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**Occurrence, distribution and fluxes of benzotriazoles along
the German large river basins into the North Sea**
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1 ***Occurrence, distribution and fluxes of Benzotriazoles along***
2 ***the German large river basins into the North Sea***

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18 **1 Abstract**

19 Benzotriazole (BT) and tolyltriazole (TT) are high production volume chemicals which
20 are used in various industrial and household applications. In this study, the
21 distribution of benzotriazoles in the estuaries of different rivers of central Europe and
22 in the North Sea was analyzed by solid-phase extraction (SPE) and liquid
23 chromatography-mass spectrometry (HPLC-MS/MS). BT as well as TT were detected
24 in all water samples. The concentrations for total benzotriazoles (BTs) ranged from
25 1.7 to 40 ng/L in the North Sea in costal areas. Concentrations in rivers are from 200
26 to 1250 ng/L, respectively. The mass flux of total benzotriazoles from the major rivers
27 of central Europe into the North Sea was calculated to 78 t/a, dominated by the
28 Rhine with an individual flux of 57 t/a of BTs. The analysis of the distribution profile in
29 the North Sea showed that the decrease of the concentration was mostly caused by
30 dilution and that the benzotriazoles are poorly degradable in the North Sea. This
31 paper presents the first report of benzotriazoles in the marine environment.

32

33 Keywords:

34 benzotriazole, tolyltriazole, river water, North Sea, HPLC-MS/MS

35

36 **2 Introduction**

37 1H-benzotriazole (BT) and 1H-methyl-benzotriazole (tolyltriazole, TT, used as a
38 technical mixture of 4- and 5-TT) are a class of high production volume chemicals
39 (HPVC) with broad applications in various industrial processes as well as in
40 households. They show metal complexing properties and are used as anticorrosive
41 additives and flame retardants in aircraft de-icers and anti-ice fluids (ADAFs) (Gruden
42 *et al.* 2001), in cooling and hydraulic fluids and for silver protection in dishwashing
43 agents (Ort *et al.* 2005, Janna *et al.* 2011). The content of BTs in ADAFs varies

44 between 0.2 -1.7% (WIPO 2002). The annual production of BTs in the United States
45 was reported to be in the range of 9000 tons per year (Hem *et al.* 2003). The content
46 of Benzotriazoles in Dishwashing agents is reported with 0.09 mg per wash to 27.8
47 mg (Janna *et al.* 2011).

48 BTs are compounds with a low vapour pressure, high water solubility and a high
49 polarity ($\log K_{ow}$ 1.44 for BT and 1.71 for TT, respectively) (US EPA 2010). Moreover,
50 they are quite persistent against biological and photochemical degradation processes
51 in the aquatic environment (Hart *et al.* 2004). Thus, they can be characterized as
52 mobile in aquatic environment. They are classified as toxic to aquatic organisms as
53 they can cause adverse long-term effects on the aquatic environments (Cancilla *et al.*
54 1998, Pillard *et al.* 2001, Cancilla *et al.* 2003, Hem *et al.* 2003).

55 In the environment benzotriazoles were firstly reported in subsurface water close to
56 airports as potential source in concentrations of 128 mg/L for BT, 17 mg/L for 4-TT
57 and 198 mg/L for total TT (Cancilla *et al.* 1998). Because of the broad applications,
58 BT and TT have high loads in waste waters treatment plants (WWTPs). The mean
59 concentrations in untreated wastewaters of WWTPs of Berlin were 12 $\mu\text{g/L}$, 1.3 $\mu\text{g/L}$
60 and 2.1 $\mu\text{g/L}$ for BT, 4-TT and 5-TT, respectively Weiss *et al.* (2006). The elimination
61 efficiency in WWTPs shows wide variations. In a study of 24 WWTPs of the Glatt
62 Valley, Switzerland elimination rates were reported between 13-62 % for BT and 23-
63 74 % for the TT-isomers (Voutsas *et al.* 2006) while Weiss *et al.* (2006) determined
64 removals of 37 % for BT and 11% for 5-TT but no significant removal for the 4-TT-
65 isomer. In sewage effluents of the UK were concentrations up to 3.6 $\mu\text{g/L}$ for BT and
66 5.7 $\mu\text{g/L}$ determined (Janna *et al.* 2011). Several studies showed that the BT and
67 TT are widely distributed in surface waters (Giger *et al.* 2006, Reemtsma *et al.* 2006,
68 Voutsas *et al.* 2006, Reemtsma *et al.* 2010). Loos *et al.* (2009) detected BT and TT in
69 94% and 81% of 122 river water samples distributed over the European Union (EU)

70 with mean concentrations of 493 ng/L and 617 ng/L for BT and TT, respectively. In
71 an EU-wide study on groundwater, BT and TT were detected in mean concentrations
72 of 1 and 4 ng/L, respectively (Loos *et al.* 2010a). Only one flux calculation is available
73 for the river Danube into the Black Sea (Loos *et al.* 2010b) . However, there are no
74 data about concentration and distribution of BTs in the marine environment.
75 The objective of the present study was to investigate the occurrence and distribution
76 of benzotriazoles in the German Bight and its major affluxes with respect to their
77 spatial distribution as well as seasonal variations. Furthermore, the mass flux of BTs
78 from the main rivers as sources of BTs into the North Sea was investigated. This
79 study presents the first data on BTs in the marine environment and improves the
80 understanding of the fate and the ecosystem risk assessment of BTs.

81

82 **3 Experimental**

83

84 **3.1 Chemicals**

85 1-H-benzotriazole (BT; 99%), 5-methyl-benzotriazole (5-tolyltriazole, 5-TT; 98%) and
86 the deuterated 1H-Benzotriazole-d4 solution were purchased from Sigma-Aldrich
87 (Steinheim, Germany). A tolyltriazole-isomer mixture was purchased from Dr.
88 Ehrenstorfer (Augsburg, Germany). Acetone (Nanograde) and methanol (Picograde)
89 were purchased from LGC Promochem (Wesel, Germany). Formic acid and
90 hydrochloric acid were purchased from Merck (Darmstadt, Germany). Pure water
91 was obtained from a Milli-Q system (Millipore, Billerica, MA, USA).

