

Caractérisation des pesticides dans les légumes cultivés sous serres agricoles au Liban: Effet de la lumière et Suivi des volatils

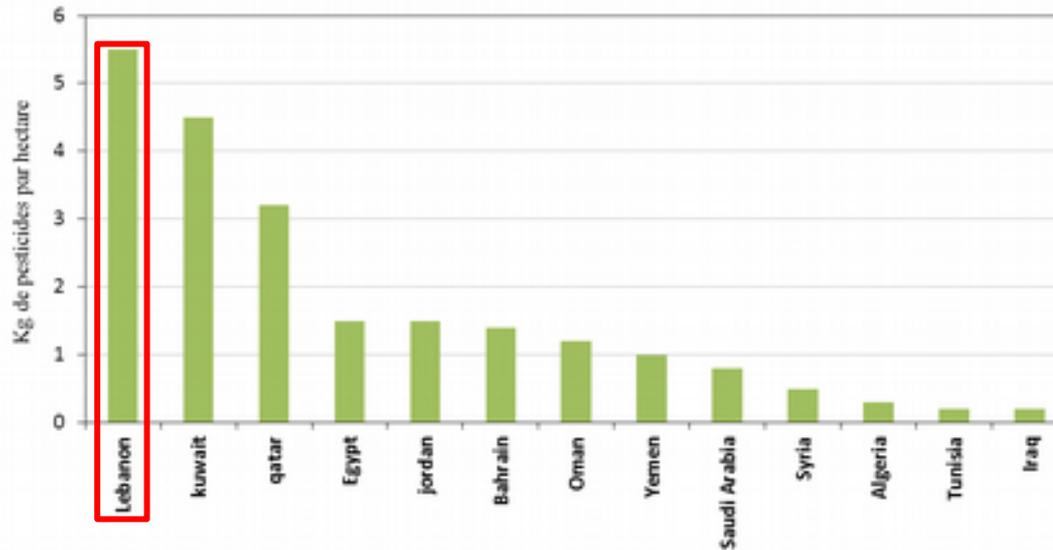
Samar Hamdache

Dr. Claire Richard, ICCF
Prof. Farouk Jaber, LACO
Dr. Mohamad Sleiman, ICCF

Choix de Menyeh -Liban Nord pour l'étude

- Liban est le premier consommateur de pesticides au Moyen-Orient

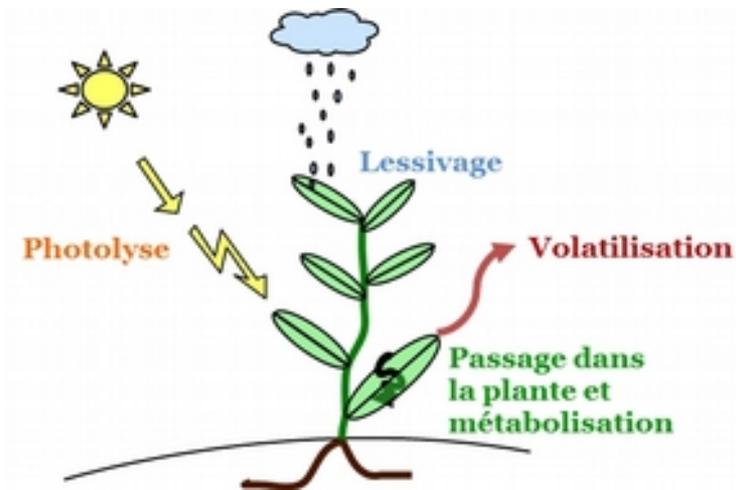
- Manque de surveillance sur l'utilisation des pesticides



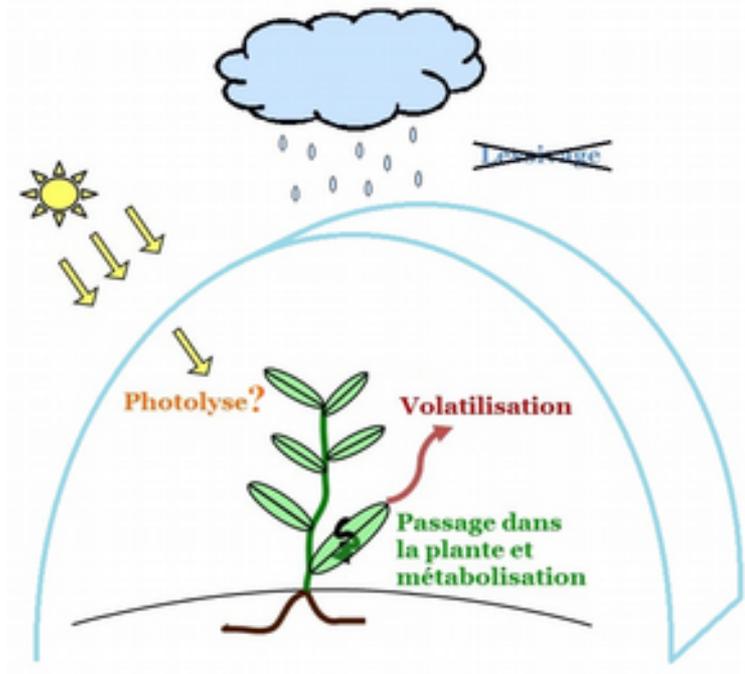
- 4000 hectares de cultures sous serres agricoles



