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Degradation of bromoxynil and trifluralin in natural water by direct photolysis and UV plus H₂O₂ advanced oxidation process

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ABSTRACT

The degradation of two pesticides, bromoxynil and trifluralin, was investigated in ultrapure and natural water solutions under ultraviolet (UV) light and a combination of UV and hydrogen peroxide (H₂O₂). The effect of pH on the photooxidation of the pesticides was also studied. The results indicated that under direct photolysis with monochromatic light at 253.7 nm and different conditions, the photochemical rates followed first-order kinetics, with fluence-based rate constants ranging from 9.15×10^{-4} to 6.37×10^{-3} cm² mJ⁻¹ and 7.63×10^{-3} to 1.47×10^{-2} cm² mJ⁻¹ for bromoxynil and trifluralin, respectively. Quantum yields, in the range of 0.08–0.25 for bromoxynil and 0.12–0.72 for trifluralin, were observed in experiments using ultrapure water. The study also found that the UV/H₂O₂ process enhanced the oxidation rate in comparison to direct photolysis. A 90% degradation with UV dose of 333 and 188 mJ cm⁻² was achieved for bromoxynil and trifluralin, respectively, in natural water, in presence of 8.8×10^{-4} M H₂O₂. To assess the aquatic toxicity, the Microtox® 81.9% screening test protocol was used before and after treatment. The test results indicated a decrease in the acute toxicity of the samples after treatment for both pesticides.

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1. Introduction

Pesticides are substances or mixture of substances used to control, repel, attract or kill pests such as weeds, insects and microbes that are considered a nuisance or threat to crops. Pesticides are also used as plant growth regulators. Even though pesticides have played a significant role in increasing agricultural production efficiency, there have been increased concerns regarding the occurrence and the impact of the use of pesticides on the environment.

More rigorous regulations and better application equipment have reduced the presence of pesticides on the environment. However, compounds such as bromoxynil and trifluralin,

together with atrazine, 2-methyl-4-chlorophenoxyacetic acid (MCPA), dicamba, mecoprop, and diuron continue to be detected in natural waters (Moore et al., 2007; LeBlanc and Kuivila, 2008; Palma et al., 2009).

The detrimental impact caused by pesticide contamination on the environment has turned attention to the use of feasible treatment technologies for their removal or degradation to other products that have no adverse effects on the environment or human health. Among the various treatment technologies for water treatment, advanced oxidation technologies have proven to be effective methods to degrade organic pollutants (Chiron et al., 2000; Ikehata and Gamal El-Din, 2005a,b). In particular, the combination of ultraviolet (UV)

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light and hydrogen peroxide (H_2O_2), the so-called UV/ H_2O_2 process has been shown to be an alternative to treat waters and wastewaters contaminated with non biodegradable organic chemicals due to the generation of hydroxyl radicals ($\cdot\text{OH}$) during the treatment process (Chen et al., 2008). The removal of pesticides from aqueous solutions has been extensively covered in the literature. However, because the characteristics of pesticides are specific and because new pesticides are continuously being developed, research work dealing with their removal and/or degradation is still required.

Bromoxynil is a phenolic benzonitrile-based pesticide used for the control of broadleaved weeds in grain crops. Trifluralin is a pre-emergence dinitroaniline pesticide used for the control of annual grasses and broadleaved weeds in beans, forage legumes, orchards, ornamentals, transplanted peppers, soy beans, sugar-beet, sunflowers, tomatoes, and vineyards. These two pesticides have not been studied extensively, even though these compounds are intensely used worldwide (Alberta Environment, 2001; Sipyagin et al., 2004). These two pesticides are classified as group C possible human carcinogens (U.S. EPA, 1998a; Greene and Pohanish, 2005), and have relatively high toxic effects on aquatic organisms. In addition, bromoxynil is considered to be developmentally toxic, and trifluralin is suspected to be an endocrine disruptor (U.S. EPA, 1998b). Photolysis of bromoxynil and trifluralin has been reported by several authors (Kochany et al., 1990; Millet et al., 1998; Sarmiento Tagle et al., 2005). However, none of these papers dealt with the use of UV/ H_2O_2 process for the degradation of these two pesticides.

The objective of this study was to assess the reactivity of two pesticides, bromoxynil and trifluralin, belonging to different families, under UV irradiation. Oxidation by hydroxyl radicals generated by the UV/ H_2O_2 process was also investigated. In addition, quantum yields and the rate constants were determined. Toxicity measurements were also conducted to monitor the effectiveness of the photooxidation processes on reducing the acute toxicity of the solutions containing these two pesticides.

2. Materials and methods

2.1. Chemicals

Bromoxynil (3,5-dibromo-4-hydroxybenzonitrile) and trifluralin (α,α,α -trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine) were purchased from Sigma–Aldrich (Oakville, ON, Canada) and were used without further purification. The chemical structures of these two pesticides are presented in Fig. 1. Hydrogen peroxide (30% w/w) was purchased from Fisher Scientific Co. (Canada). Ultrapure water (resistivity > 18.2 M Ω cm) was used in all experiments and analytical determinations. The chemicals used for solution buffers and eluents were of reagent grade and were used without further purification.

