Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21245

85 (2017) 92–102
August

Comparison of energy requirements for removal of organic micropollutants from lake water and wastewater effluents by direct UV and UV/H_2O_2 using excilamp

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Received 28 March 2017; Accepted 23 July 2017

ABSTRACT

Direct photolysis (UV) and ultraviolet/hydrogen peroxide (UV/H_2O_2) treatment using KrCl excilamp (222 nm) were studied and compared in terms of energy requirements for removal of organic micropollutants atrazine (ATZ) and triclosan (TCS) spiked into Milli-Q water, municipal wastewater effluents, deep and surface lake water with dissolved organic carbon of 1 mg/L. The obtained fluence-based rate constants in the range of $2.1–6.2 \times 10^{-2}$ cm^2/mJ and UV fluences for 90% removal (UV_{90}) in the range of 42–153 mJ/cm^2 showed that UV/H_2O_2 process was more efficient than direct UV in degrading both micropollutants in all water matrices except wastewater. In terms of electrical energy per order (E_{EO}), the addition of H_2O_2 decreased the required energy by a factor of 1.4–2.4 for ATZ removal from Milli-Q water and lake waters. For TCS, the E_{EO} was relatively constant (0.44–0.51 kWh/m^3) for both UV and UV/H_2O_2 treatments of Milli-Q water and lake waters. Regarding wastewater, similar UV_{90} fluences and the additional energy requirement for H_2O_2 increased the E_{EO} values for removal of ATZ and TCS. Despite the much lower required UV_{90} fluences compared with low-pressure mercury lamps, the low radiant efficiency of KrCl excilamp of 5% resulted in E_{EO} requirements up to 2.0 kWh/m^3.

Keywords: Organic micropollutant; Degradation; Ultraviolet; Excilamp; Energy requirements

1. Introduction

During the last decade, the presence of organic micropollutants (OMPs) in water resources has received significant public and scientific attention [1–5]. It is known that OMPs can be removed via reaction with reactive oxygen species, mainly hydroxyl radicals (•OH), generated in situ in advanced oxidation processes (AOPs). •OH often oxidize OMPs with high second-order rate constants (k_{OH}) > 5×10^9 M^{-1} s^{-1} [6,7]. Direct UV photolysis and the AOP UV/H_2O_2 with low pressure (LP) and medium pressure (MP) mercury lamps are common processes for degradation of OMPs such as pharmaceuticals and household/industrial chemicals [8–21].

Excimer and exciplex lamps (excilamps) are mercury-free sources of narrow-band vacuum UV and UV radiation with high radiant power and long lifetime, which are considered to be an environmentally safe alternative to commonly used mercury lamps in photoassisted AOPs. Many previous kinetic studies showed that excilamps are efficient in degrading organic pollutants such as chlorophenols, dyes and phenolic herbicides at relatively high initial concentrations in distilled or deionized water [22–30]. Meanwhile, energy consumption is a major parameter for the assessment of the efficiency of water and wastewater treatment technology. Earlier, Bolton et al. [31] found that UV/H_2O_2 required less electrical energy per order (E_{EO}) than UV/TiO_2 for the bleaching of methylene blue and the decay of phenol in aqueous solutions, with E_{EO} being the energy consumption needed to achieve 90% degradation of a specific compound in a cubic meter of water [32–34]. Later study [35] also showed that UV/H_2O_2 process was less energy-intensive in terms of E_{EO} than UV/TiO_2 for removal of metaldehyde, serine, leucine

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and resorcinol in the presence of background organic matter and carbonate ions. The energy requirements of ozonation, O_3/H_2O_2 and LP UV/H_2O_2 were compared for the transformation of OMPs in natural waters and wastewater [14]. It was found that ozonation is a more energy efficient technology for •OH formation in most water treatment scenarios than O_3/H_2O_2 and LP/MP-UV/H_2O_2. The serial combination of ozone/H_2O_2/LP-UV treatment was energy-saving for the surface water treatment in terms of OMPs conversion and energy consumption on a pilot scale [36]. The performance of MP-, LP- and dielectric barrier discharge (DBD)-lamp (emitting at λ ~240 nm) was modeled and compared in terms of energy requirements in various pilot UV/H_2O_2 reactors [37,38]. Particularly, results showed that for a 90% UV/H_2O_2 degradation of atrazine (ATZ) in river water LP lamps had the lowest E_{EO}, DBD lamps the highest and MP lamps in between [38]. IJpelaar et al. [39] in their study of MP removal from natural waters also showed that E_{EO} data on the LP-UV/H_2O_2 process were 30%–50% lower than for the MP-UV/H_2O_2 process. In recent years, the photoassisted AOPs for removal of OMPs from natural waters and wastewater effluents were also compared in terms of energy requirements and treatment costs [17–20,40,41]. However, energy requirements for water purification using UV excilamps remain unclear.

Based on abovementioned, this study aimed to explore the energy-efficiency of direct UV and UV/H_2O_2 treatments with KrCl excilamp (222 nm) for degradation of the selected OMPs in different water matrices in terms of UV fluences (doses) per order (UV_{90}) and E_{EO}. •OH exposure using *para*-chlorobenzoic acid (*p*CBA) as a probe compound was also estimated. The antimicrobial agent in personal care products triclosan (TCS) and S-triazine herbicide ATZ were selected as model OMPs. Three different water matrices were examined: municipal wastewater effluents, deep and surface natural water collected from Lake Baikal and Lake Gusinoe (Russia), respectively. Yet, UV excilamps have not been applied to degrade OMPs at small initial concentrations neither in pure aqueous solutions nor in real water matrices.

