Degradation dynamics and dissipation kinetics of an imidazole fungicide (Prochloraz) in aqueous medium of varying pH

Md. Wasim AKTAR 1, Dwaipayan SENGUPTA 2, Swarnali PURKAIT 2, Madhumita GANGULY 2, M. PARAMASIVAM 1

1 Pesticide Residue Laboratory, Department of Agricultural Chemicals, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur-741252, Nadia, West Bengal, INDIA
2 Department of Agricultural Chemistry and Soil Science, Institute of Agricultural Science, University of Calcutta, Kolkata, West Bengal, INDIA

ABSTRACT

Laboratory degradation studies were performed in water at pH 4.0, 7.0 and 9.2 using Prochloraz (450 EC) formulation at the concentration of 1.0 (T1) and 2.0 (T2) μg/mL. Water samples collected on 0 (2 h), 3, 7, 15, 30, 45, 60 and 90 days after treatments were processed for residue analysis of Prochloraz by HPLC-UV detector. In 60 days, dissipation was 89.1–90.5% at pH 4.0, 84.1–88.2% at pH 7.0, and 92.4–93.8% at pH 9.2 in both treatments. The results indicate that at pH 7.0 the degradation of Prochloraz was much slower as compared to other two. Between pH 4.0 and 9.2 the degradation of compound is little faster at pH 9.2. The half-life periods observed were 18.35 and 19.17 days at pH 4.0, 22.6 and 25.1 days at pH 7.0 and 15.8 and 16.6 days at pH 9.2 at T1 and T2 doses respectively.

KEY WORDS: Prochloraz; pH; dissipation; kinetics; fungicides
Materials and methods

Analytical grade of Prochloraz (99.7%) was obtained from M/S Sigma-Aldrich, USA. All the solvents like dichloromethane, acetone and ethyl acetate were glass distilled before use. Sodium sulphate was washed repeatedly with distilled acetone and activated at 110 °C for 2h before use. Stock solution (100 µg/mL) was prepared in ethyl acetate and working solution was prepared by diluting it.

The pH of aqueous solution was adjusted using buffer. Buffer capsules of pH 4.0, 7.0 and 9.2 from E.Merck were used for the purpose of preparing buffer solution. One capsule was required for 100 mL of distilled water to maintain the above mentioned pH. In a series of Winchester bottles (10L capacity) 6 L distilled water was kept and sixty capsules were added to each of the bottle. The bottles were then left in room temperature for overnight to homogenize the buffer solutions. For carrying out laboratory experiment, water (6L) of each pH triplicate was spiked at 1.0 (T1) and 2.0 (T2) µg/mL with Prochloraz formulation and was stored in Winchester bottles from October to February 2006–07 under room temperature (15–31.5 °C). Untreated control was also carried out simultaneously. Samples were drawn periodically on 0 (2h), 3, 7, 15, 30, 45, 60, and 90 days after treatments and analyzed for Prochloraz residues.

Representative 200 mL water sample was taken in 1L separating funnel and 5–10g sodium chloride was added to it. It was extracted thrice (100, 50, 50 mL) with dichloromethane by liquid-liquid partitioning. Organic phases were combined, passed through anhydrous sodium sulphate and concentrated on a rotary vacuum evaporator under reduced pressure at 40°C followed by a gas manifold evaporator till near dryness. Final solution was made to 5 mL in acetonitrile and subjected to HPLC analysis. No clean-up was required as no interference peaks were observed during analysis.

The residues of Prochloraz were analyzed on HPLC (Agilent Technologies 1200 Series) equipped with variable wavelength detector (VWD) using column (Shandon Hypersil 250 X 4.6 mm ODS 5 (RP-C18)). The wavelength (λ_max), mobile phase and flow rate was 212 nm, methanol-water (85:15, v/v) and 1mL/min, respectively. The retention time, limit of detection (LOD) and limit of quantification (LOQ) were 5.13 min, 0.01 µg/g and 0.05 µg/g, respectively.

Results and discussion

Average recoveries of Prochloraz from water fortified at 0.25 and 1 µg/mL varied from 90–96% at pH 4.0, 88–98% at pH7.0 and 88–97% at pH 9.2.

Residues of Prochloraz in water at different pH levels are presented in Table 1. As evident from the data, at pH 4.0, initial residues of 0.95 µg/mL in treatment T1 dissipated to 0.85 µg/mL in 3 days, 0.42 and 0.09µg/mL in 30 and 60 days, respectively. Corresponding dissipation were 10.5, 55.8 and 90.5%, respectively. In treatment T2, initial residues of 1.93 µg/mL dissipated to 1.64, 0.69 and 0.21 µg/mL in 3, 30 and 60 days after application with corresponding dissipation of 15.0, 64.3 and 89.1%, respectively.

At pH 7.0, initial residues of 0.93 µg/mL in T1 treatment, dissipated to 0.88, 0.45, 0.11 and 0.07 µg/mL in 3, 30, 60 and 90 days after treatment with corresponding dissipation of 5.38, 51.61, 88.17 and 92.5% respectively, whereas in T2 initial residues of 1.95 µg/mL dissipated to 1.68, 0.79, 0.31 and 0.06 µg/mL in 3, 30, 60 and 90 days after treatment showing dissipation of 13.85, 59.49, 84.10 and 91.3%, respectively.

