

## Photodegradation of Triazine Herbicides in Aqueous Solutions and Natural Waters

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The photodegradation of three triazines, atrazine, simazine, and prometryn, in aqueous solutions and natural waters using UV radiation ( $\lambda > 290$  nm) has been studied. Experimental results showed that the dark reactions were negligible. The rate of photodecomposition in aqueous solutions depends on the nature of the triazines and follows first-order kinetics. In the case of the use of hydrogen peroxide and UV radiation, a synergistic effect was observed. The number of photodegradation products detected, using FIA/MS and FIA/MS/MS techniques, suggests the existence of various degradation routes resulting in complex and interconnected pathways.

**KEYWORDS:** Photodegradation; triazines; pesticides; hydrogen peroxide; FIA/MS; FIA/MS/MS

### INTRODUCTION

The use of agricultural pesticides throughout Europe has increased dramatically during the past two decades and has consequently led to increasing concern about the environmental fate of these substances. Their use has raised some very serious ecological concerns related to their toxicity, stability, and pollution of soil, water, and air. Investigations to understand their ecological behavior are important before their application. The residues of many pesticides and their degradation products are now present in all environmental compartments because of their relatively slow rate of decomposition (1, 2).

Triazine herbicides are among the most commonly used pesticides in the world. The main compound of this family, atrazine, is found in many environmental compartments, contaminating soil and water reserves (3, 4). The EEC Directive on the Quality of Water Intended for Human Consumption sets a maximum admissible concentration (MAC) of 0.1  $\mu\text{g/L}$  per individual pesticide. The triazines listed in the 76/464/EEC Directive ("black list") on pollution are atrazine and simazine. Within the list, the herbicides cited in addition to atrazine and simazine are cyanazine, prometryn, terbutylazine, and terbutryn (5).

To evaluate the fate of pesticides in the environment, the influences of both abiotic and biotic factors should be taken into account. Among the abiotic chemical factors affecting the behavior of pesticides, photochemical reactions are important. In the surface layers of aquatic systems, photochemical reactions can play a dominant role in the conversion and degradation of pesticides. It is well known that triazines are susceptible to photochemical and oxidative degradation processes under suitable conditions (6, 7). Photodegradation of triazine herbicides under simulated solar light occurs very slowly. Thus, advanced oxidation processes (AOPs) have been developed to remove triazines from drinking water, natural waters, and industrial

effluents. Among them,  $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{O}_3/\text{UV}$ , and  $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$  combinations employ photolysis of  $\text{H}_2\text{O}_2$  and ozone to produce hydroxyl radicals ( $\cdot\text{OH}$ ) that are able to oxidize the pollutants due to their high oxidative capacity. Another interesting AOP involves the utilization of photocatalytic oxidation mediated by titanium dioxide in suspension (8–10). Many reports have been published describing the photolysis of triazines. Dechlorination, dealkylation, and alkyl chain oxidation have all been observed in these studies (4, 11–14).

The aim of this study was to elucidate the photochemical degradation potential of selected triazines in the UV and  $\text{H}_2\text{O}_2/\text{UV}$  systems for aqueous solutions and surface waters. The objectives were to evaluate the degradation kinetics in natural waters and to determine the main byproducts by using flow injection analysis (FIA) combined with mass spectrometry (MS) or tandem mass spectrometry (MS/MS) in order to estimate the photolysis mechanisms that take place in surface waters. Atrazine [2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine], simazine [2-chloro-4,6-bis(ethylamino)-*s*-triazine], and prometryn [2-methylthio-4,6-bis(isopropylamino)-*s*-triazine] were selected as the target compounds owing to their widespread use in Greece.

### MATERIALS AND METHODS

Residue analysis grade atrazine, simazine, and prometryn were supplied by Riedel-de-Haen (Germany). Hydrogen peroxide (30%), methanol, acetone, and acetonitrile (HPLC grade) were supplied by Merck. No buffer system was added to the solutions. Photolysis experiments for the aqueous solutions and surface waters were carried out in a 500 mL Pyrex UV reactor, equipped with a diving Philips HPK 125W high-pressure mercury lamp. The lamp was jacketed with a water-cooled Pyrex filter, restricting the transmission of wavelengths below 290 nm. The tap water cooling circuit maintained the temperature at 30–35 °C.