2.2. Irradiance experiments

The pesticide solutions were irradiated for various exposure times and under several conditions by using a quasi collimated beam UV apparatus (Model PSI-1-120, Calgon Carbon

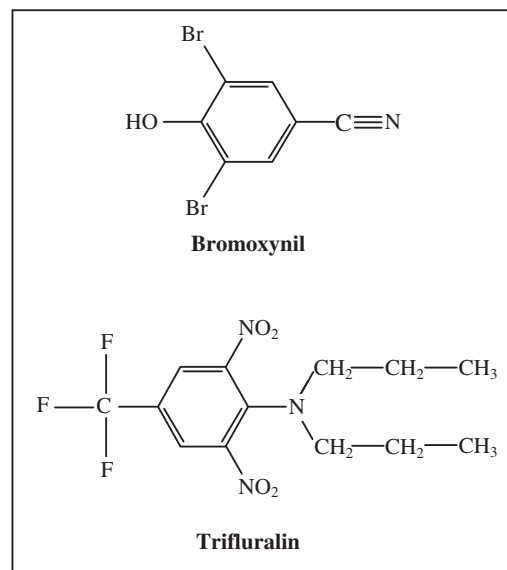


Fig. 1 – Chemical structures of bromoxynil and trifluralin.

Corporation, USA) equipped with a 10 W monochromatic low-pressure UV lamp (Ster-L-Ray Germicidal Lamp, model G12T6L 15114, Atlantic Ultraviolet Corporation, USA). A radiometer (Model IL 1400A with a SED240 Detector, International Light Inc.) calibrated at 253.7 nm, was used to measure the UV irradiance at the center of the UV beam at the level of the surface of the treated samples. The absorbance of the samples was measured using a Varian Cary 50 (Varian, Palo Alta, CA, USA) spectrophotometer with a 10 mm path length quartz cell (Fisher Scientific Co., Canada).

The treatment was conducted in a batch mode using a 50 mm diameter Petri dish as the treatment reactor. During the experiments, each reactor was placed in the center of the beam, under the open end of the collimator. The surface of the solution was 300 mm away from the UV lamp. To assure adequate mixing, a coated stir bar was used during the UV exposures to provide adequate stirring. At different time intervals, 100 μL samples were withdrawn for quantifying the residual pesticide concentration. All experiments were carried out in triplicate at room temperature (20.0 ± 0.2 °C).

The first sets of experiments were performed in ultrapure water, and the pH was adjusted using 5 mM phosphate buffer solution. Two different natural waters were selected to assess the photooxidation of these two pesticides in natural water matrices. The natural water samples were collected from two locations in the province of Alberta, Canada. Water 1 (W1) was collected from the North Saskatchewan River and Water 2 (W2) was sampled from a return flow discharging into the Redwater River. The natural waters were filtered using 0.2 μm nylon filters within 24 h after sampling and were stored at 4 °C until use. The characteristics of the two natural waters are listed in Table 1. The natural waters samples were spiked with the two pesticides (one at a time) in order to achieve an initial pesticide concentration of 3.6×10^{-6} M for bromoxynil and 3.0×10^{-6} M for trifluralin.

Prior to the UV/ H_2O_2 experiments, the two pesticides were allowed to contact H_2O_2 (5×10^{-5} M) for 24 h at room temperature to check if there was any reactivity between the

Table 1 – Characteristics of natural waters^a.

Parameter	North Saskatchewan River (W1)	Return flow water flowing into the Redwater River (W2)
pH	8.3	8.4
Turbidity (NTU)	1.0	1.3
Total organic carbon (mg/L C)	3	21
Total dissolved solids (mg/L)	213	352
Conductivity ($\mu\text{S}/\text{cm}$)	322	533
A_{254} (cm^{-1})	0.1	0.6
Total alkalinity (mg/L as CaCO_3)	136	230
Bicarbonate alkalinity (mg/L as CaCO_3)	120	202
Carbonate alkalinity (mg/L as CaCO_3)	16	28
Hardness (mg/L CaCO_3)	180	238
Magnesium hardness (mg/L CaCO_3)	24	42
Calcium hardness (mg/L CaCO_3)	156	196

^a Sampling period: May 11–12, 2008.

pesticides and H_2O_2 . The results indicated that the pesticides had no reactivity with H_2O_2 . Any hydrogen peroxide, present in the samples after UV/ H_2O_2 treatment, was quenched using catalase (2950 units/mg solid, Sigma–Aldrich, Canada) extracted from bovine liver.

Parameters such as reflection factor (RF), Petri factor (PF), water factor (WF), divergence factor (DF) as well as UV fluence (i.e., UV dose) were determined according to the procedures recommended by Bolton and Stefan (2002) and Bolton and Linden (2003).

