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

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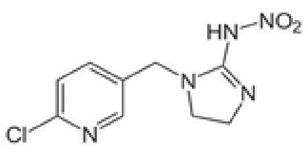
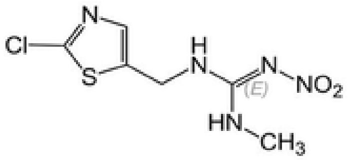
- Widely used

  --- introduced in 1990s

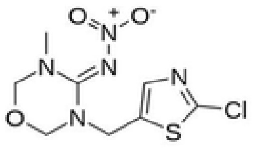
  --- represented 24% of the global market for insecticides in 2008



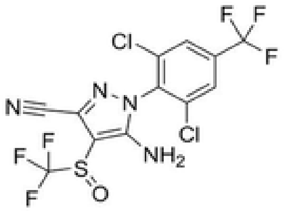
Imidacloprid



Chlothianidin



Thiometoxam



Fipronil

- Frequently detected

  --- in surface water and groundwater

  --- in drinking water

  --- in soil


- Stephen A. Todey, Ann M. Fallon, and William A. Arnold. *Environmental Toxicology and Chemistry*, **2018.**

# 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

- Peter Jeschke, Ralf Nauen, Michael Schindler, and Alfred Elbert. *J. Agric. Food Chem.*, **2011**, *59* (7), pp 2897–2908.

