



Attenuation photochemical potential of Pontal of Paranapanema river waters (Brazil) from agrochemicals: geographical and temporal assessment

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Received: 23 May 2023 / Accepted: 12 April 2024

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Abstract

Knowledge of the environmental photochemical fate of pesticides is essential to assess their potential impacts. However, there are few studies in the literature focused on the photochemical attenuation of micropollutants in Brazilian rivers. In this context, this study characterized the surface waters of the Pontal of Paranapanema region (region which concentrates more than 80% of Brazilian sugarcane cultivations), in order to determine its photochemical attenuation potential against micropollutants in different seasons. Thus, the steady-state concentrations of the photochemically produced reactive intermediates (PPRIs) (hydroxyl radical, HO[•]; singlet oxygen, ¹O₂, and triplet-excited state chromophoric dissolved organic matter, ³CDOM^{*}), formed in the rivers, were simulated by using the APEX model (Aquatic Photochemistry of Environmentally-occurring Xenobiotics), considering the sunlight irradiance, water chemistry, and depth. Based on our simulations, these concentrations vary between 0.35×10^{-15} and 4.52×10^{-14} mol L⁻¹ for HO[•], 1.3×10^{-15} and 1.2×10^{-14} mol L⁻¹ for ³CDOM^{*}, and 2.5×10^{-15} and 2.5×10^{-14} mol L⁻¹ for ¹O₂. Finally, mathematical simulations were used for predicting persistence of pesticides atrazine (ATZ) and diuron (DIR) in Pontal of Paranapanema surface waters and the half-life times (*t*_{1/2}) of the pollutants ranged from a few hours to one week.

Keywords Attenuation photochemical potential · Environmental photochemical fate · Photochemically produced reactive intermediates (PPRIs) · Mathematical simulations · Agrochemicals · Pesticides · Emerging contaminants · Pontal of Paranapanema region

Responsible Editor: Philippe Garrigues

Highlights

- Photochemically produced reactive intermediates concentrations on water bodies of Pontal of Paranapanema can be considered a little high in comparison to the usual values reported for surface water from north hemisphere countries.
- In the deeper rivers of studied region, the concentrations of HO[•], ¹O₂, and ³CDOM^{*} remained in the same range independent of season.
- In the shallow rivers of Pontal of Paranapanema region, (PPRIs) were higher in the warm seasons (spring and summer).
- Mathematical simulations were used for predicting persistence of pesticides ATZ and DIR in Pontal of Paranapanema surface waters and the half-life times (*t*_{1/2}) of the pollutants ranged from a few hours to one week.

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Introduction

Pontal of Paranapanema region is located in São Paulo State (Brazil), concentrates more than 80% of Brazilian sugarcane cultivations, and presents several agro-industries (Rocha et al. 2022; Romagnoli and Manzione 2018). Besides the land-reform settlements, private farms, and sugarcane mills, this region contains protected areas, such as the “Morro do Diabo” State Park, the second largest preserved area of Brazilian Atlantic Forest (> 30,000 ha), as well as, other forest fragments over several private farms and land-reform settlements, with sizes ranging from 2 to 2000 ha (Badari et al. 2020).

Combined with the extreme production of the sugar and alcohol industry is the increasing application of pesticides, becoming a matter of concern for the society, authorities,

and the scientific community due to issues associated with health risks arising from the gradual ingestion of these products that contaminate water, soil, and food (Remucal 2014).

Over recent decades, pesticides are recognized as emerging contaminants (ECs), which has induced growing concern due to their easy transport into the environment and their potential impacts on ecosystem and human health (Luo et al. 2014). The following effects associated with exposure to agrochemicals on human health can be cited: infertility, impotence, abortions, malformations, neurotoxicity, and hormonal dysregulation (Koifman and Koifman 2003; Meeker 2010; Oliveira et al. 2014; Stillerman et al. 2008). In addition, the International Agency for Research on Cancer (IARC) indicates that exposure to pesticides increases the risk of developing cancer in humans. In fact, several epidemiological studies consider exposure to pesticides a risk factor in the development of tumors (Martin et al. 2018).

The persistence of ECs in surface water depends, among other factors, on their transformation kinetics due to biological and abiotic processes (Carena et al. 2021). The second involves dark redox processes, hydrolysis, and photochemical reactions (Dunnivant and Anders 2006). In fact, several studies have shown that the main mechanism for the removal of micropollutants in water bodies is sunlight-induced photodegradation (Yamamoto et al. 2009; Zeng and Arnold 2013).

Photodegradation initiated by sunlight consists of two mechanisms: direct and indirect photolysis. In direct photolysis, a molecule absorbs radiation from sunlight and consequently undergoes conversion (Vione et al. 2018). In contrast, indirect photolysis is driven by reactions between the pollutant and photochemically produced reactive intermediates (PPRIs), mainly hydroxyl (HO^\bullet), singlet oxygen ($^1\text{O}_2$), and triplet-excited state chromophoric dissolved organic matter ($^3\text{CDOM}^*$). PPRIs are produced by the sunlight excitation of photosensitive chemical species, such as nitrate, nitrite, and chromophoric dissolved organic matter (CDOM), present in water media (Wang et al. 2021; Vione et al. 2018).

According to Vione (2020), most research focuses on photochemical characteristics of pollutants; on the other hand, very little research has been devoted to photochemical features of the natural medium, even though their photochemical potential can be very different from case to case. The lack of investigation on photochemical characterization of natural ecosystems hinders extrapolating results from laboratory experiments to real situations, resulting in a significant underestimation of the natural variability (Vione 2020).

Knowing the steady-state concentrations of PPRIs produced in a river is critical to the prediction of water matrix natural photochemical attenuation for ECs. Therefore, it is important to understand in what way the PPRI generation in surface water varies with change of season and so

to recognize the temporal distribution of PPRI formation (Wang et al. 2021).

The composition of natural waters has periodic trends due to combination of biological and chemical processes and can modify PPRI production; consequently, it influences the photodegradation of ECs present in the water matrix (Vione et al. 2018). However, few literature works focused on the attenuation of pollutants in rivers considering the occurrence of key photosensitizers, and to the best of our knowledge, there is no reported in literature investigation focused on the seasonal and geographical variation of PPRIs in Brazilian rivers. Thus, studies are important to determine the persistence of agrochemicals in water bodies, mainly in rivers inserted in areas with large sugarcane cultivation, as Pontal do Paranapanema region.

In this work, we modeled the potential of Pontal of Paranapanema region surface waters to induce micropollutant natural photochemical attenuation by considering the real characteristics of rivers and seasonal trends of water bodies' chemical composition and solar irradiance. We also simulated the photodegradation kinetics of two pesticides over space and time in the studied area; the pesticides atrazine (ATZ) and diuron (DIR) were selected due to their recognized occurrence in Brazilian river waters (Acayaba 2017).

The results allow for the assessment in which season environmental concern should be higher (or lower) considering natural photochemical attenuation of Pontal of Paranapanema rivers. Moreover, they enable seeing how real characteristics (solar irradiance, chemical composition, and year season) impact on emerging pollutant persistence at natural medium.

