



22 The contamination of natural waters by chemicals is a major concern in many parts of the world,  
23 and as new chemicals are introduced or others find new applications, and analytical methods  
24 improve, the occurrence of previously undetected chemicals, termed “emerging contaminants”,  
25 in wastewaters and receiving waters is frequently reported (1, 2). Much attention has focussed on  
26 compounds known to exhibit biological activity at low concentrations, in particular  
27 pharmaceuticals, steroid estrogens and other endocrine disruptors. The occurrence of these  
28 compounds began to receive attention during the 1990s when they were linked to toxicological  
29 effects in fish (3). However, consumer products such as washing powders containing detergents,  
30 bleaching agents and other ingredients are used in higher volumes than pharmaceuticals and may  
31 also contribute to the wide dispersive occurrence of xenobiotics in wastewaters (4).

32 One class of chemical corrosion inhibitors that has been incorporated into dishwashing  
33 detergents to reduce the corrosion of non-ferrous metals (5) are 1H-benzotriazole (BT) and 4- or  
34 5-methyl-1H-benzotriazole, used as a technical mixture and commonly called tolyltriazole. In  
35 addition to use in consumer products, they find more extensive use in industrial products, such as  
36 brake fluids, motor vehicle antifreeze and aircraft de-icing fluids (6). The first report on their  
37 occurrence in the aquatic environment was in the Glatt River, Switzerland, where they occurred  
38 in all sewage treatment work (STW) effluents surveyed and were detected at concentrations up to  
39 3,690 ng/L (BT) and 628 ng/L (TT) in the river (7). Subsequently, their presence has been  
40 reported in a further six Swiss rivers (8), as well as in rivers in Germany, with concentrations of  
41 BT ranging from 130 to 3,500 ng/L in the Rhine (9) and from 38 to 1,474 ng/L in the Main,  
42 Hengstbach and Hegnach collectively (10). Concentrations of BT and TT were amongst the  
43 highest of thirty six polar pollutants detected in a survey of European rivers (11). Although there  
44 are few reports on their presence in rivers from other regions of the world, BT and TT have been

45 observed in groundwater in the United States, as a result of use in aircraft de-icing fluids (12)  
46 and TT was included in a survey of source waters in the US, with an estimated maximum  
47 concentration of 360 ng/L (13).

48 Concern about any chemical is based primarily on the relationship of (eco)toxicity and exposure.  
49 In the cases of BT and TT, relatively few toxicity data are available in the open literature. Those  
50 available are almost exclusively concerned with acute toxicity. They suggest that BT and its  
51 derivative are relatively non-toxic; reported no-observed effect concentrations (NOEC) in  
52 freshwater and marine environments are usually in the mg/L range (14, 15) and that existing data  
53 are adequate for undertaking required risk assessments, although they lack, for example, any  
54 studies on the chronic effects on fish. However, many authors have commented on the lack of  
55 chronic toxicity data for these chemicals, (e.g. 15-17), and the need for a rigorous investigation  
56 of their chronic toxicity before any conclusions relevant to environmental risk assessments can  
57 be made (16).

58 Because both BT and TT have been reported to be ubiquitous in European surface waters, we  
59 undertook an evaluation of the occurrence of these compounds in the UK. We also determined  
60 the possible significance of their use in domestic dishwasher detergent formulations in relation to  
61 their environmental occurrence, because as a consequence of this use, these compounds are  
62 discharged directly to the sewer.

63

## 64 **Experimental Section**

65 Determination of environmental concentrations involved a survey of water and STW final  
66 effluent samples taken from along the River Erewash, which received discharges from eight  
67 STW above its confluence with the River Trent near Nottingham, UK. Sampling was undertaken

68 in January 2009 and consisted of 24 single grab samples; 11 from the river, five from tributaries  
69 and a final effluent from each of the eight STW. To determine if BT and TT were present in the  
70 UK potable supply, we undertook sampling on four occasions during May and June 2010 for a  
71 total of eighty tap water samples, from locations in the south-east of England. These were  
72 predominantly within a 15 km radius of Uxbridge, in west London, although some were up to 30  
73 km to the west and one location was 80 miles to the north east. To assess the potential inputs  
74 from dishwasher detergents, we analysed a range of formulations sold for domestic use during  
75 July 2010, based on information on their market share (18). Samples included tablets and powders  
76 from the two leading UK brands and “own label” products from four supermarkets with greatest  
77 overall UK market share (19).

78 **Determination of benzotriazole and tolyltriazole.** Samples of wastewaters, final effluent and  
79 river waters were chilled and extracted within 24 hours of sampling. Tap waters were sampled by  
80 householders, with taps run for 1 minute before the sample was taken, stored in polycarbonate  
81 bottles and extracted within 6 hours. The analytical methodology involved solid phase extraction  
82 (SPE), followed by quantification with positive mode electrospray ionisation-triple quadrupole  
83 mass spectrometry (7).

84 **Reagents and chemicals.** Benzotriazole (1H-benzotriazole), tolyltriazole (as 5-methyl-1H-  
85 benzotriazole) and the internal standard, 5,6-dimethylbenzotriazole, were purchased from Sigma-  
86 Aldrich (Gillingham, UK). Organic solvents, methanol and dichloromethane, were purchased  
87 from Rathburn Chemicals (Walkerburn, UK). For the SPE step, Oasis HLB (500mg/6cm<sup>3</sup>)  
88 cartridges were obtained from Waters Ltd. (Watford, UK). Reagent grade water was obtained  
89 from a MilliQ system (Millipore, Watford, UK).

