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POLICY ANALYSIS

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From Dishwasher to Tap? Xenobiotic Substances Benzotriazole and Tolyltriazole in the Environment

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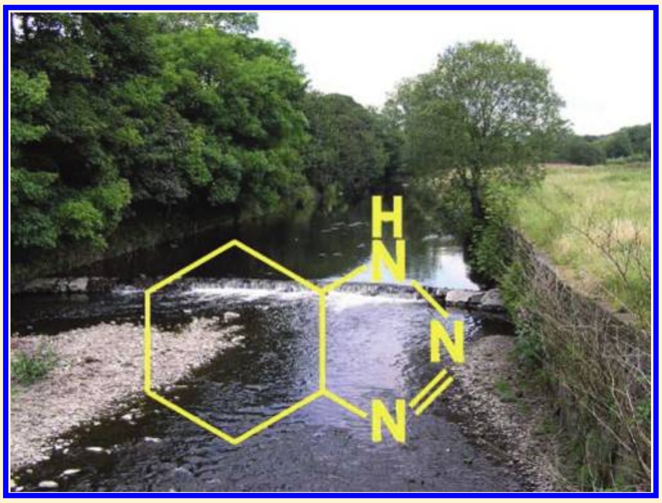
S *Supporting Information*

ABSTRACT: There is increasing evidence that the use of chemicals frequently results in widespread environmental contamination with little understanding of the toxicological implications. Benzotriazoles are used in, among other applications, dishwashing formulations for home use, and are a class of chemicals recently reported to be present in European waters. This study demonstrates their presence in UK wastewaters, rivers, and drinking water. It also estimates that their use as silver polishing agents in dishwasher tablets and powders may account for a significant proportion of inputs to wastewaters. The lack of a complete set of good quality (eco)toxicological data on possible chronic effects of these high use chemicals should caution against using them in a manner which may have contributed to such widespread environmental contamination.



■ INTRODUCTION

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

One class of chemical corrosion inhibitors that has been incorporated into dishwashing detergents to reduce the corrosion of nonferrous metals[5] is 1H-benzotriazole (BT) and 4- or 5-methyl-1H-benzotriazole, used as a technical mixture and commonly called tolyltriazole (TT). In addition to use in consumer products, they find more extensive use in industrial products, such as brake fluids, motor vehicle antifreeze, and aircraft deicing fluids.[6] The first report on their occurrence in the aquatic environment was in the Glatt River, Switzerland, where they occurred in all sewage treatment work (STW) effluents surveyed and were detected at concentrations up to 3690 ng/L (BT) and 628 ng/L (TT) in the river.[7] Subsequently, their presence has been reported in a further six Swiss rivers,[8] as well as in rivers in Germany, with concentrations of BT ranging from 130 to 3500 ng/L in the Rhine[9] and from 38 to 1474 ng/L in the Main, Hengstbach, and Hegnach collectively.[10] Concentrations of BT and TT were among the highest of 36 polar pollutants detected in a survey of European rivers.[11] Although there are few reports on their presence in rivers from other regions of the world, BT and TT have been observed in groundwater in the United States, as a result of use in aircraft deicing fluids[12] and TT was included in a survey of source waters in the U.S., with an estimated maximum concentration of 360 ng/L.[13]

Concern about any chemical is based primarily on the relationship of (eco)toxicity and exposure. In the cases of BT and TT, relatively few toxicity data are available in the open literature. Those available are almost exclusively concerned with acute toxicity. They suggest that BT and its derivative are relatively

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nontoxic, reported no-observed effect concentrations (NOEC) in freshwater and marine environments are usually in the mg/L range,[14,15] and existing data are adequate for undertaking required risk assessments, although they lack, for example, any studies on the chronic effects on fish. However, many authors have commented on the lack of chronic toxicity data for these chemicals, (e.g., refs 15−17), and the need for a rigorous investigation of their chronic toxicity before any conclusions relevant to environmental risk assessments can be made.[16]

