Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.933626

53 (2015) 3253–3262
March

Taylor & Francis
Taylor & Francis Group

Biocides in drinking water system of Ankara, Turkey

Merve Yavuz[a], Marco Oggioni[b], Ulku Yetis[a], Filiz B. Dilek[a],*

[a]*Department of Environmental Engineering, Middle East Technical University, Ankara 06800, Turkey, Tel. +90 3122105877; Fax: +90 312 2101246; email: fdilek@metu.edu.tr (F.B. Dilek)*
[b]*LAMMB, Dip. Biotecnologie, Universita'di Siena, UOC Batteriologia, Azienda Ospedaliera Universitaria Senese, Policlinico Le Scotte, Siena 3100, Italy*

Received 11 October 2013; Accepted 5 February 2014

ABSTRACT

This study focuses on the occurrence of two selected biocides, namely triclosan (TCS) and chlorhexidine (CHX), in the drinking water system of Ankara, Turkey. Samples were taken from the three main components of the drinking water system (Çamlıdere and Kesikköprü Reservoirs, Ivedik Water Treatment Plant (IWTP) and the distribution network). Seasonal variations in biocide levels as well as their relation to general water quality parameters were sought. TCS levels detected in Çamlıdere and Kesikköprü Reservoirs were in the range of 0.65–11.15 ng/L and 0.86–48.96 ng/L, respectively; whereas CHX levels detected were between <1.33–5.31 ng/L. TCS was completely removed in IWTP. In accordance with the result for the IWTP outlet, biocides in the distribution network were all below the limit of quantifications. Moreover, some conventional water quality parameters were related to the concentrations of biocides in surface waters.

Keywords: Biocides; Chlorhexidine; Drinking water; Triclosan

1. Introduction

Biocides are widely used as preservatives or as antiseptic agents in many different consumer care products such as toothpaste, mouthwash and soaps as well as household cleaners. These chemicals are increasingly added to antimicrobial surfaces and other products to kill bacteria or inhibit their growth. Biocides are also intensively used in animal husbandry and in veterinary medicines for the purposes of caring for and rearing food-producing animals. Another important use of biocides is in cooling tower systems to control the growth of some harmful bacteria such as Legionella might otherwise be released from cooling towers in aerosols.

Among the biocides, triclosan (TCS), 5-chloro-2-(2,4-dichlorophenoxy)phenol, is the most widely used one. Its use area includes the manufacturing of various cosmetic sprays, soaps, oral products, creams, detergents and hospital grade disinfectants [1–4]. It is reported that each year approximately 350 tons of TCS is produced in Europe [5] and more than 300 tons of TCS is discharged into water in USA [6]. According to the Australian statistics, yearly 15 tons of TCS is used for households and industrial cleaning products, textile additives and plastic additives [7].

TCS, when released into environment, can undergo photodegradation or biodegradation. The

---

*Corresponding author.

Presented at the International Conference WIN4Life, 19–21 September 2013, Tinos Island, Greece

photochemical conversion to dioxins, toxicity on fish, weak estrogen activity and the formation of various chlorinated and brominated derivatives has been reported as negative effects of TCS in previous studies [1–4]. Moreover, 2,4-dichlorophenol and 2,4,6-trichlorophenol have been detected as the degradation products of TCS when low concentrations of free chlorine presents in water [8]. Even low levels of dioxin are of concern; it is toxic to human since it becomes more concentrated in tissues through biomagnification.

The previous studies [5,7,9–13] indicated that TCS can be degraded and removed by 70–96% in activated sludge process, and by 58–86% in trickling filters. The remaining fraction of TCS which is not eliminated during wastewater treatment process is discharged to the aquatic environment. Previous studies in Europe, North America, Australia and China have demonstrated that occurrence of TCS in influent was in the range of 1,000–10,000 ng/L whereas in effluents was in the range of 40–2,700 ng/L [5,6,12–14]. As a result of TCS discharge to the aquatic environment, concentration of TCS was detected as ≤ 3–300,000 ng/L, 0.8 pg/L–150 ng/l, 1–35 μg/kg and 0.07–14,000 μg/l, in surface waters, in sea water, in sediments and in wastewater samples, respectively [5,11,15–23]. As can be inferred from these recorded values, the level of TCS in water courses is so variable. One interesting finding from these studies is that maximum detected values in surface waters were higher in US and Canada (up to 300,000 ng/L [15]) than those in Europe (up to 134 ng/L [22]). This could be probably a result of higher consumption of TCS in US and Canada than Europe, or surface waters studied in US and Canada were those receiving treated wastewater discharge from a specialty chemicals manufacturing facility containing TCS.

Chlorhexidine (CHX), 1,1′-Hexamethylenebis[5-(4-chlorophenyl)biguanide], is another widely used antimicrobial agent especially for surgical scrubs, health care personal soaps, skin antiseptics, skin cleanser, acne creams and oral products such as toothpastes and mouth rinses [24]. It is a positively charged hydrophobic and lipophilic molecule and so it can accumulate in the fatty tissues (e.g. lipids) of living organisms and indicate toxic effects [25,26].

In this study, the occurrence levels of selected biocides, namely TCS and CHX, in the drinking water system of the City of Ankara, Turkey were investigated. Two major surface waters, namely Çamlıdere Reservoir (CR) and Kesikköprü Reservoir (KR) that supply water to the city, Ivedik Water Treatment Plant (IWTP) that receives water from these two sources and the drinking water within the distribution network of the City that receives water from IWTP were considered. The study was carried out between May 2010 and May 2011, and the samples were collected from surface waters, inlet and outlet of the IWTP and also from several locations at the distribution network and analysed for the biocides. Seasonal variations in biocide levels as well as their relation to general water quality parameters, if any, were sought.

