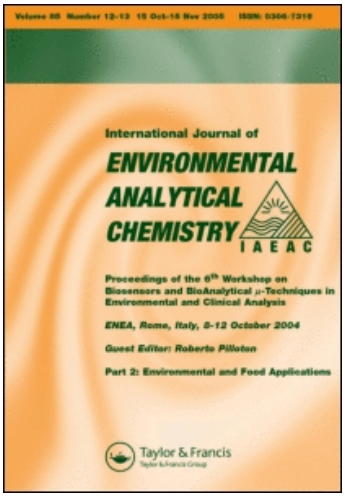

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Studying the photochemical fate of methyl parathion in natural waters under tropical conditions

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This article discusses the degradation of methyl parathion (MP) in natural and sterilized waters. Experiments were prepared using natural waters gathered in two aquatic systems (Rio de Janeiro State, Brazil), ultra-pure water and humic water solution under different conditions (i.e. in the presence/absence of light, sterilized/no sterilize solutions). The exposition to sunlight was carried out using experimental bottles without headspace immersed in a swimming pool for temperature control. Natural waters results showed that the degradation kinetic of MP is of first order and the half-lives for lake water experiments, under direct sunlight and shade, were 4.41 and 6.89 days, respectively. The kinetic curve for MP degradation in river waters showed that there are no differences when samples were sterilized and placed (or not) under shade conditions, and the half-lives ranged from 5.37 to 2.75 days for sterilized river water/absence of sunlight and natural/presence of sunlight, respectively. Therefore, our results showed that photolysis plays, in addition to bio- and chemical degradation, an important role in the decomposition of MP in aquatic environments.

Keywords: Methyl parathion; Photolysis; Natural waters; Hydrolyse

1. Introduction

The deposition of pesticides in the environment affects a wide number of living organisms which are not regarded as agricultural pests. The fate of pesticides in the environment is controlled by different processes such as retention, transformation, and transportation. The assessment of a pesticide environmental risk at a specific site is defined by the kind and dosage of the substances being used; its partitioning into air, soil, vegetation, surface water, and groundwater; the rates of degradation and persistence in each environmental compartment; the bioconcentration potentials in animal tissues; and the toxicity levels. Light-induced processes are among the most important degradation pathways for pesticides. These processes include direct photolysis in which a pesticide absorbs light and/or through photosensitization

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of dissolved components in water (e.g. natural organic matter, nitrate ions or iron (III)) [1–4].

Abiotic degradation of pesticides in natural conditions depends on many variables, such as location, natural physicochemical characteristics of water (pH, dissolved organic material, and others species) and climatic conditions (temperature, solar irradiation intensity, etc.). As a result, there are many conditions that affect the fate of the micro-pollutants in aquatic environments in different parts of the planet. However, most studies on natural waters under solar exposition were carried out in the Europe [5–12] and North America [13]. This literature, built on northern-hemisphere sites, also provides evidence about the influence of temperature [12] in the kinetics of degradation, focusing on the hydrolyse decomposition. However, it is important to note that very different conditions of temperature and solar irradiation can be found in tropical countries.

Organophosphorus pesticides are becoming highly favoured to replace organo-chloride compounds because of a widespread perception that these compounds have a relatively low persistence in the environment [14]. However, previous works have shown that such expectation is not accurate because some organophosphorous compounds can persist in soil, water, and sediment for at least 12 months [12, 15]. Moreover, even a low half-life does not necessarily indicate their total elimination from the environment. This fact is aggravated by the development of byproducts during the degradation process which are often more toxic than the original compounds [5, 6, 16]. Impacts from this compound class occur in living organisms by suppressing acetylcholinesterase activity and affecting the nervous system [17]. According to Patrick [17], this effect only occurs when organophosphorous pesticides are converted into analogous compounds, where a P=S bond is oxidized into P=O. Patrick also affirms that although mammal organisms are not capable of metabolizing organophosphorous compounds, insects can promote their oxidative desulfurization through metabolic processes which ultimately lead to their death.

