



## Research Article

# Atrazine Persistence in Sediment of Aquatic Microcosms

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**Abstract:** Atrazine is a mutagenic, carcinogenic, and environmentally persistent herbicide commonly detected in natural waters and sediment due to its broad use in corn, sugarcane, and sorghum plantations. Though largely studied, investigations on atrazine's fate and routes of transformation in freshwater environments have been somewhat scarce and fragmented. Thereby, the purpose of this study is to comprehend the physicochemical destiny of atrazine in the sediment of laboratory-based aquatic freshwater microcosms. Four microcosms with a capacity of 40 L were set up in the laboratory after the preparation of standard synthetic sediment (composed of peat moss, medium-sized grain sand, and white clay) and filled with tap water. Two of these systems (labeled 1 and 3) were contaminated with atrazine, resulting in an overall initial concentration of  $100 \mu\text{g L}^{-1}$  in each, whereas the other two systems (labeled 2 and 4) were maintained under control conditions. The assays were monitored for 43 weeks in total, for pH, dissolved oxygen (DO), total dissolved solids (TDS), apparent color, turbidity, and temperature. Atrazine was added to the systems only in the 14th week ( $100 \mu\text{g L}^{-1}$ ) and quantified in the water column in the 38th week ( $46 \mu\text{g L}^{-1}$ ) through liquid chromatography coupled to mass spectrometry, showing that the initial concentration of atrazine in the water column decayed by approximately 50% during this period. This finding indicates that the herbicide underwent biological and/or physicochemical transformations in the water column and sediment. The systems' water was replaced in the 40th week, after which the atrazine concentration in the water column returned to equilibrium ( $46 \mu\text{g L}^{-1}$ ), revealing that the sediment can function as a repository of the compound in the systems' aquatic environment.

**Keywords:** organic persistent pollutants, synthetic sediment, *triazine herbicides*

## 1. Introduction

Atrazine is a selective herbicide belonging to the class of *triazine herbicides* and is considered a persistent pollutant due to its considerably long half-life in the environment (from 10 to 5,824 days in soils and sediments) [1, 2] and high mobility between environmental compartments (soil, water, and sediment), especially due to its low solubility in water ( $35 \text{ mg L}^{-1}$ ) [2] and modest affinity for the organic carbon fraction of soils and sediments ( $K_{oc} = 10^2$ ) [3].

Atrazine concentrations in soils, superficial and groundwaters, and sediments have been measured in the range of  $0.024$  and  $0.94 \mu\text{g L}^{-1}$  [4, 5]. Although seemingly low, such concentrations are already capable of causing damage to living organisms. Singh & Singh [6] studied the toxic effects of atrazine upon the soil microbiota, plant growth, enzymatic processes, and photosynthesis as well as its impairing cellular division and lipidic synthesis, and causing hormonal deregulation in the aquatic fauna and in other animals. There are also signs that atrazine can function as a chemical barrier for fish and other aquatic animals (for instance, isolating fish populations highly sensitive to whatever

concentration of this compound is in aquatic environments) even at concentrations as low as  $0.065 \mu\text{g L}^{-1}$  [7].

Yet there have been indications that atrazine may cause adverse effects at concentrations lower than  $1 \mu\text{g L}^{-1}$ , the Brazilian legislation allows up to  $2 \mu\text{g L}^{-1}$  of atrazine in freshwater [8]. Although the use of atrazine is now restricted in the United States, the law sets a higher maximum level ( $3 \mu\text{g L}^{-1}$ ) than what is permitted in Brazil [9].

