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François Clavero, Jérôme Cachot, Christelle Clérandeau, Laure Sandoval, Fanny Meytraud, et al.. Optimization of a novel continuous treatment of viticultural wastewater using pulsed light technology. Journal of Hazardous Materials Advances, 2026, 22, pp.101165. ⟨10.1016/j.hazadv.2026.101165⟩. ⟨hal-05659886⟩

HAL Id: hal-05659886

https://hal.inrae.fr/hal-05659886v1

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Journal of Hazardous Materials Advances 22 (2026) 101165

Contents lists available at ScienceDirect

Journal of Hazardous Materials Advances

journal homepage: www.elsevier.com/locate/hazadv

Optimization of a novel continuous treatment of viticultural wastewater using pulsed light technology

François Clavero [a,b,*], Jérôme Cachot [c], Christelle Clérandeau [c], Laure Sandoval [b], Fanny Meytraud [b], Warren Albertin [a], Gilles de Revel [a], Rémy Ghidossi [a], Céline Franc [a]

[a] Univ. Bordeaux, INRAE, Bordeaux INP, Bordeaux Sciences Agro, UMR 1366, ŒNO, ISVV, Villenave d'Ornon, France
[b] SANODEV, Limoges, France
[c] Univ. Bordeaux, CNRS, INP Bordeaux, laboratoire EPOC, UMR 5805, Pessac, France

ARTICLE INFO

Keywords:
Effluent
Response surface methodology
Pesticide
Degradation
Ecotoxicity
HPLC-MS/MS
Photoproducts

ABSTRACT

A continuous Pulsed Light (PL) treatment was optimized for the degradation of pesticides in viticultural wastewater. PL uses high-intensity polychromatic light pulses to break down chemical compounds.

Optimization was performed on an aqueous solution of 20 pesticides using response surface methodology with a Box-Behnken experimental design. Pesticides and degradation products were monitored using HPLC-MS/MS. Optimal conditions, 50 mL/min flow rate, 3 Hz frequency, and 7 treatment cycles, reduced all 20 pesticides from ~300 µg/L to below quantification limits (LOQs). Dimethomorph was the most resistant to degradation. K-means clustering determined that 72 out of the 81 degradation products monitored were also degraded by the PL treatment.

The optimal PL treatment was then applied to 3 viticultural effluents. In wastewater 1, the concentrations of 5 out of 12 pesticides were reduced to below their LOQ, with 6 others degraded over 50%. In wastewater 2 and 3, all compounds except ametoctradin fell below LOQs. After PL treatment, 17 degradation products originating from 6 parent pesticides were detected.

Acute toxicity tests were conducted on bacteria (*Aliivibrio fischeri*), microalgae (*Raphidocelis subcapitata*), and fish larvae (*Oryzias latipes*). Although initial toxicity varied between the three viticultural wastewaters, PL-treatment reduced substantially toxicity up to 6 times for bacteria, up to 2 times for algae, and from 100% mortality to no toxic effects for fish in one effluent. However, acute toxicity remained high in all treated samples, likely due to high trace metal concentrations, particularly copper (7–50 mg/L) used extensively in organic and conventional viticulture.

1. Introduction

Pesticides used for agricultural purposes, also known as phytopharmaceuticals, phytosanitary products or plant protection products, play a crucial role in protecting plants and ensuring high production yields and high sanitary quality of harvests. However, phytosanitary products, while protecting plants from pests and pathogens, can also be harmful to humans and ecosystems. The escalating use of pesticides has led to an increase in pesticide residues in the different ecosystem compartments (Tudi et al., 2021). Freshwater, a precious resource, is widely contaminated by pesticides, whether surface water (Farah et al., 2024) or groundwater (Huang and Li, 2025; Suciu et al., 2020). Agricultural production, and particularly viticulture, is a major source of environmental contamination (Mauser et al., 2025). Viticulture generates large volumes of effluent, when not treated properly, can cause environmental pollution (Pigeon et al., 2006; Pussemier et al., 2004). New ways of treating pesticide-contaminated water are being searched because developing effective remediation techniques for pesticides is essential for water sustainability (Cossu et al., 2024).

Viticultural wastewater (WW) is contaminated with phytosanitary products and trace metal elements (TME), but also engine oil, fertilizers. Compounds of concern for public health and the environment (fertilizers, pesticides, and TME) have been detected at concentrations ranging from ng/L to mg/L in viticultural WW (Kyzas et al., 2016; Massot et al., 2012). Consequently, viticultural wastewater can exhibit high ecotoxicity (Clavero et al., 2025a).

* Corresponding author.
E-mail address: francois.clavero@u-bordeaux.fr (F. Clavero).

https://doi.org/10.1016/j.hazadv.2026.101165
Received 6 February 2026; Received in revised form 26 March 2026; Accepted 9 April 2026
Available online 14 April 2026
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One way to achieve the removal of unwanted organic molecules from WW is to alter their structure. Photoinduced chemical processes proved effective in degrading phytosanitary products (Reddy and Kim, 2015). Photodegradation can proceed by direct or indirect photolysis including photosensitized degradation and photocatalytic degradation (Burrows et al., 2002).

In the field of eco innovative processes pulsed light (PL) has emerged as a highly efficient method for photodegrading organic pollutants, including chlorophenol (Hadi et al., 2021), bisphenol A (Fadaei et al., 2022) and dye (Martínez-López et al., 2019). PL is a non-thermal technology that employs a capacitor to accumulate high discharge voltages. The stored electrical energy is then discharged in intermittent short pulses through a light source filled with xenon gas. This technology operates across a broad wavelength range, from 200 to 1000 nm, offering a greater likelihood of molecular interactions compared to UV-C, which typically irradiates at specific wavelengths such as 254 nm or 365 nm. Additionally, the UV irradiance of PL lamps is approximately three orders of magnitude higher than that of mercury lamps (Schaefer et al., 2007). Moreover, the presence of mercury in continuous UV-C lamps raises environmental concerns regarding the production of this process.

PL also demonstrated its ability to efficiently degrade pesticides in water spiked solutions (Baranda et al., 2012, 2014, 2017) both in continuous and static systems. The study of Baranda *et al.* (2014) focused on just 7 pesticides (simazine, atrazine, phosmet, azinphos-methyl, methyl-parathion, pirimiphos-methyl and chlorpyrifos-ethyl) and tracked only 17 degradation products whereas WW may contain dozens of pesticides giving rise to hundreds of degradation products. Moreover, the pesticides studied must be constantly updated, although atrazine, banned in Europe since 2003, still persists in the environment. Furthermore, none of these experiments investigated the impact of PL on real pesticide-contaminated wastewater samples nor on sample toxicity using in vivo bioassays.

Our recent research addressed some of these gaps. Clavero et al. (2024) described the reduction in pesticide concentration and the formation of 74 degradation products from 20 parent pesticides, using PL treatment of water samples in static mode. Moreover, we demonstrated a very significant reduction in acute toxicity of these water samples on three aquatic trophic levels, bacteria (*Aliivibrio fischeri*), microalgae (*Raphidocelis subcapitata*), and fish larvae (*Oryzias latipes*). Static PL treatment was also applied to three viticultural WWs (Clavero et al., 2025a). The reduction in pesticide concentration, although lower than for water samples, was still significant and the acute toxicity of these WW samples naturally contaminated with pesticides was also significantly reduced for the bacteria *A. fischeri*. Despite these advances, a knowledge gap remains: no study has yet applied a continuous PL system to real viticultural WW in order to process larger sample volumes with higher throughput. The parameters governing the PL photodegradation of pesticides in aqueous liquids under continuous flow conditions have to be investigated, as the transition from static to continuous systems fundamentally alters light–matter interactions and exposure conditions in a flowing medium. The use of design of experiment (DoE) to optimize pesticide-contaminated water treatment processes has already proven its effectiveness (Ngaha et al., 2019; Reddi et al., 2018). Indeed, DoEs enable the saving of a considerable amount of time by reducing the number of experiments and help to determine the factors responsible for the variability of responses.

Therefore, the aim of this work was to develop, optimize and evaluate a new PL continuous WW treatment pilot for the photodegradation of pesticides and the reduction of acute toxicity of viticultural WWs. In this context, the degradation of 20 pesticides, widely used in viticulture, enabled by the continuous PL water treatment pilot was optimized by a surface response methodology. The evolution of 81 degradation products was also studied using a clustering method to determine their stability under PL treatments. Finally, three viticultural WWs were treated by PL according to the previously optimized conditions. The concentrations of pesticides present in these treated and untreated WW samples and their degradation products were monitored by HPLC-MS/MS. The impact of PL on acute toxicity for three aquatic trophic levels (bacteria, microalgae, and fish larvae) was also studied. This approach provides new insights into pesticide photodegradation under continuous flow PL conditions and its ecotoxicological effects in viticultural wastewater, supporting the development of more sustainable treatment strategies.

2. Materials and methods

2.1. Chemicals

HPLC-grade acetonitrile was purchased from VWR International SAS (Rosny-sous-Bois, France) and LC-MS grade acetonitrile (Optima®, 100% purity), used for chromatographic separation was provided by Fisher Chemical (Illkirch, France). Ultrapure water was obtained using a Milli-Q Reference system (Merck Millipore, Fontenay-sous-Bois, France). The mobile phases employed for HPLC separation were acidified with 0.1% of formic acid (CAS RN: [64–18–6], high purity grade, 100%) from Amresco Inc. (Solon, Ohio, USA).

Stock solutions at concentration between 300 mg/L and 896 mg/L of 88 pesticides were prepared in acetonitrile for each single pesticide.

