Photolysis of Neonicotinoid Insecticide in systems simulating leaf surfaces: Rates and Toxicity Assessments

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• Widely used
  --- introduced in 1990s
  --- represented 24% of the global market for insecticides in 2008

• Frequently detected
  --- in surface water and groundwater
  --- in drinking water
  --- in soil

Why Neonicotinoids?

• Break down slowly in the environment
  --- taken up by the plant
  --- long half-lives in water
  --- degrade slowly in the absence of sunlight and micro-organisms

• Affect the insect central nervous system
  --- nervous stimulation, death and paralysis

• Susceptible to photolysis
  --- half-lives of 5-36 hours in near surface waters
  --- restricted at depths greater than 8 cm
  --- can also occur on plant surfaces

The persistence of neonicotinoids in the environment and their potential toxic effects are not fully understood.

Objectives

• Identify reaction kinetics and products on various surface upon exposure to sunlight.

• Assess toxicity of neonicotinoids to soil and aquatic species before and after photolysis.

• Disseminate the findings to stakeholders, regulators, and the public.
Imidacloprid
thiamethoxam
clothianidin
acetamiprid

• commercial product containing other active ingredients:
tebuconazole;
difenconazole;
piperonyl butoxide;
N/A
tau-fluvalinate
lambda-cyhalothrin
metofluthrin

• pure compound prepared in DI water
• Reaction kinetics
  --- real product & pure compound in H₂O
  --- various surfaces: wax, glass, alum foil, leaf

• Product identification
  --- Analysis by Orbitrap Velos LC-MSn

• Actinometry; Assessment of toxicity (in process)
Monitor the photodegradation on glass & Al foil surface

--- 1 mL of neonics deposited onto the surface
--- allow to evaporate
--- reactors exposed to artificial sunlight (765 w/m²) (5 replicates)
--- extract back into 50% ACN, 3 mL x 3 times
--- 0.2 μm filter
--- HPLC

Atlas Suntest CPS+ solar simulator, using a xenon arc lamp with a 290 nm cutoff filter.
Monitor the photodegradation on wax surface

--- melt ~ 1 gm wax

--- 1 mL of neonics deposited onto wax surface
Monitor the photodegradation of imidacloprid on strawberry leaf in solar sim

--- soak 0.25 g of strawberry leaf into imidacloprid solution for ~10 s
--- allow to dry in hood for 30 min
--- 4 replicates
--- extract back into 50% ACN, 2 mL x 3 times
- imidacloprid degradation on wax
  --- initial concentration: 550 µM

Results
• imidacloprid degradation on glass
  --- initial concentration: 550 µM

Results
Summary of kinetics

- Photolysis rates on glass and aluminum foil were much faster than those on paraffin wax and leaves.

- For imidacloprid, degradation of real product followed first order kinetics, while pure compound followed zero order kinetics.

- For thiamethoxam, degradation of real product and pure compound both followed first order kinetics.

- For clothianidin, degradation of real product followed zero order kinetics, while pure compound was observed to be relatively stable.

- No disappearance observed for acetamiprid.
Conclusions: Kinetics

• Photodegradation of commercial products were much more reactive than pure compounds.

• Various neonics on different surfaces follow different photodegradation rate laws and mechanisms.

• Paraffin wax best simulates the reaction environment on leaves.
• Reaction kinetics
  --- real product & pure compound in H₂O
  --- various surfaces: wax, glass, alum foil, leaf

• Product identification
  --- Analysis by Orbitrap Velos LC-MSn

• Actinometry; Assessment of toxicity (in process)
• Liquid chromatography coupled to a high resolution and accurate mass – tandem mass spectrometer (LC/HRAM-MS/MS; Thermo Fisher Scientific LTQ Orbitrap Velos)

• Positive & negative mode

• Compound Discoverer 3.0 (Thermo Fisher Scientific)

• work-flows: targeted and untargeted

• Products identification in various approaches.
Summary of proposed transformation products for imidacloprid
“Conclusions”: Products

• Products were observed to vary on different surfaces.

• Products for commercial and pure compounds were different on each surface.

• Nitro Reduction and dichlorination were the major reaction processes.
• Reaction kinetics
  --- real product & pure compound in H₂O
  --- various surfaces: wax, glass, alum foil, leaf

• Product identification
  --- Analysis by Orbitrap Velos LC-MSn

• Actinometry; Assessment of toxicity (in process)
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