# Why Neonicotinoids?

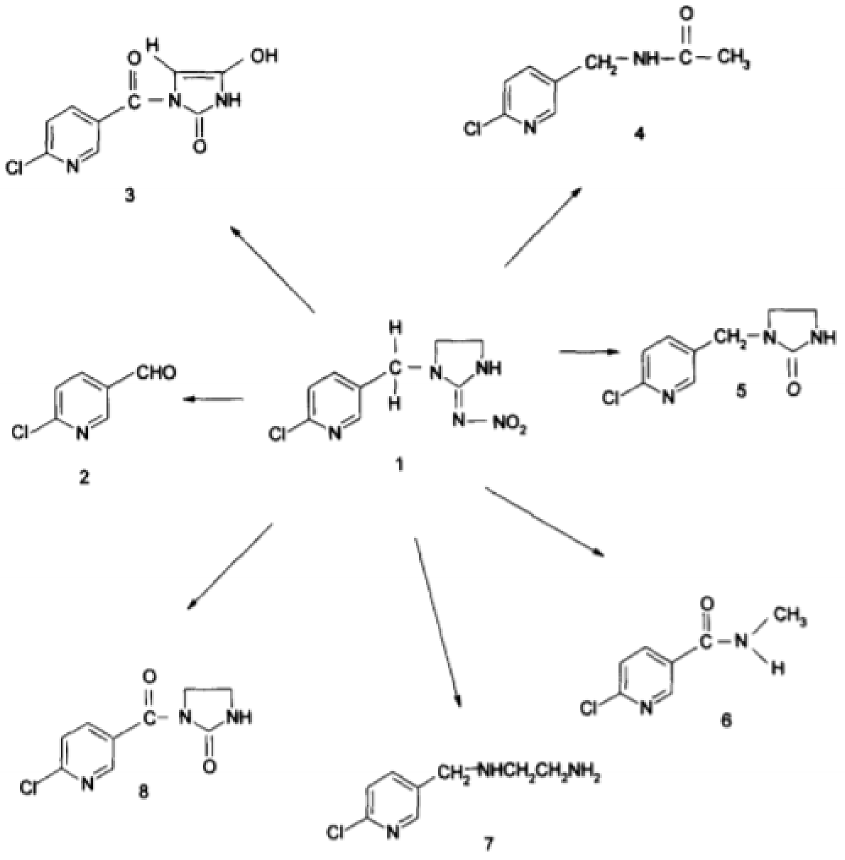
- Susceptible to photolysis

  --- half-lives of 5-36 hours in near surface waters

  --- restricted at depths greater that 8 cm

  --- can also occur on plant surfaces

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

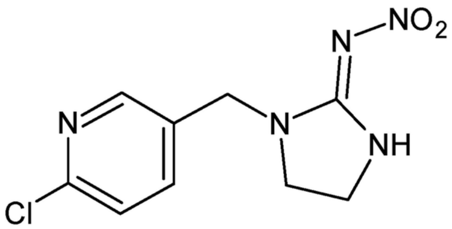


Photoproducts of imidacloprid in water

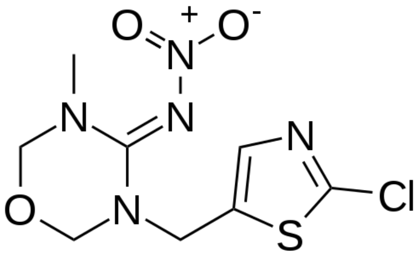

- Moza, P.N., Hustert, K .Feicht, E. Kettrup, A.. *Chemosphere*, **1998**, *36* (3), pp 497–502.

# Objectives

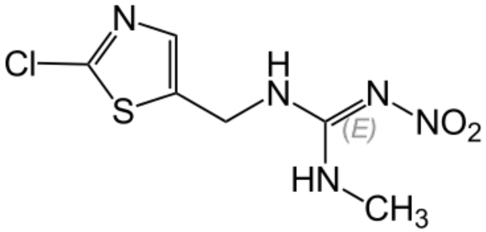
- Identify reaction kinetics and products on various surface upon exposure to sunlight.
- Assess toxicity of neonicotinoids to soil and aquatic species before and after photolysis.
- Disseminate the findings to stakeholders, regulators, and the public.

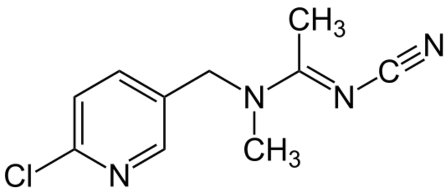
**Imidacloprid**



**thiamethoxam**



**clothianidin**



**acetamiprid**

- **commercial product containing other active ingredients:**

| Imidacloprid | thiamethoxam | clothianidin | acetamiprid |
|---|---|---|---|
| tebuconazole; tau-fluvalinate | difenoconazole; lambda-cyhalothrin | piperonyl butoxide; metofluthrin | N/A |