Atrazine's destiny in the environment has been extensively studied in soils and water; nevertheless, its presence and transformation mechanisms in sediments are still modestly investigated [10]. A good number of studies on atrazine's behavior (sorption, desorption, diffusion, and degradation) in sediments have been reported in the past decades [2, 11-14], totaling 164 scientifically relevant studies in the last 50 years (checked in Scopus on June 14, 2019). At the same time, when the following operators were combined: (atrazine AND sediment) AND (degradation OR diffusion OR sorption OR desorption), 91% of the studies returned showed that they were carried in cold to mild weather sediments, with 75 studies conducted in the United States; 22 in China; and 14 in Germany. Only seven studies addressed atrazine's behavior in tropical sediments [15-17], adding up to ten studies of scientific relevance in Brazil on the topic published between 2007 and 2018. Ten studies were returned by the Scopus database after applying the search criteria "atrazine AND sediment AND Brazil" in the title, abstract, or keywords.

In this scenario, it is important to investigate the dynamics of transformation and accumulation of the herbicide atrazine in the sediments of tropical aquatic ecosystems, longing to understand which factors may relate to the pollutant's diffusion, sorption, degradation, and volatilization in such systems. To comprehend the physicochemical destiny of atrazine in sediments, laboratory-based freshwater microcosms were constructed with synthetic sediment in order to emulate tropical aquatic ecosystems, which were put under two different conditions: no exposition to atrazine (control systems) and addition of atrazine solution (prepared as to result in a final concentration of  $100 \mu\text{g L}^{-1}$  in each system). Thus, the relevance of this study lies in the comprehension of the physicochemical destiny of a pollutant of emerging concern for studies on environmental quality in such a way that its identification and quantification in the environment may subsidize decision-making on control, recovery, and planning for the improvement of aquatic ecosystems.

## 2. Methodology

### 2.1 Sediment preparation

The synthetic sediment was prepared using common sand, clay, and peat moss, adapted from the recommendations of Method 233 of the Organization for Economic Cooperation and Development (OECD) [18], as presented in Table 1. This method originally represented sediment from mild to cold weather environments; however, it was adapted and used as a reference for this study given the absence of a standard preparation method for tropical sediments.

**Table 1.** Synthetic sediment composition

Components	Percentage of dried sediment weight (%)	Characteristics
Peat moss	5	Sphagnum, no plan residues, pH ( $7.0 \pm 0.5$ ), particles $\leq 1$ mm, air dried
Quartz sand	75	70% of particles between 0.15 - 1 mm
Clay	20	Kaolinite clay

The sand (common medium washed sand) was purchased from a construction materials store; the clay was purchased from an online beauty skincare store (pure white clay); and the *Sphagnum* peat moss was ordered from an online gardening store (specific mass:  $110 \text{ kg/m}^3$  and pH:  $6.0 \pm 0.5$ ). Prior to the preparation, the sand used was submitted to electromagnetic sieving to obtain a grain size distribution curve, according to method ABNT NBR 7181/2016 [19]. Peat moss was air-dried for 48 hours before being ground for two hours in a Marconi ball mill with jars MA 500/E to the texture of fine powder (grain average diameter  $< 1$  mm). It was then made into a suspension with

tap water using a high-performance soil mechanical agitator at a speed of 10 rps. The suspension was left to rest for 19 days for stabilization and adaptation of the microbiota to the newly created environmental conditions. After the acclimation period, the peat moss suspension was mixed with the other constituents (sand and kaolinite clay) to obtain a homogeneous sediment with water content between 30 and 50% by dry weight. This mixture was then distributed among the boxes. The solid constituents utilized in the sediment preparation were kept in a dry and fresh place at room temperature until the moment of the preparation.

The microcosms were set up in four propylene boxes with the following dimensions, measured in cm for length (L), width (W) and height (H), respectively: 48 (L) x 32 (W) x 32 (H). The boxes were filled until the mark of 26 cm, such that one-quarter of the height (6.5 cm) was filled with water-saturated synthetic sediment (corresponding to 10 L), and the remaining three-quarters were completed with tap water, according to the OECD's recommendations [18].