2.3. Analytical determination

Bromoxynil and trifluralin concentrations were monitored by using a Shimadzu high performance liquid chromatography (HPLC) instrument (LC-10AT VP) equipped with a Phenomenex Gemini 5 μm C18 110A (250 \times 4.6 mm) column. Trifluralin detection was performed using an isocratic mode with acetonitrile and ultrapure water (75%:25% v/v). For bromoxynil, the elution was carried out by pumping acetonitrile and 10 mM aqueous phosphoric acid (50%:50% v/v) isocratically. UV detection at a wavelength of 237 and 220 nm was used to quantify trifluralin and bromoxynil, respectively.

2.4. Toxicity analysis

The toxicity of bromoxynil and trifluralin solutions before and after treatment was examined by using the Microtox[®] bioassay, which involved the use of a photobacterium to determine the aquatic toxicity of the samples. A model 500 Microtox[®] analyzer (Strategic Diagnostic Inc.) was used to measure the light emitted by the photobacterium as a result of its normal metabolic processes. Freeze-dried bacteria, reconstitution solution, diluent and an adjustment solution were all

obtained from Osprey Scientific Inc. (Edmonton, Canada). Microtox[®] 81.9% screening test protocol was used for the toxicity assessment of samples. The toxicity analysis was performed using 81.9% of initial sample concentrations and within 24 h after treatment. Phenol was used as a positive control for the Microtox[®] assay. Three replicate toxicity analyses were performed for each sample.

3. Results and discussions

3.1. Direct photolysis in ultrapure water

The degradation of bromoxynil and trifluralin by monochromatic UV light was conducted in 5 mM buffered ultrapure water solutions at pH 2, 7 and 9. Fig. 2 shows the effect of pH on the degradation of these two pesticides. The results indicated an increase in degradation of bromoxynil at pH 2. On the contrary, at high pH an increase in degradation was observed for trifluralin. However, at pH 7 and 9, the degradation of trifluralin proceeded at similar rate. The results also indicate that 90% bromoxynil degradation was achieved using UV doses of 439, 2512 and 659 mJ cm^{-2} at pH 2, 7 and 9, respectively. UV doses of 302, 157 and 168 mJ cm^{-2} at pH 2, 7 and 9, respectively, were needed to degrade 90% the initial trifluralin concentration. The higher degradation of bromoxynil at pH 2 can be explained by the fact that at pH lower than the dissociation rate constant ($\text{pK}_a = 4.1$), the phenol form of bromoxynil is the major species in solution. Because the pK_a value of trifluralin is 5.3, the photooxidation is faster at pH 7 and pH 9 where the deprotonated form is the dominant species.

The influence of the initial pesticide concentration was also studied. Fig. 3 illustrates the degradation of trifluralin in ultrapure water at different initial concentrations. Degradation levels of 64% (UV fluence of 107 mJ cm^{-2}) and 66% (UV fluence of 106 mJ cm^{-2}) after 20 min of irradiation for bromoxynil and trifluralin, respectively, at a concentration of 6×10^{-6} M, were observed. There was an increase in the degradation efficiency at low concentrations for both

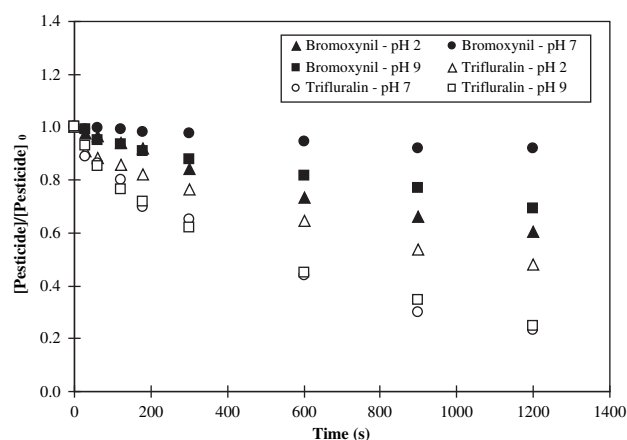


Fig. 2 – Influence of pH on pesticide degradation under direct photolysis. Experimental conditions: $[\text{bromoxynil}]_0 = 3.6 \times 10^{-6}$ M, $[\text{trifluralin}]_0 = 3.0 \times 10^{-6}$ M, average irradiance = 0.09 mW cm^{-2} .

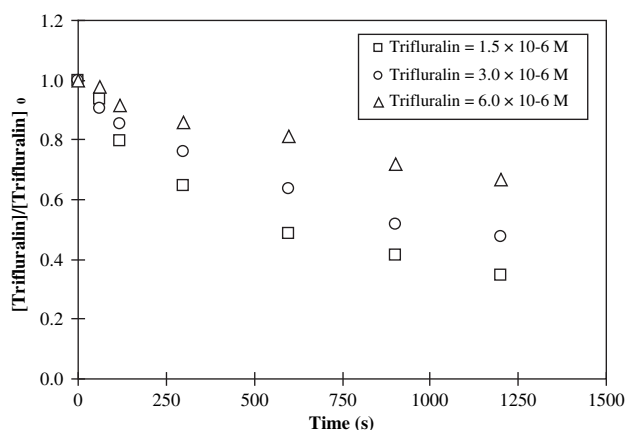


Fig. 3 – Effect of initial trifluralin concentration on direct photolysis at 253.7 nm.

pesticides. This trend has also been reported by other researchers. Hessler et al. (1993) observed an increase in the efficiency of degradation with decreasing initial concentration during the photolysis of the pesticides atrazine and metazachlor. The formation of intermediates at higher concentrations at increasing pesticide concentration may absorb part of the light available for the pesticide oxidation. Therefore, lower degradation rates can be expected at higher pesticide concentrations.