- **pure compound prepared in DI water**

- Reaction kinetics

--- real product & pure compound in $H_2O$

--- 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

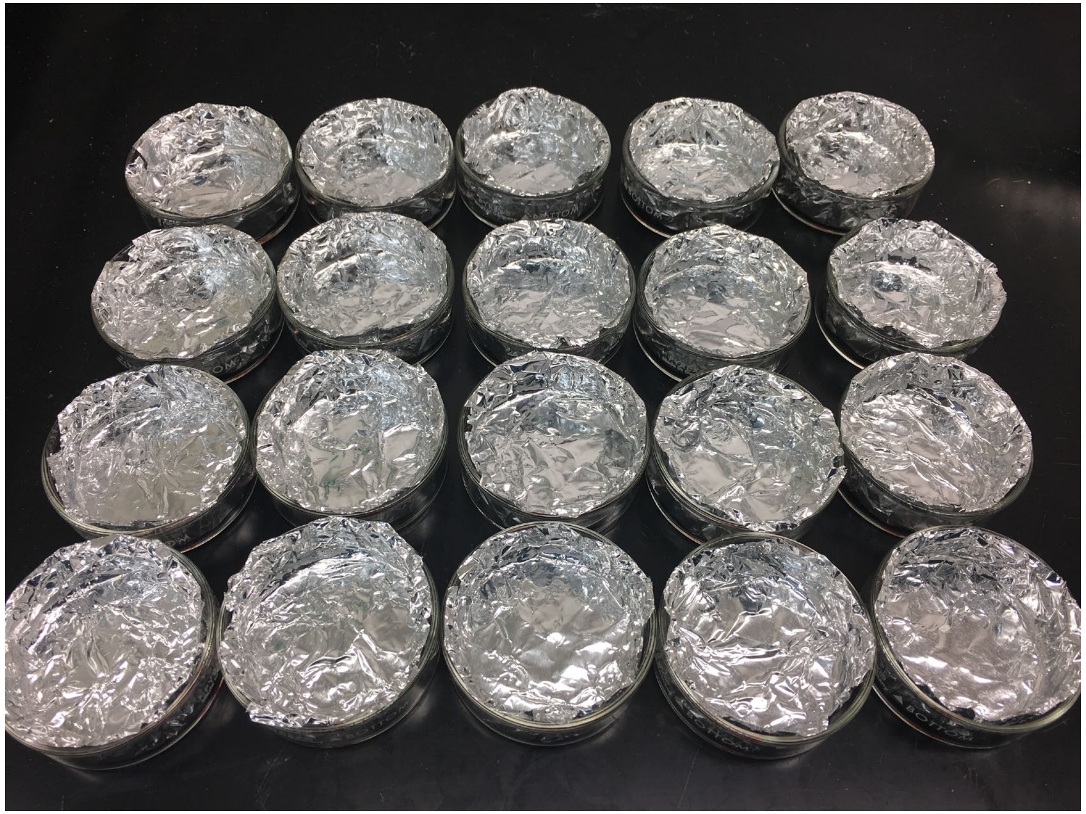
--- allow to evaporate

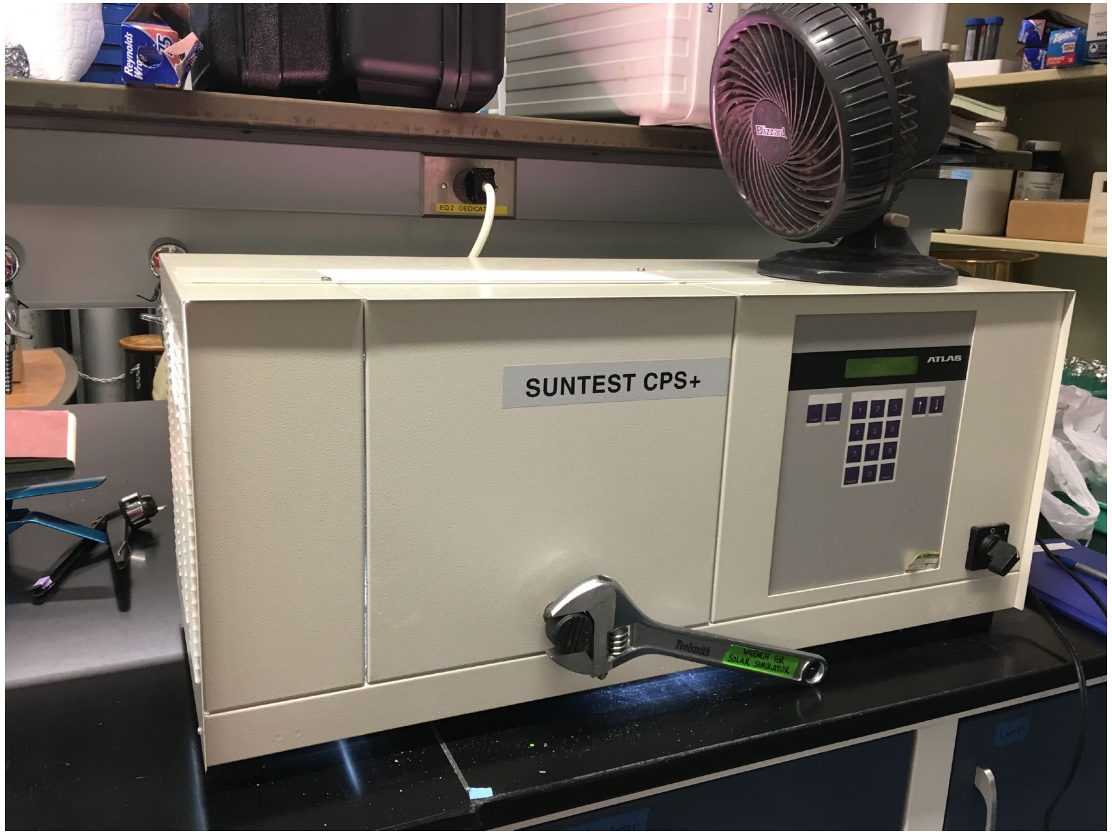
--- reactors exposed to artificial sunlight (765 w/m$^2$) (5 replicates)