2. Materials and methods

2.1. Surface waters

CR which is associated with Çamlıdere Dam is with a catchment area of 753 km^2, and an active reservoir volume of 840 hm^3. It has an annual potable water capacity of 150 hm^3. The raw water stored in the CR dam is conveyed by way of a 60 km pipeline before reaching IWTP.

KR that assures water supply during drought periods to Ankara is 110 km away from IWTP. Associated Kesikköprü Dam has a catchment's area of 354 km^2 (SHW, 2005). KR is with a 650 ha total area and 9,500 hm^3 total volume on Kızılırmak river. Five rainbow trout cage farms, each with an annual capacity between 20 and 55 ton, exist in KR [27]. Trophic state of the KR is reported to be mesotrophic with respect to the secchi-disc depth, and eutrophic with respect to the dissolved oxygen and average Chlorphyl-a values [28]. The reservoir also suffers indirectly from non-point sources due to widespread agriculture and livestock breeding and from point sources originating from due to untreated domestic and industrial wastewaters along the river [29].

2.2. Ivedik water treatment plant

IWTP is the biggest water treatment plant in Ankara (with a capacity of 1,128,000 m^3/d) serving to more than 90% of the total population. Raw waters of CR and KR are fed to IWTP in equal proportions. Transmission line from KR is also available to be used when necessary. A conventional treatment scheme is applied in the plant that consists of pre-disinfection, coagulation, flocculation–sedimentation, filtration and post-disinfection. Pre-disinfection and final disinfection are by chlorine; coagulation is by alum and/or polyaluminium chloride (PACl) at 30 mg/L together with a polyelectrolyte. The typical final-chlorination dose is reported to be 2.0 mg/L.

2.3. Distribution network

To observe the occurrence of biocides in the distribution network of Ankara, samples were

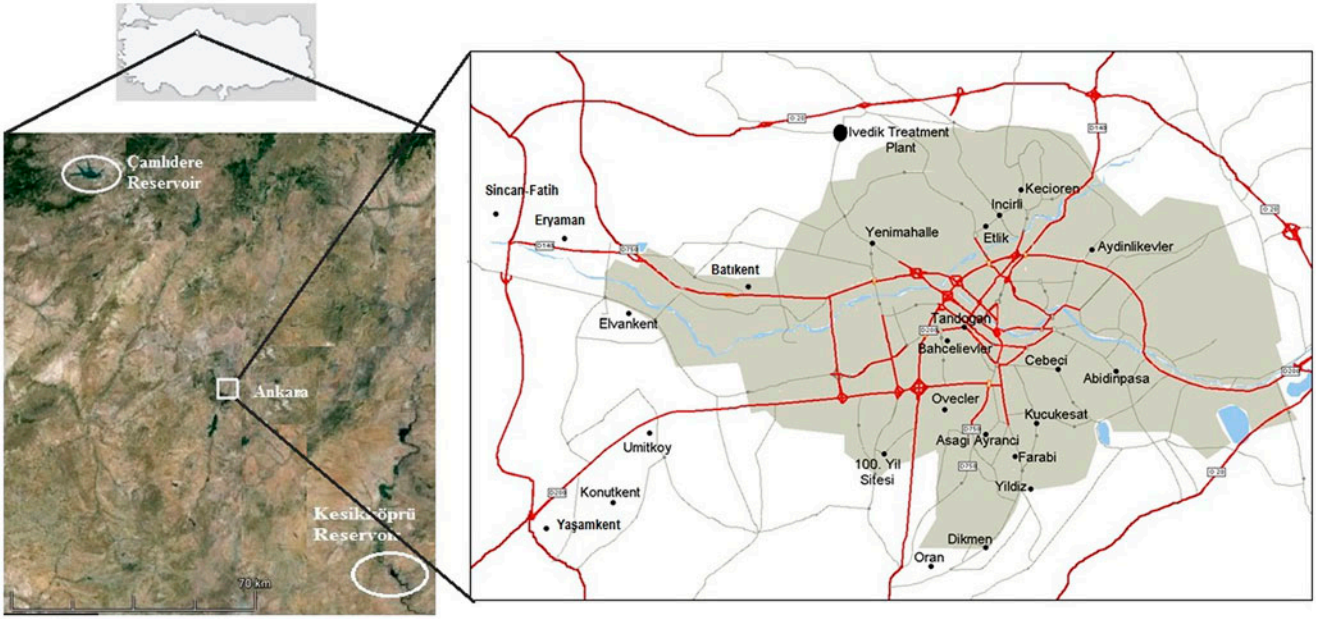


Fig. 1. Locations of the surface waters, IWTP and distribution network districts.

collected from the taps of consumers of various districts (Fig. 1). Two different samplings were conducted, one in May 2010 and the other one in May 2011. In the former sampling time, water samples from 10 different districts and in the latter one, samples from 16 different districts were taken. These districts receive water from the IWTP and are located at various distances from the plant. As shown in Fig. 1, Demetevler is the closest sampling point with a distance of about 1 km to the IWTP. Oran, Yaşamkent and Sincan-Fatih sampling points represent the terminal points. Distribution network has 7,255 km length and involve 103 storage and 62 pumping stations where additional chlorination is applied.

2.4. Target biocides

Chemical structure of the target biocides, namely TCS and CHX, and some of their physical properties are presented in Table 1.

