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

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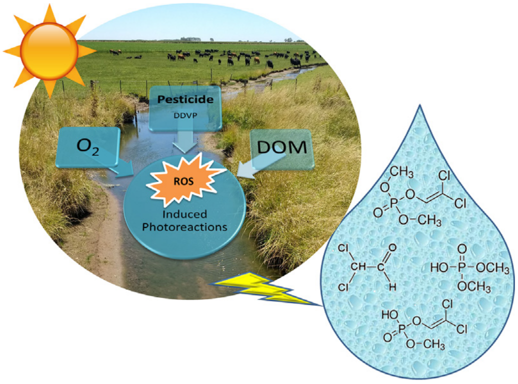
HIGHLIGHTS

- 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 ($TOC = 2\ mg\ L^{-1}$). 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}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 ($N_2 > 99.995\%$) 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 pH 3.0 ± 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 (mg $CaCO_3$ L^{-1})	463.5
pH	7.4
Turbidity (NTU)	8.1