Photodégradation des pesticides dans l'environnement



- Processus de transformation ou de transfert



- Espaces confinés / risques d'exposition

Pratiques agricoles dans les serres agricoles à Menyeh

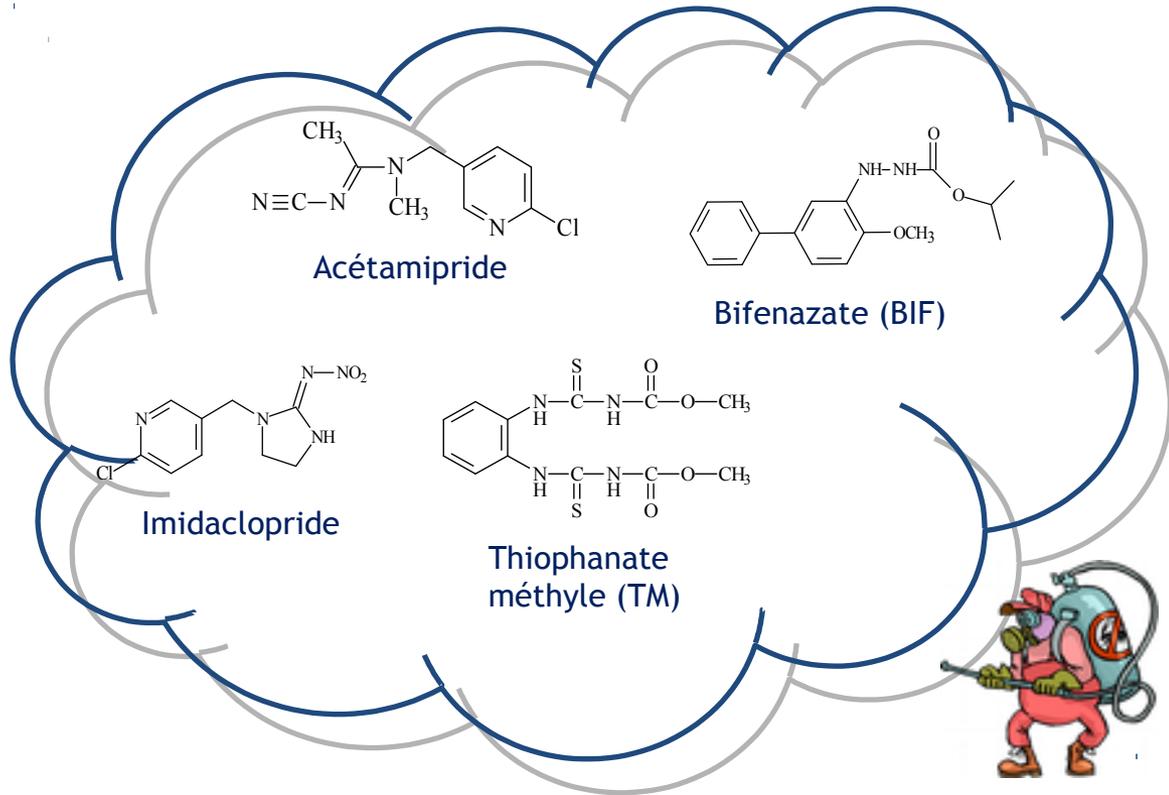
Applications
avant récolte

8

3

5

Pesticide	Doses recommandées (kg/ha)	Doses appliquées (kg/ha)
Acétamipride	0,5 - 1	0,2 - 0,6
Imidaclopride	0,3 - 0,4	0,4 - 1
BIF	0,2	0,7- 2
TM	2 - 3	4 - 11



- Pulvérisations en mélange
- Dépassement des doses recommandées pour imidaclopride , BIF et TM

Objectifs de l'étude

Composition de la phase gazeuse d'une serre agricole/
exposition



Devenir des pesticides dans une serre agricole (hydrolyse,
photolyse)? Cas du bifénazate



Echantillonnage dans les serres

- Quoi ?



Air

- Comment ?



Chaque 3 pièces ensemble
(haut, milieu et bas de la
serre)



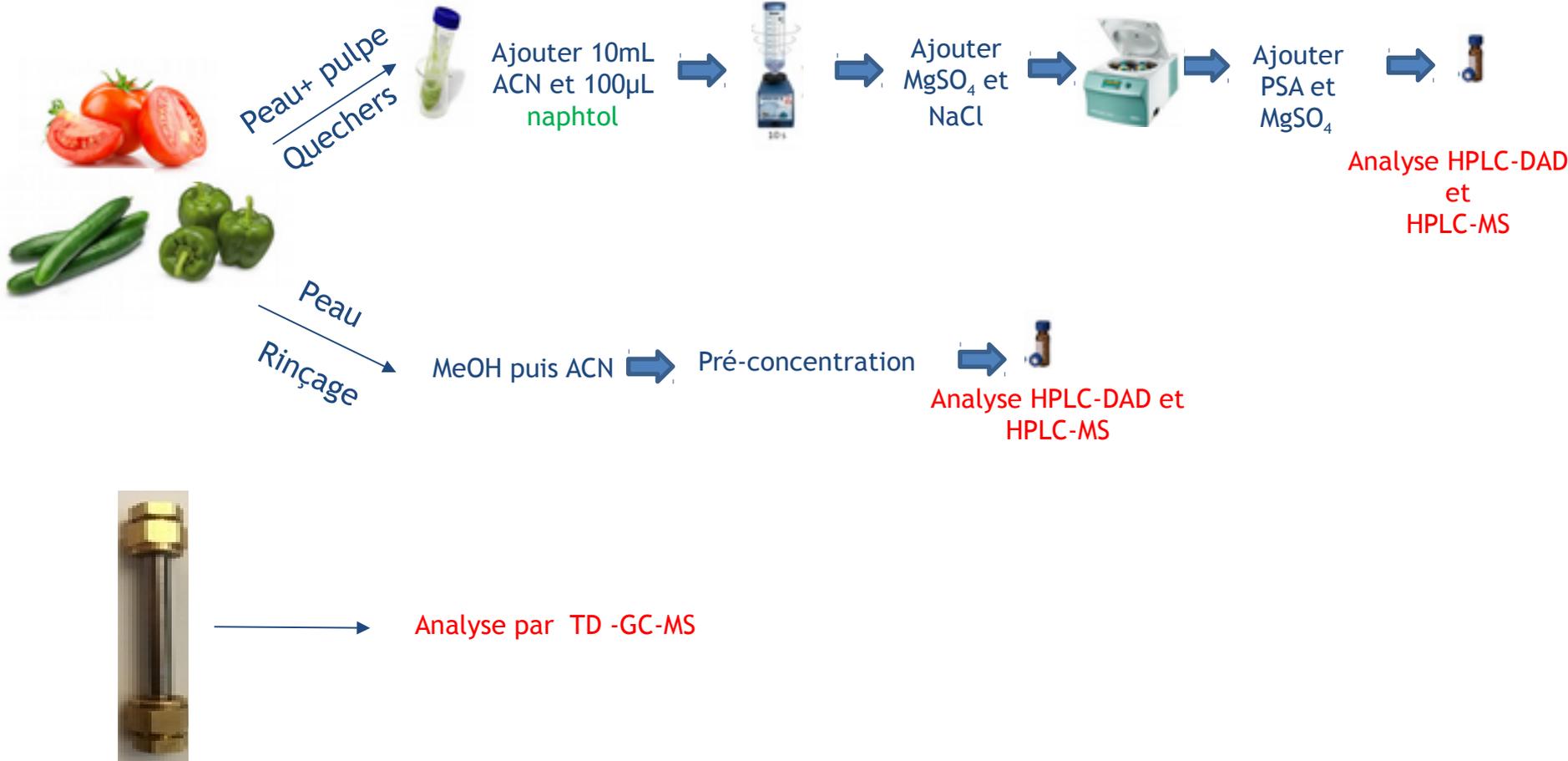
pompe automatique + tube avec
adsorbant tenax
Flux= 200ml/min , T = 60 min

- Quand ?