Methods

Water sampling

Pontal of Paranapanema is a region located in the west of São Paulo State, formed by 26 municipalities: Álvares Machado, Anhumas, Caiuá, Estrela do Norte, Euclides da Cunha Paulista, Iepé, Indiana, Marabá Paulista, Martinópolis, Mirante do Paranapanema, Nantes, Narandiba, Piquerobi, Pirapozinho, Presidente Bernardes, Presidente Epitácio, Presidente Prudente, Presidente Venceslau, Rancheira, Regente Feijó, Rosana, Sandovalina, Santo Anastácio, Taciba, and Tarabaí e Teodoro Sampaio.

According to the Pontal do Paranapanema Hydrographic Basin Committee (CBH-PP), the main rivers in the region are Paraná, Paranapanema, Santo Anastácio, and Pirapozinho (SIGRH 2022). Such rivers were characterized within the scope of this research in order to represent the characteristics of water bodies in the region; thus, three water collection points were chosen for analysis in each of the

ivers, as shown in Fig. 1, and the geographical coordinates are listed in Table 1.

Analytical procedures

Temperature, pH, nitrate, nitrite, carbonate, and total organic carbon concentrations were monitored every season, for one year in each studied point.

Spectrophotometric methods were used to determine nitrate and nitrite concentrations, and titration methods were used to determine carbonate concentrations, according to NBR 12620 standard (ABNT 1992) and NBR 13736 standard (ABNT 1992), respectively. Total organic carbon (TOC) was determined by Shimadzu TOC-L equipment. All analyses were performed in triplicates.

Photochemical modeling

The quantification of PPRIs in the environment is extremely important to understand the behavior of pollutants. In fact, similar photodegradation kinetics can be observed for a very photoreactive pollutant in a poorly photoreactive environment and a photostable pollutant in highly photoreactive surface waters (Vione 2020). The PPRIs of interest in this research are HO^\bullet , $^1\text{O}_2$, and $^3\text{CDOM}^*$, and they were measured for 12 points in the main rivers of Pontal of

Table 1 Geographic coordinates

River	Point	Coordinate (latitude/longitude)
Paraná	P1	−22,570,107/−53,064642
	P2	−22,257,682/−52,768,119
	P3	−21,759,141/−52,140,965
Paranapanema	P1	−22,6,055,178/−51,906,065
	P2	−22,555,778/−52,150,157
	P3	−22,597,949/−52,873,729
Santo Anastácio	P1	−21.850111/−52.155889
	P2	−22.023861/−51.889361
	P3	−22.204556/−51.434417
Pirapozinho	P1	−22,261,250/−52,636,944
	P2	−22,504139/−51,994369
	P3	−22,524219/−52,028281

Paranapanema region, for each season. The PPRIs are produced upon sunlight absorption by reactive species called photosensitizers and are quenched/scavenged by natural water components (Vione et al. 2018).

PPRI concentrations were simulated by using the APEX model (Aquatic Photochemistry of Environmentally-occurring Xenobiotics). The main reactions involved in the generation and sequestration of intermediate reactive species HO^\bullet , $^1\text{O}_2$, and $^3\text{CDOM}^*$ are presented by Reactions 1–17 (Souza

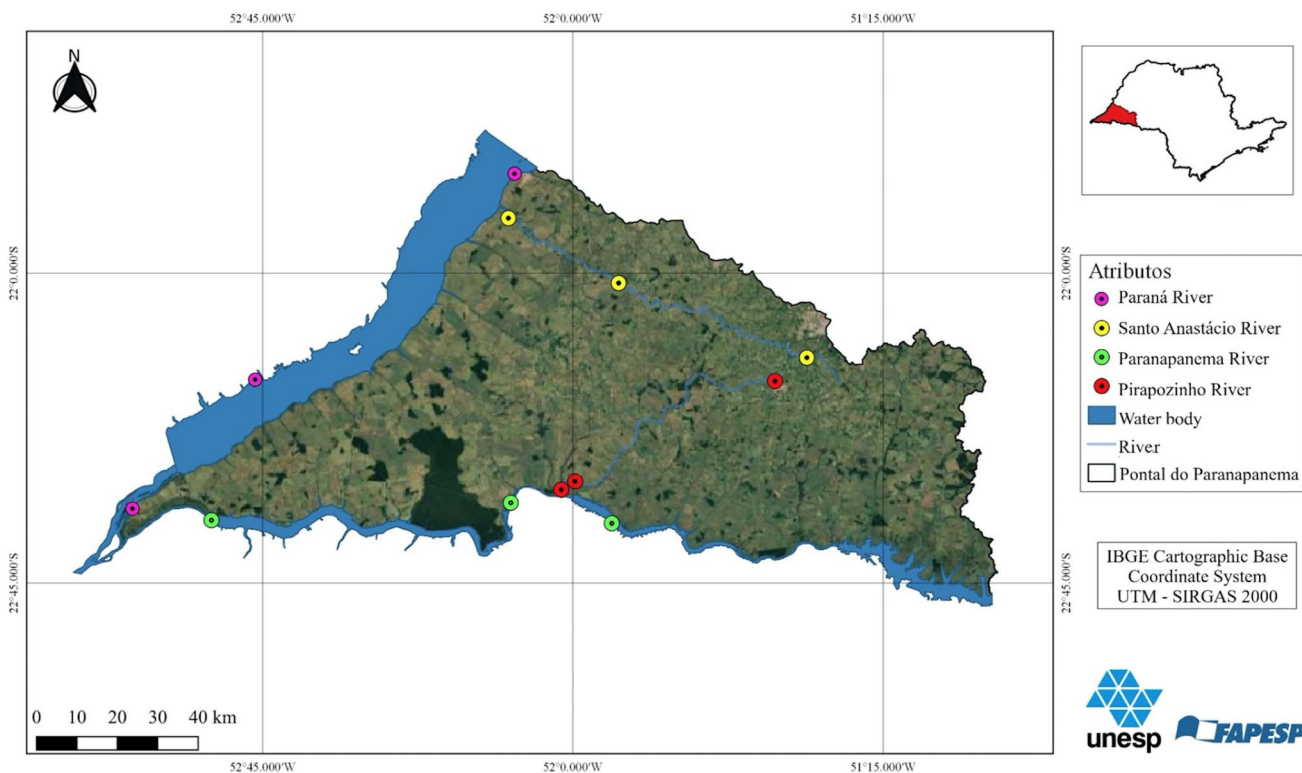
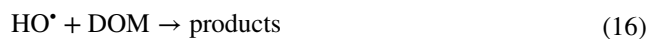
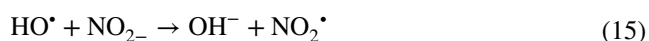
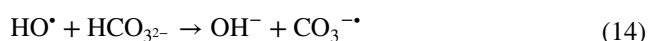
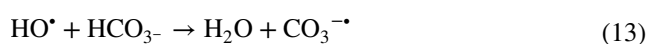
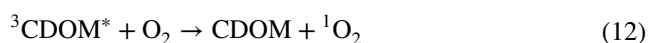
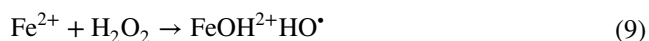
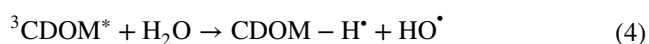


Fig. 1 Water sampling points in the main rivers of Pontal of Paranapanema region

et al. 2022). HO• radicals are formed by the absorption of light by nitrate and nitrite (Reactions 1 and 2). Additionally, HO• radicals can be generated from chromophoric dissolved organic matter (CDOM) through various pathways: CDOM photoexcitation (Reaction 3) and water oxidation by ³CDOM* (Reaction 4); O₂^{•-} generation through a charge-transfer state of CDOM (Reactions 5 and 6), followed by disproportionation to H₂O₂ (Reaction 7), which then undergoes photolysis (Reaction 8); Fenton reaction (Reaction 9); and photolysis of polyhydroxylated CDOM intermediates (Reactions 10 and 11) (Souza et al. 2022; Bacilieri et al. 2022; McNeill and Canonica 2016; Foote et al. 1995). Secondary radical formation may also occur via reactions between PPRIs and additional water components such as bicarbonate (HCO₃⁻), carbonate (CO₃²⁻), nitrite (NO₂⁻), and dissolved organic matter (DOM) (Vione 2020).



