Pesticide Behaviour in Soils, Water and Air
York 2022

Monitoring atmospheric contamination by pesticides: a single multiresidue analytical method on air and rainwater pesticide concentrations

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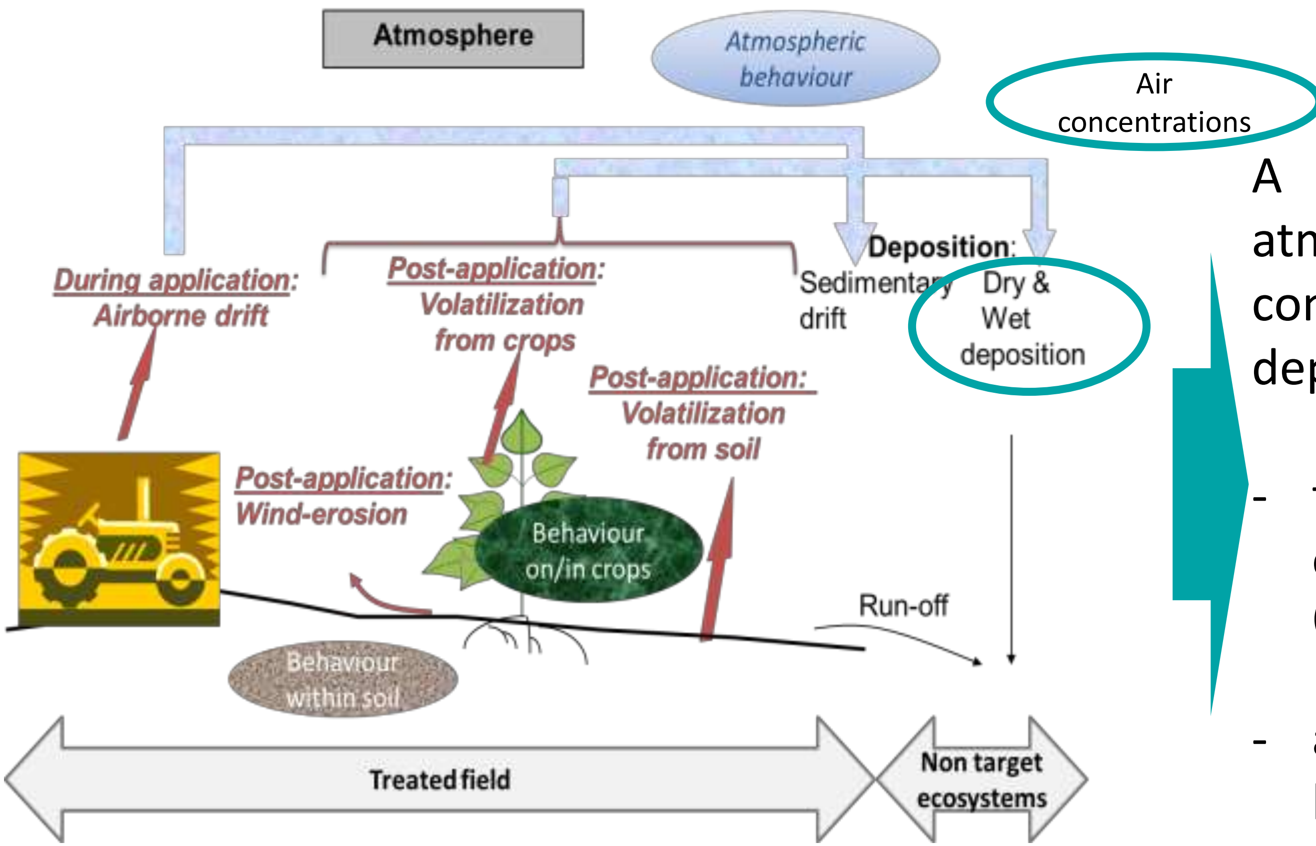
Context

Processes involved in pesticide contamination of the atmosphere



A contribution of atmospheric contamination and deposition to :

- the contamination of untreated areas (*e.g.* Pelosi et al. 2021)
- an exposure of the human population (*e.g.* Deremeaux et al. 2020)

Context

Current level ok knowledge

Few monitoring networks at national levels

- Gaseous & particulate phases, except for POPs or CUPs in few countries

  e.g. France for background concentrations (AASQAs), or for the assessment of resident exposure in vineyard conditions thanks to a recent one-year national campaign

