Environ Sci Pollut Res (2016) 23:4473–4480
DOI 10.1007/s11356-015-5655-4

RESEARCH ARTICLE

Cu^{2+} and Fe^{2+} mediated photodegradation studies of soil-incorporated chlorpyrifos

Nazia Rafique[1] · **Saadia R. Tariq**[1] · **Karam Ahad**[2] · **Touqeer Taj**[2]

Received: 11 June 2015 / Accepted: 20 October 2015 / Published online: 28 October 2015
© Springer-Verlag Berlin Heidelberg 2015

Abstract The influences of Cu^{2+} and Fe^{2+} on the photodegradation of soil-incorporated chlorpyrifos were investigated in the present study. The soil samples spiked with chlorpyrifos and selected metal ions were irradiated with UV light for different intervals of time and analyzed by HPLC. The unsterile and sterile control soil samples amended with pesticides and selected metals were incubated in the dark at 25 °C for the same time intervals. The results of the study evidenced that photodegradation of chlorpyrifos followed the first-order kinetics. The dissipation $t_{0.5}$ of chlorpyrifos was found to decrease from 41 to 20 days under UV irradiation. The rate of chlorpyrifos photodegradation was increased in the presence of both metals, i.e., Cu^{2+} and Fe^{2+}. Thus, initially observed $t_{0.5}$ of 19.8 days was decreased to 4.39 days in the case of Cu^{+2} and 19.25 days for Fe^{+2}. Copper was found to increase the rate of photodegradation by 4.5 orders of magnitude while the microbial degradation of chlorpyrifos was increased only twofold. The microbial degradation of chlorpyrifos was only negligibly affected by Fe^{2+} amendment. The studied trace metals also affected the abiotic degradation of the pesticide in the order Cu^{2+}>Fe^{2+}.

Keywords Photodegradation · Soil · Chlorpyrifos · Cu^{2+} · Fe^{2+}

Responsible editor: Philippe Garrigues

✉ Nazia Rafique
naziarafiqchem@gmail.com

Saadia R. Tariq
saadiartariq74@gmail.com

Karam Ahad
karam_ahad@yahoo.com

Touqeer Taj
touqeertaj@yahoo.com

[1] Department of Chemistry, Lahore College for Women University, Lahore, Pakistan

[2] Ecotoxicology Research Institute (ERI), Department of Plant and Environment Protection (DPEP), NARC, Islamabad, Pakistan

Introduction

Intense and massive agricultural applications led to the accumulation of high concentrations of pesticides in the soil that may ultimately become hazardous to the various forms of life. In the soil, the accumulation and dissipation of pesticides depend on the nature of pesticides and the soil characteristics (Liu et al. 2007; Morillo et al. 2000).

Chlorpyrifos (O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate) is one of the most frequently used organophosphorus insecticides that is effectively used against various pests and insects of important cash crops. It is also frequently used to control the termites, flies, mosquitoes, and various household and veterinary pests (Zhang et al., 2011). In soils, its $t_{0.5}$ usually ranges between 60 and 120 days, but different soil conditions such as pH, soil type, and temperature may extend it over 1 year. The frequent use of chlorpyrifos has been reported to contaminate the soils and water as well as destroy the non-target organisms (EC 2005; Mugni et al. 2012). Moreover, its abundant use in agriculture has been linked to various health problems that may emanate from dietary exposure to the residues of chlorpyrifos present in the food (Mugni et al. 2012). Its high acute toxicity may affect the cardiovascular system, respiratory system, and the central nervous system (Dam et al. 2000). The environmental fate of chlorpyrifos is governed by both the biotic and abiotic processes, such as chemical hydrolysis, microbial degradation, and photolysis (Sreekumaran and Pradeep 1999; Zalat et al. 2014).

A study evidenced that if chlorpyrifos is applied continuously to the soil for 360 days, the soil contained 22 % 3,5,6-trichloropyridinol (TCP), less than 8 % of 3,5,6-trichloro-2-methoxypyridine, and 27–88 % of CO_2 [Walia et al. 1988].

Chlorpyrifos degrades in the soil by photoinduced reactions. Three different photochemical reactions are reported to take place under UV irradiation involving dechlorination, hydrolysis, and oxidation (Walia et al. 1988). During photoirradiation of soil, different products are formed by dehalogenation and oxidation of chlorpyrifos that are further photolysed to yield O,O-diethyl phosphorothioic acid and chloropyridinols. The rate of hydrolysis of oxon is greater than that of chlorpyrifos so it does not accumulate in the soil. UV irradiation is also known to cause a decrease in the levels of chlorinated pyridinols thereby confirming their mineralization [Jabeen et al. 2014].

Sewerage sludge and organic wastes are frequently used as a source of organic material in agricultural soils. However, some studies have evidenced that the addition of nitrogenous and phosphate fertilizers and organic manure can alter the rate of degradation of pesticides in soils (Caracciolo et al 2005; Han et al. 2003; Topp et al. 1996; Zhou et al. 2008). The strong binding of pesticides with clay minerals and soil organic matter may cause them to persist in the soil as well as to disperse slowly. Thus, the potential of the pesticides to cause long-term effects on beneficial soil microorganisms as well as aquatic species is increased (Van Zwieten et al. 2003; Liu et al. 2007; Gaw et al. 2003). Moreover, these materials contain large quantities of hazardous heavy metals that may accumulate in the soil upon successive application of sewage sludge and thus cause the problems arising from high contents of heavy metals.