92

93 **3.2 Sample Collection**

94 Surface water samples (water depth <0.5m) were taken by stainless steel buckets in
95 pre-cleaned 1 L glass bottles on board of the research vessel *Ludwig Prandtl* along

96 the rivers Elbe and Weser during four campaigns in March, May, August and October
97 2010 with sampling intervals of 10 km. In addition, 15 spot samples were taken from
98 the shore of the rivers Elbe, Weser, Ems, the Rhine-Meuse delta and the river
99 Scheldt in August 2010. North Sea samples were taken on board of the research
100 vessel *Heincke* during three campaigns in March, July and September 2010. The
101 sampling stations are shown in Figure 1. Additional information on sampling are
102 included in the supplementary material.
103



104
105 **Figure 1 – Map showing the sampling positions in the investigated rivers and the North Sea**
106

108 **3.3 Sample Preparation**

109 Solid phase extraction (SPE) was used for compound extraction and enrichment from
110 the water samples. The unique river samples were filtered through glass fiber filters
111 (GF-C, Whatman) while seawater samples were not filtered. SPE was performed with
112 a self-designed glass based setup to prevent contaminations from plastic tubings.
113 500 – 700 mL surface water were acidified with hydrochloric acid to pH 2 and spiked
114 with 20 ng of the internal standard 1-H-benzotriazole-d4. Oasis HLB cartridges
115 (500mg, 60µm, Waters , Milfort, USA) were conditioned with 15mL acetone, followed
116 by 15mL methanol and 5 mL acidified Milli-Q-Water. The water samples were passed
117 through the pre-conditioned cartridges at a flow rate of 1-2 mL min⁻¹ and afterwards
118 washed with 5 mL acified Milli-Q-Water. The cartridges were dried under vacuum for
119 5 min. The analytes were eluted with 15 mL methanol. The extracts were roti-
120 evaporated to 5 mL and further concentrated to a volume of 150 µL under a gentle
121 stream of preheated nitrogen. The particulate phase on the filters was extracted by
122 ultrasonic with 20 mL methanol two times for 15 min. The evaporation procedures
123 were the same as described for the cartridges.

124

125 **3.4 Instrumental analysis**

126 The extracts were analysed using high performance liquid chromatography-tandem
127 mass-spectrometry (HPLC-MS/MS) in electrospray positive ionisation mode. A HP
128 1100 HPLC by Agilent Technologies was used for separation equipped with a
129 Phenomenex Synergi Hydro RP 80A column and a suitable guard column
130 (Phenomenex Synergi 2 I Hydro RP Mercury 20 2mm). The injection volume was 10
131 µL. The mobile phases were 1% formic acid as ionisation aid in Millipore water and
132 methanol, respectively. The operating flow was 200 µL/min in gradient mode, starting

133 with 90% of water as mobile phase decreasing to 0% over 25 minutes, then kept
134 constant for the next five minutes.

135 Detection and quantification of the Benzotriazoles were carried out by an API 3000
136 triple-quadrupole mass spectrometer (Applied Biosystems/MDS SCIEX) with an
137 electrospray ionization interface in positive ionization mode. The mass spectrometer
138 was operated in a multiple reaction monitoring mode (MRM) with a dwell time of 15
139 ms. The ion spray voltage was set to 5000 V and the temperature of the source block
140 was 400° C. For identification, the mass transitions 120.1 to 65.2 for BT, 134.1 to
141 77.0 for TT and 124.2 to 68.9 for the internal standard BT-d4 were monitored. The
142 chromatographical separation of the tolyltriazone isomers was not possible in this
143 study, so the isomers were as sum considered.

144

145

146 **3.5 Quality control**

147 Quality control and quality assurance included the use of a mass labelled internal
148 standard, the determination of recovery rates, of method and instrumental blanks as
149 well as breakthrough and reproducibility experiments. Method blanks were prepared
150 using 500 mL pre-cleaned Millipore water at every set of 8 samples together with the
151 samples. Blank levels were below the method quantification limits (MQL). The total
152 analytical error is calculated by 7,6% over the method.

153 Recovery rates of the mass labelled internal standard 1H-Benzotriazole-d4 in river
154 water samples ranged between $53 \pm 11\%$ for the winter season samples and $40 \pm$
155 6% for the summer season. The recovery for the seawater samples was $69 \pm 10\%$.
156 The breakthrough of BTs was found to be negligible with $<1\%$. The recovery
157 displacements were caused by matrix suppressions and losses during the solvent

158 evaporation. The MQLs were calculated based on a signal-to-noise ratio of ten. The
159 resulting MQLs are 1.2 ng/L for BT and 0.4 ng/L for TT, respectively.

160

161 **4 Results and Discussion**

162

163

164 **4.1 Occurrence in the rivers Elbe and Weser**

165 Benzotriazole and tolyltriazole were detected in the dissolved phase of all
166 investigated surface water samples. The individual concentrations of the four
167 sampling campaigns along the two rivers are shown in Table 1. In the Elbe the
168 concentrations ranged from 24 ng/L and 21 ng/L in the outer estuary of Elbe up to
169 304 ng/L and 322 ng/L in the harbour of Hamburg for BT and TT, respectively. The
170 concentrations of BT and TT in the Weser ranged from 28 ng/L in the sea water
171 influenced area up to 219 ng/L (BT) and from 21 ng/L to up to 454 ng/L (TT),
172 respectively. The maximum concentration was found in the City of Bremen. The
173 observed concentrations are comparable to Reemtsma *et al.* (2010), who reported
174 concentrations of 480 ng/L for BT and 570 ng/L for the TT-isomers, respectively, in
175 the Elbe downstream of the city of Hamburg (km 638) in January 2006.