2.5. Other water quality parameters

For surface waters, besides the biocides, other water quality parameters of total organic carbon (TOC), total dissolved solids (TDS), temperature and pH were also monitored in order to establish a relation with biocide levels, if any. For IWTP and distribution network, TOC, coliforms, residual chlorine and

Table 1
Properties of TCS and CHX

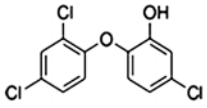
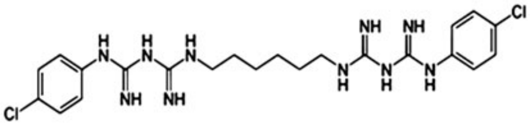
Properties	TCS	CHX
Chemical structure		
Molecular formula	$C_{12}H_7Cl_3O_2$	$C_{22}H_{30}Cl_2N_{10}$
Molecular weight	289.54	505.45
Melting point, °C	54–57.3	134–136
pKa	7.9–8.1	10.78
Log K_{ow}	4.8 at pH 7	0.08 at pH 5
Water solubility (20 °C), g/L	0.01	0.8

Table 2
Water quality parameters monitored

Parameters	Intention with selection
Surface waters	
TOC	Organic pollution indicator
TDS	Inorganic pollution indicator
Temperature	Indicator for weather/precipitation conditions and/or extent of biocide biodegradation
pH	For TCS speciation/fate understanding
IWTP and distribution network	
TOC	Organic pollution indicator
THM and HAA	Possible biocidal by-products (upon chlorination)
Residual Chlorine	As related to THM and HAA formation
Coliform	Pollution indicator

disinfection by-products of trihalomethanes (THM) and haloacetic acids (HAA) were also monitored. Intention with the selection of these parameters is indicated in Table 2.

TOC and TDS are the pollution-related water quality parameters, so, presence of wastewater inputs may be an indicator of biocides presence or possibly even abundance, as also stated by Ferguson et al. [30] in their study conducted for the pharmaceuticals. So, the measurements of these parameters were carried out during one year sampling period in order to verify the pollution state of surface water samples. TCS is present in aqueous solution as two distinct chemical species, molecular and anionic (depending on pH) in rapid dynamic equilibrium within each other [31]. So, when the concern is the fate of TCS in aquatic systems pH is important to know, as the elimination mechanism of TCS depends highly on its form, anionic or molecular. It is predominantly in its neutral form at pH 7.0 but is predominantly in its ionized form at pH 8.5 [32]. Molecular TCS is more likely to be eliminated by adsorption onto the solid matrix, whereas anionic TCS is removed from the system by a flushing process [31]. Therefore, pH was also monitored in the water sources. Moreover, temperature was included as measured parameters as it would give an idea for climatic conditions together with the recorded hydrological occurrences, like precipitation in order to claim about the dilution and/or evaporation effect on the biocide levels. Temperature would also influence the biodegradation rate of biocides.

Studies have shown that TCS and free chlorine readily react to form several different by-products including chlorinated phenoxy-phenols, chlorinated phenols and THMs [33,34]. It has also been shown that these and other phenols can act as THM precursors when they come in contact with free chlorine [35]. So, THM and HAA are taken into consideration as an indicator for biocidal reduction and conversion in drinking water samples. As related, free chlorine concentration was also monitored.

2.6. Sampling and sample preparation

Sampling from each surface water source was conducted from May 2010 to May 2011. Samples were taken from the definite sites near the water pumping stations of reservoirs and were put into amber glass bottles (2.5 L) which were transported in closed, dark and cooled conditions to the laboratory. Sampling from IWTP and distribution network was also performed in May 2010 and May 2011. Samples were taken from inlet and outlet structures of IWTP during both sampling periods.

Biocides of TCS (being hydrophobic) and CHX (being both hydrophilic and hydrophobic) tend to stay in solid phase and stick on the surface of sampling bottle. Therefore, first of all, proper cleaning of the glassware, including the sample bottles, is extremely important for biocides analyses. After detergent (Alconox) washing, glassware was cleaned firstly with tap water and then with ultrapure water. Following the drying (150˚C for 1 h) and cooling, glasswares were rinsed with acetone and methanol. Moreover, all sampling glasswares were silanized using methanol (5 mL for each 1L sample) in order to prevent the adsorption of target biocides onto their inner surfaces or onto the matrix solids.

Samples were extracted using a solid-phase extraction (SPE) method, as soon as possible (within 48 h). Prior to extraction process, samples were filtered through the 0.7 micron glass fibre filter in order to eliminate the fouling of the cartridge by particles in samples. Oasis 3 cc HLB SPE cartridge was used as a solid-phase extraction cartridge as it was found very responsive to TCS and CHX. Extracted samples were stored at −10˚C and were analysed within a month.

SPE process was optimized with respect to cartridge type, volume, capacity and pH for the maximum recovery. Firstly, SPE cartridge was conditioned with 10 mL methanol by passing its own gravity. After this step, cartridge was equilibrated with 10 mL of pure water in a same way with conditioning step. Then, sample was loaded to the cartridge and was passed through the cartridge by vacuum. During sample loading step, the flow rate was adjusted to 10 mL/min. In conditioning, equilibrating and sample loading step, it was not let to go cartridge being dried. At the end of sample loading through the cartridge, cartridge was dried under vacuum completely for 15–20 min, prior to elution. The cartridge was eluted with 25 mL of methanol by letting to pass through the cartridge with the help of gravity; vacuum was not used during elution process. Target biocides were collected in 25 mL methanol at the end of the elution step. Then, nitrogen gas was used in order to dry the sample and separate the analyte from methanol or 50°C oven was used in order to evaporate the methanol and obtain target analyte. The final step of the extraction was the collection of the dried sample to the vial with 1 mL of methanol/water mixture (25% methanol, 75% pure water). Hence, 1 L of sample was concentrated 1000 times with 100% recovery. After collection of sample into 1 mL vial, the samples were ready for the LC-ES-MSMS measurements.

