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Photolysis of chlorpyrifos in various aqueous solutions

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ABSTRACT

Kinetics of degradation of chlorpyrifos, an organophosphorus insecticide; widely used for pest control of various crops, has been investigated in different aqueous solutions using sun and UV light; in presence of calcium Ca (II), potassium K (I), magnesium Mg (II) and phosphorus PO_4^{3-} ions at 0.1 M and 0.01 M; chosen as major useful elements for crops in soil solution. Degradation of chlorpyrifos under pH (6 and 8) and temperature (22 ± 2 °C and 40 ± 2 °C) was also studied. Our results show that the degradation in all solutions tested in this study exhibited pseudo-first-order kinetics. The degradation rate of chlorpyrifos increases with the presence of Ca and K at 0.01 M under sun light irradiation and in the presence of Mg and P at 0.1 M under UV irradiation.
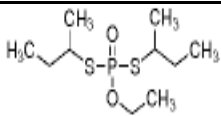
Keywords: Chlorpyrifos; Insecticide; Pollution; Hydrolysis; Minerals; Photolysis; Solar and UV irradiation

INTRODUCTION

Modern agriculture depends heavily on the use of agrochemicals such as pesticides. Throughout the 1990s, insecticide sales occupied up to 79 % worldwide (Zhang et al., 2011). Organophosphorus is the most widely used pesticide. Chlorpyrifos [O,O-diethyl-O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate] is an organophosphate insecticide, acaricide and miticide used to control foliage and soil-borne insect pests on a variety of food and feed crops, such as grain, cotton, fruit, and vegetable crops, as well as lawns and ornamental plants (Fang et al., 2006). However, part of the applied pesticides could contaminate the environment, especially groundwater (Gonçalves et al., 2007). This presence should be take in consideration due to the potential toxicity of pesticide towards fauna and humans, particularly chlorpyrifos which was noticed to be highly toxic to aquatic organisms, and a potent developmental neurotoxin at low levels of exposure (Eamkamon et al., 2012). The chemistry of the aquatic environment where pesticide is

present was identified as one of many factors influencing pesticide fate. Indeed, the processes of evaluation involve evaluating the interactions of pesticide molecules with dissolved and particulate components in aqueous solutions. Several dissolved metallic ions have been reported to promote the hydrolysis of organophosphorus pesticides, with various reasons forwarded as to the intimate mechanism of metal ion promoted hydrolysis. Several postulates have suggested metal ion co-ordination of Lewis sites to be an important factor in promoting the reaction (Meikle and Youngsong, 1978). On the other hand, different methods for water decontamination have been developed, including photochemical processes under different irradiation conditions (Gafar, 2010). Photochemical degradation of pesticides can be important in the decontamination of natural water or contaminated soils. The photochemical methods involve either a direct photodegradation reaction of pesticides by UV light, or indirect photodegradation

Table 1. Main physical-chemical properties of chlorpyrifos insecticide (Footprint 2012)

Pesticide	Chemical structure	M.M (g/mol)	S.W (mg/L)	V.P (mPa)	Kd (L mg/Kg)	$T_{1/2}$ Water(d)	$T_{1/2}$ Soil(d)
Chlorpyriphos		350.89	1.05	1.43	300	25.5	21

MM- molecular mass, S.W- solubility in water at 20 °C, V.P- vapour pressure at 25 °C, Kd- adsorption coefficient, $T_{1/2}$ water- Chlorpyrifos half life in water (day), $T_{1/2}$ soil- Chlorpyrifos half life in soil (day).

processes including H_2O_2 photolysis or photo-Fenton reagents (H_2O_2/ Fe^{3+}) (Aaron and Oturan, 2001).

Although gas chromatography coupled with mass spectrometry or liquid chromatography with diode array detection have traditionally been used for the determination of pollutants in solutions, spectrophotometric analysis has gained increased popularity for this propose in the latest years. In the present work, we have investigated the effect of pH (6 - 8) and temperature (22 – 40 °C). Also we have simulated the chemistry of aqueous solutions of soil by adding calcium, potassium, magnesium and phosphorus ions to study their effects on the hydrolysis of chlorpyrifos under sun and UV light irradiation. The analyses of samples were performed using UV spectrophotometer.

MATERIALS AND METHODS

Chemicals

Chlorpyrifos [O,O-diethyl-O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate] was purchased from Cluzeau, France. Its purity was > 99 %. All solvents were of high performance liquid chromatography (HPLC) grade and from Sigma-Aldrich, France. Table 1 shows structure as well as some physical-chemical properties of chlorpyriphos. Standard solutions were prepared in methanol (100 mg/L). Working solutions of chlorpyrifos of concentration 4 mg/L were used in this study.

