Use of L-ascorbic acid as a mean to prevent in-vial degradation of LC-amenable pesticides

Francisco José Díaz-Galiano
María Murcia Morales
Amadeo R. Fernández-Alba

Co-funded by the European Union

EURL-FV

EURL-FV WEBSITE

EURL-FV

European Union Reference Laboratory for Pesticide Residues
Fruits and Vegetables

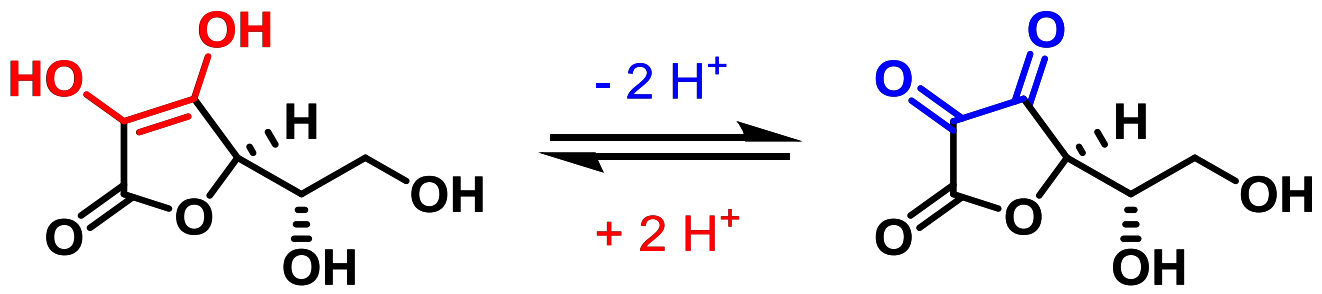
www.eurl-pesticides.eu

Use of L-ascorbic acid as a mean to prevent in-vial degradation of LC-amenable pesticides

L-ASCORBIC ACID

Properties

- Readily undergoes oxidation → antioxidant properties



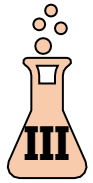
- Solubility up to 30 % (w/V) in water

- Can be employed as analyte protectant for LC analyses

METHODOLOGY

No L-ascorbic acid: 0.2 mL of the 0.050 ppm pesticide mixture, and 0.8 mL of water

12 ppm L-ascorbic acid: 0.2 mL of the 0.050 ppm pesticide mixture, 0.796 mL of water, and 0.004 mL of the 3 % (w/V) L-ascorbic acid solution

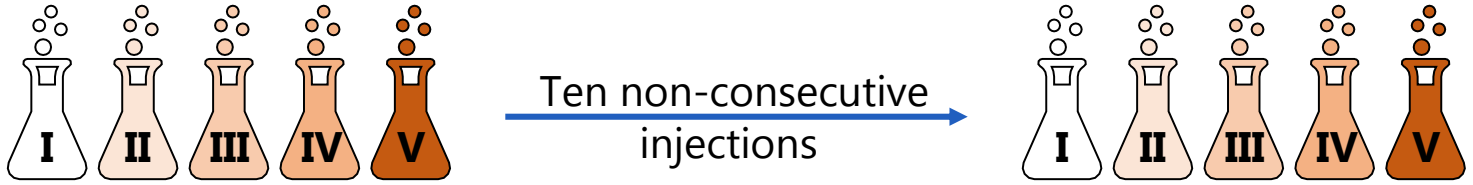


60 ppm L-ascorbic acid: 0.2 mL of the 0.050 ppm pesticide mixture, 0.78 mL of water, and 0.02 mL of the 3 % (w/V) L-ascorbic acid solution

300 ppm L-ascorbic acid: 0.2 mL of the 0.050 ppm pesticide mixture, 0.7 mL of water, and 0.1 mL of the 3 % (w/V) L-ascorbic acid solution

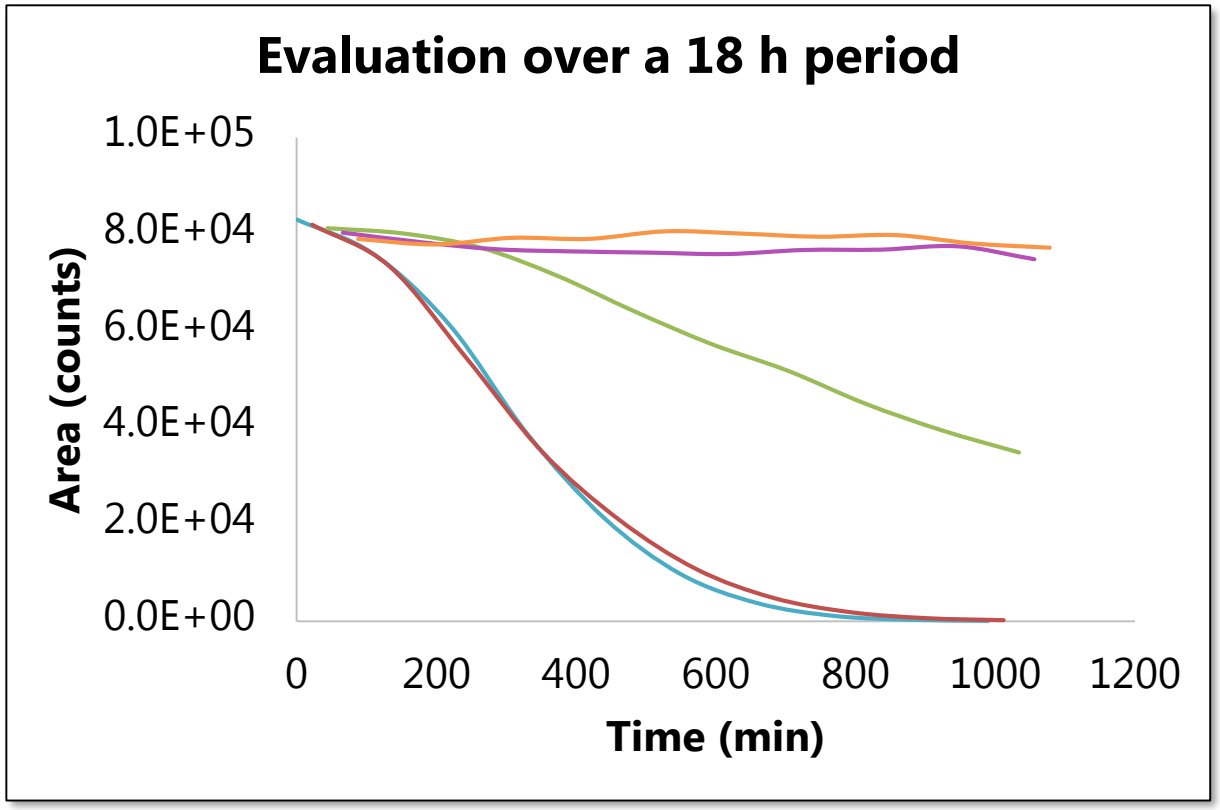
600 ppm L-ascorbic acid: 0.2 mL of the 0.050 ppm pesticide mixture, 0.6 mL of water, and 0.2 mL of the 3 % (w/V) L-ascorbic acid solution