176 In addition to the dissolved phase, the particulate phase of three samples taken in
177 the turbidity maximum of the Elbe estuary (around km 689) was analyzed. The
178 concentrations of BT and TT in the particulate phase were found to be less than 1%
179 of the dissolved phase or even below the MQL. Based on these results, the filters of
180 other stations were not analysed.

181

182

183

184

185 **Table 1: Concentrations of benzotriazoles in ng/L in Elbe (E) und Weser (W). (--) = not sampled;**
 186 **station names are stream kilometres; NE1-NE3 are positions in the North Sea; exact positions**
 187 **are included in the supplementary data**

Station	March		May		August		October	
	BT [ng/L]	TT [ng/L]	BT [ng/L]	TT [ng/L]	BT [ng/L]	TT [ng/L]	BT [ng/L]	TT [ng/L]
E570	142	191	139	231	--	--	--	--
E579	155	281	142	268	--	--	--	--
E589	139	270	136	159	--	--	--	--
E599	140	279	138	246	--	--	--	--
E609	118	229	134	209	193	142	93	64
E619	142	213	--	--	209	214	92	49
E624	134	195	136	234	228	173	98	71
E629	157	239	152	231	254	196	91	72
E639	179	323	141	177	268	195	120	101
E649	135	243	139	123	304	222	164	138
E659	156	250	128	109	257	194	163	154
E669	139	231	134	130	212	195	162	169
E679	137	235	127	133	180	186	162	146
E689	114	223	121	103	155	125	160	152
E699	103	176	115	126	144	113	148	119
E709	115	228	102	81	110	122	120	84
E719	97	180	--	--	--	--	105	93
NE1	101	203	75	114	--	--	92	73
NE2	48	74	51	85	--	--	57	41
NE3	25	37	24	34	--	--	29	21
W2	125	208	215	454	--	--	169	136
W12	138	190	219	325	--	--	186	192
W22	128	193	215	517	--	--	168	159
W32	117	146	207	426	--	--	179	180
W42	114	175	199	381	--	--	198	155
W52	134	233	188	395	--	--	203	221
W62	113	195	156	211	--	--	182	232
W72	109	160	106	189	--	--	107	133
W90	70	128	69	158	--	--	63	54
W110	31	53	39	65	--	--	28	21

188

189

190 **4.2 Mass fluxes of benzotriazoles in the Elbe**

191 For an improved comparison of the occurrence of benzotriazoles among the different
192 campaigns, riverine mass fluxes of BTs were calculated. They consider the water
193 discharge variations caused by rain events and dry periods. Mass fluxes for the Elbe
194 were calculated based on the sum concentrations of BT and TT and the daily water
195 discharges with a correction factor for sea water influence. The calculation based on
196 the following equation (1),

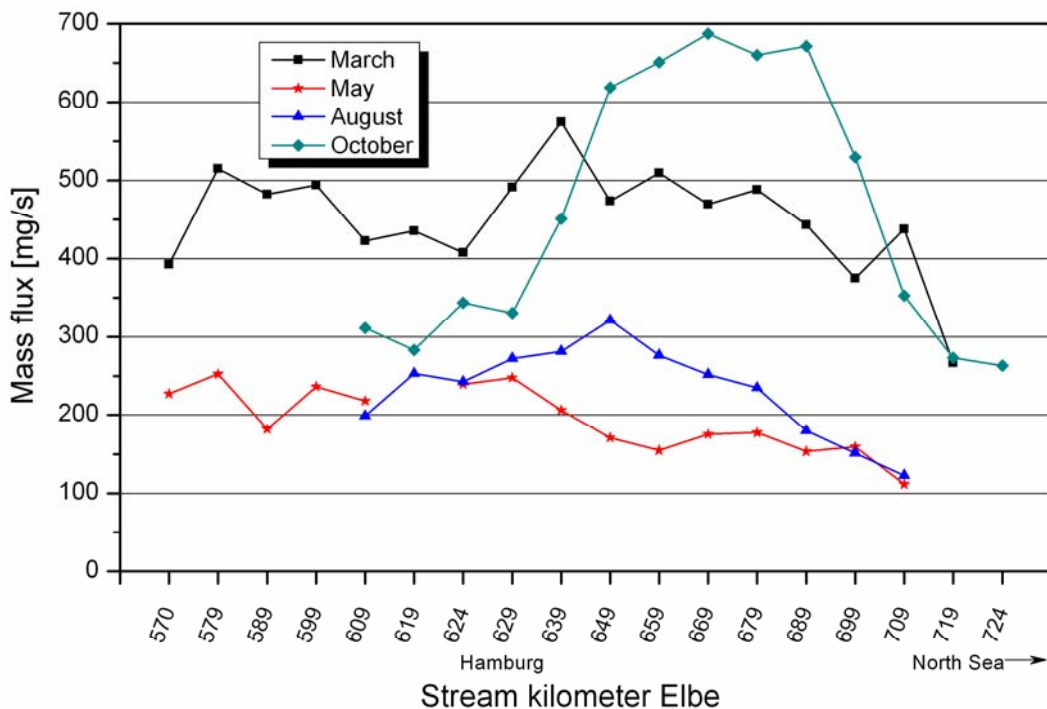
$$197 \quad f = \left(\frac{c}{\left(1 - \frac{S_{sample}}{S_{sea}}\right)} \right) * Q_{day} \quad (1)$$

198 where f is the mass flux [mg/s], c is the measured concentration [ng/L], S_{sample} means
199 salinity at sampling point in PSU (Practical Salinity Units), S_{sea} means salinity in
200 seawater (35 PSU) and Q_{day} is the water discharge [m³/s] on the sampling day. The
201 water discharge data are supplied from the FFG ELBE. The salinity of the river Elbe
202 is negligible (<1 PSU) compared to the Salinity in the North Sea. Hence, the salinity
203 of the River was in the calculation not considered. The results are shown in Figure 2.
204 The mean mass fluxes were 450 mg/s, 194 mg/s, 232 mg/s and 474 mg/s in March,
205 May, August and October 2010, respectively. The high flux in March, which was
206 constant along the entire sampling course along the river, was probably caused by
207 the first spring discharge after a strong winter season with high usage of
208 benzotriazoles containing de-icing agents during winter.