Triphenylphosphate (TPP) used as the internal standard (IS), was purchased from Sigma-Aldrich Chimie (St Quentin Fallavier, France). Difenoconazole-d_6 (99.4% isotopic purity), fenbuconazole-d_5 (98.8% isotopic purity), metrafenone-d_9 (99.9% isotopic purity), pyraclostrobin-d_6 (99.8% isotopic purity), tebuconazole-d_6 (97.5% isotopic purity), and tebufenozide-d_9 (98.9% isotopic purity) used as IS were acquired from Cluzeau info labo (Sainte Foy la Grande, France).

2.2. Pulsed light

The LPBox, manufactured by Sanodev (Limoges, France), was utilized for pulsed light treatments. The LPBox was operated at 4 kV as optimized in a previous study by Clavero et al. (2024).

The spectral distribution at 4 kV is as follows: UV-C 3.2%, UV-B 6.2%, and UV-A 19%. The LPBox delivers a fluence of 140 J/flash at 4 kV. This value is determined in electrical Joules, i.e., the energy consumed by the LPBox to produce a flash. A continuous treatment pilot system was designed by Sanodev (Fig. 1), including a rectangular reactor of 8 cm width × 25 cm length and 3.2 mm depth. The pilot system includes a pump through which aqueous solutions or WW samples are transported inside the reactor where samples are treated by PL. The reactor glass is made of quartz to limit PL radiation absorption. The total fluence (H) applied to each sample was calculated by multiplying the number of flashes by the fluence per flash depending on the residence time of the liquid in the reactor. Treatments were carried out in successive cycles. A cycle corresponds to the transfer of the entire liquid (500 mL) from the left bottle to the right bottle.

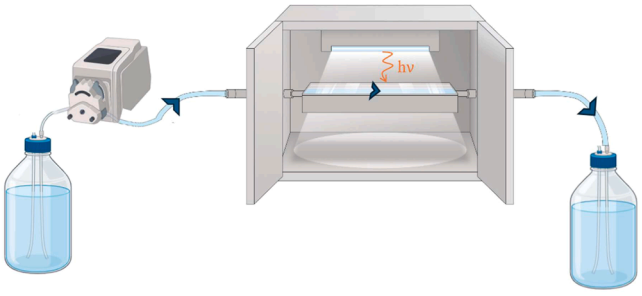


Fig. 1. Continuous PL water treatment. On the left untreated sample connected to a pump sending the liquid into the reactor -at the center of the LPBox- where it is treated before being released to a recovery bottle on the right.

2.3. Samples

2.3.1. Aqueous solutions

A cocktail solution of the 20 selected pesticides was prepared in milli-Q water from stock solutions with concentrations ranging from 267 to 354 µg/L for the DoE set and from 189 to 352 µg/L for the validation set. These pesticides were selected because they are frequently detected in wines and are therefore likely to be commonly present in viticultural wastewater. The aqueous cocktail solution was used for the single purpose of optimizing pesticide degradation parameters in a continuous system. PL treatments were applied to this sample according to the DoE and the optimized value of the DoE. For the validation set, 2 mL samples were collected after each PL treatment cycle. The validation set treatment was performed in triplicate.

2.3.2. Wastewater samples

Three viticultural WWs were obtained from three different wine estates in the Bordeaux region. WWs 1 and 2 come from wine estates where the phytosanitary treatment itinerary is conventional, allowing the use of synthetic pesticides, whereas WW 3 comes from a vineyard cultivated using organic practices. These WWs were processed using the optimized parameters obtained from the DoE (flow rate: 50 mL/min, frequency: 3 Hz and 7 cycles). These samples were further analyzed for toxicity. WWs were processed by PL in single replicate.

2.4. Sample preparation for LC-MS analysis

Regarding the aqueous solutions, the LC-MS analyses were performed in multiple reaction monitoring (MRM) mode (Table S1) on samples prepared as described in Clavero et al. (2024). Limits of detection (LODs) and quantification (LOQs) for parent pesticides are reported in Table S2.

The quantification of pesticides in the different WW samples was performed after a QuEChERS extraction (Quick, Easy, Cheap, Effective, Rugged, and Safe) using EN 15662 method and LC-MS analysis in MRM mode as described in Clavero et al. (2025b), with a slight difference: 81 photoproducts were quantified relatively (using peak area ratios) instead of 74 (Table S3). Each sample was prepared in triplicate and analysed once without dilution and once with a 10-fold dilution, in order to quantify compounds at high concentrations; i.e., out of the calibration range. Limits of detection (LODs) and quantification (LOQs) for parent pesticides are reported in Table S4.

Each HPLC-MS/MS analysis was performed after filtering 1 mL of the solution to be analyzed on 0.2 µm PTFE membrane before injection.

2.5. Quantification of trace metal elements

Aluminium, copper, iron, manganese and zinc were quantified by the EPOC laboratory (University of Bordeaux, France). The samples were first acidified with 10% nitric acid before being analysed by ICP- OES (Inductively Coupled Plasma Optical Emission Spectrometer) (Spectrometer ICP-OES 700®, Agilent Technologies).

2.6. Toxicity bioassay

For all toxicity analyses the pH of the WWs analysed were measured between 6.8 and 8.1.

2.6.1. Acute toxicity bioassay on bacteria (Aliivibrio fischeri)

Microtox® test using the heterotrophic and bioluminescent bacterium *A. fischeri* was performed as described in Clavero et al. (2025a). Treated and untreated WW samples were diluted at 20%, 10%, 5%, 2.25%, and 1.25% for WW1, 50%, 25%, 12.5% and 6.25% for WW2, 10%, 5%, 2.25%, 1.25%, 0.63%, and 0.31% for WW3, in order to determine EC50 (effective concentration 50%), the concentration for the bioluminescence inhibition of 50% of the population of bacteria. These analyses were conducted in triplicate.

2.6.2. Acute toxicity bioassay on microalgae (Raphidocelis subcapitata)

Raphidocelis subcapitata was used as a reference freshwater microalgae for the growth inhibition assay as described in Clavero et al. (2025b). Treated and untreated WW1 were diluted at 0.19%, 0.098%, 0.05%, and 0.024%; treated and untreated WW2 were diluted at 3.12%, 1.56% and 0.78%; treated and untreated WW3 were diluted at 0.39%, 0.25%, and 0.17%, in order to determine EC50, the concentration for the inhibition of growth for 50% of the population of algae. These analyses were conducted in triplicate.

2.6.3. Acute toxicity bioassay on fish larvae (Oryzias latipes)

Oryzias latipes was used as a reference freshwater fish. A 48 h acute toxicity assay on freshly hatched larvae was performed as described in Clavero et al. (2025b). All analyses were conducted in triplicate. Pre-tests were used to determine the dilutions to be applied to the 3 WWs in order to measure the toxicity of treated and untreated WWs, WW1 was diluted at 5% of its initial concentration, WW2 was not diluted and WW3 at 75%.

2.7. Experimental design

Optimization of the PL continuous water treatment was carried out using a response surface methodology. A Box-Behnken design (BBD), was used to optimize and evaluate the ability of PL to degrade 20 pesticides with a continuous water treatment system. The three independent variables of the BBD were: liquid flow rate (mL/min) (X1), LPBox frequency (flashes/s) (X2), treatment cycle (number of times the liquid passes in front of the lamp) (X3). The different experiments are conducted on three scales: low (−1), central (0), and high (+1) (Chaker et al., 2021; Nardelli et al., 2020). The BBD carried out is summarized in Table S5.

The responses considered were the percentage of degradation of each pesticide: ametoctradin to tetraconazole (Y_1-Y_{20}).

In total, 15 experiments in random order were performed with a triplicate at the center point. This triplicate enables to measure the pure error of the model.

A multi-response optimization was performed using XLSTAT Version 2023.2.1414 (Statistical Software for Excel, Quality option).

Linear, quadratic, and interaction coefficients were computed through least squares regression. Analysis of variance (ANOVA) was conducted to assess the significance and interactions of the independent variables ($p\text{-value} < 0.05$).

2.8. Statistical analysis

The evolution of the photoproducts over treatments of the experimental design (Fig. 5) was studied using k-means clustering (R package ClassDiscovery). This method allows to partition the kinetic profiles into k clusters in which each observation belongs to the cluster with the nearest mean (cluster centers or cluster centroid). The number of optimal clusters was assessed visually.

Data for each toxicity assessment were analyzed by *t*-test, two samples were considered as different for a $p\text{-value} < 0.05$.

3. Results and discussion

3.1. Design of experiment

3.1.1. Experimental design generation and statistical analysis

The degradation of pesticides with a PL continuous water treatment system depends on various parameters. The use of experimental design aims to optimize a process by reducing the number of experiments and to determine the factors responsible for the variability of responses. Moreover, BBD enables to develop predictive models of the relationship

between the factors and the responses.

More specifically, the aim of the DoE employed here was to evaluate the impact of flow rate, frequency, and cycle number of a continuous pulsed light system on the degradation of 20 pesticides. The 15 experiments of the BBD were carried out on an aqueous cocktail solution of the 20 pesticides with concentrations between 267 and 354 µg/L. The 15 BBD modalities generated (Table S5) were quantified by HPLC-MS/MS after PL-treatment.

The influence of each variable and the potential effects on the responses Yi (Degradation percentage of each pesticide, %) were examined with a response surface methodology. This allowed for the generation of a regression model to evaluate and optimize the degradation of the 20 pesticides studied in mixture.