90 Standard solutions were prepared from individual stock solutions. Around 1000 ng/mL  
91 individual stock solution of each compound was prepared in methanol. A series of mixed  
92 calibration standards containing analytes at a concentration range of 2.5 to 5000 ng/mL and the  
93 internal standard (100 ng/mL) in methanol/water (50/50), were prepared, along with a solution of  
94 benzotriazole and tolyltriazole at 1000 ng/mL for use in spiking samples to evaluate method  
95 recovery and performance. A solution of internal standard was prepared in methanol at 100  
96 ng/mL for addition to samples prior to extraction.

97 **Extraction of wastewaters, river waters and tap water.** Wastewaters, river waters and tap  
98 water were enriched by SPE. Wastewaters and river waters were filtered (GF/C, Whatman, UK)  
99 and acidified to pH <3 with 3% nitric acid (Fisher, Loughborough, UK) with addition of internal  
100 standard (0.2 mL or 1 mL of 100ng/mL in methanol, depending on the final volume that samples  
101 would be made up to). Oasis cartridges were prepared by washing with 5 mL of methanol  
102 followed by 5 mL of reagent grade water. Samples were loaded onto the cartridges at a flow rate  
103 of 5 to 10 mL/min. For wastewaters and river waters, a sample volume of 200 mL was used, and  
104 for tap waters, 1000 mL. After the extraction, cartridges were rinsed with 5 mL of reagent water  
105 and dried with air, then eluted with 5 mL of dichloromethane with 3% methanol. These eluates  
106 were concentrated on a miVac (Genevac, Ipswich, UK), evaporated to dryness with nitrogen and  
107 re-dissolved in 0.2 mL or 1ml of methanol / water (50:50) prior to quantification.

108 **Domestic dishwasher powders and tablets.** Products were weighed and approximately 20 g of  
109 the powders and whole tablets were then dissolved in 1 L of MilliQ water using a magnetic  
110 stirrer. Products were analysed in duplicate, using an external standard calibration. Dissolution of  
111 the products was determined visually, and occurred within one hour. Once dissolved, solutions  
112 were further diluted, initially 1:100 in MilliQ water, before quantification. Where necessary,

113 further dilutions were made to obtain solution concentrations within the calibrated range of the  
114 instrument. Full description of the instrumental analysis and quantification and method  
115 performance is given in Supporting information (SI) text and Tables S1 and S2.

116 **Catchment Modelling.** The catchments modelled were those of the River Trent, where the  
117 Erewash is located, and the River Thames, which was the known source for some of the tap  
118 water samples, in particular from the area around Uxbridge, west London. The model has  
119 previously been demonstrated to accurately predict concentrations of triclosan in both of these  
120 heavily urbanised catchments (20). It generates spatially explicit statistical distributions of down-  
121 the-drain chemicals using a Monte Carlo mixing-model approach to combine statistical estimates  
122 of chemical loads at specific emission points (e.g. STWs) with estimated river flow duration  
123 curves for the whole river network of interconnected model reaches (20-22).

124 The performance of the model was initially tested with measured effluent concentrations and  
125 outputs compared to observed river concentration data collected in the survey described above.

126 The STWs inputs and the upstream boundaries of the river model were set to the values  
127 measured on the day of the survey. The degradation rates of the chemicals in the river were set to  
128 zero, as they have been noted to be resistant to biodegradation (23) and no degradation of BT  
129 was observed during a 20 day river die away study (24). Although photodegradation has been  
130 reported to occur, with half lives for BT and TT of 10 and 4 days respectively (24), this is of  
131 little effect in relation to residence time in most UK rivers. For example from the source to the  
132 mouth of the Thames, which is 221 km long, this ranges from 7 to 21 days (25), and most inputs  
133 are subject to shorter residence times as they join at points far downstream of the source.

134 The model was run in the monthly mode and the model outputs were chosen from the month  
135 whose long term mean flow was closest to that on the sampling day. Because the sampling had

136 been deliberately targeted at a low flow period, this month turned out to be July, even though the  
137 actual sampling run had been made in January 2009. To run the model at a catchment scale, to  
138 obtain values for STWs discharges that could be used more widely throughout the catchment, the  
139 measured concentrations were transformed into equivalent per capita output loads (21).

140 **Estimation of the inputs of BT and TT from dishwasher detergents.** Consumer products were  
141 purchased from UK supermarkets during May and June 2010 and analysed for BT and TT. An  
142 average load of BT and TT per wash was determined by using market share information and use  
143 patterns (18, 19) (Table 1). To estimate how many washes were undertaken per day, we used the  
144 population equivalent of one of the eight the STW (44,895), assuming 2.36 people per household  
145 (26) to derive 19,023 households. With dishwasher ownership of 28% (27), this gave 5,326  
146 households with dishwashers. We then assumed each of these were used once per day,  
147 discharging the estimated average load per wash (Table 1) to the STW.

148 The calculated load was transformed to a concentration by dividing by the consented dry weather  
149 flow (as it did not rain during the week of sampling) and compared to the concentration  
150 determined by taking the average detected in seven grab samples of settled sewage (primary tank  
151 effluent) from this STW (four at 9:00 and three at 14:00) taken over a four day period during  
152 November 2008. Settled sewage was sampled to give some attenuation to likely variation of  
153 concentrations in crude sewage, and was deemed appropriate due to the solubility of the analytes.

