



Sunlight and UVC-254 irradiation induced photodegradation of organophosphorus pesticide dichlorvos in aqueous matrices

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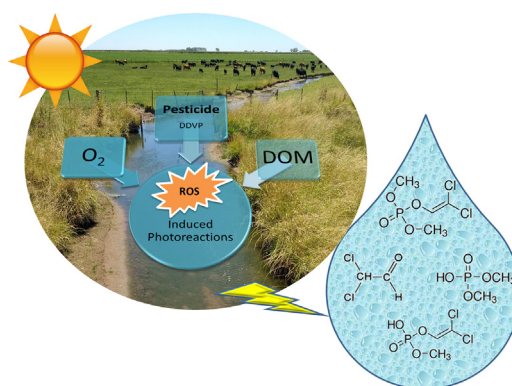
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HIGHLIGHTS

- Dichlorvos is photodegraded under simulated sunlight radiation and dissolved oxygen.
- Photogenerated hydroxyl radical plays an important role in the degradation pathway.
- Dichlorvos reduction by UV-C radiation combines photocleavage and ROS generation.
- Humic acids play a double role as accelerator and inhibitor of dichlorvos depletion.
- By-products from photoreactions have higher acute toxicity than dichlorvos.

GRAPHICAL ABSTRACT



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ABSTRACT

Dichlorvos (DDVP) is an organophosphorus pesticide that has been classified as highly hazardous chemical by the World Health organization. In this study, the fate of the pesticide DDVP in natural water compartments was examined under simulated sunlight. Moreover, the effect of UV-254 irradiation on DDVP depletion was also studied. In deionized water, DDVP was photodegraded only in the presence of dissolved molecular oxygen. The photodegradation during the first 6 h of sunlight irradiation occurred with pseudo first-order kinetics, and the rate constants were 0.040 h^{-1} at pH 7 and 0.064 h^{-1} at pH 3. A reaction mechanism for the generation of reactive oxygen species (ROS) via DDVP photoabsorption was proposed. Humic acids (HA) played a double role as photosensitizer and inhibitor, observing an enhancement on DDVP photodegradation at low HA concentration ($\text{TOC} = 2 \text{ mg L}^{-1}$). The depletion of DDVP under 254 nm UV irradiation was ascribed to direct photodegradation and oxygen mediated photoinduced reactions. Direct photodegradation of DDVP decreased with 254 nm irradiation reduction, highlighting the importance of radical mediated mechanisms at low irradiation doses. Based on LC/MS data, the main photoproducts under simulated solar light and UV-C irradiation were identified and potential reaction pathways were postulated. The three main identified products were *o*-methyl 2,2-dichlorovinyl phosphate, dichloroacetaldehyde and dimethylphosphate. Moreover, the toxicity of samples was evaluated along the irradiation exposure time using Microtox® assays. This study brings new insights into the role of oxygen in the photodegradation of DDVP and the induced and inhibition mechanisms involved in the presence of the humic acids in natural waters.

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1. Introduction

The use of organic pesticides in agricultural practices, required to ensure harvest quality and food protection, can result in the release of these substances to non-target environmental matrices, including freshwater bodies. This constitutes a problematic situation, since pesticides are generally known for having hazardous properties that can make the exposure to these chemicals a potential risk to life. Regarding human health, the increasing incidence in some types of cancer and birth defects, among other diseases, has been associated to pesticide exposure. Also, it is well-known that these compounds can represent a health risk for other living species. Because of these reasons, several classes of pesticides have been classified as Priority Substances by some of the latest European legislations regarding the monitoring and control of micropollutants in the field of water policy (Panizzi et al., 2017; Stork et al., 2017).

One of the pesticide groups with presence in these lists of priority substances are organophosphorus pesticides (OPPs), which are widely used in both agricultural (phytosanitary) and animal production (antiparasitic). OPPs have been classified from slightly to highly hazardous, according to the potential risks that each one of them could pose to human and environmental safety. Dichlorvos (2,2-dichlorovinyl dimethyl phosphate, DDVP), is one of the most employed compounds of this family. It is used as insecticide in agriculture, food storage and homes, as well as to treat infections in livestock (Gomez et al., 2013; Moraes et al., 2015; Patil and Gogate, 2015). However, it has been classified as a highly toxic pesticide by the World Health Organization (WHO) due to its hazardous properties. In humans, the acute exposure to DDVP can cause breathing problems or even death, whereas chronic exposure has been linked to other human conditions like diabetes or liver malfunction (Desai and Desai, 2008; Montgomery et al., 2008; Ragnarsdottir, 2000; Wang et al., 2014). Also, this OPP has been classified as a possible human carcinogen (IARC, 1991). Concerning other animal species, it has been found that DDVP exposure induces oxidative damage and carcinogenesis in fish (Das, 2013).

The widespread use of DDVP, together with its high solubility in water, has caused its detection in surface waters worldwide (Chen et al., 2016; Gao et al., 2009; Heidar et al., 2017; Nasrabadi et al., 2011; Sangchan et al., 2014). Still, there is little information on the fate of this pesticide in aquatic compartments. All organophosphate esters are potentially susceptible to undergo hydrolysis, but it is expected to be slow in environmental conditions (Druzina and Stegu, 2007). Moreover, the presence of organic matter and inorganic ions could affect the photodegradation processes (Bodhipaksha et al., 2017; Cristale et al., 2017; Druzina and Stegu, 2007). Natural and effluent water constituents participate in photodegradation reactions. For instance, triplet excited state of dissolved organic matter ($^3\text{DOM}^*$) participates as a sensitizer in photochemical reactions producing singlet oxygen in natural water bodies (Burns et al., 2012). The portion of DOM that absorbs light is named chromophoric DOM and this property comes principally from phenolic structures of humic substances. These compounds are generated from microbial activity or lignin degradation in soil matrix. By the way, DOM participate both as producer and scavenger of reactive oxygen species (ROS), moreover screening effect of light is described for DOM, interfering in the incident radiation on surface water (Cristale et al., 2017; Souza et al., 2014; Zhu et al., 2015). Not only DOM participates but also different ions (bicarbonate or nitrate) participate also in photoreactions under sun irradiation (Bodhipaksha et al., 2017).