The statistical analysis and the responses of the 15 observations of the DoE are listed respectively in Table 1 and Table S6. It appeared that all the compounds were 100% degraded in 3 of the 15 observations (Obs3, 7, and 12). The *p-value* of the ANOVA was below 0.05 for 11 compounds (Table 1). Compounds with a *p-value* above 0.05 have degradation kinetics that are too rapid, which probably makes model determinations incorrect. Indeed, as can be seen in Table 1, the adjusted R^2 for azoxystrobin, chlorantraniliprole, difenoconazole, fenhexamid, fludioxonil, krexoim-Me, mandipropdamid, pyraclostrobin, and tetraconazole were the lowest observed and deviate significantly from an adjusted R^2 of 0.8. This value of 0.8 was the minimum acceptable value arbitrarily chosen for the fit of the responses to obtain an accurate model (Plonsky and Ghanbar, 2018). Metrafenone and tebuconazole had significant *p-values*, but their adjusted R^2 values were slightly below 0.8, indicating a poor fit with the model. This was also probably due to their rapid degradation rates. As can be seen in Table S6, at most only 5 observations were above LOQ (i.e. not considered as 100% degraded) for these 11 compounds, and even only one for chlorantraniliprole (Obs9). PL was able to degrade all 20 compounds studied effectively, but there are significant differences in behaviour depending on the compound, as already demonstrated by Clavero et al. (2024).

Compounds whose degradation kinetic was slow enough to generate a model with a satisfactory fit were ametoctradin, benalaxyl, boscalid, cyprodinil, dimethomorph, fenbuconazole, iprovalicarb, pyrimethanil, and tebufenozide. For these models, the adjusted R^2 was between 0.802 and 0.987.

The high-quality fit of the models is depicted on the graphs in Fig. 2, which compare the observed values with the predicted values.

The 4 models with the closest fit to the responses (higher adjusted R^2) were boscalid, dimethomorph, iprovalicarb and tebufenozide. The equations of each one of the 4 models are given below, the term F is used for frequency, Fr for flow rate, and C for cycle number:

$$Y\,boscalid = 93.4 - 11.6 \times Fr + 8.7 \times F + 35.2 \times C + 0.8 \times Fr \times Fr + 9.5 \times Fr \times F + 8.2 \times Fr \times C - 8.4 \times F \times F - 0.4 \times F \times C - 28.9 \times C \times C \quad (1)$$

$$Y\,dimethomorph = 84.7 - 12.9 \times Fr + 11.6 \times F + 32.6 \times C + 3.6 \times Fr \times Fr + 8.7 \times Fr \times F + 3.1 \times Fr \times C - 8.4 \times F \times F + 6.6 \times F \times C - 27.0 \times C \times C \quad (2)$$

$$Y\,iprovalicarb = 95.4 - 9.9 \times Fr + 7.8 \times F + 31.3 \times C + 1.2 \times Fr \times Fr + 8.1 \times Fr \times F + 7.8 \times Fr \times C - 7.8 \times F \times F - 1.2 \times F \times C - 27.0 \times C \times C \quad (3)$$

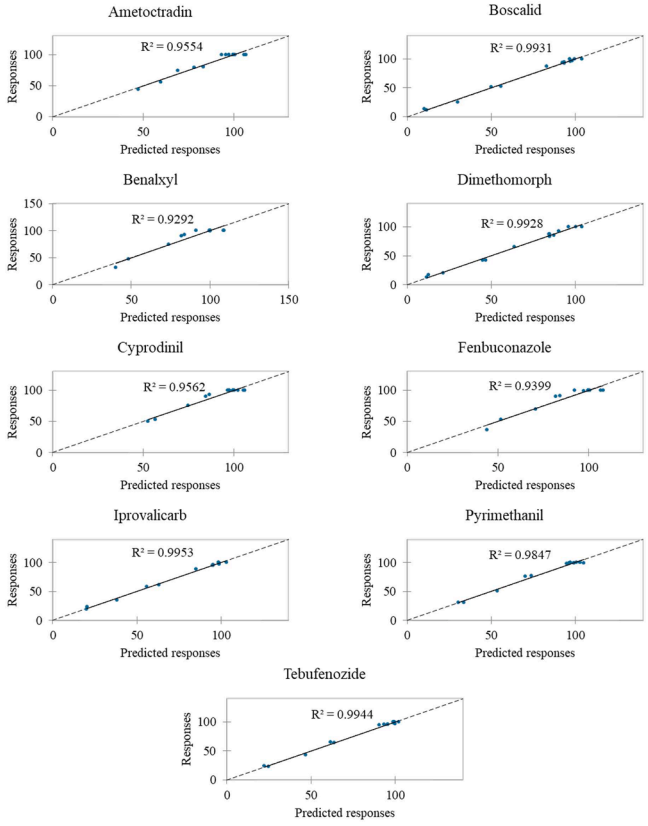


Fig. 2. Comparison of experimental response (y) with predicted response (x) for the 9 compounds with an acceptable model fit.

$$Y\,tebufenozide = 95.4 - 10.3 \times Fr + 7.5 \times F + 29.4 \times C - 4.2E02 \times Fr \times Fr + 7.3 \times Fr \times F + 9.4 \times Fr \times C - 6.3 \times F \times F - 3.5 \times F \times C - 24.0 \times C \times C \quad (4)$$

The surface plots of iprovalicarb generated by Eq. (3) (Fig. 3a, b, c) have been chosen as an example because the 9 models with adjusted $R^2 > 0.8$ evolve in a similar way. The method of least squares was used to estimate the regression coefficients.

In Box–Behnken response surface designs, main factors and interactions are modeled simultaneously to obtain a robust estimation of the experimental surface. Among the different approaches for partitioning the sum of squares (Type I, II, and III SS), the balanced nature of our design ensures that the factors remain orthogonal. In our case, all three methods (Type I, II, and III SS) yielded identical results, confirming the orthogonality of the design. Type III SS was nevertheless selected as it allows the contribution of each factor and its interactions to be assessed while accounting for the entire model (Hershberger, 2005; Winstel et al., 2024).

The type III sum of square analysis for iprovalicarb (Table 2) shows significant *p-values* for the three variables and for most of their interactions. The variable with the highest weight in the dataset was the number of cycles, followed by the flow rate and then the frequency, as observed in Table 1, with respective contributions of 86.1%, 8.6%, and 5.3%. The surface plots and the contribution of the variables demonstrated that an increasing number of cycles coupled with increased frequency and the slowest flow rate tested maximizes degradation for iprovalicarb and in the same way for the other 8 compounds.

This means that no matter how energy is transmitted, with low frequencies or fast flow rates, only the energy deposited per volume matters. Therefore, the degradation depends only on applied fluence. This

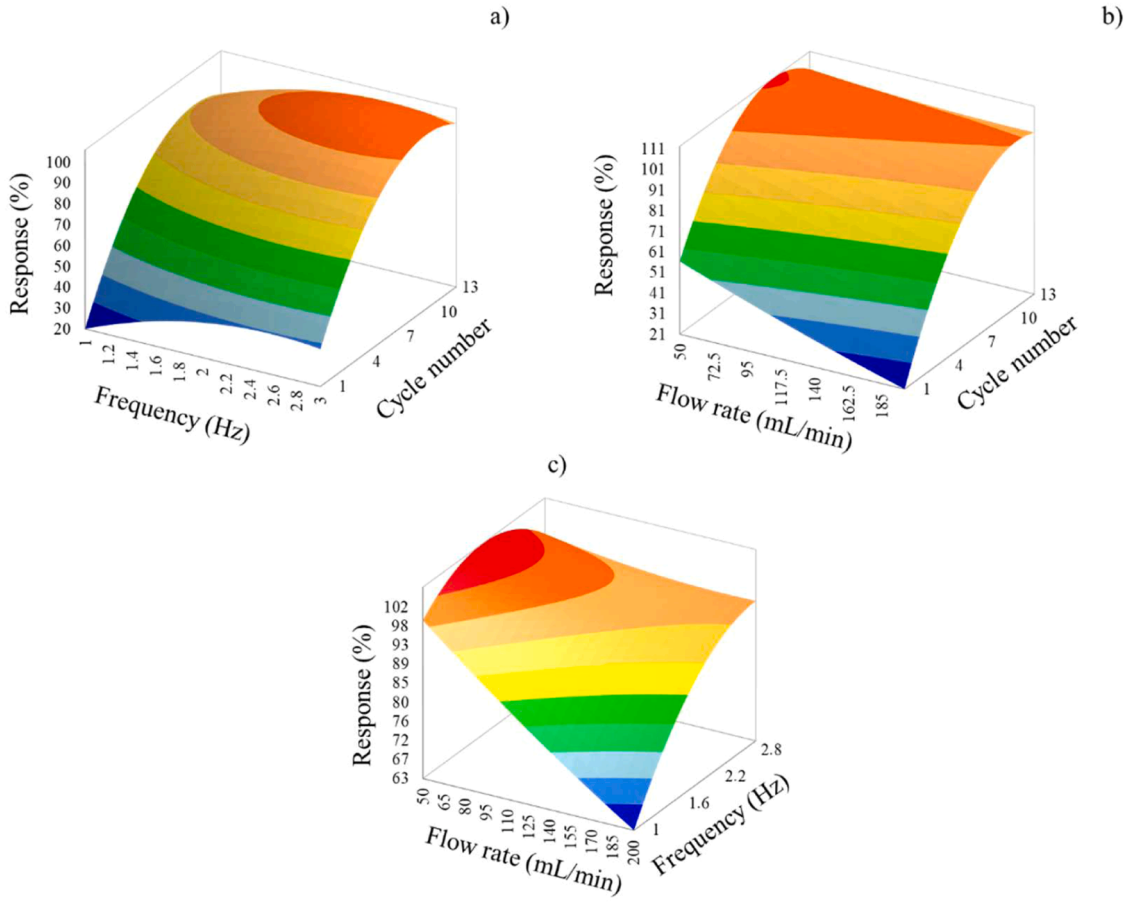


Fig. 3. Response surface plots Y as the response degradation percent of iprovalicarb: (a) frequency × cycle number; (b) flow rate × cycle number; (c) flow rate × frequency.

Table 1
Statistical analysis of the design of experiment (p-value < 0.05 in bold).

