

# Enhanced Removal of Micropollutants from Groundwater, Using pH Modification Coupled with Photolysis

Yaal Lester · Hadas Mamane · Dror Avisar

Received: 10 May 2011 / Accepted: 21 September 2011 / Published online: 18 October 2011  
© Springer Science+Business Media B.V. 2011

**Abstract** Direct ultraviolet (UV) photolysis coupled with modification of solution pH was explored as a method for the removal of organic micropollutants from groundwater. Photodegradation rates of most of the investigated compounds were pH dependent, however, its correlation with photodegradation rate varied among compounds. The potential of the pH modification during photolysis was determined for removal of a mixture of two pharmaceuticals sulfamethoxazole (SMX) and triclosan (TCS) in groundwater. The treatment included initial photolysis of the mixture at the optimal pH for TCS (i.e., 7.5–7.9), followed by pH modification to the optimal pH for SMX (i.e., 5), prior to a second irradiation period. The described procedure dramatically increased the

removal efficiency (up to threefold) of the treated mixture compared to UV treatment at constant pH.

**Keywords** Micropollutant · pH modification · Photodegradation · Polychromatic UV · Water treatment

## 1 Introduction

Numerous new and improved therapeutic drugs are being developed and consumed each year, and these molecules eventually find their way into the local waterways (Kummerer 2009). Unfortunately, the enormous increase in drug consumption worldwide has not been accompanied by substantial parallel developments in water-treatment technology, aimed at preventing these substances from reaching the environment. Consequently, some of these contaminants are being continuously discharged to aquatic environments through water used for irrigation. This may result in contamination of the groundwater, the main source of drinking water (Chefetz et al. 2008). In fact, pharmaceutical residues and other micropollutants have already been detected in groundwater wells under agricultural fields that have been continuously irrigated with wastewater effluents in Israel (Avisar et al. 2009), Europe (Hirsch et al. 1999; Sacher et al. 2001) and the USA (Batt et al. 2006; Karnjanapiboonwong et al. 2011).

---

Y. Lester · D. Avisar  
The Hydrochemistry Laboratory, Geography and the Environment, Tel Aviv University,  
Tel Aviv 69978, Israel

Y. Lester · H. Mamane  
School of Mechanical Engineering, Faculty of Engineering,  
Tel Aviv University,  
Tel Aviv 69978, Israel

D. Avisar (✉)  
Hydrochemistry, Geography and the Environment,  
Tel Aviv University,  
Tel Aviv 69978, Israel  
e-mail: droravi@post.tau.ac.il

Ultraviolet (UV) light is commonly used for the disinfection of wastewater and drinking water. UV radiation can also be used to chemically degrade or break down micro/nanopollutants via photolysis (photodegradation), a process in which a chemical species undergoes a chemical change as the result of the absorption of photons (Legrini et al. 1993). Several studies have shown that UV light can efficiently degrade various contaminant compounds, such as the anti-inflammatory agents ketoprofen (Pereira et al. 2007; Kim et al. 2009), diclofenac (Felis and Miksch 2009), and *n*-nitrosodimethylamine (NDMA; Stefan and Bolton 2002). However, the removal of organic micro/nanocontaminants by direct photolysis is only effective when the absorption spectrum of the water contaminant overlaps with the emission spectrum of the UV lamp, and when the quantum yield of the photochemical process is reasonably large.

pH is known to impact the photolysis kinetics of many organic chemicals. Canonica et al. (2008), using low- and medium-pressure mercury arc UV lamps, found the phototransformation rates of 17 $\alpha$ -ethinylestradiol, diclofenac and sulfamethoxazole to be highly pH dependent. Lee et al. (2005) showed that pH strongly influences both photolysis rate and photoproduct partitioning of NDMA, using a low-pressure UV lamp. Other researchers have demonstrated the influence of pH on the photoreactivity of different classes of antibiotics such as sulfonamide (Boreen et al. 2004; Lester et al. 2008) and fluoroquinolone (Sortino et al. 1998; Fasani et al. 1999; Mella et al. 2001), as well as other organic water pollutants (Lam et al. 2003; Shemer et al. 2005). Thus pH impacts the degradation kinetics of many organic pollutants, and in most cases this effect is related to the pollutant's characteristics and in particular to its ionic form and acid dissociation constant (pKa) values (Avisar et al. 2010).

The main goal of this study was to examine the combination of direct UV photolysis and artificial pH modification of the treated water (during the treatment itself) as a potential treatment technology for groundwater remediation. The treatment is aimed at removing target pollutants as a single compound and in a mixture, at the optimum pH value for each compound. The pH modification may affect the "electronic" structure of the target water contaminant, thereby increasing the potential

for its photolytic degradation when irradiated at the relevant wavelength.