Heavy metals play dual roles in the degradation of pesticides in soil. Enhanced levels of some pesticides in the soil such as Cu^{2+} and Zn^{2+} may reduce the dissipation of deltamethrin and cypermethrin while some other metals like Fe may enhance their rate of dissipation and thus reduce their $t_{0.5}$. This was explained in terms of reduction in the activity of bacterial biomass (Liu et al. 2007; Zheng and Ye 2001; Rafique and Tariq 2014). The persistence/dissipation of pesticides in the presence of metals has also been explained on the basis of their influence on the growth of bacterial populations involved in pesticide degradation (Vágvölgyi et al. 2010; Škrbić et al. 2010). Cu^{2+} ions have the potential to retard the dissipation of ethylenethiourea produced on degradation of ethylene bis-dithiocarbamate fungicides. On the other hand 2,4D degradation was highly accelerated by *Variovorax* in the presence of Cu^{2+} ions. Manganese, zinc, and copper (20–50 mg L^{-1}) were also found to accelerate the carbendazim and diuron degradation (Vágvölgyi et al. 2010; Škrbić et al. 2010). Guzsvany et al. studied the potential of AlFe-pillared clay and Fe-ZSM-5 catalysts for the removal of aqueous imidacloprid under UV irradiation or visible light. The comparison of the obtained results was also provided with the data obtained by using the photo-Fenton reaction and TiO2 Degussa P25 (Guzsvany et al. 2010)

Thus, the present study was formulated to determine the influence of Cu^{2+} and Fe^{2+} ions on the persistence/dissipation of soil-incorporated chlorpyrifos. The importance of the study stems from the fact that enhanced levels of certain metals present in the soil may trigger the photodegradation process of pesticides. Thus, the problems arising from repeated and excessive applications of pesticides to various crops and their subsequent accumulation in the soils may be overcome to some extent.

Materials and methods

Soil collection, pretreatment, and characterization

For the present study, bulk soil was obtained from the botanical garden of National Agricultural Research Center (NARC) Islamabad at a depth of 0–15 cm and placed in zip-mouthed, high-density, polythene bags. No pesticides or fertilizers had previously been used on the sampling site for 10 years. Prior to use, the soil samples were homogenized periodically and sieved to obtain particles of less than 2 mm mesh sizes. A water holding capacity (WHC) of 75 % was maintained for the soil samples at 0.33 bars by using the method of Frank et al. (2002)). Then, these soil samples were stored in the dark, at 20 °C until analysis. The texture of soil was determined by a hydrometer (Bao 2000). Soil physico-chemical properties (Table 1) were determined by using the standard method of Ryan et al. (2001). For bioactive control experiments, soil samples were autoclaved in capped flasks for 2 h at 121 °C for sterilization (100 mL capacity). An atomic absorption spectrophotometer was used for the estimation of metals in soil samples before use.

Materials

Chlorpyrifos (99 % purity) standard and HPLC-grade acetonitrile were obtained from Sigma Aldrich (Germany). The solutions of chlorpyrifos at a concentration of 5 mg L^{-1} were prepared in acetonitrile and stored in a freezer at 4 °C. Analytical grade $FeSO_4{\cdot}7H_2O$ and $CuSO_4{\cdot}5H_2O$ were purchased from Merck, Germany. Analytical grade reagents and chemicals were used without any further purification. Highly pure distilled water as prepared by a Milli-Q system of Millipore Waters Co. (Bedford, MA) was used during these experiments.

Spiking procedure

The spiking solution of chlorpyrifos at a concentration of 0.5 mg/mL was prepared by diluting the stock solution

Table 1 Physico-chemical properties of the studied soil

Soil type	Soil texture			M.C. %	O.M. %	pH (1:2)	CEC (mmol/kg)	P	N	K	Cu^{2+}	Fe^{2+}
	% Clay	% Sand	% Silt						(mg/kg)			
Silty clay loam	4.5	87	8.5	2.34	4.62	7.4	8.3	5.8	0.52	130	20.3	245.8

appropriately with acetonitrile. A 10.0-g portion of pre-dried soil was mixed thoroughly with water (7.5 mL) to prepare the soil slurries. This slurry was uniformly spread on the petri plate in the form of thin films of 2 mm depth and then added with pre-requisite concentrations of pesticide standards. Subsequently, these soil slurries were added with appropriate concentrations of two metals, i.e., Cu^{2+} and Fe^{2+}, separately. The final concentrations of these metals spiked with the soil are provided in Table 1. Microsyringe was used to evenly dispense the spiking solution across the soil surface. The soil samples were then thoroughly mixed and uniformly spread on the plate. In the case of control experiments, no addition of metal and pesticides was made. All the samples were prepared in triplicate. After irradiation, the controls and samples were removed from the photoreactor.