Pesticides	R^2	Adjusted R^2	*p-value*	Sumsq Model	Sums Error	Sumsq Total corrected	Mean square Model	Mean square Error	Variable contribution Cycle (%)	Variable contribution Frequency (%)	Variable contribution Flow rate (%)
Ametoctradin	0.955	0.875	**0.00698**	4,416	206	4,622	491	41	87.4	0	12.6
Azoxystrobin	0.865	0.623	0.08725	351	55	406	39	11	77.8	18.6	3.6
Benalaxyl	0.929	0.802	**0.02072**	5,990	456	6,446	666	91	83	8.5	8.5
Boscalid	0.993	0.981	**0.00007**	15,516	108	15,625	1,724	22	85.4	5.3	9.3
Chlorantraniliprole	0.805	0.453	0.1875	27	7	33	3	1	61.6	34.5	3.9
Cyprodinil	0.956	0.877	**0.00668**	3,969	182	4,150	441	36	84.5	4.2	11.2
Difenoconazole	0.794	0.423	0.20813	82	21	103	9	4	60.3	36.8	2.9
Dimethomorph	0.993	0.98	**0.00008**	14,398	104	14,502	1,600	21	78	9.8	12.2
Fenbuconazole	0.94	0.832	**0.01414**	5,311	339	5,650	590	68	84.9	7	8
Fenhexamid	0.881	0.668	0.06653	1,452	196	1,648	161	39	78	14.3	7.6
Fludioxonil	0.852	0.586	0.10653	285	50	335	32	10	78.2	20.1	1.7
Iprovalicarb	0.995	0.987	**0.00003**	12,494	59	12,553	1,388	12	86.1	5.3	8.6
Kresoxim-Me	0.895	0.707	0.05038	226	26	252	25	5	84.5	13	2.5
Mandipropamid	0.835	0.539	0.13317	23	5	28	3	1	81.9	18	0.1
Metrafenone	0.905	0.734	**0.04061**	1,775	186	1,961	197	37	76.2	0	23.8
Pyraclostrobin	0.852	0.585	0.10715	35	6	41	4	1	84.9	14.8	0.3
Pyrimethanil	0.985	0.957	**0.00052**	9,133	142	9,275	1,015	28	86.4	3.9	9.7
Tebuconazole	0.907	0.739	**0.03889**	3,493	359	3,852	388	72	80.8	10.8	8.4
Tebufenozide	0.994	0.984	**0.00004**	11,059	62	11,120	1,229	12	84.1	5.5	10.4
Tetraconazole	0.848	0.574	0.11319	749	134	883	83	27	74.2	21.3	4.5

shows that pulse functioning of the PL is not the reason for its ability to degrade compounds because continuous, not pulsed, radiation would be more effective. As a consequence, the great advantage of PL over continuous UV lamps for degrading pesticides lies in the wide range of wavelengths it irradiates (200 to 1000 nm), as well as in the high intensities made possible by accumulated high discharge voltages.

It is therefore possible to express the concentration measured in each DoE observation as a function of fluence per volume unit (J/mL). The degradation curves of the 20 pesticides (Figure S1, Table S6) show that the compounds have difference of sensitivity to PL. A majority of them

Table 2
Analysis type III sum of squares.

Source	Sum Squares	F	Pr > F	Significance *p-value* code
Flow rate	780.208	65.874	**0.0001**	***
Frequency	485.301	40.974	**0.001**	**
Cycle	7857.217	663.391	**<0.0001**	***
Flow rate*Flow rate	5.621	0.475	0.522	◦
Flow rate*Frequency	261.893	22.112	**0.005**	**
Flow rate*Cycle	241.469	20.387	**0.006**	**
Frequency*Frequency	225.167	19.011	**0.007**	**
Frequency*Cycle	5.491	0.464	0.526	◦
Cycle*Cycle	2688.869	227.023	**<0.0001**	***

Code of p-value: 0 < *** < 0.001 < ** < 0.01 < * < 0.05 < . < 0.1 < ° < 1.

was already degraded at the lowest energies, while others were only completely degraded at the highest fluences. These findings clearly demonstrated the effectiveness of the PL continuous process, which was capable of completely degrading below their LOQs the 20 compounds under the experimental conditions. Furthermore, as explained earlier, these curves clearly show that the most consistent models came from the molecules with the slowest degradation kinetics. Dimethomorph, boscalid, iprovalicarb, and tebufenozide were the 4 most difficult compounds to degrade.

The compound that was the least affected by PL was dimethomorph. In order to determine the optimal conditions to degrade this compound, the variables flow rate and frequency were set at 50 mL/min and 3 Hz, respectively, which corresponds to a dwell time in the reactor of 78 s per cycle. This enabled the determination of an optimum modality of between 7 and 8 cycles to degrade dimethomorph and all other compounds to 100%.

3.1.2. Validation of the optimal condition of the experimental design

An aqueous cocktail solution of the 20 pesticides at concentrations between 189 and 352 µg/L was subjected to increased number of cycles of PL treatment at a constant flow rate of 50 mL/min and a fixed frequency of 3 Hz (Fig. 4). The 20 pesticides, even dimethomorph, were degraded below their respective LOQs (Table S2) after the solution received 3528 J/mL which corresponds to 7 cycles. These results demonstrate the accuracy of the models. It is interesting to note that the compounds previously observed as not very sensitive to PL (dimethomorph, boscalid, iprovalicarb, and tebufenozide) were also the most difficult to degrade in this validation set, demonstrating the repeatability of the experiments.

In order to depict the difference of behaviour between compounds, a classification was performed using the equation of a first-order kinetic as decribed in Clavero et al. (2024). The half fluence ($H_{1/2}$), which represents the total fluence required to achieve a 50% reduction in the concentration of a compound, can be calculated using the equation: $H_{1/2} = Ln2/k$. The kinetic parameters, k and $H_{1/2}$, were calculated from the data set of the validation experiment for the 20 pesticides and are listed in descending order in Table 3.

From these experiments it can be noted that all compounds have $H_{1/2}$

Table 3
Degradation parameters for each pesticide treated by PL (rate constant k, half fluence $H_{1/2}$).

Pesticide	k	$H_{1/2}$ (J/mL)
Dimethomorph	0.0016	444.64
Boscalid	0.0025	282.02
Iprovalicarb	0.0025	278.90
Tebufenozide	0.0026	264.03
Ametoctradin	0.0036	191.69
Pyrimethanil	0.0042	163.35
Fenbuconazole	0.0052	132.95
Difenoconazole	0.0057	121.51
Benalaxyl	0.0061	114.06
Metrafenone	0.0064	107.67
Cyprodinil	0.0065	106.30
Tebuconazole	0.0073	95.56
Kresoxim-Me	0.0079	87.15
Fludioxonil	0.0083	83.48
Fenhexamid	0.0083	83.33
Azoxystrobin	0.0085	81.96
Pyraclostrobin	0.0086	80.66
Mandipropamid	0.0096	72.56
Tetraconazole	0.0092	75.65
Chlorantraniliprole	0.0290	23.67

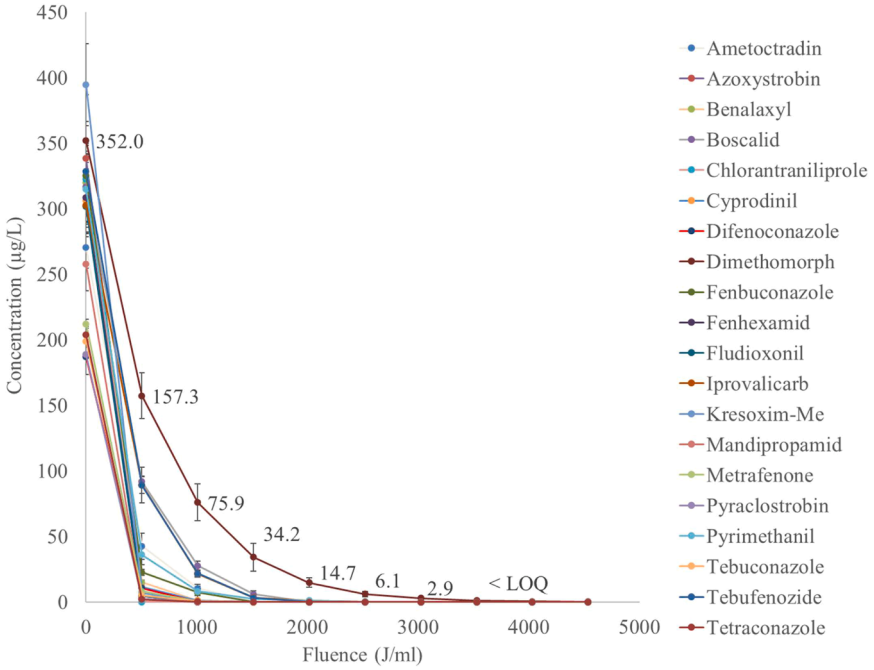


Fig. 4. Degradation of 20 pesticides in an aqueous cocktail solution by PL continuous treatment during validation of optimal condition (flow rate 50 mL/min, frequency 3 Hz, and number of cycles from 1 to 9).

below 504 J/mL which is the fluence applied after one cycle. Mathematically, it is known that to obtain 99% degradation a 7-fold $H_{1/2}$ is required, while a 8-fold $H_{1/2}$ provides a degradation above 99.5%. This is in line with the determination of the optimal condition being between 7 and 8 cycles for all compounds studied here. Thus, all compounds with $H_{1/2} < 504$ J/mL will be degraded to 99% after 7 cycles. Dimethomorph, boscalid, iprovalicarb, tebufenozide, ametoctradin, and pyrimethanil had already been categorized as the 6 most difficult compounds to degrade using a static PL treatment system. On the orther hand, chlorantraniliprole, tetraconazole, mandipropamid and pyraclostrobin were always classified as very sensitive compounds degrading readily.