## 2 Material and Methods

### 2.1 Selected Compounds

Twelve organic compounds were selected for the study based on their environmental relevance (Table 1). All compounds were purchased from Sigma-Aldrich. Stock solutions (100 mg L<sup>-1</sup>) were prepared in water or methanol according to the compound's solubility. Other high-performance liquid chromatography (HPLC)-grade solvents and chemicals (acetonitrile, methanol, formic acid, sodium hydroxide, and water) were purchased from Bio-Lab Ltd. (Jerusalem, Israel).

### 2.2 Experimental Setup

All irradiation experiments were conducted using polychromatic UV light. Specifically, photolysis was carried out in a bench-scale collimated beam apparatus using a 0.45 kW polychromatic medium-pressure (MP) Hg vapor lamp (Ace-Hanovia lamp, Ace Glass Inc., Vineland, NJ, USA). The treated solution (100 mL) was spiked with a known concentration of the selected pharmaceuticals, and then irradiated with constant gentle stirring. Samples were withdrawn at appropriate intervals for chromatographic analysis. UV dose (fluence) was determined by multiplying the average irradiance of the UV lamp between 200 and 300 nm by exposure time. The average irradiance was calculated using a calibrated spectroradiometer (spectral range 200–390 nm; USB4000, Ocean Optics, Dunedin, FL, USA) placed in the same position as the irradiated solution, using a procedure adapted from Bolton and Linden (2003). The UV absorption coefficient of the treated solutions at different pHs was measured in a UV-vis spectrophotometer (Varian, Cary 100BIO, Victoria, Australia) and the molar absorption coefficients for the target compounds were determined.

### 2.3 Experimental Procedure

#### 2.3.1 Optimal pH Determination

The optimal pH values for the photodegradation of each target contaminant were determined by testing

**Table 1** Selected target contaminants

Class	Compounds
Antibiotics	Enrofloxacin (ENR), norfloxacin (NOR), trimethoprim (TMP), tetracycline (TC), amoxicillin (AMX) and sulfamethoxazole (SMX)
Anti-epileptic drug	Carbamazepine (CBZ)
Anti-inflammatory drugs	Ketorolac (KTR) and diclofenac (DCF)
Antimicrobial agent	Triclosan (TCS)
Water pollutants	Acridine (ACR), <i>n</i> -nitrosodimethylamine (NDMA)

the photodegradation rates of each contaminant separately, at different pH values. Experiments were conducted in phosphate buffered saline (PBS, 5 mM), and pH was adjusted by adding formic acid or sodium hydroxide at the appropriate volume and concentration. Once the pH of the buffer containing the contaminant (at an initial concentration of 1 mg L<sup>-1</sup>) was adjusted, the sample was subjected to irradiation to determine the pH value that leads to the maximal photodegradation rate. It should be noted that the initial concentration of the pharmaceuticals was higher than their concentration in aquatic environments; however, it was low enough to minimize the compound's contribution to the total solution absorbance, such that first-order photodegradation rates were obtained for all compounds.

### 2.3.2 Groundwater Experiments

The main goal of the second part of this study was to determine the potential of UV photodegradation combined with artificial pH modification for the removal of a mixture of two pharmaceuticals, i.e., sulfamethoxazole (SMX) and triclosan (TCS), from groundwater, using their determined optimal pH values.

Groundwater samples were taken from three different aquifer basins in Israel: GW-1 and GW-3 were from a local carbonate aquifer in the upper Galilee (eastern slopes) and the major carbonate aquifer in the eastern slopes of the Judea Mountain Ridge in central Israel, respectively, both representative of the Judea group. GW-2 was taken from a local aquifer in the Golan Heights, which is composed of interbedded carbonate and basalt layers. The groundwater samples were spiked with the two target contaminant (initial concentration of 0.5 mg L<sup>-1</sup> for each compound), adjusted to their optimal pH value (as determined in Section 2.3.1), and then subjected to

UV irradiation (as determined in Section 2.2). The general chemical composition (major ions) of the groundwater samples used in this study is presented in Table 2.

