Chemosphere 171 (2017) 74–80

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Key environmental processes affecting the fate of the insecticide chloropyrifos applied to leaves

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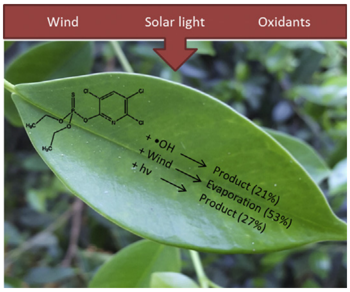
HIGHLIGHTS

- Chlorpyrifos loss paths from leaves are evaporation, direct and indirect photolysis.
- Evaporation is the dominant removal path under most environmental conditions.
- Reaction of Chlorpyrifos with atmospheric ozone is expected to be negligible.
- Half-life of Chlorpyrifos under Mediterranean climate was calculated as 0.9 – 6.9 h.
- Calculation application is limited to crops with high portion of exposed leaves.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 October 2016
Received in revised form
29 November 2016
Accepted 4 December 2016
Available online 8 December 2016

Handling Editor: Klaus Kümmerer

Keywords:
Chloropyrifos
Leaves
Evaporation
Photolysis
Indirect photolysis

ABSTRACT

Chlorpyrifos (CP) is still a commonly employed organophosphorus insecticide worldwide. In semi-arid and Mediterranean climates, applied CP is expected to remain on leaves surfaces for relatively long time due to the lack of summer rains and common use of drip irrigation. The present work examines the loss rate of CP from leaves via different surface processes: evaporation, direct photolysis and reactions with ozone and •OH radicals. Laboratory experiments showed that evaporation rate constant of CP increased from 0.109 to 0.492 h^{-1} with the increase in wind speed up to 4 m/s. First-order rate constant of direct photolysis, measured using a solar simulator, was $k'_{UV} = 1.15\ (\pm 0.01) \times 10^{-20}$ cm^2 $photon^{-1}$. Second-order rate constants for the reaction of CP with ozone and •OH were measured as 6×10^{-20} and 6×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively. The above rate constants were applied successfully in an outdoor experiment to predict the disappearance of chloropyrifos under specific environmental conditions. Further modeling showed that the insecticide half-life time on exposed surfaces under typical Mediterranean environment will be in the range of 0.9–6.9 h. Evaporation is expected to be the dominant removal path under most environmental conditions, followed by direct photolysis and reaction with •OH.

1. Introduction

Chlorpyrifos (CP) is an organo-phosphorous insecticide widely used for the control of a broad-spectrum of pests in agriculture

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http://dx.doi.org/10.1016/j.chemosphere.2016.12.013

(Sadiki and Poissant, 2008). The efficacy of CP and its potential risk to human depends in part on its persistence on treated surfaces (mainly leaves), where it is exposed to solar irradiation, atmospheric oxidants and other abiotic conditions (e.g. wind and precipitation). Consequently, applied pesticides may persist for relatively long durations at the surface-atmosphere interface, especially in semi-arid and Mediterranean climates (which are characterized by long dry and hot summers), due to the lack of precipitation and top irrigation. Indeed, Montemurro et al. (2002) measured half-life time of CP on treated orange leaves as high as 6–7 days in the dry climate conditions of southern Italy, whereas Goh et al. (1986) reported that top irrigation of treated lawn significantly increased the dissipation of CP foliar residues.

Early studies (e.g., Leistra et al., 2006) showed that in the cases of dry weather, the main paths for CP disappearance in the environment are: (i) evaporation, (ii) direct photolysis and (iii) indirect photolysis through its reaction with atmospheric oxidants (e.g. ozone and •OH radical). Meikle et al. (1983) found that volatilization was the main contributor to CP disappearance from an inert surface (filter paper), with half-life time of 0.3 days at airspeed of 0.06 m s^{-1} (about 10-fold faster than its direct and indirect photodecomposition combined). Similarly, Leistra et al. (2006) estimated that volatilization was a key process in the disappearance of CP from potato leaf surfaces, with 63%–66% decrease in CP concentration due to volatilization in the first daylight hours after application. Other researchers showed that direct photolysis of organophosphorus pesticides (including CP) is significant, exposing thin films of pesticides to UV light at 300 nm (Chen et al., 1984).

With respect to CP oxidation by different atmospheric oxidants, most studies agree that •OH radical is the dominant contributor (Meng et al., 2010; Muñoz et al., 2014). El Masri et al. (2014) measured reaction rate constants for heterogeneous oxidation of CP by •OH and ozone (on quartz plaques) to be 5.8×10^{-12} and 1.2×10^{-19} cm^3 $molecule^{-1}$ s^{-1}, respectively. Accordingly, they estimated an atmospheric lifetime of approximately 2 days for CP, controlled mostly by •OH reaction. Slightly faster rate constant (9.1×10^{-11} cm^3 $molecule^{-1}$ s^{-1}) was reported for homogeneous oxidation of gaseous CP by •OH (Muñoz et al., 2014).