Substrates were dissolved in distilled water under their solubility level by putting the appropriate volume of a stock solution in acetone to give an acetone content of <1%. The concentration of triazine

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**Table 1.** Photodegradation Kinetic Parameters: Rate Constants, Correlation Coefficients ( $R^2$ ), and Half-Lives ( $t_{1/2}$ ) of the Studied Triazines in Distilled Water and in River and Lake Waters

| herbicide | distilled water                    |       |               | lake water                         |       |               | river water                        |       |               |
|-----------|------------------------------------|-------|---------------|------------------------------------|-------|---------------|------------------------------------|-------|---------------|
|           | $k \times 10^2$ (h <sup>-1</sup> ) | $R^2$ | $t_{1/2}$ (h) | $k \times 10^2$ (h <sup>-1</sup> ) | $R^2$ | $t_{1/2}$ (h) | $k \times 10^2$ (h <sup>-1</sup> ) | $R^2$ | $t_{1/2}$ (h) |
| atrazine  | 8.4                                | 0.95  | 8.3           | 9.6                                | 0.99  | 7.2           | 10.5                               | 0.99  | 6.6           |
| symazine  | 17.6                               | 0.99  | 3.9           | 12.7                               | 0.99  | 5.4           | 27.9                               | 0.99  | 2.7           |
| prometryn | 15.2                               | 0.98  | 4.6           | 6.0                                | 0.99  | 11.6          | 10.0                               | 0.99  | 6.9           |

pesticides in water was 10 mg/L in order to facilitate the identification of intermediate products. The herbicide solution was magnetically stirred during the illumination. At specific time intervals, samples of 10 mL were withdrawn from the reactor and analyzed after direct injection. Each series of photodegradation experiments was conducted in two replicates and accompanied by dark reaction controls.

The concentrations of the selected triazines were determined by a Merck-Hitachi 655A liquid chromatograph equipped with a variable-wavelength UV detector using a 25 cm, 0.4 cm i.d. C18 Erlasil S100 column. The mobile phase was a mixture of acetonitrile and water (60/40 v/v). The eluate was delivered at a rate of 1.0 mL/min, and the detection was realized at 223 nm. The standards that were used were of 99.9% purity, purchased from Riedel-de-Haan.

For the identification of transformation products by FIA/MS and FIA/MS/MS, the irradiated solution (250 mL) was concentrated by solid-phase extraction (SPE) at the end of the total irradiation time using 1 mL SPE cartridges filled with commercial C18 material from Baker. After SPE, the cartridges were eluted with deionized water and dried in a gentle stream of nitrogen. Absorbed compounds were desorbed and eluted with small portions of methanol (altogether 2 mL). The eluates were filtered through membranes of 0.45  $\mu$ m pore size, and then solutions were used directly for FIA-MS. For the analysis, a TSQ 700 mass spectrometer (Finnigan MAT, San Jose, CA) combined with a DEC 5000/33 data station was used. The electrospray (ES) interface (positive mode) was from Finnigan MAT.

To study the influence of natural water constituents on photodegradation, river water was collected from the river Axios and lake water from the lake Volvi located in Northern Greece. The Axios River, which originates in Yugoslavia and flows into the Thermaikos Gulf, is affected by domestic and industrial wastes. The lake Volvi (area 67 km<sup>2</sup>, maximum depth 23 m) is a slightly eutrophic lake, and its water quality is affected by agricultural effluents and wastes. All water samples were stored at 4 °C and again filtered before use (membrane filters, pore size 0.45  $\mu$ m, from Schleicher & Schrell). Total organic carbon was measured with a Simatzu V-csh TOC analyzer.