--- extract back into 50% ACN, 3 mL x 3 times

--- 0.2 μm filter

--- HPLC



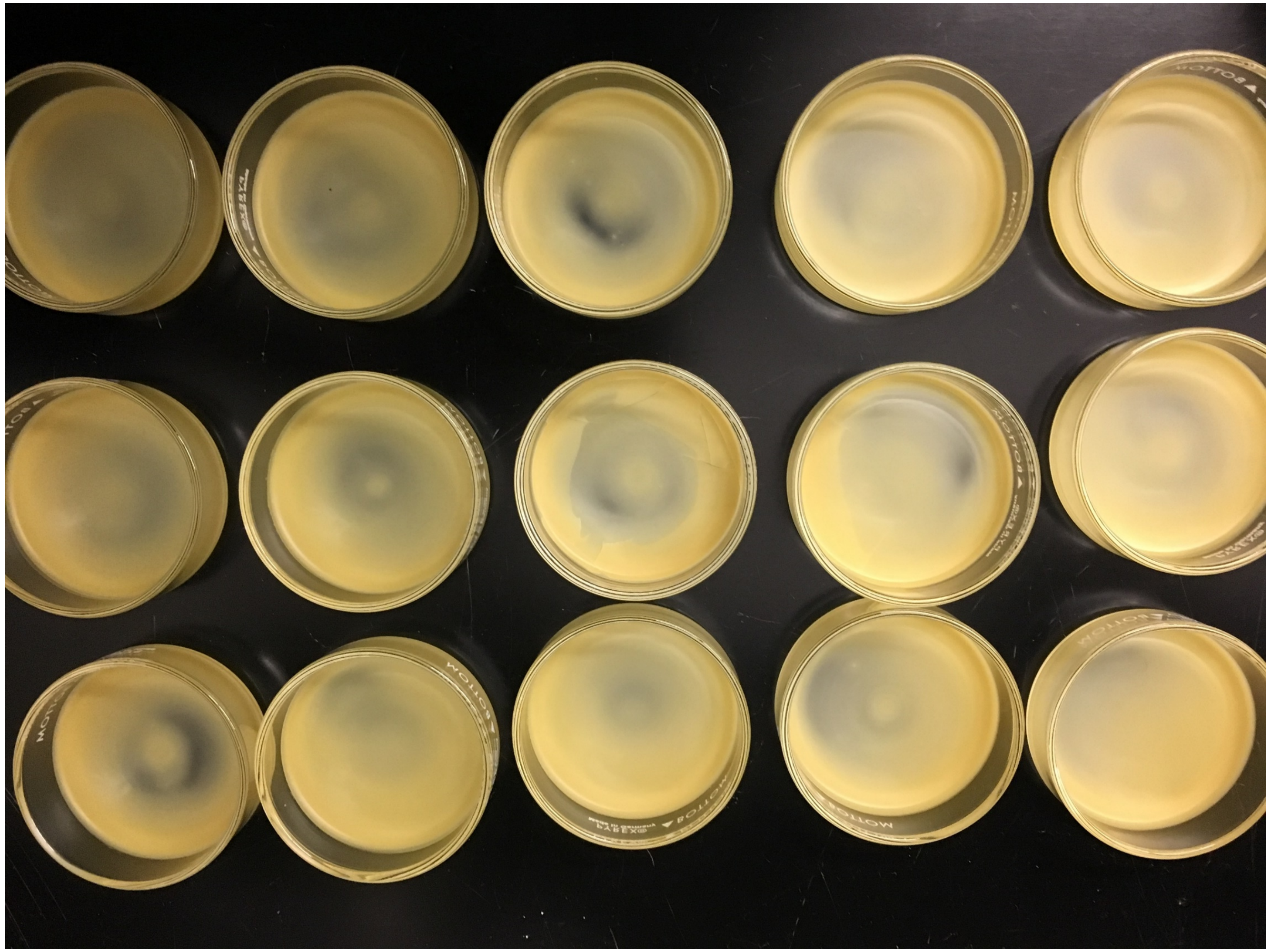



Atlas Suntest CPS+ solar simulator, using a xenon arc lamp with a 290 nm cutoff filter.