## 2.4 Analytical Methods

### 2.4.1 Chromatographic Analysis

The target compounds were detected and quantified by HPLC (HPLC-Agilent 1,100 series; ACE- RP C18 column 2.5×250 mm) equipped with a UV diode array detector and a mass spectrometer (MS, Finnigan LCQ). The HPLC consisted of a microvacuum degasser, a binary pump, and a thermostatic column compartment. The flow rate was 0.5 mL min<sup>-1</sup> and the injected volume was 100 μL. The flow from the HPLC was passed through a split connector at 60 μL min<sup>-1</sup> of effluent introduced into the MS interface. The MS was used in positive electrospray ionization mode, where ions in the range of 70–500 m/z<sup>-1</sup> were registered in the conventional scanning mode.

### 2.4.2 Data Analysis

The degradation kinetics were expressed as a natural logarithm of the ratio of the concentration ( $C_H$ )

**Table 2** General chemical composition of the three groundwater types

	pH	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	Ca <sup>++</sup>	Mg <sup>++</sup>	NO <sub>3</sub> <sup>-</sup>	Na <sup>+</sup>	SO <sub>4</sub> <sup>-</sup>
		(mg L <sup>-1</sup> )						
GW-1	7.5	19	260	70	16	17	9	7
GW-2	7.8	24	198	26	18	15	32	6
GW-3	7.9	80	236	62	31	33	46	28

remaining following a UV dose  $H$  ( $\text{mJ cm}^{-2}$ ) to initial concentration ( $C_0$ ; Eq. 1).

$$\ln \frac{C_H}{C_0} = -kH \quad (1)$$

The data were fitted using a linear regression approach resulting in pseudo-first-order reaction kinetics which reflected the difference in photo-degradation between samples. The UV dose-based degradation rate constant  $k$  ( $\text{cm}^2 \text{mJ}^{-1}$ ) was calculated as the negative slope obtained when the degradation was plotted logarithmically. The UV dose required for 90% degradation of the target contaminants was used as a comparative parameter between compounds and between pH values, to emphasize the improved energy consumption of the degradation process due to pH modification. The UV dose required for 90% degradation was calculated using the obtained value for  $k$ , by inserting the appropriate numbers:

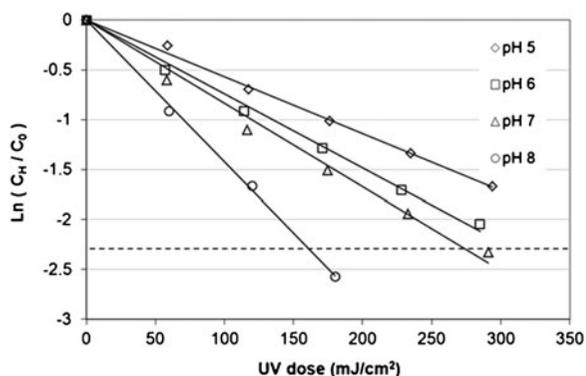
$$\ln \frac{[10\%]}{[100\%]} = -2.3 = -kH \quad (2)$$

### 3 Results and Discussion

#### 3.1 Optimal pH Determination

To better understand the effect of pH variations on photodegradation rate of pharmaceuticals and other organic micropollutants, several photodegradation tests were conducted on the selected compounds at different pH values. The pH values were in the common environmental range of 5–8. Degradation rates at the different pH values are represented in Fig. 1, which shows the photodegradation of TCS (in PBS) plotted against UV dose.

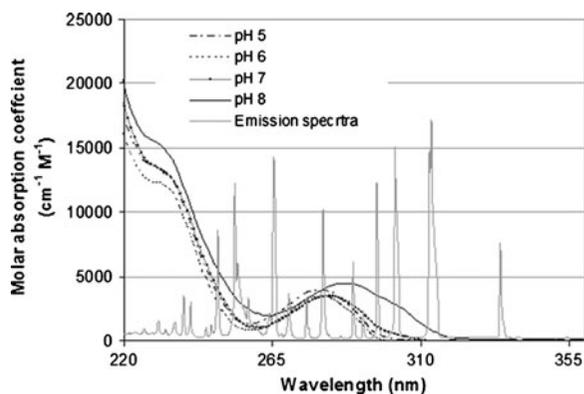
pH strongly affected the rate of direct TCS photodegradation: lowering the pH of the UV-irradiated solution from 8 to 5 resulted in a significant decrease in the pollutant's degradation rate (Fig. 1); the UV dose required for 90% removal of TCS was above  $400 \text{ mJ cm}^{-2}$  at pH 5 and  $162 \text{ mJ cm}^{-2}$  at pH 8. The pKa of TCS is approximately 7.9 (Wong-Wah-Chung et al. 2007), and there may therefore be a relation between the acid–base speciation of the compound and its photodegradation rate at different pH values.



