1 **From dishwasher to tap? Xenobiotic substances benzotriazole and tolyltriazole in the**

2 **environment**

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10 There is increasing evidence that the use of chemicals frequently results in widespread

11 environmental contamination with little understanding of the toxicological implications.

12 Benzotriazoles are used in, amongst other applications, dishwashing formulations for home use,

13 and are a class of chemicals recently reported to be present in European waters. This study

14 demonstrates their presence in UK wastewaters, rivers and drinking water. It also estimates that

15 their use as silver polishing agents in dishwasher tablets and powders may account for a

16 significant proportion of inputs to wastewaters. The lack of a complete set of good quality

17 (eco)toxicological data on possible chronic effects of these high use chemicals should caution

18 against using them in a manner which may have contributed to such widespread environmental

19 contamination.

20

21 **Introduction**

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 xenobiotocs 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 of a range of formulations sold for domestic use during

75   July 2010, based on information on their market share (*18*). Samples included tablets and powers

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 ($500mg/6cm^3$)

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.
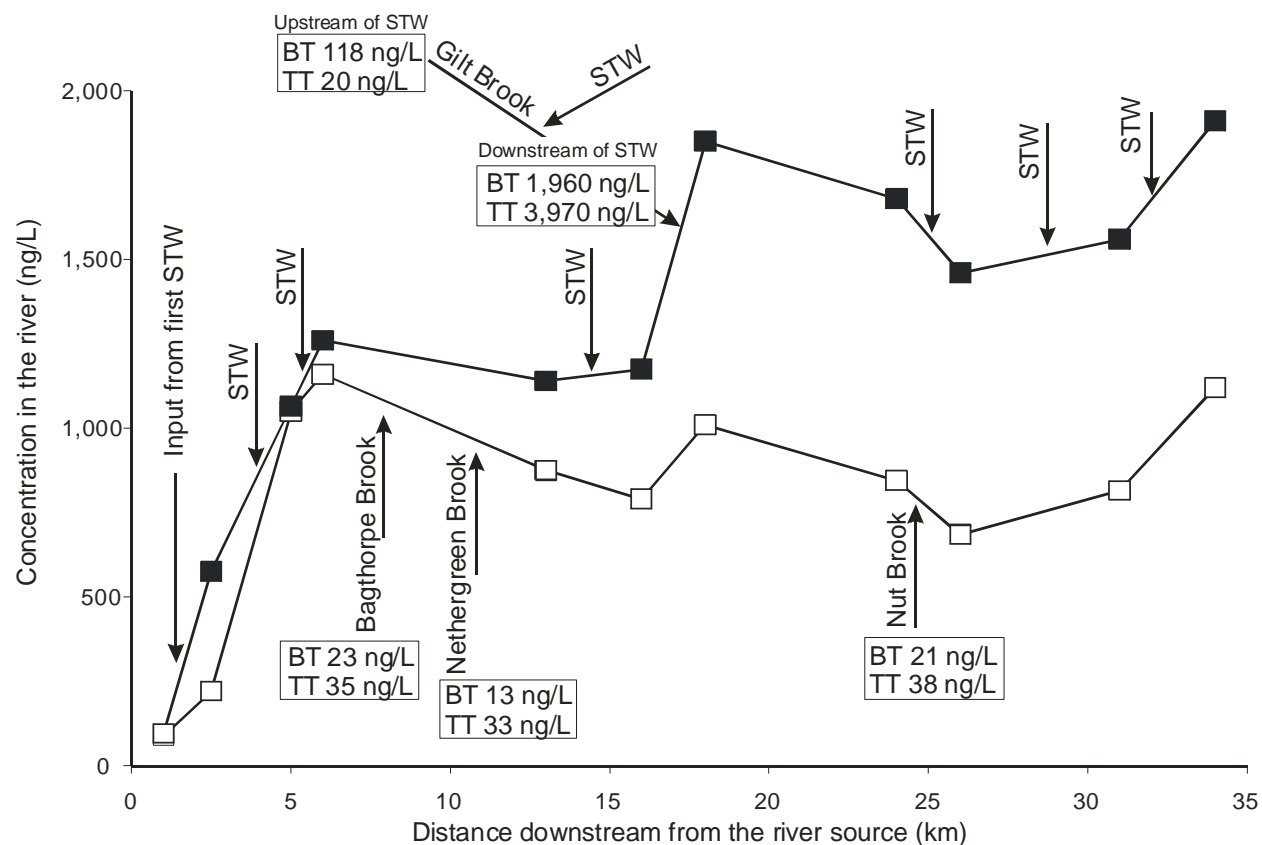
148   The calculated load was transformed to a concentration by dividing by the consented dry weather

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.

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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.

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Figure showing concentration vs distance with labels:

Upstream of STW
BT 118 ng/L
TT 20 ng/L

Gilt Brook

STW

Downstream of STW
BT 1,960 ng/L
TT 3,970 ng/L

STW   STW   STW

Input from first STW

STW

STW

STW

Bagthorpe Brook

Nethergreen Brook

Nut Brook

BT 23 ng/L
TT 35 ng/L

BT 13 ng/L
TT 33 ng/L

BT 21 ng/L
TT 38 ng/L

Y-axis: Concentration in the river (ng/L) — 0, 500, 1,000, 1,500, 2,000

X-axis: Distance downstream from the river source (km) — 0, 5, 10, 15, 20, 25, 30, 35

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

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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<< 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 <<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_3 / mg DOC, 90% removal of these compounds might be expected, and increasing the dose to

221   1.0 mg O_3 / 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).

