Chlorothalonil accelerates the photodecomposition of other pesticides exposed to sunlight on wax films

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Objective: Just after foliar application, pesticides are exposed to solar light and can potentially undergo photodegradation. This photochemical reactivity affects the pesticide efficiency. Yet, these reactions are rarely studied. Another issue poorly considered is the potential mutual effects between pesticides. To improve crop protection, it is frequent to apply pesticides in mixtures or to use successively different pesticides during annual crop treatments. Mixing pesticides might have consequence on their photostability. Here, we investigated the fate of a mixture of two pesticides (the fungicide chlorothalonil and the herbicide cycloxydime) which have been already studied alone (1,2).

Enhancing effect of CT on CD phototransformation

To model leaves that are covered with a waxy layer, photodegradation experiments were carried out on paraffinic wax films. Irradiation were conducted in a solar simulator (500 W m\(^{-2}\)).

![Figure 2: Decay of CD (200 g ha\(^{-1}\)) irradiated on paraffin wax in Solar simulator. CD alone (○, k=0.11±0.01 h\(^{-1}\)) and in the presence of CT at 150 g ha\(^{-1}\) (●, k=0.30±0.03 h\(^{-1}\)). Stratos alone (Δ, k=0.41±0.04 h\(^{-1}\)), in the presence of CT at 20 g ha\(^{-1}\) (●, k=0.58±0.06 h\(^{-1}\)), and in the presence of Fongil at 150 g ha\(^{-1}\) (▲, k=1.3±0.1 h\(^{-1}\)).](image)

CD disappears faster in the presence of CT than in its absence. In contrast, CT does not disappear in the time scale of the experiments whatever the conditions. Formulated CD (Stratos) disappears also faster in the presence of formulated CT (Fongil) than in its absence.

Laser Flash Photolysis

The reaction was studied by time-resolved spectroscopy to measure individual reaction rate constants. Excitation of CT at 266 nm yields the triplet excited state which may undergo different reactions:  
* deactivation (k\(_d\) = 5.7x10\(^4\) s\(^{-1}\)),  
* reaction with oxygen, producing singlet oxygen (k\(_{O_2}\) = 1.0x10\(^8\) M\(^{-1}\) s\(^{-1}\)),  
* reaction with CD by H-atom transfer (k\(_{CD}\) = 7.5x10\(^9\) M\(^{-1}\) s\(^{-1}\)).

![Figure 4: Absorption spectrum of CT triplet (%CT*)](image)

Photoproducts

Photoprocesses were recovered by rinsing irradiated wax films using ACN and solutions were further analyzed by HPLC-MS in the ES+ mode.

![Figure 3: TIC HPLC/MS of CD irradiated alone or in the presence of CT](image)

Irradiated alone, CD is photolysed into I, II, II and IV. These products are due i) to the cleavage of the N-O bond and ii) to an oxidation. In the presence of CT, the oxidation products I, II and IV are formed in much higher amounts. Interestingly, oxidation of wax components is also observed.

Mechanism

CT enhances CD photodegradation through two pathways: singlet oxygen production and direct oxidation of CD by triplet CT. CT is regenerated in these two processes. CT is thus a sensitizer.

![Figure 5: Reactivity of CT* with oxygen and CD](image)

Conclusions

Chlorothalonil enhances the photodegradation of cycloxydime in solar light. This reactions should have consequences in real conditions by increasing the herbicide dissipation and thus decreasing its efficiency. Similar effects might be observed with other pesticides. Therefore, it is important to investigate the fate of pesticides in mixtures together with their individual behaviours. This work also shows that wax constituents can undergo oxidation in the course of pesticides photolysis.

References