3.2. Rate constant and quantum yield under direct photolysis

The photodegradation of a pollutant “P” in an aqueous solution by UV irradiation can be represented by the reaction (Benitez et al., 2004, 2006):



where P_{oxid} represents the product(s) from the photolysis of the pollutant “P”.

Under conditions where P is the principal absorber and the absorbance is small (<0.03) so that the kinetics could be represented by a first-order model, the overall photolysis reduction (i.e., degradation) of the compound “P” during the collimated beam irradiation can be expressed as

$$\ln\left(\frac{[P]_0}{[P]_t}\right) = k_{UV}t \quad (2)$$

where $[P]_0$, $[P]_t$ are the concentrations of the pollutant “P” at the beginning of the experiment and after a time t (s), respectively, and k_{UV} is the first-order rate constant (s^{-1}).

Because k_{UV} can be affected by experimental conditions, such as irradiance, path length, and absorbance, Bolton and Stefan (2002) showed that Equation (2) can be expressed in an alternative form

$$\ln\left(\frac{[P]_0}{[P]_F}\right) = k'_{UV}F \quad (3)$$

where $[P]_0$, $[P]_F$ are the concentrations of “P” at the beginning of the experiment and after a fluence (UV dose) F ($J\ m^{-2}$) has

been applied and k'_{UV} is the fluence-based rate constant ($m^2\ J^{-1}$) given by

$$k'_{UV} = \frac{\ln(10)\Phi_P\epsilon_P}{10U_\lambda} \quad (4)$$

where Φ_P is the quantum yield ($mol\ einstein^{-1}$) for the direct UV photolysis of “P” at wavelength λ , ϵ_P is the molar absorption coefficient ($M^{-1}\ cm^{-1}$) of P at wavelength λ and U_λ is the energy per einstein at wavelength λ . The energy per einstein of UV photons at 253.7 nm is $471,528\ J\ einstein^{-1}$. Note that k'_{UV} is only a function of fundamental parameters and is not influenced by the experimental conditions.

A plot of $\ln[P]_0/[P]$ versus F for each pesticide should result in a straight line with a slope of k'_{UV} . Fig. 4 shows this plot for the experiments performed at different pHs. As illustrated in Fig. 4, the experimental points lie around a straight line, and first-order kinetics can be assumed. The fluence-based rate constants and quantum yields estimated for bromoxynil and trifluralin are listed in Table 2. The rate constants were calculated as the mean of triplicates. Uncertainty was illustrated through the standard deviation of the mean ($n = 3$ values). The molar absorption coefficient (ϵ), estimated by using the Lambert–Beer Law, is also presented in Table 2. As shown in Table 2, the highest quantum yields were observed at pH 9 for both pesticides and the lowest values were observed at pH 2, and pH 7 for trifluralin and bromoxynil, respectively. It was also noted that the degradation of trifluralin was more efficient than that of bromoxynil due to the higher quantum yield values for trifluralin.

Millet et al. (1998) recorded a quantum yield of 9.3×10^{-3} for the photolysis of bromoxynil (initial concentration of $18.8 \times 10^{-6}\ M$) in water containing 0.5% acetonitrile and using a xenon lamp ($\lambda > 290\ nm$). Previously, Kochany and Choudhry (1990) reported the quantum yield to be in the range of 0.023–0.054 for bromoxynil solution containing different sodium nitrite concentrations. The experiments were performed using $7.8 \times 10^{-6}\ M$ bromoxynil and irradiation at 313 nm. Quantum yields of 0.020–0.052 were noted by Kochany et al. (1990) after irradiating $7.8 \times 10^{-6}\ M$ bromoxynil solutions

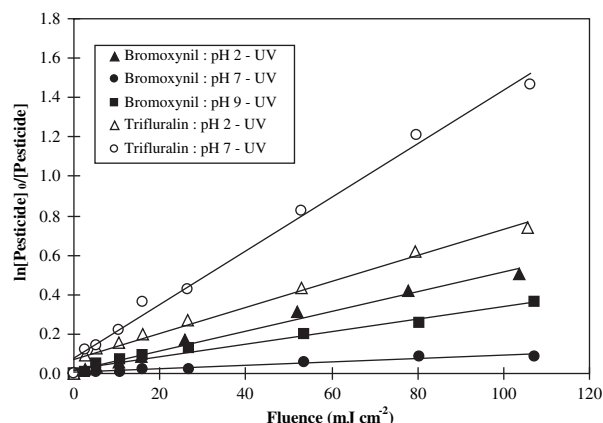


Fig. 4 – Kinetics of bromoxynil and trifluralin under UV irradiation with monochromatic light in a quasi collimated beam apparatus. Experimental conditions: $[bromoxynil]_0 = 3.6 \times 10^{-6}\ M$, $[trifluralin]_0 = 3.0 \times 10^{-6}\ M$, average irradiance = $0.09\ mW\ cm^{-2}$.