## 2.2 Systems acclimation and monitoring

The microcosms were kept in an environment of moderate light and ventilation while being monitored weekly for 300 days (43 weeks). During this period, the systems were monitored on the same day of the week, approximately at the same time of the day, and in a similar position. The parameters monitored were dissolved oxygen (DO), turbidity, apparent color, pH, total dissolved solids (TDS), and water temperature. For the monitoring of DO, a Hach multiparameter probe (model HQD Intellical) was used; and for temperature, pH, and TDS assessment, a Horiba multiparameter probe (model U50) was used. For turbidity and color measurements of the samples collected from the cosmoses, a turbidimeter (model AP2000 WT) and colorimeter (model AquaColor) of the brand Policontrol were used. Both instruments operate under the Standard Method (2120 E) for Examination of Water and Wastewater [20]. All measurements were taken in duplicate. Water lost through evaporation was reclaimed weekly (approximately 3 L in each system), while keeping sediment replenished in the systems in mind. Figure 1 presents a timeline illustrating the course and steps of the experimentation.

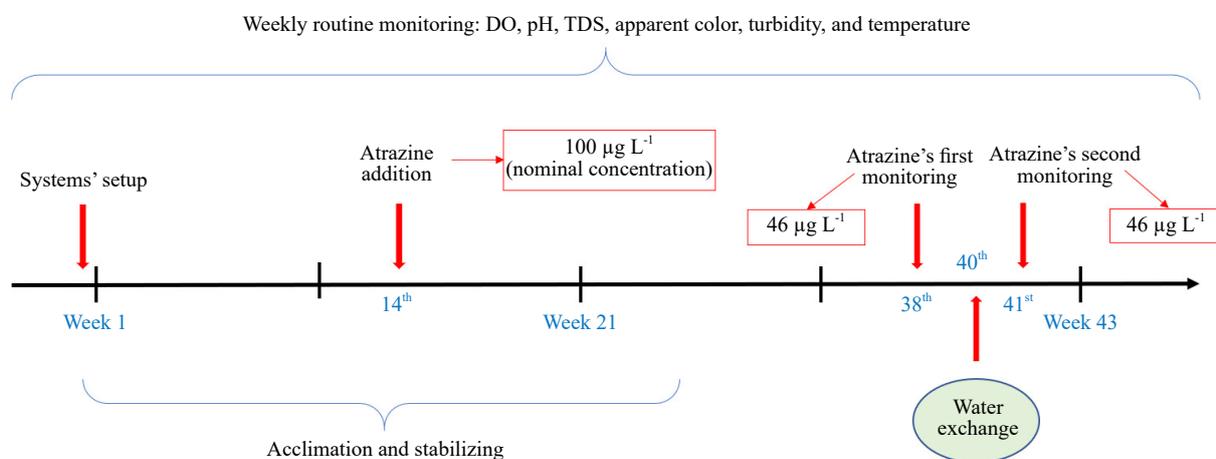
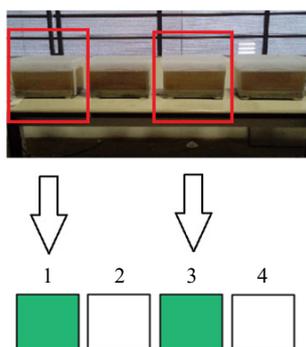


Figure 1. Experimental timeline

## 2.3 Contamination of the systems with atrazine

After the acclimation period, atrazine was added to two of the systems, and the other two were left for control purposes (Figure 2). The atrazine standard used was purchased from Sigma Aldrich, CAS number 1912-24-9. An aqueous stock solution of atrazine ( $30 \text{ mg L}^{-1}$ ) was prepared, and aliquots were carefully added to the systems so as to reach a final nominal concentration of  $100 \text{ µg L}^{-1}$ .



**Figure 2.** Microcosms built in the laboratory containing water and synthetic sediment. The systems marked in red were the ones stressed with atrazine

Vargha et al. [21] used the same concentration on a benchwork scale to simulate atrazine's gradual contamination (in small concentrations) and to approximate the experimental conditions to those of real systems that receive relatively low (though continuous) atrazine loads via leaching and runoff. Although other authors have reported atrazine concentrations in natural waters to range between 0.024 and 28.6  $\mu\text{g L}^{-1}$  [4, 5], a higher concentration was chosen in order to enable direct detection by liquid chromatography coupled to mass spectrometry (LC-MS), saving preparation steps and avoiding risks of sample contamination.