**Fig. 1** UV photodegradation of TCS ( $1 \text{ mg L}^{-1}$ ) in PBS ( $5 \text{ mM}$ ) as a function of UV dose, at different pH values (5, 6, 7, and 8), obtained by MP collimated beam apparatus. The dashed line represents 90% degradation

Key parameters in evaluating the rate of a photochemical reaction are the molar absorption coefficient of the compound and its overlap with the emission spectra of the UV lamp (together with the compound's quantum yield). These parameters quantify the light absorbance of a compound at each wavelength. pH dependence of the selected compounds' molar absorption coefficients was examined. Figure 2 illustrates the molar absorption coefficients of TCS at different pH values in the range of 5–8, as well as the emission spectra of the UV lamp. TCS absorbed light in the UV range at all examined pH values. Slight differences in absorbance peaks at around 278 nm could be seen at pH values of 5–7, whereas at pH 8, its absorbance peak was significantly shifted to the right, at 288 nm. Moreover, the peak at pH 8 was higher ( $4,410 \text{ cm}^{-1} \text{ M}^{-1}$ ) than those at pH 5, 6, and 7 ( $4,050$ ,  $3,480$ , and  $3,500 \text{ cm}^{-1} \text{ M}^{-1}$ , respectively). The apparent shift in the molar absorption coefficients of TSC between pH values (with a clear relation to its pKa) and consequently, the change in the overlap of the compound's absorption coefficients with the emission spectra of the UV lamp, could potentially explain the differences in the photodegradation kinetics of this compound at different pH values.

Similarly, Wong-Wah-Chung et al. (2007) found that TCS is more photodegradable at high pH (i.e., 11.8) than at low pH (i.e., 5.6), using UV light at different wavelengths. Moreover, the molar absorption coefficient of TCS at pH 5.5 peaked at 280 nm with a value of approximately  $4,200 \text{ cm}^{-1} \text{ M}^{-1}$ , while



**Fig. 2** Molar absorption coefficients of TCS at various pH values, demonstrated with the emission spectra of the polychromatic UV lamp

at pH 11.8, a maximum value of  $8,300 \text{ cm}^{-1} \text{ M}^{-1}$  appeared at 291 nm. Other studies also confirm the pH dependence of the TCS molar absorption coefficient and photostability (e.g., Mezcuca et al. 2004).

The UV doses required for 90% removal and the molar absorption coefficient peaks, for the studied compounds (in PBS) at different pH values are presented in Table 3. All of the removal experiments were duplicated and relative standard deviations were less than 10% in all cases. UV dose was calculated for wavelengths between 200 and 300 nm, as these are commonly used in MP UV treatments (e.g., Bolton and Linden 2003). It should be noted, however, that various compounds absorb light at wavelengths above 300 nm (e.g., ENR), and these wavelengths may influence their photolysis rate. For most of the examined compounds, the UV dose required to achieve 90% removal was strongly dependent on the pH of the treated solution (with the exception of NDMA), and could often be related to the compound's pKa value. The extent of the pH dependency and its correlation (i.e., positive or negative) with removal rate by irradiation varied between compounds. For example, increasing the pH of the treated solution from 5 to 8 significantly reduced the UV dose required for 90% removal of NOR and ENR, from 3,286 and 2,091  $\text{mJ cm}^{-2}$  to 319 and 852  $\text{mJ cm}^{-2}$ , respectively. For SMX, the opposite trend was observed: changing the pH of the buffer from 5 to 8 increased the UV dose required to achieve 90% removal (from 173 to 676  $\text{mJ cm}^{-2}$ ). Thus, by optimizing the pH of the treated solution, markedly

lower UV doses can be exploited to achieve the same log removal of a target compound.

In addition, changes in molar absorption coefficient, due to pH modifications, were observed for most compounds (Table 3), and may provide a partial explanation for the changes in their degradation rates at different pH values. However, various compounds showed significant changes in their photodegradability due to pH modification with no associated changes in their molar absorption coefficient (e.g., CBZ). Therefore, various mechanisms may be involved in the observed changes in the kinetics of the UV photodegradation of each compound by pH modification (e.g., changes in quantum yield).

It is important to note that even though the photolysis rates of several of the examined compounds were strongly pH dependent, direct photolysis was still ineffective for their degradation: UV doses above 6,765 and 10,474  $\text{mJ cm}^{-2}$  were required for 90% removal of CBZ and ACR, respectively (at their optimal pH value).