154

## 155 **Results and Discussion**

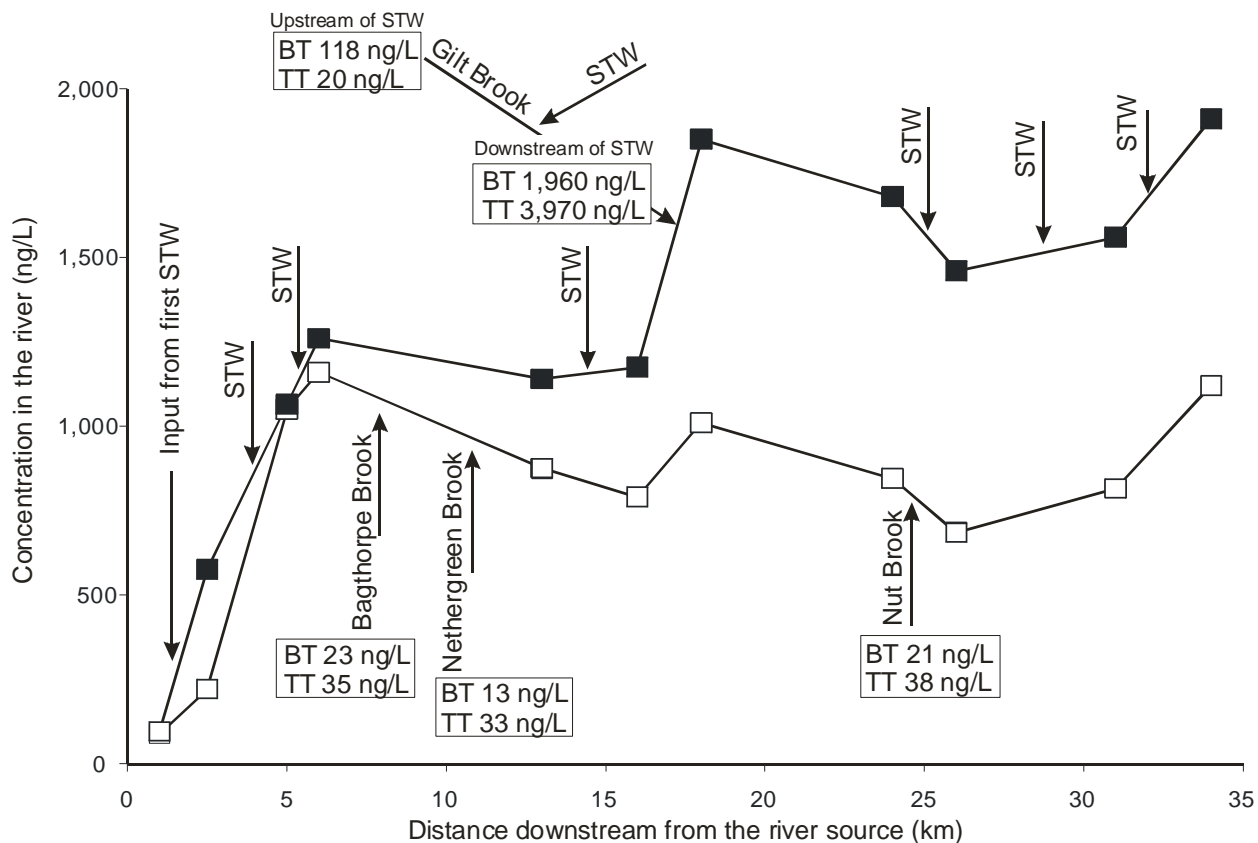
156 Concentrations of BT in the eight sewage effluents, which ranged from 840 to 3,605 ng/L, were  
157 consistently less than those of TT (2,685 to 5,700 ng/L). There was no relationship between  
158 effluent concentrations and treatment type, which were either activated sludge or biological

159 filters with or without tertiary treatment, such as nitrifying sand filters. Three of the works had  
160 older biological filters running in parallel with more recently installed activated sludge treatment.  
161 In the river, higher concentrations of TT were also consistently observed (Figure 1), as in the  
162 effluents. The river survey demonstrated that the compounds were present in all samples,  
163 including those from the small tributaries, with the highest concentration observed upstream of a  
164 STW being 118 ng/L, indicating sources other than sewage effluents, such as industrial or urban  
165 run-off. However, the increase in concentrations at around 2.5 km from the source of the river  
166 may be attributed to inputs from the first STW as may those in Gilt Brook, and subsequent  
167 increases were also attributable to discharges from STW; conversely, decreases in the  
168 concentrations of these chemicals in the river water corresponded with the confluence of less  
169 contaminated tributaries, resulting in dilution. There is no evidence that any other discharges to  
170 the river could account for the increase in BT and TT concentrations above the backgrounds  
171 observed. Although the European chemical Substances Information System (ESIS) (28),  
172 indicates an importer of TT in the area of the Erewash, they are in fact located on a nearby river,  
173 and would not be expected to contribute discharges to the Erewash. The company named on  
174 ESIS is not listed in the UK Environment Agency (EA) “What’s in your backyard?” pollution  
175 inventory (29) as having a licence to discharge, and there is no indication from the EA data set  
176 that there are any companies along the Erewash itself which are likely to contribute to the  
177 concentrations of BT and TT observed in the river.