Metal speciation studies in soil

Metal speciation studies were performed by using the modified method of Tessier et al. (1979) that distributed the metals into six operationally defined fractions. According to the method, a 1.0-g portion of air-dried, homogenized soil sample was sequentially treated with deionized distilled water, $MgCl_2$ (1.0 M), sodium acetate solution (1.0 M), hydroxylamine hydrochloride (0.04 M), nitric acid (0.02 M)+30 % H_2O_2, and HNO3+HClO4, to obtain the respective fractions such as water-soluble (S_1), exchangeable (S_2), carbonate-bound (S_3), Fe–Mn-oxide-bound (S_4), organic-bound (S_5), and residual fractions (S_6). (Salbu et al. 1998) For each extraction, the mixture was centrifuged for 30 min at 3000 rpm; the supernatants were removed with pipette, filtered with Whatman filter paper, and analyzed for metals by using atomic absorption spectroscopy (AAS). Before starting the next extraction step, the sample was shaken for 30 min with 8 cm^3 of double distilled water (DDW) water and centrifuged, and the wash solution was discarded. All extractions were conducted in triplicate.

The calibration curve method was adopted for the quantification of results while using the standard solutions in concentration range of 2–8 mg L^{-1} and recording their corresponding absorptions. At least four standard solutions were run on the instrument covering the absorption range of samples. The precision of quantitative results was ensured by running the triplicate samples. In order to check the accuracy of data obtained by AAS, standard reference material SRM 2711"Montana Soil" was run with the samples. The results of the analysis were considered to be reliable if analysis error for repeat samples was less than 5 %, and an analytical precision of ±10 % was obtained for replicate samples.

Photochemical experiments

The soils were irradiated with a UV tube of 8 W (Atlas, Linsengericht, Germany) equipped in a self-designed photoreactor. The vessels used for irradiating the samples were provided with quartz lids at the top. In order to control the temperature, water was kept circulating beneath the samples, throughout the floor of the photolysis chamber. A 3.0-V electric fan was installed inside the photoreactor to allow the sample headspace to be purged continuously. The vertical distance between spiked soil samples and UV tube was maintained at 23 cm. The reference comprised an unspiked soil sample that was irradiated in a UV photoreactor for a time interval equal to the sample. In order to maintain the WHC at 75 %, the moisture content of soil samples was regularly monitored, initially after every 60 min and later on after every 12 h. DDW was used to maintain the initial moisture content and weight of each soil sample after every sampling, where necessary. Subsequently, these soil samples were irradiated in the UV photoreactor for different time intervals, i.e., 0, 4, 24, 48, 96, 192, 384, and 762 h.

Control test experiments

The control test samples of two different types were prepared including unsterilized and sterilized ones. The unsterile dark control samples were prepared by adding a 10-g portion of soil sample with prerequisite concentration of chlorpyrifos and two metals. These samples were incubated in the dark at 25 °C for 0, 1, 2, 4, 8, 16, 32, 64, and 128 days. Before spiking, a WHC of 75 % was maintained for each of the soil samples. For sterile control experiments, 10 g soil samples were autoclaved thrice at 121 °C (at intervals of 24 h) for 30 min in air-tight flasks. A water content of 75 % was achieved by adding deionized water to the autoclaved soil samples. These samples were then added with solutions of chlorpyrifos and metals and incubated for 0, 1, 2, 4, 8, 16, 32 64, and 128 days respectively in the dark, at 25 °C.

Pesticide extraction and analysis

The chlorpyrifos-spiked soil samples were extracted after irradiation according to the procedure of Graebing and Chib (2004). In brief, UV-irradiated samples were extracted three times with (90:10) mixture of acetonitrile and water (10 mL) containing 1 N H_3PO_3. During extraction, the contents were vortexed thoroughly for 1 min and sonicated for 10 min in an ultrasonic bath (35 kHz, 50/60 Hz, D-7700 Singen/HtW T-700, Elma, Germany). Subsequently, these samples were centrifuged for 10 min. The extraction of residue was carried out twice by using the same mixture. The combined soil extracts were concentrated to 5 mL on a rotary evaporator at 40 °C, cleaned thrice with 10 mL CH_2Cl_2, and then evaporated again to 0.5 mL. These extracts were then dissolved in a 2-mL volume of acetonitrile, cleaned by passing through a 0.45-μm polyethersulfone-based filter membrane present in a syringe, and reduced to 1.0 mL at ambient temperatures, under N_2 atmosphere. The extracts obtained were analyzed by HPLC. Chlorpyrifos recoveries obtained by this method were in the range of 79.9 %±2.05 for 0.5 mg kg^{-1} to 94 % ±1.19 for10 mg kg^{-1}.

The method of Zalat et al. (2014)) was used for the determination of chlorpyrifos. The analyses by HPLC were carried out by using a reversed-phase C18 column with an internal diameter of 250×4.6 mm and a 5-μm particle size. The instrument was equipped with a binary LC Pump 250 PE Nelson 900 Series Interface UV/Vis Detector for separation. The mobile phase consisted of a mixture of glacial acetic/water/acetonitrile (0.1 *v*/10 *v*/90 *v*) that was used at a 1 mL/min flow rate and an injection volume of 20.0 μL. A wavelength of 290 nm was used for the detection of chlorpyrifos at the retention time of 6.7 min. The adopted HPLC method was observed to be linear in the concentration range of 0.05 to 50 μg mL^{-1} (with R^2=0.999±0.04). The LOD and LOQ obtained for this method were 0.05 and 0.15 μg mL^{-1}, respectively. Calibration of the instrument was performed by using external matrix-matched standards, every time before the analysis of samples and the linear regression analyses were used for quantification.