## 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

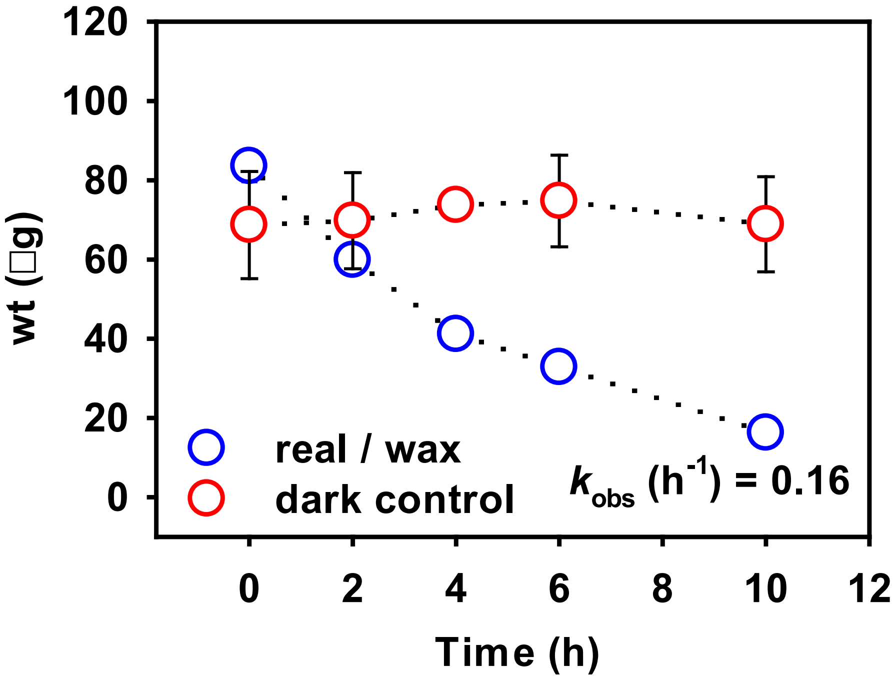
--- allow to dry in hood for 30 min

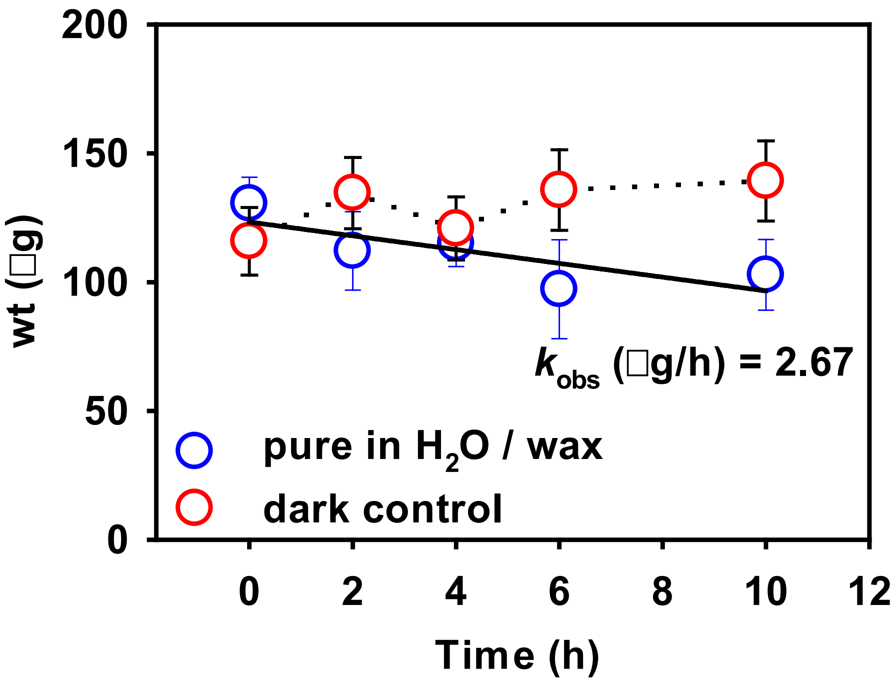
--- 4 replicates

--- extract back into 50% ACN, 2 mL x 3 times

- imidacloprid degradation on wax

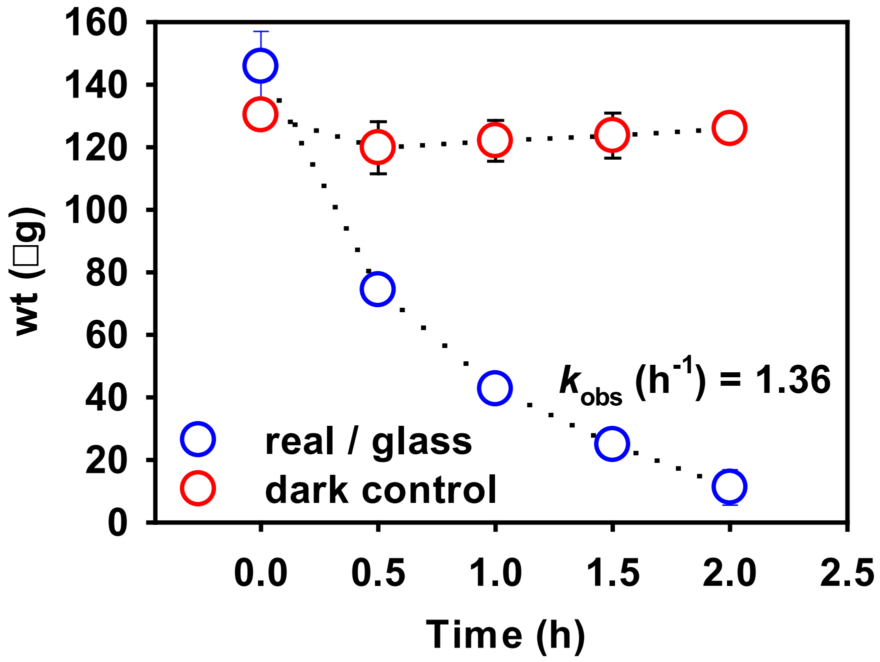