APEX predicts PPR concentrations from solar irradiance, chemical species present in water body and depth (Bodrato and Vione 2014).

The solar irradiance considered in this research was obtained from National Center for Atmospheric Research by UCAR-TUV calculator for geographic coordinates of Pontal of Paranapanema region; for each season, it generated a 24-h averaged spectrum (NCAR 2022). This calculator can be freely accessed by the following link: https://www.acom.ucar.edu/Models/TUV/Interactive_TUV/.

Sampling campaign of four main rivers under study was conducted to determine water chemistry data, the parameters, nitrate, nitrite, bicarbonate, total organic carbon, temperature, and pH were monitored monthly. Three samples from each point were collected and analyzed every month for a year.

Considering that waters in Pirapozinho and Santo Anastacio rivers are quite shallow, for these rivers, a water column depth of 0.5 m was used in the model, and for Paranapanema and Paraná rivers, the depth was fixed at 2.5 m, because these rivers are deeper. It is important to highlight that the model assumes well-mixed water, and the calculated concentrations represent the average within the depth of the column, rather than a specific point concentration at that depth.

The maps were organized using the QGIS software (QGIS Developmental Team 2022).

Pesticide photochemical persistence in environment

The photochemical environmental persistence of ATZ and DIR was predicted by the use of mathematical model APEX. Photochemical modeling yields the pseudo-first-order degradation rate constants of selected pesticides, as well as their corresponding half-life times. In the scientific literature, many publications employ the APEX software, whose modeling methodology has been substantiated through the comparison with field data pertaining to the phototransformation kinetics of diverse contaminants in surface waters. Noteworthy examples include diclofenac, naproxen, clofibrac acid, carbamazepine, atrazine, sertraline, and paroxetine (Avetta et al. 2016; De Laurentiis et al. 2012; Marchetti et al. 2013; Gornik et al. 2020, 2021).

Photodegradation in surface waters initiated by sunlight can be divided into direct and indirect photolysis. In the first, the pollutant absorbs sunlight and consequently undergoes transformation. APEX model considers pollutant direct photolysis rate P (r_p) as given by Eq. 9:

$$r_P = \int \Phi_{\text{direct phot}}(\lambda) \frac{AP(\lambda)}{A_{\text{tot}}(\lambda)} p^0(\lambda) (1 - 10^{-A_{\text{tot}}(\lambda)}) d(\lambda) \quad (9)$$

where $\Phi_{\text{direct phot}}$ is the quantum yield of photolysis; $A_P(\lambda)$ is the pollutant absorbance at λ ; $A_{\text{tot}}(\lambda)$ is reaction medium total absorbance; $p^0(\lambda)$ is the incident spectral sunlight photon flux density. The total absorbance of the reaction medium, $A_{\text{tot}}(\lambda)$ is calculated by multiplying the specific absorbance of the surface water sample over a 1 cm optical path length, measured for each collected sample, by the depth (d).

Direct photolysis pseudo-first-order rate constant is considered in the APEX model as Eq. 10:

$$k_{P,\text{direct phot}} = \frac{r_P}{[P]} \quad (10)$$

Indirect photolysis is conducted by reactions of the pollutant with PPRIs, depending on the reactivity of the given pollutant towards HO^\bullet , $^3\text{CDOM}^*$, or $^1\text{O}_2$ (Vione 2020).

The degradation kinetics of a given pollutant P by the PPRIs, $k_{P,j}$ is considered as shown in Eq. 11, where $k_{P,j}$ is the second-order rate constant of the reaction between P and PPRIs and $[j]$ are PPRIs steady-state concentrations (HO^\bullet , $^3\text{CDOM}^*$, or $^1\text{O}_2$).

$$k_{P,j} = \sum k_{P,j}[j] \quad (11)$$

The sum of the contributions of direct and indirect mechanisms is considered by APEX model, as the

pseudo-first-order rate constant of pollutant photodegradation (k_P) (Eq. 12). Finally, the half-life time of pollutant ($t_{1/2}$) is calculated in APEX model by Eq. 13.

$$k_P = k'_{P,j} + k_{P,\text{direct phot}} \quad (12)$$

$$t_{1/2} = \frac{\ln 2}{k_P} \quad (13)$$

Studied pesticide photoreactivity data were obtained from literature as reported in Table 2.

Results and discussion

Characterization of water bodies over space and time

Key physicochemical parameters of the main rivers of Pontal of Paranapanema are summarized in Tables 3, 4, 5, and 6. The pH, nitrate, nitrite and carbonate contents, and concentrations of dissolved organic carbon (DOC) were monitored for the surface water samples collected monthly for one year.

In mid-latitude regions, pH exhibits significant summer maxima (Lencina-Avila et al. 2022), while nitrate exhibits comparatively summer minima (Zhang et al. 2008). In tropical regions, such as Pontal of Paranapanema Region, seasonal variations are attenuated, and alterations in the two parameters appear less conspicuous (Tables 3 and 4).

Table 2 Second-order kinetic degradation rate constants of the pesticides with PPRIs from literature (Zeng and Arnold 2013; Marchetti et al. 2013; Fabbri et al. 2015)

Pesticide	(L mol ⁻¹ s ⁻¹)	$k_{P,1O2}$ (L mol ⁻¹ s ⁻¹)	$k_{P,3CDOM^*}$ (L mol ⁻¹ s ⁻¹)	$\Phi_{\text{direct phot}}$ (mol Einstein ⁻¹)
ATZ	$(2.5 \pm 0.4) \times 10^9$	$(2.0 \pm 0.3) \times 10^5$	$(1.2 \pm 0.2) \times 10^9$	$(1.58 \pm 0.19) \times 10^{-2}$
DIR	$(7.8 \pm 1.7) \times 10^9$	$(2.9 \pm 0.6) \times 10^5$	$(7.8 \pm 1.6) \times 10^9$	$(1.25 \pm 0.05) \times 10^{-2}$

Table 3 Average field-measured pH values for the main rivers of Pontal do Paranapanema region