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

■ EXPERIMENTAL SECTION

Determination of environmental concentrations involved a survey of water and STW final effluent samples taken from along the River Erewash, which received discharges from eight STW above its confluence with the River Trent near Nottingham, UK. Sampling was undertaken in January 2009 and consisted of 24 single grab samples: 11 from the river, 5 from tributaries, and a final effluent from each of the eight STW. To determine if BT and TT were present in the UK potable supply, we undertook sampling on four occasions during May and June 2010 for a total of 80 tap water samples, from locations in the southeast of England. These were predominantly within a 15-km radius of Uxbridge, in west London, although some were up to 30 km to the west and one location was 80 miles to the northeast. To assess the potential inputs from dishwasher detergents, we analyzed a range of formulations sold for domestic use during July 2010, based on information on their market share.[18] Samples included tablets and powders from the two leading UK brands and “own label” products from four supermarkets with greatest overall UK market share.[19]

Determination of Benzotriazole and Tolyltriazole. Samples of wastewaters, final effluent, and river waters were chilled and extracted within 24 h of sampling. Tap waters were sampled by householders, with taps run for 1 min before the sample was taken, stored in polycarbonate bottles, and extracted within 6 h. The analytical methodology involved solid phase extraction (SPE), followed by quantification with positive mode electrospray ionization-triple quadrupole mass spectrometry.[7]

Reagents and Chemicals. Benzotriazole (1H-benzotriazole), tolyltriazole (as 5-methyl-1H-benzotriazole), and the internal standard, 5,6-dimethylbenzotriazole, were purchased from Sigma-Aldrich (Gillingham, UK). Organic solvents, methanol and dichloromethane, were purchased from Rathburn Chemicals (Walkerburn, UK). For the SPE step, Oasis HLB (500 mg/6 cm^3) cartridges were obtained from Waters Ltd. (Watford, UK). Reagent grade water was obtained from a Milli-Q system (Millipore, Watford, UK).

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

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

Domestic Dishwasher Powders and Tablets. Products were weighed and approximately 20 g of the powders and whole tablets were then dissolved in 1 L of Milli-Q water using a magnetic stirrer. Products were analyzed in duplicate, using an external standard calibration. Dissolution of the products was determined visually, and occurred within 1 h. Once dissolved, solutions were further diluted, initially 1:100 in Milli-Q water, before quantification. Where necessary, further dilutions were made to obtain solution concentrations within the calibrated range of the instrument. Full description of the instrumental analysis and quantification and method performance is given in Supporting Information (SI) text and Tables S1 and S2.

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

The performance of the model was initially tested with measured effluent concentrations and outputs compared to observed river concentration data collected in the survey described above. The STWs inputs and the upstream boundaries of the river model were set to the values measured on the day of the survey. The degradation rates of the chemicals in the river were set to zero, as they have been noted to be resistant to biodegradation[23] and no degradation of BT was observed during a 20-day river die away study.[24] Although photodegradation has been reported to occur, with half-lives for BT and TT of 10 and 4 days respectively,[24] this is of little effect in relation to residence time in most UK rivers. For example from the source to the mouth of the Thames, which is 221 km long, this ranges from 7 to 21 days,[25] and most inputs are subject to shorter residence times as they join at points far downstream of the source.

The model was run in the monthly mode and the model outputs were chosen from the month whose long-term mean flow was closest to that on the sampling day. Because the sampling had been deliberately targeted at a low flow period, this month turned out to be July, even though the actual sampling run had been made in

Table 1. Amounts of BT and TT Present in Dishwasher Detergent Products from UK Supermarkets (mg per 20 g of Tablet or Powder)

		load in 20 g of product (mg)		weighted load[a] (mg)		market share (%)	load per wash[b] (mg)	
	type	BT	TT	BT	TT		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

[a] Calculated based on 80% of people using the tablet formulation: = (mg in tablet × 0.8) + (mg in powder × 0.2). [b] Calculated by taking into account the market share of the product = weighted load/100 × market share. [c] These products were only available in tablet form. [d] Market share of these products was assumed to be the same as the market share of food sold by the four major UK supermarkets.[19] [e] Summing of load per wash gives an estimated input per wash based on the amount in each product and use of that product.

January 2009. To run the model at a catchment scale, to obtain values for STWs discharges that could be used more widely throughout the catchment, the measured concentrations were transformed into equivalent per capita output loads.[21]

Estimation of the Inputs of BT and TT from Dishwasher Detergents. Consumer products were purchased from UK supermarkets during May and June 2010 and analyzed for BT and TT. An average load of BT and TT per wash was determined by using market share information and use patterns[18,19] (Table 1). To estimate how many washes were undertaken per day, we used the population equivalent of one of the eight STWs (44,895), assuming 2.36 people per household[26] to derive 19,023 households. With dishwasher ownership of 28%,[27] this gave 5326 households with dishwashers. We then assumed each of these were used once per day, discharging the estimated average load per wash (Table 1) to the STW.

