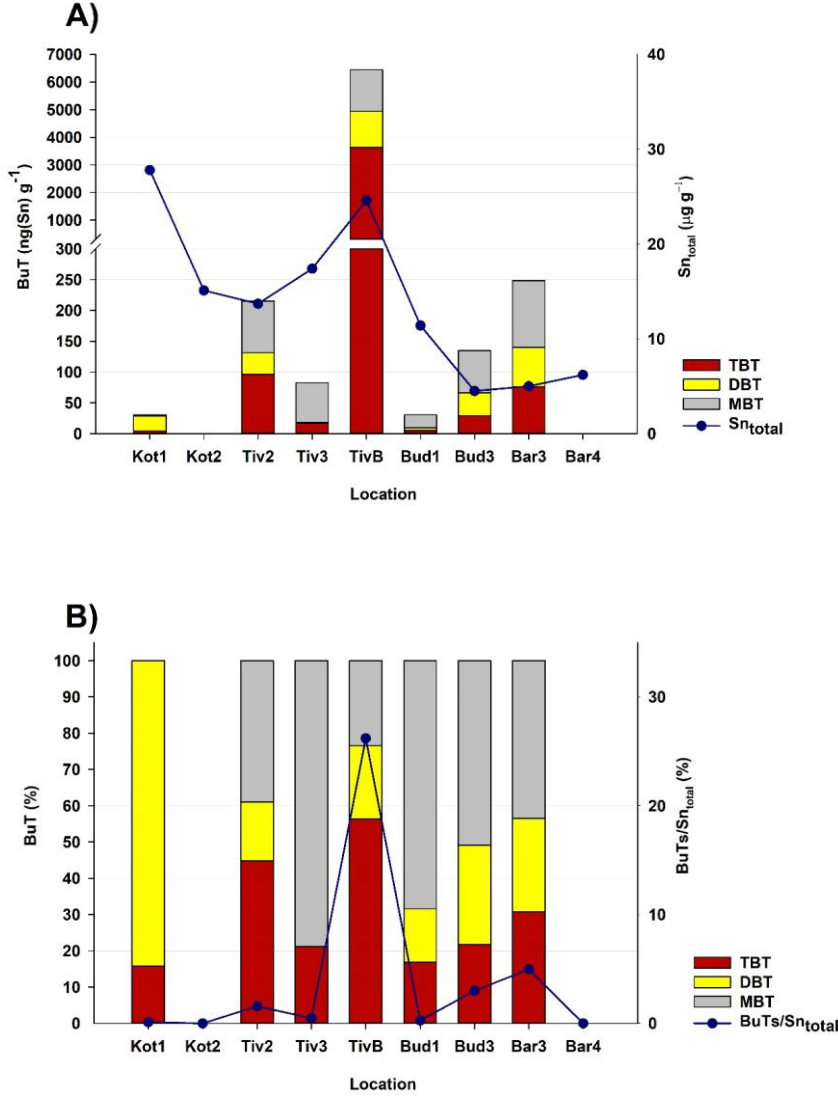


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Figure 2. The distribution of BuTs in mussel tissues: (a) MBT, DBT and TBT concentrations, and (b) percentage of each chemical species (BuT/ΣBuTs).

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Figure 3. The distribution of BuTs and total Sn in surface sediments: (a) MBT, DBT, TBT and Sn concentrations, and (b) percentage of each BuT species (BuT/∑BuTs) along with proportion of ∑BuTs/Sn_{total}. (The absence of bars for BuTs means that they were not detected – the concentrations are <LOD.)

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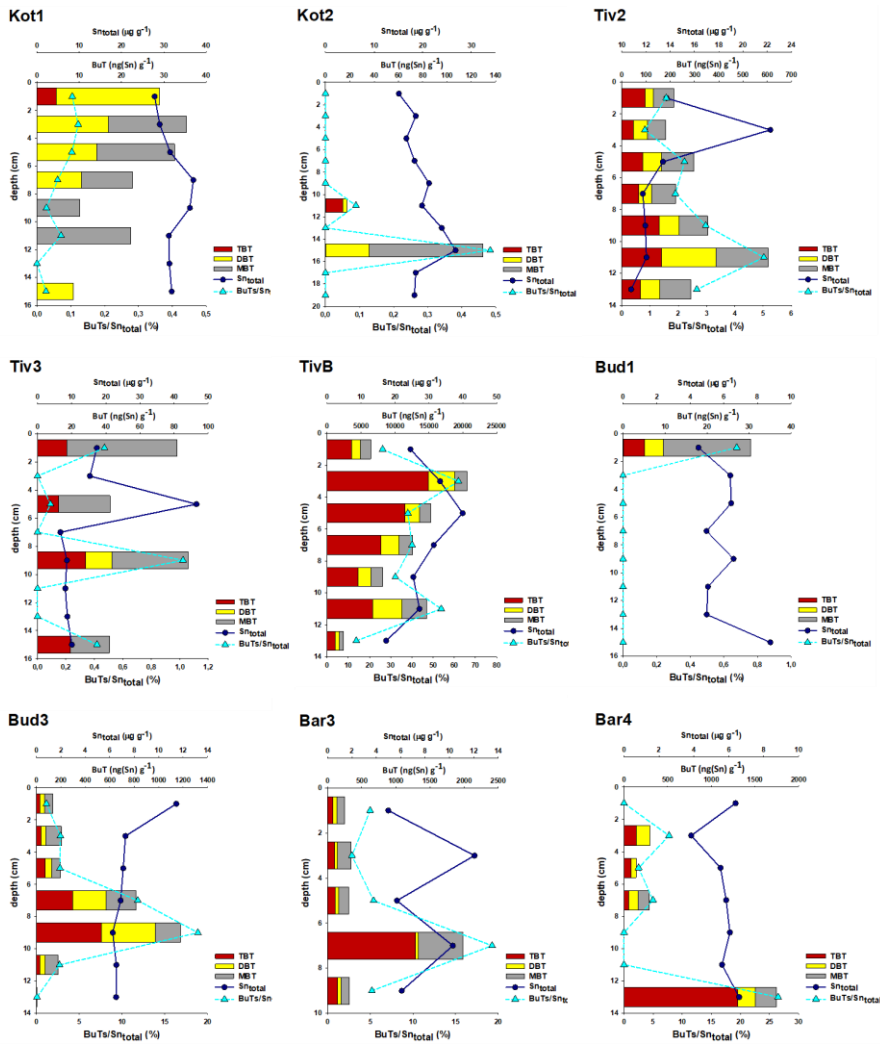