2. Materials and methods

2.1. Reagents and examined waters

TCS (99.8%, Sigma-Aldrich, St. Louis, MO, USA), ATZ (99.1%, Sigma-Aldrich) and *p*CBA (99%, Acros, Geel, Belgium) were used as received. High-pressure liquid chromatography (HPLC) grade acetonitrile (ACN) was purchased from Cryochrom (Moscow, Russia), methanol (MeOH), acetic acid and hydrogen peroxide (30%) from Khimreaktivsnab (Irkutsk, Russia). Stock solutions of compounds were prepared in Milli-Q water (18.2 mΩ cm) produced by a Simplicity® UV system from Millipore. Degradation experiments were performed separately in three different water types: deep lake water (DLW), surface lake water (SLW) and municipal wastewater (WW). DLW was collected from Lake Baikal at a depth of 220 m (as unpolluted water), SLW was collected from Lake Gusinoe and WW was obtained from the municipal wastewater treatment plant in Ulan-Ude (Fig. S1). The samples were shipped and filtered the same day (0.45 μm RC, Vladisart) and stored at 4°C until experiments were performed. Table 1 summarizes the general water quality data.

2.2. UV and UV/H_2O_2 treatment procedure

A dielectric barrier discharge KrCl excilamp (222 nm) was purchased from High Current Electronics Institute SB RAS (Tomsk, Russia). Experiments were conducted in a bench-scale quasi-collimated beam reactor under conditions described previously [25]. The incident irradiance in the center of the sample dish, measured using a calibrated radiometer (TKA-PKM-12, TKA Scientific Instruments, St. Petersburg, Russia), was 0.6 mW/cm^2 across the UVC spectrum. The irradiance, which was determined by ATZ actinometry for an optically thin solution [14,42], was 0.59 mW/cm^2 (section 1, Fig. S5 Supplementary Information).

Direct UV photolysis and UV/H_2O_2 degradation (0.6 mM H_2O_2) of selected OMPs were conducted separately in Milli-Q water, DLW, SLW and WW. The SLW and WW were preliminary diluted to have the same dissolved organic carbon (DOC)

Table 1
Hydrochemical characteristics of the examined waters

Matrix	GPS coordinates (WGS 84)	pH	Conductivity (μSm/cm)	DOC (mg/L)	COD (mg/L)	HCO_3^- (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	Cl^- (mg/L)	Total Fe (mg/L)
Deep lake water (220 m, Lake Baikal)	N52°50′; E107°58′	6.7	2	1.0	5 ± 1.6	67 ± 2	0.51 ± 0.06	<0.01	0.53 ± 0.07	<0.1
Surface lake water (Lake Gusinoe)	N51°17′; E106°27′	8.3	434	39 ± 7	20 ± 3	193 ± 3	0.61 ± 0.08	<0.01	3.86 ± 0.50	<0.1
Municipal wastewater effluents (Ulan-Ude City)	N51°54′; E107°29′	7.5	1,335	24 ± 4	87 ± 9	56 ± 2	212	5.4	281.9 ± 36.6	<0.1 (0.05)

GPS, Global Positioning System.
Note: CO_3^{2-} was not determined (pH < 8.5).

as in DLW (1 mg/L) in order to elucidate the role of dissolved organic matter. The water samples (50 mL) were placed in an open glass dish (7.2 cm diameter), spiked with an individual micropollutant and were irradiated by KrCl excilamp with magnetic stirring (RCT IKAMAG, Germany). •OH scavenging tests were conducted in the selected waters using *p*CBA as a probe compound at natural pH. The steady-state •OH concentration ($[\bullet OH]_{ss}$) was evaluated by the rate of *p*CBA degradation (Fig. S4), as previously described [43,44]. Experiments were conducted in triplicate at an initial OMPs concentration of 1 mg/L and at unadjusted pH; run time was 5 min. This concentration was set in order to follow the degradation of the micropollutants by direct injection using HPLC. Samples were withdrawn after each exposure at 0, 15, 30, 60, 120 and 180 s and analyzed by HPLC for residual micropollutant concentration. The average UV fluence rate throughout the water volume was calculated using the modified spreadsheet (https://www.iuva.org) with the standard method for determining UV fluence [45] (Tables S1 and S2). The applied fluence was subsequently obtained by multiplying the average fluence rate with the irradiation time. The energy requirements were calculated using a methodology [14,32–34], and an example of such calculation is given in section 2 (Supplementary Information).

2.3. Analytical methods

The target compounds were analyzed using an Agilent 1260 Infinity HPLC system with a UV detector equipped with a Zorbax SB-C18 column (4.6 × 150 mm). The eluents MeOH and 1% CH_3COOH (30:70), ACN and 75 mM CH_3COOH (40:60) were used for *p*CBA and ATZ analysis, respectively. The analytes were detected at 220 nm (ATZ) and 230 nm (*p*CBA), flow rate of 0.5 mL/min, injection volume of 40 μL. pH measurements were performed using a Metrohm 827 pH meter with a Primatrode NTC glass electrode (Metrohm, Switzerland), which was calibrated with Certipur® buffer solutions (Merck, Germany). DOC was measured by TOC-L CSN (Shimadzu, Japan). The absorbance of the waters spiked with the selected OMPs with and without H_2O_2 was measured in a 1 cm cell by a Shimadzu UV-1800 spectrophotometer. Water quality analysis was performed using the standard methods listed in the Environmental Normative Federal Documents (Federal Center of Analysis and Assessment of Technogenic Exposure, Moscow, Russia).