The calculated load was transformed to a concentration by dividing by the consented dry weather flow (as it did not rain during the week of sampling) and compared to the concentration determined by taking the average detected in seven grab samples of settled sewage (primary tank effluent) from this STW (four at 9:00 and three at 14:00) taken over a 4-day period during November 2008. Settled sewage was sampled to attenuate likely variation of concentrations in crude sewage, and was deemed appropriate due to the solubility of the analytes.

RESULTS AND DISCUSSION

Concentrations of BT in the eight sewage effluents, which ranged from 840 to 3605 ng/L, were consistently less than those of TT (2685 to 5700 ng/L). There was no relationship between effluent concentrations and treatment type, which were either activated sludge or biological filters with or without tertiary treatment, such as nitrifying sand filters. Three of the works had older biological filters running in parallel with more recently installed activated sludge treatment. In the river, higher concentrations of TT were also consistently observed (Figure 1), as in the effluents. The river survey demonstrated that the compounds were present in all samples, including those from the small tributaries, with the highest concentration observed upstream of a STW being 118 ng/L, indicating sources other than sewage effluents, such as industrial or urban runoff. However, the increase in concentrations at around 2.5 km from the source of the river may be attributed to inputs from the first STW as may those in Gilt Brook, and subsequent increases were also attributable to discharges from STW; conversely, decreases in the concentrations of these chemicals in the river water corresponded with the confluence of less contaminated tributaries, resulting in dilution. There is no evidence that any other discharges to the river could account for the increase in BT and TT concentrations above the backgrounds observed. Although the European chemical Substances Information System (ESIS),[28] indicates an importer of TT in the area of the Erewash, they are in fact located on a nearby river, and would not be expected to contribute discharges to the Erewash. The company named on ESIS is not listed in the UK Environment Agency (EA) "What's in your backyard?" pollution inventory[29] as having a license to discharge, and there is no indication from the EA data set that there are any companies along the Erewash itself which are likely to contribute to the concentrations of BT and TT observed in the river.

The sampling and analysis of large catchments is a challenge in terms of resources and costs, and it is therefore often appropriate to model concentrations of chemicals in river systems.[30] Before modeling of a more extensive area was undertaken, the LF2000-WQX model was calibrated using the measured effluent concentrations to predict concentrations in the Erewash. When using the measured concentrations in effluents from municipal STWs to drive the inputs, the fit for BT with the observed values slightly underestimated concentrations (regression slope = 0.8; $R^2 = 0.76$; $p \ll 0.001$) (SI Figure S1), However, it was able to reproduce the concentrations measured throughout the river very well for TT (regression slope = 1.2; $R^2 = 0.88$; $p \ll 0.001$) (SI Figure S2), indicating that the municipal effluents are the predominant source of these compounds. The predicted concentrations calculated based on per capita loads gave fits to the measured data very similar to those using the municipal effluent concentrations (SI Figures S1 and S2). For BT, the average underestimate of the observed values was unchanged, and those

