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Decomposition of selected organic micropollutants under solar radiation

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ABSTRACT

Natural solar radiation is considered a free energy source, continuously reaching the earth's surface. Next to biological processes, it plays a crucial role in the decomposition of pollutants introduced by humans into the environment. Integrating of natural photo-decomposition with other physico-chemical processes becomes a current and effective water purification method. The research focused on investigating the decomposition of selected micropollutant water solutions exposed to the direct action of sunlight. Model aqueous solutions (deionized water, salt water, and surface water) were spiked with analytical standards of diclofenac, triclosan, butylated hydroxytoluene, and 4-*tert*-octylphenol and subjected to solar radiation during European winter, spring, summer, and fall periods. The samples were tested using gas chromatography, the Microtox bioassay, and the *Lemna minor* Growth Inhibition Test (GIT). It has been shown that the decomposition rate of all tested compounds strongly depends on the period of the year. It relates to the different intensities of solar radiation reaching the earth's surface. The highest number of by-products of the decomposition of individual compounds was observed in the spring and autumn periods. These post-process solutions were also characterized by higher toxicity than those processed in summer and winter.

Keywords: Organic micropollutants; Sunlight; By-products; Toxicity

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1. Introduction

The sun, as a free source of energy reaching the surface of our planet, shows the most significant natural potential for the decomposition of contaminants, especially those of organic origin. This decomposition is possible due to energy applied to the chemical bonds of organic molecules and comes directly from solar radiation, which has the range of UV-C, UV-B, UV-A, visible light, and infrared. Mainly UV-C radiation can be used as an effective promotor of the decomposition of organic micropollutants [1]. Fatta-Kassinos et al. [2] showed that the absorption of UV-B rays could oxidize some compounds from the group of pharmaceuticals. Not only the season of the year affect the amount of solar energy reaching individual elements of ecosystems. Atmospheric aerosols and water vapor deiced about the Earth's radiation balance [3] by scattering and absorption processes [4]. This direct photo-decomposition process in water bodies can be supported by the action of other oxidizing species, that is, hydroxyl radicals, carbonate radicals, and the triple states coloured dissolved organic *matter* which was generated during the indirect action of solar radiation, and the compounds occurring in the water matrix [5]. The direct and indirect photodegradation mechanisms of compounds depend on their molecule structure, which defines the absorption spectrum and the quantum yield of a compound [6]. Vione et al. [7] pointed out that the environmental condition plays a significant role during indirect photodegradation and decides to support or inhibit the production of reactive transient species. Mathon et al. [5] state that the efficiency of micropollutant decomposition under the influence of natural solar radiation depends not only on the physico-chemical composition of water but also on the type of reservoir (its volume, depth, and

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localization) and the season of the year. This is especially important for water bodies located in a temperate climate, where there is a significant variation in solar energy reaching the Earth's surface during the year.

Sunlight-supported advanced oxidation processes can be a promising method for removing a bride range of contaminants [8]. Sunlight acts in such processes as a source of energy that activates some agents [9,10] or leads to the generation of reactive species like hydroxyl radicals $HO^\bullet$ or sulphate radicals $SO_4^{\bullet-}$ [11]. The radicals interact selectively or nonselective with the molecules of the organic micropollutants and initiate the progressive decomposition of the compounds [12]. The current operating solar light degradation system has only been designed for regions with a constant amount of solar radiation and is based on the photocatalytic treatment processes of compounds [13–15]. However, designing solutions based on the action of sunlight requires fundamental knowledge about the decomposition of pollutants under the influence of the photodegradation process. It becomes necessary to know the decomposition pathways of pollutants to properly select the reagents required for the complete mineralization of compounds and, thus, to produce water streams devoid of harmful substances. Batchu et al. [16] assessed the possibility of the decomposition of antibiotics under the influence of solar radiation. They showed that this decomposition is possible but requires time and access to radiation of appropriate energy. Also, the decomposition of benzotriazoles can be initiated by the action of natural sunlight in deionized water solutions and in solutions with a dissolved organic matter content [17,18]. Compounds from the group of non-steroidal anti-inflammatory drugs and endocrine-disrupting chemicals have mostly been found to be photoactive. The photoactivity is possible due to their structural composition, which can directly absorb solar radiation at wavelengths $\lambda > 290$ nm or indirectly react with radicals generated by the solar irradiation of photosensitizers occurring in water solutions [19].

The research compares the photo-decomposition process of four anthropogenic micropollutants: diclofenac, triclosan, butylated hydroxytoluene, and 4-*tert*-octylphenol during European winter (January), spring (April), summer (July), and autumn (October) periods. In order to determine the influence of the physico-chemical composition of the water matrix on the course of the photo-decomposition process, the tests were carried out on both deionized water, brackish water (containing sodium chloride, magnesium chloride, magnesium sulfate, calcium sulfate, potassium sulfate, and calcium carbonate) and surface water. The possible micropollutant decomposition by-products were identified by using solid–phase extraction followed by gas chromatography combined with mass detection. The analyzes were supplemented with toxicological tests at the Microtox® bioassay and the *Lemna minor* Growth Inhibition Test (GIT).

2. Material and methods

2.1. Water samples

Model water solutions subjected to solar radiation were prepared based on deionized water, salt water and surface water with the addition of analytical standards of diclofenac, triclosan, butylated hydroxytoluene, and 4-*tert*-octylphenol, which were previously dissolved in methanol. The concentration of the selected micropollutants was set at 0.5 mg/dm^3, and the characteristics of the compounds were given in Table 1. The deionized water was obtained from a laboratory water distillation station Arium Comfort II UV, by Sartorius AG (Göttingen, Germany). The salt water solution was prepared using deionized water with the addition of sodium chloride 27.2 mg/dm^3 (NaCl), magnesium chloride 3.8 mg/dm^3 ($MgCl_2$), magnesium sulfate 1.6 mg/dm^3 ($MgSO_4$), calcium sulfate 1.3 mg/dm^3 ($CaSO_4$), potassium sulfate 0.8 mg/dm^3 (K_2SO_4) and calcium carbonate 1.2 mg/dm^3 ($CaCO_3$). Salt concentrations were selected based on literature data [20–22]. The surface water came from a pond located in Upper Silesia, Poland. The qualitative characteristic of the surface water is presented in Table 2.

2.2. Solar radiation

The solar irradiation process for all prepared solutions was conducted on an outdoor testing stand. The solutions were placed in open quartz glass batch reactors optionally cooled or heated with tap water (Fig. 1.). The volume of the reaction solutions was 1.0 dm^3. The depth of the water layer was in all reactors equal to 15 cm. The reactors were placed on a magnetic stirrer to ensure even access of the entire reaction mixture to the light rays. The reactors were exposed to direct sun irradiation. Table 3 summarizes the average direct solar radiation per horizontal surface in Upper Silesia, Poland, during the research. The temperature of the reaction solutions during all experiments was kept in the range from 20°C to 21°C. All experiments were parallel conducted in a dark chamber without the influence of solar radiation. The tests performed with the solar radiation and in the dark chamber were carried out for 5, 15, 30, 60, and 120 min and then imminently analyzed. Each experiment was performed three times.