3. Results and discussion

3.1. Fluence-based degradation rates

The fluence-based rate constants were obtained from the corresponding pseudo-first-order plots of micropollutant degradation as a function of applied fluence by direct UV and UV/H_2O_2 in Milli-Q water, DLW, SLW and WW (Fig. S2). Table 2 illustrates that the fluence-based rate constants of TCS degradation by direct UV in all examined waters are 3–4 times higher than those observed for ATZ. Although the excilamp emission wavelength and ATZ absorption spectra are overlapped (Fig. 1), the calculated quantum yield of direct photolysis of TCS in the protonated form is one order of magnitude higher than that of ATZ (Table S3).

Comparing rates of micropollutant degradation in different water matrices by direct UV alone, the rate constants in Milli-Q water and lake waters were similar, whereas a fastest degradation was observed in WW. This result suggests the possibility of indirect photolysis of these compounds and the formation of •OH and other oxidative species. Though DOC values in lake waters and diluted WW are close (1 mg/L), WW has a much higher absorption coefficient at 222 nm (0.44 cm^{-1}) compared with lake waters (Fig. S3). Radical probing with *p*CBA showed involving •OH in oxidation processes under UV treatment of WW (Table 3). In general, the enhancement of degradation rates of micropollutants in natural water and wastewater effluents without H_2O_2 addition is consistent with the previous similar reports for removal of carbamazepine and other pharmaceuticals from surface waters by simulated sunlight [46–48].

Comparing the fluence-based rate constants of degradation by UV and UV/H_2O_2 within the same water matrix (Table 2), it is seen that the removal of micropollutants is faster by UV/H_2O_2 in all selected matrices except for WW. In Milli-Q water lacking any •OH scavengers and having the highest steady-state •OH concentration ($[\bullet OH]_{ss} = 2.6 \times 10^{-12}$ M),

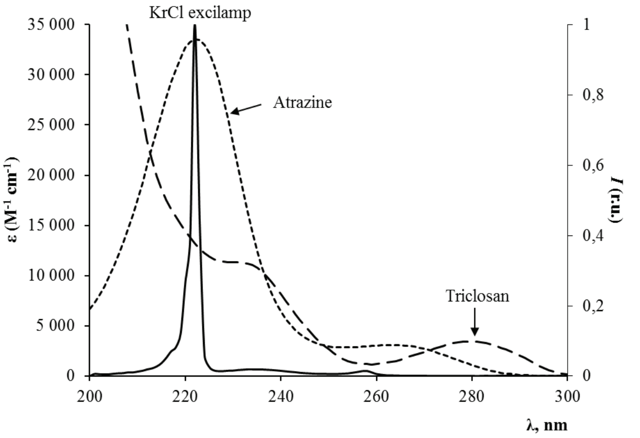

Fig. 1. Molar absorption coefficients (ε) of the selected micropollutants in Milli-Q water and the relative emission spectrum of the KrCl excilamp.

Table 2
Fluence-based rate constants (10^{-2}, cm^2/mJ) of direct UV and UV/H_2O_2 degradation of micropollutants in the selected waters

Micropollutant	Milli-Q		DLW		SLW		WW	
	UV	UV/H_2O_2	UV	UV/H_2O_2	UV	UV/H_2O_2	UV	UV/H_2O_2
ATZ	0.9 ± 0.07	3.2 ± 0.3	1.1 ± 0.07	2.1 ± 0.2	0.8 ± 0.06	2.1 ± 0.2	1.8 ± 0.1	1.7 ± 0.1
TCS	2.7 ± 0.2	6.2 ± 0.3	2.9 ± 0.1	5.1 ± 0.4	2.8 ± 0.07	4.7 ± 0.4	5.8 ± 0.3	5.5 ± 0.3

Note: $C_0 = 1$ mg/L and $[H_2O_2]_0 = 0.6$ mM.

the difference is more pronounced. ATZ reacts slower with •OH ($k_{OH} = 3 \times 10^9$ M^{-1} s^{-1} [49]) than TCS ($k_{OH} = 5.4 \times 10^9$ M^{-1} s^{-1} [50]) and was degraded with lower fluence-based rate constants within the same water type under UV/H_2O_2 treatment. Regarding WW with the same DOC after dilution, the degradation rates did not increase on adding H_2O_2 and were similar for both treatment schemes. This is consistent with the lowest •OH level found in WW under UV/H_2O_2 (1.2×10^{-12} M), which can be attributed to recombination reactions under •OH excess and the scavenging effect caused by Cl^- ions (Table 1).

3.2. UV_{90} fluences and E_{EO}

The UV fluences required for 90% removal of the selected micropollutants (UV_{90}) in different water matrices are presented in Fig. 2. ATZ was poorly degradable compound by direct UV with relatively high fluences of 230–360 mJ/cm^2 needed to achieve 90% removal. Lower UV fluences (60–90 mJ/cm^2) were required to degrade 90% TCS by UV alone. UV/H_2O_2 treatment of Milli-Q water and lake waters decreased the corresponding fluences by a factor of 1.6–3.3. However, the difference between fluences for UV and UV/H_2O_2 became minor for WW assuming the possibility of indirect photodegradation processes (Fig. 2).