This article presents a study on the photochemical behaviour of Folisuper-600Br^{TM} (Agripec; ingredient active: methyl parathion) in natural waters under sunlight in the southeast Brazil. These experimental conditions are deemed to be highly important because many studies about the fate of organophosphorous compounds in the environment found in the literature [1, 2, 5, 15, 18] were carried out using synthetic water, artificial light, or sunlight from non-tropical regions. Finally, our study has given special attention to the simulation of natural conditions, a dimension which is often neglected in most studies about the fate of micro-pollutants in the environment.

2. Experimental

2.1 *Materials*

The commercial formulation of methyl parathion (active ingredient: methyl parathion, 600 g L^{-1}), Folisuper-600BR^{TM}, was purchased from Agripec (Ceará, Brazil). Methyl parathion (99.8% purity) was purchased from Riedel-de Haën (Seelze, Germany). Pesticide-grade ethyl acetate was obtained from TediaBrazil (Rio de Janeiro). The anhydrous sodium sulfate was purchased from Quemis (São Paulo) and was heated to

400°C for 4 h before use. Humic acid-sodium salt was purchased from Sigma/Aldrich (Steinheim, Germany). The stock solution of 5.5 mg L^{-1} of humic acid (HA) was prepared according 40-CFR EPA (40-Code Federal Regulations—Environmental Protection Agency) Test Guidelines for Indirect Photolysis [19]. The Super Optimal Broth (SOB) medium agar was prepared with tryptone, and yeast extract, NaCl, KCl, $MgCl_2$, and agar were purchased from VETEC (Rio de Janeiro). Tryptone and yeast extract provide sources of nitrogen and growth factors, which allow the bacteria to recover from the stress of adaptation and grow well. Sodium chloride provides essential ions. Magnesium sulfate is a source of magnesium ions required in a variety of enzymatic reactions, including DNA replication. All the other chemical compounds used were of analytical grade. Water was purified using a Milli-Q system from Millipore-Waters Co. (Mississauga, ON, Canada).

The borosilicate bottles with a capacity of 40 mL were supplied from Wheaton (Millville, NJ). Light attenuation by glass was 14% at 300 nm, 21% at 310 nm, 32% at 300 nm, 52% at 290 nm, and 74% at 280 nm. These attenuation rates were smaller than those cited by Vialaton and Richard in their work [7]. All glassware was cleaned using a 10% alkaline Extran HA 01 (Merck, Rio de Janeiro) solution by immersion. The complete cleaning was done by rinsing with pesticide-grade solvents.

2.2 *Natural waters sampling*

Natural waters used in experiments were collected in Campos dos Goytacazes, the most important municipality in the northern region of Rio de Janeiro state, Brazil. This region has a high agricultural activity dominated by extensive plantations of sugar cane and pineapple.

Water samples were collected from the Zumbi dos Palmares Lake (latitude 21° 35.560′ S and longitude 41° 11.650′ W), in November 2005, and from the Paraíba do Sul River (latitude 21° 45′ 15″ S and longitude 41° 19′ 28′W) in March 2006. Natural water samples were gathered from the top metre of both aquatic bodies. We determined pH and dissolved oxygen in the field (table 1). The dissolved oxygen was measured with oxygen metre (Lutron DO5510), and the pH was determined with a pH metre (Lutron pH 206).

Natural water samples were filtered through a 11-μm qualitative filter (Whatman no. 1) and divided into two parts: (1) natural water for direct use in the degradation experiments; (2) autoclaved at 120°C and 1.1 atm for 20 min. Some of the physicochemical properties of these natural waters and stock solution of humic acid are displayed in table 1.

Sterilization efficiency and qualitative information about microbial population was proven by plating (in duplicates) lake and river water (25 μL), natural and sterilized, on SOB medium agar in sterile conditions. Plates were maintained for 24 h at 37°C, in a stove with 5% of carbon dioxide. After the incubation period, plates were analysed, and results were recorded using a digital camera (figure 1).

2.3 *Degradation experiments*

Lake water (‘in natura’ and sterilized) and river water (‘in natura’ and sterilized), and humic acid solutions were spiked with Folisuper-600Br^{TM}. The actual concentration of

Table 1. Physicochemical properties of the natural waters before being spiked with methyl parathion.