## RESULTS AND DISCUSSION

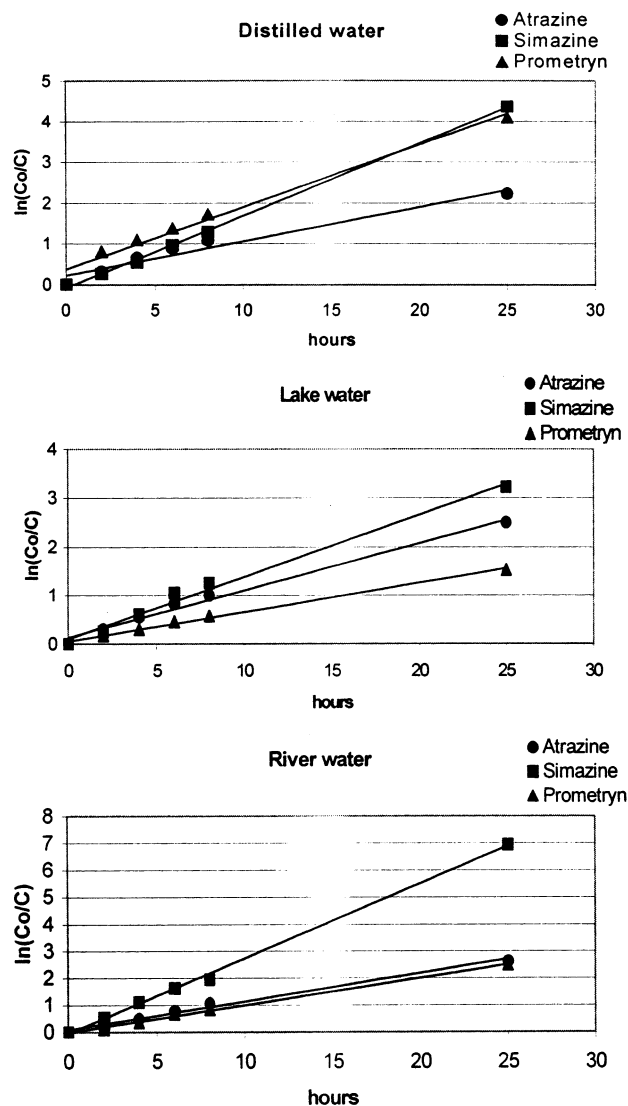
No obvious degradation of triazines in darkness at 25 °C was observed within 24 h. This means that the hydrolytic processes of triazines during the course of the experiment can be ignored. Moreover, dark degradation was not observed in the presence of hydrogen peroxide.

The kinetics of all the investigated pesticides follow an apparent first-order degradation curve (Figure 1). The logarithm of the ratio of the initial concentration ( $C_0$ ) to the concentration at a given time ( $C$ ) vs time ( $t$ ) was plotted, and the rate constant ( $k$ ) was determined by calculating the slope of the line obtained. The half-lives could then be determined from the equation

$$t_{1/2} = \ln 2/k$$

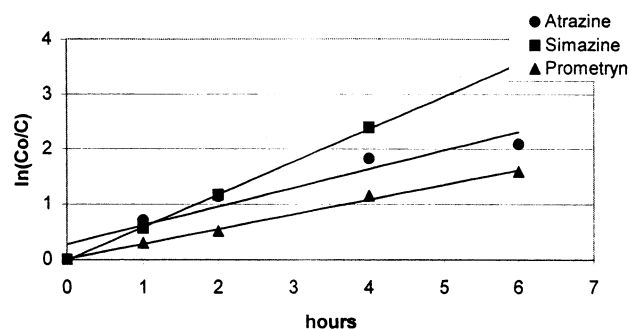
Table 1 list the values of  $k$  and the linear regression coefficients for kinetics of the photodegradation of the studied compounds. According to these values, the appropriate first-order relationship appears to fit well.

All investigated pesticides were sufficiently degraded in aqueous solutions. The half-lives ranged from 2.7 to 11.6 h for the studied triazines in the examined waters (distilled water and surface waters).