  --- initial concentration: 550 µM

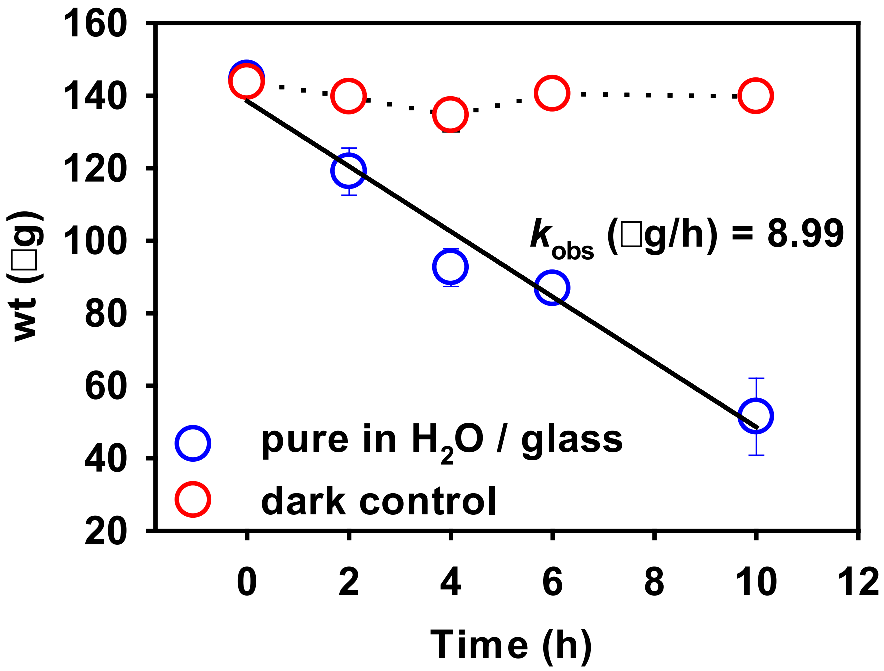


- imidacloprid degradation on glass

  --- initial concentration: 550 μM




# Results

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# 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 $H_2O$