The presence of micropollutants in wastewater treatment plants (WWTP) has developed concern in recent years due to their persistence over biological treatment, so novel tertiary treatments have been developed (Debabrata and Sivakumar, 2018; Pablos et al., 2013; Teijon et al., 2010; Yuval et al., 2016). UV-C irradiation can be used, not only as disinfection method, but also to eliminate emerging micropollutants such as pharmaceutical products and pesticides (Zhu et al., 2015). UV

disinfection systems (UV-DS) constitute an alternative to chemical disinfection and could be used simultaneously in wastewater treatment plants for micropollutants control. Shorter residence times (Paleologou et al., 2007) and the low generation of toxic byproducts during the process (Le Roux et al., 2017), in comparison to other technologies, are additional advantages of the employment of UV-DS systems in water and wastewater treatment facilities.

DDVP presents low molar absorptivity (ϵ) in the UV-C and UV-B range compared with other organophosphorus pesticides (Feigenbrugel et al., 2005). Consequently, most of the scientific publications regarding the abatement of this pesticide by alternative water technologies are focused on the application of photocatalytic or other advanced oxidation processes (AOP's) (Chen and Gengyu, 2005; Cruz-Alcalde et al., 2018; Debabrata and Sivakumar, 2017; Evgenidou et al., 2006; Gomez et al., 2013; Liu et al., 2009; Naman et al., 2002; Oancea and Oncescu, 2008; Oncescu et al., 2010; Patil and Gogate, 2015).

In order to throw light on the fate of the pesticide dichlorvos in natural water compartments, as well as the potential degradation through a hypothetical UV-C disinfection system, the aim of this investigation was to deeply study the photodegradation of dichlorvos under simulated sunlight and UV-254 irradiation. The influence on this process of dissolved oxygen and dissolved organic matter –especially the humic fraction of DOM– on DDVP degradation were both carefully considered. Reaction intermediates and possible degradation pathways were also studied through LC-MS analysis, and finally the potential risks caused by formed phototransformation products were evaluated by means of bacteria bioluminescence inhibition assays.

2. Materials and methods

2.1. Chemicals and reagents

2,2-dichlorovinyl dimethyl phosphate, *tert*-butyl alcohol (TB) and humic acid sodium salt were purchased from Sigma Aldrich (Germany). Methanol was acquired from Merck (Darmstadt, Germany). Potassium hydrogen phosphate, potassium dihydrogen phosphate and sodium azide (AzNa) were supplied by Panreac (Spain). High purity nitrogen gas ($\text{N}_2 > 99.995\%$) was supplied by Abelló Linde (Spain). Ultrapure water was produced by a filtration system (Millipore, USA). Secondary effluent collected from the Gavà-Viladecans WWTP, located near Barcelona was also employed in some experiments, previously filtered with 0.7 μm glass fiber filters. Table 1 includes its main characteristics. Effluent samples were stored at 4 °C prior to use.

2.2. Photodegradation experiments

Characterization of phototransformation processes under simulated sunlight and UV-254 nm irradiation were performed employing solutions of 4.5 μM of DDVP daily prepared before conducting the experiments. Prepared solutions were buffered at $\text{pH } 3.0 \pm 0.2$ and 7.0 ± 0.2 with a 10 mM phosphate buffer. Phosphate buffer did not modify the UV-visible spectra of OPs in the aqueous solution and did not absorb at $\lambda > 240$ nm. In order to evaluate the hydrolysis process in the absence of radiation, dark controls were performed in amber bottles equipped with magnetic stirring. The whole set of experiments was performed

Table 1
Main physicochemical properties of Gavà-Viladecans WWTP effluent.

TOC (mg C L^{-1})	30
UVA_{254} (m^{-1})	28.9
Alkalinity ($\text{mg CaCO}_3 \text{ L}^{-1}$)	463.5
pH	7.4
Turbidity (NTU)	8.1

in duplicate at 20 °C. Aliquots from the photoreactors and dark controls were collected throughout the entire reaction time (6 and 24 h, respectively). Obtained samples were placed in amber glass vials and stored at –20 °C until analysis.

Three types of DDVP solutions ($C_0 = 4.5 \mu\text{M}$) were exposed to simulated sunlight during experimentation: buffered Milli-Q solutions, buffered Milli-Q solutions in presence of humic acids (HA) (2.0, 3.2 and 10.0 mg TOC L^{-1}) and effluent from a municipal wastewater treatment plant (30 mg TOC L^{-1}). These were continuously pumped (peristaltic pump Ecoline VC-280) into a SolarBox (Co. fo.me.gra 220 V, 50 Hz) device and recirculated back to a reservoir. A Duran glass tubular photoreactor (0.078 L) was placed in the axis of a parabolic mirror located inside the simulation chamber. Then, the medium was irradiated by a Xe-OP lamp (Phillips 1 kW). Irradiation with wavelengths under ~290 nm was cut off by the effect of the Duran glass, thus avoiding the influence of the UV-C sunlight component. The photonic flow of the photoreactor in the 290–400 nm range was evaluated by o-nitrobenzaldehyde actinometry (De la Cruz et al., 2013), being 2.98 $\mu\text{Einstein s}^{-1}$. The temperature of the stirred tank was kept at 20 °C with an ultra-thermostat bath (Haake K10).

Buffered DDVP in Milli-Q solutions ($C_0 = 4.5 \mu\text{M}$) were subjected to UV-C irradiation in two different irradiation setups. The first irradiation system included a 2-L jacketed reactor with one 4 W low-pressure Hg UV lamp (Philips TUV G4T5), whereas the second encompassed a 2-L jacketed reactor with three 8 W low-pressure Hg UV lamps (Philips TUV 8W, G8T5), all of them emitting at 254 nm and located inside quartz sleeves (equally separated). The light emission of the lamps was stabilized for 15 min before each experiment. The reactor was completely covered with aluminum foil to avoid irradiation losses. The actinometrical measurement used to determine the photon flow in the photoreactor was based on the photochemical decomposition of atrazine, as described in the literature (Canonica et al., 2008). According to this actinometrical determination, the reactor with one 4 W UV lamp had an incident photonic flow of 1.52 $\mu\text{Einstein s}^{-1}$, and the corresponding value for the three 8 W lamps system was 9.15 $\mu\text{Einstein s}^{-1}$.

The effect of dissolved oxygen in the photodegradation processes was evaluated in experiments employing DDVP solutions in Milli-Q water. For that purpose, DDVP solutions were bubbled with N_2 gas during the entire irradiation time to minimize dissolved oxygen content. In all experiments, O_2 concentration was continuously measured with a WTW Oxi-340i Oximeter. ROS generation in irradiated DDVP solutions was evaluated by adding radical scavengers to the reaction medium. *tert*-Butanol (TB 3 mM) was used as probe of the presence of hydroxyl radicals ($\text{HO}\cdot$) and sodium azide (AzNa 2.5 mM) as singlet oxygen ($^1\text{O}_2$) quencher (Burns et al., 2012).