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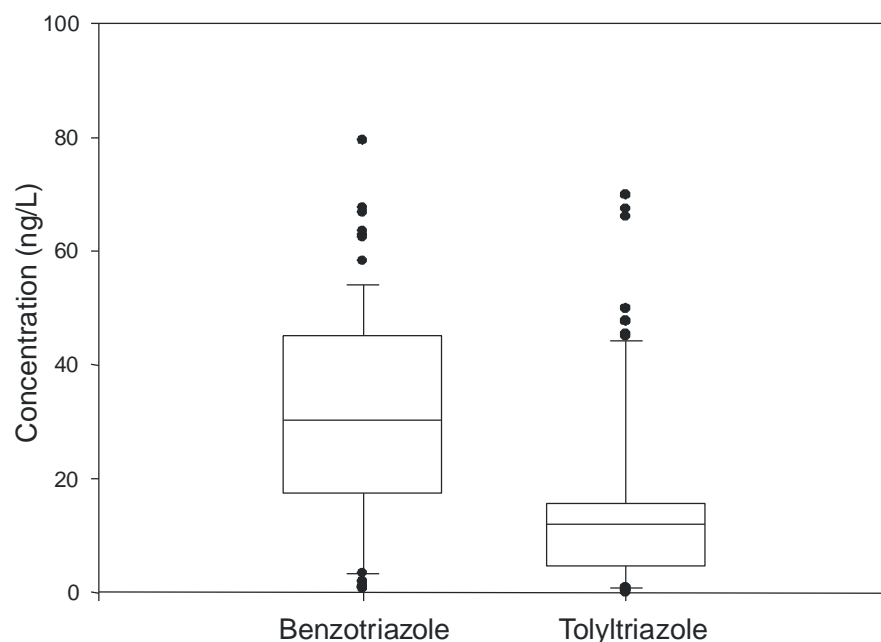
FIGURE 2. Box plots of concentrations of BT and TT in tap water. Median concentrations and the 25-75 percentile range are shown in the box with whiskers at 5 and 95 percentiles.

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

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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.
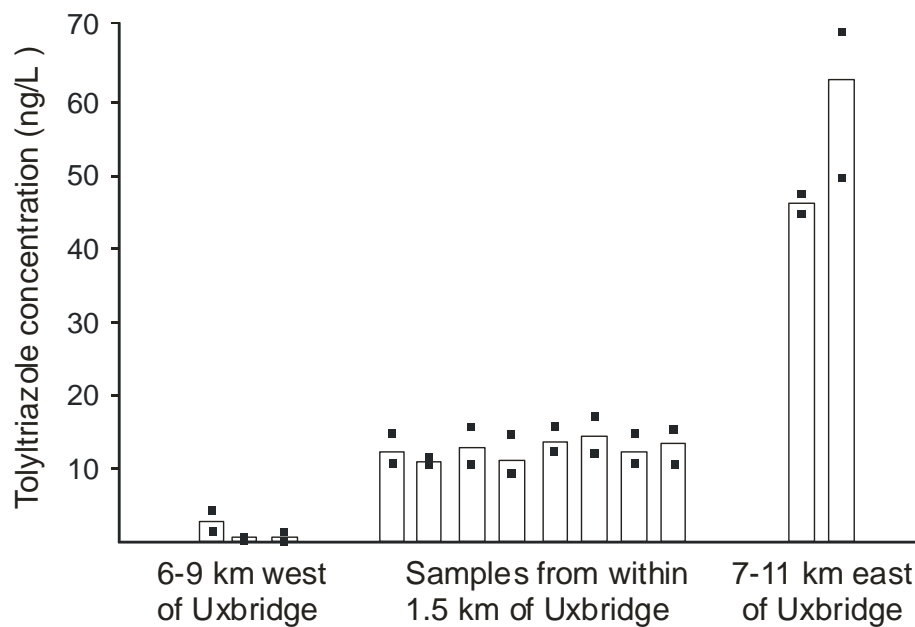
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258   **FIGURE 3. Change in concentration of tolyltriazole in tap water from 13 of the 20**

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.**

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

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

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) BT	TT	Weighted load[a] (mg) BT	TT	Market share (%)	Load per wash[b] (mg) BT	TT
Brand 1	tablet		60.0		51.4	54		27.8
	powder		17.0					
Brand 2	tablet[c]	4.5		4.5		17	0.77	
Own label 1	tablet	0.9		3.9		5.4[d]	0.21	
	powder	16.0						
Own label 2	tablet	0.5		3.8		4.0[d]	0.15	
	powder	17.0						
Own label 3	tablet	2.2		1.5		5.8[d]	0.09	
	powder	1.3						
Own label 4	tablet[c]	2.3		2.2		10.8[d]	0.24	
Total market share						97.0		
Average load per wash[e]							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 uncertainly, 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.

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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

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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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