Table 2 – Fluence-based rate constants and calculated quantum yields for direct photolysis.

pH	ϵ_P ($M^{-1} cm^{-1}$)	k'_{UV} ($cm^2 mJ^{-1}$)	Φ_P
<i>Bromoxynil</i>			
2	1.26×10^4	$(5.2 \pm 0.2) \times 10^{-3}$	0.08
7	4.97×10^3	$(9.1 \pm 0.2) \times 10^{-4}$	0.04
9	2.91×10^3	$(3.5 \pm 0.1) \times 10^{-3}$	0.25
<i>Trifluralin</i>			
2	1.26×10^4	$(7.6 \pm 0.1) \times 10^{-3}$	0.12
7	4.97×10^3	$(1.5 \pm 0.2) \times 10^{-2}$	0.60
9	3.87×10^3	$(1.4 \pm 0.1) \times 10^{-2}$	0.72

containing different amount of soil fulvic acid ($\lambda > 313$ nm). Experiments performed in the present study using ultrapure water spiked with bromoxynil at an initial concentration of 3.6×10^{-6} M, resulted in a quantum yield of 0.24 under irradiation at 253.7 nm.

3.3. Direct photolysis in natural water

To investigate the influence of water quality on the photooxidation of bromoxynil and trifluralin, two natural waters and non-buffered ultrapure water were used. Fig. 5 shows the degradation of bromoxynil and trifluralin in natural water under direct photolysis.

The results indicate 50% degradation after 30 min and 56 min of UV exposure in North Saskatchewan River water (W1) and an irrigation canal return flow water flowing into the Redwater River (W2) for bromoxynil, and after 15 min and 25 min in waters W1 and W2 for trifluralin. In addition, 90% degradation was achieved with UV dose of 362, 483 and 574 $mJ cm^{-2}$ in ultrapure water, water W1 and water W2 during direct photolysis of bromoxynil, and at UV dose of 197, 234 and 255 $mJ cm^{-2}$ for trifluralin.

By using Equation (4), the fluence-based rate constants were determined. As shown in Table 3, the highest values of

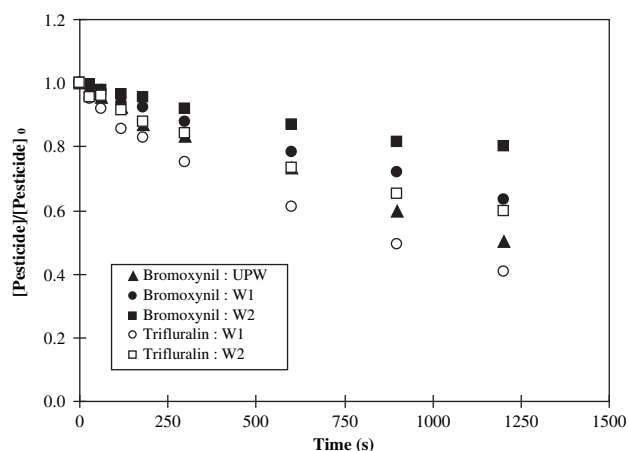


Fig. 5 – Influence of the type of water on pesticide degradation under direct UV photolysis. UPW: ultrapure water, W1: North Saskatchewan River water, W2: return flow water flowing into the Redwater River. Experimental conditions: $[bromoxynil]_0 = 3.6 \times 10^{-6}$ M, $[trifluralin]_0 = 3.0 \times 10^{-6}$ M, average irradiance = $0.09 mW cm^{-2}$.

the fluence-based rate constants were observed in direct photolysis using ultrapure water for both pesticides. The rate constants in water W2 (return flow water) recorded the lowest values. The results also indicate that there is high efficiency of direct photolysis on degrading trifluralin.

3.4. Degradation by UV/H₂O₂

The degradation of bromoxynil and trifluralin by UV/H₂O₂ was studied in ultrapure water at different pHs and in two natural waters (see Fig. 6). The degradation of both pesticides was also investigated in the presence of different initial H₂O₂ concentrations. It was found that an increase in the H₂O₂ concentration (from 4×10^{-4} M to 8×10^{-4} M) increased the rate of degradation of bromoxynil. However, the increase in the degradation rate was not significant when the H₂O₂ concentration increased from 8×10^{-4} M to 18×10^{-4} M. The same trend was observed for the degradation of trifluralin in ultrapure water.

