REACTIVE INTERMEDIATE SPECIES GENERATION IN THE PARANAPANEMA RIVER : TEMPORAL EVALUATION

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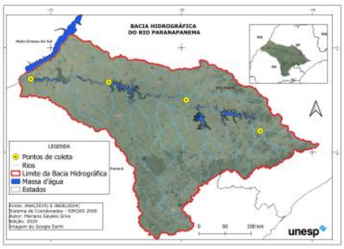

This study focuses on evaluating the photochemical reduction capacity of the Paranapanema River from 2000 to 2020 through literature review and mathematical simulations, alongside investigating the persistence of fluoxetine, an antidepressant, within the river ecosystem. The mechanismis involve the degradation of pollutants through solar radiation absorption and photo-initiated degradation facilitated by transient species like oxygen, hydroxyl radicals, and triplets from organic matter. It was noticiabled that the variations in singlet oxygen concentrations between the different points are more pronunced than the temporal variations observed over the period studied. No significant variations were observed in the concentrations of hydroxyl radicals over the period from 2000 to 2021 in the points analysed.Thus, it can be inferred that points P1 and P2 along the Paranapanema river hold a higher potential for photochemical attenuation concerning micropollutants, as the concentrations of reactive intermediates are elevated at these locations.

Introduction

Understanding the mechanisms affecting the impact the fate and transport of pollutants in the environment is a key focus within the field of environmental sciences. Considerable attention has been devoted to the presence of persistent organic pollutants (POPs) in surface waters. These substances have garnered significant interest due to their environmental impact and effects on human health.[1]

The mechanisms of photoinduced degradation processes are the primary contributors to the removal of POPs from natural waters. These involve direct and indirect photolysis, where in the former, the pollutant is degraded via absorption of solar radiation, while the photo-initiated mechanisms refer to the degradation of a compound with the assistance of transient species generated photochemically (RI), such as singlet oxygen ($^1O_2$), hydroxyl radicals and ($^•OH$) and triplets from organic matter ($^3CDOM^*$). [2] Understanding the concentration of reactive intermediate species (RIs) in rivers is crucial to determining the river's photochemical attenuation capacity in relation to persistent pollutants.[3] The Paranapanema River is one of the most important watercourses in the interior of the state of São Paulo, Brazil.

The aim of this study was to determine the photochemical reduction capacity of the Paranapanema River between 2000 and 2020, using a literature review and mathematical simulations. Additionally, we also studied the persistence of the antidepressant fluoxetine in the Paranapanema River over the years.

Material and Methods

Using the data provided by CETESB (São Paulo State Environmental Company), the pH and concentrations of nitrate, nitrite and total organic carbon were analyzed at four points on the Paranapanema River between 2000 and 2021.

Based on this data, the mathematical model APEX (Aqueous Photochemistry of Environmental-Occurring Xenobiotics), developed by Brodato and Vione (2014), was used to estimate the potential generation of reactive intermediate species (RIs) -$^•OH$, $^1O_2$ and $^3CDOM^*$ - in the Paranapanema River.Using QGIS software, it was possible to spatially analyze the generation of RIs in the Paranapanema River over the years.

For the simulation of FLX persistence, data provided by CETESB and the reactivity constants of FLX with the RIs found in the literature were used, along with the quantum yield of direct photolysis of the antidepressant (Table 1).

Table 1. Second-order kinetic rate constants of the reactions between FLX and RIs ($^1O_2$, $•OH$,3CDOM*).

$k_{FLX,OH}$ (10^9 L mol^{-1} s^{-1})	$k_{FLX,^1O_2}$ (10^7 L mol^{-1} s^{-1})	$K_{FLX,^3CDOM^*}$ (10^9 L mol^{-1} s^{-1})	Direct photolysis quantum Yield
2.54±0.06	1.37±0.07	2.67±0.05	$1.37x10^{-5}$ mol Einstein^{-1}

Results and Discussion.