At pH 9.2, from treatment T1 initial residues of 0.97 µg/mL dissipated to 0.73, 0.28 and 0.06 µg/mL in 3, 30 and 60 days after treatment with corresponding dissipation of 24.74, 71.13 and 93.8%, respectively. In T2 residues of 1.96 µg/mL dissipated to 1.13, 0.45 and 0.15 µg/mL in 3, 30 and 60 days after treatment showing dissipation of 42.4, 71.1 and 85.2%.

Table 1

<table>
<thead>
<tr>
<th>Time (in days)</th>
<th>pH 4.0</th>
<th>pH 7.0</th>
<th>pH 9.2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0 µg/mL</td>
<td>2.0 µg/mL</td>
<td>1.0 µg/mL</td>
</tr>
<tr>
<td>0</td>
<td>0.95±0.09</td>
<td>1.93±0.01</td>
<td>0.93±0.03</td>
</tr>
<tr>
<td>3</td>
<td>0.85±0.03</td>
<td>1.64±0.03</td>
<td>0.88±0.06</td>
</tr>
<tr>
<td>7</td>
<td>0.73±0.05</td>
<td>1.47±0.09</td>
<td>0.76±0.13</td>
</tr>
<tr>
<td>15</td>
<td>0.62±0.01</td>
<td>1.24±0.01</td>
<td>0.64±0.04</td>
</tr>
<tr>
<td>30</td>
<td>0.42±0.04</td>
<td>0.69±0.06</td>
<td>0.45±0.08</td>
</tr>
<tr>
<td>45</td>
<td>0.19±0.02</td>
<td>0.39±0.03</td>
<td>0.27±0.06</td>
</tr>
<tr>
<td>60</td>
<td>0.09±0.05</td>
<td>0.21±0.02</td>
<td>0.15±0.04</td>
</tr>
<tr>
<td>90</td>
<td>BDL</td>
<td>BDL</td>
<td>0.07±0.07</td>
</tr>
</tbody>
</table>

BDL=Below Detectable Limit
on 0 (2h) day dissipated to 1.54, 0.59 and 0.15 in 3, 30 and 60 days after treatment and corresponding dissipation was 21.4, 69.9 and 92.4%, respectively.

It is clear that Prochloraz residues in water dissipated more than 80% in 60 days at pH levels of 4.0, 7.0 and 9.2 in both treatments under laboratory conditions under temperature ranging from 15 to 31.5°C. The degradation was slow during first 3 days followed by relatively faster degradation from 3rd day onward to 45 days after which it became slow.

Almost identical degradation ranging from 89.1 to 93.8% at two pH levels (viz. pH 4.0 and 9.2) during 60 days study indicate that there was no significant effect of these two pH on degradation, although dissipation was a little faster at pH 9.2 throughout the studies. More than 91% degradation at 90 days after treatment indicates that degradation was much slower at pH 7.0 than that of other two. Half-life values at pH levels of 4.0, 7.0 and 9.2 varied from 18.4 to 19.2, 22.6 to 25.1 and 15.8 to 16.6 days, respectively (Table 2). At all pH levels degradation was observed to be faster in T1 than T2. The slow dissipation at higher rate could attribute to inhibition of microbial activity.

Similar observations have been reported in degradation of fenoxanil in water where dissipation was independent of pH and was subject to photodegradation following pseudo first order kinetics. Dissipation of Nonylphenol Diethoxylates residues has also been reported following pseudo first order kinetics in river waters (Cravedi et al., 2001). Whereas in another studies, decomposition of Nonylphenol Ethoxylates and bixafen in water as pH and dose dependent, resulted in faster dissipation under alkaline conditions and at low dose of application (Debrauwer et al., 2001; Gac et al., 2001). Slightly faster dissipation of Prochloraz at alkaline pH has been observed in our studies also.

Conclusions

Considering rapid dissipation of Prochloraz at the tested doses in water system, its much faster degradation can be expected under field condition. Consumption of vegetables from Prochloraz treated field could not be independent of health as no residues of the herbicide would be found in the harvested plant samples as the dissipation of Prochloraz would be higher in plant system due to higher enzymatic activity. Hence, the tested doses can be considered safe from the point of view of health hazards, environmental pollution and ground water contamination due to its residual effects.

Acknowledgement

The authors are grateful to Head, Dept. of Bio-Chemistry, Institute of Agricultural Science, University of Calcutta, Kolkata, West Bengal, India for providing the necessary instrumental facilities.

Table 2.
Regression equation, Correlation Co-efficient and half-life for the dissipation of Prochloraz in water at different pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>Treatments (μg/mL)</th>
<th>Regression Equation</th>
<th>Correlation Co-efficient</th>
<th>Half-life (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>1.0 y = 2.007 – 0.0164x</td>
<td>0.977</td>
<td>18.35</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>y = 2.29 – 0.0157x</td>
<td>0.995</td>
<td>19.17</td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>1.0 y = 1.9863 – 0.0133x</td>
<td>0.975</td>
<td>22.64</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>y = 2.2641 – 0.0121x</td>
<td>0.992</td>
<td>25.08</td>
<td></td>
</tr>
<tr>
<td>9.2</td>
<td>1.0 y = 1.953 – 0.019x</td>
<td>0.992</td>
<td>15.84</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>y = 2.2824 – 0.0181x</td>
<td>0.995</td>
<td>16.63</td>
<td></td>
</tr>
</tbody>
</table>

REFERENCES