2.3. Analytical methods

DDVP was determined through a high performance liquid chromatography (HPLC) system (Agilent 1260 Infinity) equipped with a UV detector. The mobile phase consisted of a 65:35 volumetric mixture of 1 mM phosphoric acid and acetonitrile. The employed column was a Teknokroma Mediterranea™ Sea₁₈ (25 cm × 4.6 mm, particle size 5 μm), which was preconditioned at 25 °C. The flow rate was set at 1.2 mL min^{-1} and the detection was performed at 205 nm. All samples were previously filtered with 0.45 μm PVDF/L filters. LOD and LOC were determined to be 0.049 μM and 0.113 μM respectively.

DDVP photodegradation products (PDBP) were analyzed by Liquid chromatography-Mass Spectrometry (LC-MS). In order to avoid interferences from phosphates present in buffered solutions, experiments for PDBP determination were conducted in unbuffered Milli-Q water under same conditions of irradiation than previous experiments. An Agilent 1100 HPLC coupled with a G1969A LC/MSD-TOF mass spectrometer was employed. Interface was operated in negative mode and the ion transfer capillary temperature was at 325 °C. Nitrogen was used as carrier gas at 30 psi and the samples were injected by HPLC

system using a mobile phase consisting of 80:20 water and acetonitrile with a flow rate of 300 $\mu\text{L min}^{-1}$. Data-dependent scan mode was used in order to identify by-products, the scan range was 25–1100 m/z and the collision energy was set at 35 eV. The MS^2 scan could confirm the structures of compounds related to DDVP.

Sample toxicity was determined following the bioluminescence inhibition test of *Vibrio fischeri* bacteria (MicroTox® method). The bioluminescence of *V. fischeri* was registered by the Microtox® M500 analyzer (Modern Water, UK) after a 15-min exposure time. The osmotic pressure in samples was adjusted by adding a NaCl solution, to a final concentration of 2% of NaCl. The pH value was adjusted to 7 ± 1 by adding NaOH or HCl 100 mM solutions. Serial dilutions of each sample were performed in order to establish dose-response relationships and calculate the EC_{50} value (Bundy et al., 1997).

3. Results and discussion

Dark controls in pure water revealed that neither hydrolysis, absorption nor volatilization occurred significantly during the exposure period (<1.12% in 6 h), which indicates that the observed decreases in DDVP concentrations during photodegradation experiments were mainly caused by photochemical processes.

In surface waters, the photochemical transformation of organic compounds could take place by direct photolysis or indirect photoreactions. Direct photolysis takes place when irradiation absorption by a molecule triggers its transformation. A key prerequisite for a molecule to undergo direct photolysis is its ability to absorb light. In order to determine the possibility of undergoing photodegradation, the absorption spectrum of DDVP solution was recorded (Fig. 1).

The UV absorption spectrum of DDVP in Milli-Q water presents an absorption maximum at 192 nm, with a light absorption band that extends to the 295 nm region, slightly overlapping the solar spectrum at sea level (see inset in Fig. 1). The findings are consistent with the UV absorptivity of DDVP reported by Feigenbrugel et al. (2005), which were $\epsilon = 0.08 \text{ M}^{-1} \text{ cm}^{-1}$ and $0.03 \text{ M}^{-1} \text{ cm}^{-1}$ at 290 and 295 nm, respectively. These results, therefore, illustrate the ability of DDVP to absorb irradiation at the UV-B range. Although UV-B is only a small portion of the solar spectra, it is sufficient to induce photolytic transformation of organic compounds (De la Cruz et al., 2013).

3.1. Photodegradation of DDVP in pure water with simulated sunlight

To study the photodegradation of DDVP, changes of the dimensionless concentration (C/C_0 ; $C_0 = 4.5 \mu\text{M}$) in buffered (pH = 7) Milli-Q

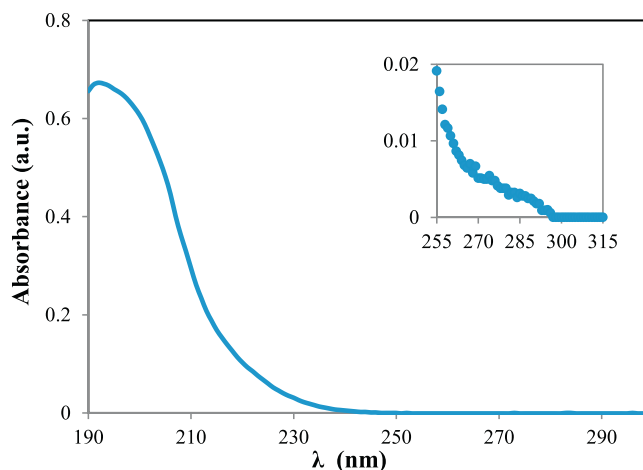


Fig. 1. UV-Vis absorption spectrum of DDVP at 4.5 mM. The insert graph includes detail of the DDV absorption spectrum between 255 and 315 nm.

water solutions versus irradiation time, in the presence of oxygen (average concentration: $6.03 \pm 0.5 \text{ mg L}^{-1}$) and in N_2 bubbled solution (O_2 concentration $< 0.3 \pm 0.1 \text{ mg L}^{-1}$), are depicted in Fig. 2. The dark control (DC) is also included. The plot presents results for the first 6 h of experimentation since in this period clear differences between the photodegradation rates of the tested compound were observed. However, irradiation under simulated sunlight was extended up to 24 h.

Under the studied conditions, DDVP underwent around 20.6% photodegradation in average after 6 h of irradiation time, in the presence of dissolved oxygen. This value extended to ca. 50% when the exposure time was 24 h (data not shown). However, when the dissolved O_2 was very low due to continuous N_2 bubbling, the removal of DDVP dropped to only 2.6%. The degradation of DDVP under simulated solar light fitted pseudo first-order kinetics during the 6 h experimentation and the observed transformation rate constants decreased 10 times (from 0.04 h^{-1} to 0.004 h^{-1}) when dissolved oxygen was removed of the reaction medium.