  PESPAT project at the european scale (L. Mayer, presentation on Wednesday)

- Rainwater

  e.g. Kreuger et al. (2017) in Sweden, wet deposition rates ranging from 9 to 800 $mg \cdot ha^{-1} \cdot y^{-1}$

Different methodologies for quantifying pesticide concentrations in the atmosphere and in the rainwater

Main goals

Within the framework of the Rescape and Ping projects

the contamination by pesticides of environmental matrices (air, rainwater and soils) and soil macro-fauna (earthworms, carabids and small mammals)

through samples collected in natura in an intensive agricultural landscape

Specific objectives of the presented study:

- a multiresidue analysis method using a single analytical pipeline to quantify both atmospheric and rainwater pesticide concentrations

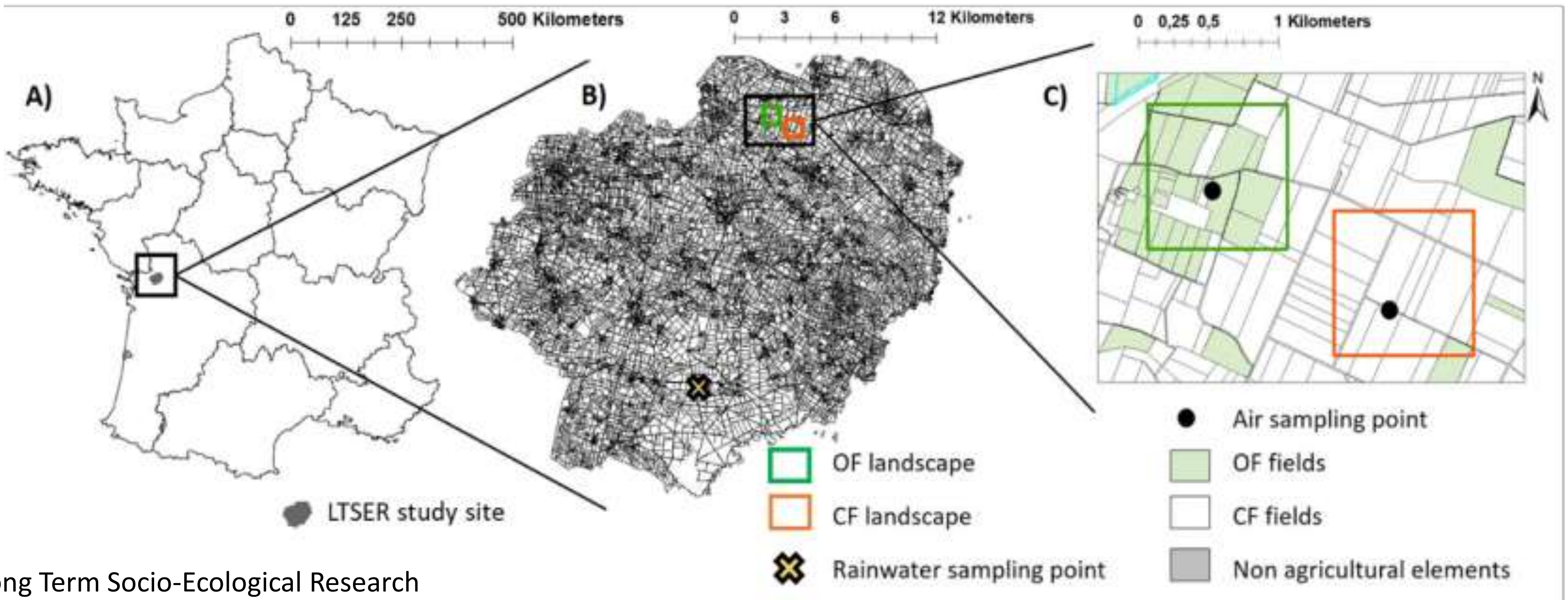
- wet deposition calculation

- the data *vs* existing data on air contamination in the same region and year (regional association AASQA)

Materials and Method

Study area : « Zone Atelier Plaine & Val de Sèvre »

ZAPVS study site | **Rainwater and air sampling**



Long Term Socio-Ecological Research
Villiers-en-Bois, France *(Bretagnolle et al. 2018)*

- Intensive cereal plain (435km²)
  - Biodiversity, ecological functions
  - Farmer practices and land use are annually monitored

Materials and Method

Rainwater and air sampling

Rainwater collect

Weekly basis : from March to November 2018

- refrigerated collector at 4°C
- stored in polyethylene terephthalate bottles at -20°C (in dark)