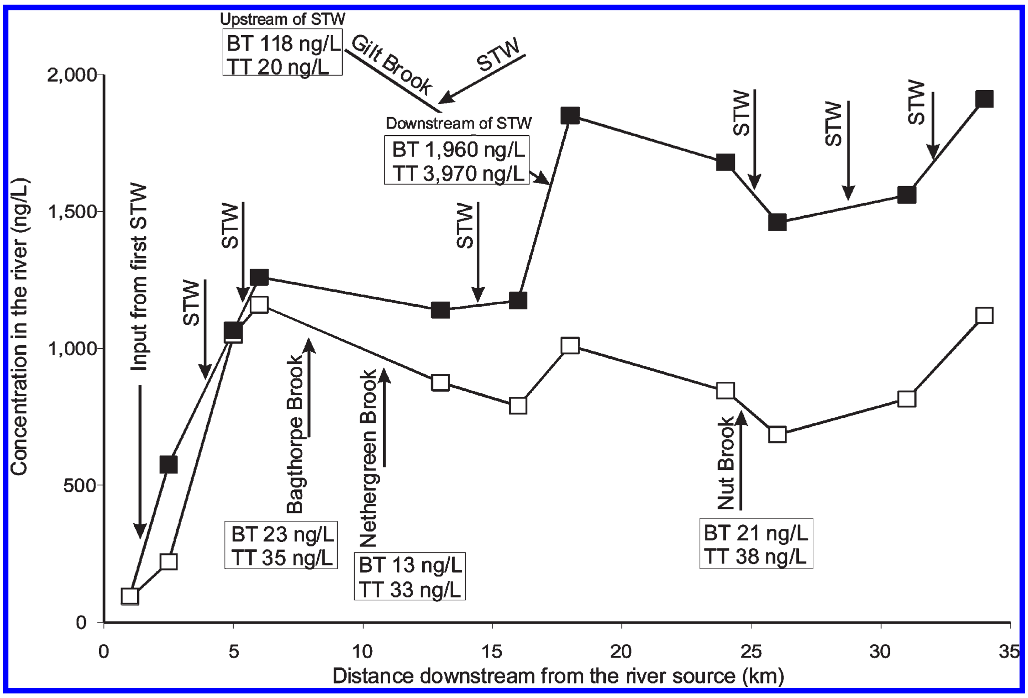

Figure 1. Graphical representation of the River Erewash showing concentrations of BT (□) and TT (■) increasing downstream from the river source. Values in boxes indicate concentrations (ng/L) in tributaries.

for TT were similar to those obtained with effluent data (regression slope = 1.3; R^2 = 0.87; $p \ll 0.001$). These results indicated that the use of calculated per capita loads to STW for making predictions across a catchment, with no degradation in the river, was a reasonable approach.

The model results highlighted that concentrations of BT between 400 and 1000 ng/L would frequently occur in river waters in the Trent catchment, with values below 400 ng/L in more upstream areas, less impacted by discharges from STW. For TT, modeled concentrations were higher, with 10% of the river falling in the 2000−3000 ng/L range and 1000−2000 for a further 15% of the catchment (SI Figure S3). Modeling of the River Thames catchment was undertaken to give an indication of concentrations that could be expected in the area where the drinking water samples were sourced. Throughout the catchment, concentrations of BT and TT were predicted to range from 1 to 1000 ng/L below the first STW inputs, with increasing values of 401 to 1000 ng/L and TT frequently in the 1000−2000 ng/L range in the lower reaches (SI Figure S4). A single grab sample taken from the River Colne, a tributary of the River Thames, in September 2010 corroborated these predictions, with average modeled values (BT 337 ng/L and TT 508 ng/L) and measured values of 224 and 453 ng/L, respectively.

Occurrence in Drinking Water. Given the presence of these compounds at such concentrations in surface waters, and that surface waters are frequently abstracted for drinking water supply, it is reasonable to ask if they are likely to be present in the potable supply. Potable treatment relies on a number of steps to purify water, increasingly involving processes using granular activated carbon (GAC) and ozone to remove chemical contaminants. However, there is some evidence that such processes may not be fully effective at removing BT and TT. Studies on the treatment of municipal wastewaters (not potable water) using ozone suggest that at ozone doses of 0.8 mg O_3/mg DOC, 90% removal of these compounds might be expected, and increasing the dose to 1.0 mg O_3/mg DOC appeared to increase removal to 99%.[6,31] It has been shown that activated carbon can remove the less polar TT more effectively than BT, and that for BT, breakthrough can occur.[9] However, given the river concentrations measured and modeled in this and other studies, even if removal efficiencies of 99% could be consistently achieved, residual concentrations of 20−60 ng/L of BT and TT could potentially occur following drinking water treatment.

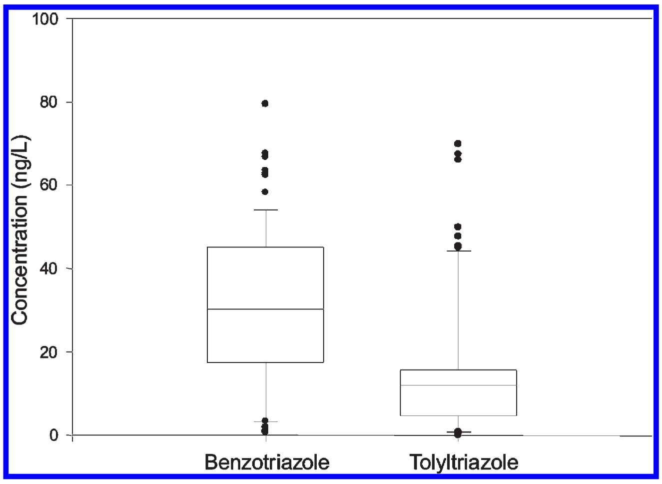

Figure 2. Box plots of concentrations of BT and TT in tap water. Median concentrations and the 25−75 percentile range are shown in the box with whiskers at 5 and 95 percentiles.