Photocatalytic degradation kinetics

The data for the photodegradation of pesticides in the soil was studied by fitting the Langmuir–Hinshelwood (L–H) model according to the equation:

$$r = dC/dt = kKC/2 + KC$$

where C represents the pesticide concentration, k=rate constant, r=rate of pesticide mineralization, and K=adsorption coefficient of the pesticide.

If the initial concentration of pesticide is in the range of parts per billion or parts per million, then L–H kinetics may be approximated to first-order kinetics according to the equation:

$$r = dC/dt = k'C = kKC$$

The integrated forms of equation are:

$$Ct = C_o e^{-k't} or \ln(C_o/C_t) = -kKt = -k't$$

where k=first-order rate constant ($time^1$) [Konstantinou and Albanis 2003). The $t_{0.5}$ of pesticide is determined by the equation=(1/k) ln 2.

Results and discussion

Chlorpyrifos is degraded in the soil on exposure to chemical reactions, sunlight, and microorganisms (Reddy et al. 2013; Luebke and Hum 2002). Its half-life has been recorded to range from 48–190 days in the dark, but it may exceed 1 year depending on its formulation, rate of application, soil type, climate, etc. pH of soil was found to have a profound influence on the degradation of pesticide. On increasing the pH from 7 to 8, an increase in rate of degradation was observed with a corresponding decrease in $t_{0.5}$ from 100 to 1.5 days.

The microorganism-assisted degradation of chlorpyrifos is a good technique for its dissipation, but incomplete and slow degradation are the major constraints that limit this process [Walia et al. 1988; Roberts and Hutson 1999]. In water, the photodegradation $t_{0.5}$ of chlorpyrifos was found to be 3–4 weeks. So far, no studies have been reported focusing the metal-assisted photodegradation of chlorpyrifos in the soil.

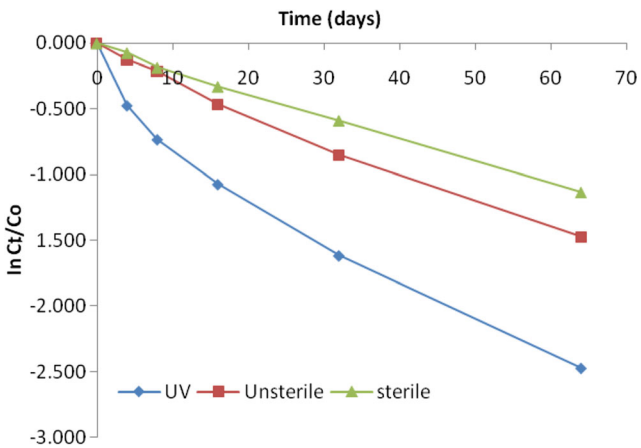

Fig. 1 Photodegradation profile of chlorpyrifos in soil

Table 2 Dissipation statistics for chlorpyrifos in soil amended with trace metals

Pesticide	Trace metal	Cultivation environment	K (day^{-1})	$t_{1/2}$ (days)	r^2
Chlorpyrifos (50 mg kg^{-1})	No metal	UV	3.5×10^{-2}	19.80±2.31	0.988
		Dark unsterile	2.3×10^{-2}	30.13±1.13	0.992
		Dark sterile	1.7×10^{-2}	40.76±0.96	0.997
	Cu^{2+}	UV	1.58×10^{-1}	4.39±1.23	0.950
		Dark unsterile	5.3×10^{-2}	13.07±2.1	0.998
		Dark sterile	3.7×10^{-2}	18.73±1.09	0.993
	Fe^{2+}	UV	5.6×10^{-2}	12. 37±1.38	0.998
		Dark unsterile	2.8×10^{-2}	24.75±2.04	0.979
		Dark sterile	2.6×10^{-2}	26.65±1.82	0.995

Photodegradation studies of soil-incorporated chlorpyrifos

On exposure to sunlight, the degradation rate of chlorpyrifos in the soil was observed to be 3.5×10^{-2} day^{-1} with $t_{0.5}$ of 19.8±2.3 days (r=0.988). The natural logarithmic decline corresponding to the photodegradation of soil-incorporated chlorpyrifos on UV irradiation verses irradiation time is provided in Fig. 1. The photodegradation curves for dark unsterile and sterile controls are also cast in this figure for comparison. In moist soil, chlorpyrifos photodegradation followed the first-order kinetics. It was found that the photodegradation of chlorpyrifos in soil was quite rapid under UV irradiation with half-life being reduced to 19.8 days from an initial half life of 40.8 days (R^2 of 0.988, Table 2). The reaction rate was observed to be varied from 1.7×10^{-2} to 3.5×10^{2} per day, at a p value of <0.05.