The designated guidelines for atrazine detection through LC-MS were based on the method number 536.0, adapted by Thermo Fischer Scientific and originally devised by the United States Environmental Protection Agency (USEPA) [22], for the determination of trace herbicides in superficial waters. For the analyses hereby executed, the method was slightly modified to fit the characteristics of the equipment in use (Agilent 6460 Triple Quadrupole LC-MS with Jet Stream Technology) and to match the reactants available in the laboratory. The equipment settings are listed in Table 2.

**Table 2.** Equipment setup for atrazine detection through liquid chromatography coupled with mass spectrometry

Column	Agilent ZORBAX Eclipse Plus C18; 2.1 × 150 mm; 3.5 $\mu\text{m}$ (p/n 959763-902)		
Solvent A	Ammonium acetate 5 mM + 0.1% acetic acid		
Solvent B	Methanol + 0.1% acetic acid		
Flow rate	400 $\mu\text{L min}^{-1}$		
Volume of injection	100 $\mu\text{L}$		
Wavelength	230 nm		
Injection gradient	Time (min)	% A	% B
	0	98	2
	10	98	2
	20	10	90
	25	10	90
	25.1	98	2
	30	98	2

Water samples were collected at the subsurface of each cosmos with a small, clean plastic container, positioning the collector at the center of each system. The samples were placed in Falcon tubes of 20 mL and kept refrigerated under -20 °C until the day of analysis. All samples were filtered through 0.45  $\mu\text{m}$  hydrophilic polytetrafluorethylene (PTFE)

filters and analyzed in duplicates.

## 2.4 Systems decontamination

After 265 days (the 38th week), the four systems had their water columns drained and replenished with uncontaminated tap water, leaving a 1-cm-thick sheet of water over the sediment to avoid turmoil. The microcosms were rested for one week before the physicochemical parameters were monitored again.