METHODOLOGY



VIAL COMPOSITION

Acetonitrile:Water (20:80, V/V)



L-ascorbic acid in-vial concentration

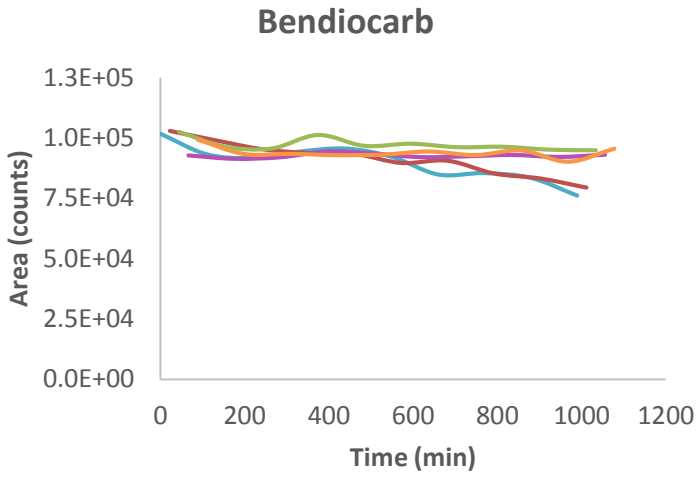
- 0 ppm
- 12 ppm
- 60 ppm
- 300 ppm
- 600 ppm

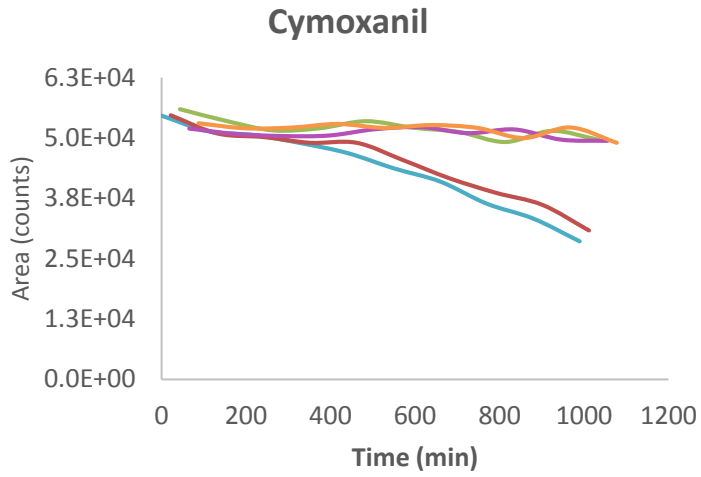
278 LC-amenable compounds evaluated

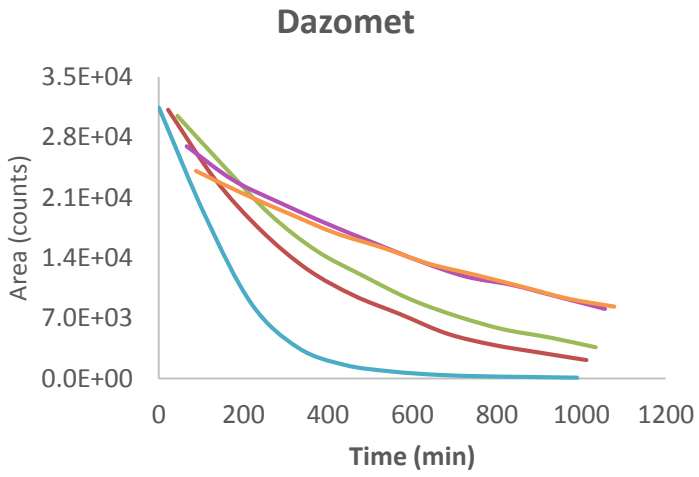
Non-thermostatted autosampler

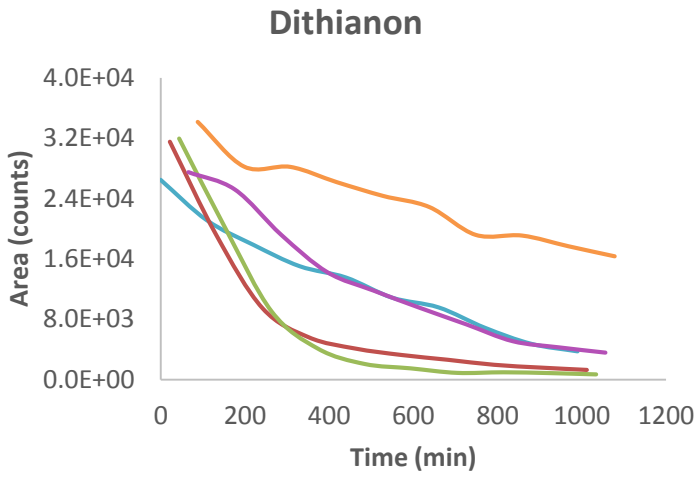
(20 °C ≤ T ≤ 30 °C)

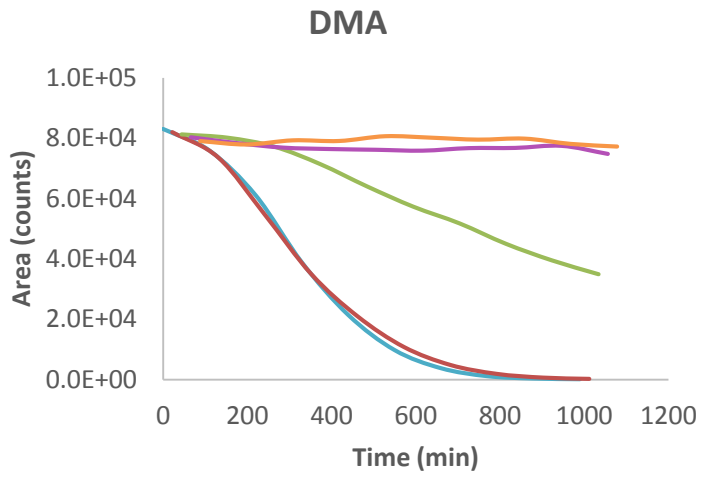
COMPOUNDS POSITIVELY AFFECTED (PRESERVATION)