River	Point	Summer	Autumn	Winter	Spring
Santo Anastácio	P1	7.12 ± 0.01	6.77 ± 0.16	7.07 ± 0.12	7.02 ± 0.09
	P2	7.19 ± 0.11	6.92 ± 0.02	6.99 ± 0.05	7.05 ± 0.06
	P3	7.17 ± 0.07	7.71 ± 0.74	7.19 ± 0.15	7.59 ± 0.28
Paranapanema	P1	7.50 ± 0.13	7.71 ± 0.31	7.56 ± 0.17	7.89 ± 0.39
	P2	7.30 ± 0.09	7.30 ± 0.22	7.18 ± 0.31	7.50 ± 0.19
	P3	7.30 ± 0.09	7.32 ± 0.17	7.18 ± 0.34	7.45 ± 0.12
Pirapozinho	P1	7.29 ± 0.01	7.31 ± 0.01	7.33 ± 0.01	7.34 ± 0.05
	P2	7.48 ± 0.07	7.58 ± 0.39	7.43 ± 0.15	7.57 ± 0.32
	P3	7.42 ± 0.09	7.41 ± 0.07	7.24 ± 0.37	7.50 ± 0.20
Paraná	P1	7.30 ± 0.31	7.17 ± 0.12	7.63 ± 0.03	7.32 ± 0.21
	P2	7.57 ± 0.07	7.24 ± 0.16	7.72 ± 0.07	7.67 ± 0.11
	P3	7.34 ± 0.10	7.35 ± 0.13	7.20 ± 0.29	7.46 ± 0.09

Table 4 Average field-measured nitrate concentrations for the main rivers of Pontal do Paranapanema region (mg L^{-1})

River	Point	Summer	Autumn	Winter	Spring
Santo Anastácio	P1	6.99 ± 1.34	4.42 ± 0.01	5.17 ± 1.46	3.73 ± 0.81
	P2	5.28 ± 0.73	5.04 ± 0.01	6.02 ± 1.07	6.43 ± 2.74
	P3	4.73 ± 2.35	4.56 ± 2.18	2.65 ± 0.56	1.80 ± 0.69
Paranapanema	P1	1.06 ± 0.57	1.10 ± 0.05	1.00 ± 0.39	0.53 ± 0.06
	P2	2.91 ± 2.34	3.12 ± 3.35	1.51 ± 0.99	0.92 ± 0.80
	P3	1.97 ± 1.10	1.37 ± 0.28	1.14 ± 0.26	0.68 ± 0.11
Pirapozinho	P1	5.28 ± 2.03	2.93 ± 1.92	4.42 ± 1.91	3.02 ± 0.56
	P2	2.98 ± 0.34	3.06 ± 0.01	4.10 ± 0.97	2.59 ± 0.72
	P3	4.56 ± 3.02	2.94 ± 0.01	2.53 ± 0.71	2.17 ± 0.26
Paraná	P1	0.91 ± 0.48	0.90 ± 0.48	0.48 ± 0.09	0.45 ± 0.01
	P2	1.56 ± 0.88	1.27 ± 0.04	1.20 ± 0.45	0.52 ± 0.01
	P3	1.47 ± 0.93	1.23 ± 0.81	0.53 ± 0.45	0.67 ± 0.01

Table 5 Average field-measured nitrite concentrations for the main rivers of Pontal do Paranapanema region ($\mu\text{g L}^{-1}$)

River	Point	Summer	Autumn	Winter	Spring
Santo Anastácio	P1	30.24 ± 5.80	21.13 ± 0.01	20.55 ± 0.01	16.32 ± 0.01
	P2	54.92 ± 12.99	59.92 ± 27.07	116.76 ± 28.25	179.92 ± 10.02
	P3	27.10 ± 13.67	25.72 ± 8.97	18.63 ± 6.01	18.90 ± 15.31
Paranapanema	P1	9.64 ± 2.28	11.14 ± 1.61	10.38 ± 2.28	11.46 ± 11.87
	P2	11.48 ± 3.42	18.96 ± 8.61	11.68 ± 2.04	9.02 ± 8.08
	P3	9.79 ± 2.15	11.44 ± 0.34	11.78 ± 4.34	11.95 ± 7.85
Pirapozinho	P1	242.59 ± 13.10	73.25 ± 7.32	94.26 ± 25.37	110.77 ± 0.01
	P2	12.90 ± 2.07	15.77 ± 0.01	15.50 ± 2.22	20.92 ± 0.01
	P3	17.19 ± 7.26	14.77 ± 0.01	13.31 ± 1.83	18.88 ± 0.01
Paraná	P1	10.54 ± 2.84	11.07 ± 1.39	11.48 ± 3.28	14.15 ± 0.01
	P2	6.39 ± 1.90	12.37 ± 0.82	10.84 ± 2.83	8.26 ± 5.81
	P3	9.41 ± 2.67	10.44 ± 0.18	11.50 ± 4.75	16.98 ± 0.01

Table 6 Average field-measured TOC concentrations for the main rivers of Pontal do Paranapanema region (mg L^{-1})

River	Point	Summer	Autumn	Winter	Spring
Santo Anastácio	P1	12.12 ± 2.53	13.75 ± 0.30	10.84 ± 3.27	15.32 ± 0.01
	P2	17.07 ± 2.28	17.17 ± 0.96	26.58 ± 1.70	16.70 ± 12.26
	P3	23.76 ± 9.79	31.28 ± 4.38	38.21 ± 9.61	38.66 ± 7.91
Paranapanema	P1	12.32 ± 0.66	12.20 ± 1.84	8.53 ± 3.34	12.21 ± 6.46
	P2	9.74 ± 1.50	4.77 ± 0.09	13.37 ± 1.56	9.46 ± 5.72
	P3	11.30 ± 1.24	8.95 ± 3.51	8.02 ± 6.40	9.18 ± 3.62
Pirapozinho	P1	17.56 ± 6.48	16.82 ± 0.94	6.98 ± 2.06	7.81 ± 0.10
	P2	7.77 ± 0.65	10.75 ± 5.97	14.04 ± 5.54	4.24 ± 1.98
	P3	7.85 ± 0.89	9.84 ± 1.02	8.35 ± 1.95	9.85 ± 0.10
Paraná	P1	8.95 ± 0.34	11.23 ± 2.26	13.70 ± 2.79	10.27 ± 2.35
	P2	7.16 ± 0.68	7.18 ± 3.62	4.98 ± 0.27	10.89 ± 2.10
	P3	11.78 ± 0.41	12.35 ± 3.56	11.29 ± 2.13	11.19 ± 0.82

The pH values vary between 6.77 and 7.72 in all studied points; this parameter does not suffer considerable variations with seasons or with location. Other authors also observed values in agreement with those reported here for

Pontal of Paranapanema rivers (Rocha and Thomaz 2004; Filho et al. 2010).

Paranapanema and Paraná rivers presented low contents of nitrate compared with Santo Anastácio and Pirapozinho

ivers, the low nitrate values observed in the deeper rivers (Paraná and Paranapanema) can be explained by the action of microorganisms that change nitrate into organic nitrogen and by consumption of this nutrient by algal growth more pronounced in these mediums, and the same trend was reported by Vione et al. (2018) for Guadiana River in Spain.

Nitrite concentrations do not present a trend variation with season; in fact, the more pronounced differences between nitrite concentrations were observed by geographic position, with deeper rivers presenting low values of nitrite. It is also possible to observe that P1 of Pirapozinho river presents higher values of this nutrient, possibly due to this location receiving the discharge of a wastewater treatment plant.