209

210 In March the median concentrations were very similar to the concentrations in May
211 and August. The variations of the mass flux are caused by different water discharges,
212 a constant flux level is not observed.

213 An elevated input in the area of the city of Hamburg was observed in August and
 214 especially in October. On this input based the high averages in October. A possible
 215 reason for this increase could be a discontinuous emission by a WWTP or another
 216 source located in the harbour area of Hamburg. In contrast, no influence of the city of
 217 Hamburg was observed in March and May. In October, to the outer estuary the high
 218 mass flows disappear. Probably there leave the sampling transect a waste water
 219 plume, which is responsible for the high contamination downstream from Hamburg.
 220 In all cruises slightly decreasing mass fluxes were observed downstream of the city
 221 of Hamburg. This could be caused by dilution with fresh waters of inflows of tributary
 222 streams and surface run off. Based on the study in part 4.6. degradation processes
 223 are implausible. The exchange with other compartments like air or sediment seems
 224 not to be an important process for BTs, due to their physical-chemical properties.
 225



226

227 **Figure 2: Calculated benzotriazole mass fluxes [mg/s] of the river Elbe**

228 **4.3 Occurrence of benzotriazoles in the tributary rivers of the North Sea**

229 Spot samples taken in the estuaries of the tributary rivers were investigated. The
230 concentrations of BTs in the investigated affluxes of the North Sea are shown in
231 Table 2. The concentrations, which were not influenced by seawater, ranged from
232 172 ng/L for BT and 232 ng/L for TT in the river Elbe, and up to 390 ng/L (BT) and
233 1114 ng/L for TT in the river Scheldt. Especially upstream of the city of Antwerp, the
234 river Scheldt is in comparison to other large rivers with 1500 ng/L for benzotriazoles
235 highly contaminated. In the Rhine and its anthropogenic modified delta the
236 concentrations ranged from 155 – 369 ng/L for BT and 184 – 431 ng/L for TT. In the
237 rivers Ems and Weser, concentrations were within 278 – 291 ng/L for BT and 312 –
238 357 ng/L for TT, which are relatively comparable to those in the Elbe and Rhine.
239 Obviously the concentrations of BTs decreased towards the mouth from Ems-1 to
240 Ems-2 and Weser-W2 to Weser-W90, even under consideration of the seawater
241 influence. It is assumable that this is due to dilution processes from a diffuse inflow of
242 the rural surrounding areas and probably degradation processes occurring.

243 In comparison to other studies for BTs in surface waters, the results in this study
244 showed relatively similar concentrations. In an European survey on more than 100
245 rivers from 27 countries *Loos et al. (2009)* found median concentrations of 226 ng/L
246 for BT and 140 ng/L for TT, respectively. In the river Main, which is influenced by
247 discharge of the Frankfurt airport, median concentrations were 132 ng/L for BT and
248 162 ng/L for TT, respectively.

249 Reemtsma et al. (2010) reported increasing concentrations along the rivers Elbe (by
250 means of 5 samples) and Rhine (by means of 4 samples) over distances of 650 and
251 700 km, respectively. In the present study their results were affirmed. This increasing
252 of concentration could be caused by an industrial input of the high industrial density
253 along estuaries due to the logistical connection from rivers and the sea and a

254 accumulation along the rivers. This indicate a bad degradation of the investigated
 255 compounds.
 256 Especially noticeable in the present study is that the concentration of TT in relation to
 257 BT is elevated. In studies in Switzerland (Giger *et al.* 2006, Voutsas *et al.* 2006) as
 258 well as in the European survey study on polar organic contaminations (Loos *et al.*
 259 2009) higher median concentrations for BT than TT are reported. In the study on the
 260 Rhine and Elbe (Reemtsma *et al.* 2010), a decrease of the BT/TT ratio along the
 261 rivers was observed. Since 5-TT is known to be more degradable than BT and 4-TT
 262 (Weiss *et al.* 2006), this effect is likely not related to degradation processes. A
 263 possible explanation could be different usages of benzotriazoles in the upper reaches
 264 regions of the rivers than in the lower reaches regions.

265

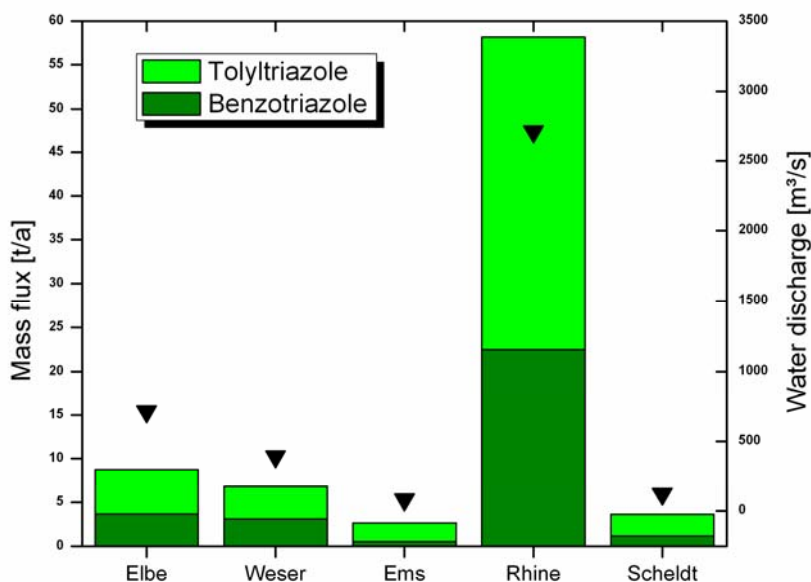
266 **Table 2: Concentrations of benzotriazoles of the North Sea feeder rivers in ng/L; exact**
 267 **positions are included in the supplementary data**
 268