## 3. Results and discussion

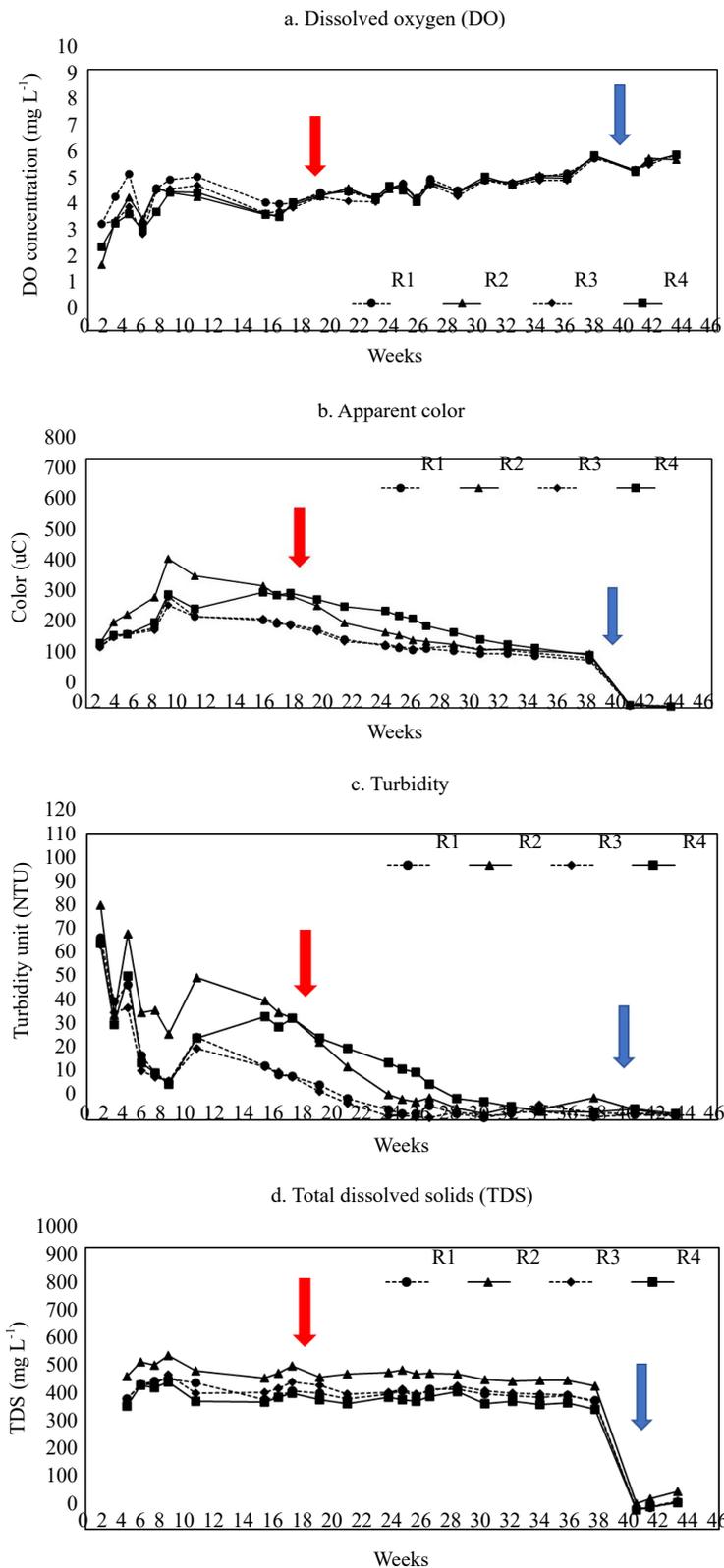
The sand grain distribution analysis showed that the average grain diameter was between 0.14 and 4.75 mm, with 95% of the particle size above 0.15 mm. The specific surface area of the sand grains is relatively small when compared to the dimension of colloidal clay particles ( $d < 0.002 \mu\text{m}$ ) [23], which suggests that clay and peat moss fractions could be the major causes for the retention of atrazine on their surfaces, both due to their chemical and electrostatic properties and due to their extensive contact surfaces [24]. Given that sand (composed of quartz and silicates) does not have electrostatic properties that could favor pollutant retention nearly as similar to clays and organic matter, it is reasonable to conclude that the sand fraction contributed little to atrazine retention (which is related to persistence; once adsorption occurs, it may hinder bioavailability to degrading organisms).

Seybold et al. [25], who have also investigated the adsorption of atrazine in synthetic sediments, did not use sand in the formulation of the sediment employed in the experiments. Instead of synthesizing the sediment gathering fractions of different origins, the authors utilized agricultural soils of the state of Virginia, in the United States, to produce sediments with only the silty and clayey fractions of those (particle diameter  $< 53 \mu\text{m}$ ); likewise, the authors support that those fractions are mostly responsible for herbicide (and other chemical) retention in soils and sediments. In the present study, nevertheless, sand was added in order to attain the recommendations posed by the OECD guidelines [18], enabling the creation of more predictable and controlled environments.

### 3.1 Parameters monitored

The systems took, on average, 23 weeks to achieve equilibrium after the sediment incorporation (the parameters chosen as equilibrium indicators were pH and DO). Atrazine was added only 100 days after the systems were set up (14th week) and had no discernible or significant effect on the tendency monitored between this point and that of the water exchange, as shown in Figures 3 (a) to (d) (red arrow). The water temperature was kept between 18 and 25 °C during the entire monitoring period, holding above 21 to 22 °C most of the time. In the subsequent period (weeks 22 to 37), a rise of 9% in DO concentration in the water column was observed, which can be justified by seasonality in the region (winter period, lower water temperature), favoring DO's solubility. The pH remained within the range of  $7.2 \pm 0.5$  throughout the experiment, most likely due to the acid buffering effect commonly observed in matrices with high organic matter content [26]. After the water exchange as shown in Figures 3 (a) to (d) (blue arrow), some alterations were observed in the apparent color and the concentration of TDS. The former showed evident attenuation, while the latter declined by an average of 90% compared to the moment preceding the water exchange in systems 1 and 3.