For THM/HAA and coliform analysis, samples from distribution network were collected separately in 300-mL glass bottles and 1 mL of 0.1 N sodium thiosulphate was added for 100 mL sample to eliminate any remaining residual chlorine and to stop further disinfection by product formation. Household taps were flushed for 15 min prior to sampling. Sample bottles were carefully filled just to overflowing for the prevention of passage of air bubbles into the bottles. The samples were stored at 4°C.

2.7. Analysis

Biocide concentrations were measured using a modified EPA 1694 method [36] in which a liquid chromatography with tandem mass spectrometry (LC-ES-MSMS) following SPE is applied. Agilent 6410B Triple Quadrupole MSMS was used and operated in negative ESI mode in conjunction with Agilent C-18 Capillary column. Optimization studies revealed the mobile phase for both of the compounds as 5 mM ammonium formate + 0.1% formic acid + methanol. Other conditions determined as optimum for TCS and CHX measurements are presented in Table 3. Signal to noise ratio was always greater than 10. Limit of detection (LoD) and limit of quantification (LoQ) values determined are 0.26 and 0.87 ng/L for TCS and 0.39 and 1.33 ng/L for CHX, respectively.

Table 3
Optimum conditions applied during HPLC-MSMS measurements

	TCS	CHX
Dwell time (ms)	150	150
Delta EMV	400	400
Capillary voltage (V)	3,000	3,000
Gas temperature (ºC)	300	350
Injection volume (µL)	30	30

Analyses were carried out with duplicate samples and three injections for each sample were made and the average of the measurements was reported.

THM and HAA quantification was carried out as described by [37]. Temperature, TDS and pH of samples were determined by on-site measurements using the calibrated Hach-equipment (Hach Sension 378). TOC of samples was measured by Shimadzu TOC device (TOC-5000A) according to SM 3510B [38]. Coliform analysis was performed using membrane filtration method according to SM 9222 B [38].

3. Results and discussion

3.1. Biocides in the surface waters

Monitoring study conducted for both general water quality parameters and biocides in the surface waters between May 2010 and May 2011 revealed the results presented in Table 4.

As can be seen from Table 4, in CR, pH values varied between 6.7 and 9.0, whereas its TDS content did not exhibit any significant change during the sampling period. There was an unexpected increase in TOC between November 2010 and February 2011. This could recall a possible illegal wastewater discharge(s) or transportation of natural organic matters (NOMs) from the drainage basin due to heavy raining during this time period. Nevertheless, the latter attribution seems more possible as this watercourse is a well protected one being currently used as a drinking water supply for the city of Ankara.

Regarding the biocides, TCS levels were higher than CHX during the sampling period, except May 2010 (Table 4), as the public usage of TCS is probably more widespread as compared with CHX. Indeed, for the samples after September 2010, concentration of CHX could not be measured exactly as the level of sample concentration was lower than LoQ value of LC/MSMS for CHX measurement (i.e. 1.33 ng/L). Relatively high CHX concentrations in May 2010 and

Table 4
Genaral water quality parameters and biocide levels in the surface waters of CR and KR

	pH		Temperature (℃)		TDS (mg/L)		TOC (mg/L)		TCS (ng/L)		CHX (ng/L)	
Sampling time	CR	KR	CR	KR	CR	KR	CR	KR	CR	KR	CR	KR
May’10	8.3	8.4	19.7	21.6	82	831	6.2	3.7	2.15	2.37	5.31	5.31
July’10	9.0	8.3	25.7	23.5	89.2	826	6.5	4.7	5.4	8.21	1.53	1.46
Sept.’10	8.8	8.5	21.8	20.8	100	834	6.3	4.7	4.44	16.47	<1.33	<1.33
Oct.’10	7.2	7.6	15.7	15.2	89	951	5.9	4.3	0.65	2.03	<1.33	<1.33
Nov.’10	8.3	7.7	10.2	12.4	99	1,035	8.8	5.9	3.61	5.00	<1.33	<1.33
Jan.’11	6.7	–	5.8	−1.0	91	1,100	10.8	4.3	0.86	2.92	<1.33	<1.33
Feb.’11	7.6	7.5	7.6	8.0	88	824	14.5	5.2	8.77	0.86	<1.33	<1.33
Mar.’11	7.5	7.8	9.3	10.7	85.7	847	6.3	5.7	5.45	11.3	<1.33	<1.33
Apr.’11	7.8	7.9	10.3	11.5	88.1	862	5.21	4.2	10.42	15.52	<1.33	<1.33
May’11	7.9	8.1	16.2	15.8	88.9	874	5.28	4.9	11.15	48.96	<1.33	<1.33

July 2010 as compared with other sampling months could be attributed to the hot weather conditions leading to higher degree of evaporation and hence, higher CHX levels. On the other hand, CHX concentration did not increase back in May 2011, probably due to relatively low temperature conditions and heavy rain experienced, unlike May 2010. The data obtained from the Turkish State Meteorological Institute (TSMI) supports this attribution as the region received a precipitation 50% higher than the normal during spring 2011 [39]. Nevertheless, the same trend was not observed for TCS. As can be seen from Table 4, highest TCS concentration was observed in May 2011 (being also high in April 2011), unlike CHX. The reason for this could be the possible excess public use of antimicrobials containing TCS, but not CHX, owing to the great public concern rose on the inflectional flu disease (H1N1) during those days. As a matter of fact, when TCS variation alone was examined, it was seen that during winter season, TCS concentrations were generally lower than that of summer and spring seasons, except February 2011. This observation could have arisen from evaporation of water from reservoir basin during summer period and heavy rain during winter period (except Feb 2011) as supported by TSMI (2012). In a study conducted by Ferguson et al. [30], the temperature was found to be one of the factors affecting the concentration of some pharmaceuticals with a negative correlation. They reported that temperature would be negatively correlated with total pharmaceutical concentration following biotic degradation potential, as temperature influences biodegradation rates of these compounds. However, in our study, such a correlation was not observed. Additionally, lower TCS values observed in October 2010 and January 2011 could be due to lower pH conditions (7.2 and 6.7, respectively), as TCS would be in molecular form and hence, could have been eliminated from water through its adsorption onto the solid matrix.