Hydrolysis experiments

The hydrolysis of chlorpyrifos was studied under two parameters: pH and temperature. The effect of pH on degradation of chlorpyriphos was studied in buffered solutions at pH 6 and 8. pH solutions were prepared as described by Weast (1977). Chlorpyrifos degradation was also observed under temperature conditions. Two temperatures were chosen 22 ± 2 °C (room temperature) and 40 ± 2 °C (Thermo scientific bain-marie). A scanning of wavelength have shown a maximum absorbance of chlorpyrifos (4 mg/L) at λ = 290 nm.

Photolysis experiments

Photolysis of chlorpyrifos was carried out under laboratory conditions at room temperature and natural sunlight. Five different solutions were prepared in distilled water by adding Ca^{2+} ($CaCl_2$), K^+ (KCl), Mg^{2+} ($MgSO_4$), and PO_3^{-4} (KH_2PO_4) at 0.1 M and 0.01 M further control one (C) in order to investigate any catalytic effects of those minerals. All prepared solutions have also shown a maximum absorbance at 290 nm.

The solutions were irradiated for the first part by natural sun light. In the second part they were prepared in Pyrex beakers reactor. The samples were irradiated continuously for 2 hours using the lamp High-pressure mercury lamp HPLK 125W-Phillips. All solutions were stirred using magnetic stirrer and samples from considered solutions were taken at regular time intervals (10 min) and then analysed directly without preconcentration by UV 1600 Mapada photometer set at 290 nm. The pH (7) and temperature (22 ± 2 °C) remained constant during experiment. All experiments were performed in duplicate. Test controls were incubated in the dark to ensure that the transformation of chlorpyrifos was only due to light absorption. The concentrations were determined from the calibration curve (concentration vs absorbance) produced from known concentrations.

RESULTS AND DISCUSSION

Effect of pH

Many organophosphorus insecticides are particularly susceptible to hydrolysis under different pH conditions. Chemical hydrolysis of chlorpyrifos was investigated at buffered solutions of pH 6 and pH 8. Data was fitted to first order model. All plots of ln (C/C_0) versus time, where C_0 is the reactant concentration at T = 0 min, C is the reactant concentration at various times, showed linear trend at both pH tested (figure 1). It appeared that hydrolysis is more susceptible at alkaline than acidic pH. Values of hydrolysis rate constant and half times deduced from data were 0.009 hours^{-1} (half life 75 hours),
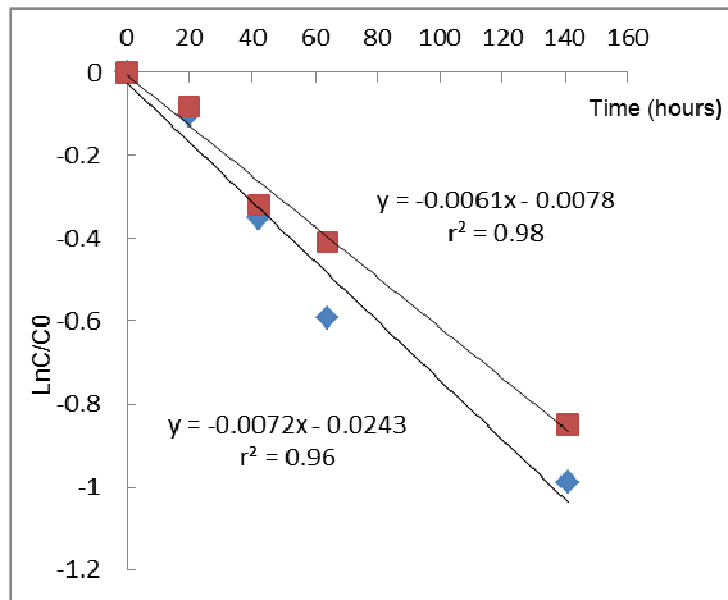
Figure 1. Semi-log plots of Ln (C/C_0) over time for chlorpyrifos hydrolysis at pH 6 (♦) and pH 8 (■)
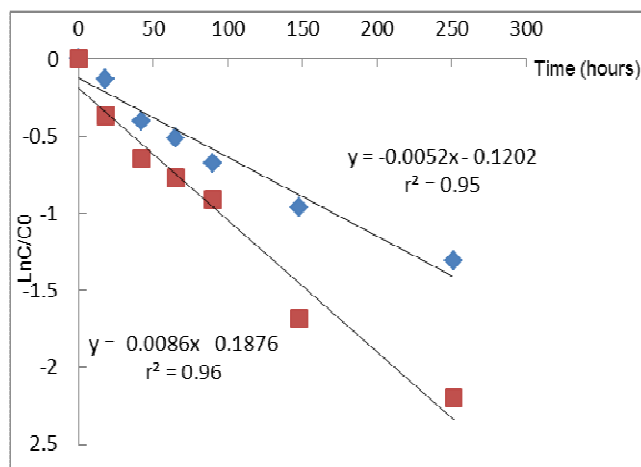
Figure 2. Semi-log plots of Ln (C/C_0) over time for chlorpyrifos hydrolysis at 22 °C (♦) and 40 °C (■).