2.3. Analytical procedure

The collected post-processed samples were subjected to chromatographic analysis, which allowed for the determination of the changes in the concentration of individual micropollutants in the sample and to identify possible decomposition by-products.

The chromatographic analysis was preceded by solid–phase extraction (SPE). The SPE procedure allowed for the extraction of all analytes present in the sample. The volume of the extracted samples was 0.02 dm^3. Supelclean™ ENVI-8 and Supelclean™ ENVI-18 by Merck KGaA (Darmstadt, Germany) were used to analyze the tested compounds and their intermediates. The procedure was detailed described in Kudlek [23,24]. The organic solvents used during the SPE were from Avantor Performance Materials Poland S.A. (Gliwice, Poland). The calculated recovery of diclofenac (DCF), triclosan (TCS), butylated hydroxytoluene (BHT), and 4-*tert*-octylphenol (OP) after the implemented SPE conditions exceeded 99%, 98%, 99%, and 97%, respectively.

The 7890B gas chromatograph with mass detection by Agilent Technologies (Santa Clara, United States) was implemented for the qualitative and quantitative analysis of extracts. The chromatograph worked with a capillary column

Table 1
Characteristics of tested organic cosmetic ingredients

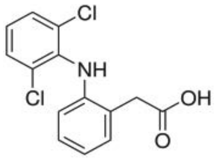
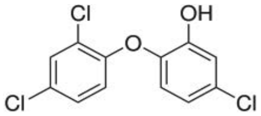
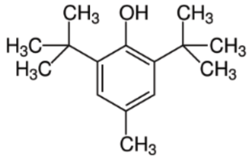
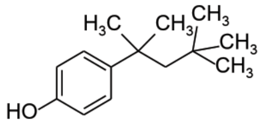
Compound	Structural formula	Molecular formula	Molar mass, g/mol	Solubility in H_2O, mg/dm^3	logK_{ow}, –
Diclofenac, DCF		$C_{14}H_{11}Cl_2NO_2$	296.10	2.37	4.51
Triclosan, TCS		$C_{12}H_7Cl_3O_2$	289.54	10.00	4.76
Butylated hydroxytoluene, BHT		$C_{15}H_{24}O$	220.35	0.60	5.10
4-*tert*-octylphenol, OP		$C_{14}H_{22}O$	206.32	5.11	5.30

Table 2
Physico-chemical characteristic of the surface water

Parameter	Mean value
pH	7.01
Conductivity, µS/cm	930.25
Absorbance (λ = 254 nm)	0.120
Total organic carbon, mg/dm^3	23.15
Ion current, mg/dm^3	50.71
Total current, mg/dm^3	73.86
Chemical oxygen demand, mg·O_2/dm^3	30.52
Biochemical oxygen demand$_5$, mg·O_2/dm^3	4.52
Total nitrogen, mg/dm^3	5.69
N–NH_4, mg/dm^3	1.52
N–NO_3, mg/dm^3	3.14

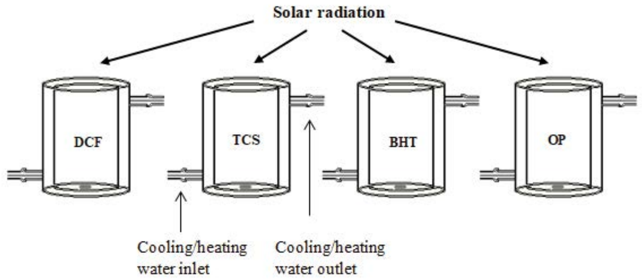


Fig. 1. Scheme of the laboratory set-up during the solar radiation experiment.

Table 3
Average direct solar radiation per horizontal surface and ambient temperature

Period	Month	Mean solar radiation, W/m^2	Mean ambient temperature, °C
Winter	January	23	1.1
Spring	April	79	6.7
Summer	July	136	18.9
Autumn	October	59	11.2

SLB™ – 5 ms (30 m × 0.25 mm of 0.25 µm film thickness) by Sigma-Aldrich (Poznań, Poland). Helium 6.0 from SIAD Poland sp z o.o. (Ruda Śląska, Poland) acts as the carrier gas. The injection speed of the samples was set at 3,000 mm^3/min while the injector operated at a temperature of 250°C. The oven temperature program was divided into three stages:

- Stage 1: 80°C held for 6 min;
- Stage 2: 5°C/min up to 260°C;
- Stage 3: 20°C/min up to 300°C held for 2 min

The ion trap temperature and the ion source operated at 150°C and 230°C, respectively. The quantitative analysis of micropollutant concentrations was operated in the selected ion monitoring (SIM) mode, whereas the intermediates were identified in the total ion current (TIC) mode. The mass spectra of the intermediates were compared with the United States National Institute of Standards and Technology NIST v17 Mass Spectral Library using the MassHunter

Software. A compound was considered identified if the similarity of its mass spectrum to that of the standard compound exceeded 70%.

The percentage of micropollutant removal (R, %) was calculated by determining the initial C_i concentrations of the individual compound in the sample before solar radiation and post-processed C_p micropollutant concentration (mg/dm^3) according to Eq. (1):

$$R,\% = \frac{C_i - C_p}{C_i} \times 100 \tag{1}$$

The results presented in all figures present the arithmetic mean of three replicates. The error bars (which did not exceed 4%) were estimated based on standard deviation. One-way ANOVA variance of analyses ($\alpha < 0.05$) was applied for the statistical analysis of the obtained results and the verification of the hypothesis that the level of insolation in particular seasons affects the decomposition of micropollutants in water solutions. The Fisher's Least Significant Difference LSD Test was used to determine the smallest significant differences in micropollutant concentration measured in water samples between individual seasons.

The total kinetic constant k for each water solution was calculated based on the micropollutant concentration (C_i) in the initial time t_0 and the concentration (C_p) after the given process elongation t according to Eq. (2). Whereas, the $t_{1/2}$ was calculated according to Eq. (3).

$$C_p = C_0 \cdot e^{-(kt)} \tag{2}$$

$$t_{1/2} = \left(\frac{\ln 2}{k}\right) \tag{3}$$

2.4. Toxicity tests

The toxicity of the prepared solutions was tested before and after the exposure to solar radiation. Toxicity assessment was made based on the Microtox® bioassay and the *Lemna minor* GIT analysis results. The test procedure of the Microtox® bioassay is based on the measurement of the changes in the intensity of light emitted by the test organisms – bioluminescent salt water bacteria *Aliivibrio fischeri*, exposed to the tested samples. The measurements were carried out on the Microtox analyzer model 500 by Modern Water (London, United Kingdom) with the use of the MicrotoxOmni Software according to the OECD 150 Guideline 202 and ISO 6341:2012.