178

179





180

181 **FIGURE 1. Graphical representation of the River Erewash showing concentrations of BT**  
 182 **(□) and TT (■) increasing downstream from the river source. Values in boxes indicate**  
 183 **concentrations (ng/L) in tributaries.**

184

185 The sampling and analysis of large catchments is a challenge in terms of resources and costs, and  
 186 it is therefore often appropriate to model concentrations of chemicals in river systems (30).  
 187 Before modelling of a more extensive area was undertaken, the LF2000-WQX model was  
 188 calibrated using the measured effluent concentrations to predict concentrations in the Erewash.  
 189 When using the measured concentrations in effluents from municipal STWS to drive the inputs  
 190 the fit for BT with the observed values slightly under estimated concentrations (regression  
 191 slope=0.8;  $R^2=0.76$ ;  $p << 0.001$ ) (SI, Figure S1), However, it was able to reproduce the

192 concentrations measured throughout the river very well for TT (regression slope=1.2;  $R^2=0.88$ ;  
193  $p \ll 0.001$ ) (SI Figure S2), indicating that the municipal effluents are the predominant source of  
194 these compounds. The predicted concentrations calculated based on per capita loads gave very  
195 similar fits to the measured data as did those using the municipal effluent concentrations (SI  
196 Figures S1 and S2). For BT, the average underestimate of the observed values was unchanged,  
197 and those for TT were similar to those obtained with effluent data (regression slope=1.3;  
198  $R^2=0.87$ ;  $p \ll 0.001$ ). These results indicated that the use of calculated per capita loads to STW  
199 for making predictions across a catchment, with no degradation in the river, was a reasonable  
200 approach.

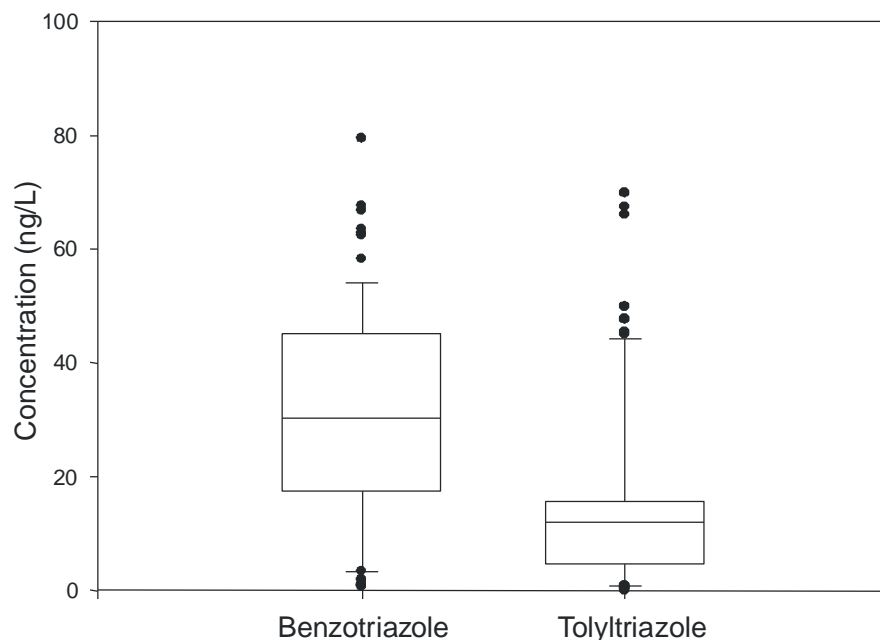
201 The model results highlighted that concentrations of BT between 400 – 1000 ng/L would  
202 frequently occur in river waters in the Trent catchment, with values below 400 ng/L in more  
203 upstream areas, less impacted by discharges from STW. For TT, modelled concentrations were  
204 higher, with 10% of the river falling in the 2,000 to 3000 ng/L range and 1,000 to 2,000 for a  
205 further 15% of the catchment (SI Figure S3). Modelling of the River Thames catchment was  
206 undertaken to give an indication of concentrations which could be expected in the area where the  
207 drinking water samples were sourced. Throughout the catchment, concentrations of BT and TT  
208 were predicted to range from 1 to 1,000 ng/L below the first STW inputs, with increasing values  
209 of 401 to 1,000 ng/L and TT frequently in the 1,000 to 2,000 ng/L range in the lower reaches (SI  
210 Figure S4). A single grab sample taken from the River Colne, a tributary of the River Thames, in  
211 September 2010 corroborated these predictions, with average modelled values (BT 337 and TT  
212 508 ng/L) and measured values of 224 and 453 ng/L, respectively.

213 **Occurrence in drinking water.** Given the presence of these compounds at such concentrations  
214 in surface waters, and that surface waters are frequently abstracted for drinking water supply, it

215 is reasonable to ask if they are likely to be present in the potable supply. Potable treatment relies  
216 on a number of steps to purify water, increasingly involving processes using granular activated  
217 carbon (GAC) and ozone to remove chemical contaminants. However, there is some evidence  
218 that such processes may not be fully effective at removing BT and TT. Studies on the treatment  
219 of municipal wastewaters (not potable water) using ozone suggest that at ozone doses of 0.8 mg  
220 O<sub>3</sub> / mg DOC, 90% removal of these compounds might be expected, and increasing the dose to  
221 1.0 mg O<sub>3</sub> / mg DOC appeared to increase removal to 99% (6, 31). It has been shown that  
222 activated carbon can remove the less polar TT more effectively than BT, and that for BT,  
223 breakthrough can occur (9). However, given the river concentrations measured and modelled in  
224 this and other studies, even if removal efficiencies of 99% could be consistently achieved,  
225 residual concentrations of 20 to 60 ng/L of BT and TT could potentially occur following  
226 drinking water treatment.

227 Benzotriazole and / or TT were detected in all tap water samples analysed. Concentrations of BT  
228 were higher than those of TT, opposite to that seen in the river survey, possibly a consequence of  
229 higher adsorption of TT to activated carbon (9), which is often used in potable water treatment  
230 processes. For BT, concentrations in samples ranged from 0.6 to 79.4 ng/L, with an average of  
231 30.9 ng/L. Tolyltriazole concentrations ranged from <0.2 ng/L up to 69.8 ng/L, with an average  
232 of 15.1 ng/L (Figure 2).