The microbial degradation and abiotic hydrolysis are responsible for transforming the chlorpyrifos. The significance of biotic degradation of soil-incorporated chlorpyrifos was indicated by a large difference in degradation rates of pesticide in unsterilized and sterilized soils, i.e., 6×10^{-2} day^{-1} and $t_{0.5}$ of 25 days (Fig. 1 and Table 2), thus evidencing the significant role of microbes in dissipating and detoxifying the residues of chlorpyrifos in the soil (Jabeen et al. 2014; Rokade and Mali 2013). Chlorpyrifos also inhibits the growth of bacterial populations present in the soil and interrupts the degradation of soil organic matter. As is mostly applied aerially, it accumulates in the top soil where it affects the soil biochemical properties. It also retards the growth of nitrogen-fixing symbiotic bacteria and adversely affects the enzyme activity of soil that is the degradation index for organic matter in the soil [Laksmikantha 2000].

The data furnished in Table 2 shows that in comparison with photodegradation, the $t_{0.5}$ of chlorpyrifos in unsterilized treatments was enhanced from 19.84 to 30.13 days. These results agreed well with those of Singh et al. (2002)) who reported the $t_{0.5}$ of chlorpyrifos to be in the range of 34–46 days (Singh et al. 2002). TCP has been reported as the antimicrobial degradation product of chlorpyrifos that is accumulative in the soil and slows the rate of microbial degradation (Robertson et al. 1998).

Under sterilized conditions, the soil microbial population was eliminated and thus the pesticide became persistent. The degradation of chlorpyrifos was very slow in the dark sterile soil conditions with a rate constant being 1.7×10^{-2} and a $t_{0.5}$ double than that under UV irradiation (Fig. 1). Hydrolysis was the main process that caused the dissipation of chlorpyrifos in sterile soil kept in the dark because the possibilities of microbial dissipation and photodegradation were eliminated by incubating the samples in the dark. Racke et al. (1996) also reported a small degradation of chlorpyrifos in soils with high pH, under sterile conditions (Racke et al. 1996).

Table 3 Dissipation statistics for different concentrations of chlorpyrifos

Pesticide concentration (mg/kg)	Cultivation environment	K (day^{-1})	$t_{1/2}$ (days)	r^2
25	UV	5.41×10^{-2}	12.81±1.82	0.993
	Dark	1.95×10^{-2}	35.53±1.01	0.975
50	UV	3.50×10^{-2}	19.8±2.31	0.988
	Dark	1.71×10^{-2}	40.76±0.96	0.997
100	UV	2.44×10^{-2}	28.40±1.32	0.826
	Dark	9.42×10^{-3}	73.72±1.61	0.864

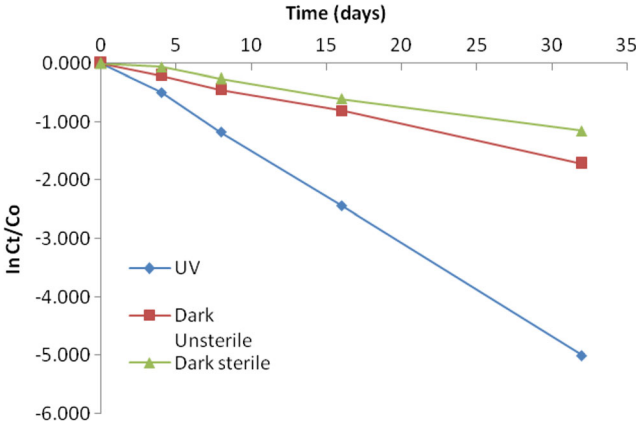

Fig. 2 Degradation profile of chlorpyrifos in Cu^{2+}-amended soil

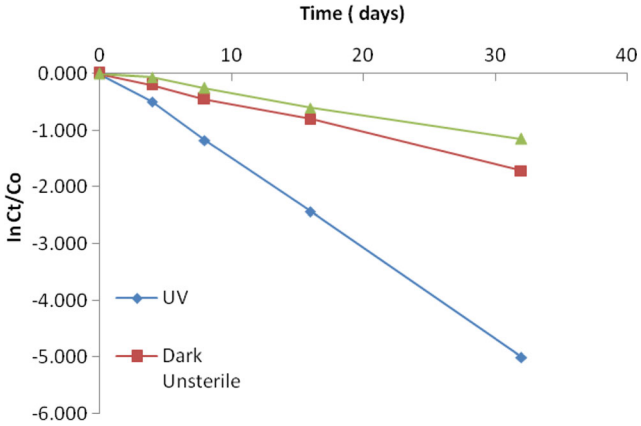

Fig. 3 Degradation profile of chlorpyrifos in Fe^{2+}-amended soil

Effect of initial pesticide concentration on photodegradation

An increase in initial concentration of chlorpyrifos in soil was observed to decrease its rate of photodegradation. The data in Table 3 evidenced that on increasing the initial concentration of soil-incorporated chlorpyrifos from 50 to 100 mg/kg, a decrease in its rate of degradation to 2.4×10^{-2} took place. Simultaneously, the $t_{0.5}$ of pesticide was enhanced from the initial half-life of 19.74 to 28.40 days at $p<0.05$. Further confirmation was obtained by reducing the chlorpyrifos concentration to 25 mg kg^{-1}, where $t_{0.5}$ was significantly reduced to 12.81 days. It was also depicted by an increase in degradation rate constants from 3.51×10^{-2} to 5.41×10^{-2}. Thus, the degradation rate of chlorpyrifos was dependent on its initial concentration. In fact, UV sources produce photons. On increasing the initial concentration of chlorpyrifos, the competition between TCP and chlorpyrifos for UV photons was increased which led to a reduction in dissipation of chlorpyrifos.