### 3.2 Groundwater Experiments

The removal of SMX and TCS from groundwater is of particular interest, since TCS has been identified by the EU water framework directive priority substance list (together with diclofenac, ibuprofen, and clofibric acid) as a future emerging priority candidate of particular environmental concern due to its wide usage (as cited by Ellis 2006); while SMX is one of the most commonly detected antibiotics worldwide (e.g., Sacher et al. 2001; Barnes et al. 2008). Figure 3 demonstrates the UV dose-based photodegradation rate constants of the two pharmaceuticals (measured separately) in PBS at various pH values. SMX and TCS photolysis rates both exhibited strong pH dependency, but with opposite effects: increasing solution pH from 5 to 8 led to a higher TCS degradation rate and lower SMX degradation rate. Accordingly, the optimal pH values to achieve the highest photodegradation rate for TCS and SMX were 8 and 5, respectively.

The following treatment of groundwater containing TCS and SMX in a mixture was therefore proposed: (a) irradiation of the mixed solution at the groundwater's original pH (i.e., 7.5–7.9) for a predetermined optimal irradiation time (explained below), to maximize TCS degradation, and (b) modification of the

**Table 3** UV dose required for 90% removal, and molar absorption coefficient peaks, of the studied compounds (in PBS) at different pH values

Compounds	Relevant pKa	UV dose for 90% removal (mJ cm <sup>-2</sup> ) (molar absorption coefficient peak, cm <sup>-1</sup> M <sup>-1</sup> ; wavelength, nm)			
		pH 5	pH 6	pH 7	pH 8
TCS	7.9	403 (4,050; 279)	311 (3,480; 280)	274 (3,500; 282)	162 (4,410; 288)
NOR	6.3, 8.7	3,286 (40,445; 277) (11,879; 314)	1,533 (38,079; 275) (11,753; 319)	523 (36,771; 272) (13,191; 323)	319 (38,265; 272) (15,062; 324)
ENR	5.94	2,091 (38,194; 277) (11,512; 316)	1,278 (36,532; 276) (11,361; 316)	697 (32,844; 271) (12,615; 323)	852 (32,702; 271) (13,041; 323)
SMX	5.7	173 (17,234; 264)	338 (19,259; 259)	605 (19,615; 257)	676 (16,324; 256)
TMP	6.6	11,500 (6,240; 272)	11,500 (5,622; 276)	2,875 (5,312; 278)	1,437 (6,265; 287)
KTR	3.5	2,091 (7,031; 249) (20,284; 322)	1,917 (6,519; 249) (20,073; 323)	1,278 (6,678; 249) (20,177; 323)	605 (6,324; 246) (19,230; 322)
CBZ	13.9	17,692 (11,227; 285)	17,695 (11,334; 285)	10,952 (11,755; 285)	6,765 (11,939; 285)
ACR	5.5	38,333 (53,497; 255)	23,000 (435,420; 249)	14,375 (438,824; 249)	10,474 (474,354; 249)
AMX	6.9	2,091 (9,531; 229) (1,414; 272)	2,091 (9,805; 228) (1,125; 273)	1,278 (9,720; 227) (1,241; 273)	1,278 (9,819; 227) (1,696; 273)
TC	4.5, 7.3	5,750 (14,525; 275) (14,450; 358)	1,437 (14,898; 276) (14,918; 357)	767 (14,854; 275) (15,131; 360)	460 (14,848; 271) (15,879; 367)
DCF	4.0	207 (9,620; 275)	198 (10,342; 276)	192 (10,164; 276)	165 (10,328; 276)
NDMA		622 (7,714; 227)	621 (7,709; 227)	610 (7,679; 227)	609 (7,540; 228)

groundwater pH to a value of 5, followed by an additional irradiation period, to accelerate the degradation of SMX. The mixture was considered 90% removed when the most slowly degraded compound in the mixture was 90% removed.

The pH modification point was determined using linear programming (LP) which allows optimizing the treatment to achieve maximum removal of the mixture at minimum UV dose (or irradiation time). The LP goal was to minimize the objective function as follows:

Minimize:

$$H_1 + H_2 \quad (3)$$

Subject to constraints:

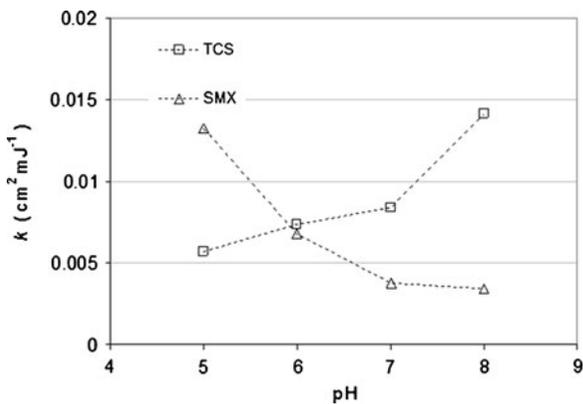
$$-k_1 \times H_1 - k_2 \times H_2 \leq \text{Ln} \left( \frac{10\%}{100\%} \right) \quad (4)$$

$$-k'_1 \times H_1 - k'_2 \times H_2 \leq \text{Ln} \left( \frac{10\%}{100\%} \right) \quad (5)$$

where,  $H_1$  and  $H_2$  are the UV dose applied (mJ cm<sup>-2</sup>) from time 0 to pH modification point and from the pH modification point to at least 90% removal of the mixture, respectively;  $k_1$  and  $k_2$  are the dose-based photodegradation rate constants of SMX at pH~7.5–7.9 and pH 5, respectively, measured during preliminary control irradiation tests on a groundwater mixture of TCS and SMX under constant pH;  $k'_1$  and  $k'_2$  are the degradation rate constants of TCS under the same conditions. These dose-based rate constants for TCS and SMX at the groundwater's original pH (7.5–7.9) and at the modified pH value of 5 were obtained using data in Fig. 4a.

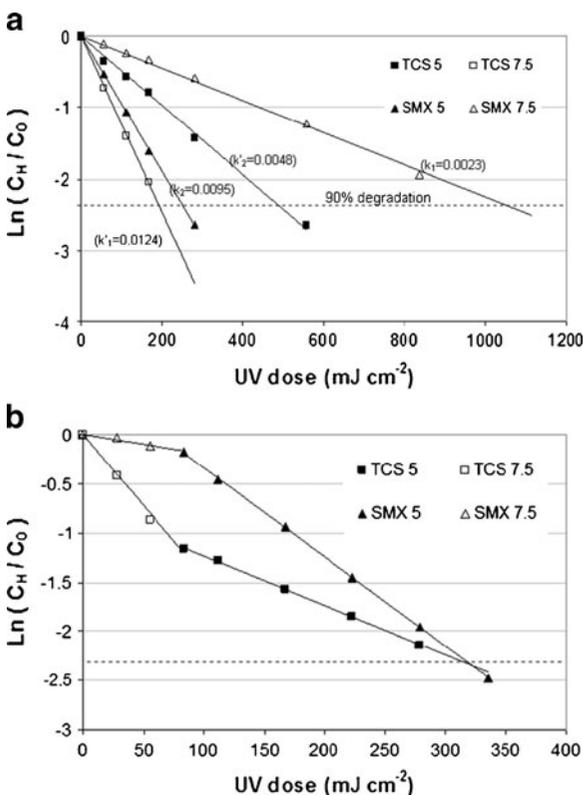
UV absorbance of the water was taken into consideration when calculating the average UV dose (fluence) in the collimated beam apparatus. The UV dose was then the product of the average irradiance and residence time. Thus, ideally, the dose-based photodegradation rate constants should be independent of water quality (dissolved constituents) in the dose calculations. Nevertheless, minor variations were observed in the rate constants for SMX and TCS when measured in buffer and groundwater.

Figure 4b illustrates the removal of TCS and SMX in a mixture from GW-1, following the irradiation protocol in which the water pH was modified from



**Fig. 3** UV dose-based photodegradation rate constant for TCS and SMX, measured separately in PBS (5 mM), as function of pH. The dashed lines represent 90% degradation

7.5 to 5 during the experiment. The pH modification point determined using LP was obtained after 1.5 min of irradiation (UV dose of 84 mJ cm<sup>-2</sup>), following an



**Fig. 4** UV dose-based photodegradation of TCS and SMX, measured in a mixture (0.5 mg L<sup>-1</sup> each compound) in GW-1, using medium-pressure collimated beam apparatus under **a** constant pH values of 5 and 7.5, and **b** pH modification of the treated water from 7.5 to 5 after irradiation dose of 84 mJ cm<sup>-2</sup>. The dashed lines represent 90% degradation

additional 4.5 min of irradiation (UV dose of 254 mJ cm<sup>-2</sup>) to achieve 90% removal of the mixture.

During the first irradiation period (at pH 7.5), the degradation of TCS was strongly accelerated, while SMX degradation was relatively slow (Fig. 4b). In the second irradiation set, after adjusting the pH to 5, the opposite trend was observed: the UV dose required for 90% removal of the mixture was only 310 mJ cm<sup>-2</sup>, whereas when the pH of the irradiated groundwater was maintained constant (pH 7.5 or 5, Fig. 4a), significantly higher UV doses of 1,000 and 479 mJ cm<sup>-2</sup>, respectively, were needed to achieve 90% removal of the mixture. Therefore, modifying the treated groundwater pH during the photodegradation process significantly improved the efficiency of the target mixture’s removal relative to UV treatment at constant pH.