233



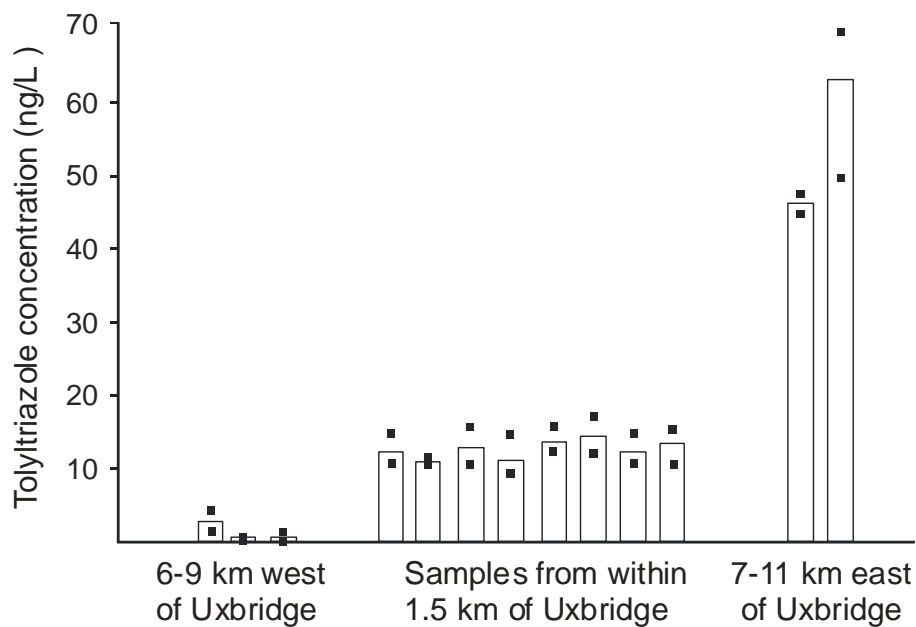
234

235 **FIGURE 2. Box plots of concentrations of BT and TT in tap water. Median concentrations**  
 236 **and the 25-75 percentile range are shown in the box with whiskers at 5 and 95 percentiles.**

237

238 However, there was evidence that taking average concentrations, without consideration of spatial  
 239 distribution of the data, may be misleading in terms of estimating actual human exposure through  
 240 tap water. Concentrations of BT and TT in the samples exhibited spatial variation, most clearly  
 241 demonstrated for TT, in samples from 13 of the 20 locations which lay on an east – west line.  
 242 Concentrations of <5 ng/L to the west, increased by an order of magnitude within 20km east,  
 243 where values ranged from 50 to 70 ng/L (Figure 3). Such differences, which exhibited little  
 244 temporal variation within individual locations, would indicate that there are real differences in  
 245 exposure of populations living in relatively close proximity. There are two major water supply  
 246 companies within the London area with complex distribution systems which mix water from a  
 247 number of sources. However, samples from the Uxbridge area are supplied by Veolia Water  
 248 from a large treatment plant approximately 2.5 km distant, which abstracts directly from the

249 River Thames, where the catchment model predicted average concentrations of 400 ng/L BT and  
 250 840 ng/L TT. The water treatment works uses coagulation / flocculation followed by ozonation  
 251 and finally GAC filtration to supply 237 megalitres of water per day. Locations to the east and  
 252 west of Uxbridge in Figure 3 are supplied by Thames Water, and differences in concentrations  
 253 may be attributable to factors such as the source of drinking water supply (e.g. groundwater or  
 254 surface water), treatment processes and mixing in distributions systems. Four of the 7 samples  
 255 excluded from Figure 3 were to the north of Uxbridge, and had between 5 and 12 ng/L of TT.  
 256 The other three samples were from between 40 to 100 km distant, with 1 to 28 ng/L TT.



257

258 **FIGURE 3. Change in concentration of tolyltriazole in tap water from 13 of the 20**  
 259 **locations sampled over a 20 km distance from east to west around Uxbridge, west London.**  
 260 **Bars show the average value of four samples taken at weekly intervals, with maximum and**  
 261 **minimum values shown by black squares.**

262 **Estimation of possible inputs from dishwasher formulations.** The analysis of dishwasher  
263 powders and tablets confirmed the presence of either BT or TT in all products, with a minimum  
264 of 0.5 mg per 20 g in one own brand tablet to 60 mg in a leading brand tablet product. Using  
265 market share information, we calculated an “average load per wash” of 1.45 mg of BT and 27.8  
266 mg of TT (Table 1). Using estimates of the number of households using a dishwasher (5,326) in  
267 one of the STW catchments, as described in the Experimental Section, with an assumption of one  
268 use per household per day, this resulted in estimated inputs of 7.72 g of BT (5,326 x 1.45 mg)  
269 and 148 g of TT (5,326 x 27.8 mg) per day to this particular STW (Table 1). With a flow of 10  
270 ML/day, the estimate of concentrations in the influent at the STW was 772 ng/L BT and 14,800  
271 ng/L TT.