To understand the role of oxygen on DDVP photodegradation, the pesticide was subjected together to simulated sunlight irradiation for 6 h in Milli-Q water in presence of sodium azide (3 mM) and *tert*-butanol (2.5 mM). *tert*-Butanol presents a very high reaction rate with $\text{HO}\cdot$ ($6.10^8 \text{ M}^{-1} \text{ s}^{-1}$) (Piechowski et al., 1992), and azide is a known scavenger for both $^1\text{O}_2$ and $\text{HO}\cdot$, with rate constants of $2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, respectively (Catalán et al., 2004). At the used concentrations, light absorption competition between scavengers and DDVP was totally avoided. Other typical radical scavengers and probes, like furfuryl alcohol and benzoquinone, which are known to be used as singlet oxygen probe and superoxide radical ($\text{O}_2^{\cdot-}$) scavengers, respectively, could not be used since they present a higher absorbance than DDVP in the UV-B region and they would completely screen irradiation to DDVP. As it can be observed in Fig. 2, the same level of inhibition in DDVP photodegradation was observed when azide was present in the reaction medium (total degradation in 6 h: 2.4%), compared with the depletion obtained in the absence of oxygen. Nevertheless, degradation in the presence of *tert*-butanol was slightly higher, about 5%. These results confirm that reactive oxygen species (ROS) would be involved in the photolytic degradation mechanisms of DDVP in water, in the presence of dissolved oxygen.

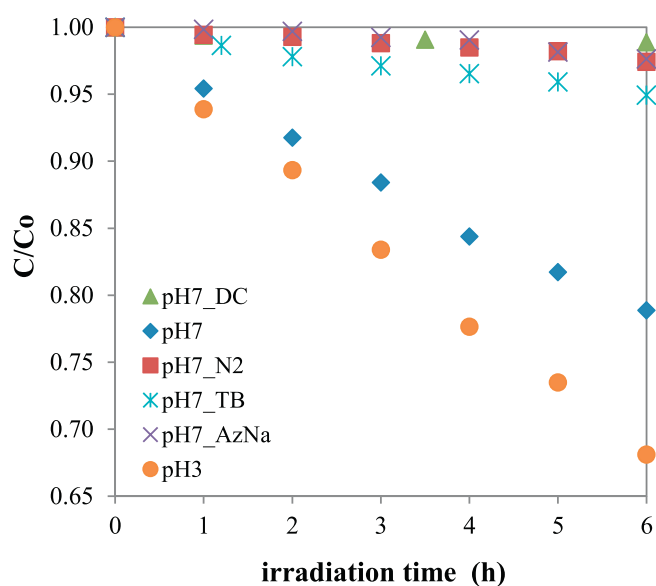
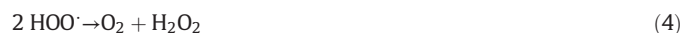
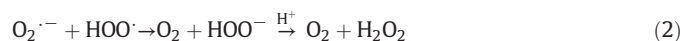


Fig. 2. DDVP relative concentration evolution during irradiation experiments with simulated sunlight ($C_0 = 4.5 \mu\text{M}$). DC: dark control; N_2 : nitrogen bubbled solution (O_2 concentration $< 0.3 \pm 0.1 \text{ mg L}^{-1}$); TB: *tert*-butanol (2.5 mM); sodium azide (3 mM).

The absorption of irradiation by a molecule can lead to the production of an electronically excited species that can exhibit new chemistry that is different than that of the parent, ground-state species. The photo-initiated oxidation of organic substances in water in the presence of molecular oxygen is usually based of the formation of reactive oxygen species (ROS) (Chen et al., 2008). Subsequently to the generation of the excited species, and in the presence of dissolved oxygen, they can promote electron transfer to an oxygen molecule with formation of a superoxide radical anion and a substrate radical cation (Type I reactions). The electronic excited state of the absorbing molecule may also be quenched by molecular oxygen with formation of singlet molecular oxygen (Type II reactions) (Oppenländer, 2003).

Superoxide is the one-electron reduced form of triplet O_2 and the conjugate base of the hydroperoxyl radical ($\text{HOO}\cdot$) (Eq. (1)). Because of its relatively low pKa (4.69), the $\text{O}_2^{\cdot-}$ anion dominates over $\text{HOO}\cdot$ in most aqueous environments. The $\text{O}_2^{\cdot-}$ anion readily undergoes disproportionation through reaction with $\text{HOO}\cdot$ (Eq. (2)). The apparent second-order rate constant for disproportionation is highly pH dependent, with a maximum value of $9.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at pH 4.69 (the pKa of $\text{O}_2^{\cdot-}/\text{HOO}\cdot$), that decreases by an order of magnitude for each unit increase in pH where the $\text{pH} > \text{pKa}$ (Burns et al., 2012). Thus, at low pH ($\text{pH} < \text{pKa}$), more reactive acid form ($\text{HOO}\cdot$) will generate further hydroxyl radicals ($\text{HO}\cdot$) via H_2O_2 formation (Eq. (3.1) & (3.2)). Moreover, hydroperoxyl radical rapidly self-reacts ($k = 8.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) (Eq. (4)) promoting a new generation source of hydrogen peroxide. In neutral conditions ($\text{pH} > \text{pKa}$), slower $\text{O}_2^{\cdot-}$ disproportionation together with very low rate constant of self-reaction of the anion ($k \approx 10^1 \text{ M}^{-1} \text{ s}^{-1}$) (Eq. (5)) will decrease overall photo-oxidation performance (Burns et al., 2012).



Photoionization of DDVP by electron transfer to dissolved oxygen and subsequent superoxide radical formation and final $\text{HO}\cdot$ yield appears to be the principal mechanism of degradation taking place during photolysis, since most of the inhibition observed during experiments with N_2 bubbling or the presence of azide is also observed during experiments with the addition of *tert*-butanol. In order to corroborate this, the same initial concentration of DDVP ($C_0 = 4.5 \mu\text{M}$) in buffered Milli-Q water solutions at $\text{pH} = 3$ was irradiated in the solar simulator and the relative concentration evolution (C/C_0) with time is also represented in Fig. 2. DDVP does not show basic or acidic properties in water (Cruz-Alcalde et al., 2018), therefore reactivity of this compound with UV irradiation was not expected to change with the medium pH. However, in our experiments, pH 3 conditions increased DDVP photodegradation up to 32%, with a degradation rate constant of 0.064 h^{-1} . That represents an improvement on DDVP photo-oxidation rate constant ca. 50%. Although further research would be necessary to finally corroborate the complete photo-degradation pathway of DDVP under solar irradiation, our experiments point out to the generation of ROS, mainly hydroxyl radicals, through DDVP excitation prior UV-B irradiation absorption (Eq. (6)) of the pesticide molecule and subsequent electron transfer to dissolved oxygen (Eq. (7)). The slightly higher photo-degradation inhibition exhibited in the presence of azide would indicate a possible residual contribution of type II mechanism on the

overall photo-degradation mechanism, that is, energy transfer to molecular oxygen to form singlet oxygen (Eq. (8)).