In an attempt to explore if wastewater discharge(s) is the reason for TCS increase, TCS and TOC values were compared. TOC content in water samples can be accepted as a good indicator for water quality. Therefore, higher TCS concentrations would be expected at higher TOC concentrations. In this respect, Fig. 2 illustrates the variation of TOC and TCS concentrations in CR during the sampling period from May 2010 to May 2011.

As seen from Fig. 2, in CR, the variations of TCS and TOC were generally in accordance except few cases. TCS concentration was high during winter time period due to higher consumption of antibacterial agents during this time period, as expected. However, for January 2011, TCS concentration indicated an abrupt decrease although TOC concentrations

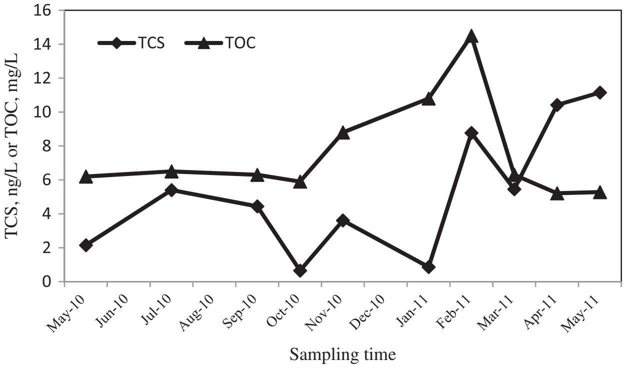


Fig. 2. TCS and TOC concentration variation in Çamlıdere reservoir.

continued to increase. The rainy days in winter might have been the reason of this decrease in TCS concentration due to the dilution effect. On the other hand, it seems that rain did not create dilution effect on TOC concentration, possibly due to transportation of high amount of NOMs from the basin. Moreover, for April 2011 and May 2011 samples, TCS and TOC concentrations indicated different trends with respect to each other and TOC concentrations decreased while TCS concentration was rising. This increase in TCS during April 2011 and May 2011 could be the result of evaporation due to hot weather conditions or possible occurrence of overturn in surface water during spring. Adsorbed TCS on the sediment layer could be mixed with upper part of the water body and so TCS concentration could arise. On the other hand, the decrease of TOC could arise from the uptake of TOC in water samples by micro-organisms/bacteria with increase in temperature, but not TCS. This might have been as a result of low biodegradability of TCS in aquatic environments.

In KR, higher pollutant concentrations are expected as compared with CR. Evidently, TDS concentration of KR was comparably higher than that of CR (Table 4). Nevertheless, this difference could be partly due to geological nature of the basin. TOC concentrations for both water sources did not exhibit a significant difference, indicating a similar NOMs entry to the courses.

Similar to CR case, TCS concentration in KR was always higher than CHX concentrations during the sampling period except May 2010 (Table 4). The concentration of CHX was generally so low in water samples, its concentration remained under the LoD and LoQ value of method and so it could not be measured exactly. However, TCS was detected during the whole sampling period and it was seen that TCS concentrations remained low during winter season as compared with spring and summer times. The reason for this could be the possible excess public use of antimicrobials containing TCS, but not CHX, owing to the great public concern rose on the inflectional flu disease (H1N1) during spring 2011. The relatively high concentration of TCS in spring and summer time might also arise from evaporation of water from reservoir during sunny days. However, other factors which could affect the TCS occurrence in water samples must be explored in order to determine the exact reason. In this respect, correlation between TCS and TOC was sought (Fig. 3). As seen from this figure, especially from March to May 2011 period, TCS trend was different than that of TOC. During this period, TOC concentration started to decrease while TCS concentration reached to its maximum level. This situation could have arisen from the overturn in aquatic environment during spring season, resulting in the TCS previously bound tightly to the bottom sediments to release to the overlying water.

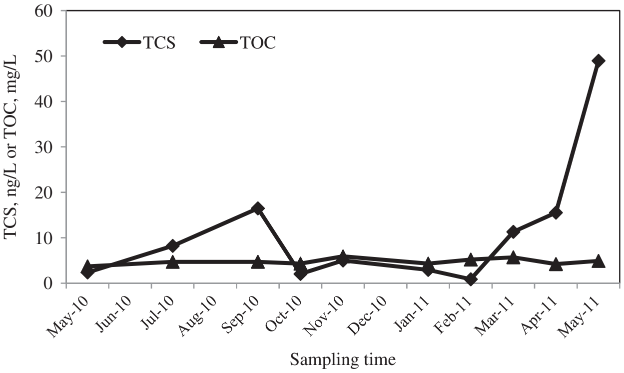


Fig. 3. TOC and TCS concentration variation in Kesikköprü reservoir.

When TCS concentrations in KR were assessed in relation to pH of water, it was clearly seen that TCS concentration is low when pH is low, with an exception in May 2010 (Table 4). The lowest TCS concentration (i.e. 0.86 ng/L) was measured in February 2011 where pH is also the lowest (i.e. 7.5). Like for CR, this could be attributed to the fact that at low pH condition TCS would be in molecular form and hence, could have been eliminated from water through its adsorption onto the solid matrix.