J-1
jour de la pulvérisation
(J)
J+1
J+3
J+6

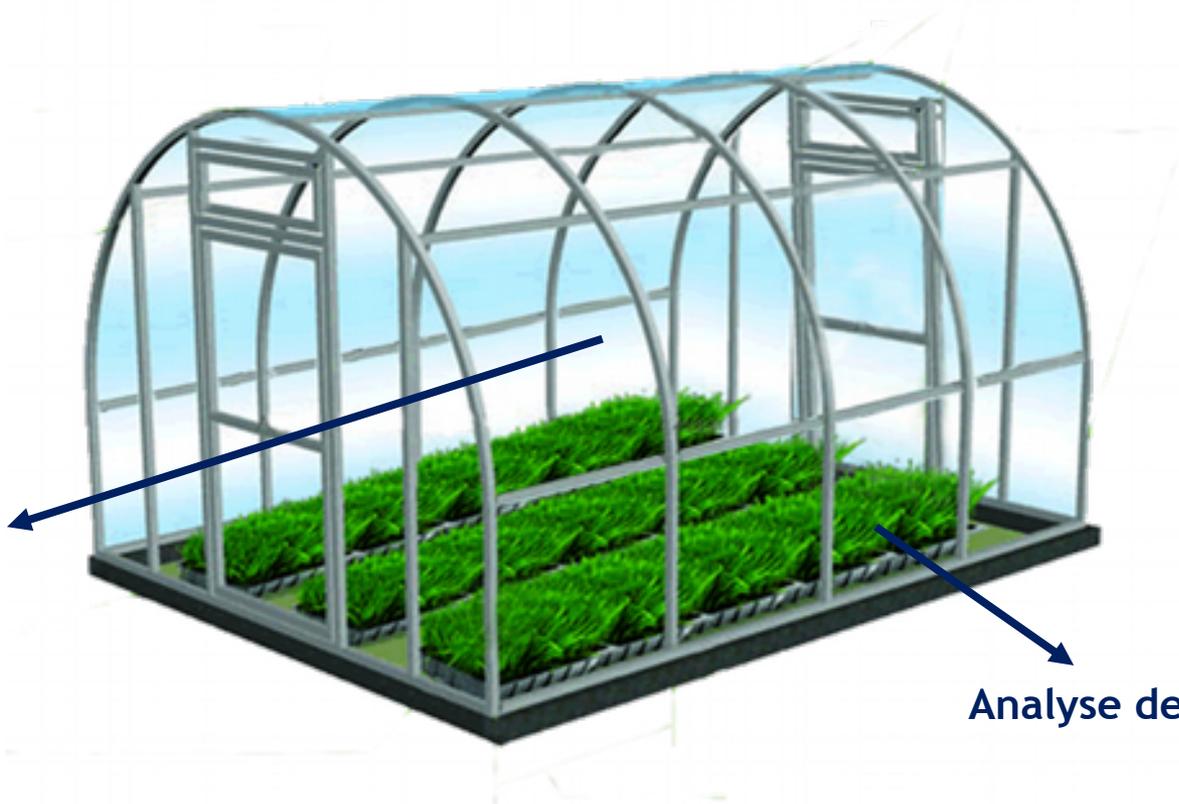


Extractions et analyses des échantillons naturels



Caractérisation de la serre

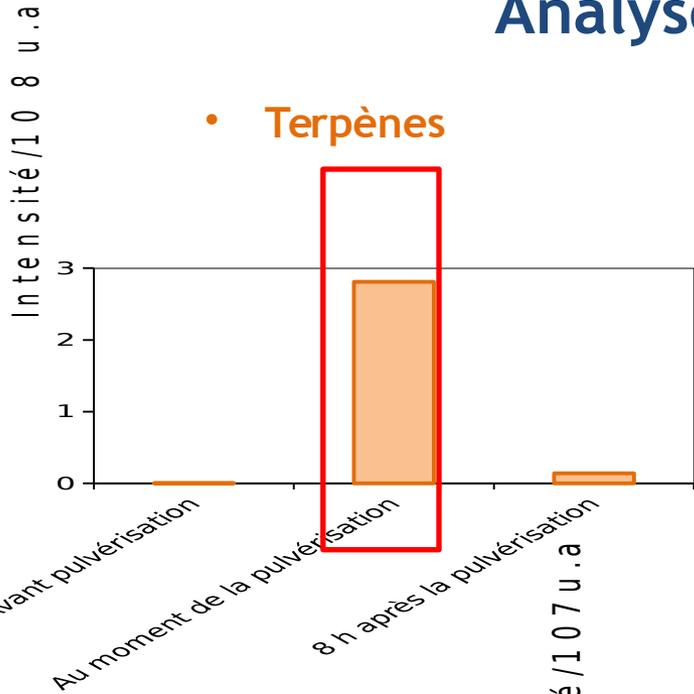
Analyse de la
phase
gazeuse



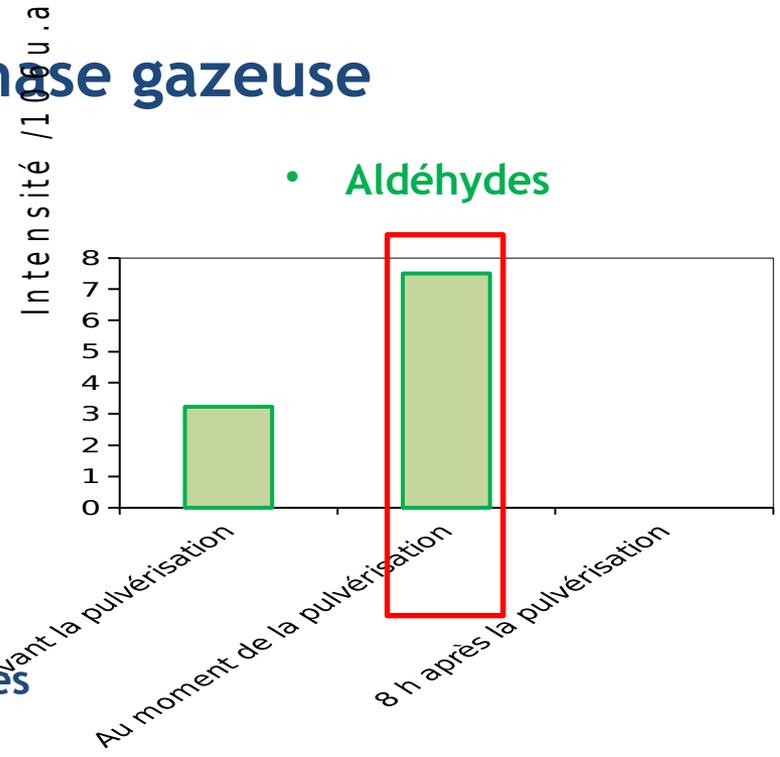
Analyse des légumes

Analyse de la phase gazeuse

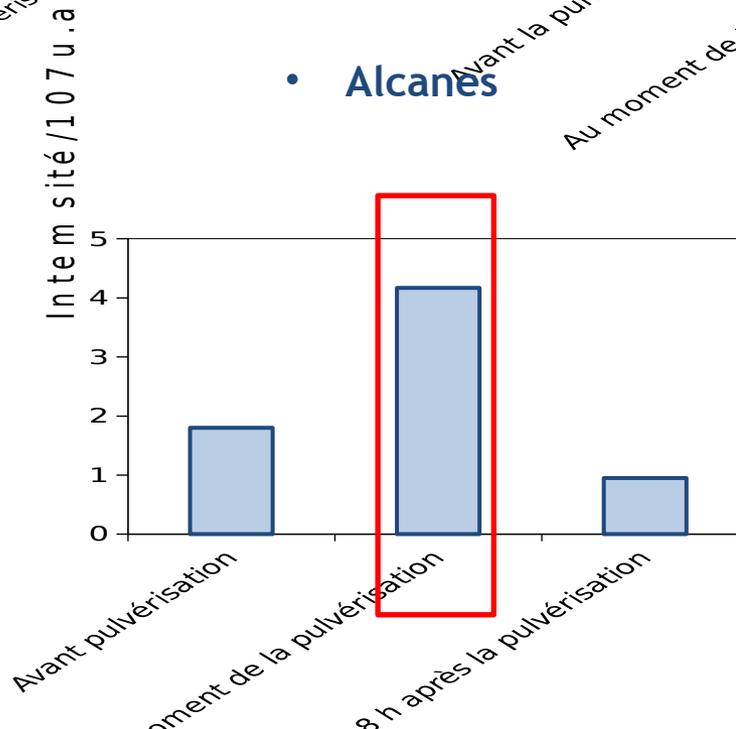
• Terpènes



• Aldéhydes

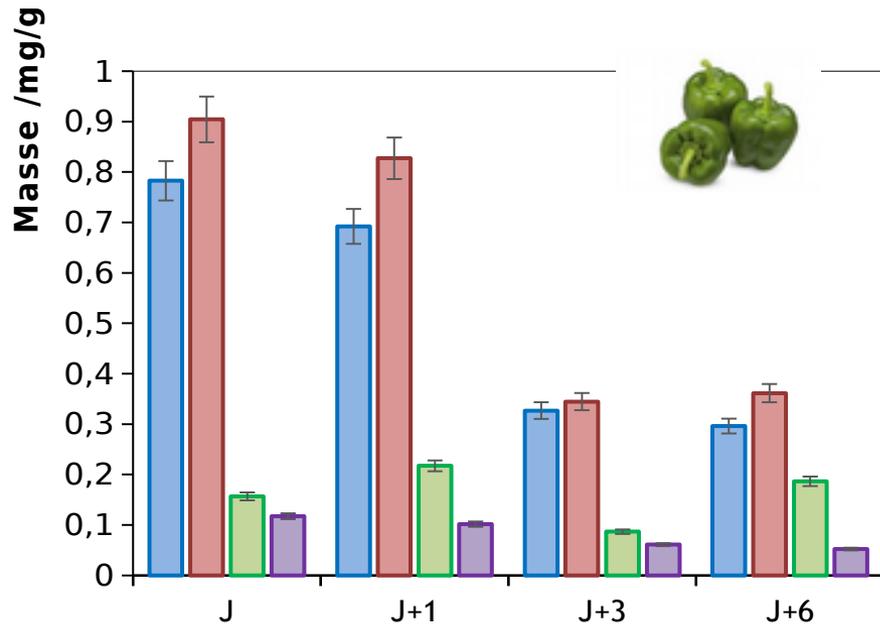


• Alcanes



• Terpènes les plus abondants