At an initial H₂O₂ concentration of 8.8×10^{-4} M, the degradation of bromoxynil and trifluralin at different pHs was investigated. The results show an increase in the degradation of these pesticides compared to the degradation efficiencies under direct photolysis. For trifluralin, pH had little effect on the degradation rate. Meanwhile, a pronounced enhancement in the rate of bromoxynil degradation was observed at pH 9.

As expected, the fastest degradation occurred in ultrapure water, and the slowest in the water W2 (return flow water) for both pesticides (see Fig. 6). The presence of natural organic matters (such as humic acid) and bicarbonate ions in natural water reduced the concentration of $\cdot OH$ radicals available to react with the pesticides. The bicarbonate and carbonate ions are scavengers of hydroxyl radicals; therefore, they are expected to reduce the rate of the radical-mediated reactions of organic compounds (Tuhkanen, 2004). Humic substances adsorb UV light, therefore, they reduce the photolysis of H₂O₂ as well as they scavenge $\cdot OH$ radicals (Crittenden et al., 1999). The results also show that a 90% degradation with UV doses of 333 and 188 $mJ cm^{-2}$, respectively, was achieved for bromoxynil and trifluralin in water W1 (North Saskatchewan River water), in the presence of 8.8×10^{-4} M H₂O₂. UV doses of 366 and 159 $mJ cm^{-2}$ for bromoxynil and trifluralin, respectively, were needed to achieve the same degradation levels in the return flow water (water W2). Lower UV doses were needed in

Table 3 – Fluence-based rate constants for direct photolysis in natural waters.

Water type	ϵ_P ($M^{-1} cm^{-1}$)	k'_{UV} ($cm^2 mJ^{-1}$)
<i>Bromoxynil</i>		
UPW	5.43×10^3	$(6.4 \pm 0.2) \times 10^{-3}$
W1	3.47×10^3	$(4.8 \pm 0.9) \times 10^{-3}$
W2	2.34×10^3	$(4.0 \pm 0.4) \times 10^{-3}$
<i>Trifluralin</i>		
UPW	4.99×10^3	$(9.9 \pm 0.2) \times 10^{-3}$
W1	5.31×10^3	$(9.8 \pm 0.5) \times 10^{-3}$
W2	2.09×10^3	$(9.0 \pm 0.5) \times 10^{-3}$

UPW: ultrapure water, W1: North Saskatchewan River water, W2: return flow water flowing into the Redwater River.

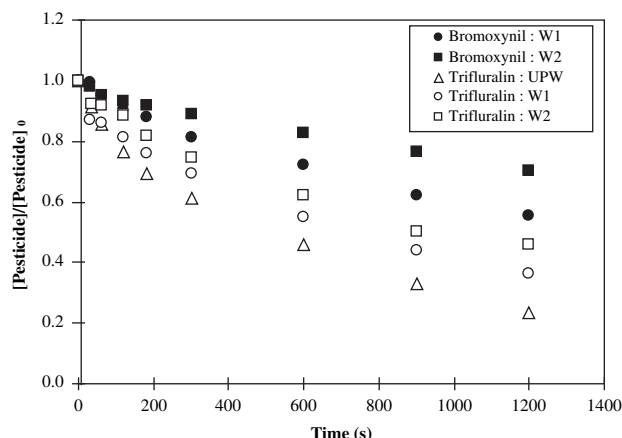


Fig. 6 – Influence of the type of water on pesticide degradation using UV/H₂O₂. UPW: ultrapure water, W1: North Saskatchewan River water, W2: return flow water flowing into the Redwater River. Experimental conditions: [bromoxynil]₀ = 3.6 × 10^{−6} M, [trifluralin]₀ = 3.0 × 10^{−6} M, [H₂O₂]₀ = 882 × 10^{−6} M, average irradiance = 0.09 mW cm^{−2}.

this study in comparison to previous studies focused on other pesticides. Kruithof et al. (2002) reported that several pesticides such as atrazine and diuron could be degraded up to more than 70% by using a UV dose in the range of 500–4000 mJ cm^{−2}. Wu and Linden (2008) used 500 mJ cm^{−2} and 7 × 10^{−4} M H₂O₂ to achieve 60% degradation of parathion (initial concentration of 7.6 × 10^{−6} M) present in a river water.

3.5. Kinetics of UV/H₂O₂ oxidation

The mechanisms of oxidation by UV/H₂O₂ have been investigated extensively, and it has been found that the rate of degradation of an organic compound using UV/H₂O₂ process results from the contribution of two pathways: direct photolysis and hydroxyl radical attack (Tuhkanen, 2004; Rosenfeld and Linden, 2007):

$$\frac{d[P]}{dt} = k_{UV}[P] + k_{OH-P}[\cdot OH][P] \quad (5)$$

where k_{OH-P} is the second-order rate constant of hydroxyl radical with the pollutant “P”. Because $\cdot OH$ radical concentration can be assumed to be constant over the range of reaction (Benitez et al., 2006), the product ($k_{OH-P}[\cdot OH]$) can be converted into a pseudo first-order rate constant k'_{OH-P} . Thus, the following equation may be used to describe the degradation of the pollutant “P” during UV/H₂O₂ process:

$$\ln \frac{[P]_0}{[P]} = k_{UV}t + k'_{OH-P}t = (k_{UV} + k'_{OH-P})t = k_Tt \quad (6)$$

where k_T represent the pseudo first-order rate constant for the overall degradation of the compound “P” during the UV/H₂O₂ treatment. As shown in Fig. 6 and according to Equation (6), a plot of $\ln[P]_0/[P]$ versus reaction time should lead to straight lines, with a slope equal to k_T . These values are presented in Table 4 for three different pHs and the different waters. Table 4 also shows the first-order rate constant k_{UV} , estimated using Equation (2), obtained under direct photolysis.