**Figure 1.** Photodegradation rates of triazine herbicides in distilled water, lake water, and river water (concentration level, 10 mg/L).**Table 2.** Quality Characteristics of Different Types of Water Used

| type of water   | pH  | conductivity (mS/cm) | DO (mg/L) | TOC (mg/L) |
|-----------------|-----|----------------------|-----------|------------|
| distilled water | 7.1 | 456                  | 8.0       | 0.8        |
| lake water      | 8.7 | 985                  | 6.9       | 13.6       |
| river water     | 8.5 | 678                  | 8.2       | 4.5        |

On the basis of the water systems examined, no distinct order of photodecomposition can be observed. Nevertheless, river water appears to have a higher degradation capacity for all the examined pesticides than lake water. This fact is attributed, in addition to other factors, to the oxygen content of river water (Table 2). On the other hand, the high concentration of suspended organic matter which was observed in the lake water influences the absorption of sunlight and consequently the



**Figure 2.** Photodegradation rates of triazine herbicides (concentration level, 10 mg/L) in distilled water in the presence of H<sub>2</sub>O<sub>2</sub> (200 mg/L).

**Table 3.** Photodegradation Kinetic Parameters: Rate Constants, Correlation Coefficients ( $R^2$ ), and Half-Lives ( $t_{1/2}$ ) of the Studied Triazines in Distilled Water, in the Presence of H<sub>2</sub>O<sub>2</sub> (200 mg/L)

| herbicide | $k \times 10^2$ (h <sup>-1</sup> ) | $R^2$ | $t_{1/2}$ (h) |
|-----------|------------------------------------|-------|---------------|
| atrazine  | 34.0                               | 0.95  | 2.0           |
| symazine  | 59.4                               | 0.99  | 1.2           |
| prometryn | 26.9                               | 0.99  | 2.6           |

**Table 4.** Variation of the First Apparent Kinetic Constant with the Initial Hydrogen Peroxide Concentration

| [H <sub>2</sub> O <sub>2</sub> ] (mg/L) | $k$ (h <sup>-1</sup> ) |
|---|------------------------|
| 0                                       | 8.4                    |
| 100                                     | 23.8                   |
| 200                                     | 34.0                   |
| 300                                     | 47.7                   |

degree of photodegradation of the examined triazines (15, 16). All the studied pesticides disappeared by more than 90% after 25 h of UV radiation in the examined water systems.

Indirect photolysis (UV with H<sub>2</sub>O<sub>2</sub>) of the tested pesticides also follows first-order kinetics (Figure 2). The values of the rate constants, regression coefficients, and half-lives are listed in Table 3. Hydrogen peroxide in combination with UV light can significantly enhance the degradation efficiency of the studied pesticides. These compounds disappeared by more than 80% after 6 h of radiation (4 times faster for atrazine). The reason for this behavior is a radical mechanism. New reactions occur as a consequence of the presence of radicals (especially •OH and HO<sub>2</sub>•) from the decomposition of hydrogen peroxide by UV radiation (12).

For prometryn, a smaller difference in the rate constants between direct photolysis and UV/H<sub>2</sub>O<sub>2</sub> system was observed, implying that the degradation of prometryn was due primarily to direct photolysis.

To determine the influence of the hydrogen peroxide concentration on the degradation rate of atrazine, experiments were carried out in the UV reactor with solutions at an initial atrazine concentration of 10 mg/L and with various concentrations of hydrogen peroxide, ranging from 100 to 300 mg/L. The rate of photodegradation follows a first-order kinetic law. The variation of the first-order kinetic apparent constant with the initial hydrogen peroxide concentration is given in Table 4.

The kinetics of atrazine photodegradation can be described as the sum of two mechanisms, direct photolysis and photo-oxidation (13):

$$-\frac{d[C]}{dt} = k_1[C] + k_2[H_2O_2][C]$$

with  $k_1 = 8.4 \times 10^{-2} \text{ h}^{-1}$  and  $k_2 = 0.13 \times 10^{-2} \text{ mg}^{-1} \text{ L h}^{-1}$ .