Suivi des résidus des pesticides- Méthode Quechers

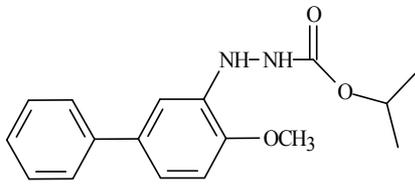


Molécule	MRLs (mg/g)	Poivron vert	
		Quantité de résidu (mg/g)	
Acétamipride	0,0003	J+6	0,3
Imidaclopride	0,001	J+6	0,3
TM	0,0001	x1000	0,19
BIF	0,003	J+6	0,05

Pesticide	t _r (min)	m/z en ES ⁺
Imidaclopride	3,46	256,05914
Acétamipride	3,9	223,07420
TM	5,3	343,05231
BIF	7,7	301,15384

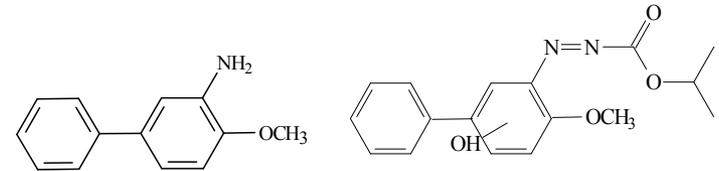
- Quantités les plus faibles des résidus >>>> MRLs imposées