3.2. Biocides in the treatment plant

When raw water sources containing biocides are subjected to treatment in water treatment plants, their biocide content may experience reduction and/or conversion to other by-products, depending on the physicochemical process(es) applied in the water treatment plants. Accordingly, the effect of physiochemical treatment applied in IWTP on biocide levels in drinking water was evaluated.

Like for the surface water samples, biocide presenting the highest concentration at the inlet of the treatment plant was TCS. Chlorhexidine was present at level below LoQ. The main result is that TCS is completely removed from the drinking water treatment plant, as indicated in Table 5. These data are consistent with the fact that TCS is easily absorbable in the sludge. So, probable removal mechanism is the adsorption onto the alum sludge as it is hydrophobic and has a tendency to adsorb onto the sludge.

Regarding the removal of biocides from raw waters in the water treatment plants, other options could be adsorption, advanced oxidation or membrane

Table 5
Treatment performance of IWTP for biocides and other related quality parameters

	TCS (ng/L)		CHD (ng/L)		TOC (mg/L)		THM (μg/L)	HAA (μg/L)	Coliforms (/100 mL)	
	2010	2011	2010	2011	2010	2011	2010	2010	2010	2011
In	2.51	10.51	<1.33	<1.33	6.5	5.5	NA	NA	85	Too much
Out	<0.87	<0.87	<1.33	<1.33	3.9	3.1	8.5	10.7	0	0

Table 6
Biocides and other related quality parameters in the water distribution network

	TCS (ng/L)		CHD (ng/L)		TOC (mg/L)		Coliforms (/100 mL)		Residual chlorine (mg/L)		THM (μg/L)		HAA (μg/L)
District	2010	2011	2010	2011	2010	2011	2010	2011	2010	2011	2010	2011	2010
Ümitköy	–	<0.87	–	<1.33	–	3.9	–	0	–	0.67	–	49.9	–
Çukurambar	V	<0.87	–	<1.33	–	4.1	–	0	–	0.87	–	44.1	–
Bahçelievler	<0.87	<0.87	<1.33	<1.33	4.5	4.3	0	0	0.89	1.10	61.4	46.4	23.9
Batıkent	<0.87	<0.87	<1.33	<1.33	4.4	4.9	0	0	0.91	0.97	50.3	–	–
Birlik Mah.	–	<0.87	–	<1.33	–	4.5	–	0	–	0.49	–	56.3	–
K. Esat	–	<0.87	–	<1.33	–	4.4	–	0	–	1.35	–	38.8	–
Oran	<0.87	<0.87	<1.33	<1.33	4.4	3.6	0	0	0.99	1.18	47.3	7.0	20.1
Dikimevi	<0.87	<0.87	<1.33	<1.33	4.2	4.3	0	0	1.10	1.29	53.4	40.7	–
Yaşamkent	<0.87	<0.87	<1.33	<1.33	4.4	4.2	0	0	0.51	0.06	50.1	60.7	4.3
100.yıl	–	<0.87	–	<1.33	–	3.6	–	0	–	1.51	–	40.2	–
Gölbaşı	<0.87	<0.87	<1.33	<1.33	4.1	4.1	0	0	1.05	1.11	50.6	39.3	13.6
Eryaman	–	<0.87	–	<1.33	–	3.6	–	0	–	0.76	–	45.7	–
Sincan-Fatih	–	<0.87	–	<1.33	–	4.5	–	0	–	0.16	–	53.2	–
Ayrancı	–	<0.87–	–	<1.33	–	4.7	–	0	–	0.45	–	55.3	–
Anıttepe	–	<0.87	–	<1.33	–	3.0	–	0	–	0.09	–	51.0	–
Demetevler	<0.87	–	<1.33	–	3.9	–	0	–	1.12	–	8.5	–	10.7
Etlik	<0.87	–	<1.33	–	4.4	–	0	–	0.09	–	39.1	–	27.5
Yenimahalle	<0.87	–	<1.33	–	4.2	–	0	–	1.11	–	54.3	–	25.2
Örnek mah.	<0.87	–	<1.33	–	4.7	–	0	–	0.87	–	43.5	–	16.5

processes [40–42]. For example, several studies have been published in the literature indicating considerably high TCS removals, over 99% in ozonation [43,44] and 87% in membrane filtration [42]. However, adsorption of TCS onto the experimental systems utilized owing to its quite high hydrophobicity is an important issue to be considered when evaluating the results [45]. Moreover, possible by-products with ozonation application need to be carefully assessed [46]. In addition, these processes are costly. However, considering the promising results obtained in a conventional water treatment plant (as presented in Table 5), there seems, luckily, no need to apply these costly and advanced treatment methods.

3.3. Biocides in the distribution system

In an attempt to assess the biocide levels throughout the water distribution system of Ankara, samples were collected and analysed for their biocide contents as well as for TOC, coliform, residual chlorine, THM and HAA contents. It was also attempted to see if any further biocidal reduction/conversion occurs due to intermediate chlorination applied within the distribution system. Results obtained are present in Table 6. As seen from this table, biocide levels were all below the detection limits. This is in accordance with the result for the water treatment plant outlet for which biocides were also below the LoQ.

Table 7
Summary of biocides levels (ng/l) in drinking water system of Ankara

Water source	TCS	CHX
Çamlıdere reservoir	0.65–11.15	<1.33–5.31
Kesikköprü reservoir	0.86–48.96	<1.33–5.31
IWTP	2.51–10.51 (inlet) <0.87 (outlet)	<1.33 (inlet and outlet)
Distribution network	<0.87	<1.33

Results belonging to the possible biocidal by-products, THM and HAA did not confirm the contribution of biocides to their formation since these by-products are also formed due to reaction between chlorine and NOM. Because biocide levels were detected as very low, contribution of biocides to their formation was not determinable.