The above could be explained by the following hypothesis: the apparent yellow color is usually related to the amount of dissolved organic matter (DOM) in the water column, as discussed by Mitchell [27], Midwood and Felbeck [28], and the U.S. Water Science School [29]. The initial 38 weeks gave it enough time for the system to settle and for part of the sediment's organic matter to dissolve into the water column until the system reached equilibrium. However, when the systems underwent water exchange, the apparent color returned to low marks once the water column was replaced by municipally treated tap water. We could see a soft rising trend after the 43rd week in the TDS (which stands for mostly DOM, like tannin and other organic acids in general [29]), indicating that the apparent color could also intensify in the following weeks. To verify this, the experiment would have to be replicated and left to rest for several weeks after the water exchange before additional measurements could be taken. Regarding the turbidity, the readings showed consistent oscillation in the first 13 weeks, probably due to the acclimation period of the systems. After that, turbidity decreased until it reached equilibrium, from the 27th week on.



**Figure 3.** Monitoring of microcosms system parameters of (a) DO ( $\text{mg L}^{-1}$ ), (b) apparent color ( $\mu\text{C}$ ), (c) turbidity (NTU), and (d) TDS ( $\text{mg L}^{-1}$ ). Red arrows indicate the moment in which atrazine was added to the systems, and blue arrows indicate the moment of water exchange. The dotted lines represent the systems that received atrazine loads (R1 and R3)

### 3.2 Atrazine quantification in the systems

After 150 days of the addition of atrazine to the systems, the initial nominal concentration ( $100 \mu\text{g L}^{-1}$ ) dropped by approximately 50%, being quantified at  $47.5 \mu\text{g L}^{-1}$  in system 1 and  $44.3 \mu\text{g L}^{-1}$  in system 3. No detection signal was registered for atrazine above the equipment's detection limit in systems 2 and 4 ( $10 \mu\text{g L}^{-1}$ ). Likewise, no signal was registered for the samples from the four systems prior to atrazine's contamination. The result obtained is coherent with what has been reported in the literature: atrazine's half-life in the liquid phase of aquatic lentic ecosystems varies, on average, between 60 and 190 days [2, 30, 31].

Atrazine decay in the water column may have occurred through five routes: sorption to dissolved and suspended organic matter, biodegradation, redox reactions, hydrolysis, and photolysis [32]. It is expected that a considerable quantity of atrazine may be complexed with the DOM in the water column once the interaction between the herbicide and this fraction has been reported in the literature by several authors [32-37]. According to Katagi [32], pesticide interaction with the functional groups of dissolved organic carbon (fulvic, humic, and hydrophilic acids) present in the organic matter increases its apparent solubility and can retard or catalyze the compound hydrolysis via adsorption or reaction to these functional groups (carboxylic acids, carbonyls, hydroxyls, and phenolic hydroxyls).

Besides DOM's influence on pesticide persistence in natural waters, sediment particles should be considered as potential adsorbents of atrazine and other chemicals. Droppo et al. [38] showed that sediment flock micropores house a complex web of inorganic compounds, microorganisms, and organic polymers secreted by this bacterial community lodged within the flocks. A similar activity may have contributed to the biodegradation of atrazine in the systems investigated in the present study; moreover, the suspended flocks were removed from the solution in the filtration step, suggesting that part of the mass of atrazine added initially may have been retained or degraded biologically in this phase.