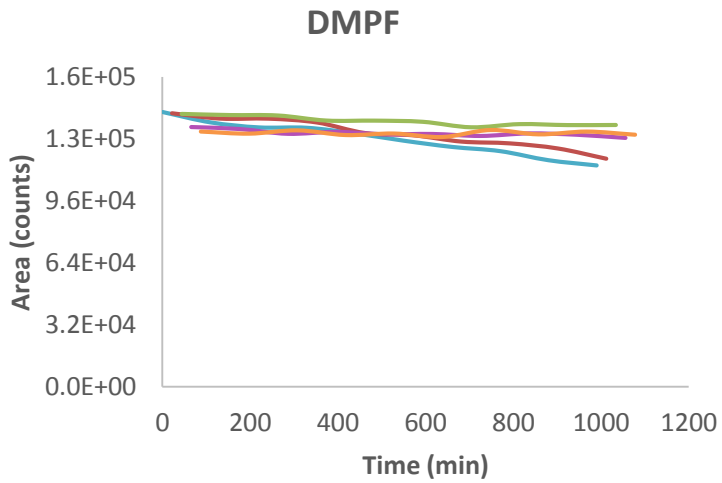






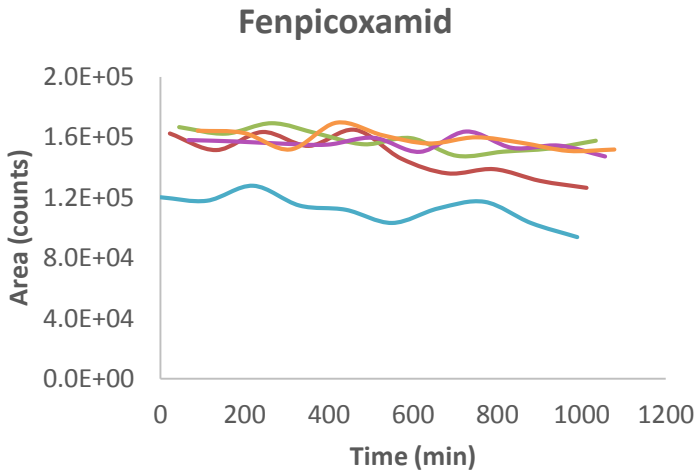


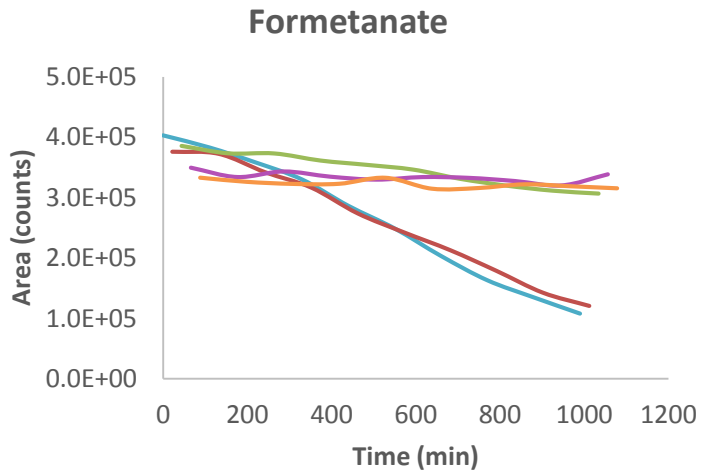


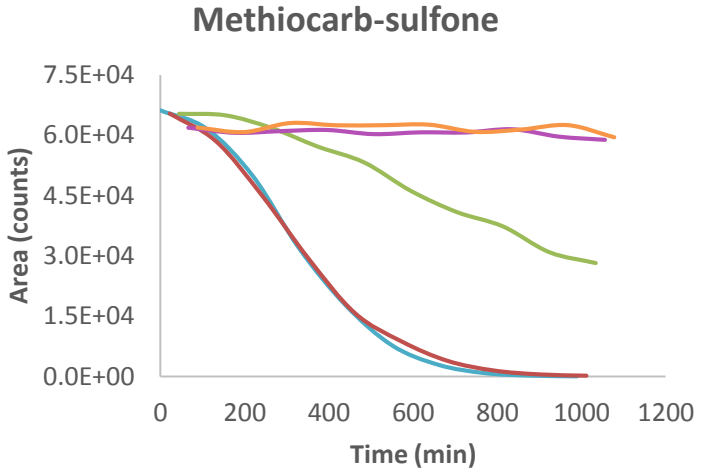


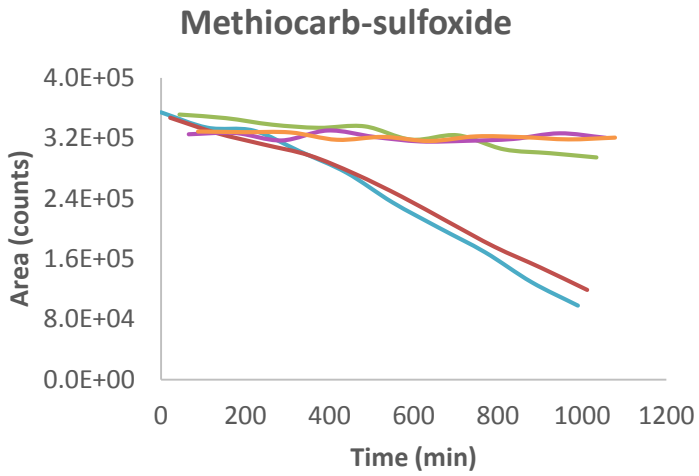
0 ppm 12 ppm 60 ppm 300 ppm 600 ppm

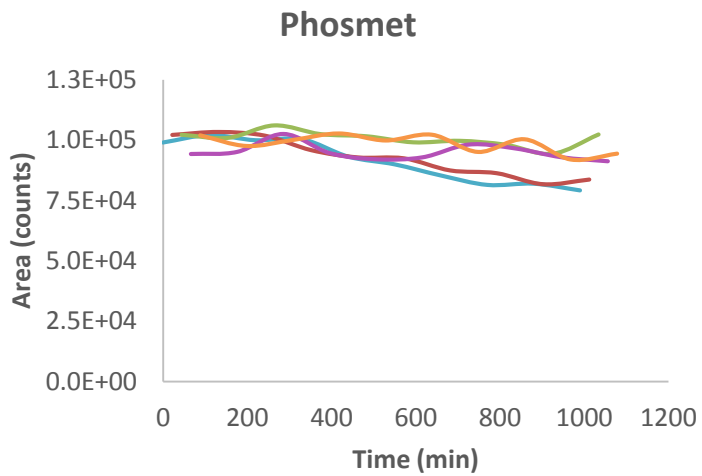
COMPOUNDS POSITIVELY AFFECTED (PRESERVATION)