Table 6 shows the total organic carbon (TOC) findings. The highest concentrations of TOC were observed at P3 of the Santo Anastácio river (38.66 mg L^{-1}) in the municipality of Presidente Prudente-SP; this region is highly urbanized, which can directly influence the composition of river in terms of organic matter. The lowest DOC concentrations were found at P2 of Pirapozinho river (4.24 mg L^{-1}). As for the other parameters analyzed, there was no seasonal trend for the TOC concentration.

Modeled RI steady-state concentration

Photochemically produced reactive intermediates (PPRIs), generated upon sunlight irradiation of chemical species present in water matrices, had their concentrations determined through the APEX photochemical model in this research.

Figures 2, 3, and 4 present the geographical distribution of the main PPRIs, hydroxyl radical (HO^\bullet), the excited triplet states of chromophoric dissolved organic matter ($^3\text{CDOM}^*$), and singlet oxygen ($^1\text{O}_2$) in the Pontal of Paranapanema region, at different seasons.

PPRIs are produced in sunlit surface waters mainly by the photosensitization of CDOM, followed by nitrate and nitrite: (i) CDOM generates HO^\bullet and $^3\text{CDOM}^*$; (ii) $^3\text{CDOM}^*$ produces $^1\text{O}_2$ by reaction with, their main sink, dissolved oxygen; (iii) HO^\bullet radicals could oxidize $\text{HCO}_3^-/\text{CO}_3^{\bullet-}$; (iv) nitrite and nitrate generate HO^\bullet radicals (Vione et al. 2018; McNeill and Canonica 2016; Yan et al. 2019; Carena and Vione 2020).

Since PPRI formation/consumption is very fast, the steady-state concentrations of these species are usually very low, as already reported for northern hemisphere countries (Vione 2014). Vione et al. (2014) observed concentrations in order of $10^{-17} \text{ mol L}^{-1}$ for HO^\bullet and 10^{-16} – $10^{-15} \text{ mol L}^{-1}$ for $^3\text{CDOM}^*$ and $^1\text{O}_2$. Carena et al. (2021) modeled the (PPRIs) in the Piedmont region (NW Italy), obtaining 0.1 to $18 \times 10^{-16} \text{ mol L}^{-1}$ for HO^\bullet and 3 to $47 \times 10^{-16} \text{ mol L}^{-1}$ for $^3\text{CDOM}^*$ and $^1\text{O}_2$.

In turn, Ayeni et al. (2021) characterized samples collected from nine rivers located in Japan and obtained steady-state concentration ranges of $(1.53\text{--}16) \times 10^{-16} \text{ mol L}^{-1}$ for HO^\bullet and $(3.79\text{--}53.4) \times 10^{-14} \text{ mol L}^{-1}$ for $^1\text{O}_2$. Koehler et al. (2018) using photochemical kinetics modeling estimated the steady-state concentrations of PPRIs of lakes from Sweden and estimated $[\text{HO}^\bullet] = (5\text{--}15) \times 10^{-18} \text{ mol L}^{-1}$ and $[^3\text{CDOM}^*] = (7\text{--}20) \times 10^{-17} \text{ mol L}^{-1}$.

Fig. 2 Geographical distribution of the hydroxyl radical (HO^\bullet) in the Pontal of Paranapanema rivers at different seasons

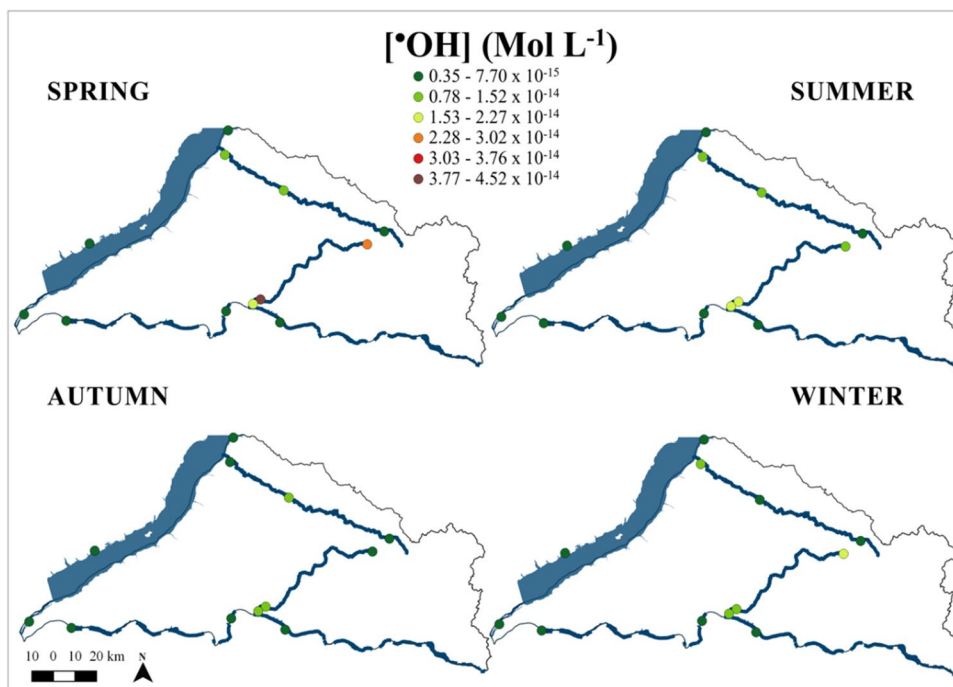


Fig. 3 Geographical distribution of the excited triplet states of chromophoric dissolved organic matter ($^3\text{CDOM}^*$) in the Pontal of Paranapanema rivers at different seasons