The rate of degradation of chlorpyrifos in the dark was also found to be dependent on the initial pesticide concentration in the soil (Table 3). A four-time increase in chlorpyrifos concentration (i.e., from 25 to 100 mg kg^{-1}) led to a twofold increase in $t_{0.5}$. Singh et al. (2003)) have reported that even after repeated applications of chlorpyrifos, no chlorpyrifos-degrading microbial population was developed in the soil (Singh et al. 2003).

Metal speciation studies in soil

The form of the metal in soil decides its behavior in the soil. Thus, the metal speciation analysis in the soil was performed after spiking the soil with metals according to the modified Tessier's scheme. The results of the study pertaining to the distribution of the metals in various operationally defined fractions in surface soil evidenced that Cu and Fe mostly belonged to Fe–Mn-oxide-bound fraction and organic fraction. The appreciable concentration of Cu was also present in residual fraction. The least amount of the two metals was present in water-soluble and exchangeable fractions, respectively.

Effect of Cu^{2+} on degradation of soil-incorporated chlorpyrifos

When the soil-incorporated chlorpyrifos was spiked with Cu^{2+} at a concentration of 20 mg kg^{-1}, the rate of its photodegradation was increased from 3.5×10^{-2} to 1.6×10^{-1} day^{-1} ($p<0.05$, Fig. 2). A sudden reduction in chlorpyrifos $t_{0.5}$ was also observed from 19.84 to 4.4 days (Table 2). In fact, Cu compounds are known to catalyze the photodegradation of various pesticides under UV irradiation (Tariq et al. 2014). An increase in Cu^{2+} concentration from C_0+20 mg kg^{-1} to C_0+40 mg kg^{-1} caused an increase in the rate of photodegradation from 1.58×10^{-1} to 1.65×10^{-1} day^{-1}. Thus, a clear reduction in the dissipation half-

Table 4 Dissipation statistics for chlorpyrifos in soil amended with different Cu^{2+} and Fe^{2+} levels under UV irradiation

Pesticide	Trace metal	Metal conc	K (day^{-1})	$t_{1/2}$ (days)	r^2
Chlorpyrifos (50 mg kg^{-1})	Cu^{2+}	20	1.58×10^{-1}	4.38±1.23	0.997
		40	1.65×10^{-1}	4.20±2.16	0.999
		80	1.71×10^{-1}	4.05±0.74	0.991
	Fe^{2+}	20	5.6×10^{-2}	12.6±1.38	0.998
		40	6.6×10^{-2}	10.5±0.91	0.997
		80	7.6×10^{-2}	9.12±1.31	0.986

life of the pesticide was recorded from 105 to 98 h (Table 4). Figure 2 depicts that during 32 days of incubation, the rate of chlorpyrifos dissipation was increased significantly in unsterilized soil at $p>0.05$ in comparison with the control dark sterile treatments.

In unsterile control treatments, chlorpyrifos $t_{0.5}$ was reduced from 22.8 to 13.1 days that evidenced that Cu^{2+} influenced the activity of the microbes in the soil that degrade the pesticide. Copper also influenced the abiotic dissipation of chlorpyrifos. Thus, the $t_{0.5}$ of chlorpyrifos dissipation was reduced from 40.8 to 18.73 days when it was spiked with catalytic amounts of Cu^{2+} but on UV exposure, a further decrease in half-life was observed from 18.73 to 4.4 days. This was explained on the basis of the photon capturing potential of Cu^{2+} ions and their subsequent efficient role in catalyzing the photolysis of chlorpyrifos.

Effects of Fe^{2+} on chlorpyrifos degradation

Fe^{2+} is known to boost the photodissipation of numerous halogenated herbicides and pesticides due to its photosensitizing ability (Rafique and Tariq 2014; Salah et al. 2006; Tajeddine et al. 2010). When the soil-incorporated chlorpyrifos was spiked with Fe^{2+}, an increase in the rate of photodegradation of chlorpyrifos was observed from 3.5×10^{-2} to 5.5×10^{-2} ($p<0.05$) and its $t_{0.5}$ was decreased from 19.74 to 12.6 days (Table 2). The role of Fe^{2+} in catalyzing the photodegradation of pesticides has also been reported by other authors (Guzsvany et al. 2010; Kochany 1992; Tariq et al. 2014; Zheng and Ye 2001).

The increased soil Fe^{2+} levels have been reported to enhance the degradation of chlorpyrifos in soil (Satapanajaru et al. 2003; Sayles et al. 1997). The data provided in Table 4 and Fig. 3 evidenced that in comparison with controls, a 94 to 96 % of initial chlorpyrifos concentration was dissipated when it was continuously irradiated with UV light for 4 days in the presence of increased Fe^{2+} concentration (C_0+10 and C_0+30 mg kg^{-1}). This increased degradation was due to the direct photodegradation catalyzed by Fe^{2+} or by an indirect photolysis resulting from the reaction of iron ions with hydroxyl radicals present in the moist soil (Sayles et al. 1997).