272 The average concentrations actually detected in effluent from the primary settling tanks (settled  
273 sewage) at this STW during four days in November 2009 were 1,610 ng/L of BT and 2,303 ng/L  
274 TT. It is apparent that the exercise underestimated the measured load of BT, and overestimated  
275 that of TT. As only one branded product contained TT, then the relative inputs of BT and TT  
276 from dishwasher detergents will depend very much on market share of that brand and on the  
277 proportion of people who use the tablet form of that brand. Given the assumptions made in  
278 calculating inputs, and possible limitations of the limited sampling regime in assessing true  
279 inputs, it would appear that the use of these chemicals in dishwasher formulations may account  
280 for a significant proportion (at least 30%) of the inputs to the STW and subsequently the  
281 environment. To further improve this estimate, more accurate, catchment specific data on sales  
282 and use of dishwasher detergents would be required, along with a more comprehensive sampling  
283 strategy at the STW. A full source apportionment exercise has not been undertaken; and other  
284 uses, such as in corrosion inhibitors for heating systems and motor vehicles could also contribute

285 to the load to sewer, however the estimation has highlighted that the use of BT and TT in “down  
 286 the drain” products may make a significant contribution to their concentrations in UK rivers.

287 **TABLE 1. Amount of BT and TT present in dishwasher detergent products from UK**  
 288 **supermarkets (mg per 20g of tablet or powder).**

289

	Type	Load in 20 g of product (mg)		Weighted load <sup>a</sup> (mg)		Market share (%)	Load per wash <sup>b</sup> (mg)	
		BT	TT	BT	TT		BT	TT
Brand 1	tablet		60.0		51.4	54		27.8
	powder		17.0					
Brand 2	tablet <sup>c</sup>	4.5		4.5		17	0.77	
Own label 1	tablet	0.9		3.9		5.4 <sup>d</sup>	0.21	
	powder	16.0						
Own label 2	tablet	0.5		3.8		4.0 <sup>d</sup>	0.15	
	powder	17.0						
Own label 3	tablet	2.2		1.5		5.8 <sup>d</sup>	0.09	
	powder	1.3						
Own label 4	tablet <sup>c</sup>	2.3		2.2		10.8 <sup>d</sup>	0.24	
Total market share						97.0		
Average load per wash <sup>e</sup>							1.45	27.8

290 a calculated based on 80% of people using the tablet formulation. = (mg in tablet x 0.8) + (mg in  
 291 powder x 0.2)

292 b calculated by taking into account the market share of the product = weighted load/100\*market  
 293 share

294 c These products were only available in tablet form

295 d Market share of these products was assumed to be the same as the market share of food sold by  
 296 the four major UK supermarkets (19)

297 e Summing of load per wash gives an estimated input per wash based on the amount in each  
 298 product and use of that product

299 Although the presence of chemicals in the environment and drinking water does not in itself pose  
300 a risk to health and the environment, there is concern that the possible effects of long term  
301 exposure to individual chemicals and / or mixtures of chemicals are not fully understood (32,  
302 33). The implications of our findings depend to a large extent on the degree of (eco)toxicity of  
303 BT and TT. As stated in the Introduction, there appear to be gaps in knowledge, as a  
304 consequence of the lack of any chronic ecotoxicity data for fish and for the range of toxicity  
305 endpoints evaluated (16), of particular importance for these chemicals in relation to exposure.  
306 Chemicals are usually more toxic when administered chronically (long-term) than when  
307 exposure is acute (short-term). This difference can be expressed as the acute : chronic ratio. For  
308 many industrial chemicals, this ratio is 10 or less, meaning that the LOEC and NOEC derived  
309 from chronic toxicity tests are not appreciably lower than those derived from acute toxicity tests.  
310 However, if chemicals have specific modes of action (as, for example, pharmaceuticals do), then  
311 chronic toxicity tests often demonstrate that chemicals can be very much more toxic than  
312 anticipated based on the results of acute toxicity tests (34). For example, the acute : chronic ratio  
313 of ethinyl estradiol is around 100,000 (35). This illustrates the importance of the current data gap  
314 with BT and TT; it is imperative to determine their chronic ecotoxicities (16) and data on  
315 carcinogenicity is conflicting (24). Although there seems to be no particular reason to think that  
316 BT and/or TT will have a high acute: chronic ratio, and hence be of more concern than appears  
317 to be the case based on acute ecotoxicity data, caution should be exercised for the following  
318 reason. Many azoles are very active chemicals, with specific modes of action: many (imidazoles  
319 and triazoles) are fungicides used in agriculture, and others (e.g. fadrazole) are used for anti-  
320 estrogen treatment in diseases such as breast cancer (36). Recent results have demonstrated that  
321 many commonly-used fungicides act as endocrine disrupters in vivo in both mammals (37) and



322 fish (38). Structural alerts such as these can be useful in aiding the selection of appropriate  
323 chronic toxicity tests that should be helpful in determining whether or not BT and/or TT are  
324 significantly more toxic chronically than they are acutely.

325 Adding further uncertainty to the toxicity of BT and TT is the possibility that BT is a human  
326 carcinogen. A Dutch committee (39) concluded that the weight of evidence indicated that BT  
327 may be a possible genotoxic carcinogen, although it was highlighted that the database was  
328 inconclusive. Based on that assessment, and structural analogy, Australian drinking water quality  
329 guidelines suggest a maximum permissible concentration of TT of 7 ng/L (40). Given this  
330 uncertainty, it could be strongly argued that the Precautionary Principle should be applied to both  
331 BT and TT, and exposure concentrations (to both aquatic wildlife and humans) minimised until  
332 appropriate chronic toxicity data become available on which to base any risk assessments.

333

### 334 **Acknowledgments**

335 The authors are grateful to the EPSRC for funding to undertake parts of this study  
336 (EP/G009775/1).

337

### 338 **Supporting Information Available**

339 Details on the instrumental analysis and quantification, and two tables summarising information.  
340 Two Figures showing modelled outputs and measured values for the Erewash and two Figures  
341 showing the catchment modelling outputs (Trent and Thames). This information is available free  
342 of charge via the Internet at <http://pubs.acs.org/>.