Figure 4. The depth distributions of butyltins (MBT, DBT, TBT and Σ BuTs) and total Sn in sediment cores along with proportions of Σ BuTs/S_{total}. (The absence of bars for BuTs means that they were not detected – The concentrations are <LOD.)

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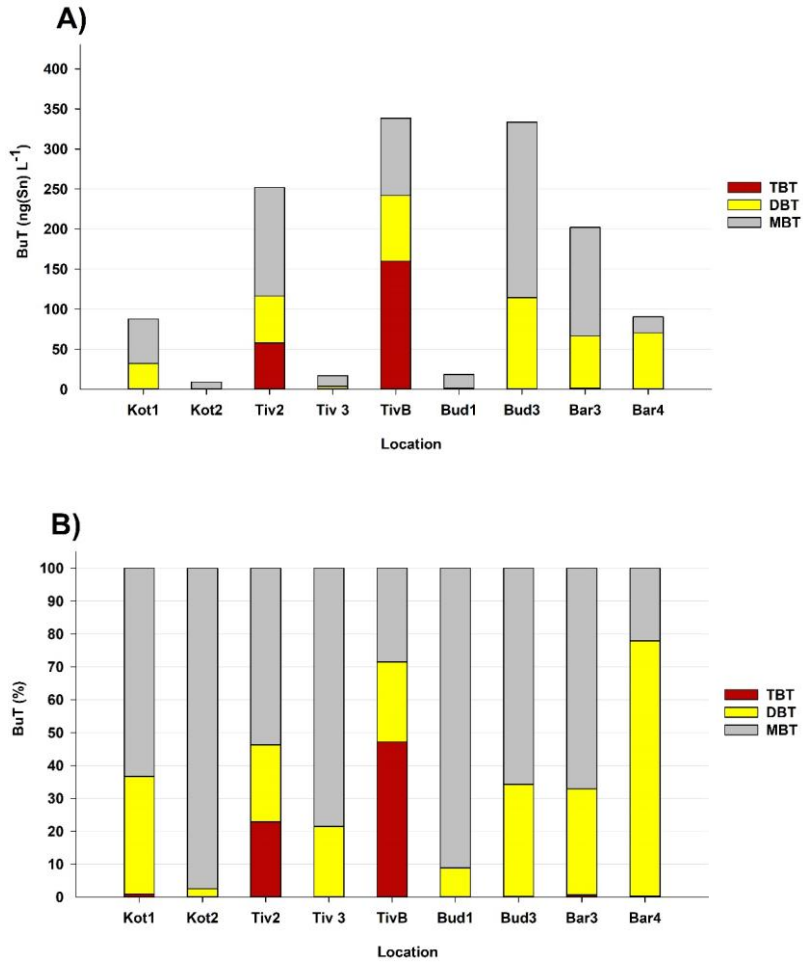


Figure 5. The distribution of BuTs in waters overlying sediment: (a) MBT, DBT and TBT concentrations, and (b) percentage of each BuT species ($BuT/\sum BuTs$).

Table S1. The description of sampling locations along the Montenegrin coast.

Location	Type of samples	Description of location	Water depth (m)
Kotor Bay			
Kot1	sediment, mussels	marina in Kotor	7
Kot1a	mussels	marina in Kotor	3
Kot2	sediment, mussels	cruise port in Kotor	15
Kot3	mussels	small local port (Dobrota)	5
Kot3a	mussels	small local port (Dobrota)	3
Tivat Bay			
Tiv1	mussels	marina in Tivat	8
Tiv2	sediment, mussels	marina in Tivat	6
Tiv3	sediment, mussels	outside the marina in Tivat	21
TivB	sediment	shipyard	24
City of Budva			
Bud1	sediment, mussels	marina	4
Bud1a	mussels	local port	3
Bud3	sediment	marina (near the hoist)	5
Bud4	mussels	marina	4
City of Bar			
Bar1	mussels	cargo port	15
Bar3	sediment, mussels	marina	6
Bar4	sediment, mussels	military port	7

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Nevenka Mikac: Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing, Visualization, Funding acquisition. **Martina Furdek Turk:** Conceptualization, Methodology, Formal analysis, Investigation, Writing – review & editing, Visualization, Supervision. **Dragana Petrović:** Investigation. **Miljan Bigović:** Formal analysis, Investigation. **Sladjana Krivokapić:** Investigation, Funding acquisition.