Recherche des produits de transformation/ rinçage de la peau



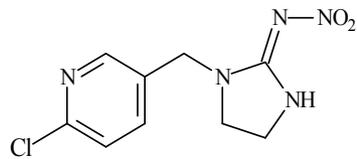
BIF

$m/z=301,15384$



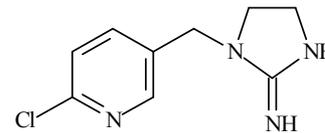
$m/z=200,1066$
Coupure NH-NH

$m/z=315,1338$
-H+O



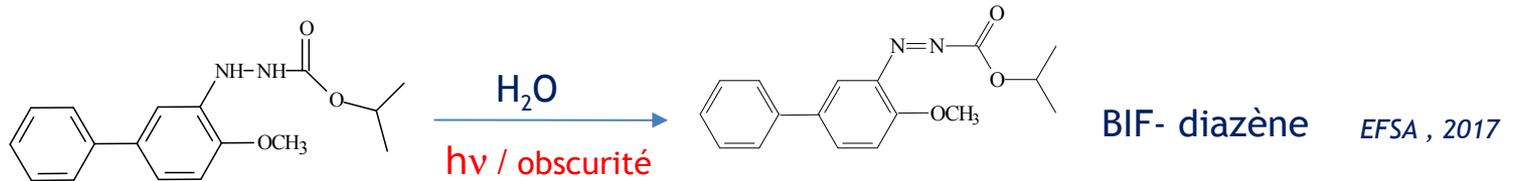
Imidaclopride

$m/z=256,05914$



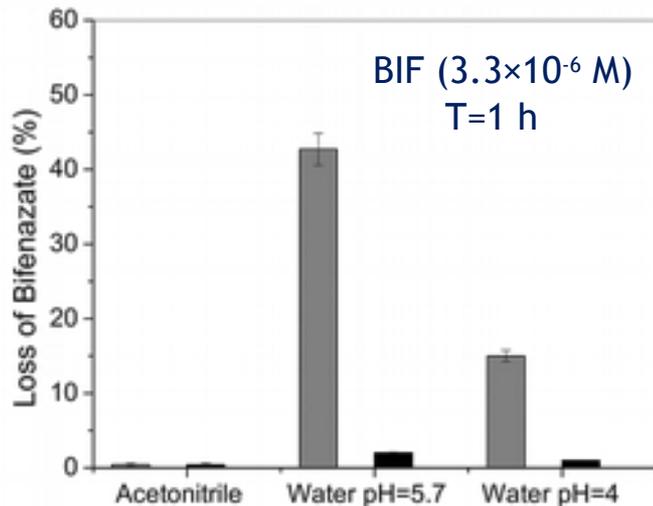
$m/z=211,07423$
-NO₂ + H

Réactivité de BIF à l'obscurité



Autoxydation du phénylhydrazine en diazène

Misra et al , 1976



- ACN : Dégradation négligeable

- Eau : pH ↑ , [O₂] ↑ = Dégradation ↑



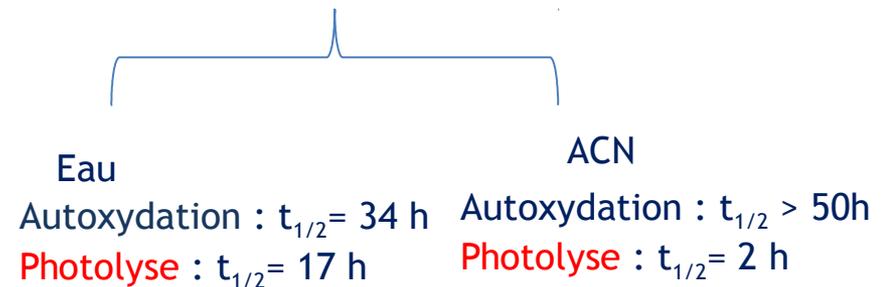
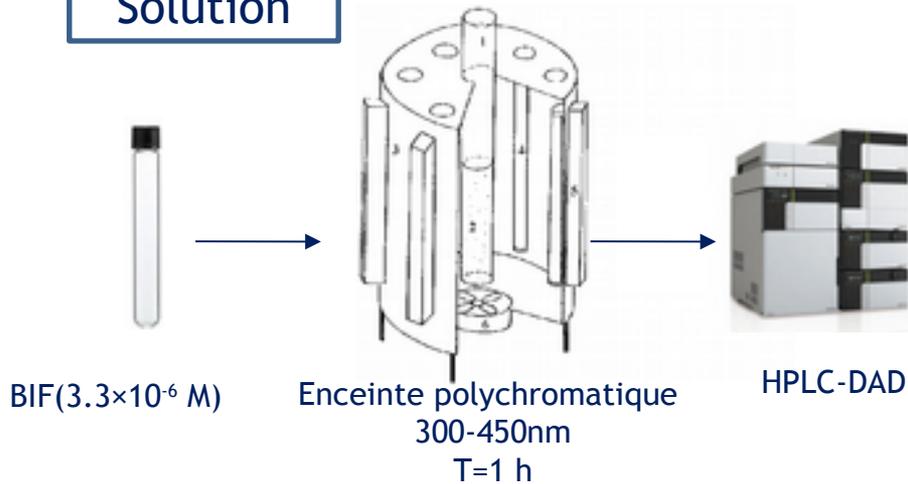
Réaction favorisée dans solvant protique, avec le pH et O₂

■ Obscurité sous air

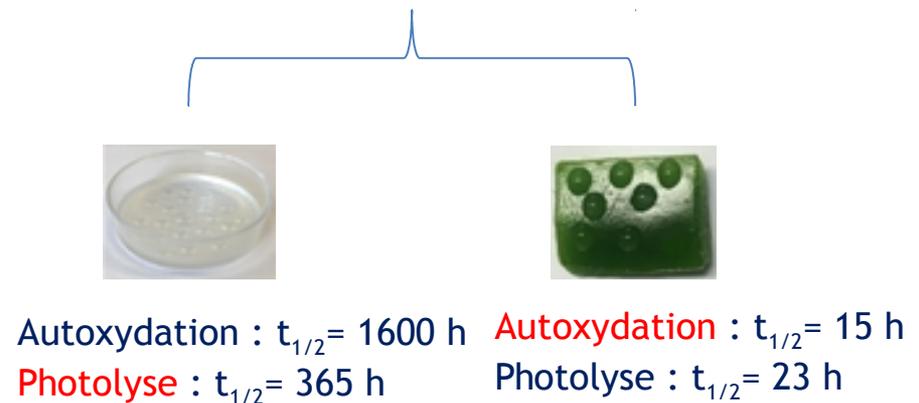
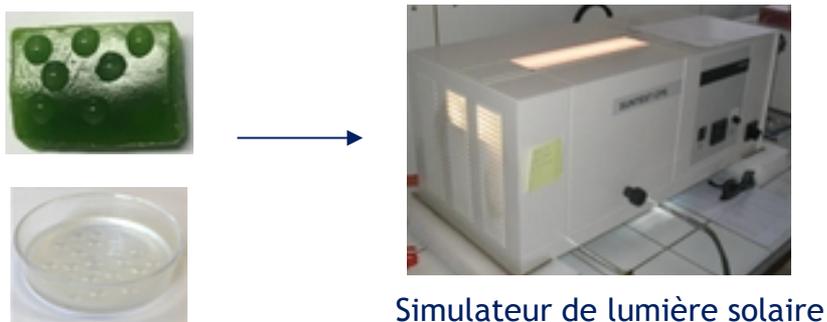
■ Obscurité sous O₂