Although photo-transformation of DDVP and other organophosphate pesticides (OPP) in natural waters has been previously studied in literature (Zamy et al., 2004; Druzina and Stegu, 2007), this is the first time in literature that the contribution and role of dissolved molecular oxygen on the photo-transformation of pesticide under solar irradiation has been pointed out. The capability of DDVP to undergo photo-degradation in contact with oxygen could have implication also in atmospheric media due to its relatively high vapor pressure (229 MPa) compared with other OPP (Druzina and Stegu, 2007; Feigenbrugel et al., 2006).

3.2. Irradiation of DDVP in humic acids solution and WWTP effluent with simulated sunlight ($\lambda > 290 \text{ nm}$)

Phototransformations in natural waters can be indirectly induced by dissolved organic matter. It is well known that sunlight induced ${}^3\text{DOM}^*$ are important transient species in surface waters. They can promote the transfer of electrons or hydrogen atoms from the substrate to the triplet state. Besides, ${}^3\text{DOM}^*$ is considered to be the main precursor of singlet oxygen in natural waters by quenching with dissolved molecular oxygen. On the other hand, however, it has been demonstrated that DOM may inhibit the excited triplet-induced oxidation of several water contaminants due to phenolic antioxidant moieties, by reaction with intermediate superoxide anions and reduction of the substrate back to its initial state, thereby inhibiting its transformation (Wenk et al., 2013). This dual behavior of DOM as photosensitizer and redox inhibitor has been attributed to HA. Moreover, inorganic components present in wastewater effluents such as nitrite, nitrate and carbonate may also contribute or inhibit the indirect photodegradation of contaminants (Cristale et al., 2017).

To study the influence of DOM on the DDVP photodegradation process, 4.5 μM DDVP solutions with different HA content (0, 2, 3.2 and 10 mg TOC L^{-1}) were irradiated with artificial sunlight ($\lambda > 290 \text{ nm}$). Moreover, a wastewater secondary effluent ($\text{TOC} = 30 \text{ mg L}^{-1}$) doped with 4.5 μM of DDVP was also subjected to the same irradiation conditions. The obtained sunlight photodegradation pseudo-first order rate constants are presented in Fig. 3.

As it can be observed, HA concentration played an important role during DDVP photodegradation. In fact, the DDVP degradation rate was 25% faster at lower HA concentration (2 mg TOC L^{-1} ; $k = 0.050 \text{ h}^{-1}$) than in pure water ($k = 0.039 \text{ h}^{-1}$), indicating that indirect phototransformation contribution of HA is likely to be a significant process. However, at higher humic acid content (i.e., simulated DOM at 3.5 and 10 mg TOC L^{-1}), the observed rates ($k = 0.032 \text{ h}^{-1}$ and $k = 0.031 \text{ h}^{-1}$) were about 20% slower than in the control experiment and ca. 40% when compared with rate constant in the presence of HA at low concentration. Moreover, the photodegradation rate constants did not seem to strongly depend on the HA concentration. Finally, wastewater exhibited the lowest rate ($k = 0.008 \text{ h}^{-1}$), with a decrease close to 80% compared with rate depletion of DDVP in pure water.

According to the triplet-induced oxidation and subsequent inhibition mechanism previously exposed, under simulated solar irradiation, observed photodegradation of DDVP could be enhanced in the presence of low concentration of ${}^3\text{HA}^*$ by promoting the electron transfer from DDVP, endorsing its transformation (Eqs. (9), (10)). In the presence of molecular oxygen, the back reaction (Eq. (11)) would be inhibited by the scavenging of $\text{HA}^{\cdot-}$ by oxygen generating superoxide radical

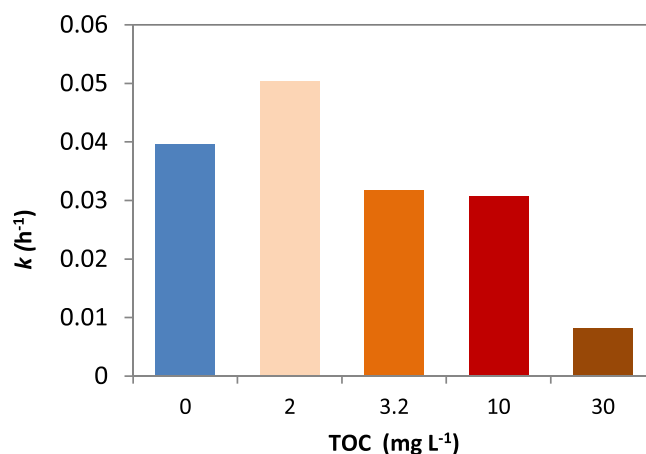
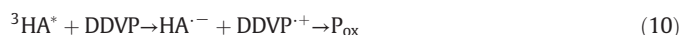


Fig. 3. Pseudo-first order degradation constants of DDVP for solutions containing 0, 2, 3.2 and 10 mg TOC L^{-1} of humic acid and wastewater effluent (30 mg TOC L^{-1}) under simulated solar irradiation ($\lambda > 290 \text{ nm}$) ($R^2 > 0.97$).

anion (Eq. (12)). Contribution of singlet oxygen generation according to Eq. (13) should also be taken into account. However, HA contains antioxidant moieties (e.g. phenolic compounds) that may inhibit $\text{DDVP}^{\cdot+}$ further transformation by reducing it back to the initial state DDVP (Eq. (14)) (Wenk et al., 2013). Moreover, quinone functionalities of humic substances can participate in the inhibition mechanisms by oxidizing superoxide radical anions (Eq. (15)) (Kouras-Hadef et al., 2012).