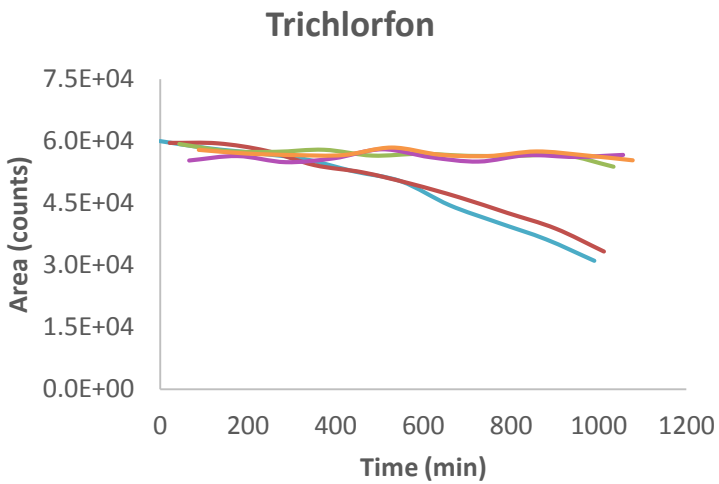






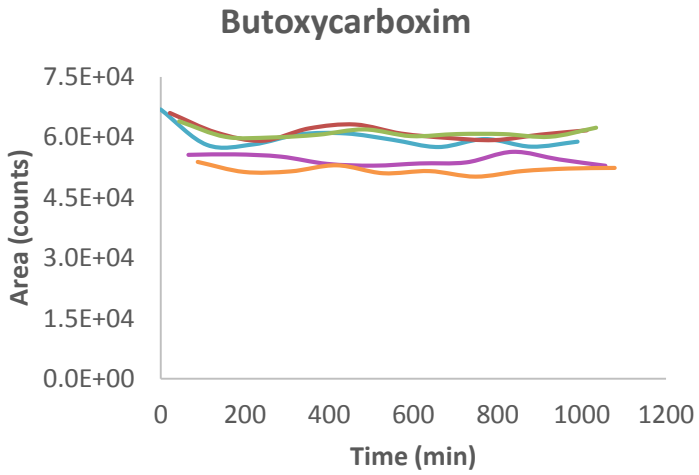


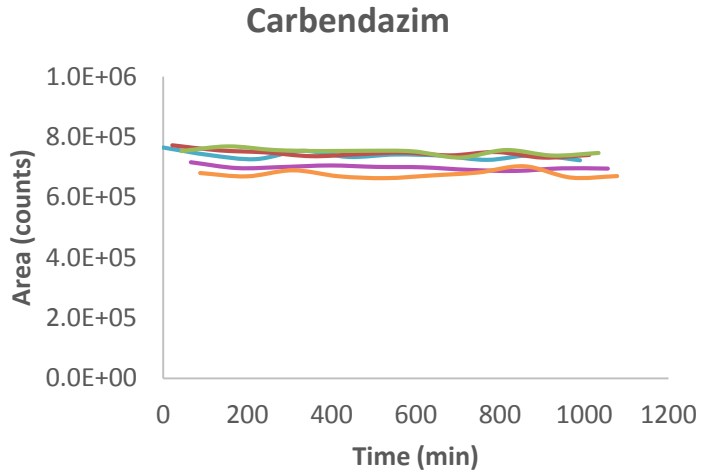


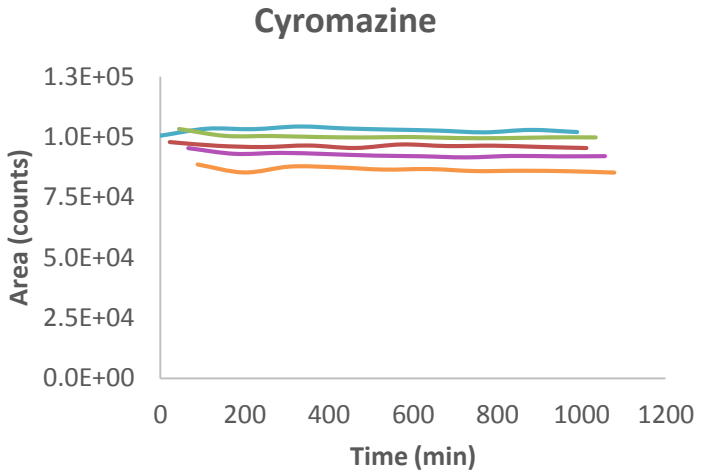


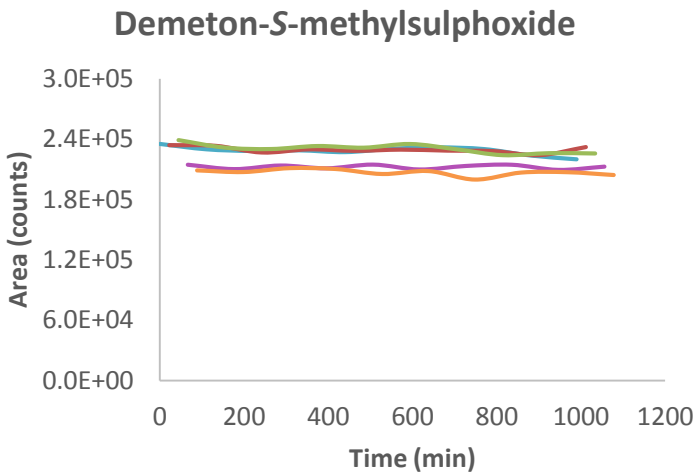
0 ppm 12 ppm 60 ppm 300 ppm 600 ppm

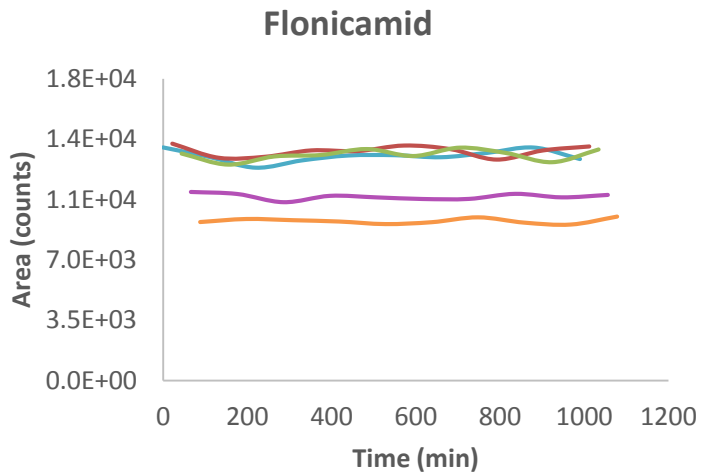