Air sampling

Daily basis : 2 days in May & 2 days in June 2018

(preliminary test)

Air pump

Volumetric controller

12V power supply

- Pesticides trapped on cartridges Tenax
- Air volume sampled measured
- stored in at 4°C (in dark)

=> no need of a nearby power source

Materials and Method

Pesticides selected

- 27 pesticides selected
  (+ their isomeric form)
  - 12 Herbicides
  - 8 Fungicides
  - 7 Insecticides
- Selected for their
  - frequency of use in the area
  - atmospheric emission potential
  - compatibility with analytical tools

Compound	log K_{OW}	Vapour pressure (mPa)	Water solubility ($mg.L^{-1}$)
Acetochlor	4.14	2.20E-02	282
Aclonifen	4.37	1.60E-02	1.4
Bifenthrin	6.6	1.78E-02	0.001
Boscalid	2.96	7.20E-04	4.6
Clomazone	2.54	2.70E+01	1212
Cloquintocet-mexyl	5.03	5.31E-03	0.59
Cycloxydim	1.36	1.00E-02	53
Cypermethrin[a]	5.5	6.78E-03	0.009
Cyproconazole [b]	3.09	2.60E-02	93
Deltamethrin	4.6	1.24E-05	0.0002
Diflufenican	4.2	4.25E-03	0.05
Dimethachlor	2.17	6.40E-01	2300
Epoxiconazole	3.3	3.50E-04	7.1
Fenpropidin	2.6	1.07E+01	530
Lambda-Cyhalothrin	5.5	2.00E-04	0.005
Metazachlor	2.49	9.30E-02	450
Metconazole	3.85	2.10E-05	30.4
Metrafenone	4.3	1.53E-01	0.492
Napropamide	3.3	2.20E-02	74
Pendimethalin	5.4	3.34E+00	0.33
Pirimicarb	1.7	4.30E-01	3100
Prochloraz	3.5	1.50E-01	26.5
Propiconazole [c]	3.72	5.60E-02	150
Pyraclostrobin	3.99	2.60E-05	1.9
S-metolachlor	3.05	3.70E+00	480
Tau-fluvalinate [d]	7.02	9.00E-08	0.00103
Thiamethoxam	-0.13	6.60E-06	4100

Materials and Method

Extraction and analysis

Rain water

Stir Bar Sorptive Extraction (SBSE)

PDMS bar (*Gerstel*)

Extraction conditions : factors modifying equilibrium

- 25°C
- Stirring speed: 800 rpm
- 10mL water volume
- pH unmodified
- addition of an inert salt (NaCl,),
- addition of an organic modifier (Acetone)
- extraction time

Literature & instrumention

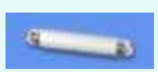
Bourdat-Deschamps 2007, Prieto 2010

Experimental design

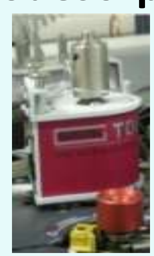
2 extraction conditions: 135 min ; 10% (v/v) acetone ; 30% (m/v) NaCl

Stir bar and Tenax

A single extraction method: **Thermodesorption and GCMS**



Up to two Stir bar analysed together
=
2 extraction conditions possible



Thermo Desorption Unit (TDU, Gerstel)

(GCMS, Agilent)

Results

Rainwater sample extraction efficiency : trueness recovery

	Trueness Experimental recovery (%)				Trueness Experimental recovery (%)		
Acetochlor	93.0	+/-	1.4	**Fenpropidin**	107.1	+/-	7.2
Aclonifen	88.8	+/-	5.9	**Lambda-Cyhalothrin**	41.9	+/-	3.7
Bifenthrin	57.2	+/-	4.7	**Metazachlor**	93.0	+/-	10.2
Boscalid	89.0	+/-	0.4	**Metconazole**	93.5	+/-	3.2
Clomazone	90.7	+/-	7.1	**Metrafenone**	91.6	+/-	14.2
Cloquintocet-mexyl	83.1	+/-	6.5	**Napropamide**	95.6	+/-	7.3
Cycloxydim	130.8	+/-	69.1	**Pendimethalin**	87.5	+/-	3.7
Cypermethrin 1	NA*	+/-	NA*	**Pirimicarb**	94.2	+/-	2.3
Cypermethrin 2	43.7	+/-	0.8	**Prochloraz**	98.1	+/-	8.8
Cypermethrin 3	52.0	+/-	10.9	**Propiconazole 1**	98.6	+/-	0.6
Cypermethrin 4	49.3	+/-	1.7	**Propiconazole 2**	99.7	+/-	1.3
Cyproconazole 1,2	94.1	+/-	6.7	**Pyraclostrobin**	86.8	+/-	11.8
Deltamethrin	49.1	+/-	14.9	**S-metolachlor**	97.5	+/-	1.1
Diflufenican	87.5	+/-	12.6	**Tau-fluvalinate 1**	59.0	+/-	20.0
Dimethachlor	91.8	+/-	3.8	**Tau-fluvalinate 2**	56.0	+/-	21.3
Epoxiconazole	96.6	+/-	0.5	**Thiamethoxam**	UE*	+/-	UE*