The calculated energy requirements in terms of E_{EO} reflect the trends observed when comparing the corresponding UV fluences (Table 4). Considering the E_{EO} values of 2.65 kWh/m^3 or less are favorable [51], both schemes using excilamp for all examined matrices represent an economically viable option. The UV/H_2O_2 process for a given H_2O_2 concentration requires less energy for removal of ATZ from Milli-Q water and lake waters. TCS showed the lowest and roughly the same energy requirements of 0.44–0.51 kWh/m^3 for both UV and UV/H_2O_2 treatments of Milli-Q water and lake waters. Regarding WW, direct UV treatment showed better electrical efficiency in comparison with UV/H_2O_2 process for removal of both micropollutants (Table 4). Adding energy for H_2O_2 production to similar E_{EO} values for UV and UV/H_2O_2 schemes resulted in higher energy demands for WW treatment.

3.3. Comparison with the literature data

Comparison of the obtained results with literature data is rather difficult due to different experimental conditions or the time-based kinetic data presented. However, presenting results in terms of UV_{90} or E_{EO} could enable such comparison. Table 5 summarizes the literature data on degradation of ATZ and TCS as individual compounds using UV and UV/H_2O_2 schemes.

A KrCl excilamp appears to be more efficient than LP/MP lamps for direct UV and UV/H_2O_2 degradation of ATZ in Milli-Q water at the same initial concentration of 1 mg/L (Table 5). The k values are one order of magnitude higher than those reported by Sanches et al. [12] and Khan et al. [40]. Although the reported UV_{90} fluence for UV/H_2O_2 treatment [40] is one order of magnitude higher (1,300 vs. 94.5 mJ/cm^2), the E_{EO} is the same (0.7 kWh/m^3). Sanches et al. [12] showed approximately 70% degradation of ATZ in surface water by using both UV and UV/H_2O_2 schemes at a high fluence of 1,500 mJ/cm^2.

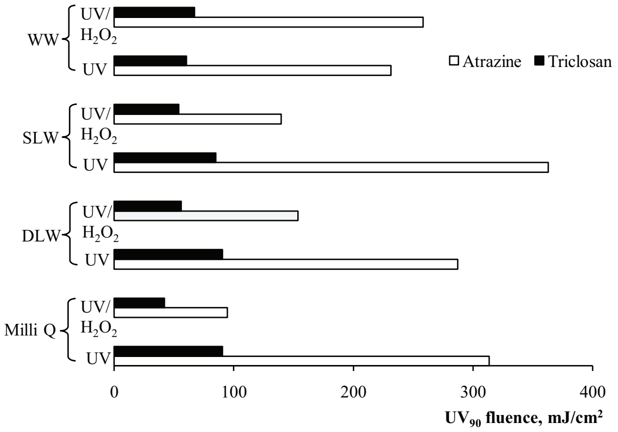

Fig. 2. UV fluences required for 90% removal of micropollutants by direct UV and UV/H_2O_2 in Milli-Q water, deep lake water (DLW), surface lake water (SLW) and wastewater (WW) using a KrCl excilamp. Compound concentration = 1 mg/L and $[H_2O_2]_0$ = 0.6 mM.

Table 3
First-order rate constants of pCBA degradation (k) and steady-state hydroxyl radical concentration ($[•OH]_{ss}$)

Matrix	Milli-Q		DLW		SLW		WW	
	UV	UV/H_2O_2	UV	UV/H_2O_2	UV	UV/H_2O_2	UV	UV/H_2O_2
$k \times 10^{-2}$, s^{-1}	0.06	1.3	0.07	1.1	0.06	0.9	0.34	0.6
$[•OH]_{ss} \times 10^{-12}$, M	–	2.6	–	2.3	–	1.8	0.68	1.2

Note: C_0 = 1 mg/L and $[H_2O_2]_0$ = 0.6 mM.

Table 4
Energy requirements (kWh/m^3) for 90% removal of micropollutants in examined waters by direct UV (222 nm) and UV/H_2O_2

Micropollutant	Milli-Q		DLW		SLW		WW	
	UV	UV/H_2O_2	UV	UV/H_2O_2	UV	UV/H_2O_2	UV	UV/H_2O_2
ATZ	1.74	0.73	1.60	1.06	2.02	0.98	1.29	1.64
TCS	0.50	0.44	0.50	0.51	0.47	0.50	0.34	0.58

Note: Compound concentration = 1 mg/L and $[H_2O_2]_0$ = 0.6 mM. Optical path length = 1 cm.

Table 5
Literature values on pseudo-first-order fluence-based rate constants (k), UV fluences per order and electrical energy per order (E_{EO}) for UV and UV/H_2O_2 treatments of atrazine and triclosan as individual compounds

Treatment	Conditions	Matrix	k, cm^2/mJ	UV_{90}, mJ/cm^2	E_{EO}, kWh/m^3	Reference
UV	UV-254 nm 4.64 μM ATZ (1.0 mg/L) pH 3.0, 5.7, 11.0	Milli-Q	$6.72–7.73 \times 10^{-4}$	–	–	[40]
UV/H_2O_2	See above 92.80 μM H_2O_2 (3.15 mg/L), unadjusted pH	Milli-Q	1.77×10^{-3}	1.30×10^3	7.09×10^{-1}	[40]
UV	LP lamp 2.6 ± 0.2 mg/L ATZ 1.7 ± 0.16 mg/L TCS	Ultrapure water	–	900 (59% ATZ) 900 (92% TCS)	–	[21]
UV/H_2O_2	See above 10 mg/L H_2O_2	Ultrapure water	–	900 (>90% ATZ) 900 (~95% TCS)	–	[21]
UV	MP lamp, 1 mg/L TCS	5 mM PBS	$\sim 7.5 \times 10^{-3}$ $\sim 8.4 \times 10^{-3}$	311 (pH 6) 274 (pH 7)	–	[52]
UV/H_2O_2	LP lamp, 100 μg/L ATZ, 5.0 mg/L H_2O_2	SE[a] SE with low alkalinity Deionized water	–	16,884 12,060 1,206	0.59 (SE)	[17]
UV	LP lamp 1 mg/L ATZ	LGW[b] GW[c] SW[d]	7.56×10^{-4} 8.21×10^{-4} 8.51×10^{-4}	1,500 (~70%) for SW	–	[12]
UV/H_2O_2	See above 40 mg/L H_2O_2	LGW SW	7.43×10^{-4} 8.64×10^{-4}		–	[12]