River	Sample station	BT [ng/L]	TT [ng/L]	Salinity [PSU]	Position	
					E	N
Elbe	E679 - Glückstadt	172	232	0,6	9,40	53,79
Elbe	E 712 - Cuxhaven	55	77	20,1	8,71	53,87
Weser	W 90 - Bremerhaven	105	126	19,8	8,58	53,53
Weser	W2 - Hemelingen	278	357	0,5	8,86	53,06
Ems	Ems2 - Emden	146	208	10,7	7,31	53,32
Ems	Ems1 - Herbrum	291	312	0,6	7,32	53,03
Rhine - IJssel	R1 - Kampen	369	332	0,0	5,92	52,56
Rhine - North Sea Canal	R2 - Ijmuiden	155	184	10,0	4,61	52,47
Rhine - New Waterway	R3 - Maassluis	246	431	1,1	4,25	51,91
Rhine - Hollands Diep	R4 - Bovensluis	241	428	0,1	4,41	51,70
Rhine - GER/NED border	R5 - Lobith	262	378	0,0	6,10	51,85
Waal	R6 - Andelst	233	342	0,0	5,74	51,88
Meuse	R7 - Meegen	397	417	0,1	5,57	51,83
Scheldt	S2 - Schaar van Ouden Doel	180	374	16,7	4,21	51,40
Scheldt	S1 - Schelle	390	1114	3,6	4,33	51,13

269

270 **4.4 Mass fluxes of European Rivers into the North Sea**

271 The mass flux estimations are based on one sampling campaign in August 2010
272 only. Mass fluxes were calculated by equation (1) with the modification that the
273 average annual water discharges were used. The mass fluxes are shown in Figure 3.
274 The overall total input from all investigated rivers into the North Sea was calculated
275 with 30 t/a for BT and 47 t/a for TT, respectively. The dominate source is the Rhine
276 with his 4 main inflows into the North Sea (North Sea Canal, New Waterway Canal,
277 Ijssel and Hollands Diep/Haringvliet) with approximately 22 t/a for BT and 35 t/a for
278 TT, respectively. This accounted for 72% of the discharge of the investigated rivers.
279 Seasonal variations are not considered in this estimation. In a previous study, (Giger
280 *et al.* 2006) showed no significant seasonal trends in the Rhine. The seasonal
281 variations of the mass flux of BTs from the Elbe to the North Sea estimated in this
282 study is correlated to the water discharge. For more specified conclusions of the
283 seasonal trends is a details analyses with smaller time intervals required.



284

285 **Figure 3: Estimated mass fluxes in t/a of European rivers into the North Sea; Triangles show**
286 **the water discharge of the river**

287

288 **4.5 Occurrence in the North Sea**

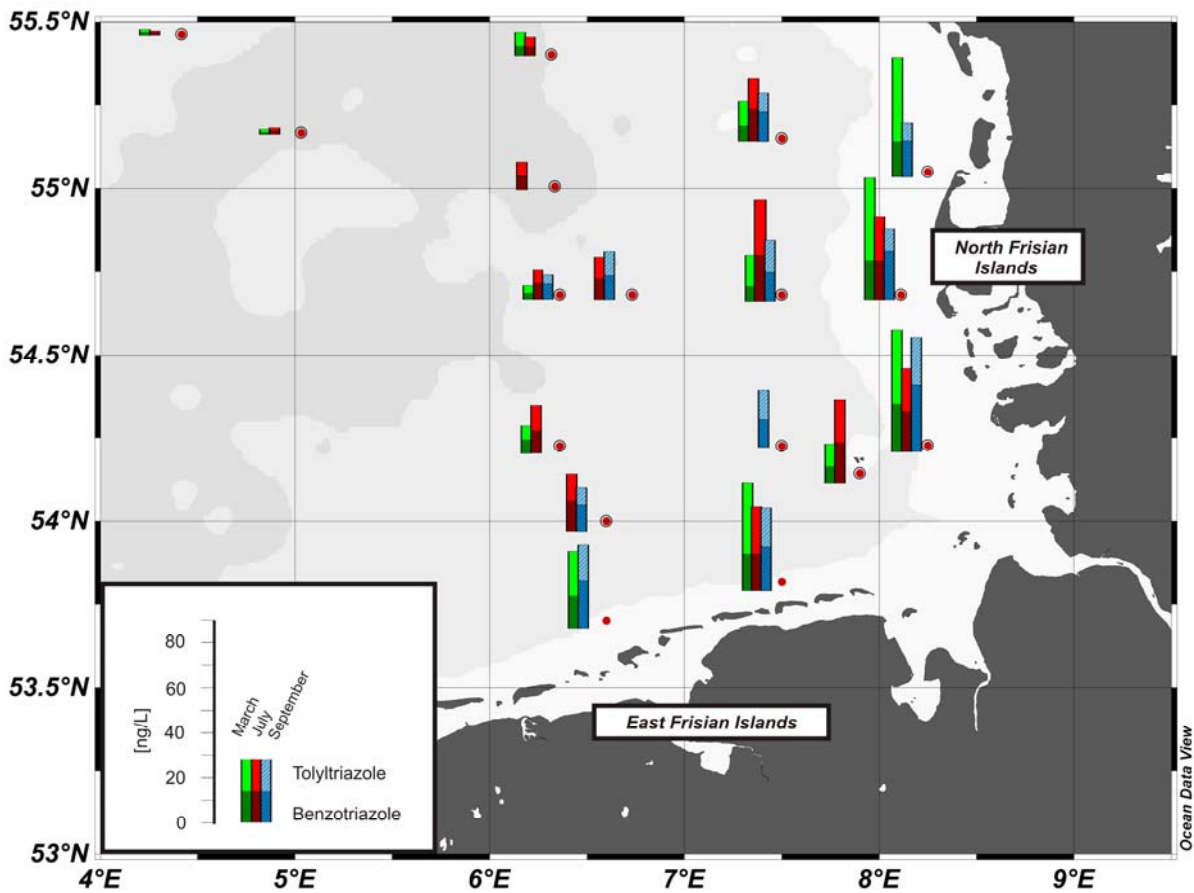
289 BT and TT were detected above the MQL in all seawater samples from the German
290 Bight. The results are shown in Figure 4. In the coastal area concentrations up to 21
291 ng/L and 37 ng/L were found for BT and TT, respectively. In the open sea in
292 approximately 300 km distance to the coast, concentrations of BT and TT were 1.4
293 ng/L and 1.1 ng/L, respectively, which are just above the MQL.