Seybold et al. [30] have studied atrazine's degradation in anaerobic conditions in natural wetlands; the authors discuss that atrazine's concentration is reduced to 50% in approximately 38 weeks in the water and soil of swamped systems and that the methanogenic conditions contribute to the chemical stability of the herbicide because of its low oxidation capacity. This suggests that a considerable amount of the atrazine mass removed from the water may have been preserved in the bottom sediment. The concentration of atrazine metabolites monitored in the water column - hydroxyatrazine (HA) and deisopropylatrazine (DEA) - reached a peak in only 25 days; then, it declined abruptly [30]. This fact indicates that atrazine's biodegradation is likely to be accelerated in the first weeks of its presence in the aquatic system, when it is still reaching equilibrium.

Similar to the results obtained in this study, it is assumed that the gradients present prior to equilibrium (high quantity of suspended soils being deposited or redissolved; DO and pH oscillations) contributed to atrazine diffusing more rapidly between the phases, increasing its contact with the water, solid particles and bacteria present in the medium, and favoring molecular breakup.

Barchanska et al. [35] have concluded that atrazine's adsorption to sediment particles occurs by forming hydrogen bonds between the carboxyl groups of humic acids and the secondary amines of triazine groups. This explains the relatively high octanol-water partition coefficient of atrazine ( $\log K_{ow} = 2.61$ ) and points to its hydrophobicity as a determining factor dictating its distribution in the environment.

Although organic carbon may have a key role in the adsorption of organic pollutants to soils and sediments, Katagi [32] has encountered values of  $K_{OC}$  for atrazine in the order of  $10^2$ , which is lower than the majority of the known persistent organic pollutants (whose coefficient ranges from  $10^3$  to  $10^7$ , according to Felix et al. [3]). Thus, despite demonstrating considerable affinity for organic matter, atrazine has higher mobility between the sediment and the water column than the majority of the organic persistent pollutants currently listed, considering that the bottom sediment is usually rich in organic matter [39].

Atrazine transformation through biodegradation, hydrolysis, and oxi-reduction are the most reported in the literature, producing intermediate metabolites such as hydroxyatrazine, desethyl-desisopropyl-hydroxyatrazine and N-dealkylated atrazine [2, 24, 30, 40]. Although known from the literature, these metabolites were not monitored in this study due to the tight schedule of experiments and some instrumental impairments.

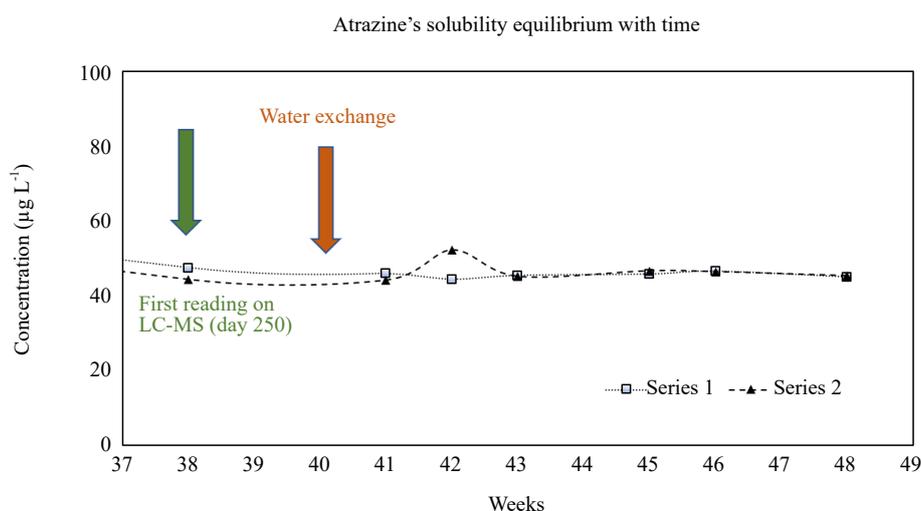
Atrazine can also undergo photolysis, although this degradation path is not pointed to as one of the main mechanisms of degradation of atrazine in aquatic ecosystems, possibly due to its small contribution to the process when compared with other degradation routes [24]. Katagi [32] supports the idea that the compound's biodegradation in the