[a] Secondary effluents.
[b] Laboratory grade water.
[c] Groundwater.
[d] Surface water.

High fluences of ~10^3 mJ/cm^2 or above were also reported earlier for ATZ removal at μg/L level in a mixture with other micropollutants in model and real water matrices by UV/H_2O_2 treatment using LP lamps [18,20]. However, a lower fluence of 600 mJ/cm^2 was needed for 80% ATZ degradation at 2–4 μg/L in surface natural waters [39]. Lekkerkerker-Teunissen et al. [15] mentioned that MP lamps were more efficient than LP lamps for ATZ degradation in deionized water at the high dose of 700 mJ/cm^2 (47% vs. 27% removed). However, high initial ATZ concentration of 6.62 mg/L was used in this study. Addition of 5 and 10 mg/L H_2O_2 increased the removal efficiency by 10%–15% for the LP lamps, whereas this trend was not observed in case of MP lamps [15].

Regarding TCS, the obtained rate constant of direct UV in Milli-Q water is by a factor of 3.6 higher and the corresponding UV_{90} fluence is by a factor of 3.4 lower than those obtained earlier in phosphate-buffered saline (PBS) at pH 6 with MP-lamp [52]. Rosaz et al. [21] also reported high fluence of 900 mJ/cm^2 for LP-UV and UV/H_2O_2 treatment of TCS in ultrapure water (Table 5).

Despite the low UV_{90} fluences required, the calculated E_{EO} values with excilamp are within the same range as reported previously for ATZ removal as an individual compound as in a mixture with other micropollutants using LP/MP lamps. This could be attributed to the much lower radiant efficiency of excilamp compared with LP lamp (5% (data from the manufacturer) vs. 30% [53]). Antoniou and Andersen [18] reported the comparable E_{EO} for LP-UV/H_2O_2 ATZ removal at 100 μg/L from demineralized water and tap water to be 0.41 and 1.12 kWh/m^3, respectively. IJpelaar et al. [39] also showed that the energy demands were below 1.0 kWh/m^3 for 2–4 μg/L ATZ transformation in Dunea water by LP-UV/H_2O_2 (10 mg/L). The obtained energy requirements for lake waters with 1 mgC/L were nearly comparable with those (0.98 kWh/m^3) reported by Katsoyiannis et al. [14] for 0.5 μM (0.11 mg/L) ATZ degradation in Lake Zürich (1.3 mgC/L) using LP lamp. Lee et al. [20] in their comprehensive study of LP-UV and UV/H_2O_2 abatement of various OMPs in a mixture reported a bit higher E_{EO} values for 1 μg/L ATZ and TCS degradation at 20 mg/L H_2O_2 and light path length of 10 cm. Particularly, for 90% abatement in a hypothetical drinking water matrix (1 mgC/L) ATZ required 0.38 (UV) and 0.26 (UV/H_2O_2) kWh/m^3, whereas TCS required less energy of 0.07 (UV) and 0.22 (UV/H_2O_2) kWh/m^3 [20]. Note that the calculated E_{EO} values for excilamp will be one order of magnitude lower for optical path length of 10 cm (section 2, Supplementary Information).

In general, the energy demands for KrCl excilamp are not noticeably higher than those reported previously for LP/MP lamps despite the much lower radiant efficiency. If the higher efficiency of excilamps in converting electrical energy to UV light is attained as in case of recently engineered vacuum UV

Xe_2-excimer lamp (172 nm, η = 40%) [30], the final energy requirements will be significantly lower with excilamp.

4. Conclusions

The UV/H_2O_2 treatment with KrCl excilamp (222 nm) employing UV fluences up to 153 mJ/cm^2 and 0.6 mM (20.4 mg/L) H_2O_2 was a more energy-efficient process for degradation of ATZ and TCS in Milli-Q water, DLW and SLW with DOC of 1 mg/L. Among the examined waters, only the diluted wastewater enhanced degradation of ATZ and TCS by direct UV treatment. This assumes a predominant contribution of sensitized DOM in wastewater as a source of reactive oxygen species. The comparative assessment of similar studies shows that the obtained fluence-based rate constants are one order of magnitude higher and UV fluences per order are significantly lower than those reported earlier for LP and MP lamps. However, taking into account the higher radiant efficiency of LP lamps, the final E_{EO} values with excilamp-UV or UV/H_2O_2 is within the same range as reported with LP-UV/H_2O_2. Considering the energy of 2.65 kWh/m^3 or less favorable, an excilamp-UV/H_2O_2 scheme was found to be economically competitive against LP/MP-UV/H_2O_2 for treatment of low DOC aqueous matrices. The development of excilamps with higher radiant efficiency makes their practical application promising for water treatment.