The *Lemna minor* GIT measurement consists in counting the number of plant fronds of freshwater vascular plants *Lemna minor* [25]. The fronds were counted after 7 d of plant growth in the tested samples. Plants from their own culture were used for the study. The culture and toxicity test were performed according to OECD Guideline 221.

The toxicity effect (E, %) for the *Lemna minor* GIT was calculated using Eq. (4):

$$E,\% = \frac{N_C - N_T}{N_C} \times 100 \tag{4}$$

where N_C – number of green and healthy plant fronds in the control sample; N_T – number of green and healthy in the test sample.

The obtained test results were interpreted based on a four-class toxicity classification system presented in Table 4 [26].

Table 4
Toxicity classification system of water samples [26]

Toxicity class	E, %	Interpretation
I	<25.00	Nontoxic sample
II	25.00–50.00	Low toxic sample
III	50.01–75.00	Toxic sample
IV	75.01–100	Highly toxic sample

3. Results and discussion

3.1. Effectiveness of micropollutant photo-decomposition process

The micropollutants occurring in the prepared water solutions decompose very slowly under the action of solar radiation. The removal degrees for compounds observed in deionized water during different seasons of the year were summarized in Fig. 2. The lowest removal degree of all testes micropollutants was noted during winter. For example, the removal of DCF increased from about 1% after 15 min of radiation to 15% after 120 min (Fig. 2a). It should be noted that the 1% removal of DCF cannot be considered statistically significant. Therefore, 15 min of solar radiation was not enough to start the decomposition of this micropollutant. During the winter season, the decomposition of OP started first after 15 min of exposure to sunlight (Fig. 2d). The same relationship was also observed for salt water and surface water solutions of this compound. The low decomposition ability during winter was also confirmed by the determined half-life of DCF and OP (Table 6). The half-life of OP in deionized water during the winter season was about 854 min, while during spring, it decreased to about 165 min.

Higher removal degrees in the winter season were noted for BHT and TCS. The concentration of BHT after 30 min of radiation reached 5%, and after 120 min, 26%. It should be noted that 5 min of solar radiation was insufficient to initiate the decomposition of the tested micropollutants in deionized water, salt water, and surface water solutions. This is related to the lower energy amount which reaches the earth's surface during the winter season in Europe [27]. The sunlight comes to the surface at a low angle and is dispersed over a larger area [28]; therefore, the energy which potentially reaches the reaction vessels is insufficient to start the decomposition of compounds.

The solar radiation emitted during summer allowed to speed up the compound decomposition process. After 5 min of irradiation, the removal of DCF and OP in deionized water (Fig. 2) was higher than 1.5%, the TCS concentration decreased by 8%, and the BHT removal reached 5%. Similar results were also noted for the surface water solution. Only in the case of salt water solutions the decomposition of TCS and BHT start after 15 min of irradiation and for DCF and OP after 30 min. The same dependence was

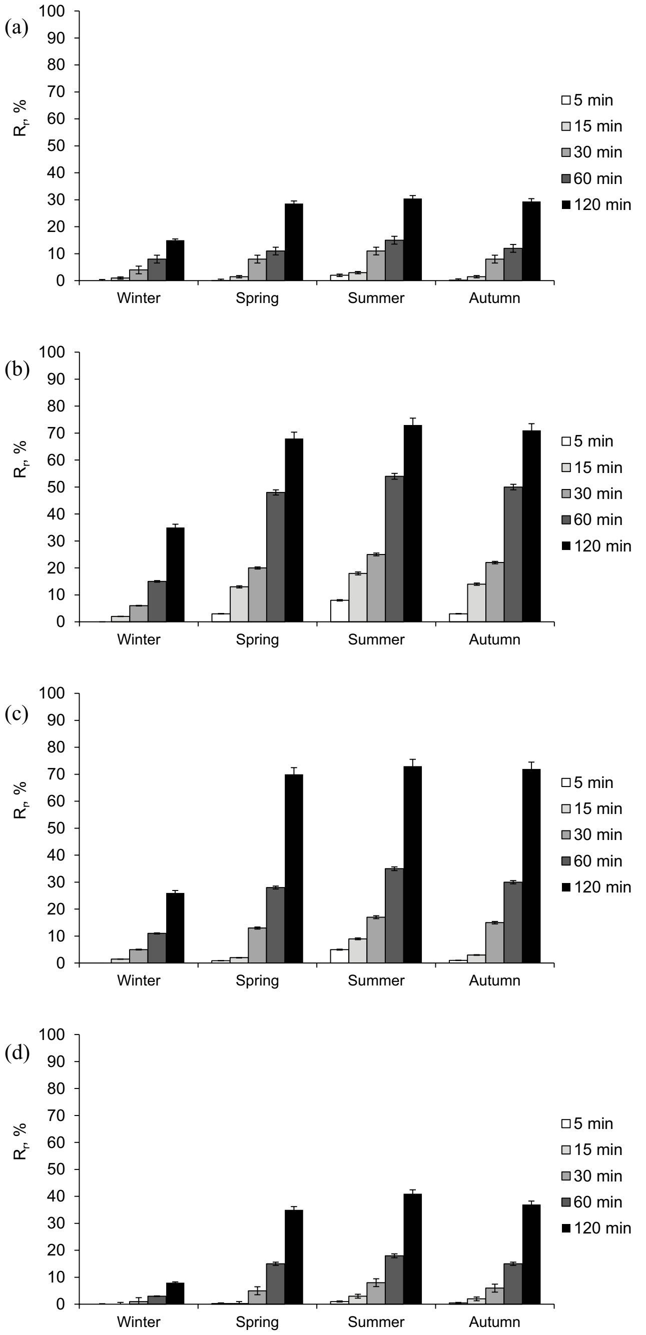


Fig. 2. Comparison of the (a) diclofenac, (b) triclosan, (c) butylated hydroxytoluene and (d) 4-*tert*-octylphenol removal degree noted in deionized water solutions after irradiation with sunlight during different seasons.

observed in salt water samples exposed to solar radiation during spring and autumn.

The removal degrees noted during the spring and autumn in all tested water samples in the measured periods did not differ significantly. However, the removal degree of OP and TCS was higher during autumn than during spring. For example, the TCS removal in deionized water solutions after 60 min of irradiation during autumn was equal to 50% (Fig. 2b), and during spring, it did not exceed 48%.

The one-way ANOVA variance of analyses showed that the different rations of solar radiation measured in all seasons of the year significantly affect the decomposition of the tested micropollutants in water solutions. The test carried out in the dark chamber during all seasons of the year showed no statistically significant changes in the concentrations of the tested micropollutants. This confirms the assumption that the decomposition of pollutants is initiated by solar radiation.

Fig. 3 compares the removal degrees of the tested micropollutants after 120 min of process elongation. It was noted that inorganic compounds present in salt water solutions inhibited the decomposition of the micropollutants. For example, the removal degree of TCS during winter was equal to 24%, during spring 48%, during summer 51%, and during autumn did not range over 50% in salt solutions. In comparison, the values of the removal degree of this compound in the deionized water solution were 35% in winter, 68% during spring, 73% during summer, and 71% in the winter, respectively.