Under dark unsterile conditions, the rate of chlorpyrifos dissipation was only negligibly affected (0.02 at $p<0.05$) due to increased Fe^{2+} levels that eliminated the possibility of microbial dissipation (Fig. 3). The $t_{0.5}$ of chlorpyrifos in Fe^{2+}-amended soil was decreased from 43.36 to 26.6 days ($p<0.05$) indicating that Fe^{2+} also affected the abiotic degradation of chlorpyrifos (Table 2). Under anoxic conditions, Fe^0 has been successfully used to remediate the chlorpyrifos-contaminated soils at acidic pH. Thus, hydrolysis followed by reductive dechlorination was the major process for bringing about abiotic degradation of chlorpyrifos (Sayles et al. 1997).

Conclusions

The presence of selected trace metals, i.e., Cu^{2+} and Fe^{2+}, caused an increase in the rate of chlorpyrifos photodegradation with a resultant decrease in $t_{0.5}$ from 19.8 to 4.39 and 19.25 days, respectively. Cu^{2+} caused a six-time increase in photodegradation rate and a twofold increase in microbial degradation of chlorpyrifos. Fe^{2+}, on the other hand, negligibly affected the biotic chlorpyrifos degradation. The selected trace metals also influenced the abiotic degradation in the order $Cu^{2+}>Fe^{2+}$.

Acknowledgments We are highly obliged to the Higher Education Commission, Pakistan for providing the financial support under the scheme of Indigenous Ph.D. Fellowship. We also acknowledge the assistance provided by Dr. Fayyaz Hussain, Principle Scientific Officer, Land Resource Research Institute (LRRI), for carrying out the physico-chemical and metal analysis of reference soil samples.

References

Bao SD (2000) Soil and agricultural chemistry analysis. China Agricultural Press, Beijing, pp 25–114

Caracciolo AB, Giuseppe G, Grenni P, Cremisini C, Ciccoli R, Ubaldi C (2005) Effect of urea on degradation of terbuthylazine in soil. Environ Toxicol Chem 24:1035–1040

Dam K, Seidler F, Slotkin T (2000) Chlorpyrifos exposure during a critical neonatal period elicits gender selective eficits in the development of coordination skills and locomotor activity. Dev Brain Res 121(2):179–187

EC (2005) Review report for the active substance chlorpyrifos. Sanco/3059/99-Rev.1.5.Health and consumer protection directorate-general, European commission.http://ec.europa.eu/sanco_pesticides/public/index.cfmevent= active substance. Selection

Frank MP, Graebing PW, Chib JS (2002) Effect of soil moisture and sample depth on pesticide photolysis. J Agric Food Chem 50: 2607–2614

Gaw SK, Palmer GT, Kim ND, Wilkins AL (2003) Preliminary evidence that copper inhibits the degradation of DDT to DDE in pip and stone fruit orchard soils in the Auckland region, New Zealand. Environ Pollut 122:1–5

Graebing P, Chib JS (2004) Soil photolysis in a moisture and temperature-controlled environment. insecticides. J Agric Food Chem 52:2606–2614

Guzsvany V, Banic N, Papp Z, Gaal F, Abramovic B (2010) Comparison of different iron-based catalysts for photocatalytic removal of imidacloprid. React Kinet Mech Catal 99:225–233

Han KH, Kim CS, Ro HM, Lee SM, Yoo SH (2003) Degradation of ethoprophos in three physicochemically different soils treated with composted manure and chemical fertilizer. Bull Environ Contam Toxicol 70:520–526

Jabeen H, Iqbal S, Anwar S (2014) Biodegradation of chlorpyrifos and 3,5,6-trichloro-2-pyridinol by an ovelrhizobial strain Mesorhizobiumsp. HN_3. Water Environ J. doi:10.1111/wej.12081

Kochany LE (1992) Degradation of nitrobenzene and nitrophenols in homogeneous aqueous solution. Direct photolysis versus photolysis in the presence of hydrogen peroxide and the Fenton reagent. Water Qual Res J Can Water 27:97–122

Konstantinou IK, Albanis TA (2003) Photocatalytic transformation of pesticides in aqueous titanium dioxide suspension susing artificial

and solar light: intermediates and degradation pathways. App Catal B Environ 42:319–335

Laksmikantha, H.C (2000) Effect of foliar insecticides on soil microorganisms and their biochemical processes in soils of Gulbarga. M.Sc(Agri.)Thesis, University of Agricultural sciences, Dharwad

Liu T-F, Sun C, Ta N, Hong J, Yang SG, Chen CX (2007) Effect of copper on the degradation of pesticides cypermethrin and cyhalothrin. J Environ Sci 19:1235–1238

Luebke B, Hum B (2002) Pesticide-induced immunotoxicity: are humans at risk? Ecol Risk Assess 8:293

Morillo E, Undabeytia T, Maqueda C, Ramos A (2000) Glyphosate adsorption on soils of different characteristics. Influence of copper addition. Chemosphere 40:103–107

Mugni H, Demetrio P, Paracampo A, Pardi M, Bulus G, Bonetto C (2012) Toxicity persistence in runoff water and soil in experimental soybean plots following chlorpyrifos application. B Environ Contam Toxicol 89(1):208–212

Racke KD, Steele KP, Yoder RN, Dick WA, Avido E (1996) Factors effecting the hydrolytic degradation of chlorpyrifos in soil. J Agric Food Chem 44:1582–1592