COMPOUNDS NEGATIVELY AFFECTED (SUPPRESSION)

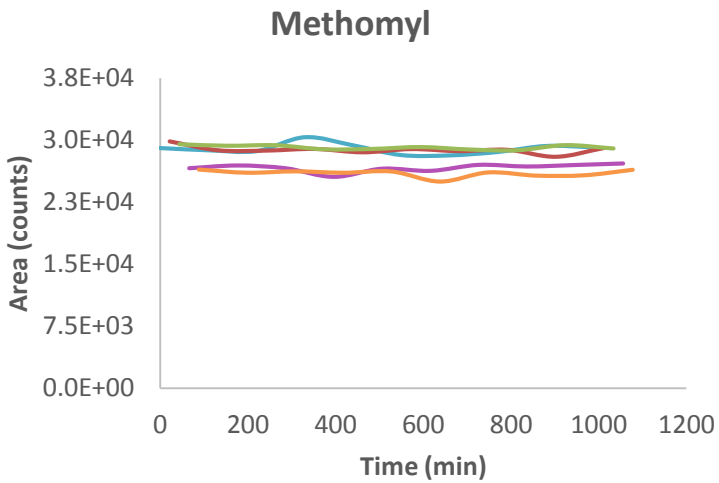






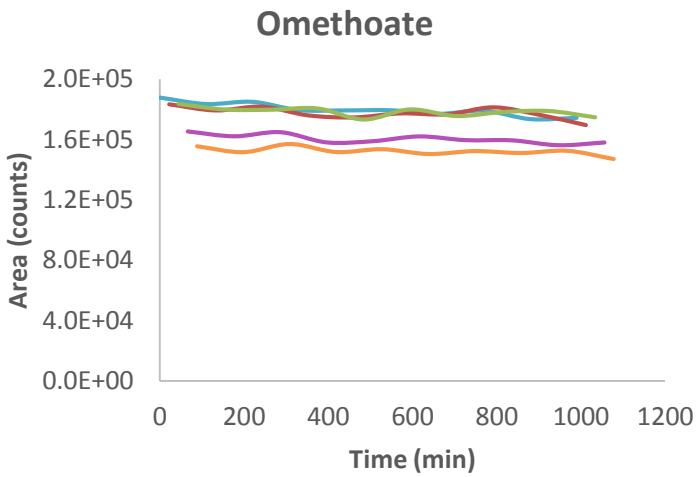


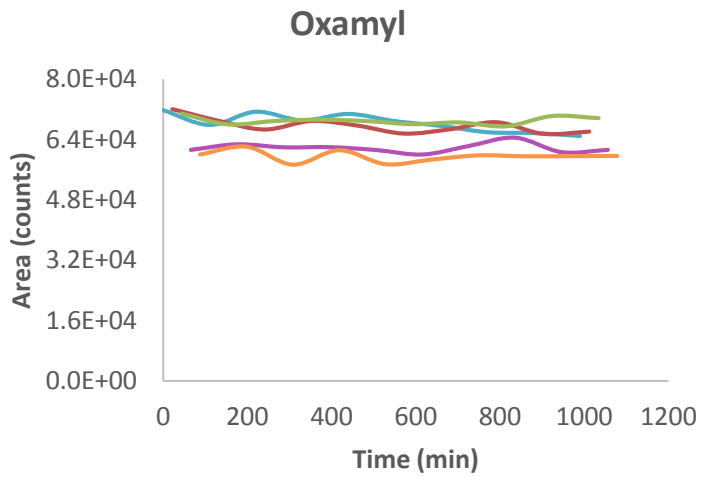


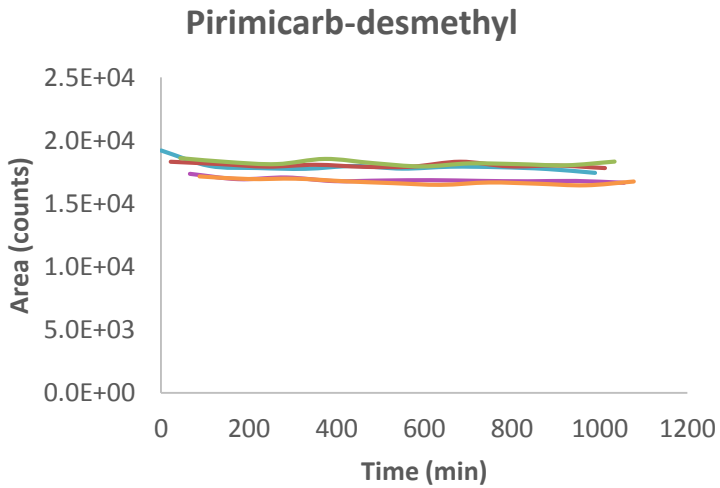


0 ppm 12 ppm 60 ppm 300 ppm 600 ppm

COMPOUNDS NEGATIVELY AFFECTED (SUPPRESSION)