and 0.01 hours[-1] (half life 64 hours) for pH 6 and pH 8 respectively. At the end of experiment the rate degradation of chlorpyrifos varied from 58 % to 67 % at pH 6 and 8 respectively.

Alkaline pH caused degradation of chlorpyrifos, which could be explained by the attack of the phosphorus atom by the nucleophilic hydroxide ion. There are two hypotheses regarding the relationship between increased pH value and the rate of chlorpyrifos hydrolysis (Xiao, 1997). First hypothesis suggests the hydrolysis rate increases fairly consistently with increased pH. The second one suggests that the hydrolysis rate of chlorpyrifos is fixed, while it proceeds at an increased

rate under alkaline conditions. Our results agree with those reported by Druzina and Stegu (2007). They have conducted a study over the same pH range used (6–8.5). They reported faster degradation at higher pH values. However, Liu et al. (2001) found no relationship between pH and rate of hydrolysis ($r^2 = 0.09$), with half-lives of 45.9, 56.3, 126.0, 26.5 and 24.4 days at pH 5.72, 7.66, 7.93, 7.99 and 8.15 respectively.

Effect of temperature

Seasonal changes influence groundwater temperatures

Table 2. Rate constant (k) and half-life ($t_{1/2}$) of chlorpyrifos degradation under sun light photolysis spiked mineral aqueous solutions at 0.01 M and at 0.1 M

Solutions	Ca		K		Mg		P	
	0.01	0.1	0.01	0.1	0.01	0.1	0.01	0.1
$T_{1/2}$ (min)	206	-	224	699	160	206	216	184
K (min^{-1}).10^4	33	-	30	9	43	33	32	37
r^2	0.94	0.93	0.98	0.95	0.96	0.90	0.96	0.92

and may influence the rate of pesticide of chemical breakdown. Chemical hydrolysis of chlorpyrifos was investigated under two different temperatures 40 °C and 22 °C. It was found that hydrolysis was rapid at 40 °C when compared with 22 °C. The reaction tends to be pseudo first order as indicated in figure 2 above. At 40 °C, the hydrolysis half life varied from 42 hours to 90 hours at 22 °C, and rate of constant from 0.016 to 0.007 hours^{-1} respectively. At the end of experiment, the rate of degradation of chlorpyrifos varied from 73 % to 89 % at 22 °C and 40 °C respectively. Close focus on the values of rate constants showed that rate of constant fairly doubled subsequent to an increase of 10.

The activation energy can be derived from the Arrhenius equation:

$$K = A \exp(-\frac{Ea}{R.T})$$

Increased rates of chlorpyrifos degradation occur at higher temperatures. In fact, Meikle and Youngson (1978) reported that the rate of chlorpyrifos hydrolysis increased an average of 3.5-fold for each 10 °C rise in temperature. Freed et al. (1979) revealed that the half-lives of chlorpyrifos hydrolysis at pH 7.4 were 53 and 13 days at 20 °C and 37.5 °C respectively. Hui et al. (2010) found that the half-life of chlorpyrifos in distilled water at pH 7.0 was 12.3 and 8.12 days at 16 °C and 40 °C, respectively. Increased temperature elevates the energy of nucleophilic attack on chlorpyrifos molecules, which has an average 21.1 kcal/mol activation energy for the hydrolytic reaction (1979). Our calculated active energy was 3 fold weaker of the average; it was likely due to the catalytic effect of microorganisms present in aqueous solution.