Rafique, N. and Tariq, S.R (2014) Photodegradation of a-cypermethrin in soil in the presence of trace metals (Cu^{2+}, Cd^{2+}, Fe^{2+} and Zn^{2+}), Environ Sci Processes Impacts

Reddy, A., Vijaya, B., Madhavi,V., Gangadhara,R.K. and Madhavi,G (2013) Remediation of chlorpyrifos-contaminated soils by laboratory-synthesized zero-valent Nano iron particles: Effect of pH and Aluminiumsalts. J Chem 7

Robertson LN, Candler KJ, Stickely BDA, Cocco RF, Ahmetagic M (1998) Enhanced microbial degradation implicated in rapid loss of chlorpyrifos from the controlled release formulation SUSCON BLUE in soil. Crop Prot 17:29–33

Rokade KB, Mali GV (2013) Biodegradation of chlorpyrifos by pseudomonas Desmolyticumncim 2112. Int J Pharm Bio Sci Apr 4(2):609–616

Ryan, J., Estefan G. and Rashid, A (2001) Soil and Plant Analysis Laboratory Manual, 2nd edition, Syria, ICARDA,x+172pp

Salah R, Gilles M, Mohamed S (2006) Highly efficient photodegradation of the pesticide metolcarb induced by Fe complexes. Environ Chem Lett 4(4):213–217

Salbu B, Krekling T, Oughton DH (1998) Characterization of radioactive particles in the environment. Analyst 123:843–849

Satapanajaru T, Comfort SD, Shea PJ (2003) Enhancing metolachlor destruction rates with aluminum and iron salts during zerovalent iron treatment. J Environ Qual 3(5):1726–1734

Sayles GD, You G, Wang M, Kupferle MJ (1997) DDT, DDD and DDE dechlorination by zero-valent iron. Environ Sci Technol 31(12): 3448–3454

Shiping Z, Changqun D, Wang X, Michelle WHG, Yu Z, Hui F (2008) Assessing cypermethrin-contaminated soil with three different earthworm test methods. J Environ Sci 20(11):1381

Singh BK, Walker A, Wright DJ (2002) Degradation of chlorpyrifos, fenamiphos and chlorothalonil alone and in combination and their effects on microbial activity. Environ Toxicol Chem 21:2600–2605

Singh BK, Walker A, Morgan AJW, Wright DJ (2003) Effects of soil pH on the biodegradation of chlorpyrifos and isolation of a chlorpyrifos-degrading bacterium. Appl Environ Microbiol 69(95):198–5206

Škrbić,B.,Vágvölgyi,Cs.,Tjapkin,A.,Predojević,Z.,Krisch,J.,Manczinger, L.(2010).Development of xenobiotic-degrading bioaugmentation products-BIOXEN project. International Conference on Science and Technique in the agri-food business. ICoSTAF 2010, 3-4th November 2010, Szeged. Abstracts

Sreekumaran, N.A. and Pradeep T (1999) Extraction of chlorpyrifos and Malathion from water by metal Nanoparticles, JNN7,1–7 Roberts, T.R. and Hutson, D.H. Metabolic path ways of agrochemicals-Part2: Insecticides and Fungicides; The Royal Society of Chemistry: Cambridge,UK,235-242

Tajeddine L, Mountacer H, Sarrakha M (2010) Effect of iron and humic acid on photodegradation of some pesticides adsorbed on clay surfaces. Arabian J Chem 3:73–77

Tariq SR, Rafique N, Kiran S, Khan AM (2014) Photo-induced degradation of emamectin benzoate: effect of iron amendments and solvent system. Environ Earth Sci 72(4):983–988

Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedures for the speciation of particulate trace metals. Anal Chem 51: 844–851

Topp E, Tessier L, Gregorich EG (1996) Dairy manure in corporation stimulates rapid atrazine mineralization in an agricultural soil. Can J Soil Sci 76:403–409

Vágvölgyi,Cs.,Škrbić,B.,Krisch,J.,Manczinger,L (2010) Remediation of pesticide-polluted soils by microbial bioaugmentation. In:12th Regional Conference on Environment and Health, 14/15 September 2010. NoviSad, Serbia

Van Zwieten L, Ayres MR, Morris SG (2003) Influence of arsenic co-contamination on DDT break down and microbial activity. Environ Pollut 124:331–339

Walia S, Dureja P, Mukerjee SK (1988) New photodegradation products of chlorpyrifos and their detection on glass, soil, and leaf surfaces. Arch Environ Contam Toxicol 17:183–188

Zalat, O.A., Elsayed, M.A., Fayed, M.S. and Megid A.E. M.K (2014) Sources of uncertainty for the determination of chlorpyrifos by gas chromatography equipped with Flame Photometric Detector, ILCPA,6:48–55

Zhang Y, Hou Y, Chen F, Xiao Z, Zhang J and Hu X (2011) The degradation of chlorpyrifos and diazinon in aqueous solution by ultrasonic irradiation: effect of parameters and degradation pathway. Chemosphere 82(8):1109–1115

Zheng H, Ye C (2001) Photodegradation of acetochlor and butachlor in waters containing humic acid and inorganic ion. B Environ Contam Toxicol 67(4):601–608