These results validate the initial observations of Clavero et al. (2024) where a clear hierarchy of sensitivity to pulsed light was established based on degradation kinetics. Compounds such as dimethomorph, boscalid, iprovalicarb, tebufenozide, ametoctradin, and pyrimethanil were already identified as the most resistant, whereas chlorantraniliprole, tetraconazole, mandipropamid, and pyraclostrobin consistently exhibited high susceptibility to PL treatment. This consistency across studies, despite differences in reactor configuration (static vs continuous), supports the hypothesis that degradation behavior is primarily governed by intrinsic molecular properties, particularly structural features such as aromaticity and conjugation degree, rather than process conditions alone. This implies that there is no difference in terms of molecular sensitivity between a continuous processing system and a static PL system.

3.2. Evolution of photoproducts

To specifically investigate the stability of the degradation products toward PL treatment, 81 photoproducts (Table S1) were monitored using HPLC-MS/MS on samples of the experimental design. The evolution of the peak areas of the photoproducts was classified using the k-means clustering method, as described in Clavero et al. (2024). In this experiment, the trends in the peak areas of degradation products as a function of fluence were used to classify the different photoproducts into two categories (Fig. 5): (i) compounds formed and degraded during the experiment and (ii) compounds formed and not degraded during the experiment. In total, 72 compounds followed kinetics of the group (i) and only 9 of the group (ii). This result demonstrates that PL continuous water treatment is able to degrade pesticides and their photoproducts. This corroborates the hypothesis of Clavero et al. (2024), which assumed that the degradation products would be totally degraded as the PL treatment increased, leading to complete mineralization of the organic pesticide molecules. Transformation products (TPs) that persisted after the highest PL treatment at 5376 J/mL were Bosca-325–2, Chlo-368–1, Cypro-226–1, Cypro-226–2, Fenhex-142, Ipro-225, Pyri-124, Tebuco-196 and Tebuco-224.

3.3. Application to viticultural wastewater

3.3.1. Chemical analysis

3.3.1.1. Pesticide content. Three viticultural WWs of different origin (see Section 2.3.2) were treated with our PL continuous treatment pilot in the optimized conditions obtained from the experimental design (flow rate: 50 mL/min, frequency: 3 Hz and 7 cycles). PL-treated and untreated WW samples were then extracted using the QuEChERS EN 15662 method and quantified in LC-MS/MS by standard addition of 88 pesticides.

The quantification results show important differences in the composition of these three WWs (Fig. 6a, b and c).

WW1 had the highest number of compounds and also the highest concentrations with 12 compounds at initial concentrations between 32 and 2320 µg/L, 7 of them at concentrations above 200 µg/L and even four of them exceeding 1 mg/L. WW2 only contained 10 compounds at concentrations between 9 and 1456 µg/L, with 2 of them at concentrations above 200 µg/L and even above 1 mg/L. WW3 contained only one pesticide at low concentration (63 µg/L), which is not surprising given that the cultivation method used by the estate that generated it, is organic. The presence of this pesticide in WW3 may be due to poor rinsing of the storage tank, environmental contamination, the persistence of this pesticide or a recent conversion to organic viticulture. Five

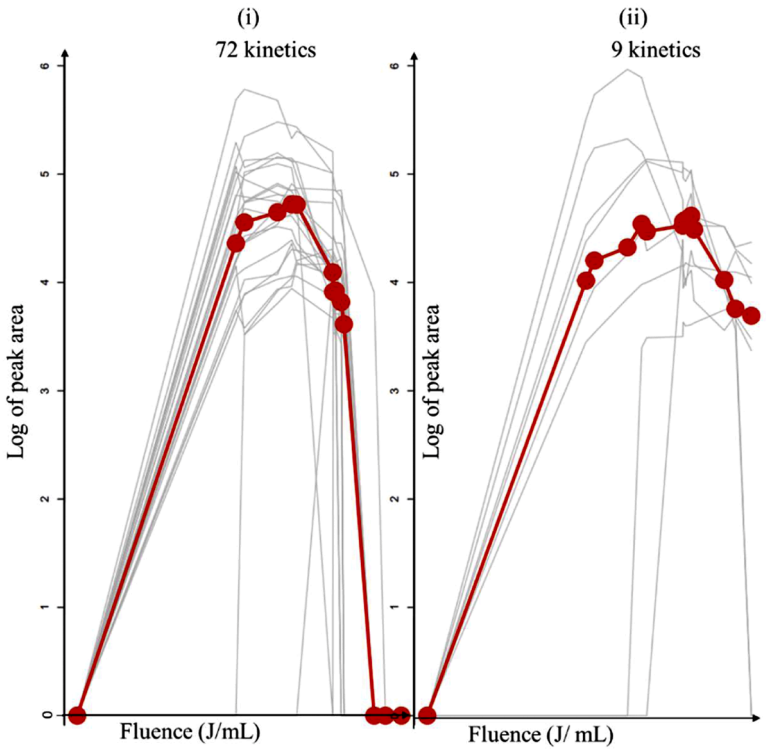


Fig. 5. Clustering using kinetic profiles of degradation products formed in an aqueous cocktail solution of 20 pesticides applying fluences from 0 to 5376 J/mL.

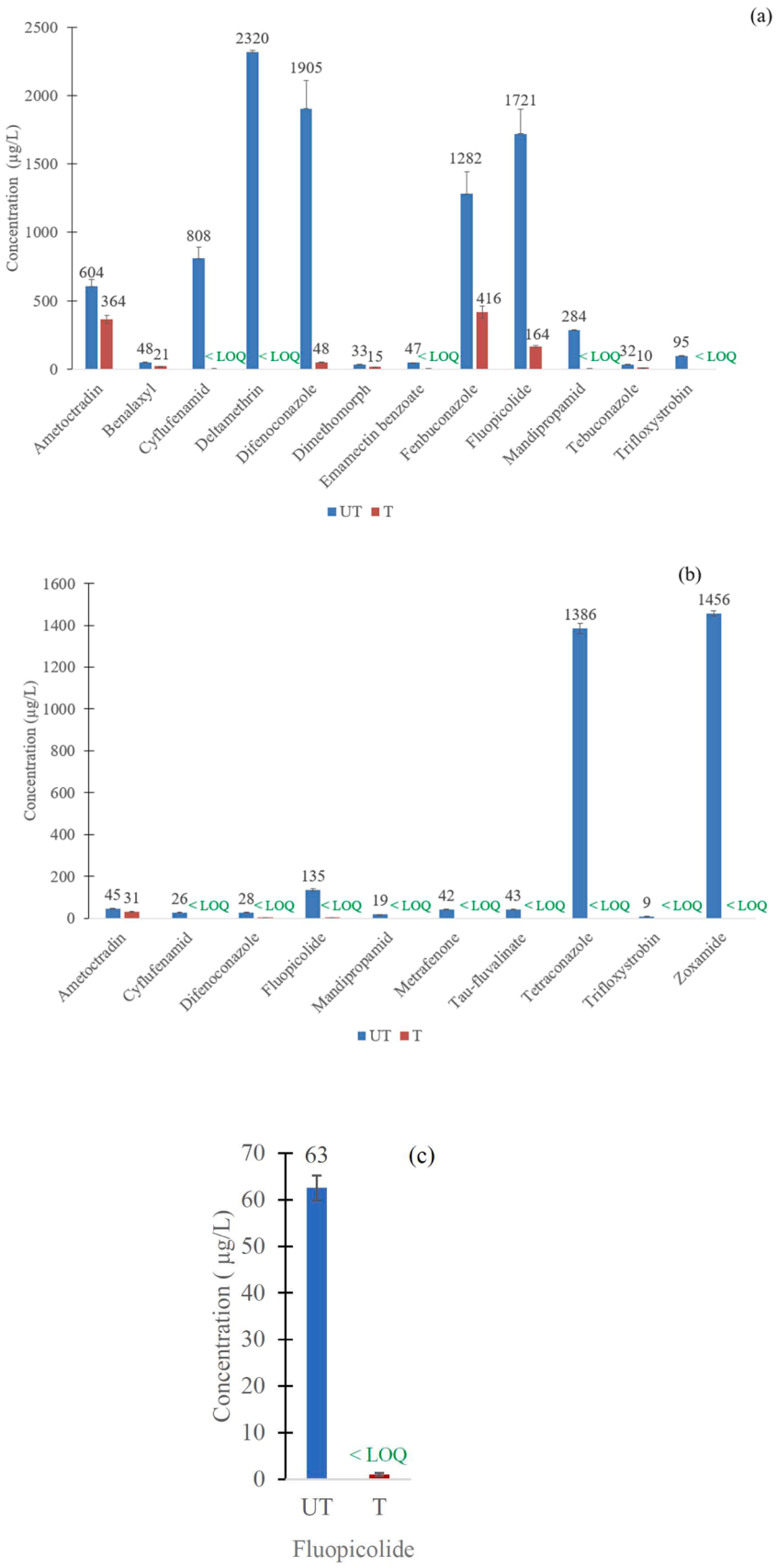


Fig. 6. comparison of pesticide concentrations in viticutural wastewater between treated (T) and untreated (UT) WWs for (a) WW1; (b) WW2 and (c) WW3.

compounds were common to both WW1 and WW2 (ametoctradin, cyflufenamid, difenoconazole, mandipropamid, and trifloxystrobin), and fluopicolide was common to all three WWs. In the end, 16 active substances were represented in these WW samples, 9 of them being also present in our aqueous cocktail solution of 20 pesticides.