Acknowledgments

This research was carried out under the Program of Basic Research of SB RAS (Project IX.138.3.2) and partially supported by Russian Foundation for Basic Research (grant no. 14-08-31733). We thank Dr. Dmitry Matafonov (IGEB SB RAS) for help in deep water sampling and mapping.

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Supplementary information

1. Calculation of the incident irradiance

The incident irradiance, E_λ (Einstein/m^2 s), was determined by atrazine actinometry at low optical density [2,7] using 5 μM atrazine solution in Milli-Q water as an actinometer (buffered at pH 7.0 with 5 mM phosphate) assuming a wavelength-independent quantum yield of 0.046 mol/Einstein [3] and an absorption coefficient of 3,210 m^2/mol at 222 nm (Table S3) according to:

$$E_\lambda = \frac{k_\lambda}{2.303\Phi_\lambda\varepsilon_\lambda} \quad \text{([2] adapted for monochromatic radiation)}$$

where k_λ is the photolysis rate constant (s^{-1}), ε_λ is the molar absorption coefficient (m^2/mol) and Φ_λ is the quantum yield (mol/Einstein) at the wavelength λ.

$k_\lambda = 0.0037$ s^{-1} (Fig. S5)
$\Phi_\lambda = 0.046$ mol/Einstein
$\varepsilon_\lambda = 3{,}210$ m^2/mol

Finally,

$$E_\lambda = \frac{0.0037}{2.303 \times 0.046 \times 3210} = 1.088 \times 10^{-5}\ \text{Einstein m}^{-2}\text{s}^{-1}$$

At 222 nm, the energy of 1 mol photons is 5.387×10^5 J/Einstein. 1.088×10^{-5} Einstein/m^2 s $\times$ 5.387×10^5 J/Einstein = 5.862 W/m^2 or 0.59 mW/cm^2.

2. Example of calculation of the electrical energy per order (E_{EO}) for atrazine degradation in deep Lake Baikal water using KrCl excilamp

Deep Lake Baikal water (at 222 nm)

UV/H_2O_2 treatment, $[ATZ]_0 = 1$ mg/L, $[H_2O_2]_0 = 0.6$ mM.

For 1 cm optical path length (Table S2):

$A_{222} = 0.3302$ cm^{-1} (lake water containing 0.6 mM H_2O_2 and 1 mg/L ATZ, measured).
Water factor = 0.70

The fluence required for 90% removal, that is, per order (UV_{90}') was calculated from the first-order fit (Fig. S2):

$k = 0.0214$ cm^2/mJ
$\ln(C/C_0) = -0.0214 \times UV_{90}'$

$UV_{90}' = \ln(0.1)/-0.0214 = 2.3/0.0214$ cm^2/mJ = 107.5 mJ/cm^2

From the fluence UV_{90}' we can calculate the fluence per order for 1 cm optical path length (UV_{90}):

$UV_{90} = UV_{90}'$/Water factor ($l = 1$ cm) = 107.5/0.70 = 153 mJ/cm^2

Energy requirements for 90% micropollutant degradation were calculated according to the methodology established by Bolton and Cater [4], Bolton et al. [5,6] and described in the SI by Katsoyiannis et al. [7].

- The energy content of the used H_2O_2.
  The energy cost for the production of H_2O_2 is 10 kWh/kg [7,8].
  The consumption is 0.6 mol/m^3, that is, 20.4 g/m^3.
  The energy consumption is then 0.204 kWh/m^3.
- The electrical energy per order (E_{EO}) required to achieve the fluence per order UV_{90} (kWh/m^3). The efficiency of the KrCl excilamp (η_{UV}) is 0.05 (data from the manufacturer [10]) and the water absorbance has been already considered. This result in the following equation:

$$EEO = \frac{UV_{90}}{1 \times \eta_{UV}} \times \frac{kWh}{3.6 \times 10^6 J}$$

For a 1 cm optical path length we get:

$$EEO = \frac{1530\ J\ m^{-2}}{10^{-2} m \times 0.05} \times \frac{kWh}{3.6 \times 10^6 J} = 0.85\ kWh/m^3 + 0.204$$

(energy consumption due to 0.6 mM H_2O_2) = 1.06 kWh/m^3.

For 10 cm optical path length we get:

$$EEO = \frac{1530\ J\ m^{-2}}{10^{-1} m \times 0.05} \times \frac{kWh}{3.6 \times 10^6 J} = 0.085\ kWh/m^3 + 0.204$$

(energy consumption due to 0.6 mM H_2O_2) = 0.289 kWh/m^3.

Table S1
Direct UV photolysis of micropollutants in the selected waters

Micropollutant	Absorbance at 222 nm for 1 cm	Water factor for 1 cm	Average irradiance[a], mW/cm^2
	Milli-Q water		
ATZ	0.1834	0.82	0.411
TCS	0.0456	0.95	0.496
Deep lake water			
ATZ	0.2650	0.75	0.367
TCS	0.1335	0.86	0.427
Surface lake water			
ATZ	0.1746	0.82	0.416
TCS	0.0254	0.97	0.513
Wastewater			
ATZ	0.5853	0.55	0.247
TCS	0.3941	0.66	0.288

Note: Compound concentration = 1 mg/L.
[a] The average UV irradiance throughout the water volume was calculated using the modified spreadsheet (https://www.iuva.org) with the standard method for determining UV fluence [1].