343

### 344 **Literature Cited**

- 345 1) Bolong, N.; Ismail, A. F.; Salim, M. R.; Matsuura, T. A review of the effects of emerging  
346 contaminants in wastewater and options for their removal. *Desalination* **2009**, *239*, 229-246.
- 347 (2) Ternes, T. A.; Joss, A.; Siegrist, H. Scrutinizing pharmaceuticals and personal care  
348 products in wastewater treatment. *Environ. Sci. Technol.* **2004**, *38*, 392A-399A.
- 349 (3) Jobling, S.; Nolan, M.; Tyler, C. R.; Brighty, G.; Sumpter, J. P. Widespread sexual  
350 disruption in wild fish. *Environ. Sci. Technol.* **1998**, *32*, 2498-2506.
- 351 (4) Wind, T.; Werner, U.; Jacob, M.; Hauk, A. Environmental concentrations of boron, LAS,  
352 EDTA, NTA and Triclosan simulated with GREAT-ER in the river Itter. *Chemosphere* **2004**, *54*,  
353 1135-1144.
- 354 (5) Wäschenbach, G.; Robinson, P.; Sandmann, B.; Magg, H.; Höflinger, W. Dishwasher  
355 product in tablet form. US Patent US 6,194,368 B1, February 27, 2001.
- 356 (6) Weiss, S.; Jakobs, J.; Reemtsma, T. Discharge of three benzotriazole corrosion inhibitors  
357 with municipal wastewater and improvements by membrane bioreactor treatment and ozonation.  
358 *Environ. Sci. Technol.* **2006**, *40*, 7193-7199.
- 359 (7) Voutsas, D.; Hartmann, P.; Schaffner, C.; Giger, W. Benzotriazoles, alkylphenols and  
360 bisphenol a in municipal wastewaters and in the Glatt River, Switzerland. *Environ. Sci. Pollut.*  
361 *Res.* **2006**, *13*, 333-341.
- 362 (8) Giger, W.; Schaffner, C.; Kohler, H. P. E. Benzotriazole and tolyltriazole as aquatic  
363 contaminants. 1. Input and occurrence in rivers and lakes. *Environ. Sci. Technol.* **2006**, *40*, 7186-  
364 7192.
- 365 (9) Reemtsma, T.; Miehe, U.; Duennbier, U.; Jekel, M. Polar pollutants in municipal  
366 wastewater and the water cycle: Occurrence and removal of benzotriazoles. *Water Res* **2010**, *44*,  
367 596-604.

- 368 (10) Kiss, A.; Fries, E. Occurrence of benzotriazoles in the rivers Main, Hengstbach, and  
369 Hegbach (Germany). *Environ. Sci. Pollut. Res. Int.* **2009**, *16*, 702-710.
- 370 (11) Reemtsma, T.; Weiss, S.; Mueller, J.; Petrovic, M.; Gonzalez, S.; Barcelo, D.; Ventura,  
371 F.; Knepper, T. P. Polar pollutants entry into the water cycle by municipal wastewater: A  
372 European perspective. *Environ. Sci. Technol.* **2006**, *40*, 5451-5458.
- 373 (12) Hart, D. S.; Davis, L. C.; Erickson, L. E.; Callender, T. M. Sorption and partitioning  
374 parameters of benzotriazole compounds. *Microchem. J.* **2004**, *77*, 9-17.
- 375 (13) US Geological Survey. *Anthropogenic organic compounds in source water of nine*  
376 *community water systems that withdraw from streams, 2002-2005*; Report 2008-5208, USGS:  
377 Reston, Virginia, 2008.
- 378 (14) Pillard, D. A.; Cornell, J. S.; Dufresne, D. L.; Hernandez, M. T. Toxicity of benzotriazole  
379 and benzotriazole derivatives to three aquatic species. *Water Res.* **2001**, *35*, 557-560.
- 380 (15) Kadar, E.; Dashfield, S.; Hutchinson, T. H. Developmental toxicity of benzotriazole in  
381 the protochordate *Ciona intestinalis* (Chordata, Ascidiaceae). *Anal. Bioanal. Chem.* **2010**, *396*, 641-  
382 647.
- 383 (16) Harris, C. A.; Routledge, E. J.; Schaffner, C.; Brian, J. V.; Giger, W.; Sumpter, J. P.  
384 Benzotriazole is antiestrogenic in vitro but not in vivo. *Environ. Toxicol. Chem.* **2007**, *26*, 2367-  
385 2372.
- 386 (17) la Farre, M.; Perez, S.; Kantiani, L.; Barcelo, D. Fate and toxicity of emerging pollutants,  
387 their metabolites and transformation products in the aquatic environment. *Trends Anal. Chem.*  
388 **2008**, *27*, 991-1007.
- 389 (18) *Dishwashing Detergents - UK - April 2009*; Mintel International: London, 2009.
- 390 (19) *Food Retailing - UK - November 2009*; Mintel International: London, 2009.