**Table 5.** Identified Photoproducts in Photolytic Degradation of Atrazine, Simazine, and Prometryn in Natural Waters

| herbicide | basic ions detected by FIA/MS  |
|-----------|--|
| atrazine  | $m/z$ 202/204: 2-chloro-4-(ethylamino)-6-isopropylamino- <i>s</i> -triazine (atrazine) |
|           | $m/z$ 197: 2-hydroxy-4-(ethylamino)-6-isopropylamino- <i>s</i> -triazine (1)           |
|           | $m/z$ 188/190: 2-chloro-4-amino-6-isopropylamino- <i>s</i> -triazine (2)               |
|           | $m/z$ 174/176: 2-chloro-4-(ethylamino)-6-amino- <i>s</i> -triazine (3)                 |
| simazine  | $m/z$ 202/204: 2-chloro-4,6-bis(ethylamino)- <i>s</i> -triazine (simazine)             |
|           | $m/z$ 184: 2-hydroxy-4,6-bis(ethylamino)- <i>s</i> -triazine (1)                       |
|           | $m/z$ 174/176: 2-chloro-4-amino-6-(ethylamino)- <i>s</i> -triazine (2)                 |
|           | $m/z$ 146/148: 2-chloro-4,6-diamino- <i>s</i> -triazine (3)                            |
| prometryn | $m/z$ 242: 2-methylthio-4,6-bis(isopropylamino)- <i>s</i> -triazine (prometryn)        |
|           | $m/z$ 196: 2,4-bis(isopropylamino)- <i>s</i> -triazine (1)                             |
|           | $m/z$ 212: 2-hydroxy-4,6-bis(isopropylamino)- <i>s</i> -triazine (2)                   |
|           | $m/z$ 200: 2-methylthio-4-amino-6-isopropylamino- <i>s</i> -triazine (3)               |

The basic ions that were detected by FIA/MS, after the photochemical degradation of the studied triazines in natural waters, are presented in Table 5.

As a result of the soft ionizing interface and the ionization conditions in the MS mode used, only molecular ions,  $[M + H]^+$ , of the compounds were generated. Therefore, every signal in the FIA/MS spectra represents at least one compound with a defined molar mass (17). All the identified products were confirmed by FIA/MS/MS.

According to Table 5, the double peaks 216/218 and 202/204 correspond to the initial compounds of atrazine and simazine, respectively.

The molecular ions of each double signal appear to be in a ratio of 3:1 due to the natural ratio of the isotopes of chloride  $Cl^{35}/Cl^{37}$ . According to this, the products (2) and (3) of atrazine and simazine can be confirmed as compounds that contain chloride (18).

The ion with  $m/z$  242 is the molecular ion of prometryn. No double peaks were observed in this mass spectrum, which indicates the absence of compounds that contain chloride.

FIA/MS spectra provide information about the quality of the compounds formed after the photodegradation of the herbicides. By FIA/MS/MS, it is then possible to confirm these results because isomers can be differentiated in this way, but not by the application of FIA/MS (17, 19). Tandem mass spectrometry can make chromatographic separation unnecessary, and, because of fragmentation, standards also can become unnecessary (19).

The main photoproducts of the studied triazines after photochemical degradation in natural waters are presented in Figure 3.

According to the above scheme, one photodegradation pathway for the two chlorotriazines (atrazine and simazine) is the formation of products (1) after dechlorination and hydroxylation. For prometryn, cleavage of the methylthio group from the triazine ring is observed first, resulting in the formation of compound (1) and the hydroxylated compound (2). The second possible route is the oxidation of the alkylic side chains attached to the nitrogen atoms in positions 4 and 6, leading to the formation of the dealkylated derivatives [compounds (2) and (3) for the chlorotriazines and compound (3) for the methylthio-triazine]. The mechanism of indirect photolysis is different from the one observed for UV photolysis alone (13). The hydroxylation of triazines appears to be the primary photodegradation stage in direct photolysis. In contrast, in indirect photolysis, dealkylation is the dominant photodegradation pathway (14). The identified hydroxylated and dealkylated photoproducts in the present study indicate that, in surface waters, both direct and indirect photolysis takes place.