Schaefer and Dupras (1970) have studied the effect of temperature and light on the stability of chlorpyrifos (dursban). They found that the stability did not decrease as the season advanced, but was much more seriously affected by temperature. Miles et al. (1983) have reported the implications of temperature effects on the rate of microbial degradation. Thus, chlorpyrifos efficacy and persistence were studied in sterile, natural mineral and organic soils at 3 °C, 15 °C and 28 °C. They found that chlorpyrifos in organic soil had half-lives of 24, 15 and 6 weeks, and in mineral soil of 16, 6 and 2.5 weeks, respectively at 3 °C, 15 °C and 28 °C.

Effect of metallic ions and sun light

The rate of hydrolysis is influenced by the intensity and spectrum of sunlight, length of exposure, and the properties of the pesticide. Several experiments were made in order to evaluate the influence of dissolved metals (Ca, K, Mg, and P) at 0.01 M and 0.1 M, under sun light irradiation on the degradation of chlorpyrifos at 4 mg/L. The solutions were prepared in transparent glass bottles of 20 mL closed to avoid the loss of chlorpyrifos by evaporation. The sunlight excitation was conducted over a period of 2 hours, with regular sampling every 10 minutes. Data showed good fit with first-order model. Deduced data of half-lives ($T_{1/2}$), hydrolysis rates (K) and correlation coefficients (r^2) are shown in table 2.

Photolysis rates varied from 0.0030 min^{-1} to 0.0043 min^{-1} at 0.01 M, and from 0.0009 min^{-1} to 0.0037 min^{-1} at 0.1 M concentration. The corresponding calculated half lives ranged from 160 to 224 days at 0.01 M and from 184 to 699 days at 0.1 M. The results could be related to the fact that microorganisms suspended in the water may scatter incidental light, greatly reducing the penetration of light beneath the surface of the molecule (Shiller et al., 2006). Wu and Laird (2002) speculated that the degradation of chlorpyrifos in aqueous systems is more complex than the simple hydrolysis reaction. They have studied the hydrolysis of chlorpyrifos in the filtered river water which was dominated by Ca but also contained Al, Mg, Fe, Mn, and Na. They indicated that although there is little evidence in the literature for microbial degradation of chlorpyrifos, the possibility cannot be entirely discounted.

The results indicate a steady decrease of degradation at 0.01 M for all minerals, while at 0.1 M, degradation decreased with a stimulating degradation in presence of Mg and P with correlation coefficient r^2 of 0.90 and 0.92 respectively (figure 3). At the end of experiment, the rate degradation of chlorpyrifos at concentration 0.01 M was 39.2 % in the presence of Ca, 36.8 % in the presence of K, 34.5 % in the presence of Mg and 38.1 % in the presence of P. While at 0.1 M, the rate degradation of chlorpyrifos was 11.2 % in the presence of Ca, 20.2 % in the presence of K, 41.7 % in the presence of Mg and 39.3 % in the presence of P. The comparison of data from the two concentration experiments showed that the photodegradation of samples was faster in presence of Ca and K at 0.01 M and in presence of Mg and P at 0.1 M.
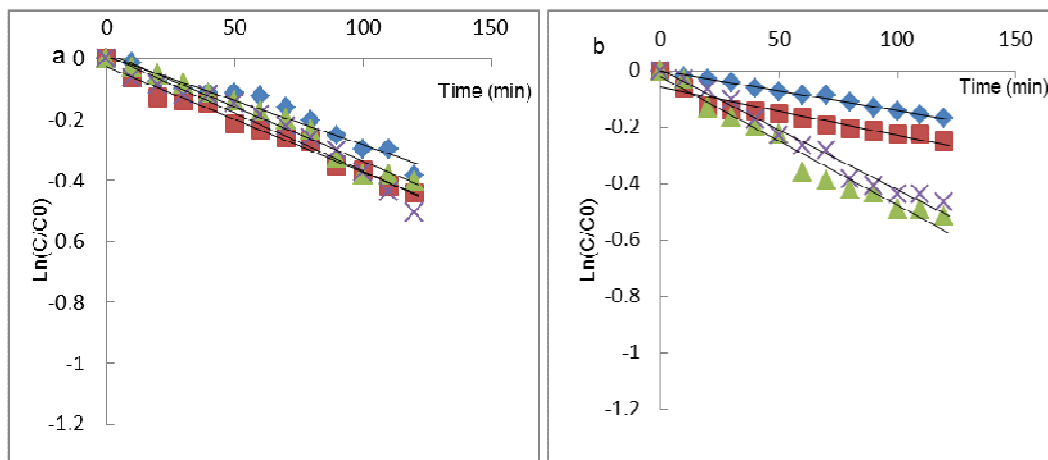
Figure 3. Semi-log plots of Ln (C/C_0) over time for chlorpyrifos photolysis under sunlight irradiation in spiked mineral aqueous solutions (Ca (♦), K (■), Mg (▲) and P (×)) at 0.01 M (a) and at 0.1 M (b).