294 The main current conditions in the German Bight are dominated on an eastern
295 current the "Continental Coastal Water". This transported water masses from the
296 Dutch Coast into the German Bight and turned than to the north (Turrell 1992). The
297 benzotriazoles distribution in the North Sea indicates an input from the rivers Elbe
298 and Weser from the south-east into the German Bight. The high contamination in
299 front of the East Frisian Islands can be traced back to the input of the rivers Rhine
300 and Scheldt. The contamination in the area of the North Frisian Islands is based of
301 the input over the Rhine and Scheld as well as from the Elbe and Weser. The
302 samples from the open sea were mainly influenced by Atlantic Ocean water
303 streamed along the Scottish Coast as central and south North Sea waters into this
304 area (Turrell 1992).

305 A slight seasonal variation was observed. In comparison to the summer in spring
306 high concentrations were detected in the coastal area, with a strong decreasing trend
307 towards the open sea. In summer the concentrations in the coastal area were slightly
308 lower, but interestingly, the open sea stations showed higher concentrations in
309 summer than in spring. This is against the theory that the highest photo- and
310 biodegradation is in summer. In autumn the trend followed the summer pattern.

311 The contamination of Benzotriazoles in the North Sea is relatively high in comparison
312 to other organic pollutants. For example, concentrations of polyfluoroalkyl
313 compounds (PFCs) such as perfluorooctanoic acid (PFOA) and perfluorooctane

314 sulfonate (PFOS) are one order of magnitude lower (Ahrens *et al.* 2009),
315 concentrations of the endocrine disruptor Triclosan are three orders of magnitude
316 lower as benzotriazoles (Xie *et al.* 2008). The sum concentrations of
317 organophosphate flame retardants (OPE) showed comparable concentrations to
318 single concentrations of BT and TT (Andresen *et al.* 2007).
319



320
321 **Figure 4: Distribution of benzotriazoles in the North Sea in ng/L**

322
323 **4.6 Study of dilution and persistency**

324 To investigate if decreasing concentrations are based on degradation or merely on
325 dilution, a comparison with salinity is useful. The correlation of dilution versus salinity
326 was assessed with utilization of the equations (2) and (3).

328 **Dilution Factor (DF) = salinity sampling point / salinity sea water** (2)

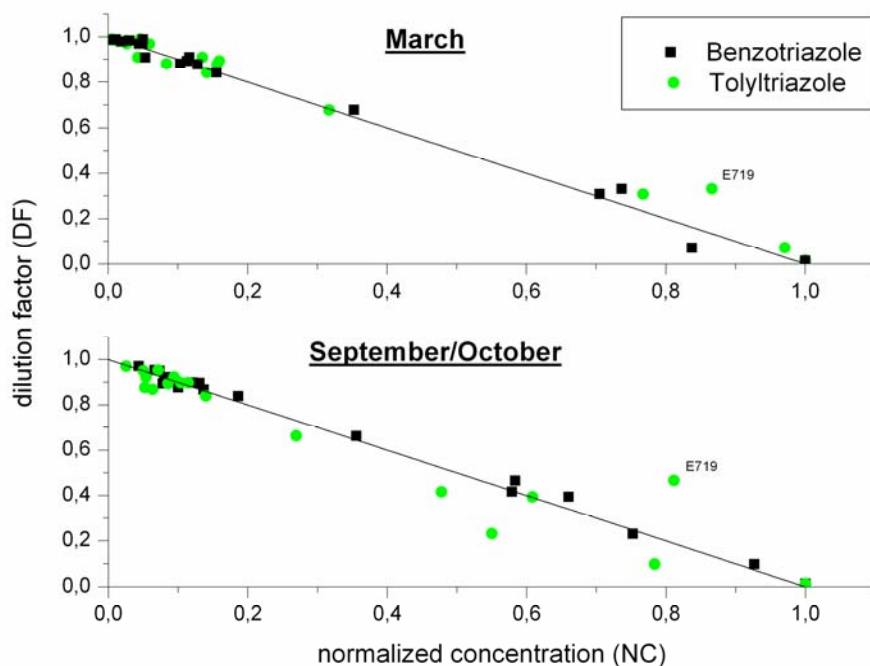
329 **Normalized concentration (NC) = concentration sampling point / concentration freshwater** (3)

330

331 The salinity of sea water was assumed with 35 PSU. The freshwater concentration
332 was set to the last sampling point in the estuary with a salinity < 1 PSU.

333 Figure 5 displays the dilution factor (DF) at each sampling point with sea water
334 influence (salinity > 1 PSU) of the March and September/October sampling in the
335 Elbe and the North Sea in comparison to the normalized concentration (NC) for BT
336 and TT.

337 The mostly linear observed relationship signifies that the decrease of the
338 concentration is mainly due to dilution with seawater. Only for TT in autumn, a
339 slight degradation can be ascertained in autumn, because the most points are under
340 the line. This can be explained by higher degradability of the 5-TT isomer than BT
341 and the 4-TT isomer (Weiss *et al.* 2006). In both graphs the sampling station a point
342 E719 for TT is located in the front of the harbour of Cuxhaven and has assumedly a
343 local source of tolyltriazole. Based on this analysis, the seasonal variations which are
344 described in chapter 4.5 were caused by seawater currents and dilution processes
345 rather than degradation.