- 391 (20) Price, O. R.; Williams, R. J.; van Egmond, R.; Wilkinson, M. J.; Whelan, M. J. Predicting  
392 accurate and ecologically relevant regional scale concentrations of triclosan in rivers for use in  
393 higher-tier aquatic risk assessments. *Environ. Internat.* **2010**, *36*, 521-526.
- 394 (21) Williams, R. J.; Keller, V. D.; Johnson, A. C.; Young, A. R.; Holmes, M. G.; Wells, C.;  
395 Gross-Sorokin, M.; Benstead, R. A national risk assessment for intersex in fish arising from  
396 steroid estrogens. *Environ. Toxicol. Chem.* **2009**, *28*, 220-230.
- 397 (22) Rowney, N. C.; Johnson, A. C.; Williams, R. J. Cytotoxic Drugs in Drinking Water: A  
398 prediction and risk assessment exercise for the Thames Catchment in the United Kingdom.  
399 *Environ. Toxicol. Chem.* **2009**, *28*, 2733-2743.
- 400 (23) Leitner, N. K. V.; Roshani, B. Kinetic of benzotriazole oxidation by ozone and hydroxyl  
401 radical. *Water Res.* **2010**, *44*, 2058-2066.
- 402 (24) USEPA: High Production Volume (HPV) Challenge Program, USEPA **2010**.
- 403 (25) Johnson, A. C.; Acreman, M. C.; Dunbar, M. J.; Feist, S. W.; Giacomello, A. M.; Gozlan,  
404 R. E.; Hinsley, S. A.; Ibbotson, A. T.; Jarvie, H. P.; Jones, J. I.; et al.. The British river of the  
405 future: How climate change and human activity might affect two contrasting river ecosystems in  
406 England. *Sci. Total Environ.* **2009**, *407*, 4787-4798.
- 407 (26) The Office for National Statistics. *Census 2001 - People and their homes in England and*  
408 *Wales*; The Office for National Statistics: London, 2003.
- 409 (27) Waterwise. *Water and energy consumptions of dishwashers and washing machines: An*  
410 *analysis of efficiencies to determine the possible need and options for a water efficiency label for*  
411 *wet white goods*; Waterwise: London, 2008; 48 pp.
- 412 (28) European Commission. ESIS (European chemical Substances Information System), 2011.  
413 <http://ecb.jrc.ec.europa.eu/esis/> .

- 414 (29) Environment Agency. What's in your backyard? 2011 <http://www.environment->  
415 [agency.gov.uk/homeandleisure/](http://www.environment-agency.gov.uk/homeandleisure/).
- 416 (30) Johnson, A. C.; Ternes, T.; Williams, R. J.; Sumpter, J. P. Assessing the concentrations  
417 of polar organic microcontaminants from point sources in the aquatic environment: Measure or  
418 model?. *Environ. Sci. Technol.* **2008**, *42*, 5390-5399.
- 419 (31) Hollender, J.; Zimmermann, S. G.; Koepke, S.; Krauss, M.; McArdell, C. S.; Ort, C.;  
420 Singer, H.; von Gunten, U.; Siegrist, H. Elimination of organic micropollutants in a municipal  
421 wastewater treatment plant upgraded with a full-scale post-ozonation Followed by sand filtration.  
422 *Environ. Sci. Technol.* **2009**, *43*, 7862-7869.
- 423 (32) Snyder, S. A.; Westerhoff, P.; Yoon, Y.; Sedlak, D. L. Pharmaceuticals, personal care  
424 products, and endocrine disruptors in water: Implications for the water industry. *Environ. Eng.*  
425 *Sci.* **2003**, *20*, 449-469.
- 426 (33) Jones, O. A.; Lester, J. N.; Voulvoulis, N. Pharmaceuticals: a threat to drinking water?  
427 *Trends Biotechnol.* **2005**, *23*, 163-167.
- 428 (34) Fent, K. Effects of pharmaceuticals on aquatic organisms. In *Pharmaceuticals in the*  
429 *Environment 3rd Edition*; Kümmerer, K., Ed.; Springer-Verlag: Berlin, Heidelberg, 2008.
- 430 (35) Webb, S. F. Data-based perspective on the environmental risk assessment of human  
431 pharmaceuticals. I. Collation of Avila vale ecotoxicology data. In *Pharmaceuticals in the*  
432 *Environment 2nd Edition*; Kümmerer, K., Ed.; Springer-Verlag: Berlin, Heidelberg, New York,  
433 2004.
- 434 (36) Trosken, E. R.; Scholz, K.; Lutz, R. W.; Volkel, W.; Zarn, J. A.; Lutz, W. K.  
435 Comparative assessment of the inhibition of recombinant human CYP19 (aromatase) by azoles  
436 used in agriculture and as drugs for humans. *Endocrine Res.* **2004**, *30*, 387-394.

437 (37) Taxvig, C.; Vinggaard, A. M.; Hass, U.; Axelstad, M.; Metzdorff, S.; Nellemann, C.  
438 Endocrine-disrupting properties in vivo of widely used azole fungicides. *Int. J. Androl.* **2008**, *31*,  
439 170-176.

440 (38) Rime, H.; Nguyen, T.; Bobe, J.; Fostier, A.; Monod, G. Prochloraz-induced oocyte  
441 maturation in Rainbow Trout (*Oncorhynchus mykiss*), a molecular and functional analysis.  
442 *Toxicol. Sci.* **2010**, *118*, 61-70.

443 (39) DECOS. *1,2,3-benzotriazole. Health-based recommended occupational exposure limit:*  
444 Dutch Expert Committee for Occupational Standards: The Hague, 2000.

445 (40) NRM-MC-EPHC-NHMRC *Australian Guidelines for Water Recycling: Augmentation of*  
446 *drinking water supplies*; Natural Resource Management Ministerial Council, Environment  
447 Protection and Heritage Council, and National Health and Medical Research Council: Adelaide,  
448 2008.

449

450 **Brief**

451 Benzotriazole and tolyltriazole were determined and the possible contribution from use in  
452 dishwasher detergents assessed; the need for more data on their chronic toxicity was highlighted.

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