4. Conclusion

Monitoring study conducted in two surface water sources near Ankara revealed that TCS and CHX levels lied within ranges given in Table 7. Higher TCS levels were recorded in KR than in CR, while CHX remained more or less same and comparably low. Monthly variation of biocides levels could be attributed to the differences in hydrological and meteorological conditions in the region, as well as other factors governing the fate of these biocides in the water courses. Removal of TCS in the water treatment plant was evident. Biocides in the water distribution system were all found below the detectable levels.

Acknowledgement

Work was supported by EC project KBBE-227258 (BIOHYPO).

References

[1] S. Onodera, M. Takahashi, M. Ogawa, S. Suzuki, Mutagencity of polychlorophenoxyphenols (predioxins) and their photo-degradation products in aqueous solution, Jpn. J. Toxicol. Environ. Health 41 (1995) 212–219.

[2] D.E. Latch, J.L. Packer, W.A. Arnold, K. McNeill, Photochemical conversion of triclosan to 2,8-dichlorodibenzo-p-dioxin in aqueous solution, J. Photochem. Photobiol. A 158 (2003) 63–66.

[3] N. Tatarazako, H. Ishibashi, K. Teshima, K. Kishi, K. Arizono, Effects of triclosan on various aquatic organisms, Environ. Sci. 11(2) (2004) 133–140.

[4] K. Inaba, T. Doi, N. Isobe, Formation of bromo-substituted triclosan during chlorination by chlorine in the presence of trace levels of bromide, Water Res. 40 (2006) 2931–2937.

[5] H. Singer, S. Müller, C. Tixier, L. Pillonel, Triclosan: Occurrence and fate of a widely used biocide in the aquatic environment: Field measurements in wastewater treatment plants, surface waters, and lake sediments, Environ. Sci. Technol. 36 (2002) 4998–5004.

[6] R.U. Halden, D.H. Paull, Co-occurrence of triclocarban and triclosan in US water resources, Environ. Sci. Technol. 39 (2005) 1420–1426.

[7] A.S. Stasinakis, A.V. Petalas, D. Mamais, N.S. Thomaidis, G. Gatidou, T.D. Lekkas, Investigation of triclosan fate and toxicity in continuous flow activated sludge systems, Chemosphere 68 (2007) 375–381.

[8] J.L. Wu, N.P. Lam, D. Martens, A. Kettrup, Z. Cai, Triclosan determination in water related to wastewater treatment, Talanta 72(5) (2007) 1650–1654.

[9] T. Heberer, Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: A review of recent research data, Toxicol. Lett. 131 (2002) 5–17.

[10] L. Samsoe-Petersen, M. Winther-Nielsen, T. Madsen, Fate and Effects of Triclosan, Danish Environmental Protection Agency, Project Number 861, Copenhagen, Denmark, 2003.

[11] D.C. McAvoy, B. Schatowitz, M. Jacob, A. Hauk, W. Eckhoff, Measurement of triclosan in wastewater treatment systems, Environ. Toxicol. Chem 21 (2002) 1323–1329.

[12] K. Bester, Triclosan in sewage treatment process- balances and monitoring data, Water Res. 37(16) (2003) 3891–3896.

[13] G.G. Ying, R.S. Kookana, Triclosan in wastewaters and biosolids from Australian wastewater treatment plants, Environ. Int. 33 (2007) 199–205.

[14] S. Weigel, U. Berger, E. Jensen, R. Kallenborn, T. Hilde, H. Huhnerfuss, Determination of selected pharmaceuticals and caffeine in sewage and seawater from tromso/norway with emphasis on ibuprofen and its metabolites, Chemosphere 56 (2004) 583–592.

[15] G.A. Jungclaus, V. Lopez-Avila, R.A. Hites, Organic compounds in an industrial wastewater: A case study of their environmental impact, Environ. Sci. Technol. 12 (1978) 88–97.

[16] A. Lopez-Avila, R.A. Hites, Organic compounds in an industrial wastewater their transport into sediments, Environ. Sci. Technol. 14 (1980) 1382–1390.

[17] T. Okumura, Y. Nishikawa, Gas chromatography—mass spectrometry determination of triclosans in water, sediment and fish samples via methylation with diazomethane, Anal. Chim. Acta 325 (1996) 175–184.

[18] A. Lindström, I.J. Buerge, T. Poiger, P.A. Bergqvist, M.D. Müller, H.R. Buser, Occurrence and environmental