346

347 **Figure 5: Correlation of dilution factor and normalized concentrations for benzotriazole and**
 348 **tolyltriazole in the river Elbe and the North Sea**

349

350

351 5 Conclusions

352 Benzotriazoles are poorly degradable polar organic pollutants which are present in
 353 the anthropogenic water cycle. This study has shown that approximately 80 tonnes
 354 per year of these chemicals are discharged via the investigated rivers into the North
 355 Sea, mainly via the river Rhine. Further it is shown that the decrease of the
 356 concentration in the German Bight is mostly attributed to dilution.

357 On the one hand the toxicity of these substances is reported to be moderate, the
 358 bioaccumulation potential is low and the detected concentration are two magnitude
 359 lower as the chronic predicted no effect concentrations. But on the other hand the
 360 benzotriazoles are observed concentrations of benzotriazoles in the aquatic
 361 environment rank among the highest in the group of polar organic pollutants in the
 362 water cycle. Thus the widespread distribution in European lakes, groundwater, rivers
 363 and the North Sea in addition to the shown persistence in aquatic samples has to be

364 noted. Further studies have to focus on the occurrence and degradation of the
365 benzotriazoles in the marine water cycle, especially separate investigation of the
366 tolyltriazole isomers.

367

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375 **7 References**

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Supplementary data

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Table S1: Additional data of North Sea sampling campaigns

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Station		Position		March campaign			July campaign			September campaign		
		Longitude [E°]	Latitude [N°]	Date	Time	Salinity [PSU]	Date	Time	Salinity [PSU]	Date	Time	Salinity [PSU]
Tiefe Rinne	N1	7,900	54,142	04.03.2010	17:30	31,80	13.07.2010	16:39	32,5	-	-	-
Eiderstedt	N2	8,250	54,227	04.03.2010	19:40	29,47	-	-	-	18.09.2010	09:52	29,4
Deutsche Bucht	N3	7,504	54,225	-	-	-	-	-	-	19.09.2010	09:17	31,3
Amrum	N4	8,113	54,680	08.03.2010	10:30	30,75	15.07.2010	10:28	30,9	18.09.2010	14:07	30,4
List	N5	8,250	55,050	08.03.2010	14:20	31,25	-	-	-	18.09.2010	17:32	30,7
Langeoog	N6	7,500	53,817	05.03.2010	23:30	31,84	15.07.2010	21:49	31,4	19.09.2010	12:57	31,44
Borkum	N7	6,600	53,702	05.03.2010	18:18	30,82	-	-	-	19.09.2010	19:50	31,43
Emssüd	N8	6,360	54,225	05.03.2010	12:30	33,95	16.07.2010	13:17	33,3	-	-	-
Fino 1	N9	6,600	54,000	-	-	-	16.07.2010	09:08	35,2	19.09.2010	22:08	33,3
NSB 2	N10	6,335	55,005	06.03.2010	18:10	34,64	16.07.2010	21:44	34,1	-	-	-
NSB 3	N11	6,732	54,680	-	-	-	19.07.2010	06:44	33,5	20.09.2010	07:38	33,4
Nordsee 1	N12	6,317	55,402	09.03.2010	01:15	34,42	17.07.2010	12:42	34,1	-	-	-
Nordsee 2	N13	7,500	54,680	06.03.2010	09:00	33,92	15.07.2010	14:24	31	19.09.2010	04:06	32,3
Nordsee 3	N14	6,360	54,680	06.03.2010	21:20	34,30	14.07.2010	08:41	33,7	20.09.2010	05:21	34
Nordsee 4	N15	7,500	55,150	06.03.2010	13:00	34,63	19.07.2010	15:18	32,4	18.09.2010	22:14	32,3
Nordsee 6	N16	5,033	55,167	09.03.2010	08:00	34,54	17.07.2010	20:40	34,5	-	-	-
Entenschnabel	N17	4,418	55,462	09.03.2010	12:30	34,55	18.07.2010	04:18	34,7	-	-	-

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Table S2: Additionally data of estuary sampling campaigns