The PL continuous treatment appeared to have had a very significant impact on the concentration of all the pesticides present in all WWs studied. Indeed, in WW2 and WW3, the concentrations of all compounds decreased to levels below their LOQs, except for ametoctradin in WW2. Regarding WW1, the concentrations of 5 out of 12 compounds were also below their respective LOQs (Table S4). Concentrations of other compounds also fell sharply, with decreases of >50% for benalaxyl, difenoconazole, dimethomorph, fenbuconazole, fluopicolide, and tebuconazole. Ametoctradin was the compound the least affected by PL, with a concentration reduction of around 30–40% between the treated and untreated sample in WW1 and WW2. Considering all compounds in these WWs, ametoctradin, benalaxyl, and dimethomorph and in a lesser extent fenbuconazole and tebuconazole were the most difficult to degrade. This is similar to what was observed using static PL treatment of WWs (Clavero et al., 2025a).

However, given the results of the DoE, these compounds should have been degraded more efficiently than observed. It is likely that the degradation caused by the PL was attenuated by the WW matrix components that absorb radiations as explained in Clavero et al. (2025a). Indeed, WW1 was the WW which absorbed mostly radiations in the UV wavelengths. It could explain why WW1 was the one that underwent the least pesticide degradation. Nevertheless, it can be said that the treatment of viticultural effluent in a continuous flow system with a thin layer of liquid resulted in a better degradation of all the compounds compared to the treatment in static system (Clavero et al., 2025a). Indeed, in our previous study, performed with the static system, no compound was degraded below its LOQ and all compounds had been degraded to much lower percentages. The continuous treatment of thin layers of liquid (3.2 mm) by PL is thus far more effective than static treatment but it could be further optimized by using thinner layers, or clarification of the matrix.

Some pesticides widely used in viticulture contain metal elements, such as fosetyl-aluminium, Bordeaux mixture, ferric phosphate, mancozeb, metiram. The concentrations of aluminum (Al), copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn) were quantified by ICP-OES (Table 4). The results show no differences according to PL treatment. Indeed, no effect of UV-radiation is expected on metal elements. On the other hand, differences in concentrations can be observed between the various WWs. WW3 had the highest content of copper. WW1 had the highest concentrations of aluminium and zinc and the second highest copper content. Very high concentrations of copper were observed in these three WW samples, which is consistent with copper derivatives being widely used to combat downy mildew. It is important to underline that such high TME concentrations are likely to have significant effects on the toxicity of the WWs studied.

Table 4
Concentrations of trace metal elements in the three WWs (n = 2), T for treated and UT for untreated samples.

	TME concentration (mg/L)				
Samples	Al	Cu	Fe	Mn	Zn
WW1 UT	2.76 ± 0.34	28.90 ± 3.75	0.74 ± 0.26	0.38 ± 0.11	2.02 ± 0.46
WW1 T	2.13 ± 1.59	19.82 ± 8.37	0.63 ± 0.36	0.40 ± 0.25	1.95 ± 0.88
WW2 UT	0.12 ± 0.03	10.49 ± 4.07	1.71 ± 1.03	3.03 ± 1.04	0.11 ± 0.04
WW2 T	0.08 ± 0.02	7.11 ± 2.54	1.38 ± 0.42	1.95 ± 0.85	0.09 ± 0.01
WW3 UT	0.33 ± 0.07	38.73 ± 7.89	0.47 ± 0.08	0.58 ± 0.01	0.24 ± 0.01
WW3 T	0.42 ± 0.06	50.03 ± 5.19	0.79 ± 0.10	0.57 ± 0.1	0.33 ± 0.06
LOQ (mg/L)	0.066	0.008	0.021	0.006	0.013

3.3.1.2. Photoproduct analysis. Nine pesticides present in WW1 and WW2 were previously deeply studied regarding their photoproducts (Clavero et al., 2025a) and among them, ametoctradin and dimethomorph did not give any observable photoproduct. The 42 photoproducts arising from the 7 remaining pesticides (benalaxyl, difenoconazole, fenbuconazole, mandipropamid, metrafenone, tebuconazole, and tetraconazole), were searched by LC-MS (MRM) in the WW samples. Only 17 photoproducts out of 42 were detected (Fig. 7a and b). For WW1, 12 photoproducts were observed out of 32 observables. Degradation products were observed for all the pesticides initially present and targeted in the MRM method (i.e. benalaxyl, difenoconazole, fenbuconazole, and tebuconazole), with the exception of mandipropamid. This is consistent with the fact that the concentration of mandipropamid was initially quite low in WW1. Moreover, the response of its photoproduct is particularly weak with the MRM method, making it difficult to observe the formation of mandipropamid degradation product. For the specific case of WW2, 5 photoproducts were observed out of 20 possibly observable. The low initial concentrations of difenoconazole, mandipropamid and metrafenone probably prevented the observation of some degradation products, with none observed for difenoconazole and mandipropamid, and only one out of three for metrafenone. On the other hand, four degradation products out of 8 were detected for tetraconazole. By comparing the degradation products detected after continuous PL-treatment of WWs with those detected after static PL-treatment (Clavero et al., 2025a) it can be noted that for WW1, four additional degradation products were detected in the continuous experiment (TP bena-240, TP difeno-370–1, TP difeno-388–1, and TP tebuco-272.2). On the other hand, regarding WW2, TP metrafen-331 was missing after continuous PL-treatment. These results can be attributed to a more effective degradation in the continuous PL-treatment. Indeed, some transformation products only form at higher fluences while others begin to degrade.

The hypothetical structures of the photoproducts observed are given in Clavero et al. (2024). These structures imply as major transformation reactions, hydroxylation and dehalogenation for the compounds containing halogen atoms like difenoconazole, fenbuconazole, metrafenone, tebuconazole, and tetraconazole. For benalaxyl, which does not contain halogens, a probable carbon-nitrogen bond cleavage between the anilide nitrogen and the other groups has been observed with a loss of phenylacetyl or methylpropionate moieties.

Another interesting thing to note is that as observed by Clavero et al. (2025a), the WW1 sample shows an ion of $m/z = 303$ already in the untreated samples at the same retention time (12.34 min) and with the same fragmentation pattern as in the treated samples. Its peak area increases by around 45 times in the treated samples. This compound seems to be the major PL-degradation product of fenbuconazole corresponding to the replacement of the chlorine atom of the molecule by a hydrogen. However, not only PL-induced photodegradation may be able to produce it, but also sunlight-induced photodegradation or other degradation mechanisms may also be involved. Alike, a compound of $m/z = 240$, never described in the literature to our knowledge, and originating from the degradation of benalaxyl (replacement of methylpropionate group) was already detected in the untreated WW1 sample. It would be valuable in future studies to monitor the degradation of these pesticides using alternative methods in order to investigate if these degradation products may form under various conditions (pH, temperature, time). Additionally, it would be worthwhile to search for these transformation products in food matrices treated with fenbuconazole or benalaxyl, or in surfacewater and groundwater close to plots treated with these pesticides, as they could serve as a marker for their degradation, which has not yet been described or monitored to our knowledge.

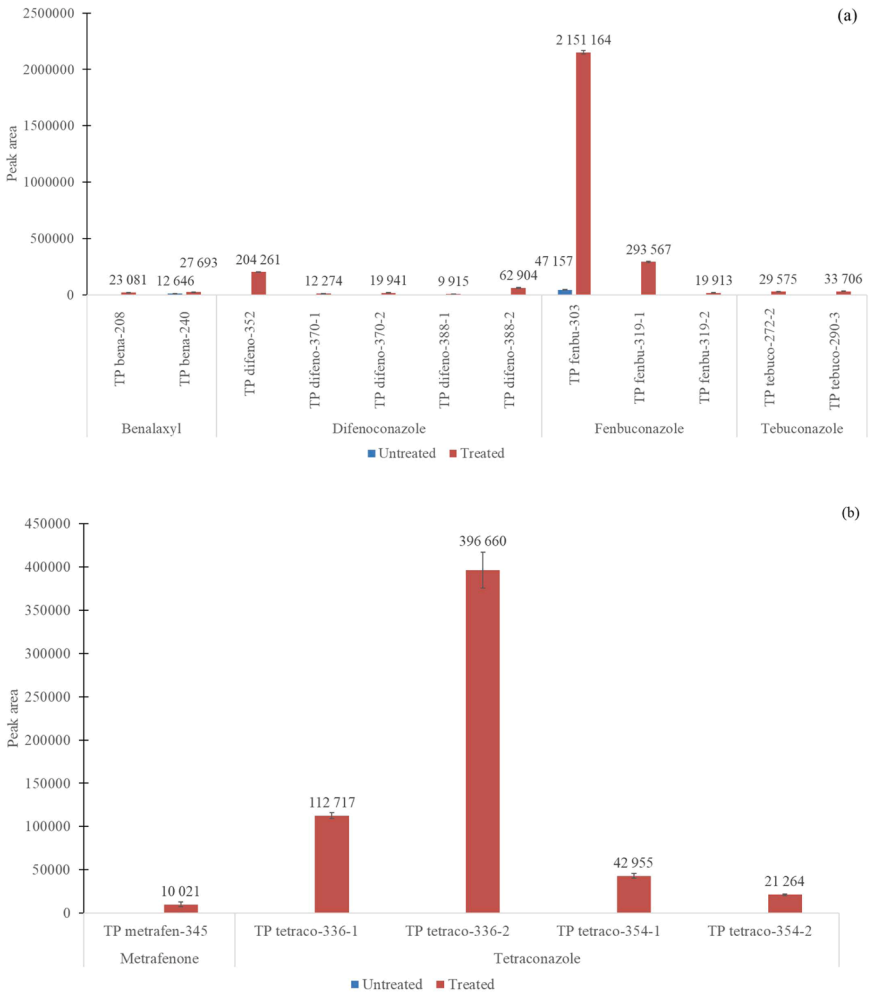


Fig. 7. Peak area of the photoproducts in (a) WW 1 and (b) WW2.