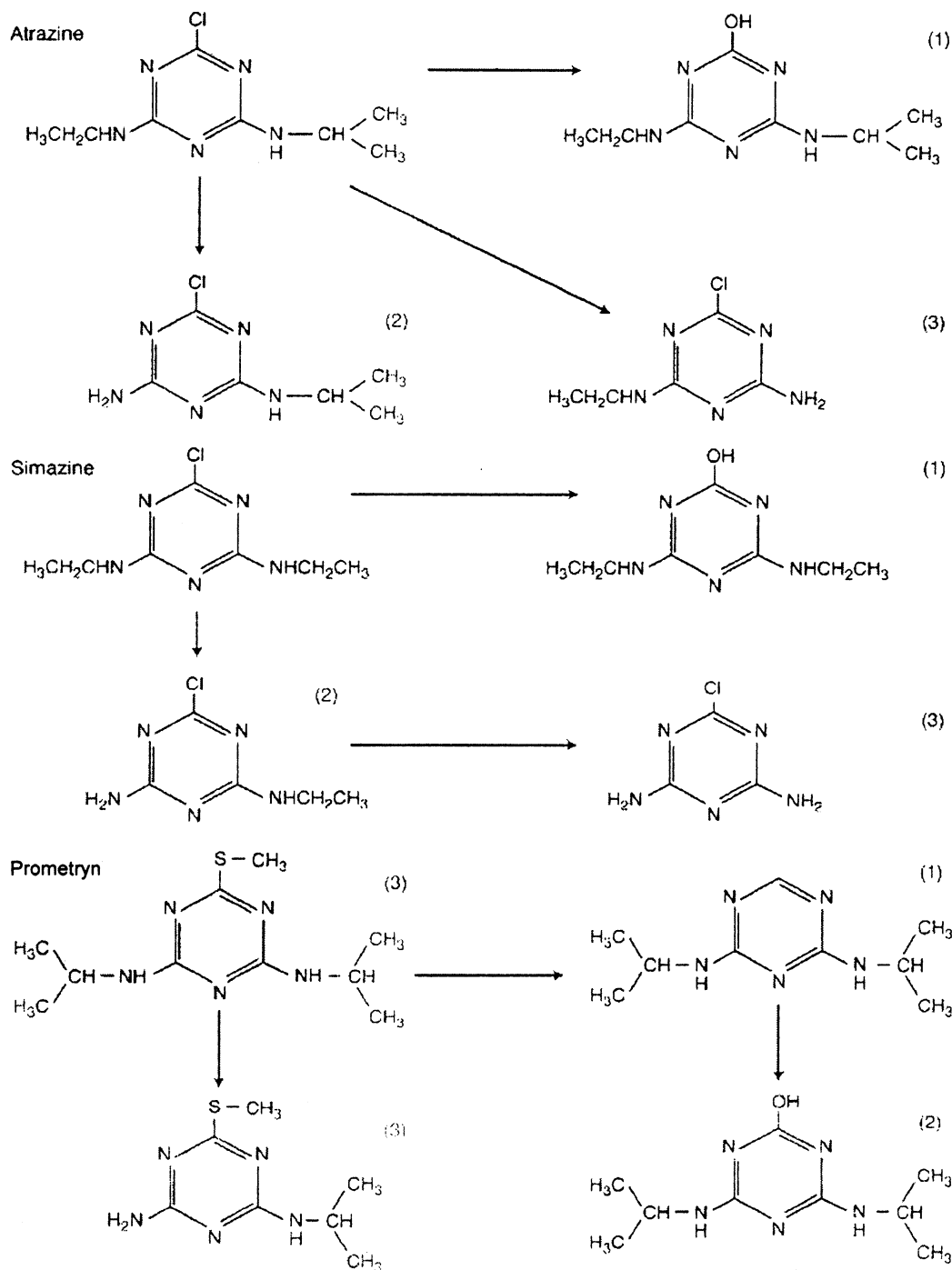


Figure 3. Main photoproducts of atrazine, simazine, and prometryn after photochemical degradation in natural waters (river and lake waters).

## CONCLUSIONS

Results obtained in this study demonstrate that the dark decomposition of triazines in aqueous solution is negligible with respect to the photochemical decomposition.

The rate of photodecomposition of aqueous solutions depends on the nature of the triazines and follows first-order kinetics.

In the case of the use of hydrogen peroxide and UV radiation, a synergistic effect is observed.

In conclusion, the number of compounds detected during the degradation of the above compounds shows the complexity of the photochemical process and suggests the existence of various degradation routes, resulting in complex and interconnected pathways.

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