From Equation (6), the subtraction of k_{UV} from k_T yields the pseudo first-order rate constant k'_{OH-P} . These values are presented in Table 4. The results suggest that the presence of H₂O₂ enhanced the oxidation rate in comparison to direct photolysis. The results also suggest that direct photolysis tends to be dominant under the tested conditions since k_{UV} and k'_{OH-P} values were closer. Previous studies have shown comparable k_{UV} and k'_{OH-P} values. Sundstrom et al. (1989) found $k_{UV} = 0.043 \text{ min}^{-1}$ and $k_{OH-P} = 0.038 \text{ min}^{-1}$ for 2,4-dichlorophenol, and $k_{UV} = 0.078 \text{ min}^{-1}$ and $k_{OH-P} = 0.022 \text{ min}^{-1}$ for 2,4,6-trichlorophenol using UV/H₂O₂. Benitez et al. (2004) found k_{UV} value of $1.8 \times 10^2 \text{ min}^{-1}$ and k_{OH-P} equals to $1.1 \times 10^2 \text{ min}^{-1}$ for the degradation of propachlor in lake water using UV/H₂O₂. A value of k_{UV} equals to $25.1 \times 10^3 \text{ min}^{-1}$ and k_{OH-P} equals to $12.0 \times 10^3 \text{ min}^{-1}$ was found for the degradation of diuron in ultrapure water using UV/H₂O₂ (Benitez et al., 2006). Shen et al. (1995) suggested that the direct photolysis effect would be more apparent for the

Table 4 – Pseudo first-order rate constants for UV and UV/H₂O₂ processes.

pH or water type	$k_{UV} \text{ (s}^{-1}\text{)}$	$k_T \text{ (s}^{-1}\text{)}$	$k'_{OH-P} \text{ (s}^{-1}\text{)}$
Bromoxynil			
2	$(4.5 \pm 0.2) \times 10^{-4}$	$(5.9 \pm 0.3) \times 10^{-4}$	1.4×10^{-4}
7	$(0.8 \pm 0.1) \times 10^{-4}$	$(3.6 \pm 0.4) \times 10^{-4}$	2.8×10^{-4}
9	$(3.1 \pm 0.1) \times 10^{-4}$	$(13.2 \pm 0.2) \times 10^{-4}$	10.1×10^{-4}
UPW	$(5.7 \pm 0.2) \times 10^{-4}$	$(6.5 \pm 0.2) \times 10^{-4}$	0.8×10^{-4}
W1	$(3.8 \pm 0.1) \times 10^{-4}$	$(5.2 \pm 0.3) \times 10^{-4}$	1.4×10^{-4}
W2	$(2.1 \pm 0.2) \times 10^{-4}$	$(3.0 \pm 0.1) \times 10^{-4}$	0.9×10^{-4}
Trifluralin			
2	$(6.7 \pm 0.9) \times 10^{-4}$	$(12.4 \pm 0.1) \times 10^{-4}$	5.7×10^{-4}
7	$(13.0 \pm 1.0) \times 10^{-4}$	$(15.0 \pm 1.0) \times 10^{-4}$	2.0×10^{-4}
9	$(12.2 \pm 0.2) \times 10^{-4}$	$(13.9 \pm 0.3) \times 10^{-4}$	1.8×10^{-4}
UPW	$(10.4 \pm 0.4) \times 10^{-4}$	$(12.6 \pm 0.4) \times 10^{-4}$	2.1×10^{-4}
W1	$(7.8 \pm 0.4) \times 10^{-4}$	$(9.1 \pm 0.4) \times 10^{-4}$	1.3×10^{-4}
W2	$(4.6 \pm 0.2) \times 10^{-4}$	$(7.2 \pm 0.8) \times 10^{-4}$	2.6×10^{-4}

UPW: ultrapure water, W1: North Saskatchewan River water, W2: return flow water flowing into the Redwater River.

photooxidation of 2,4,6-trichlorophenol than the effect of hydroxyl radicals. In a previous study, Millet et al. (1998) reported a rate constant for the direct photolysis of bromoxynil of $4.2 \times 10^{-4} \text{ s}^{-1}$ in a hexane solution and $1.38 \times 10^{-5} \text{ s}^{-1}$ in a solution of water plus acetonitrile ($\lambda > 290 \text{ nm}$). Kochany et al. (1990) estimated the rate constant to be $1.12 \times 10^{-3} \text{ s}^{-1}$ for the direct photolysis of bromoxynil in distilled water (initial concentration of $7.8 \times 10^{-6} \text{ M}$). In the present study, a rate constant of $(5.7 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$ was calculated for the photolysis of bromoxynil in ultrapure water (initial concentration of $3.6 \times 10^{-6} \text{ M}$).