	Lake water		River water		
Sample/analysis	'In natura'	Sterilized	'In natura'	Sterilized	Humic acid solution
pH[a]	6.60	–	7.20	–	–
Dissolved oxygen ($mg\,L^{-1}$)[a]	1.1	–	5.2	–	–
pH	6.8	7.0	7.8	8.0	7.0
Conductivity ($\mu S\,cm^{-1}$)	290	312	72	79	1995
TOC[b] ($mg\,L^{-1}$)	15.7	19.4	8.6	6.4	6.5
K^+ ($mg\,L^{-1}$)	5.86	5.86	2.74	3.13	na[c]
Na^+ ($mg\,L^{-1}$)	42.55	42.55	5.29	6.21	na
Ca^{2+} ($mg\,L^{-1}$)	13.17	14.29	8.08	8.29	na
Mg^{2+} ($mg\,L^{-1}$)	7.45	9.65	1.71	1.46	na
Fe^{3+} ($mg\,L^{-1}$)	1.45	2.05	1.90	2.25	na
Cu^{2+} ($mg\,L^{-1}$)	nd[d]	nd	nd	0.01	na
Zn^{+2} ($mg\,L^{-1}$)	0.01	0.02	nd	0.01	na
Mn^{2+} ($mg\,L^{-1}$)	0.01	0.03	nd	nd	na
Carbonate ($mg\,L^{-1}$ CO_3^{2-})	nd	nd	nd	1.95	na
Bicarbonate ($mg\,L^{-1}$ HCO_3^-)	14.94	15.40	13.11	11.44	na
Sulfates ($mg\,L^{-1}$ SO_4^{2-})	4.20	4.00	4.70	4.50	na
Chlorides ($mg\,L^{-1}$ Cl^-)	50.00	52.00	3.00	2.00	na

[a]Measures done in the field. [b]Total organic carbon. [c]na: not analysed. [d]nd: not detected.

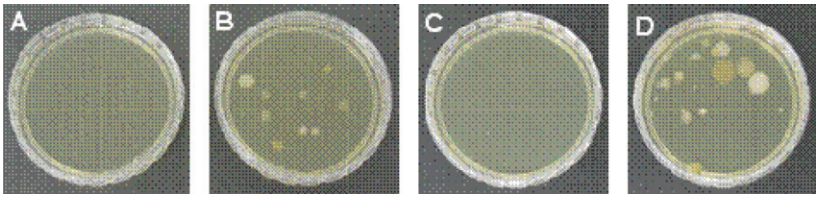


Figure 1. Plates after being spiked with different kind of waters (25 μL), inoculation in SOB medium and incubation period (24 h at 37°C). (a) filtered and sterilized lake water; (b) filtered lake water; (c) filtered and sterilized river water; and (d) filtered river water.

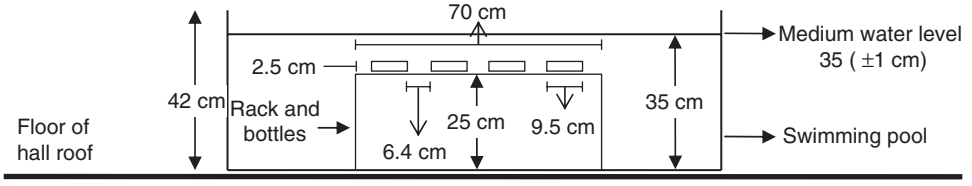
methyl parathion in the commercial formulation was determined by gas chromatography prior to this procedure, and the result was 585.00 ($\pm$4.71) $g\,L^{-1}$. Initial concentrations of methyl parathion in each solution are described in table 2.

Irradiation experiments under sunlight were conducted at the top of the Sciences and Technologies Centre building at the Universidade Estadual do Norte Fluminense (Rio de Janeiro, Brazil). The first experiment was carried out between 21 November 2005 and 11 December 2005, and the second between 5 March 2006 and 18 March 2006. Experiments were performed using a borosilicate bottle of 40 mL without head space immersed in a swimming pool for temperature control (scheme 1 and figure 2). Some bottles were immersed in the pool covered with aluminium foil for hydrolysis control (figure 2a). The borosilicate bottle totally absorbed the irradiation bellow 250 nm and approximately 50% next to 290 nm. Given the low quantity of photons with wavelength below 290 nm and anywhere below 280 nm arriving on the Earth surface [20], we inferred that the use of borosilicate glass did not represent interference in our experimental results.