Benzotriazole and/or TT were detected in all tap water samples analyzed. Concentrations of BT were higher than those of TT, opposite that seen in the river survey, possibly a consequence of higher adsorption of TT to activated carbon,[9] which is often used in potable water treatment processes. For BT,

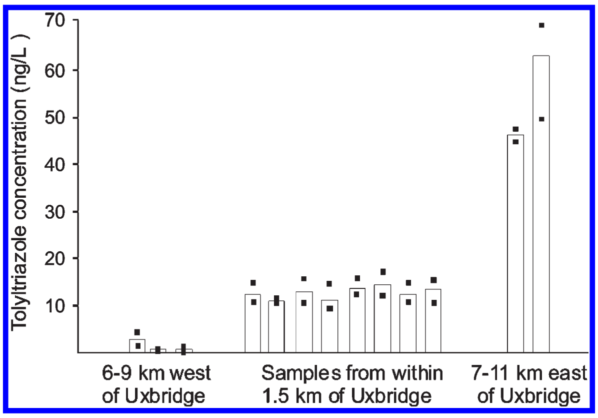

Figure 3. Change in concentration of tolyltriazole in tap water from 13 of the 20 locations sampled over a 20-km distance from east to west around Uxbridge, west London. Bars show the average value of four samples taken at weekly intervals, with maximum and minimum values shown by black squares.

concentrations in samples ranged from 0.6 to 79.4 ng/L, with an average of 30.9 ng/L. Tolyltriazole concentrations ranged from <0.5 to 69.8 ng/L, with an average of 15.1 ng/L (Figure 2).

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

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 (5326) 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 (5326 × 1.45 mg) and 148 g of TT (5326 × 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 1610 ng/L of BT and 2303 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; 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-the-drain" products may make a significant contribution to their concentrations in UK rivers.

Although the presence of chemicals in the environment and drinking water does not in itself pose a risk to health and the environment, there is concern that the possible effects of long-term exposure to individual chemicals and/or mixtures of chemicals are not fully understood.[32,33] The implications of our findings depend to a large extent on the degree of (eco)toxicity of BT and TT. As stated in the Introduction, there appear to be gaps in knowledge, as a consequence of the lack of any chronic ecotoxicity data for fish and for the range of toxicity end points evaluated,[16] of particular importance for these chemicals in relation to exposure. Chemicals are usually more toxic when administered chronically (long-term) than when exposure is acute (short-term). This difference can be expressed as the acute:chronic ratio. For many industrial chemicals, this ratio is 10 or less, meaning that the LOEC and NOEC derived from chronic toxicity tests are not appreciably lower than those derived from acute toxicity tests. However, if chemicals have specific modes of action (as, for example, pharmaceuticals do), then chronic toxicity tests often demonstrate that chemicals can be very much more toxic than anticipated based on the results of acute toxicity tests.[34] For example, the acute:chronic ratio of ethinyl estradiol is around 100 000.[35] This illustrates the importance of the current data gap with BT and TT; it is imperative to determine their chronic ecotoxicities[16] and data on carcinogenicity are conflicting.[24] Although there seems to be no particular reason to think that BT and/or TT will have a high acute:chronic ratio, and hence be of more concern than appears to be the case based on acute ecotoxicity data, caution should be exercised for the following reason. Many azoles are very active chemicals, with specific modes of action: many (imidazoles and triazoles) are fungicides used in agriculture, and others (e.g., fadrazole) are used for antiestrogen treatment in diseases such as breast cancer.[36] Recent results have demonstrated that many commonly used fungicides act as endocrine disrupters in vivo in both mammals[37] and fish.[38] Structural alerts such as these can be useful in aiding the selection of appropriate chronic toxicity tests that should be helpful in determining whether BT and/or TT are significantly more toxic chronically than they are acutely.

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

■ ASSOCIATED CONTENT

S Supporting Information. Details on the instrumental analysis and quantification, and two tables summarizing that information; two figures showing modeled outputs and measured values for the Erewash and two figures showing the catchment modeling outputs (Trent and Thames). This information is available free of charge via the Internet at http://pubs.acs.org/.

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