Réactivité de BIF à la lumière

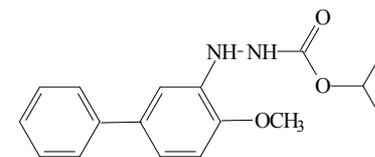
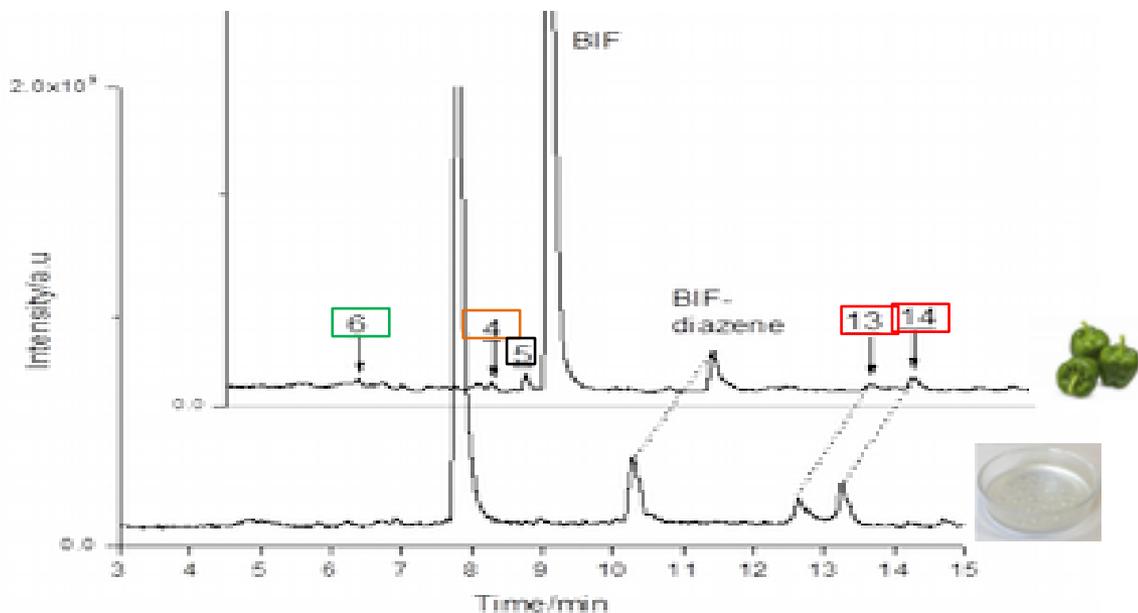
Solution



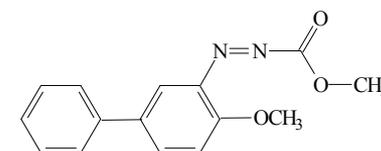
Solide



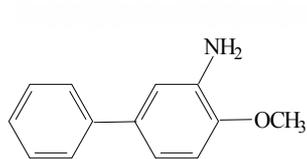
Formation des photoproduits sur poivron



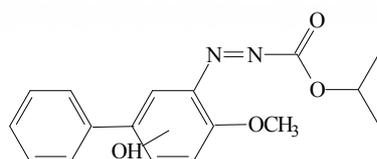
Bif



Bif-diazène

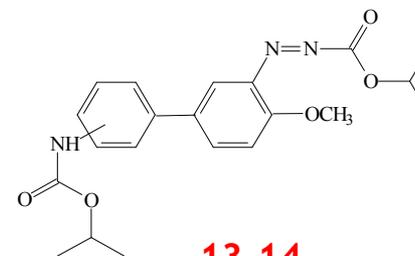


6
ACN



4
Photolyse
dans l'eau

5
Autoxydation
dans l'eau



13,14
Cire

Légumes dans les serres agricoles

Unravelling the reactivity of bifenazate in water and on vegetables: Kinetics and byproducts



Samar Hamdache^{a,b}, Mohamad Sleiman^a, Pascal de Sainte-Claire^a, Farouk Jaber^b, Claire Richard^{a,*}

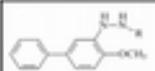
^a Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de Clermont-Ferrand, F-63000 Clermont-Ferrand, France

^b Laboratory of Analysis of Organic Compounds, Faculty of Sciences I, Lebanese University, Hadath, Beirut, Lebanon

HIGHLIGHTS

- Bifenazate undergoes degradation in the dark and under simulated solar light.
- Rates and byproducts are affected by the medium and oxygen.
- Autooxidation takes place in oxygenated water and methanol.
- The reactivity on green pepper is affected by the water contained in the vegetable.
- Using wax or solvent is not adequate to mimic reactions on vegetables.

GRAPHICAL ABSTRACT

 Bifenazate	 Wax	 Green Pepper	 Water
	-	Bif-diazene P1	Bif-diazene P1
	Bif-diazene + Adducts	Bif-diazene P2 + Adducts	Bif-diazene P2

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ABSTRACT

In this study, we aimed to better understand the transformation mechanisms of bifenazate, a biphenyl hydrazine derivative insecticide poorly studied up to now. For this, we compared its reactivity in the dark and under simulated solar light irradiation in different media (water, non-aqueous polar solvent, surface of apolar wax films, skin of vegetable). In air-saturated pH = 5.7 water, bifenazate underwent both autooxidation in the dark ($t_{1/2} = 34$ h) and photolysis ($t_{1/2} = 17$ h). In an aprotic polar solvent such as acetonitrile, bifenazate was stable in the dark but was quickly photodegraded in the presence of oxygen ($t_{1/2} = 2$ h). The phototransformation of bifenazate was due to the oxidation of excited states by oxygen and to the cleavage of the N—N bond, while the autooxidation in water started by the initial oxidation of the molecule by oxygen and involved the superoxide anion as chain carrier. On paraffinic wax film, photodegradation ($t_{1/2} = 365$ h) and dark autooxidation ($t_{1/2} = 1600$ h) were very slow. On green pepper skin, bifenazate disappeared both in the dark ($t_{1/2} = 34$ h) and through photolysis ($t_{1/2} = 23$ h) at rates close to those measured in water. This shows that on green pepper skin, bifenazate is affected by water contained in the vegetable and possibly released by transpiration. Bifenazate diazene was the major degradation product in all studied conditions. Minor byproducts were detected too. They depended on the experimental conditions showing that degradation pathways are governed by the nature and properties of the medium. In particular, on green pepper one found byproducts generated in acetonitrile and on wax by photolysis and in water by autooxidation. This finding highlights the need for a better model than wax to mimic photolysis on plant surfaces.

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Conclusions et perspectives

- ❑ Présence de COVs dans la phase gazeuse d'une serre agricole ⇒ nécessité de prendre plus de mesures de sécurité pour l'agriculteur
- ❑ Détection des résidus de pesticides pulvérisés à Menyeh avec des taux >> MRLs
- ❑ Possibilité de photodégradation des pesticides à l'intérieur des serres agricoles à Menyeh
- ❑ Renforcement des mesures réglementaires pour l'utilisation des pesticides au Liban