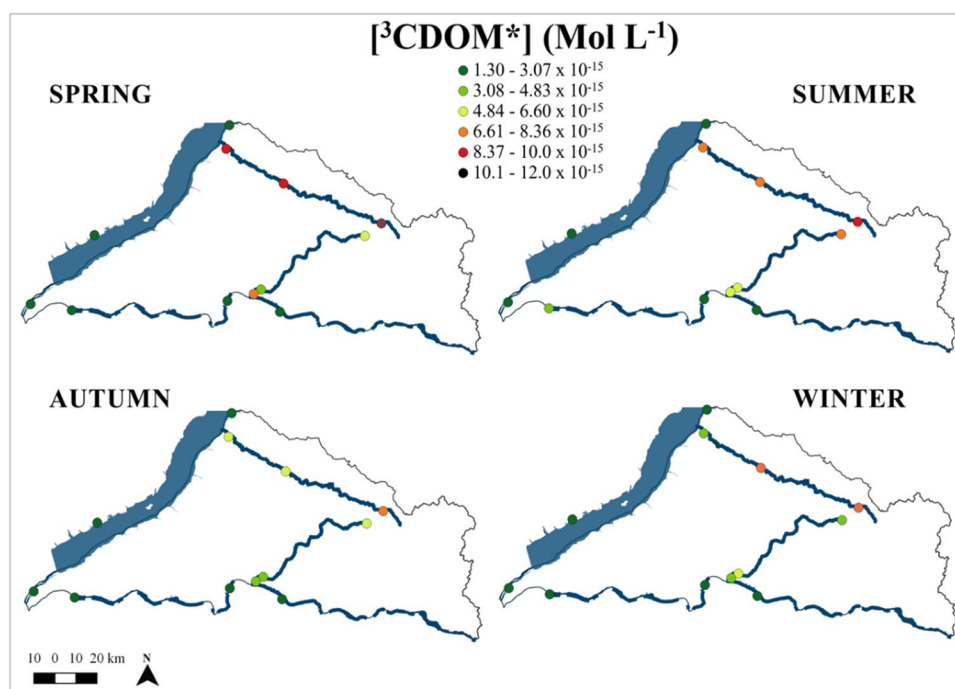
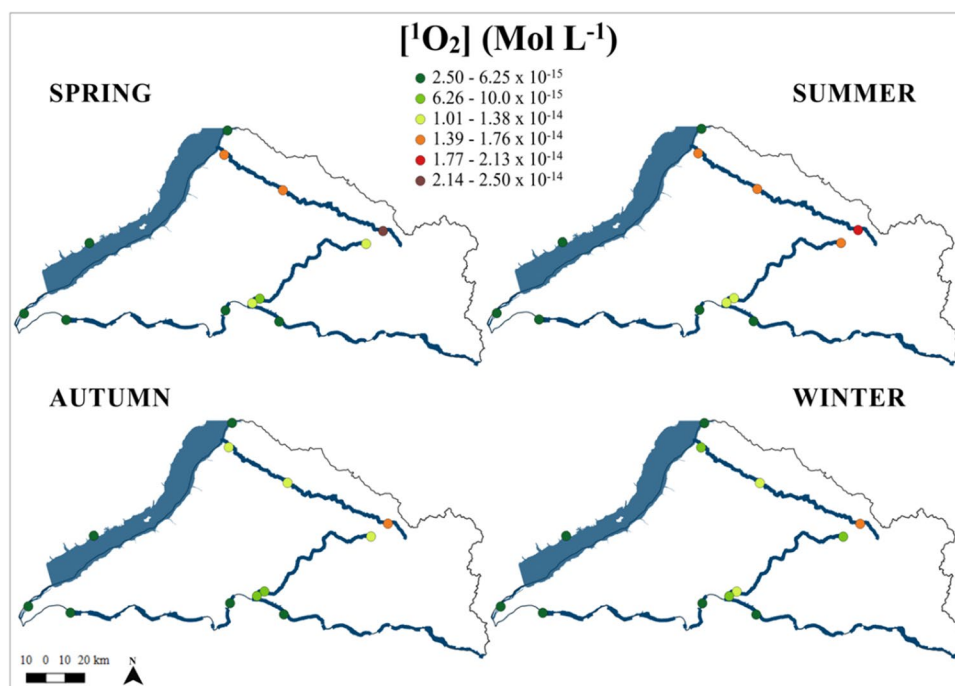


Fig. 4 Geographical distribution of the singlet oxygen ($^1\text{O}_2$) in the Pontal of Paranapanema rivers at different seasons



In this research, the simulated steady-state PPRI molar concentrations can be considered high, considering the usual values reported in the literature (Vione 2014; Carena and Vione 2020; Peterson et al. 2012). According to our mathematical simulations, the values vary from 0.35×10^{-15} to 4.52×10^{-14} mol L $^{-1}$ for HO^\bullet , 1.3×10^{-15} to 1.2×10^{-14} mol L $^{-1}$ for $^3\text{CDOM}^*$, and 2.5×10^{-15} to

2.5×10^{-14} mol L $^{-1}$ for $^1\text{O}_2$. These higher values could be explained because this is the first investigation that considers solar irradiance from southern hemisphere. Furthermore, it is essential to highlight that the investigated areas are situated within a tropical region, where the average irradiance differs significantly from that in temperate areas (Roxburgh and Noble 2001).

In the deeper studied rivers, Paraná and Paranapanema, PPRI concentrations do not present seasonal variation; the concentrations of HO^\bullet , $^1\text{O}_2$, and $^3\text{CDOM}^*$ were maintained in the same range independent of season. On the other hand, in the shallow rivers (Santo Anastácio and Pirapozinho), a trend could be observed: (PPRIs) are higher in the warm seasons (spring and summer) when the incident solar irradiance is higher.

These results suggest the influence of water depth on the photochemical processes, as reported in literature. In fact, Parizi et al. (2018) performed a factorial design at two levels of each variable (nitrate, nitrite, bicarbonate, dissolved organic matter concentrations, pH, and water depth) to determine the variables that present greater importance in the degradation of synthetic hormone sodium levothyroxine-T4 in surface waters. The authors concluded that water depth was the variable that most influenced the photochemical degradation of the studied pollutant. Furthermore, our results suggest that water depth also affects PPRI generation more than incident solar irradiance, in the study area.

Figure 2 presents the modeled concentrations of HO^\bullet by APEX. Hydroxyl radical is an important oxidant in water bodies, with significant contributions to natural waters, a very reactive species, with typical second-order reaction rate constants in the order of 10^{-8} – $10^{-10} \text{ M}^{-1} \text{ s}^{-1}$ (Buxton et al. 1988).

The steady-state concentrations of HO^\bullet in sunlit waters are in order of 10^{-14} to $10^{-17} \text{ mol L}^{-1}$ (Rosario-Ortiz and Canonica 2016), in general agreement with the values obtained in this research (0.35×10^{-15} to $4.52 \times 10^{-14} \text{ mol L}^{-1}$).

In Paraná and Paranapanema rivers, the HO^\bullet concentration remained in the range of 0.35 to $7.70 \times 10^{-15} \text{ mol L}^{-1}$. The highest HO^\bullet concentrations were obtained in Pirapozinho river, reaching $4.52 \times 10^{-14} \text{ mol L}^{-1}$ in P2 at spring season. The higher $[\text{HO}^\bullet]$ observed in this point could be explained by the fact that here in spring we observed the minimum value of dissolved organic matter DOM (measured as the TOC), which is an important sink of hydroxyl radical (Rosario-Ortiz and Canonica 2016).

In agreement with our findings, Carena et al. (2021) investigated photodegradation kinetics of agrochemicals usually applied in the Piedmont region (NW Italy) and also concluded that regions with higher $[\text{HO}^\bullet]$ had less concentrated sinks as DOM or more concentrated sources (e.g., NO_3^-). Similar behavior was seen by Zeng and Arnold (2013) who reported that water bodies with a high level of DOC show lower HO^\bullet concentrations.

Figure 3 presents the geographical distribution of $[\text{CDOM}^*]$ on Pontal of Paranapanema-SP. The photoexcitation of CDOM results in the formation of excited triplet states because CDOM consists of a complex mixture of organic molecules that produce $^3\text{CDOM}^*$ by sunlight photon

absorption. The assessment of their steady-state concentration is important in the elucidation of micropollutant photochemical persistence in aquatic environment (Rosario-Ortiz and Canonica 2016).

The results obtained for $[\text{CDOM}^*]$ simulations in Pontal of Paranapanema region range from 1.3 to $12.0 \times 10^{-15} \text{ mol L}^{-1}$, with the higher seasonal variations at Pirapozinho and Santo Anastácio rivers. The higher value of $^3\text{CDOM}^*$ was observed in P3 of Santo Anastácio that presented higher values of DOC during all studied seasons. The increase of $[\text{CDOM}^*]$ with increasing DOC derives from the fact that $^3\text{CDOM}^*$ states are formed by irradiated CDOM, but they are not significantly scavenged by DOM (Vione 2014). In fact, the lifetime of $^3\text{CDOM}^*$ in aerated aqueous solutions, as surface waters, is in the μs range; this lifetime is too short to allow an important scavenging of $^3\text{CDOM}^*$ by DOM (Wenk et al. 2013).