The test results indicated a beneficial influence of the complex chemical composition of the surface water solution on the decomposition of compounds. The obtained compound removal degrees were significantly higher (confirmed by the one-way ANOVA results) than those noted in the salt water solution but achieved higher values than those noted in deionized water. For example, the DCF removal in deionized water during summer was not higher than 30%. At the same time, in surface water solutions, this micropollutant was reduced by over 35%. The removal degrees of BHT in deionized and surface water were very similar; the difference does not exceed 1%, which is within the limit of measurement error. It should be emphasized that the dissolved organic matter can reduce the amount of radiation reaching the particles of individual micropollutants by absorbing UV rays [29]. However, this phenomenon was not observed during the conducted research.

The LSD test results, summarized in Table 5, indicated a significant difference in micropollutant concentration measured in water samples between individual seasons. The LSD values for the tested micropollutants were, in all cases, higher than the absolute value of the difference in the mean removal degree of individual micropollutants.

In the considered period of the solar irradiation process, no complete removal of any of the tested micropollutants was achieved. Therefore, it is necessary to extend the exposure process, which is also indicated by Koumaki et al. [19].

It was observed that the degradation kinetics of the micropollutants in the tested water solutions during the direct solar radiation followed pseudo-first-order reaction kinetics. The calculated coefficient of determination (R^2) ranged from over 0.95 to 0.99. The calculated compound half-life values were lowest in summer and highest in winter (Table 6). This confirms the highest efficiency of the decomposition process in the summer period and a significant inhibition of the decomposition of compounds in the winter period.

Table 5
LSD test results calculated for different seasons and all tested water solutions

Deionized water solutions									
Diclofenac	Winter	Spring	Summer	Autumn	Triclosan	Winter	Spring	Summer	Autumn
Winter	–				Winter	–			
Spring	13.6	–			Spring	33.0	–		
Summer	15.5	1.9	–		Summer	37.9	4.9	–	
Autumn	14.4	0.8	1.1	–	Autumn	36.1	3.1	1.8	–
Butylated hydroxytoluene	Winter	Spring	Summer	Autumn	4-*tert*-octylphenol	Winter	Spring	Summer	Autumn
Winter	–				Winter	–			
Spring	43.9	–			Spring	27.1	–		
Summer	46.9	3.0	–		Summer	33.2	6.1	–	
Autumn	45.9	2.0	1.0	–	Autumn	29.0	2.0	4.1	–
$LSD_{DCF} = 0.4$; $LSD_{TCS} = 1.2$; $LSD_{BHT} = 1.0$; $LSD_{OP} = 1.6$									
Salt water solutions									
Diclofenac	Winter	Spring	Summer	Autumn	Triclosan	Winter	Spring	Summer	Autumn
Winter	–				Winter	–			
Spring	10.2	–			Spring	24.0	–		
Summer	12.4	2.2	–		Summer	27.0	3.0	–	
Autumn	11.0	0.9	1.3	–	Autumn	25.6	1.6	1.4	–
Butylated hydroxytoluene	Winter	Spring	Summer	Autumn	4-*tert*-octylphenol	Winter	Spring	Summer	Autumn
Winter	–				Winter	–			
Spring	29.9	–			Spring	13.4	–		
Summer	32.1	2.2	–		Summer	17.0	3.6	–	
Autumn	30.9	1.0	1.2	–	Autumn	14.9	1.5	2.0	–
$LSD_{DCF} = 0.7$; $LSD_{TCS} = 0.3$; $LSD_{BHT} = 0.1$; $LSD_{OP} = 0.1$									
Surface water solutions									
Diclofenac	Winter	Spring	Summer	Autumn	Triclosan	Winter	Spring	Summer	Autumn
Winter	–				Winter	–			
Spring	15.9	–			Spring	33.1	–		
Summer	18.4	2.5	–		Summer	36.8	3.6	–	
Autumn	17.0	1.1	1.4	–	Autumn	34.8	1.7	2.0	–
Butylated hydroxytoluene	Winter	Spring	Summer	Autumn	4-*tert*-octylphenol	Winter	Spring	Summer	Autumn
Winter	–				Winter	–			
Spring	43.7	–			Spring	29.0	–		
Summer	46.8	3.1	–		Summer	34.0	5.0	–	
Autumn	44.8	1.1	2.1	–	Autumn	29.9	0.9	4.1	–
$LSD_{DCF} = 0.5$; $LSD_{TCS} = 0.8$; $LSD_{BHT} = 0.8$; $LSD_{OP} = 0.5$									

The half-life values of all tested micropollutants noted in salt water solutions were significantly higher than those noted in surface water and deionized water solutions. The half-life of OP in salt water during winter exceeds 1719 min and during spring 396 min. While the half-life of this compound noted in deionized water was about 854 min in winter and 165 min in spring. This proves the negative impact of the adopted salty water composition on the decomposition of compounds. The observation is consistent with previous research studies [30,31]. However, it should be emphasized that compounds such as bicarbonate ions in the matrixes can lead to the formation of carbonate radicals ($HCO_3^{\bullet}$, $CO_3^{\bullet-}$), which can additionally support the process of pollutant decomposition [32]. Lair et al. [33] noted that small amounts of Cl^- can force the initial degradation of micropollutants such as naphthalene.

Despite the slight differences between the compound removal degrees in the spring and autumn seasons, the obtained half-life values indicate a faster course of the decomposition process in autumn. For example, the half-life