Wyer (2008) has studied the effect of phosphorus on the hydrolysis of diazinon an organophosphorate insecticide. He has revealed that nucleophilic attack on the central phosphorus atom or, alternatively, attack at a carbon atom on the aliphatic chain are the expected modes of action for the hydrolysis of diazinon. This hypothesis may explain our results related to the catalytic effect of phosphorus on the hydrolysis of chlorpyrifos. Some studies have demonstrated that the presence of cations in aqueous solutions may catalyze cleavage of the P–O bond. Mortland and Raman (1967) reported nearly 100% hydrolysis of chlorpyrifos (2.8 mg/L) within 24 h in aqueous methanol (50 % v/v) containing 0.1 mM Cu^{2+}, limited hydrolysis (10 % in 24 h) in the presence of 0.1 mM $MgCl_2$, and negligible hydrolysis in the presence of $CaCl_2$. They also studied the effect of $CoCl_2$, $ZnSO_4$, $AlCl_3$, $CaCl_2$, $MgCl_2$ and Cu-organic soil; they found no catalyzed effect on the chlorpyrifos hydrolysis in the presence of those minerals.

Hui et al. (2010) have studied the effect of concentration of chlorpyrifos in its hydrolysis in 0.02 M $CaCl_2$ solution. They demonstrate that degradation of chlorpyrifos occurred very fast when the initial concentration of chlorpyrifos was low (0.5 mg/L). However, at higher initial concentration (1.8 and 1.0 mg/L), the half-life for chlorpyrifos was 1.5-2 times longer. This result is in contradiction with our case study in presence of Ca. We noticed that at concentration of chlorpyrifos of 4 mg/L and concentration of 0.01 M of Ca, this ion catalyses the chlorpyrifos hydrolysis. Further experiments studying the effect of concentration are needed.

Hossain et al. (2013) have investigated the direct sun light photodegradation of chlorpyrifos in both distilled and lake water. They revealed that the degradation of chlorpyrifos by sun light in distilled water was 10.4 %, 18.75 %, 25.5 % and 33.5 % after 3, 6, 8 and 10 days, respectively, whereas degradation in lake water was 17.2 %, 31.45 %, 38.85 % and 47.15 % after 3, 6, 8 and 10 days respectively.

Effect of metallic ions under UV-light

The direct UV excitation of a solution containing 4 mg/L of chlorpyrifos was conducted over a period of 2 hours, with regular sampling every 10 minutes. Analysis by UV photometer of solutions showed a decrease in the concentration of chlorpyrifos in both solutions at 0.01 M and 0.1 M (figure 4).

Deduced data of half-lives ($T_{1/2}$), hydrolysis rates (K) and correlation coefficients (r^2) are shown in table 3. At the end of experiment, the rate degradation of chlorpyrifos at concentration 0.01 M was 72.7 % in the presence of Ca, 69.6 % in the presence of K, 34.5 % in the presence of Mg and 38.6 % in the presence of P. While at 0.1 M, the rate degradation of chlorpyrifos was 33.3 % in the presence of Ca, 29.6 % in the presence of K, 41.4 % in the presence of Mg and 49.1 % in the presence of P.