The warm season samples of Santo Anastácio river produced the highest concentration of $^1\text{O}_2$ upon simulations performed by APEX, $(1.39 \text{ to } 2.5) \times 10^{-14} \text{ mol L}^{-1}$, and a similarly high concentration was obtained at P1 of Pirapozinho river at summer time $(1.39 \text{ to } 1.76) \times 10^{-14} \text{ mol L}^{-1}$. Lower values ranging from 2.5 to $6.25 \times 10^{-15} \text{ mol L}^{-1}$ were obtained for the deeper rivers, Paraná and Paranapanema. As for $^3\text{CDOM}^*$, $[\text{O}_2]$ increases with increasing DOC because $^1\text{O}_2$ is produced by irradiated CDOM, while it is not scavenged significantly by DOM (Vione 2014). Our results are in agreement with literature that reported that in surface waters irradiated by sunlight, the steady-state concentration of $^1\text{O}_2$ ranges from 10^{-15} to $10^{-12} \text{ mol L}^{-1}$ (Rosario-Ortiz and Canonica 2016). Peterson et al. (2012) examined the variation of singlet oxygen production in Lake Superior over space and season, the measurement results in range of 0.7 to $1.6 \times 10^{-15} \text{ mol L}^{-1}$ which is the same order obtained in this study.

Photochemical environmental persistence of the pesticides

The simulated phototransformation rate constants of atrazine (ATZ) in the different seasons are shown in Fig. 5. It can be inferred that ATZ would mainly be photodegraded by $^3\text{CDOM}^*$ and HO^\bullet , and its half-life times ($t_{1/2}$) reach seven days in Paraná River at winter. In deeper rivers, as Paraná and Paranapanema, the contribution of $^3\text{CDOM}^*$ was more pronounced (on average 45%) than in shallow waters as Pirapozinho and Santo Anastácio (on average, 25%). In turn, the attack of $^1\text{O}_2$ on pollutant molecules is not expected to be an important degradation pathway in the Pontal of Paranapanema rivers. Despite the selectivity of PPRI in reactions with organic pollutants, $^1\text{O}_2$ is very important in the mechanism of photochemical inactivation of pathogens in natural environments (Rosario-Ortiz and Canonica 2016).

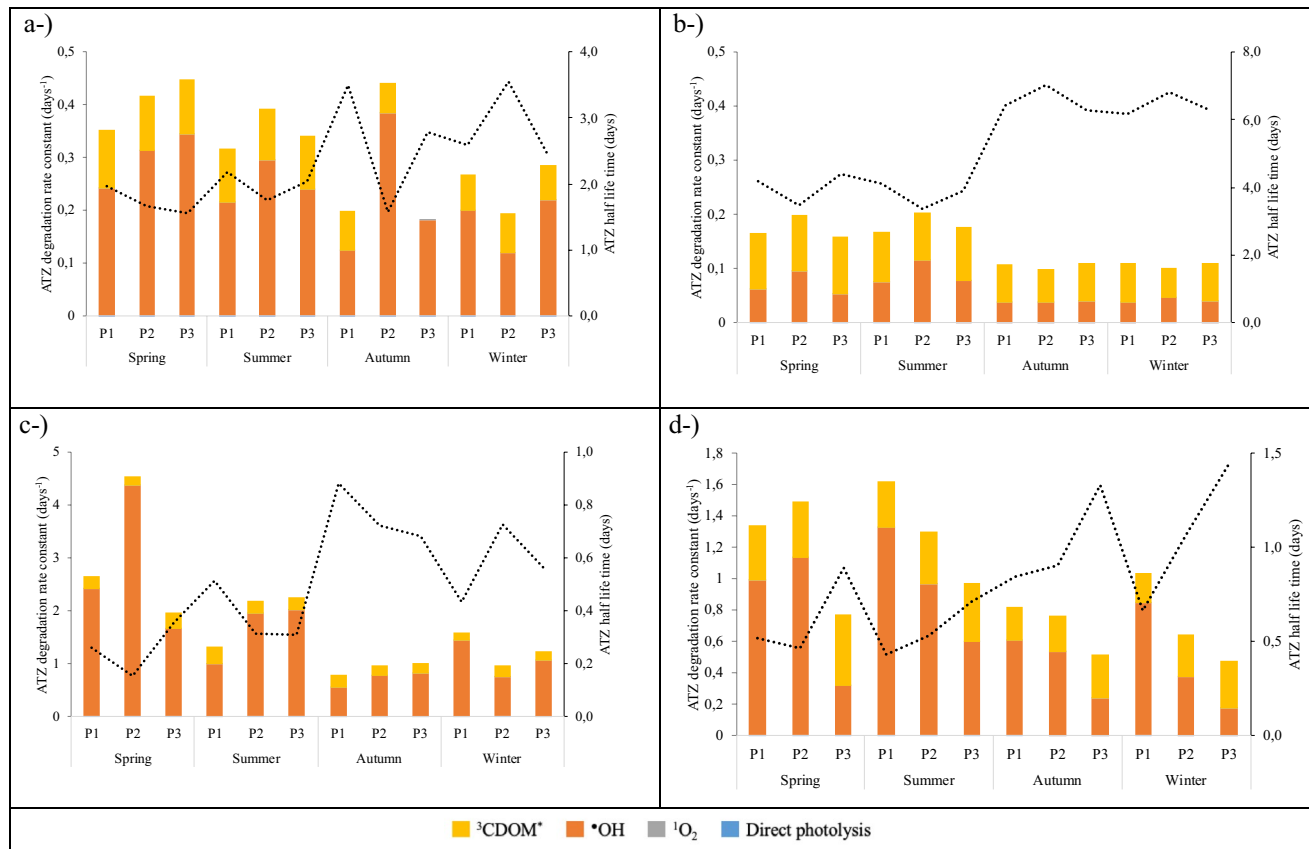


Fig. 5 Predicted rate constant of ATZ photodegradation in rivers **a** Paranapanema, **b** Paraná, **c** Pirapozinho, and **d** Santo Anastácio, induced by photochemical processes (HO^\bullet , $^1\text{O}_2$, and $^3\text{CDOM}^*$ and direct photolysis) in different seasons

As shown by Fig. 6 for diuron (DIR), the main pathways involved in the photodegradation of this pollutant in the Pontal of Paranapanema rivers are the reactions with hydroxyl radicals and $^3\text{CDOM}^*$, with singlet oxygen and direct photolysis playing a minor role. According to the kinetic simulations, the values of $t_{1/2}$ vary from 0.2 to 1 day in the deeper rivers (Paraná and Paranapanema). Contrary, in shallow waters such as Pirapozinho and Santo Anastácio rivers, the pollutant is degraded in a few hours. In fact, the photodegradation of DIR is expected to be slower in deeper water bodies due to the lower penetration of sunlight and, consequently, a lower rate of photochemically produced reactive intermediates formation. This behavior was observed by Lastre-Acosta et al. (2022), who reported $t_{1/2}$ of 2-chlorobiphenyl increasing almost linearly with increasing depth of the water column.