Table 2. Methyl parathion experimental using natural waters.

Experiment	Solution		Exposure	Code	I.C. ($\mu g\,L^{-1}$)[a]	Sample day no.
1	Lake	'In natura'	Bright	LNB	209	i[b], 1, 2, 3, 4, 6, 7, 9, 11, 13.
			Shadow	LNS		i, 1, 3, 6, 7, 9, 11, 13.
		Sterilized	Bright	LSB	224	i, 3, 6, 9, 13.
			Shadow	LSS		i, 3, 6, 9, 13.
	HA	–	Bright	HAB1	185	i, 1, 2, 3, 4, 6, 7, 9, 11,13.
2	River	'In natura'	Bright	RNB	187	i, 1, 2, 3, 4, 5, 7, 9, 11, 13.
			Shadow	RNS		i, 1, 3, 5, 7, 9, 13.
		Sterilized	Bright	RSB	210	i, 1, 3, 5, 9, 13.
			Shadow	RSS		i, 3, 5, 9, 13.
	HA	–	Bright	HAB2	218	i, 1, 2, 3, 4, 5, 7, 9, 11, 13.

[a]Initial concentration (I.C.) of methyl parathion at samples. [b]Initial time; L: lake water; R: river water; N: natural; S: sterilized; B: bright; S: shade; HA: humic acid.



Scheme 1. Schematic representation of the experimental swimming pool.

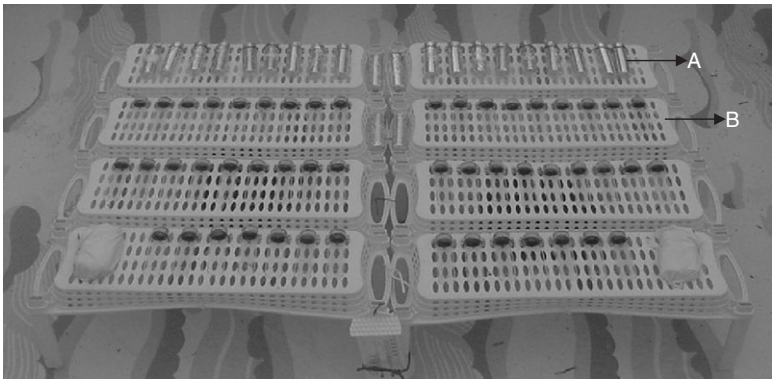


Figure 2. Borosilicate bottles immersed in the water and exposed to sunlight (frontal vision). (a) shade bottle; (b) bright bottle.

Pesticide concentration was determined by a liquid–liquid extraction followed by CG/MS, in duplicates, at the beginning of each experiment (initial time) and in each of the daily samples (table 2). Environment and swimming pool water temperatures were measured using a thermometer of maximum and minimum temperatures (Incoterm, Rio Grande do Sul, Brazil). Solar irradiation and precipitation were measured using a Pyranometer CM 11 no. 7.1415.01.000 from Adolf Thies & Co.KG (Göttingen, Germany) located in a meteorological station located at the campus of the Federal Rural University of Rio de Janeiro (21° 75′ S; 41° 30′ W and 11 m height). The spectral range analysed by Pyranometer was 305 and 2800 nm. Samples received approximately

Table 3. Climatic conditions during the degradation experiments.

		Inside water temperature (°C)		Outside water temperature (°C)		Average irradiation ($W\,m^{-2}$)		
Experiment	Season	Max.	Min.	Max.	Min.	All day	5 a.m.[a]–6 p.m.[b]	Precipitation (mm)
1	Fall[c]	30[d] (2)	23 (2)	36 (2)	21 (3)	244	437	85
2	Summer[c]	32 (1)	25 (2)	43 (2)	22 (2)	243	431	39

[a]Approximate time of sunrise. [b]Approximate time of sunset. [c]Seasons in Brazil (5–18 March 2006 and 21 November to 11 December 2005). [d]Mean temperature (SD).