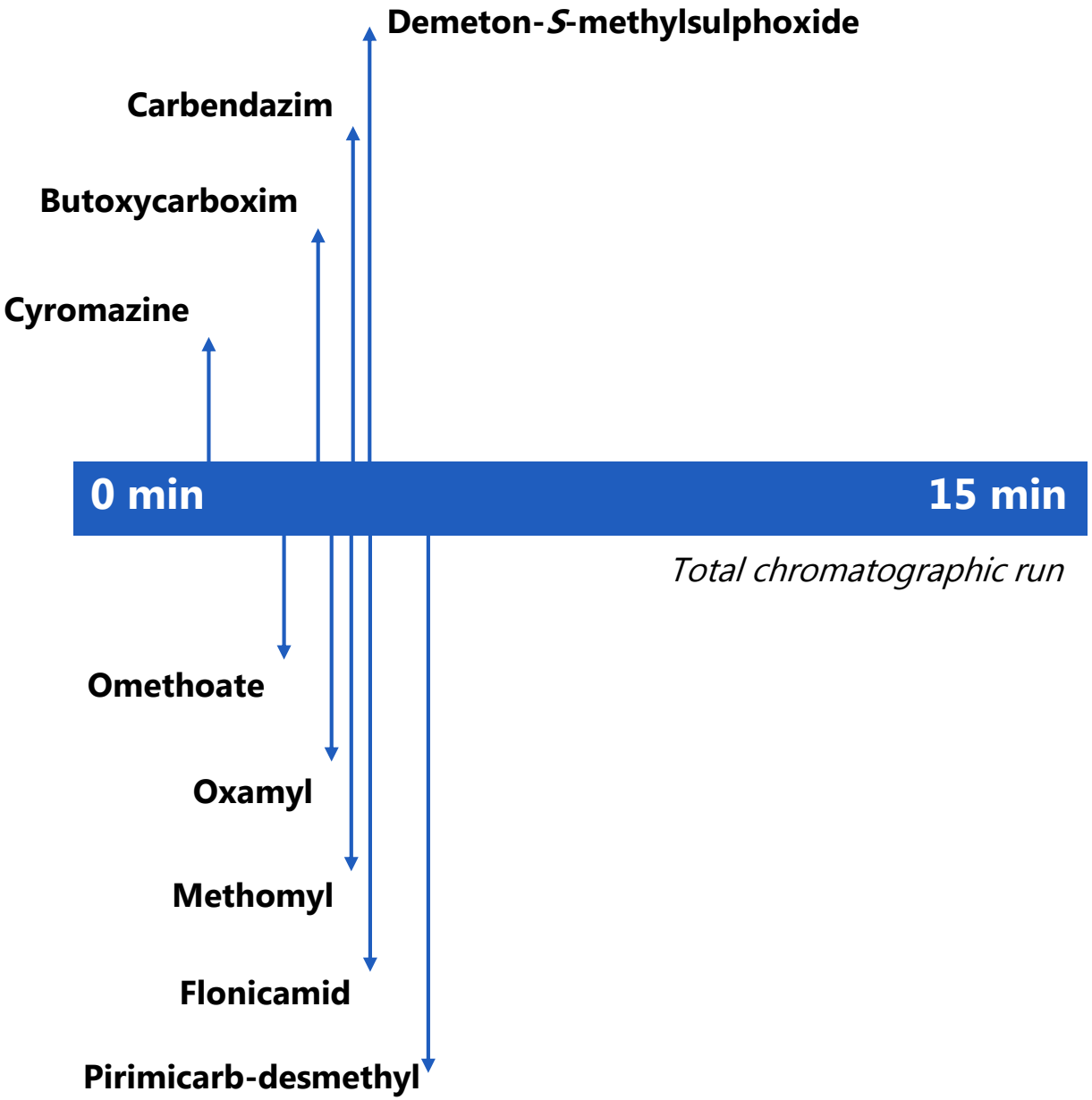






0 ppm 12 ppm 60 ppm 300 ppm 600 ppm

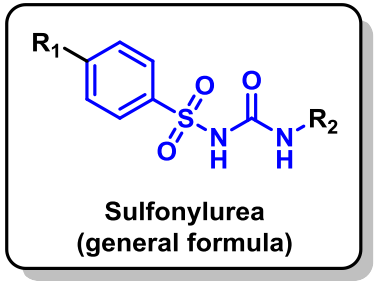
COMPOUNDS NEGATIVELY AFFECTED (SUPPRESSION)

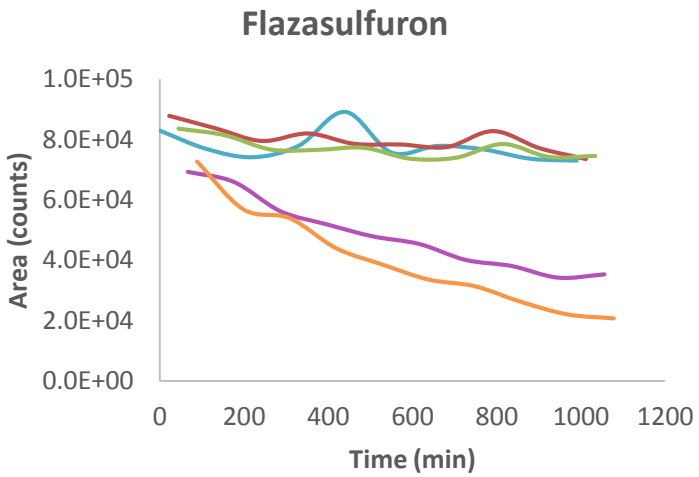


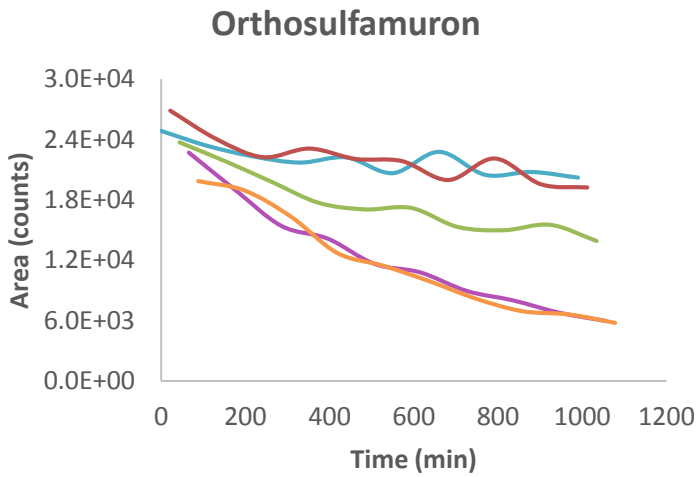
Signal suppression due to high L-AA concentration