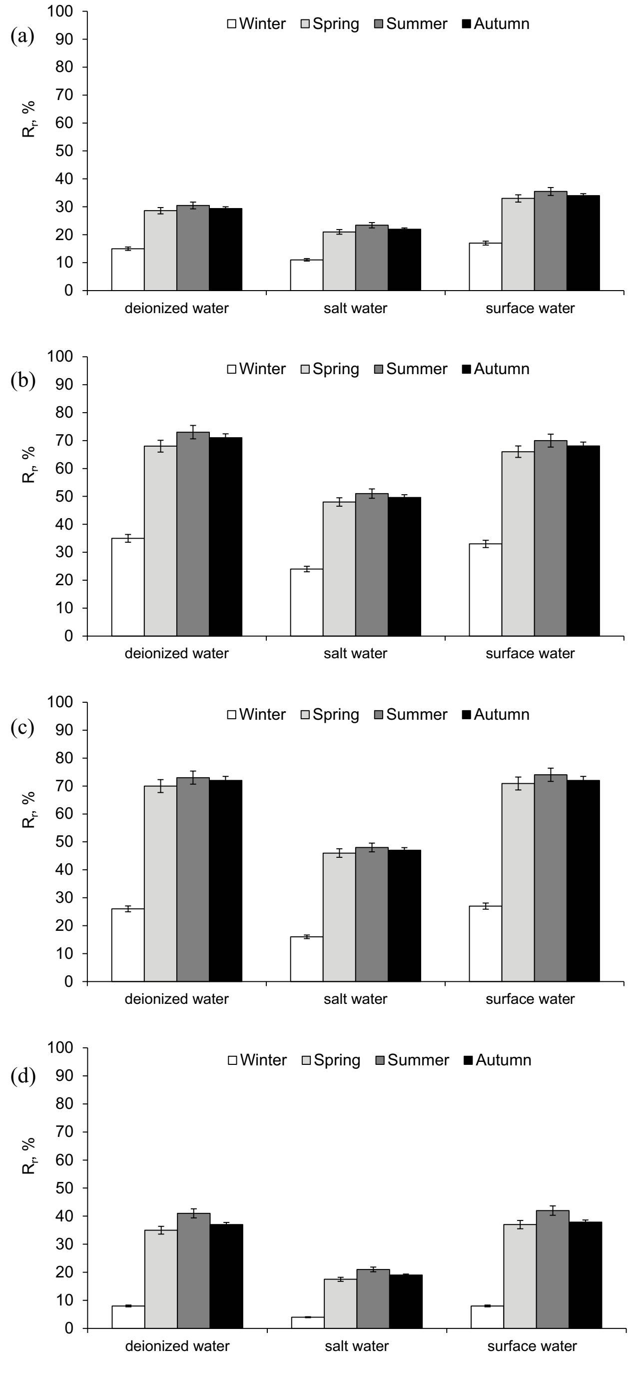


Fig. 3. Removal degree of (a) diclofenac, (b) triclosan, (c) butylated hydroxytoluene and (b) 4-*tert*-octylphenol in different water solutions after 120 min of solar radiation during in all seasons of the year.

of TCS in surface water in autumn was about 41 min, and in spring increased to over 73 min. This means that micropollutants much better absorbed the radiation emitted by the sun in autumn than in spring.

Table 6
Micropollutant half-life $t_{1/2}$, min calculated for different seasons of the year

Compound	Solution type		
	Deionized water	Salt water	Surface water
Winter			
Diclofenac	490.6	621.5	428.5
Triclosan	172.0	256.4	178.9
Butylated hydroxytoluene	257.1	399.4	239.6
4-*tert*-octylphenol	854.2	1719.1	856.1
Spring			
Diclofenac	231.4	340.2	196.2
Triclosan	69.2	125.4	73.2
Butylated hydroxytoluene	106.4	175.5	104.5
4-*tert*-octylphenol	165.5	396.4	157.5
Summer			
Diclofenac	231.6	289.4	200.8
Triclosan	56.1	97.0	57.1
Butylated hydroxytoluene	99.4	103.5	93.7
4-*tert*-octylphenol	159.4	316.4	138.6
Autumn			
Diclofenac	223.4	322.9	184.7
Triclosan	59.7	120.5	41.6
Butylated hydroxytoluene	98.7	170.6	73.6
4-*tert*-octylphenol	184.2	374.9	156.2

3.2. Identification of photo-decomposition intermediates

The chromatographic analysis carried out in the TIC mode indicated the presence of micropollutant intermediates in the samples after contact with solar radiation. Table 7 summarize compounds matched in samples exposed to solar radiation during winter, spring, summer, and autumn. The number of identified newly formed compounds increased with the duration of the irradiation process. In addition, the surface area corresponding to the peaks of individual intermediates was larger in samples exposed longer to radiation. This indicates an increase in the concentration of individual by-products in the tested aqueous solutions. Only in the case of samples irradiated during summer a decrease in the peak area of the intermediates or their complete decomposition was observed between 60 and 120 min of the process duration.

The exposure of pharmaceutical compounds to UV rays, including sunlight, leads to the breaking of bonds between atoms contained in the molecule structure of these compounds, which has been proven in numerous studies also conducted on compounds in the form of powders or liquids and occurring in aqueous solutions [34–36]. Kovacic et al. [37] indicate that during the irradiation of the DCF molecule, the chlorine atom is detached, and the compound molecule cyclizes. This process results in the formation of (8-chloro-9H-carbazol-1-yl)acetic acid, the presence of which in samples exposed to sunlight was also noted by Agüera et al. [38]. According to literature data [39–41], two DCF photo-decomposition pathways can be distinguished. The first

Table 7
By-products of the decomposition of compounds in water solutions subjected to sunlight irradiation in different seasons

Compound	By-product	Time, min														
		5			15			30			60			120		
Winter																
	Water solution	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Diclofenac	4′,5-dihydroxydiclofenac	–	–	–	–	–	–	–	–	–	–	–	+	–	+	+
Triclosan	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Butylated hydroxytoluene	2,6-di-*tert*-butylhydroquinone	–	–	–	–	–	–	–	–	–	–	–	+	+	+	+
	tert-butylhydroquinone	–	–	–	–	–	–	–	–	–	–	–	–	–	+	–
	2,6-di-*tert*-butylbenzoquinone	–	–	–	–	–	–	–	–	–	–	–	–	–	+	–
4-*tert*-octylphenol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Spring																
	Water solution	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Diclofenac	4′,5-dihydroxydiclofenac	–	–	–	–	–	–	–	–	–	–	–	+	+	+	+
	5-hydroxydiclofenac	–	–	–	–	–	–	–	–	–	–	–	+	+	+	+
	2,6-dichloroaniline	–	–	–	–	–	–	–	–	–	+	+	+	+	+	+
	2,6-dichloro-4-aminophenol	–	–	–	–	–	–	–	–	–	–	–	–	+	+	+
Triclosan	2,4-dichlorophenol	–	–	–	–	–	–	–	–	–	+	+	+	+	+	+
	4-chlorophenol	–	–	–	–	–	–	–	–	–	+	+	+	+	+	+
Butylated hydroxytoluene	2,6-di-*tert*-butylhydroquinone	–	–	–	–	–	–	–	–	+	+	+	+	+	+	+
	tert-butylhydroquinone	–	–	–	–	–	–	–	–	+	+	+	+	+	+	+
	2,6-di-*tert*-butylbenzoquinone	–	–	–	–	–	–	–	–	–	+	+	+	+	+	+
4-*tert*-octylphenol	1,4-benzenediol	–	–	–	–	–	–	–	–	–	–	–	+	+	+	+
Summer																
	Water solution	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Diclofenac	4′,5-dihydroxydiclofenac	–	–	–	–	–	+	–	+	+	+	+	+	+	+	+
	5-hydroxydiclofenac	–	–	–	–	–	–	–	–	+	–	–	–	+	+	–
	2,6-dichloroaniline	–	–	–	–	–	–	–	–	+	–	–	–	–	–	–
	2,6-dichloro-4-aminophenol	–	–	–	–	–	–	–	–	+	–	–	+	–	–	+
Triclosan	2,4-dichlorophenol	–	–	–	+	+	+	+	+	+	+	+	+	+	–	+
	4-chlorophenol	–	–	–	–	–	+	+	–	–	+	–	–	–	–	–
Butylated hydroxytoluene	2,6-di-*tert*-butylhydroquinone	–	–	–	–	–	–	–	–	–	–	–	–	–	+	+
	tert-butylhydroquinone	–	–	–	–	–	–	–	+	+	+	+	+	+	+	+
4-*tert*-octylphenol	1,4-benzenediol	–		–	–		–	–	+	–	–	+	–	+	–	–
Autumn																
	Water solution	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Diclofenac	4′,5-dihydroxydiclofenac	–	–	–	–	–	–	–	–	–	–	–	+	+	+	+
	5-hydroxydiclofenac	–	–	–	–	–	–	–	–	–	–	–	+	+	+	+
	2,6-dichloroaniline	–	–	–	–	–	–	–	–	–	+	+	+	+	+	+
	2,6-dichloro-4-aminophenol	–	–	–	–	–	–	–	–	–	–	–	+	+	+	+
Triclosan	2,4-dichlorophenol	–	–	–	–	–	–	–	–	+	+	+	+	+	+	+
	4-chlorophenol	–	–	–	–	–	–	–	–	+	+	–	+	+	+	+
Butylated hydroxytoluene	2,6-di-*tert*-butylhydroquinone	–	–	–	–	–	–	–	–	+	+	+	+	+	+	+
	tert-butylhydroquinone	–	–	–	–	–	–	–	–	+	+	+	+	+	+	+
	2,6-di-*tert*-butylbenzoquinone	–	–	–	–	–	–	–	–	–	+	+	+	+	+	+
4-*tert*-octylphenol	1,4-benzenediol	–	–	–	–	–	–	–	–	+	+	+	+	+	+	+