Despite the above-mentioned data on the environmental fate of CP, very limited information is available regarding its heterogeneous reactivity while sorbed on real-field surfaces. Hence implication of the reported kinetic data to ambient conditions may not be straight forward. Furthermore, no single study has examined all main CP heterogeneous decay paths, demonstrating the contribution of each path and its relevancy to CP decay on leaves under environmental conditions. The goals of this study were to measure and calculate kinetic parameters of CP loss from leaves surfaces by evaporation, direct and indirect photolysis, as well as to determine the relative contribution of each mechanism under typical environmental conditions.

2. Materials and methods

2.1. Chemicals

Chlorpyrifos (CP) was obtained from Sigma-Aldrich at analytical grade (>98%). A popular commercial formulation of CP, Dorsban (active compound content 480 g/L), was purchased from Liad Chemicals Ltd (Israel). Squalane analytical standard (99%) was obtained from Acros Organics. All chemicals were used with no further purification.

2.2. Experimental setup

Kinetics of CP evaporation, oxidation and direct photolysis while sorbed on leaves, were measured separately in controlled laboratory experiments. The obtained data was then used to assess the contribution of each pathway and to model CP loss rate under ambient conditions. The model results were validated against an outdoor experiment.

2.2.1. Evaporation experiments

Evaporations tests were done in a standard chemical hood. Pesticide-doped leaves (lemon, persimmon and apple) were attached to a wooden plate that was placed at the hood's opening. Control of the wind speed at the samples environment was achieved by controlling the opening of the hood's window. Wind speed near the samples was measured by wind anemometer (Eole, JDC Electronic, Switzerland), placed next to the wooden plate. Samples were prepared by applying 10 μl of 500 mg/L pesticide solution (in millipore water 18.2 MΩ) on pre-washed leaves (taken from a pesticides-free tree), and letting the water evaporate for 30–60 min prior to the beginning of the experiment. This application created a multilayer deposit with surface density of approximately 3×10^{16} $molecules/cm^2$ (based on film's geometry). As surface density may affect film reactivity (El Masri et al., 2016), similar density was used throughout the study. At long exposure periods (i.e., 24 h), the leaves' stems were kept with constant water supply. Extraction of pesticide residues was done by placing the leaves in glass beakers with 5 ml ethanol, then sonicating at 50 °C for 15 min (recovery 90 ± 5%; Dinerman, 2013). Extracts were then centrifuged for 10 min at 4500 RPM prior to GC-MS analysis. All experiments were done at least in duplicates.

2.2.2. Direct photolysis experiments

Direct photolysis was carried out using a quasi-collimated solar simulator with 150-W ozone-free xenon arc lamp (Sciencetech Inc., SS150W, Canada). Incident irradiance, measured using a spectroradiometer placed at the same position as the irradiated samples (International Light, Model ILT900R, USA), was 710 W m^{-2} (integrated between 280 and 950 nm), including UVA irradiance of 21.5 W m^{-2} and UVB irradiance of 0.9 W m^{-2}. A manual shutter was used to control exposure time. CP samples for direct photolysis experiments were prepared by applying 40 μl of Dorsban solution (250 mg/L in ethanol) on clean glass slide and letting the solvent to fully evaporate prior to irradiation. After photolysis, the samples were placed in a small glass beaker, covered with 3 ml Acetonitrile and sonicated for 15 min at 50 °C. The extracted solutions were then analyzed by GC-MS.

2.2.3. Reaction rate with ozone

Chlorpyrifos (CP) reaction rate with ozone was measured using a 1L cylindrical flow-through glass reactor, described in details elsewhere (Petrick et al., 2013). In a typical experiment, six glass slides with 10 μg CP film on each, were placed at the bottom of the reactor and then exposed to a gaseous ozone streams. Chlorpyrifos (CP) films were obtained as in the direct photolysis experiments. Ozone was generated upstream of the reactor by photolyzing a dry flow of air/N_2 gas mixture in a Jelight 600 ozone generator (ozone concentration was controlled by adjusting the air/N_2 ratio). Flow rate of the carrier gas was set at 290 cm^3 min^{-1} (±5%) using mass flow controllers. Ozone steady state concentration was measured at the reactor's outlet using an ozone monitor (2BTechnologies M202). Samples were extracted using the same procedure as the photolysis experiments and analyzed with GC-MS.

2.2.4. Reaction rate with •OH

Exposure of CP to •OH was carried out in a reactor similar to the one used for ozone, center mounted with a 25W 254 nm UV lamp (Jelight, model 81-3306-7). •OH radicals were generated in-situ via