For both pesticides, shorter half-lives were obtained in the Pirapozinho and Santo Anastácio rivers. This may be due to the fact that, in these rivers, the highest values of DOC (in this work assessed through the concentration of TOC) were observed during all seasons. According to Vione et al. (2018), in waters with high DOC, the reactions with $^3\text{CDOM}^*$ tend to be favored. Furthermore, Pirapozinho and Santo Anastácio rivers are quite shallow compared to the other two (Paranapanema and Paraná),

and the photodegradation of pollutants tends to be faster in shallower environments.

Conclusions

This study investigated the Pontal of Paranapanema surface water potential to degrade agrochemicals by photochemical natural processes on a geographical and temporal scale. The concentrations of the photochemically produced reactive intermediates (PPRIs) (HO^\bullet , $^1\text{O}_2$, and $^3\text{CDOM}^*$) were simulated by using the APEX model, from sunlight irradiance, water chemistry, and depth.

Based on our results, the simulated steady state PPRI molar concentrations in Pontal of Paranapanema surface waters vary between 0.35×10^{-15} and 4.52×10^{-14} mol L $^{-1}$ for HO^\bullet , 1.3×10^{-15} and 1.2×10^{-14} mol L $^{-1}$ for $^3\text{CDOM}^*$, and 2.5×10^{-15} and 2.5×10^{-14} mol L $^{-1}$ for $^1\text{O}_2$. These values can be considered a little high in comparison to the usual values reported in literature. This can be explained because this is the first investigation that considers solar irradiance from southern hemisphere. In the deeper rivers (Paraná and Paranapanema), the concentrations of HO^\bullet , $^1\text{O}_2$, and $^3\text{CDOM}^*$ remained in

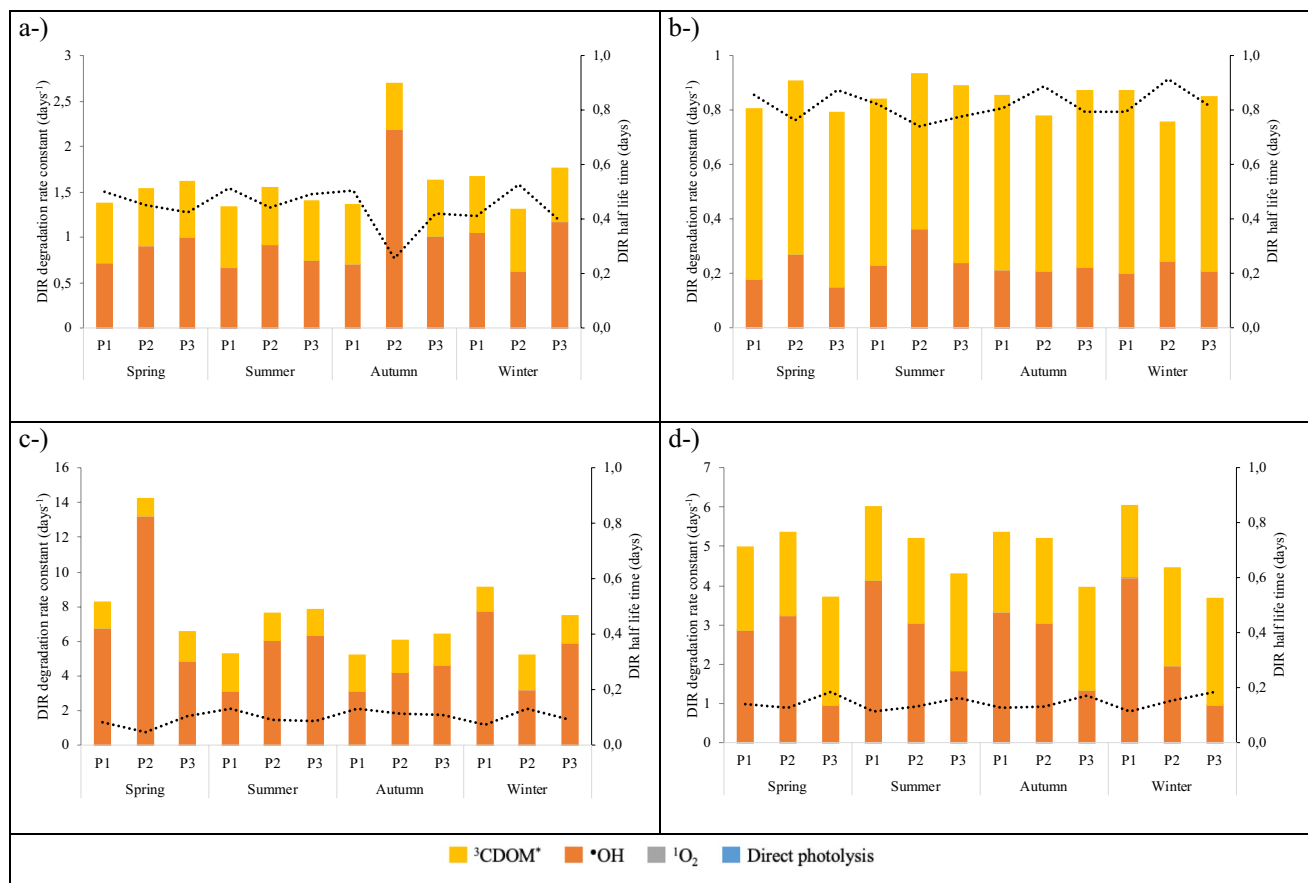


Fig. 6 Predicted rate constant of DIR photodegradation in rivers **a** Paranapanema, **b** Paraná, **c** Pirapozinho, and **d** Santo Anastácio induced by photochemical processes (HO^\bullet , $^1\text{O}_2$, and $^3\text{CDOM}^*$ and direct photolysis) in different seasons

the same range independently of season. In turn, in the shallow rivers (Santo Anastácio and Pirapozinho), (PPRIs) were higher in the warm seasons (spring and summer) when the incident solar irradiance is higher.

Finally, mathematical simulations were used for predicting persistence of pesticides atrazine (ATZ) and diuron (DIR) in Pontal of Paranapanema surface waters. The half-life times ($t_{1/2}$) of the pollutants in different sampling points ranged from a few hours to one week. For both pesticides, shorter half-lives were obtained in the Pirapozinho and Santo Anastácio rivers, which showed the highest values of TOC and lower depth.

In summary, the results of this study presented the potential of Pontal of Paranapanema region surface waters to induce the natural photochemical attenuation of pesticides by considering the real characteristics of rivers and seasonal trends of water bodies' chemical composition and solar irradiance.

Acknowledgements The authors are thankful to São Paulo Research Foundation (FAPESP) for the financial support.

Author contribution GSF: methodology and investigation. NGR: methodology and investigation. AMLA: formal analysis and writing—review and editing. LFP: validation and formal analysis. ACSCT: resources and supervision. MSP: conceptualization, methodology, validation, formal analysis, investigation, writing—original draft, writing—review and editing, supervision, and funding acquisition.

Funding This work was financially supported by São Paulo Research Foundation (FAPESP) grant #2019/0696–1; Coordenação de Aperfeiçoamento de Pessoal de Nível Superior Brasil (CAPES) Finance Code 001 and post-doc grant #88887.340964/2019–00; and National Council for Scientific and Technological Development (CNPq).

Data availability All data generated or analyzed during this study are included in this published article.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication We affirm that the article has been studied and accepted by all listed authors.

Competing interests The authors declare no competing interests.

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