A – deionized water solutions; B – salt water solutions; C – surface water solutions; + – compound identified in the sample; – – compound not identified in the sample.

pathway indicates the elimination of chlorine atoms from the structure of the molecule and the formation of by-products with carbazole structures. On the other hand, the second pathway focuses on reactions in the acetic acid group of the molecule, which may lead to the formation of indoline or aldehyde structures [39,40]. The concocted analysis of the post-processed samples confirmed the presence of four DCF intermediates in ale types of water solutions exposed to 120 min of solar radiation during spring and autumn and in selected samples during summer. Only during the winter season one intermediate – 4′,5-dihydroxydiclofenac was detected in surface water samples after 60 and 120 min of sunlight exposure and in salt water solutions after 120 min of process duration. 4′,5-dihydroxydiclofenac, and 5-hydroxydiclofenac identified in the tested samples during spring, summer, and autumn may indirectly indicate the initiation of the first photo-decomposition pathway. In contrast, 2,6-dichloroaniline and 2,6-dichloro-4-aminophenol may be classified as further decomposition products formed in the first or second DCF decomposition pathway.

In the case of TCS water solutions, only two by-products, that is, 2,4-dichlorophenol and 4-chlorophenol, were identified in post-process solutions during spring, summer, and autumn. However, no TCS by-products were formed in solutions exposed to solar radiation in the winter. This may be related to the low removal of TCS during this period and the formation of possible by-products at concentrations below the detection limit of the analytical method used. Sunlight-initiated BHT photo-decomposition was affected to produce three by-products of its decomposition, that is, 2,6-di-*tert*-butylhydroquinone, *tert*-butylhydroquinone and 2,6-di-*tert*-butylbenzoquinone. Those intermediates were identified in samples after 60 and 120 min of irradiation during spring and autumn, regardless of the physico-chemical composition of the solution. The test carried out in the winter season led to the formation of all three compounds only in salt water after 120 min of irradiation. While the presence of only 2,6-di-*tert*-butylhydroquinone was noted in surface water after 60 and 120 min of solar radiation and in deionized water after 120 min. During summer, *tert*-butylhydroquinone in the highest concentration was detected in salt water and surface water solution after 30 min of radiation, and then its concentration gradually decreased.

In the post-processed OP solutions, only one intermediate – 1,4-benzenediol was noted. This compound occurs in all types of water solutions exposed to 120 min of solar radiation during spring and in surface water solutions after 60 min of irradiation. During summer 1,4-benzenediol was noted in salt water solutions after 30 and 60 min of process duration and in deionized water samples after 120 min. The highest picks areas of the OP intermediate in all tested solutions were noted for samples collected after 60 and 120 min of solar radiation during autumn. This proves a much higher concentration of this compound in solutions irradiated in autumn than in solutions exposed to sunlight in other seasons. Moreover, the presence of 1,4-benzenediol was not noted in the samples taken in the winter season.

Sonntag and Schuchmann [42] indicate various possible mechanisms of OP decomposition under the action of solar radiation. While Brand et al. [43] pointed out that OP intermediates such as benzoquinones and 4-hydroxyacetophenone were formed due to the excitation of the molecule of this compound and the formation of phenoxy radicals, which are then oxidized to alkoxy radicals.

The largest number and concentration of micropollutant decomposition by-products were noted in surface water solutions. It should be noted that in the case of those solutions, some intermediates could be not only the decomposition by-products of the tested micropollutant but also come from other phenolic compounds occurring in this media. Particular attention should be paid to the photo-decomposition by-products of TCS which belong to the group of chlorophenols. Due to their toxic nature and potentially carcinogenic action, those compounds are catalogued as priority pollutants (Clean Water Act and by European Directive 2013/39/EU) [44,45]. The detection of any micropollutant by-product in post-processed water solutions necessitates conducting toxicological analyses to check the biological activity of newly formed compounds and to determine their harmfulness to the environment.

3.3. Toxicity analysis of post-processed retentate samples

The formation of potentially toxic by-products of phenolic compounds is a well-known phenomenon, especially during advanced oxidation processes which use strong oxidation agents [46]. However, Karci et al. [47] and Munoz et al. [48] noted that the most toxic compounds are formed during the initial stages of the compound decomposition processes and can be attributed to direct photolysis. Therefore, the appearance of micropollutant intermediates during the conducted solar radiation process requires the implementation of toxicological tests.

Fig. 4 presents the results of the toxicity effect measurement carried out on the tested water solutions before exposure to solar radiation. The results obtained from the Microtox® bioassay and the *Lemna minor* GIT indicated high toxicity ($E > 75\%$) for the solutions containing TCS. DCF and BHT water solutions, were, in all cases, assigned to non-toxic solutions ($E < 25\%$). While a low toxic nature ($25\% < E < 50\%$) was measured by the use of the Microtox® test for OP prepared based on deionized water and salt water. The salt water OP solution was also low toxic to the *Lemna minor* vascular plants. The OP solution prepared based on surface water was non-toxic to the test organisms.

The toxicity effect E for the micropollutant solutions was generally lower in the surface water solutions than in the solutions prepared based on deionized water and salt water. This is due to the presence of chemical compounds in the surface water, which may have a beneficial effect on the indicator organisms and disturb the proper interpretation of the test results [49].