Table 4. Recovery ratios and calibration curves for the experimental matrices.

Samples	Calibration equation	R^2	%R (SD)
Lake water	$y = 138.7x - 1483.5$	0.9943	66 (6)
Lake water—sterilized	$y = 58.6x - 281.0$	0.9984	56 (4)
HA solution	$y = 93.6x + 299.8$	0.9940	86 (1)
River water	$y = 132.0x - 672.6$	0.9990	64 (5)
River water—sterilized	$y = 122.7x - 682.0$	0.9964	70 (8)
HA solution	$y = 65.9x - 277.7$	0.9962	86 (1)

13 h of sunshine daily (≈ from 5 a.m. to 6 p.m.). Table 3 contains the most environmental conditions present in the study.

2.4 *Extraction and analysis*

Water samples of 25 mL were extracted three times with aliquots of 10 mL of ethyl acetate with 2.5 g of NaCl and dried with Na_2SO_4. The extracts were reduced to 0.5 g and injected in the system GC-MS (gas chromatograph with mass spectrometer) (Shimadzu GC-17A and MS-QP 5050) using the Single Ion Monitoring (SIM) mode (injection volume: 1 µL; split ratio of 15). Ions monitored for methyl parathion detection were: m/z 263, 125, 109, and 79. A DB-5, fused-silica capillary column (J&W Scientific, Folsom, CA) of 30 m, film thickness was 0.25 µm and an internal diameter (i.d.) of 0.25 mm was used. The programmed temperatures were: 100°C for 1 min, 100–280°C with a $12°C\,min^{-1}$ rate, and 280°C for 1 min. Helium was used as the carrier gas. Temperatures were set at 250°C for the injector and 280°C for the detector. A split ratio of 15 and a detector gain of 1.5 kV were used.

2.5 *Quantification and recoveries*

A standard-addition calibration method was used to quantify the extracts injected by GC/MS and to calculate the half-lives of methyl parathion in different matrices. All curves were separated according to their respective matrices (i.e. lake and river water, no sterile and sterile, and HA solutions). Water samples were spiked with Folisuper-600Br^{TM} to create solutions with a known concentration of methyl parathion. Curves with five points—198.1, 148.6, 99.1, 49.6, and 9.9 $\mu g\,L^{-1}$ (in duplicates)—were constructed (table 4). The methyl parathion recovery ratio was determined by

Table 5. Kinetic data from lake-water MP degradation.[a]

	LNB	LNS	LSB	LSS	HAB1
k (day^{-1})	0.1570	0.1070	0.1554	0.0286	0.2300
R^2	0.82	0.77	0.88	1.00	0.97
$t_{1/2}$ (day)	4.41	6.48	4.46	24	3.01
Degradation after 13 days (%)	91	84	89	32	97

[a]L: lake water; N: natural; S: sterilized; B: bright; S: Shadow; HA: humic acid.

comparing peak areas from water samples spiked with a known amount of methyl parathion Folisuper-600BR^{TM} (198.1 μg L^{-1}) to non-extracted pure standards.

3. Results and discussion

3.1 *Importance of experimental conditions*

Our first experiments using only ultrapure water showed an increase in the temperature inside the experimental bottle when exposed directly to sunlight (47°C), a condition that differs highly from the temperatures found in surface waters even in tropical countries. In addition, results of the kinetic degradation of methyl parathion in experiments carried inside (22°C) and outside (47°C) the laboratory (with direct solar exposition) showed a large temperature influence in the hydrolysis of the studied compounds. The resulting half-lives were 32 and 12 days, respectively. As described previously, a swimming pool was used to minimize and control changes in temperature, and the silicate bottles were immersed in the water in a depth of 1 cm to avoid light refraction and loss of intensity. The maximum and minimum temperature measured outside and inside the swimming pool showed a small difference within 14 days of the experiment, ranging from 25 (inside of the laboratory) to 32°C (outside), and the hydrolysis process was small, with half-lives of 32 days for both experiments. Similar outcomes were found by Noblet *et al.* [12], who observed a variation in the half-life of 96–10 days in the degradation of the methyl parathion in pure waters when temperature values varied from 32 to 40°C. All experiments were then carried out in the swimming pool.