sediment occurs primarily by dealkylation (the loss of an alkyl radical,  $C_nH_{2n+1}$ ), whereas atrazine's abiotic degradation occurs by hydrolytic substitution of the chlorine in position six (the breakdown of the chemical bond by the addition of a water molecule), catalyzed by acids. The author adds that, in the case of tests carried out in micro- and mesocosms, the contribution of photodegradation is limited to shallow water columns. In the results obtained in this work, however, it has been admitted that the contribution of photolysis to atrazine degradation was negligible, since the systems were hindered from daylight most of the time, being subjected to poor illumination mostly on occasions of sample collection and monitoring. In order to assess the exact contribution of each of atrazine's degradation routes to its mineralization in the conditions described, further studies are required.

Besides undergoing transformation in the water column, atrazine can also suffer biological, physical, and chemical transformations in the bottom sediment. Katagi [24, 32] have demonstrated that the sediment interstitial pores show a different dynamic than that of the water column and are directly involved in the process of physicochemical partitioning of pesticides in a water body. As the sediment is an overly complex compartment constituted by minerals, organic matter and living organisms, factors such as the sediment's adsorption capacity for pesticide molecules, redox potential, and amount of biomass in the matrix may also affect the fate of a persistent compound in the environment. Nevertheless, in the systems reproduced in this study, benthonic organisms were left out, and their contribution can therefore be disregarded, so that only microbiological interactions with the herbicide were considered.

### 3.3 Water column exchange and replenishment

Three weeks after the water exchange in the systems, the concentration of free atrazine in the water column returned to the previous equilibrium value ( $46 \mu\text{g L}^{-1}$ ), as shown in Figure 4.



**Figure 4.** Atrazine concentrations detected in the microcosms immediately before (green arrow) and three weeks after (orange arrow) the water exchange in the two contaminated systems

It was expected that the sediment would work as a sink for atrazine, causing a reduction in its concentration in the water column due to the compound's adsorption to the clay particles and organic matter present in the bottom sediment. However, the sediment worked as a repository for this pollutant in the stressed systems (R1 and R3). This may have happened because of the weak interaction between the atrazine molecule and the functional groups of the organic matter; besides, the synthesized sediment bears a smaller quantity of organic carbon and clay than the natural tropical sediments. It is anticipated that atrazine's adsorption would be higher. Another possible explanation is that the systems did not suffer any significant turmoil, such that atrazine could have been adhered only to sedimented particles at the water-sediment interface, which could have enabled its constant redissolution into the water column.

## 4. Conclusion

Atrazine concentration in the water column suffered a reduction of approximately 50% (from 100 to 46  $\mu\text{g L}^{-1}$ ) after 150 days from its addition to the systems. The compound decay may be attributed to the adsorption of atrazine to the particles of the sediment as well as to the physicochemical processes that may have been responsible for atrazine's breakdown, such as biodegradation, hydrolysis, oxi-reduction and photolysis, though the last one has been disregarded in this study due to its scarce mentioning in the literature.

Apart from its probable degradation in the water column, atrazine may also have suffered degradation in the interior of the suspended sediment flocks or been adsorbed to the bottom sediment. Part of the initial mass added to the systems may have been complexed with the DOM in the inner pores of the sediment and preserved under the anaerobic conditions of the interstitial waters, establishing a hypothesis for why atrazine persists in aquatic lentic environments.

The water exchange in the microcosm reservoirs did not affect the concentration equilibrium of atrazine throughout the whole experiment, demonstrating that sole water decontamination may not be enough to maintain atrazine concentration values below those permitted by Brazilian law (2  $\mu\text{g L}^{-1}$ ). Furthermore, this conclusion highlights the need for specific and more strict regulations regarding sediment quality assessment, establishing maximum deposition limits for atrazine and other compounds in this environmental compartment, given that water quality monitoring may not be enough to represent the overall environmental quality of a water body with respect to the contaminant of interest.

## Conflict of interest

The authors declare no conflict of interest for this study.

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