behavior of the bactericide triclosan and its methyl derivative in surface waters and in wastewater, Environ. Sci. Technol. 36(11) (2002) 2322–2329.
[19] A.P. Van Wezel, T. Jager, Comparison of two screening level risk assessment approaches for six disinfectants and pharmaceuticals, Chemosphere 47 (2002) 1113–1128.
[20] D. Sabaliunas, S.F. Webb, A. Hauk, M. Jacob, W.S. Eckhoff, Environmental fate of triclosan in the river aire basin, UK, Water Res. 37(13) (2003) 3145–3154.
[21] T. Poiger, A. Lindstrom, I.J. Buerge, H. Buser, P.A. Bergqvist, M.D. Muller, Occurrence and environmental behaviour of the bactericide triclosan and it s methyl derivative in surface waters and in wastewater, Chimia 57(1–2) (2003) 26–29.
[22] I. Nishi, T. Kawakami, S. Onodera, Monitoring of TCS in the surface water of the tone canal, Japan, Bull. Environ. Contam. Toxicol. 80 (2008) 163–166.
[23] Z. Xie, R. Ebinghaus, G. Flöser, A. Caba, W. Ruck, Occurrence and distribution of triclosan in the German Bight (North Sea), Environ. Pollut. 156 (2008) 1190–1195.
[24] J.J. Dynes, J.R. Lawrence, D.R. Korber, D.W. Swerhone, G.G. Leppard, A.P. Hitchcock, Quantitative mapping of chlorhexidine in natural river biofilms, Sci. Total Environ. 369 (2006) 369–383.
[25] J.A. Castillo, A. Pinazo, J. Carilla, M.R. Infante, M.A. Alsina, I. Haro, P. Clapés, Interaction of antimicrobial arginine-based cationic surfactants with liposomes and lipid monolayers, Langmuir 20(8) (2004) 3379–3387.
[26] E. Akaho, Y. Fukumori, Studies of adsorption characteristics and mechanism of adsorption of chlorhexidine mainly by Carbon Black, J. Pharm. Sci. 90 (2001) 1288–1297.
[27] U. Asir, S. Pulatsu, Estimation of the nitrogen-phosphorus load caused by rainbow trout (Oncorhynchus mykiss Walbaum, 1792) cage-culture farms in Kesikköprü Dam Lake: A comparison of pelleted and extruded feed, Turk J. Vet. Anim. Sci. 32(6) (2008) 417–422.
[28] SHW, Studies on the Biology, Ecology and Control Methods of Zebra Mussels Causing Problems in Hydroelectric Power Plants' of Turkey, Ministry of Energy and Natural Resources, State Hydraulic Works General Directorate, Ankara, 2005.
[29] S.C. Ayaz, Ö. Aktaş, S. Dağlı, C. Aydöner, E.A. Atasoy Aytış, L. Akça, Pollution loads and surface water quality in the Kızılırmak Basin, Turkey, Desal. Water Treat. 51 (2013) 1533–1542.
[30] P.J. Ferguson, M.J. Bernot, J.C. Doll, T.E. Lauer, Detection of pharmaceuticals and personal care products (PPCPs) in near-shore habitats of southern Lake Michigan, Sci. Total Environ. 458–460 (2013) 187–196.
[31] C. Tixier, H. Singer, S. Canonica, S. Müller, Phototransformation of triclosan in surface waters: A relavent elimination process for this widely used biocide-laboratory studies, field measurements, and modeling, Environ. Sci. Technol. 36 (2002) 3482–3489.
[32] D.R. Orvos, D.J. Versteeg, J. Inauen, M. Capdevielle, A. Rothenstein, V. Cunningham, Aquatic toxicity of triclosan, Environ. Toxicol. Chem. 21(7) (2002) 1338–1349.
[33] P. Canosa, S. Morales, I. Rodríguez, E. Rubí, R. Cela, M. Gómez, Aquatic degradation of triclosan and formation of toxic chlorophenols in presence of low concentrations of free chlorine, Anal. Bioanal. Chem. 383 (2005) 1119–1126.
[34] K.L. Rule, V.R. Ebbett, P.J. Vikesland, Formation of chloroform and chlorinated organics by free-chlorine-mediated oxidation of triclosan, Environ. Sci. Technol. 39 (2005) 3176–3185.
[35] H. Gallard, U. von Gunten, Chlorination of phenols: Kinetics and formation of chloroform, Environ. Sci. Technol. 36 (2002) 884–890.
[36] EPA Method 1694, Pharmaceuticals, personal care products in water, soil, sediment, and biosolids by HPLC/MS/MS, EPA-821-R-08-002, 2007.
[37] N. Ates, S.S. Kaplan, E. Sahinkaya, M. Kitis, F.B. Dilek, U. Yetis, Occurrence of disinfection by-products in low DOC surface waters in Turkey, J. Hazard. Mater. 142 (2007) 526–534.
[38] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, twentieth ed., American Public Health Association, Washington, DC, 1998.
[39] TSMI, Climate Assessment in Turkey 2011, Turkish State Meteorological İnstitute (TSMI), Ankara, 2012.
[40] I. Arslan-Alaton, Degradation of a commercial textile biocide with advanced oxidation processes and ozone, J. Environ. Manage. 82 (2007) 145–154.
[41] M.C. Dodd, H.P.E. Kohler, U. von Gunten, Oxidation of antibacterial compounds by ozone and hydroxyl radical: elimination of biological activity during aqueous ozonation processes, Environ. Sci. Technol. 43 (2009) 2498–2504.
[42] Y. Yoon, P. Westerhoff, S.A. Synder, E.C. Wert, Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products, J. Membr. Sci. 270 (2006) 88–100.
[43] L. Hernandes-Leal, H. Temming, G. Zeeman, C.J.N. Buisman, Removal of micropollutants from aerobically treated grey water via ozone and activated carbon, Water Res. 45 (2011) 2887–2896.
[44] S. Suarez, M.D. Dodd, F. Omil, U. Gunten, Kinetics of triclosan oxidation by aqueous ozone and consequent loss of antibacterial activity: Relevance to municipal wastewater ozonation, Water Res. 41 (2007) 2481–2490.
[45] A. Koc, K.B. Orhon, A. Ogutverici, L. Yilmaz, L. Furi, M.R. Oggioni, F.B.U. Dilek Yetis, Is adsorption an artifact in experimentation with Triclosan? Desal. Wat. Treat. (in press). doi: 10.1080/19443994.2013.831780.
[46] X. Chen, J. Richard, Y. Liu, E. Dopp, J. Tuerk, K. Bester, Ozonation products of triclosan in advanced wastewater treatment, Water Res. 46 (2012) 2247–2256.