The Microtox® test was more sensitive to the action of the micropollutants than the *Lemna minor* GIT. Niemirycz et al. [50] also indicated that the Microtox® bioassay is one of the most sensitive topological tests of water solutions. Therefore, further toxicological analyzes were only based on the Microtox® test.

The changes in the toxicity effect in the micropollutant solutions based on deionized water subjected to solar radiation during different seasons of the year were presented in Fig. 5. The results obtained for surface water solutions

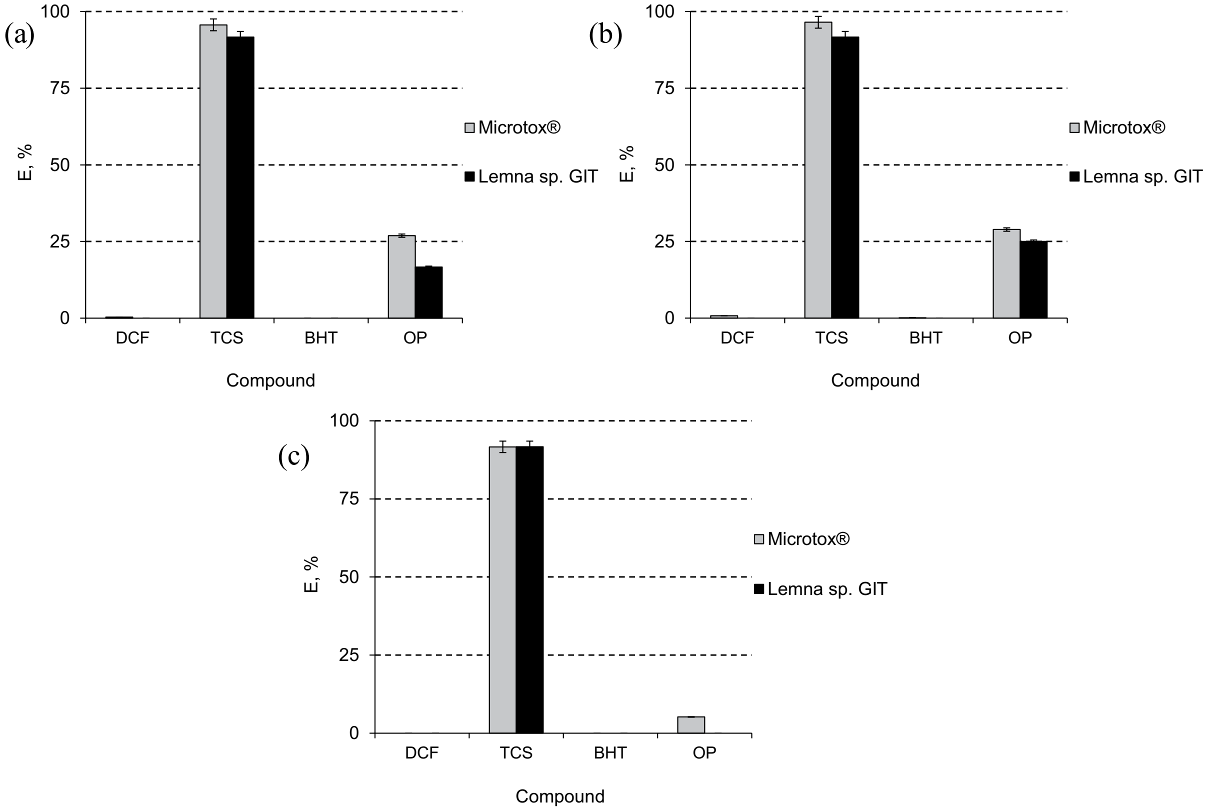


Fig. 4. Toxic effect observed for micropollutant solutions prepared on the basis of (a) deionized water, (b) salt water and (c) surface water.

were summarized in Fig. 6. The toxicity effect observed in deionized water micropollutant solutions and those prepared using salt water was very similar (results not presented). The difference between the values did not exceed 2.5%, which is close to the measurement error value of the analytical apparatus. It can therefore be concluded that the presence of the chosen salts did not significantly affect the results of the toxicological analysis, which is also confirmed by slight differences between the identified intermediates in the post-process solutions of both solutions. However, it should be emphasized that the presence of salt influenced the inhibition of the pollutant decomposition process. Therefore, the emerging toxic effect may also be related to the interaction of micropollutants with inorganic compounds.

Despite the presence of the largest number of by-products in post-process DCF solutions, no toxic character of these solutions was noted. Only in the case of deionized water (Fig. 5) and salt water solutions a slight increase in the toxic effect was noted after 30, 60, and 120 min of the process duration. However, this effect remains below 25%. Whereas in DCF and BHT solutions prepared based on surface water (Fig. 6), the toxic effect remained below 1% throughout the whole time of the irradiation process, regardless of the season of the year. In BHT solutions prepared based on deionized water and salt water in the spring, summer, and autumn seasons (Fig. 5b–d), an increase in toxicity was noted along with the lengthening of the irradiation process. This proves the toxic nature of the formed BHT intermediates. Especially *tert*-butylhydroquinone, present in all mentioned samples, is considered a carcinogenic compound, although the literature also indicates its chemoprotective effect on living organisms [51]. Also, 2,6-di-*tert*-butylhydroquinone can be cytotoxic and genotoxic to diverse cells and animals [52].

The toxicity of the TCS deionized water, salt water, and surface water solutions decreased with the increase of the solar radiation time. In the case of conducting the process in the winter period (Figs. 4a and 6a), the reduction of the toxic effect was negligible. However, in the summer period, the TCS deionized and salt water solutions, after 120 min of exposure to solar radiation, decreased their toxic character from high toxic to toxic ($50\% < E < 75\%$). Also, a decrease in toxicity was observed in the case of TCS solutions prepared based on surface water. The TCS surface water solutions (Fig. 6c and d) become toxic after 60 min of solar radiation during autumn and summer. It can therefore be concluded that despite the formation of compounds such as 2,4-dichlorophenol and 4-chlorophenol, which were generally considered to be very toxic [53,44], the reduction of the TCS concentration alone contributes most to the toxic effect. However, Kwean et al. [54] pointed out that even small amounts of 4-chlorophenol (ranging from 5 ng/dm^3 to 20 μg/dm^3) present in the aquatic environment exhibit a chronic effect on humans.