Dimou et al. (2004) investigated the degradation of trifluralin under natural sunlight irradiation. The authors reported a half life of 726 min for the degradation of trifluralin in distilled water. A half life of 11.1 min was estimated for the oxidation of trifluralin in ultrapure water in the present study. Sarmiento Tagle et al. (2005) estimated the rate constant to be $4.39 \times 10^{-5} \text{ s}^{-1}$ for the direct photolysis of trifluralin in distilled water and $1.94 \times 10^{-4} \text{ s}^{-1}$ in acetonitrile solution by the action of UV–Vis light (wavelength $> 300 \text{ nm}$). The big difference in the previously published results with those of the current study can be explained by the different experimental conditions such as wavelength, irradiance, path length, and reactor geometry.

3.6. Toxicity study

Since bromoxynil and trifluralin are toxic to aquatic organisms, the Microtox® bioassay was used to test the aquatic toxicity. The toxicity of both pesticides on *Vibrio fischeri* after 15 min of exposure based on the Microtox® 81.9% screening test protocol is illustrated in Fig. 7. Because the test bacteria are sensitive to pH, with a minimal pH effect between 6.0 and 8.0, the pH of the samples prior to the analysis was measured. It was found that the sample pH was in the recommended range, thus, no pH adjustment was needed.

As illustrated in Fig. 7, toxicity was evaluated regularly during the course of UV and UV/H₂O₂ process. The toxic

effects of the treated samples on the photobacterium were found to be significantly low for both pesticides. It was also noted that during the preliminary stages of direct photolysis, a decrease of the toxicity of bromoxynil and trifluralin was observed. Following that, an increase of the toxicity was noted. This increase in the toxicity may be due to the production of some intermediate metabolites more toxic to the photobacterium. However, this increase was always lower than the toxicity of the sample at time zero ($t = 0 \text{ min}$, before treatment). For the UV/H₂O₂ experiments, no increment in the toxicity was observed. The same trend was noted for the experiments performed in ultrapure water at different pHs (data not shown).

4. Conclusions

The photodegradation of bromoxynil and trifluralin in ultrapure water and two natural waters by ultraviolet irradiation alone and a combination of UV and hydrogen peroxide was investigated. The results show that under direct photolysis with monochromatic UV light at 253.7 nm, the degradation rates followed first-order kinetics, with fluence-based rate constants ranging from 9.15×10^{-5} to $6.37 \times 10^{-4} \text{ m}^2 \text{ J}^{-1}$ for bromoxynil and from 7.63×10^{-3} to $1.47 \times 10^{-2} \text{ cm}^2 \text{ mJ}^{-1}$ for trifluralin under different experimental conditions. In the presence of $8.8 \times 10^{-4} \text{ M H}_2\text{O}_2$ and a UV dose of 333 and 188 mJ cm^{-2} , 90% degradations were observed for bromoxynil and trifluralin, respectively, in both natural waters. The Microtox® 81.9% screening test was conducted before and after treatment to assess the toxicity of the untreated and treated samples. The outcomes show a decrease in the toxicity of the samples on *V. fischeri* after treatment for both pesticides

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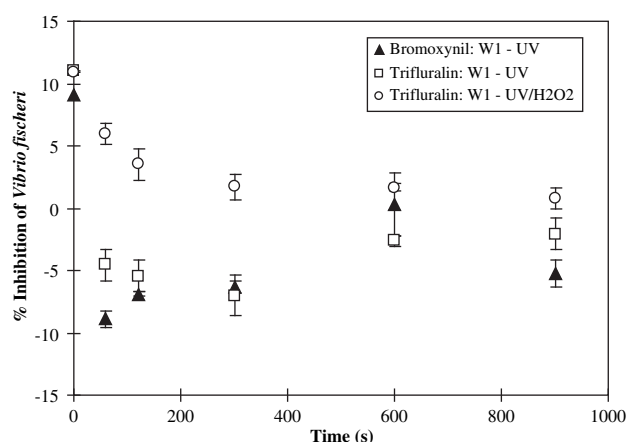


Fig. 7 – Toxic effects of bromoxynil and trifluralin on *Vibrio fischeri* using 81.9% screening test Microtox® protocol. Experimental conditions: $[\text{bromoxynil}]_0 = 3.6 \times 10^{-6} \text{ M}$, $[\text{trifluralin}]_0 = 3.0 \times 10^{-6} \text{ M}$, $[\text{H}_2\text{O}_2]_0 = 8.8 \times 10^{-4} \text{ M}$, average irradiance = 0.09 mW cm^{-2} .

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