Therefore, at low HA concentration similar to those present in natural waters ($\text{TOC} < 2 \text{ mg L}^{-1}$), the effectiveness of DDVP photodegradation relies on the balance between the ability of excited state of DDVP to produce ROS via electron transfer to dissolved oxygen and the photosensitizing capability of HA, according to reactions of Eqs. (9)–(13). In contrast, HA exhibited an overall inhibiting effect at higher HA concentrations (TOC content $> 3.2 \text{ mg L}^{-1}$), (Eqs. (14)–(15)), which could be favored by the reduction of direct DDVP light absorption due to HA scattering and absorption competition (Bodhipaksha et al., 2017; Cristale et al., 2017). All these inhibiting mechanisms were increased when irradiating wastewater effluent, in accordance to its high organic matter content. Moreover, the light screening effect promoted by turbidity must be added to the high alkalinity content of this effluent which endorsed the scavenging of radical species, mainly hydroxyl radicals (Table 1). Encompassing all inhibition mechanisms, it is expected that DDVP photoinduced transformations do not significantly account in wastewater effluents under solar sun irradiation.

3.3. UV-254 irradiation of DDVP in ultrapure water

DDVP relative concentration in solutions exposed to 254 nm irradiation in the presence of dissolved oxygen and in N_2 bubbled solutions

(concentration of oxygen $< 0.2 \text{ mg L}^{-1}$) are presented in Fig. 4. Two different photon flows were applied: one at low UV-C photon flow, by means of a 4 W lamp, and the other at higher irradiation flow ($3 \times 8 \text{ W lamps}$). Table 2 includes pseudo-first order kinetic constants obtained in the different experimental conditions applied, both with sunlight and UV-C irradiations.

Unlike experiments with simulated solar irradiation, DDVP triggered photodegradation under UV-C irradiation, both in the presence and absence of oxygen. The degradation was almost complete (97%) under 254 nm irradiation dose of about $0.1 \text{ Einstein L}^{-1}$ ($3 \times 8 \text{ W}$ and 6 h irradiation) in oxygenated water solutions. This efficiency decreased to 71% (about 30% lower) for the same irradiation dose but in the absence of oxygen. At lower photon flow, the eliminations fell from 64% to 22% under a irradiation of $0.016 \text{ Einstein L}^{-1}$ (4 W and 6 h irradiation) when oxygen was removed from the solution. That represents a decrease of about 66% of DDVP concentration in the absence of oxygen. These results evidences that ROS are involved in DDVP degradation under oxygenated UV-C irradiated solution, particularly at low photon flow. DDVP direct photolysis would be accounting at high irradiation doses, far from the conditions applied in disinfection systems (Zhu et al., 2015). Absorptivity of DDVP at high energy irradiation of 254 nm wavelength is significantly higher ($\epsilon = 5.5 \pm 0.5 \text{ M}^{-1} \text{ cm}^{-1}$) compared with the value at 290 nm ($\epsilon = 0.08 \text{ M}^{-1} \text{ cm}^{-1}$) and 295 nm ($0.03 \text{ M}^{-1} \text{ cm}^{-1}$) (Feigenbrugel et al., 2005), thus being enough to trigger DDVP direct photodegradation. Still, phototransformation rate constants improved in oxygenated waters by a factor of 3.2 at high irradiation dose, and by a factor of 4.2 at low UV-C irradiation (Table 2).

Checking the rate constants presented in Table 2, it can be observed that irradiation at 254 nm increased rate constant 4.1 times at low irradiation dose (4 W with O_2) or by a factor of 16.8 ($3 \times 8 \text{ W}$ with O_2), when compared with solar light irradiation (pH 7 with O_2). These results represent a better understanding of DDVP in solution with presence of dissolved oxygen, both in natural waters and UV-C disinfection systems.

3.4. DDVP Photodegradation by-products

Simulated sunlight and UV-C irradiated DDVP solutions, in the presence and absence of oxygen, were analyzed by LC-MS for relevant

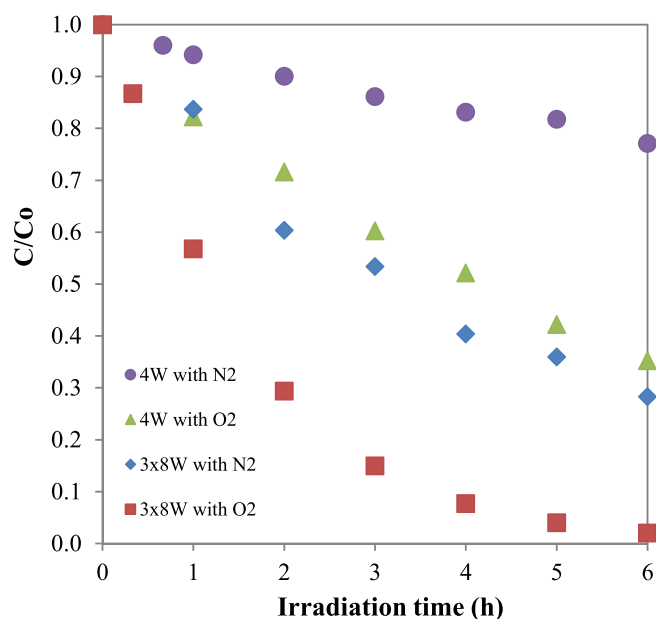


Fig. 4. DDVP relative concentration evolution during UV-254 nm irradiation ($C_0 = 4.5 \mu\text{M}$). O_2 : in the presence of dissolved oxygen (O_2 concentration $6.03 \pm 0.5 \text{ mg L}^{-1}$) N_2 : nitrogen bubbled solution (O_2 concentration $< 0.3 \pm 0.1 \text{ mg L}^{-1}$).

Table 2

Pseudo-first order degradation constants obtained irradiating with simulated sun light (SSL) and UV-C irradiation at different experimental conditions ($R^2 > 0.97$).

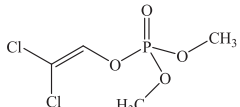
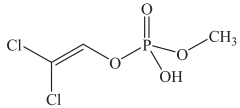
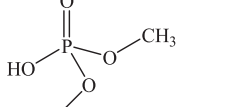
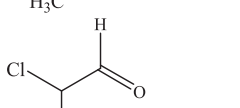
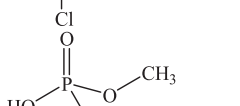
	Experimental conditions	$k \text{ (h}^{-1}\text{)}$
SSL	pH 7 with O_2	0.040
	pH 7 with N_2	0.004
	pH 3 with O_2	0.064
	HA_2mg TOC L^{-1}	0.050
	HA_3,2 mg TOC L^{-1}	0.032
	HA_10mg TOC L^{-1}	0.031
UV-C	$3 \times 8 \text{ W}$ with O_2	0.655
	$3 \times 8 \text{ W}$ with N_2	0.210
	4 W with O_2	0.171
	4 W with N_2	0.041

intermediates detection and elucidation during the pesticide photodegradation process. The detected masses and proposed molecular structures after 1, 3 and 6 h of irradiation are gathered in Table 3.