Hydrolysis rates varied from 0.0024 min^{-1} to 0.0119 min^{-1} at 0.01 M and from 0.0023 min^{-1} to 0.0063 min^{-1} at 0.1 M concentration. Comparison of data from the two irradiation experiments showed that the photodegradation of samples exposed to the UV light was faster than in those subjected to the direct sunlight, especially in presence of Ca and K at 0.01 M and in presence of Mg and P at 0.1 M. The emission spectra of UV light mainly focus on the ultraviolet band, having the advantageous of short-wave emission and high energy to initiate photodegradation of compounds. In aqueous solution, Meikle et al. (1983) investigated the photolysis-hydrolysis rate of chlorpyrifos at pH 5.0, 6.9, and 8.0 aqueous buffers exposed to ultraviolet radiation. In these buffers,
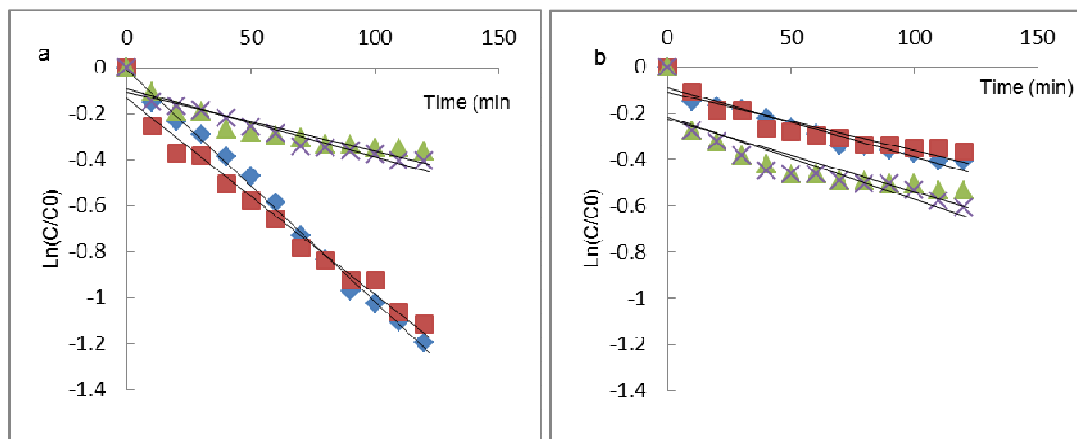
Figure 4. Semi-log plots of Ln (C/C_0) over time for chlorpyrifos photolysis under UV irradiation in spiked mineral aqueous solutions (Ca (♦), K (■), Mg (▲) and P (×)) at 0.01 M (a) and at 0.1 M (b).

Table 3 Rate constant (k) and half-life ($t_{1/2}$) of degradation of chlorpyrifos during UV light photolysis spiked mineral aqueous solutions at 0.01 M and at 0.1 M

Solutions	Ca		K		Mg		P	
	0.01	0.1	0.01	0.1	0.01	0.1	0.01	0.1
$T_{1/2}$ (min)	58	201	70	292	283	155	207	110
K (min^{-1}).10^{-4}	119	34	99	23	24	44	33	63
r^2	0.96	0.91	0.95	0.81	0.85	0.67	0.93	0.91

the half-lives after combined photolysis-hydrolysis were 11.0, 12.2, and 7.8 days respectively, and the corresponding calculated photolysis half-lives were 13.9, 21.7 and 13.1 days respectively. Table 3.

The pathways of chlorpyrifos photodegradation are not clearly understood, but partial photodegradation products have been isolated and identified (Meikle et al., 1983). Racke et al. (1996) and Hui et al. (2010) explain that the degradation of chlorpyrifos in aquatic environments involves the breakdown of the thiophosphoric esters, forming 3,5,6-trichloropyridinol (TCP) and desethylchlorpyrifos (DEC) as main metabolites. Walia et al. (1988) determined nearly 14.5 % of chlorpyrifos was converted to TCP in light, while only approximately 0.5 % was converted to TCP under dark conditions. Studies regarding the environmental fate of TCP are limited.

CONCLUSIONS

The study presents the degradation of chlorpyrifos under different indoor laboratory conditions similar to outdoor ones. The following were the major conclusions of the study:

Temperature, pH, radiation, and metal ions all significantly affect chlorpyrifos hydrolysis in water. The half-life is decreased with increasing water pH, temperature, irradiation, and metal ion concentrations.

Our results demonstrate that pH and temperature have

a large influence on the rate and half-life of chlorpyriphos hydrolysis. Alkaline conditions (pH 8) favour the degradation of chlorpyrifos, as well as the high temperature (40 °C). The hydrolysis and the photolysis of chlorpyrifos have been studied in water solutions, containing selected inorganic ions as Ca, K, Mg and P. The degradation of chlorpyrifos depends on the nature and the intensity of irradiation. The kinetic is more important under UV light than natural solar light irradiation. Adding minerals has showed a pseudo-first-order reaction. The photolysis rate of chlorpyrifos increases with the presence of Ca and K at 0.01 M under sun light irradiation and in the presence of Mg and P at 0.1 M under UV irradiation.

Further experiments with detailed characterization are needed in order to make extrapolations and predict long term changes in soil and water properties. Additional studies related to TCP under same conditions are required, in order to clarify the photolytic decomposition behaviour of pesticides and their metabolites, also to be capable of right interpretation of the complete mechanisms

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