3.3.2. *Acute toxicity of viticultural wastewater on 3 aquatic trophic levels*

3.3.2.1. Acute toxicity test on bacteria. The acute toxicity of the PL-treated (T) and untreated (UT) WW1, WW2, and WW3 was evaluated using the bacteria *Aliivibrio fischeri*, following the Microtox® protocol. The results of the acute toxicity assessments show that the inhibition percentage of WW1 and WW3 decreased after treatment, indicating a reduction in toxicity with the PL treatments. This is demonstrated by the EC50 values (Fig. 8a and c), which increased by a factor of 3.6 for WW1 and a factor of 6 for WW3. These increases in EC50 indicate a reduction in toxicity by factors of 3.6 and 6, respectively for WW1 and WW3, as EC50 is inversely correlated with toxicity. These findings are consistent with those of Clavero et al. (2025b), in which a significant reduction in toxicity was observed for PL-treated aqueous pesticide cocktail samples for *Aliivibrio fischeri*.

However, no change in toxicity was observed for WW2 (Fig. 8b). This can be attributed to the fact that this sample is the least toxic of the three, making it difficult to detect differences.

It is worth noting that, although toxicity was significantly reduced for WW1 and WW3, it remains very high even after treatment. EC50 could only be obtained after dilution of the treated WWs to 82% for WW1 and 94% for WW3. This toxicity is likely due to trace metals or residual organic compounds present in the effluent. The lower toxicity of WW2 is probably due to its lowest TME concentration especially for copper, compared to the other WWs.

Similarly to Clavero et al. (2025a), WW3 showed the highest initial toxicity followed by WW1 and then WW2. However, a decrease in initial toxicity for all three WWs compared to our previous work was observed. It may be attributed to decreases in the concentrations of the majority of compounds due to natural degradation that occurred during storage of these viticultural effluents.

3.3.2.2. Acute toxicity test on algae. The acute toxicity of the treated and untreated WW1, WW2, and WW3 was measured using the freshwater microalgae *R. subcapitata* after 96 h of exposure (Fig. 9a, b and c). A growth rate greater than 16 was observed for all the negative controls, with a mean development of 61.8×10^5 cells/mL. The population was multiplied by 305 in 96 h, indicating favorable algal development. The assays were validated using a positive control ($K_2Cr_2O_7$) with a EC50 (effective median concentration) at 0.57 mg/L after 96 h which complies with the supplier's provided value ranging 0.42–0.63 mg/L.

Regarding algal development of untreated WWs, WW1 showed the highest acute toxicity followed by WW3 and then WW2. This order is slightly different from the one observed for *A. fischeri*. It is well known that different biological models may react differently to stresses because they may exhibit various sensitivity, hence the need to test multiple models.

Next, acute toxicity of PL-treated and untreated WWs is compared. Regarding WW1, the toxicity of the PL-treated samples was significantly lower than the one of untreated samples. In fact, the EC50 (Fig. 9a) of untreated WW1 was 2 times lower than that of the treated samples, implying a toxicity reduction by a factor of 2 for the algae between the untreated and treated samples. These observations followed the same pattern as those on the bacterial model. Regarding WW2, the toxicity

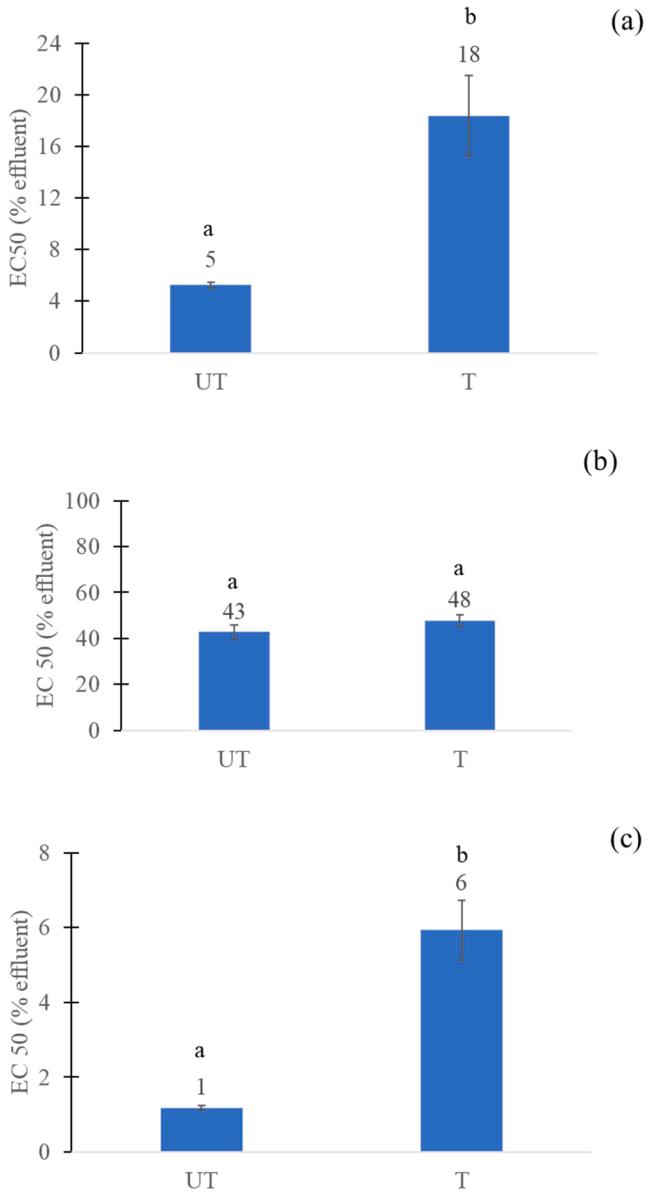


Fig. 8. *A.* fischeri EC50 of a 30 min exposure to three treated and untreated viticultural wastewaters: (a) WW1, (b) WW2, (c) WW3 (T-test, n = 3, p-value < 0.05).

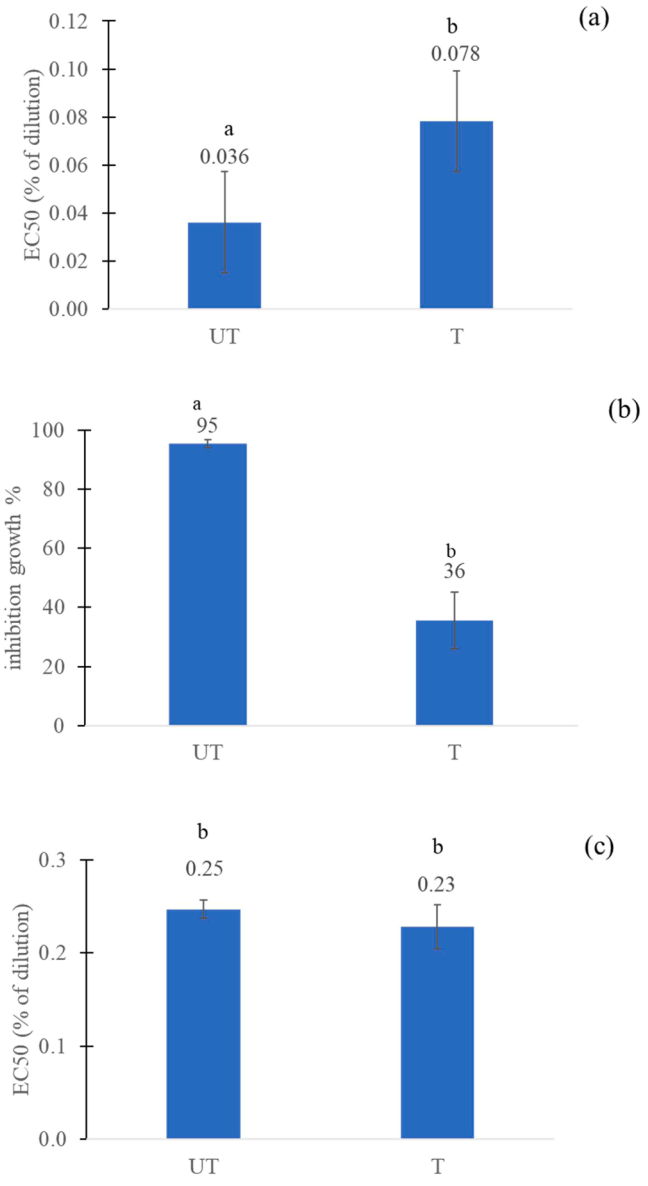


Fig. 9. Toxicity on microalgae *R.* subcapitata after 96 h of exposure to three viticultural wastewaters: EC50 of treated and untreated WW1 (a), inhibition growth at 0.78% of the initial concentration of WW2 (b) and EC50 of treated and untreated WW3 (c), (T-test, n = 3, p-value < 0.05).

was greatly reduced for the PL-treated samples, its EC50 was 0.88% of the initial concentration. However, for the untreated sample, the EC50 could not be calculated because even at the lowest dilution used (0.78% of the initial concentration of WW2), the inhibition growth percentage was high i.e. 95%. In contrast, the growth inhibition was significantly decreased for the treated sample i.e. 36% (Fig. 9b). These results highlight that PL can significantly reduce the toxicity of samples contaminated with pesticides for algae. However, no effect on toxicity was observed in WW3 (Fig. 9c), whereas it was greatly reduced in the bacterial model. It is important to note that WW3 is the sample with the highest TME content, particularly copper, and algae are highly sensitive to TME (Knauert and Knauer, 2008). It is possible that the toxicity of the TME contained in this effluent completely masked the reduction in toxicity brought by PL.

It is also important to note that, although no increase in toxicity was observed with PL treatment, the toxicity of all the PL-treated samples remained very high. Indeed, the EC50 of each sample could be determined only after a dilution of >99% for each matrix. This is probably due to the excessive concentrations of copper in the three WWs. In addition, as with the bacterial tests, WW2 was observed to be the least toxic effluent before or after treatment, probably due to its lower TME concentration.