The analysis revealed the presence of dimethyl phosphate (DMP m/z 125.000), monomethyl phosphate (MMP m/z 109.976) and dichloroacetaldehyde (DCA m/z 110.940) in almost all the analyzed samples. For its part, 2,2-dichlorovinyl methyl phosphate (MDVP m/z 205.922) was detected during most of the experiments, except for the one irradiated by means of the $3 \times 8 \text{ W}$ UV-C system, in the presence of dissolved oxygen. This particular finding can be attributed to the simultaneous contribution of both DDVP photodegradation mechanisms, direct and indirect, taking place under these experimental conditions, as well as to the larger photon flow received by the reaction medium in comparison to the system employing only a UV-C lamp. These two factors together enhanced the degradation of DDVP in this particular case, resulting in the detection of further oxidized products than the primary intermediate MDVP.

In the presence of oxygen, a ROS-mediated oxidation is expected to be the principal mechanism for DDVP indirect photodegradation. Particularly, and according to the previously obtained results, hydroxyl radicals appears to play a major role in this process. Considering this, and also in agreement with the detected intermediate species, the reaction pathways shown in Fig. 5 were proposed as potential, main DDVP photo-induced oxidation mechanisms taking place in the studied reaction systems. DDVP demethylation to yield MDVP could take place either by hydrogen abstraction followed by a formaldehyde molecule yield (mechanism 1), or through initial $\cdot\text{OH}$ addition and the subsequent removal of a methanolate group (mechanism 2). This will depend on the initial DDVP site attacked by hydroxyl radicals, as the H-abstraction will occur at one of the methyl groups, whereas the addition reaction should take place at the phosphate group of the pesticide molecule. $\cdot\text{OH}$ can also undergo addition reactions with the double bond of the dichlorovinyl moiety, resulting this in the formation of DCA and DMP (mechanism 3). Additionally, DCA could be formed if further $\cdot\cdot\text{OH}$ attack on MDVP is produced, as reported by Evgenidou et al. (2006). The three proposed mechanisms for DDVP photo-induced oxidation are similar to those reported by Cruz-Alcalde et al. (2018) in a recent study dealing with DDVP removal by ozonation. This observation is completely consistent with the fact that in both process (photo-induced oxidation and ozonation) hydroxyl radicals are involved in the degradation mechanisms. However, two main differences were observed in this work, both of them concerning the detected intermediates. On one hand, if dichloroacetaldehyde (DCA) was identified in the present work, the formation of dichloroacetic acid –a further oxidized intermediate species– was instead observed during DDVP ozonation; also, monomethyl phosphate (MMP) was identified as a reaction intermediate of DDVP photo-induced oxidation. This compound, presumably formed through DMP demethylation via mechanisms 1 and/or 2 (see Fig. 5), was neither detected in the work developed by Cruz-Alcalde et al. (2018) regarding DDVP oxidation by O_3 and $\cdot\text{OH}$. The different

Table 3
DDVP detected transformation products and their corresponding molecular structures for photodegradation experiments under different irradiation conditions. SSL: simulated solar light; O₂: in presence of O₂; N₂: in absence of O₂ (nitrogen-bubbled solutions).

m/z	Name	Proposed structure	SSL _{O₂}		UVC 4W _{O₂}		UVC 3x8W _{O₂}		UVC 3X8W _{N₂}				
			1 h	3 h	6 h	1 h	3 h	6 h	1 h	3 h	6 h		
220 (m-1)	Dichlorvos (DDVP)		Parent compound in all experiments										
206 (m-1)	DDVP-206 2,2-dichlorovinyl methyl phosphate (MDVP)		✓	✓	✓	✓	✓	✓				✓	✓
125 (m-1)	DDVP-125 Dimethyl phosphate (DMP)		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
111 (m-1)	DDVP-111 Dichloro acetaldehyde (DCA)		✓	✓	✓	✓	✓	✓		✓	✓	✓	✓
110 (m-1)	DDVP-110 Monomethyl phosphate (MMP)		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

medium conditions in both processes (i.e., photo-induced oxidation and ozonation) could be connected to the observed differences.

The photocleavage transient intermediates identified under UV-C irradiation in the absence of oxygen did not differ from the ones obtained with the contribution of hydroxyl radicals mediated reactions.

Additional research, therefore, should be carried out in order to elucidate reaction pathways for this direct mechanism. However, reaction intermediates have been already identified, and direct photolysis through UV₂₅₄ light is not expected to have a significant role in DDVP photodegradation during water or wastewater disinfection, as

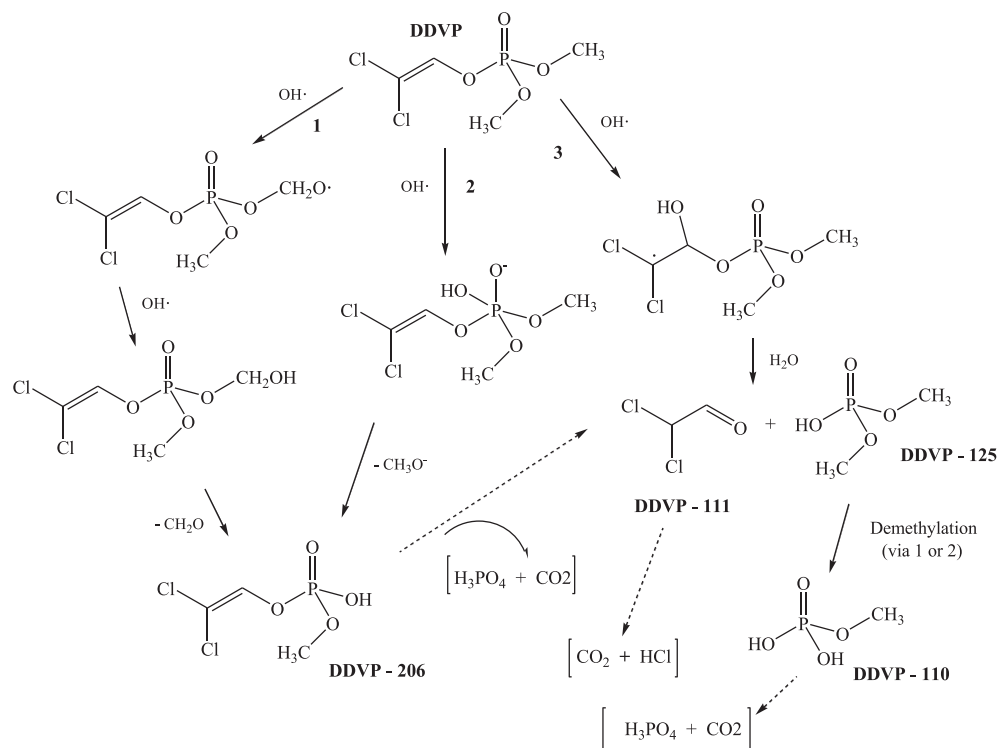


Fig. 5. Potential reaction pathways for DDVP photo-induced oxidation by hydroxyl radicals.