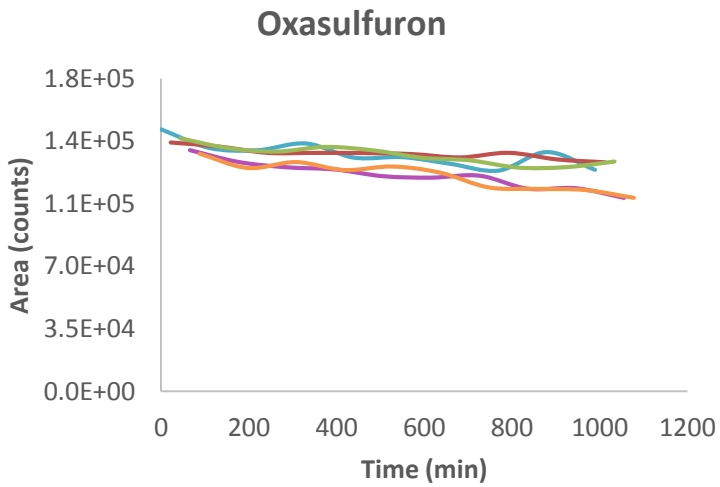
- The elution times of the nine compounds presenting signal suppression were between 2.0 min and 5.3 min
- Not all compounds with $t_R \leq 5.3$ min showed signal suppression
  - Further evaluation necessary

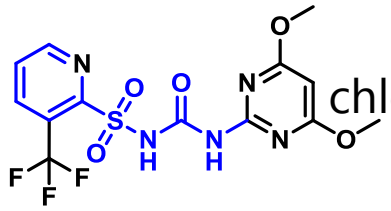
COMPOUNDS NEGATIVELY AFFECTED (DEGRADATION)



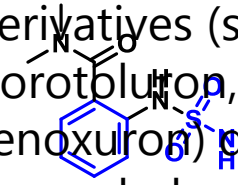


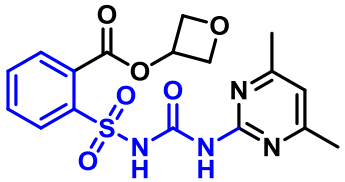






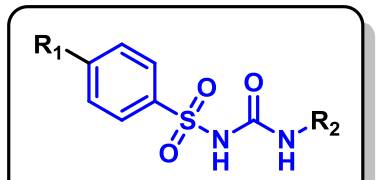
Other urea derivatives (such as chlorbromuron, chlorfluazuron, chlorotoluron, difenoxuron, diflubenzuron, diuron or flufenoxuron) did not showcase such a behaviour





0 ppm 12 ppm 60 ppm 300 ppm 600 ppm

COMPOUNDS NEGATIVELY AFFECTED (DEGRADATION)



Sulfonylurea
(general formula)

4572 J. Agric. Food Chem. 2002, 50, 4572–4575

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

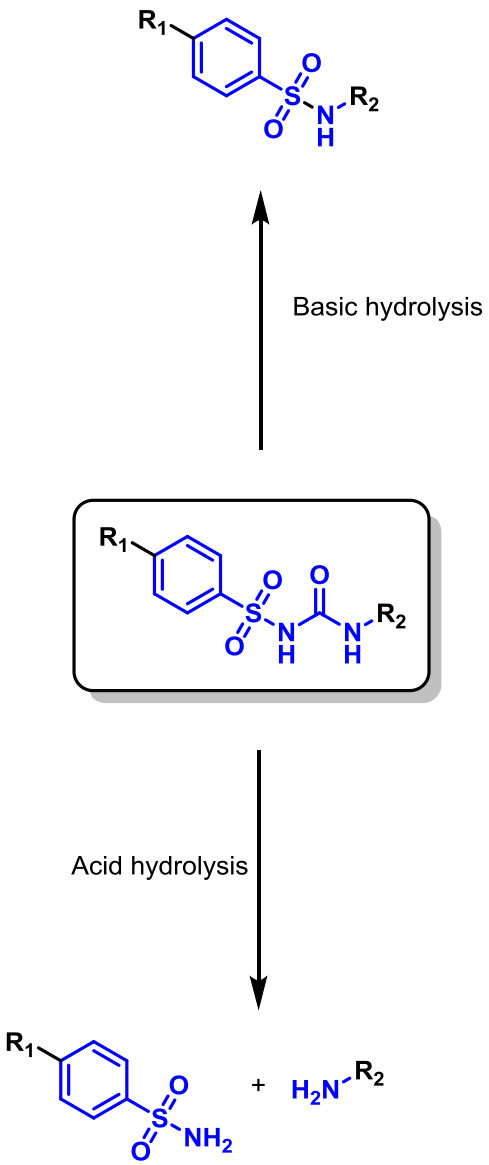
Degradation of Sulfosulfuron, a Sulfonylurea Herbicide, As Influenced by Abiotic Factors

SUPRADIP SAHA AND GITA KULSHRESTHA*

Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi 110012, India

A laboratory experiment was conducted to study the stability of sulfosulfuron [1-(2-ethylsulfonylimidazo-[1,2-*a*]pyridin-3-ylsulfonyl)-3-(4,6-dimethoxypyrimidin-2yl) urea] in a controlled environment of pH, temperature, solvent, and surface. In another experiment the photostability of sulfosulfuron was studied after irradiation under sunlight. Under alkaline condition, it yielded 1-(2-ethylsulfonylimidazo[1,2-*a*]-pyridin-3-yl-3-(4,6-dimethoxypyrimidin-2-yl) amine, and under acidic condition it degraded to 1-(2-ethylsulfonylimidazo[1,2-*a*] pyridin)-3-sulfonamide and 4,6-dimethoxy-2-aminopyrimidine. Photodegradation included breaking of a sulfonylurea bridge, as in the case of acidic hydrolysis and contraction of the sulfonylurea bridge was the major pathway of alkaline hydrolysis.