Table S2
UV/H_2O_2 oxidation of micropollutants in the selected waters

Micropollutant	Absorbance at 222 nm	Water factor for 1 cm	Average irradiance, mW/cm^2
	Milli-Q water		
ATZ	0.2406	0.77	0.379
TCS	0.1076	0.89	0.446
Deep lake water			
ATZ	0.3302	0.70	0.336
TCS	0.1902	0.81	0.390
Surface lake water			
ATZ	0.2329	0.77	0.383
TCS	0.0898	0.90	0.459
Wastewater			
ATZ	0.6451	0.52	0.231
TCS	0.4522	0.62	0.266

Note: Compound concentration = 1 mg/L and $[H_2O_2]_0$ = 0.6 mM.

Table S3
Quantum yields[a] of direct photolysis of micropollutants in Milli-Q water using KrCl excilamp (222 nm)

Micropollutant	k_{222} (s^{-1})	ε_{222} (m^2/mol)	Φ_{222}[a] (mol/Einstein)
ATZ	0.0037	3,210	0.046
TCS (protonated, pH 6.0)	0.0133	1,321	0.401

[a] Quantum yields values were estimated according to the following equation [9]:

$k_\lambda = 2.303 E_\lambda \times \varepsilon_\lambda \times \Phi_\lambda$

where k_λ is the photolysis rate constant (s^{-1}), E_λ is the photon fluence rate (1.088×10^{-5} Einstein/m^2 s), ε_λ is the molar absorption coefficient (m^2/mol) and Φ_λ is the quantum yield (mol/Einstein) at the wavelength λ.

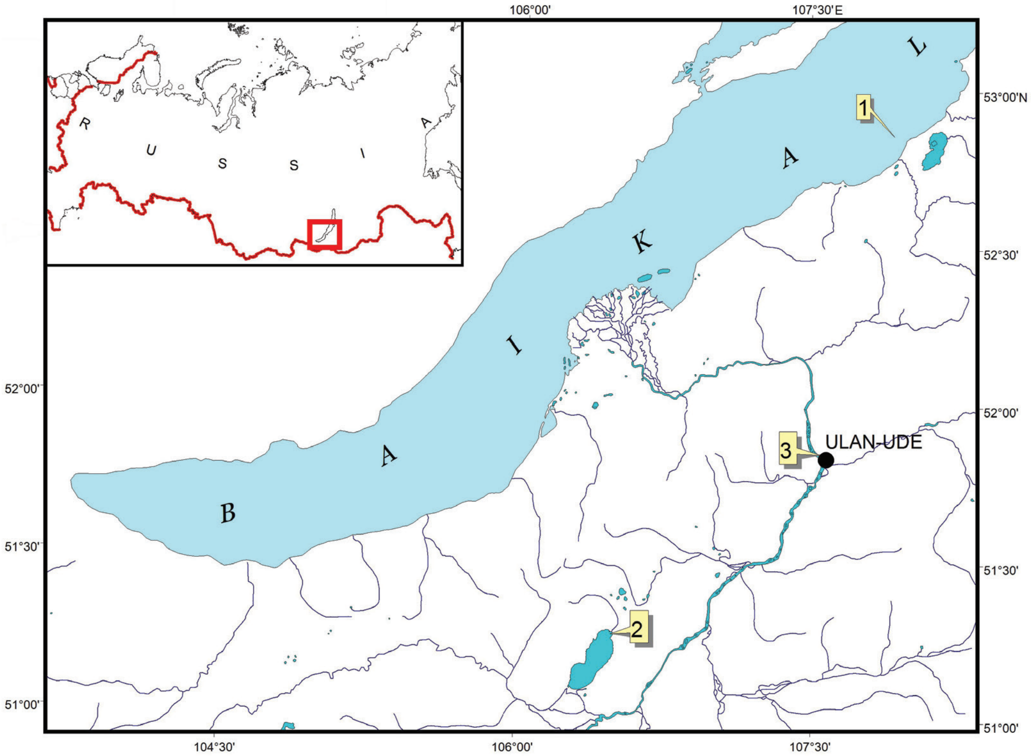

Fig. S1. Sampling points map: deep lake water (1), surface lake water (2) and wastewater effluents collected from WWTP of Ulan-Ude (3).