3.2 *Decomposition of methyl parathion in lake water*

Results of lake water degradation showed that the kinetic of methyl parathion degradation is of first order (table 5), except for lake water in the shadow (LNS), where R^2 is 0.77, and a different profile curve was obtained for the variation of concentration during the experiment (figure 3). These results allowed the identification of hydrolysis, biodegradation, and photolysis processes. First, experiments conducted with sterilized lake water under shade conditions (LSS) showed that hydrolysis is responsible for the degradation of 32% of MP. The lowest half-life was found under LNS, showing the influence of biodegradation processes in natural waters. The contribution of biological processes can also be observed in the differences found between LNS (lake water non-sterilized in the shadow) and LSS conditions. In fact, the profile of MP concentration decay in the lake water shows a similar behaviour in the first day of exposure, but the

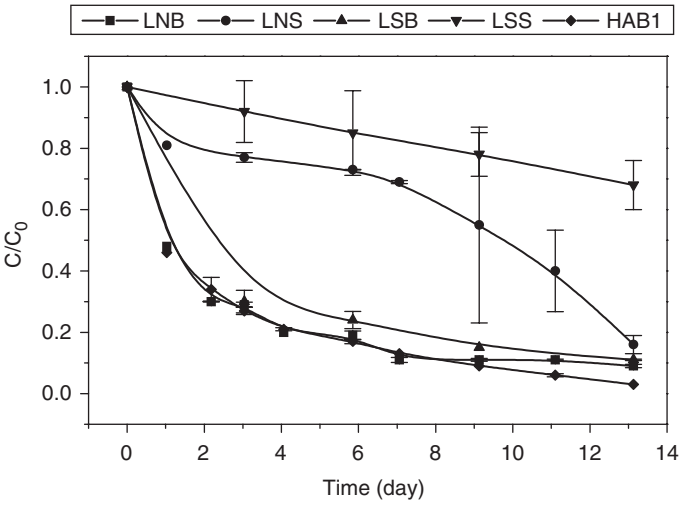


Figure 3. Degradation of MP in lake waters in natural conditions and in the presence of humic acid.

MP degradation rate is higher in the non-sterilized system (LNS) 6 days later (figure 3). On the other hand, when the systems were exposed to sunlight (LNB: lake-water natural bright; LSB: lake-water sterilized bright) the results showed that photolysis is a predominant process under biotic conditions (table 5). The comparison of MP degradation from natural water and HAB1 (humic acid bright 1) samples indicated a similar degradation profile between the two samples but a different half-life (i.e. LNB 4.41 day and HAB1 3.01 day). This latter result is probably a reflex of the lake water characteristics. On the other hand, the small difference in half-life does not seem to preclude the use of synthetic waters to preview abiotic degradation in natural systems.

3.3 *Decomposition of the methyl parathion in river waters*

Differently from lake waters, kinetics data from MP degradation in river waters showed minor differences when the water samples were sterilized and kept under shade conditions (figure 4 and table 6). Similar degradation and half-lives ($t_{1/2}$) were observed in all experiments, showing a small difference in the system exposed to irradiation and important abiotic processes caused by compounds found in the river water. However, irradiated samples showed an inferior half-life (i.e. RNB (river-water natural bright)—2.75 days; RSB (river water sterilized bright)–3.47 days; and HAB2 (humic acid bright 2)—2.82 days) than shade samples (i.e. RNS (river waters natural shade)—3.72 days and RSS (river water sterilized shade)—5.37 days). Sterilized samples showed a higher $t_{1/2}$ than natural samples. The $t_{1/2}$ and decay profile obtained for HAB2 were similar to HAB1, showing data reproducibility for artificial samples.