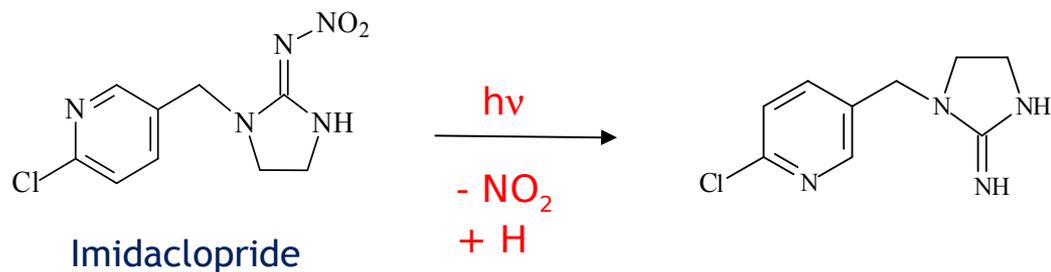
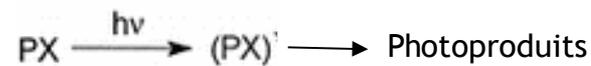
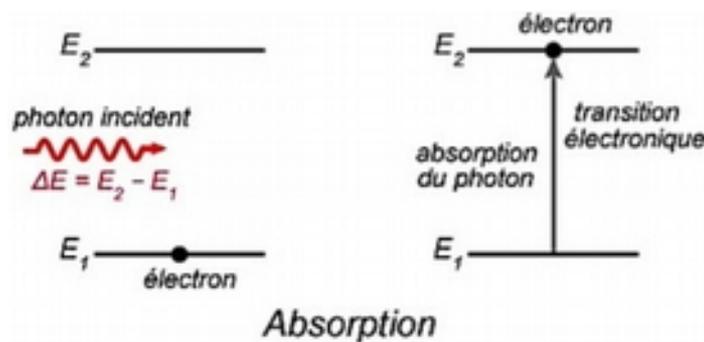
**Fin de la
présentation**



**Merci pour
votre attention**

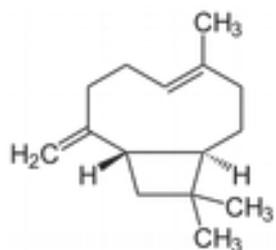
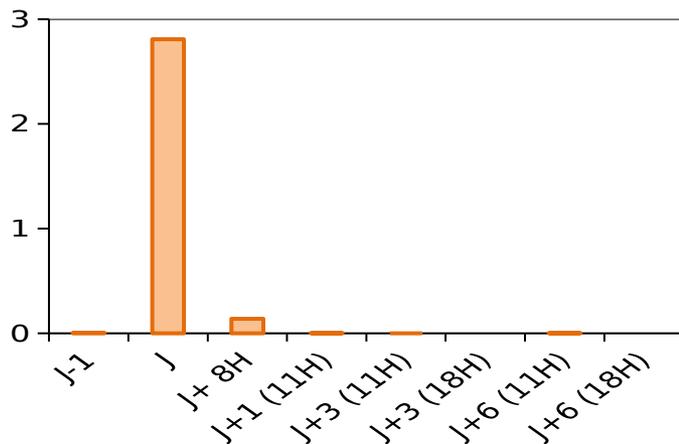
Photodégradation des pesticides dans l'environnement