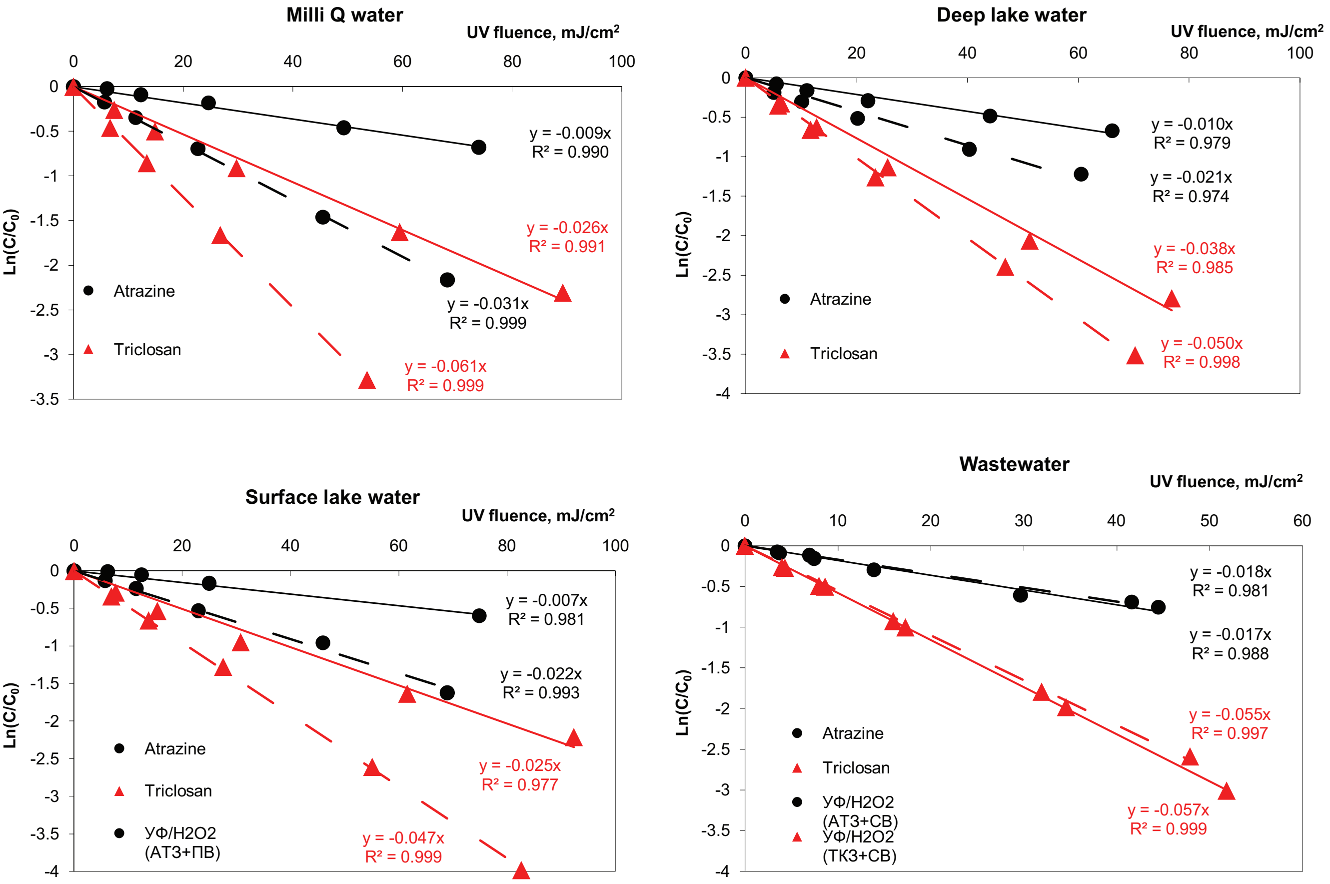

Fig. S2. Pseudo-first-order plots of atrazine and triclosan degradation as a function of fluence by direct UV (solid lines) and UV/H_2O_2 (dashed lines) in different water matrices. Compound concentration = 1 mg/L and $[H_2O_2]_0$ = 0.6 mM.

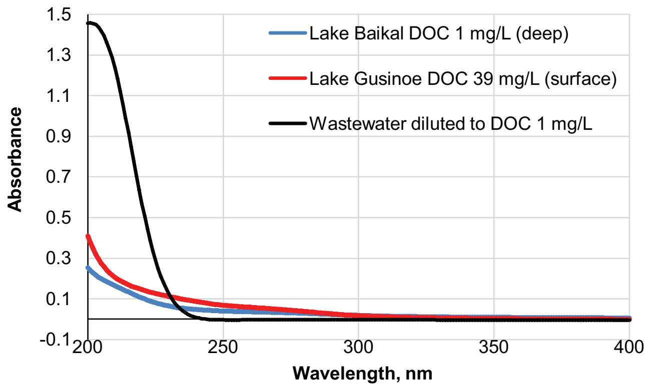

Fig. S3. UV absorbance spectra of the selected water matrices.

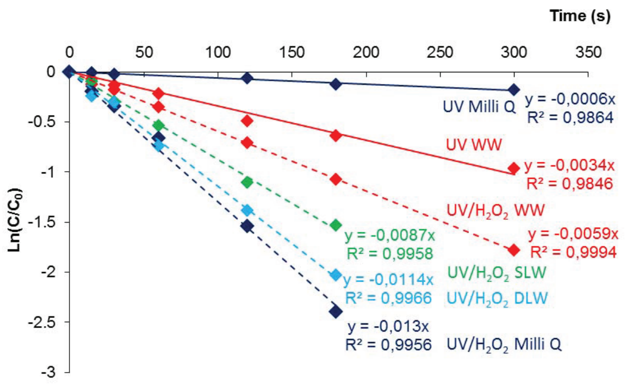

Fig. S4. First-order plots of *p*CBA degradation in Milli-Q water, DLW, SLW and WW. *p*CBA concentration = 1 mg/L and $[H_2O_2]_0$ = 0.6 mM.

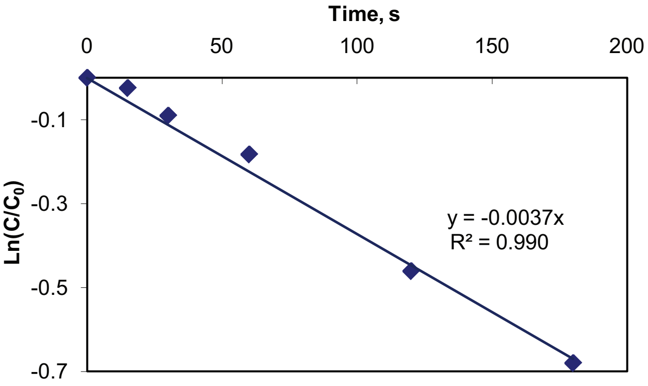

Fig. S5. First-order graph of ATZ degradation with time in Milli-Q water (5 μM and pH 7).

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