Table 4 presents the UV dose required to achieve 90% removal of TCS and SMX (in a mixture) from the three different groundwater types tested, using the described irradiation procedures. Modifying the groundwater pH during the photodegradation process from its original pH value to pH 5 markedly decreased the UV dose required for removal of TCS and SMX in a mixture relative to photodegradation at constant pH. Consequently, pH modification improved the treatment efficiency. Applications for this UV irradiation coupled with pH modification treatment are detailed in Avisar et al. (2010).

**4 Conclusions**

The pH of a treated solution impacted the photodegradation kinetics of most of the investigated

**Table 4** UV dose required to achieve 90% removal of TCS and SMX (in a mixture) in different groundwater samples, using constant pH and pH modification during irradiation

	UV dose for 90% removal (mJ cm <sup>-2</sup> )		
	Constant pH		pH modification during the treatment
	pH 7.5–8	pH 5	
GW-1	1,000	479	310
GW-2	958	469	307
GW-3	958	561	334

compounds (with the exception of NDMA). Different compounds showed different pH dependencies, with some compounds degrading rapidly at high pH values and some at low pH values (in association with their pKa). Changes in photodegradation rate at different pH values could be partially attributed to changes in the compounds' molar absorption coefficient. However, other mechanisms may be involved, thus warranting further studies should be conducted on various micro-pollutants, representing different classes of pharmaceuticals and other organic compounds of relevance.

Formation of by-products may occur during the photodegradation process of the examined pollutants and these could influence the treatment. For example, in an earlier study, we detected the formation of four major by-products during the UV photolysis of sulfadimethoxine (Lester et al. 2008). However, this issue was beyond the scope of the present study.

Experiments conducted on groundwater showed the potential of the combined pH modification during photodegradation treatment for the removal of a mixture of two pharmaceuticals (SMX and TCS). The treatment procedure included irradiation of the target mixture at a UV dose of  $84 \text{ mJ cm}^{-2}$  at pH 7.5–7.9, followed by pH modification of the solution to pH 5, followed by a second irradiation. This treatment dramatically increased the removal efficiency of the mixture relative to UV treatment at constant pH.

**Acknowledgments** The authors would like to thank Mr. Yair Lakretz for his essential comments. This study was funded by the Israeli Water Authority.