The observed differences in the degradation profiles between lake and river waters for no irradiated and sterilized samples can be explained by the physicochemical characteristics of the water samples which control (and probably stabilize) the hydrolysis process. The two natural-water samples showed differences in pH, dissolved organic material, and high ion concentrations (table 1). Other studies have reported

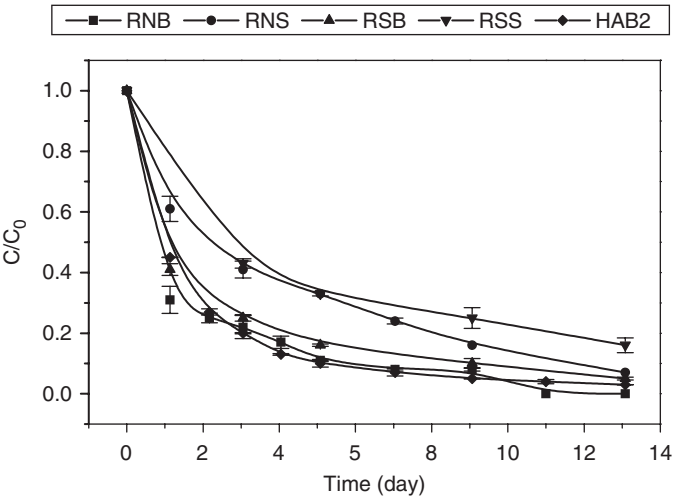


Figure 4. Degradation of MP in river waters in natural conditions and in the presence of humic acid.

Table 6. Kinetic data from river water MP degradation.[a]

	RNB	RNS	RSB	RSS	HAB2
k (day^{-1})	0.2523	0.1863	0.1996	0.1291	0.2457
R^2	0.85	0.98	0.91	0.92	0.90
$t_{1/2}$ (day)	2.75	3.72	3.47	5.37	2.82
Degradation after 13 days (%)	100	93	95	84	97

[a]R: river water; N: natural; S: sterilized; B: bright; S: Shadow; HA: humic acid.

greater degradation rates when pH values rise [21, 22]. Sakellarides *et al.* [5] affirm that pH differences (5.9 for distilled water to 8.5 for lake water) did not strongly influence degradation rates. Although there is a difference from pH values between lake water and river water, 7.0 and 8.0, respectively, this condition does not seem to be sufficient to explain the different behaviour observed in our study. A document produced jointly by the United Nations Environmental Program and Food and Agricultural Organization of the United Nations about methyl parathion shows that hydrolytic stability decreases with increasing pH values [23]. Significant differences in dissolved organic material and ion concentration found in both lake and river waters may provide a better explanation for our different profiles of MP degradation. Other studies about degradation of methyl parathion in different naturals waters, either in the presence or absence of sunlight [5, 22] or only under sunlight [8], demonstrate the complexity of pesticide behaviours and the difficulty surrounding their comparison in different environments. For instance, Lartiges and Garrigues [22] observed acceleration in degradation after sunlight exposure of samples collected in the Bourdeu River water but an inverse behaviour in seawater samples. Sakellarides *et al.* [5] have also observed greater degradation rates in waters irradiated with sunlight, and significant differences between samples collected from different aquatic ecosystems. For example, the half-lives for lake and river waters were 25.6 and 24.6 days, respectively, while the half-life for seawater was 27.6 days.

However, when groundwater and distilled water samples were analysed, similar or higher half-lives were observed (i.e. 27.5 days for groundwater and 35.4 days for distilled water). Finally, Castillo *et al.* [8] observed a lower half-life (3 days) when groundwater samples were compared with other water samples (4 days for river water).

4. Conclusions

Our results show that in order to enhance the understanding of pesticide degradation pathways in aquatic environments, we must include the study of photolysis, hydrolysis, and biodegradation processes. Degradation results of lake water showed that the degradation kinetics of methyl parathion under solar irradiation is of first order and faster than in a shade bottle. The half-lives for experiments under irradiation and in the shade were 4.41 and 6.89 days, respectively. Experiments conducted in the shade showed that the hydrolysis process was responsible for degrading 32% of MP in sterilized lake water. The estimated half-life for this sample was the highest (24 days), showing the importance of both the biodegradation and photolysis processes for methyl parathion. Kinetics data from MP degradation in river water samples showed no difference when the water was sterilized, and a similar degradation and $t_{1/2}$ were observed in all experiments. Moreover, our findings regarding the different behaviours of the organophosphorous MP in two kinds of aquatic systems reinforce the need to further study the fate of pesticides compounds in the environment.

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