The increase of the toxicity of OP solutions was noted in all types of samples, except for the surface water solution

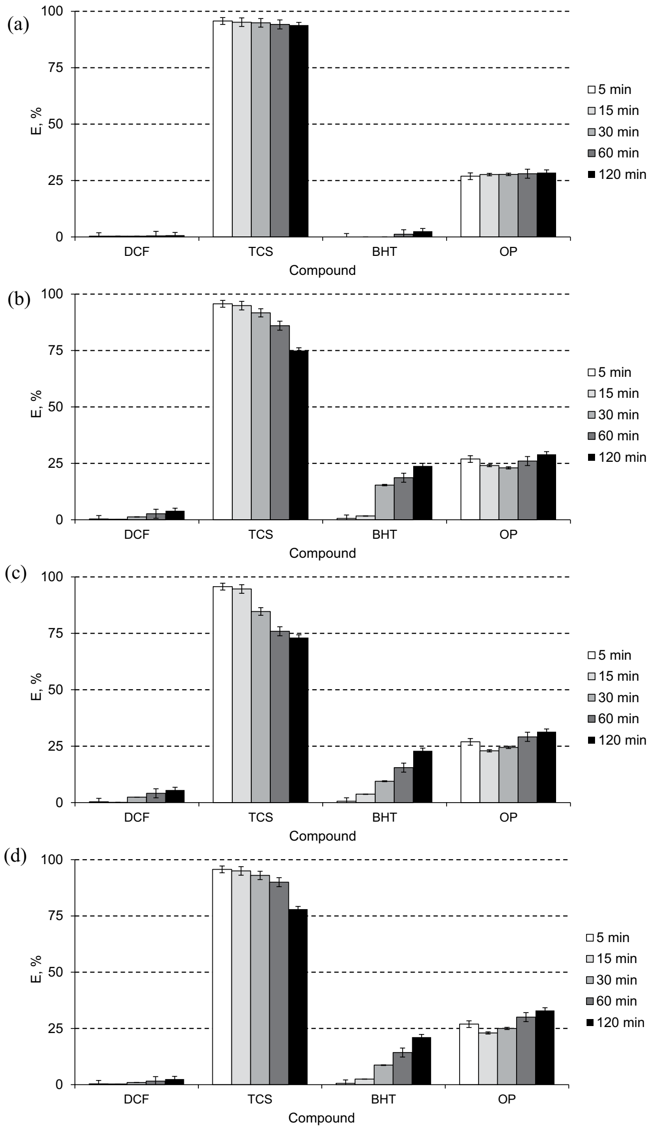


Fig. 5. Changes in the toxic effect during solar irradiation of deionized water solutions during (a) winter, (b) spring, (c) summer and (d) autumn.

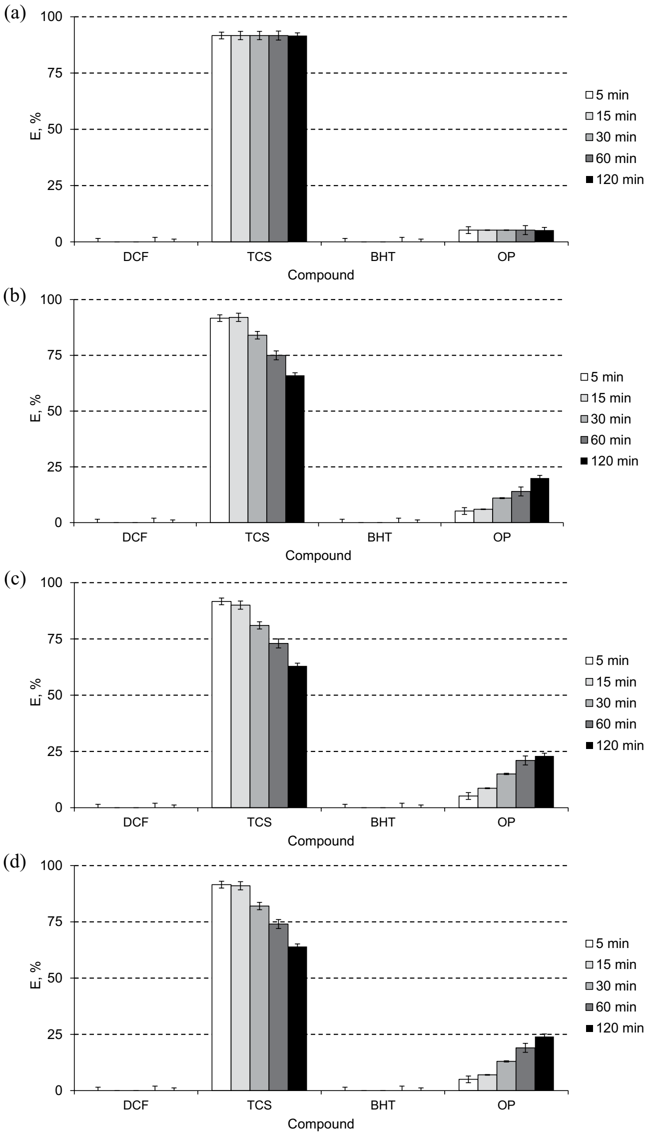


Fig. 6. Changes in the toxic effect during solar irradiation of surface water solutions during (a) winter, (b) spring, (c) summer and (d) autumn.

in winter and is related to the formation of 1,4-benzenediol and the possible formation of other compounds like *p*-benzoquinone or catechol, which presence was not proven in this study. Santos et al. [55] pointed out that 1,4-benzenediol and *p*-benzoquinone contribute the most to the increase of the toxicity of post-processed phenolic compound solutions. These observations were also proven by Ferreiro et al. [56]. Consequently, solutions of this micropollutant prepared especially based on surface water, from initially non-toxic nature, became low toxic.

The selection of an appropriate method of pollutant decomposition can lead to their complete mineralization and formation of CO_2, and thus contribute to a significant reduction in the toxicity of aqueous solutions [57]. Therefore, it is necessary to support the natural photo-decomposition of micropollutants to accelerate it and reduce the formation of harmful intermediates.

4. Conclusions

The results indicated that solar radiation could decompose different types of organic micropollutants. However, this process requires time and access to solar radiation of the appropriate intensity. Therefore, it can only be effective in the temperate climate in spring, summer, and autumn. In addition, the presence of inorganic compounds inhibited the decomposition process of pollutants, which resulted in the extension of the half-life of micropollutants decomposition in salt water solutions compared to solutions prepared with deionized water and surface water. The obtained results showed that the number of by-products of the decomposition of individual compounds could depend on the season of the year. The highest number of newly formed intermediates was observed in all tested water solutions exposed to 120 min of sunlight during spring and autumn. The higher intensity of solar radiation in the summer period contributed to the decomposition of the tested micropollutants and their decomposition by-products. The complete mineralization of compounds seems to be possible only if other physico-chemical methods support the photo-decomposition process. Nevertheless, natural solar radiation can be used as an alternative but a temporary source of energy in pollutant advanced oxidation processes, which are based on the action of artificial UV radiation. The toxicological analyses conducted on vascular plants *Lemna minor* and salt water bacteria *Aliivibrio fischeri* indicated the toxic nature only of TCS water solutions. The toxicity effect of these solutions gradually decreased with the duration of the irradiation process. The opposite relationship was observed in the case of solutions containing OP. Particularly, solutions of this micropollutant prepared based on surface water, from initially non-toxic nature, became low toxic.

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