## References

- Avisar, D., Lester, Y., & Mamane, H. (2010). pH induced polychromatic UV treatment for the removal of a mixture of SMX, OTC and CIP from water. *Journal of Hazardous Materials*, 175(1–3), 1068–1074.
- Avisar, D., Lester, Y., & Ronen, D. (2009). Sulfamethoxazole contamination of a deep phreatic aquifer. *Science of the Total Environment*, 407(14), 4278–4282.
- Barnes, K. K., Kolpin, D. W., Furlong, E. T., Zaugg, S. D., Meyer, M. T., & Barber, L. B. (2008). A national reconnaissance of pharmaceuticals and 12 other organic wastewater contaminants in the United States-I groundwater. *Science of the Total Environment*, 402(2–3), 192–200.
- Batt, A. L., Snow, D. D., & Aga, D. S. (2006). Occurrence of sulfonamide antimicrobials in private water wells in Washington County, Idaho, USA. *Chemosphere*, 64(11), 1963–1971.
- Bolton, J. R., & Linden, K. G. (2003). Standardization of methods for fluence (UV dose) determination in bench-scale UV experiments. *Journal of Environmental Engineering-ASCE*, 129(3), 209–215.
- Boreen, A. L., Arnold, W. A., & McNeill, K. (2004). Photochemical fate of sulfa drugs in the aquatic environment: Sulfa drugs containing five-membered heterocyclic groups. *Environmental Science and Technology*, 38(14), 3933–3940.
- Canonica, S., Meunier, L., & Von Gunten, U. (2008). Photo-transformation of selected pharmaceuticals during UV treatment of drinking water. *Water Research*, 42(1–2), 121–128.
- Chefetz, B., Mualem, T., & Ben-Ari, J. (2008). Sorption and mobility of pharmaceutical compounds in soil irrigated with reclaimed wastewater. *Chemosphere*, 73(8), 1335–1343.
- Ellis, J. B. (2006). Pharmaceutical and personal care products (PPCPs) in urban receiving waters. *Environmental Pollution*, 144(1), 184–189.
- Fasani, E., Rampi, M., & Albini, A. (1999). Photochemistry of some fluoroquinolones: effect of pH and chloride ion. *Journal of the Chemical Society-Perkin Transactions*, 2(9), 1901–1907.
- Felis, E., & Miksch, K. (2009). Removal of analgesic drugs from the aquatic environment using photochemical methods. *Water Science and Technology*, 60(9), 2253–2259.
- Hirsch, R., Ternes, T., Haberer, K., & Kratz, K. L. (1999). Occurrence of antibiotics in the aquatic environment. *Science of the Total Environment*, 225(1–2), 109–118.
- Karnjanapiboonwong, A., Suski, J. G., Shah, A. A., Cai, Q. S., Morse, A. N., & Anderson, T. A. (2011). Occurrence of PPCPs at a wastewater treatment plant and in soil and groundwater at a land application site. *Water, Air, and Soil Pollution*, 216(1–4), 257–273. 13.
- Kim, I., Yamashita, N., & Tanaka, H. (2009). Photodegradation of pharmaceuticals and personal care products during UV and UV/H<sub>2</sub>O<sub>2</sub> treatments. *Chemosphere*, 77(4), 518–525.
- Kummerer, K. (2009). The presence of pharmaceuticals in the environment due to human use-present knowledge and future challenges. *Journal of Environmental Management*, 90(8), 2354–2366.
- Lam, M. W., Tantuco, K., & Mabury, S. A. (2003). PhotoFate: a new approach in accounting for the contribution of indirect photolysis of pesticides and pharmaceuticals in surface waters. *Environmental Science and Technology*, 37(5), 899–907.
- Lee, C., Choi, W., Kim, Y. G., & Yoon, J. (2005). UV photolytic mechanism of *N*-nitrosodimethylamine in water: dual pathways to methylamine versus dimethylamine. *Environmental Science and Technology*, 39(7), 2101–2106.
- Legrini, O., Oliveros, E., & Braun, A. M. (1993). Photochemical processes for water treatment. *Chemical Reviews*, 93(2), 671–698.
- Lester, Y., Gozlan, I., Avisar, D., & Mamane, H. (2008). Photodegradation of sulphadimethoxine in water by medium pressure UV lamp. *Water Science and Technology*, 58(5), 1147–1154.

- Mella, M., Fasani, E., & Albini, A. (2001). Photochemistry of 1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(piperazin-1-yl)quinoline-3-carboxylic acid (ciprofloxacin) in aqueous solutions. *Helvetica Chimica Acta*, 84(9), 2508–2519.
- Mezcua, M., Gomez, M. J., Ferrer, I., Aguera, A., Hermado, M. D., & Fernandez-Alba, A. R. (2004). Evidence of 2,7/2,8-dibenzodichloro-*p*-dioxin as a photodegradation product of triclosan in water and wastewater samples. *Analytica Chimica Acta*, 524(1–2), 241–247.
- Pereira, V. J., Linden, K. G., & Weinberg, H. S. (2007). Evaluation of UV irradiation for photolytic and oxidative degradation of pharmaceutical compounds in water. *Water Research*, 41(19), 4413–4423.
- Sacher, F., Lang, F. T., Brauch, H. J., & Blankenhorn, I. (2001). Pharmaceuticals in groundwaters—analytical methods and results of a monitoring program in Baden-Wurttemberg, Germany. *Journal of Chromatography A*, 938(1–2), 199–210.
- Shemer, H., Sharpless, C. M., & Linden, K. G. (2005). Photodegradation of 3,5,6-trichloro-2-pyridinol in aqueous solution. *Water, Air, and Soil Pollution*, 168(1–4), 145–155.
- Sortino, S., De Guidi, G., Giuffrida, S., Monti, S., & Velardita, A. (1998). pH effects on the spectroscopic and photochemical behavior of Enoxacin: a steady-state and time-resolved study. *Photochemistry and Photobiology*, 67(2), 167–173.
- Stefan, M. I., & Bolton, J. R. (2002). UV direct photolysis of *N*-nitrosodimethylamine (NDMA): kinetic and product study. *Helvetica Chimica Acta*, 85(5), 1416–1426.
- Wong-Wah-Chung, P., Rafqah, S., Voyard, G., & Sarakha, M. (2007). Photochemical behaviour of triclosan in aqueous solutions: kinetic and analytical studies. *Journal of Photochemistry and Photobiology A-Chemistry*, 191(2–3), 201–208.