3.3.2.3. Acute toxicity test on fish larvae. The acute toxicity of PL-treated (T) and untreated (UT) WWs was measured with the freshwater fish *O. latipes* larvae after 48 h exposure. It appears that WW1 displays higher toxicity than WW3, which in turn exceeds WW2. As for the bacteria, the toxicity of the treated samples of WW1 and WW3 was significantly reduced (Fig. 10a and c). Especially for WW1, the acute tests conducted on the untreated solution led to mortality of 100% after 48 h of exposure, while the mortality of the PL-treated samples was only 2%. This result demonstrates a drastic reduction in acute toxicity for WW1 toward *O. latipes*. It is also important to note that the toxicity of WW3 was reduced even though it originated from a biological itinerary and no acute toxicity was observed on fish larvae after exposure to PL-treated WW3.

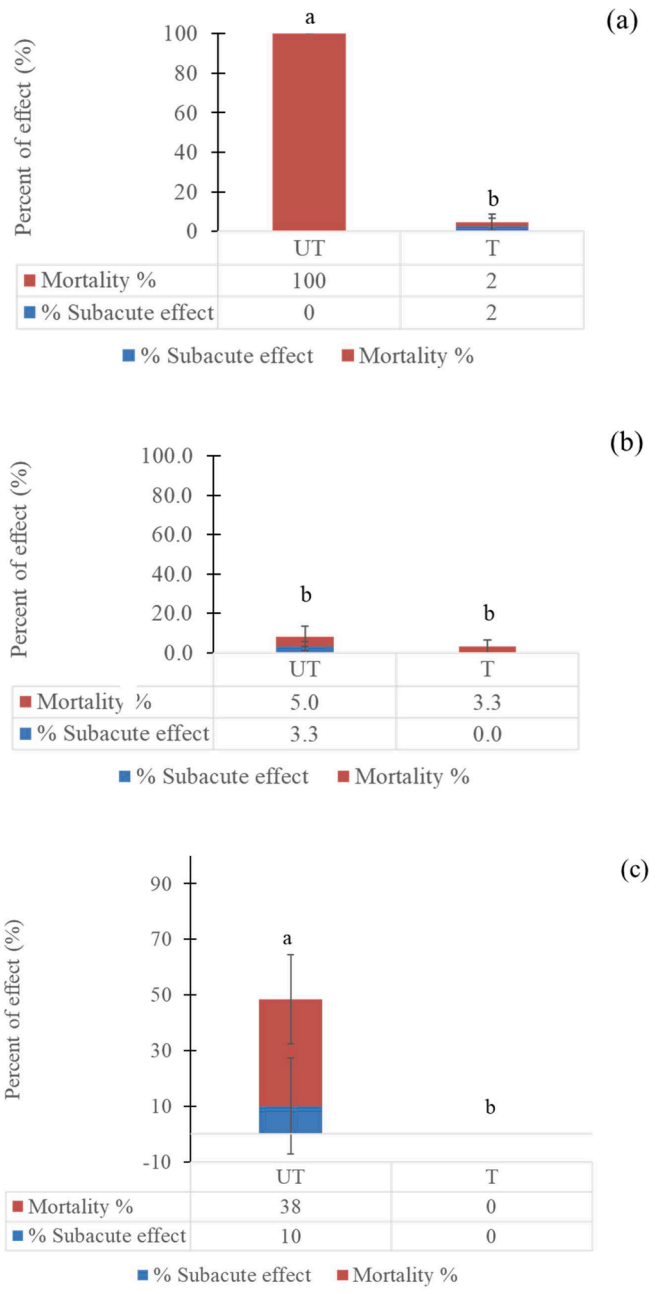


Fig. 10. Acute toxicity on O. latipes fish larvae after a 48h-exposure to three untreated and treated viticultural wasterwaters: (a) WW1 diluted at 5%;(b) WW2 without dilution and (c) WW3 diluted at 75% for O. latipes embryos after 48 h exposure. (T-test, n = 3, p-value <0.05).

WW2 had not been diluted and no toxicity was noted in either the treated or untreated samples. It corroborates the hypothesis of a lower toxicity of WW2 compared to WW1 and WW3 as observed for the bacteria and algae acute toxicity tests. This could be due to its lower TME content.

Concerning subletal effects, they were negligeable for PL treated samples for all the WWs studied (bellow 2%).

These results therefore show that PL appears to be very effective in reducing the acute toxicity for fish embryos. However, a residual toxicity remained in the experimental conditions. Indeed, WW1 was diluted to 5% of its initial concentration in order to measure its toxicity for fish, and WW3 was also diluted to 75% of its initial concentration.

3.3.2.4. Synthesis of acute toxicity results. Generally, PL-treatment of WWs significantly reduced the acute toxicity of the treated solutions for all trophic levels studied. In particular, WW1, the WW most contaminated by pesticides showed reductions in toxicity for all models.

These decreases in toxicity are consistent with our previous findings Clavero et al. (2025b), where PL treatment of pesticide mixtures led to a marked reduction in acute toxicity across multiple trophic levels. This effect can be attributed to the formation of TPs with generally lower acute toxicity than their parent compounds, resulting from typical photochemical reactions such as oxidation, hydroxylation, and dehalogenation (Man et al., 2021; Stamatis et al., 2015). In particular, the partial loss of halogenated moieties and the alteration of aromatic structures are known to reduce bioactivity and bioaccumulation potential, thereby contributing to the observed detoxification. Similar trends have been reported in photolysis studies, where degradation of pesticides was associated with reduced ecotoxicity across several trophic levels (Del Puerto et al., 2022).

Decreases in toxicity were also observed for the other two WWs, but it was dependent on the model and it seems to be influenced by the presence of copper and the sensitivity of the different biological models to copper. The presence of trace metal elements in the WWs studied seems to have had a very negative impact on the toxicities measured. Indeed, Clavero et al. (2025b) have already demonstrated that the toxicity of an aqueous solution containing 20 pesticides could be greatly reduced for the 3 trophic models studied. However, the toxicity of metal-containing pesticides such as copper derivatives remains impossible to mitigate with PL. Further studies should investigate the use of a process that flocculates and then filters the copper before treating the sample with PL.

4. Conclusion

An optimization of a continuous PL process was conducted on a mixture of 20 pesticides at 300 µg/L. A design of experiments approach identified fluence as the main parameter controlling degradation, with compound-dependent behaviors and dimethomorph being the most recalcitrant molecule. In model aqueous solutions, all target pesticides were reduced below the limit of quantification under optimized conditions (50 mL min^{-1}, 3 Hz, 7 cycles), confirming the robustness of the process under controlled conditions.

The monitoring of transformation products showed that increasing fluence promotes not only parent compound degradation but also the removal of most photoproducts, with 72 out of 81 transformation products fully degraded, thereby limiting their accumulation.

When applied to three real viticultural wastewaters, the optimized PL conditions resulted in a substantial reduction of pesticide concentrations. Most compounds were reduced below the limit of quantification, although some fungicides (e.g., ametoctradin, benalaxyl, dimethomorph, fenbuconazole, and tebuconazole) showed lower degradation efficiencies ranging from 31 to 69%, highlighting matrix-induced limitations compared to model solutions.

Ecotoxicological assessment across three trophic levels (*Aliivibrio fischeri, Raphidocelis subcapitata*, and *Oryzias latipes* embryos) showed that PL treatment reduced or maintained acute toxicity, with no increase observed. In particular, significant toxicity reductions were observed for the most pesticide-contaminated wastewater across all models. However, residual toxicity remained high in real effluents, with EC50 values only measurable at high dilutions, and could be attributed to TMEs, particularly copper.

These results indicate that PL alone is insufficient to fully mitigate the environmental hazard of viticultural wastewaters. Nevertheless, the successful implementation of a continuous thin-layer PL system operating under flow conditions, combined with high degradation efficiencies achieved within short treatment times, provides a proof of concept supporting the potential scalability of this technology toward industrial applications. From an operational perspective, this process represents a promising tool for the viticultural sector and agriculture in

general due to its rapid kinetics and compatibility with continuous flow systems. Its implementation at the industrial scale should therefore rely on its integration within treatment trains, combining upstream physicochemical steps (e.g., coagulation, flocculation and filtration) to remove inorganic contaminants, and/or coupling with complementary advanced oxidation processes such as photocatalysis to enhance overall degradation efficiency while optimizing energy consumption.

Further studies based on comprehensive non-target LC-HRMS approaches are required to elucidate the formation pathways and transformation mechanisms of photoproducts generated during PL treatment. In parallel, QSAR-based toxicity predictions would provide valuable insight into the potential ecotoxicological impact of these transformation products, particularly regarding chronic effects. Such combined approaches are essential to better understand the relationship between degradation efficiency and environmental safety, and to support the development of reliable and applicable PL-based treatment strategies.

5. Funding information

This research did not receive any specific grants from public, commercial, or nonprofit funding agencies.

CRediT authorship contribution statement

François Clavero: Writing – original draft, Validation, Investigation, Formal analysis, Data curation, Conceptualization. **Jérôme Cachot:** Writing – review & editing, Supervision. **Christelle Clérandeau:** Writing – review & editing. **Laure Sandoval:** Writing – review & editing, Resources. **Fanny Meytraud:** Writing – review & editing. **Warren Albertin:** Writing – review & editing, Software, Methodology, Data curation. **Gilles de Revel:** Writing – review & editing. **Rémy Ghidossi:** Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization. **Céline Franc:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Clavero Francois reports financial support was provided by Sanodev. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

We are grateful to Emilie Dassié and Yann Combes (EPOC laboratory) for trace metal analyses.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.hazadv.2026.101165.

Data availability

Data will be made available on request.

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