- Photodégradation directe

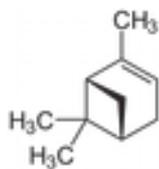


Composition chimique des terpènes

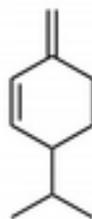
Intensité/10⁸ u.a



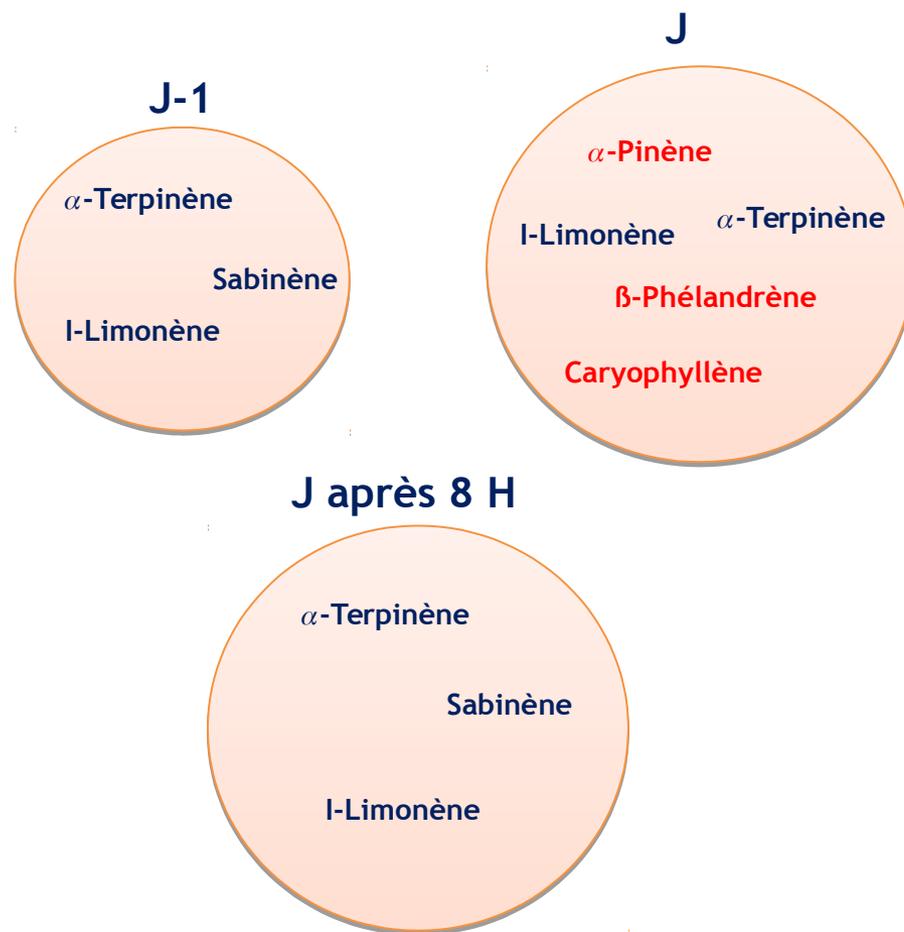
Caryophyllène



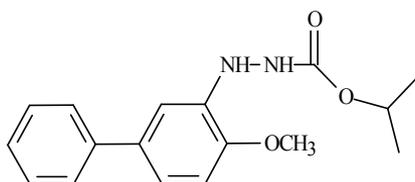
α -Pinène



β -Phélandrène

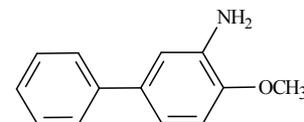


Recherche des produits de transformation/ rinçage de la peau

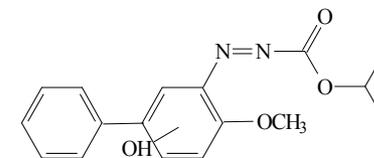


BIF

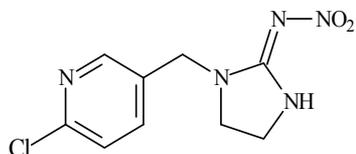
m/z=301,15384



m/z=200,1066
Coupure NH-NH

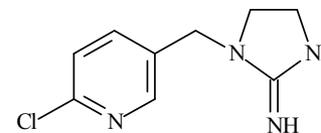


m/z=315,1338
-H+O



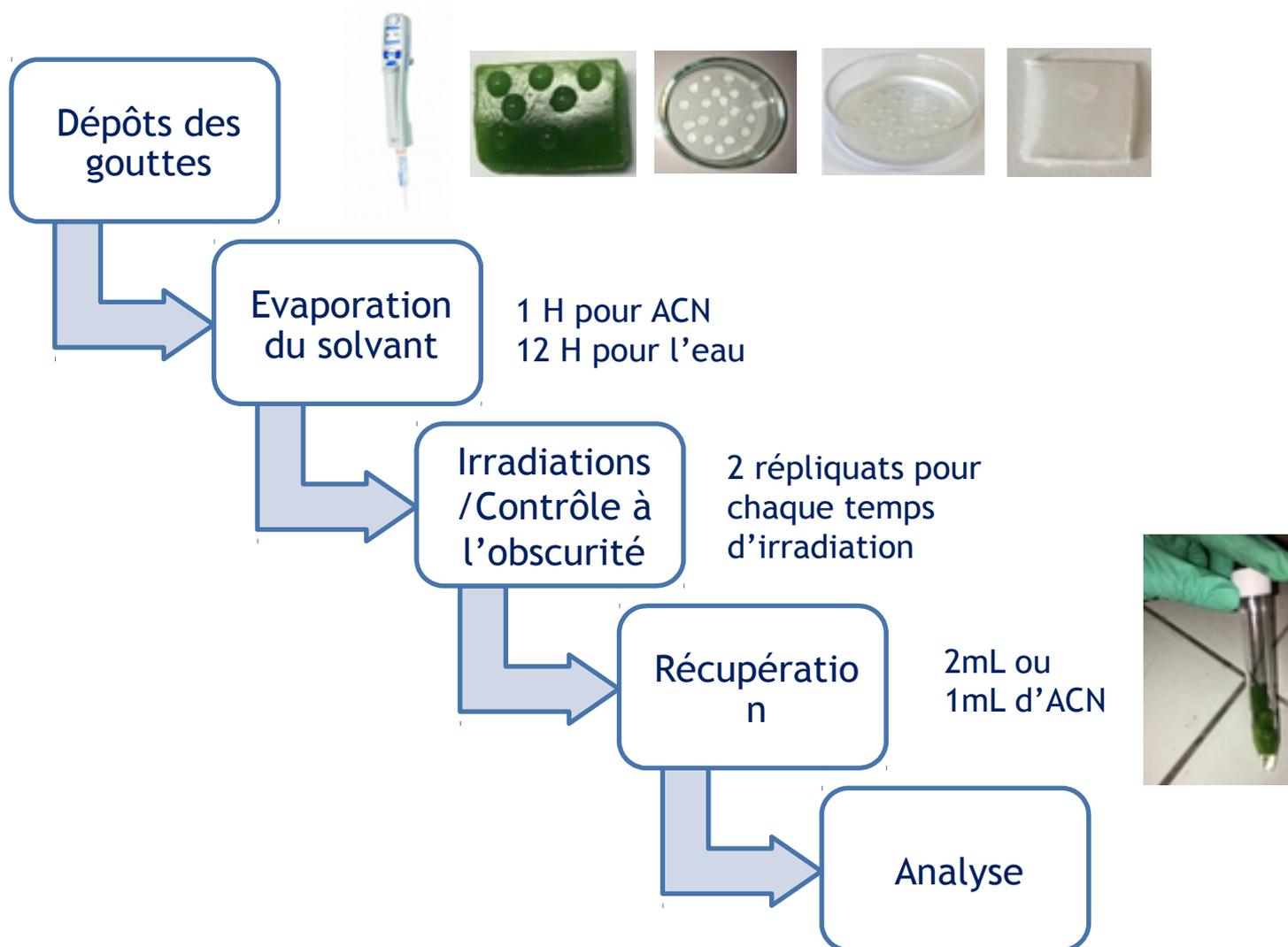
Imidaclopride

m/z=256,05914



m/z=211,07423
-NO₂ + H

Préparation des dépôts solides



Analyses

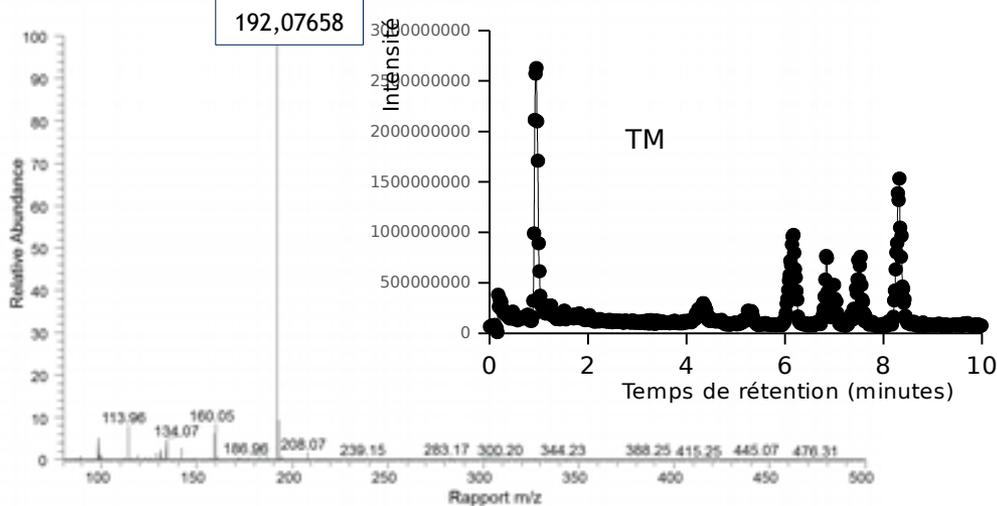
- Méthodes chromatographiques



HPLC-DAD



HPLC-ESI-HR-MS

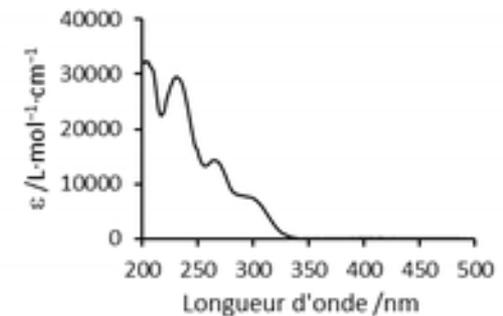


GC-MS

Quantification par
étalonnage interne

- Méthodes Spectroscopiques

Spectroscopie UV-Vis

Spectroscopie de
fluorescence

Spectroscopie Infrarouge(IR)

Transmission

ATR