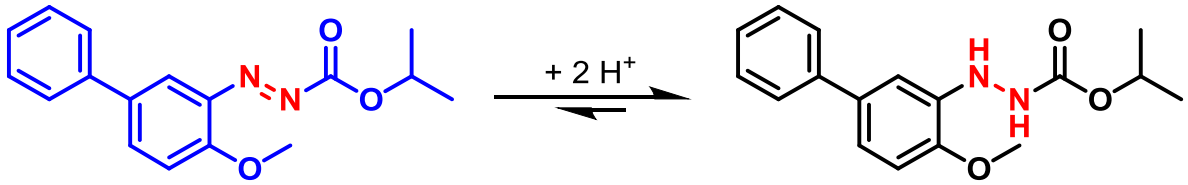
KEYWORDS: Sulfosulfuron; stability; pH; temperature; photolysis



COMPOUNDS AFFECTED BY INTERCONVERSION

Bifenazate

- Bifenazate (sum of bifenazate plus bifenazate-diazene expressed as bifenazate) Annex II

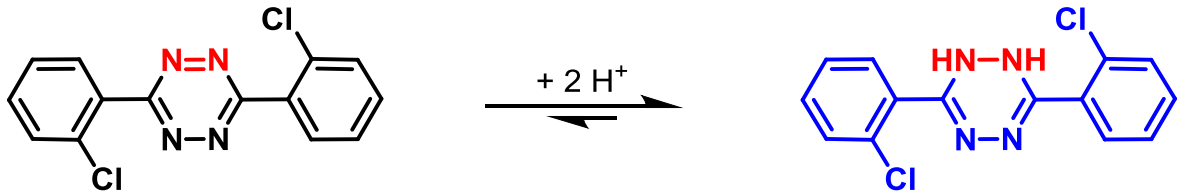


Bifenazate-diazene

Bifenazate

Clofentezine

- Clofentezine Annex IIIB



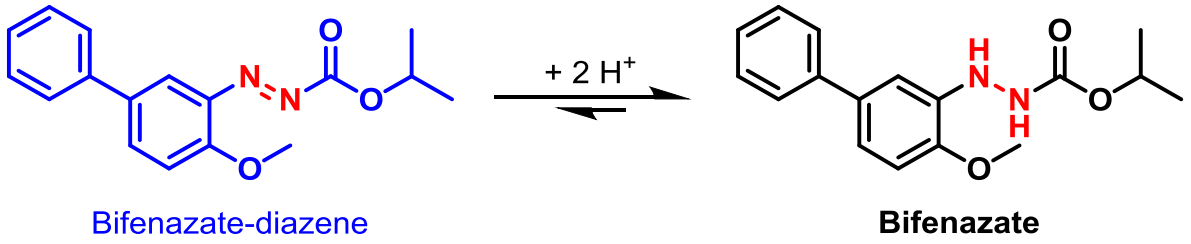
Clofentezine

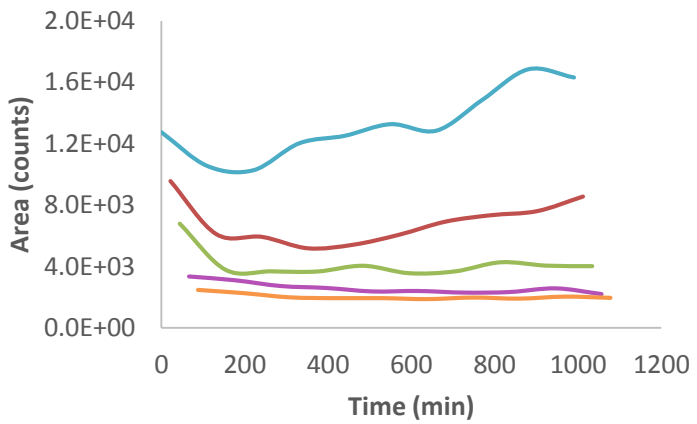
1,2-Dihydroclofentezine

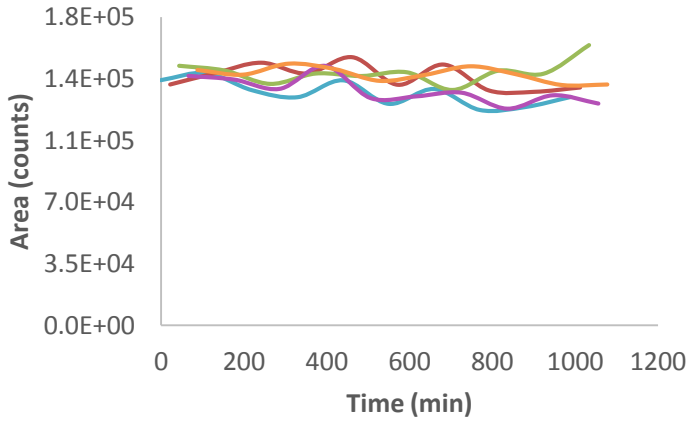
COMPOUNDS AFFECTED BY INTERCONVERSION

Bifenazate

- Bifenazate (sum of bifenazate plus bifenazate-diazene expressed as bifenazate) Annex II







0 ppm 12 ppm 60 ppm 300 ppm 600 ppm

EFFECT OF L-ASCORBIC ACID ON VARIOUS COMPOUNDS

POSITIVE EFFECT (STABILISATION)

- Bendiocarb
- Cymoxanil
- Dazomet
- Dithianon
- DMA
- DMPF
- Fenpicoxamid
- Formetanate
- Methiocarb-sulphone
- Phosmet
- Methiocarb-sulphoxide
- Trichlorfon

NEGATIVE EFFECT (SUPRESSION)

- Bendiocarb
- Carbendazim
- Cyromazine
- Demeton-*S*-methylsulphoxide
- Flonicamid
- Methomyl
- Omethoate
- Pirimicarb-desmethyl
- Oxamyl

NEGATIVE EFFECT (DEGRADATION)

- Flazasulfuron
- Oxasulfuron
- Orthosulfamuron

OTHER CASES (INTERCONVERSION)

- Bifenazate
- Clofentezine

CONCLUSIONS

- Several compounds undergo degradation processes in injection vials in an acetonitrile:water (20:80, V/V) solvent at room temperature (20 ºC ≤ T ≤ 30 ºC)

- Concentrations equal to or higher than 300 mg/L of L-ascorbic acid have been shown to **decrease or halt in-vial degradation processes** for 12 compounds
  - Accurate concentration is made possible in some cases, at least detection in others

- Some compounds present decreased signal due to **ion suppression**

- Sulphonylureas can undergo **degradation processes** in the acidified solution

THANK YOU

Co-funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Health and Digital Executive Agency (HaDEA). Neither the European Union nor the granting authority can be held responsible for them.

Co-funded by the European Union

Use of L-ascorbic acid as a mean to prevent in-vial degradation of LC-amenable pesticides

Francisco José Díaz-Galiano
María Murcia Morales
Amadeo R. Fernández-Alba

Co-funded by the European Union

EURL-FV