irradiation doses employed in disinfection are far lower than that applied for UV-C experiments carried out in the present work.

3.5. Effect of photodegradation in toxicity samples

Due to the changes in the reaction medium caused by the degradation of DDVP (i.e., the parent compound) and the generation of new products, the photodegradation of this pesticide can also involve changes in the solution toxicity (Rizzo, 2011). The values of DDVP solution toxicity with UV-C and simulated sunlight are registered in Fig. 6 by the inverse of the EC_{50} value, which represents the effective sample dilution that inhibits a 50% of bacteria light emission. Therefore, higher $1/EC_{50}$ values represent higher toxicities, and so on.

Microtox assays showed that samples taken during the experiments were in general more toxic than initial samples, following a similar pattern during their corresponding irradiation times: an initial increase in toxicity followed by a decreasing tendency of this parameter. This trend showed a delay in the case of the experiment with simulated sunlight and presence of dissolved O_2 , due probably to a slower formation of those intermediates responsible for the overall increase in toxicity of the medium. Among the three systems for which toxicity was monitored, only in the UV-C assay with the presence of dissolved oxygen a lower final $1/EC_{50}$ value was observed in comparison to that measured for the initial solution. This appears to be consistent, as both UV-C direct photolysis and ROS-mediated photooxidation were combined in this system, resulting this in a higher degradation of the chemical species present in the reaction medium and potentially responsible for the sample toxicity. Without the presence of dissolved oxygen (i.e., in experiments with nitrogen bubbling), the degradation conditions were less efficient, as the contribution of the indirect photodegradation was inhibited. Thus, the observed initial increase in toxicity was more pronounced, and the final reduction of this parameter slower in comparison to that observed for the 3X8W_0₂ process. This, together with the results obtained in the experiment performed under simulated solar irradiation in the presence of oxygen, allows the drawing of two key conclusions: alone, UV₂₅₄ direct photolysis appears to increase the sample toxicity, although no differences in the detected intermediates were observed; and the contribution of ROS-mediated photodegradation is essential for the reduction of toxicity. Concerning the chemical species responsible for the observed increase in sample toxicity, synergistic effects between residual DDVP and newly formed intermediates could constitute a plausible explanation for its increase, as previously reported

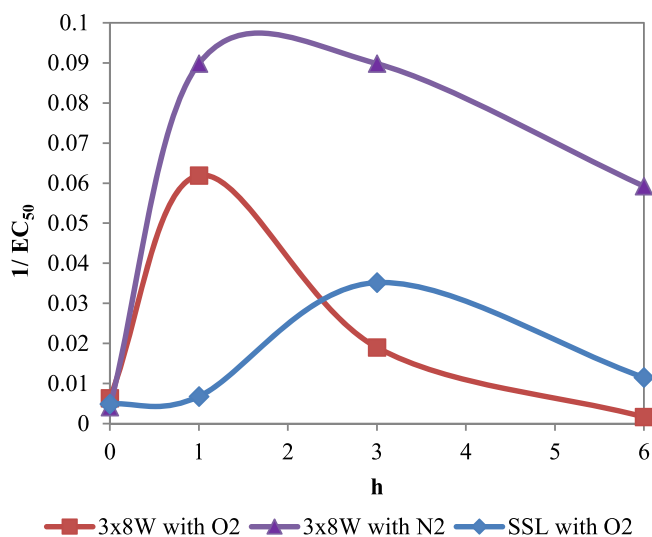


Fig. 6. Acute toxicity of the reaction medium during DDVP photodegradation experiments. 3 × 8 W: UV-C irradiation; SSL: simulated sun light.

in the work by Cruz-Alcalde et al. (2018). The sole presence of intermediates with suspected toxicity –such as MDVP– was not considered to be responsible for the observed $1/EC_{50}$ increases, as this compound was not detected in experiments in which UV-C direct photolysis was the main degradation mechanism. An accumulation of those degradation products without UV-C absorption (and therefore, not affected by direct photolysis) appears to be a more consistent interpretation of the obtained results.

4. Conclusions

Our results showed that photodegradation DDVP could occur under simulated sunlight in the presence of dissolved oxygen providing an alternative degradation mechanism to the typically suggested partial hydrolysis in water. Reactions performed in the presence of different scavengers (sodium azide and *tert*-butanol) and pH conditions allowed us to propose the main photo-induced mechanism based on the photoionization of excited DDVP by electron transfer to dissolved oxygen and the subsequent formation of superoxide and hydroxyl radicals. The absence of dissolved oxygen in ultrapure water prevented DDVP photodegradation, confirming the importance of the role of oxygen on the pesticide degradation in natural waters under solar light irradiation. DDVP depletion combines direct photocleavage and photo-induced ROS generation when submitted to UV-C (254 nm) irradiation. Although removal kinetics improved compared with solar light irradiation, the photon flow needed to a significant DDVP degradation is far from the typical UV-C disinfection applied doses. Humic substances, typically found in natural water and wastewater matrices, played also an important role on the fate of DDVP, showing an accelerating influence at low concentration by being probably involved in redox reactions with the pesticide molecule. Acute toxicity of DDVP solutions increased during the first hours of irradiation. This work highlights the importance and complexity of photoinduced oxygen mediated reactions of DDVP, even though having one of the lowest molar absorptivity coefficients of solar irradiation among organophosphorus pesticides. Thus, the role of photinduced chemical reactions on the fate of organophosphorus pesticides in oxygenated natural waters would deserve to be studied in detail due to their important environmental implications.

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