--- 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

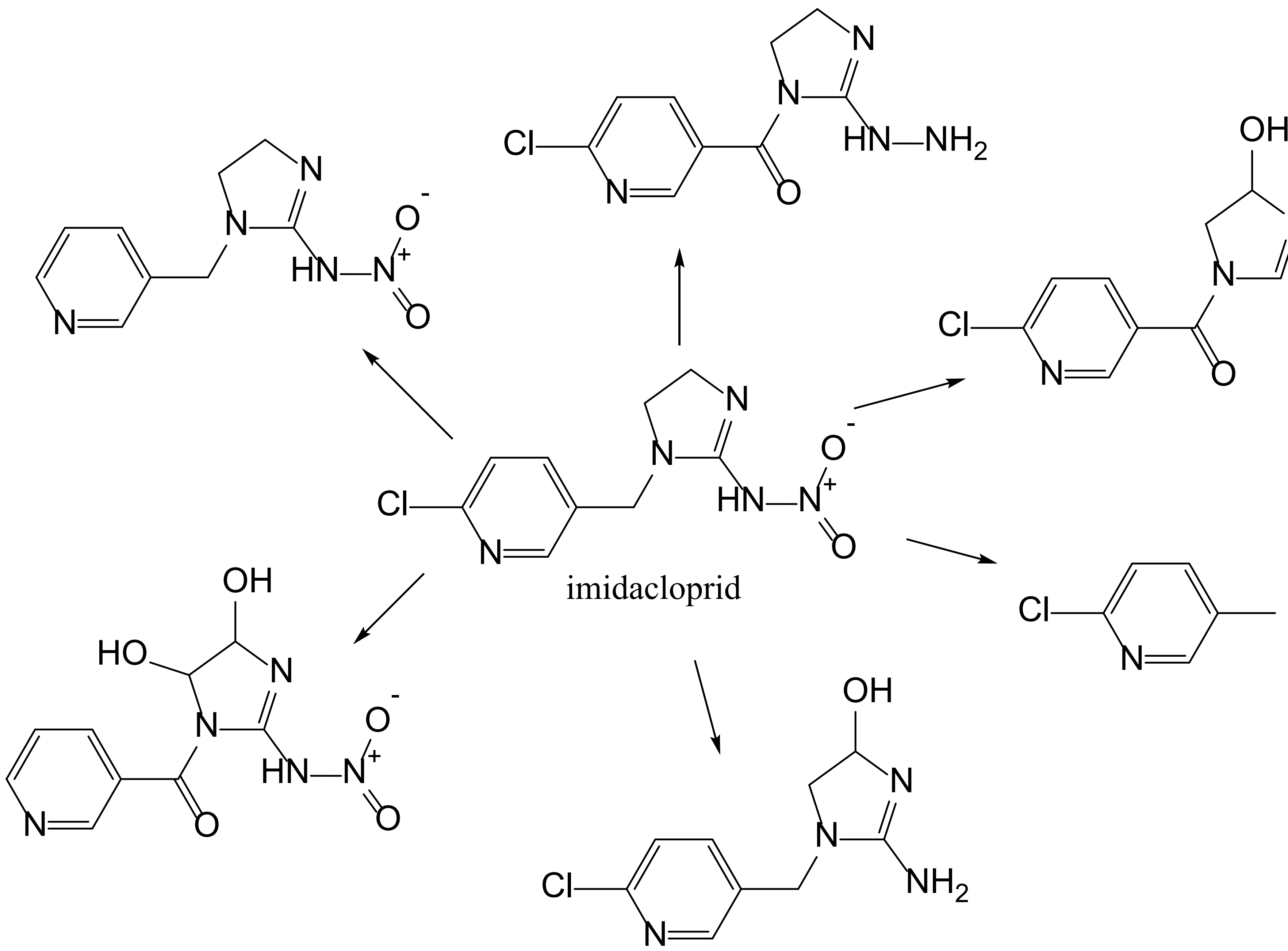
- Compound Discoverer 3.0 (Thermo Fisher Scientific)

- work-flows: targeted and untargeted

- Products identification in various approaches.

# Methods

# 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 $H_2O$

--- various surfaces: wax, glass, alum foil, leaf

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