Station	Position		March campaign		May campaign		August campaign		October campaign		
	[E°]	[N°]	Date	Time	PSU*	Date	Time	PSU*	Date	Time	PSU
E570	10,54	53,37	25.03.2010	12:35	-	06.05.2010	12:22	-	-	-	-
E579	10,43	53,40	25.03.2010	11:48	-	06.05.2010	11:29	-	-	-	-
E589	10,30	53,43	25.03.2010	10:08	-	06.05.2010	9:28	-	-	-	-
E599	10,18	53,40	25.03.2010	09:27	-	06.05.2010	8:50	-	-	-	-
E609	10,07	53,46	24.03.2010	17:54	-	06.05.2010	8:00	-	10.08.2010	16:06	-
E624	9,94	53,54	24.03.2010	17:10	-	05.05.2010	20:54	-	10.08.2010	15:20	-
E629	9,88	53,54	24.03.2010	16:32	-	05.05.2010	20:39	-	10.08.2010	15:06	-
E639	9,73	53,56	24.03.2010	16:46	-	05.05.2010	20:07	-	10.08.2010	14:47	-
E644	9,66	53,57	24.03.2010	15:51	-	05.05.2010	19:50	-	10.08.2010	14:18	-
E649	9,59	53,60	24.03.2010	15:12	-	05.05.2010	19:30	-	10.08.2010	13:50	-
E659	9,51	53,66	24.03.2010	14:32	-	05.05.2010	19:02	-	10.08.2010	13:22	-
E669	9,43	53,73	24.03.2010	13:55	0,77	05.05.2010	18:28	-	10.08.2010	12:54	-
E679	9,36	53,81	24.03.2010	13:08	0,74	05.05.2010	18:01	0,61	10.08.2010	12:27	0,53
E689	9,25	53,87	24.03.2010	12:25	0,72	05.05.2010	17:28	1,02	10.08.2010	12:00	1,11
E699	9,09	53,87	24.03.2010	11:35	0,94	05.05.2010	17:00	2,45	10.08.2010	11:34	3,49
E709	8,95	53,84	24.03.2010	10:49	3,27	05.05.2010	16:32	5,38	10.08.2010	11:04	7,44
E719	8,81	53,84	24.03.2010	09:53	11,48	05.05.2010	16:01	8,87	10.08.2010	10:31	11,47
NE1	8,671	53,914	22.03.2010	13:35	11,61	05.05.2010	14:55	13,20	-	-	-
NE2	8,437	53,976	22.03.2010	12:37	23,75	05.05.2010	14:07	20,86	-	-	-
NE3	8,081	53,926	22.03.2010	11:14	30,45	05.05.2010	12:51	29,84	-	-	-
W2	8,790	53,081	22.03.2010	09:52	0,58	03.05.2010	09:26	-	-	-	0,50
W12	8,655	53,127	22.03.2010	10:28	0,55	03.05.2010	10:08	-	-	-	0,30
W22	8,555	53,183	22.03.2010	11:07	0,52	03.05.2010	10:42	-	-	-	0,30
W32	8,484	53,258	22.03.2010	11:21	0,52	03.05.2010	11:14	-	-	-	0,30
W42	8,500	53,344	22.03.2010	11:55	0,47	03.05.2010	11:43	0,07	-	-	0,70
W52	8,493	53,433	22.03.2010	12:31	0,49	03.05.2010	12:13	0,75	-	-	3,00
W62	8,545	53,517	22.03.2010	13:11	0,53	03.05.2010	12:50	2,08	-	-	7,70
W72	8,525	53,587	22.03.2010	08:41	8,55	05.05.2010	10:19	11,64	-	-	19,20
W90	8,332	53,704	22.03.2010	09:22	15,52	05.05.2010	11:07	19,02	-	-	24,40
W110	8,127	53,824	22.03.2010	10:19	26,01	05.05.2010	12:08	26,30	-	-	30,10

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*Salinity in [PSU]

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Table S3: Additionally data of river sampling campaigns

River	Sample station	Acronym	Latitude [°E]	Longitude [°N]	Date	Local time	pH	T _w [°C]	Salinity [PSU]	Discharge [m ³ /s]
Elbe	Glückstadt	E1	9,40	53,79	02.08.2010	14:16	7,55	23,0	0,6	
Elbe	Cuxhaven	E719	8,71	53,87	02.08.2010	16:30	8,08	19,3	20,1	712
Weser	Bremerhaven	W90	8,58	53,53	02.08.2010	17:15	7,92	20,8	19,8	390
Weser	Hemelingen	W2	8,86	53,06	02.08.2010	18:30	8,35	21,9	0,5	
Ems	Emden	Ems1	7,31	53,32	03.08.2010	10:50	7,70	20,8	10,7	80
Ems	Herbrum	Ems2	7,32	53,03	03.08.2010	12:03	7,53	21,2	0,6	
Rhine - IJssel	Kampen	R1	5,92	52,56	03.08.2010	14:45	7,02	21,4	0,0	340
Rhine - North Sea Canal	Ijmuiden	R2	4,61	52,47	03.08.2010	17:30	7,92	22,4	10,0	95
Rhine - New Waterway	Maassluis	R3	4,25	51,91	03.08.2010	19:20	7,92	21,3	1,1	1335
Rhine - Hollands Diep	Bovensluis	R4	4,41	51,70	04.08.2010	09:35	7,96	21,8	0,1	940
Rhein - GER/NED Border	Lobith	R5	6,10	51,85	04.08.2010	17:20	8,18	21,4	0,0	
Waal	Andelst	R6	5,74	51,88	04.08.2010	15:35	8,20	21,2	0,0	
Meuse	Megen	R7	5,57	51,83	04.08.2010	14:30	8,00	21,8	0,1	
Scheldt	Schaar van Ouden Doel	S1	4,21	51,40	04.08.2010	10:45	8,01	20,2	16,7	120
Scheldt	Schelle	S2	4,33	51,13	04.08.2010	12:10	7,90	21,9	3,6	

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Table S4: Instrumental parameters

HLPC-MS/MS Parameter

Autosampler Modell:	Agilent 1100 Autosampler
Syringe Size:	100 µL
Injection Volume:	10 µL
Needle Level:	5 mm
Eject Speed:	200 µl/min
Pump Modell:	Agilent 1100 LC Binary Pump
Equalisation time:	5 min
Gradient ramp	
Time	Solvent Ration
0	90/10
3	90/10
5,5	50/50
8	30/70
12	10/90
16	0/100
24	0/100
24,5	90/10
25	90/10

Mass Spectrometer

Type	API 3000 Applied Biosystems/MDS Sciex
Scan Type	MRM
Polarity	positiv
Ion source	Electronen spray ionization
MRM detection window	240 sec
Nebulizer Gas	10
Curtain Gas™	6
IonSpray Voltage	5000 V
Source Temperature	400°C

Compound-Dependent Parameters:

Analyts	BT	TT	BT-d4
Q1 Mass	120.20	134.13	124.21
Q3 Mass	65.20	77.00	68.90
Retention time	14.00	15.21	14.04
Declustering Potential	6	11	11
Focusing Potential	190	190	180
Entrance Potential	33	35	35
Collision Energy	2	4	4

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Table S5: Relative recovery of target compounds in preliminary tests; Samples were spiked with 100ng/L of each target compound and 20 ng/ of internal standard

Sample	BT	TT
Milli-Q Water		
Sample A	108%	94%
Sample B	96%	92%
Sample C	113%	105%
Avarage	105%	97%
Sea Water (Arctic)		
Sample D	99%	89%
Sample E	112%	115%
Sample F	95%	119%
Avarage	102%	108%

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