Figure 1 shows the simulated concentration of reactive intermediate specie $^•OH$ at the four points on the

Paranapanema River over two decades, with values oscillating between 2.06×10^{-17} and 1.51×10^{-16} mol L^{-1}. These results are similar to data found in the literature, which generally range from 10^{-17} to 10^{-15} mol L^{-1}.[4]

Although a slight increase in $^{\bullet}OH$ concentration was observed at point P2 in 2015 (Figure 1), this increase was not significant over the years and did not vary in the space analyzed.

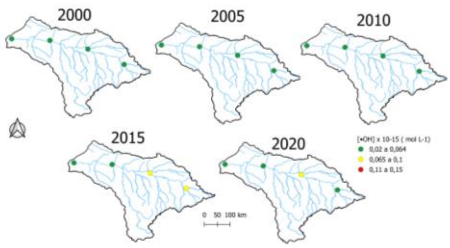

Figure 1. Concentration of $^{\bullet}OH$ in the Paranapanema River in different years.

Figure 2 shows singlet oxygen ($^1O_2$) concentrations in the Paranapanema River, oscillating between $4.06\text{x}10^{-16}$ and $3.06\text{x}10^{-15}$ mol L^{-1}.

The values found in the literature are generally in the range of 10^{-13} mol L^{-1}.[5]

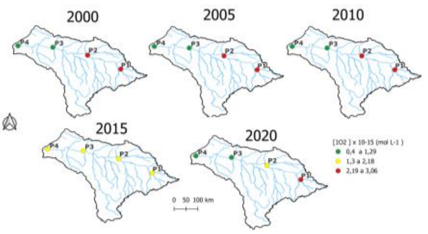

Figure 2. Concentration of ($^1O_2$) in the Paranapanema river in different years.

Figure 3 shows the concentrations of $^3CDOM^*$ over the 20 years considered in this study. The calculated values oscillate over $2.08\text{x}10^{-16}$ e $1.57\text{x}10^{-15}$ mol L^{-1}, with a trend towards higher values at points P1 and P2 compared to points P3 e P4, in line with the pattern observed in $^1O_2$ concentrations. The highest concentration of triplestes $1.57\text{x}10^{-15}$ mol L^{-1} was recorded at point P1 in 2019. The values documented in the literature are usually in the range of 10^{-16} mol L^{-1}.

Figure 4 shows the half-life of fluoxetine over the years of 2000, 2010, 2015 and 2020.It is possible to observe that in the years 2000 and 2010 the half-life did not change, while in the years 2015 and 2020 the changes occurred. Point 2 had a shorter half-life. The change between the values in the years 2015 and 2020 was given by the difference in the concentration of singlet oxygen in the rivers.

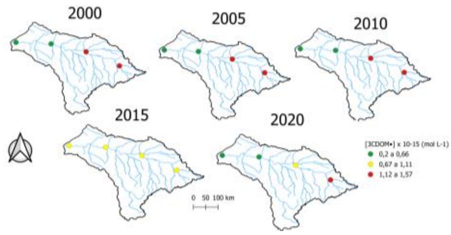

Figure 3. Concentration of ($^3CDOM^*$) in the Paranapanema River in different years

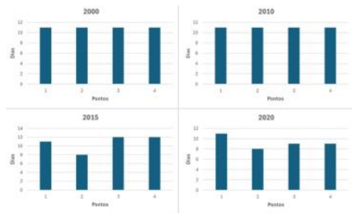

Figure 4. Shows the half-life of fluoxetine over the years of 2000, 2010, 2015 and 2020

Conclusions

It was observed that there were no significant variations in $^{\bullet}OH$ radicals over time (from 2000 to 2021) and in the space analysed (P1, P2, P3 and P4). As for the reactive species $^1O_2$ and $^3CDOM^*$, differences were observed between the points studied, with higher concentrations of these RIs at points P1 and P2 throughout the period. However, no significant differences were identified over time, as the consentrations remained consistent over the years at each point.

Therefore, it can be concluded that points P1 and P2 of the Paranapanema river have a greater potential for photochemical attenuation in relation to micropollutants, since the concentrations of RIs are higher at these sites, wich favors the degradation of micropollutants.

Acknowledgments

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