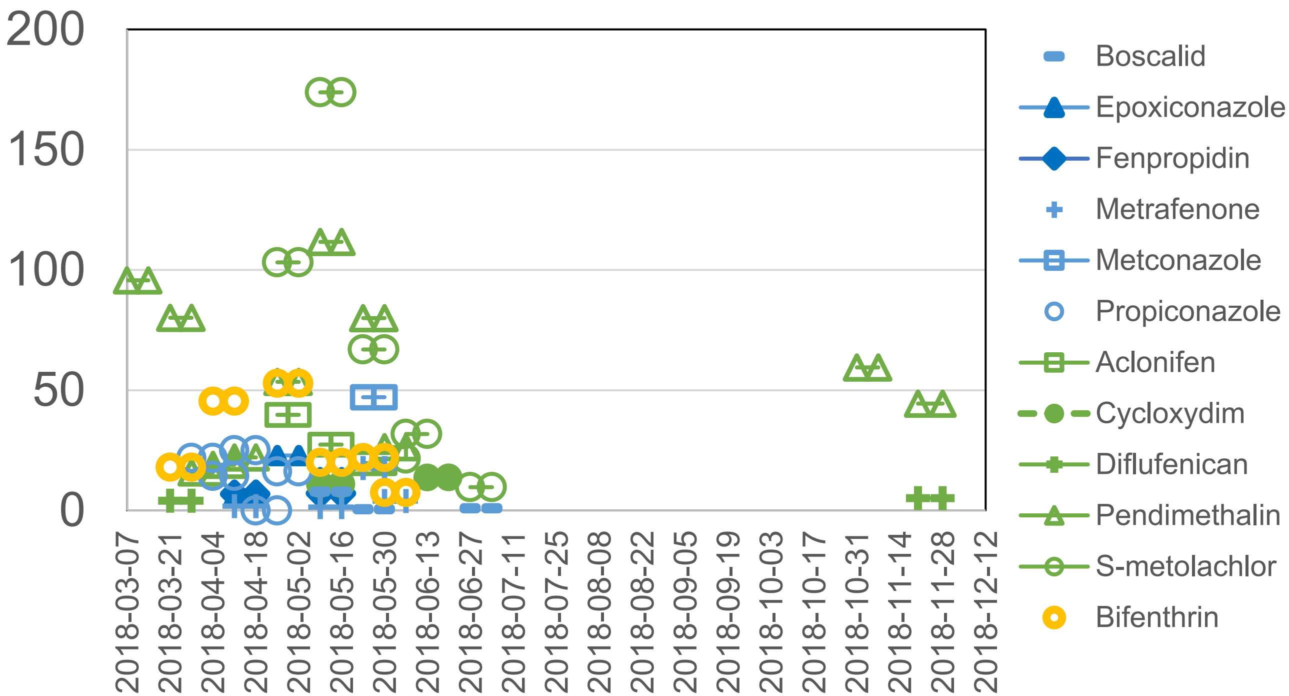
Recovery
- higher than 80% (22/32 ai)
- ranged from 40% to 59% (8/32 ai)

a good compromise to efficiently extract all the molecules under study

⇒ a correction factor for molecules with trueness recovery < 80 %

Results

Rainwater concentrations (ng l^{-1}) : seasonal evolution



- All pesticide types detected
- 0.5 ng.L^{-1} to 174 ng.L^{-1}
- Herbicide : highest concentrations
- Fungicides & Insecticides: similar concentrations

rainwater contamination mostly observed in spring

To be noticed: winter was less well represented (no samples before 7 of March and after the 28 of November)

Results

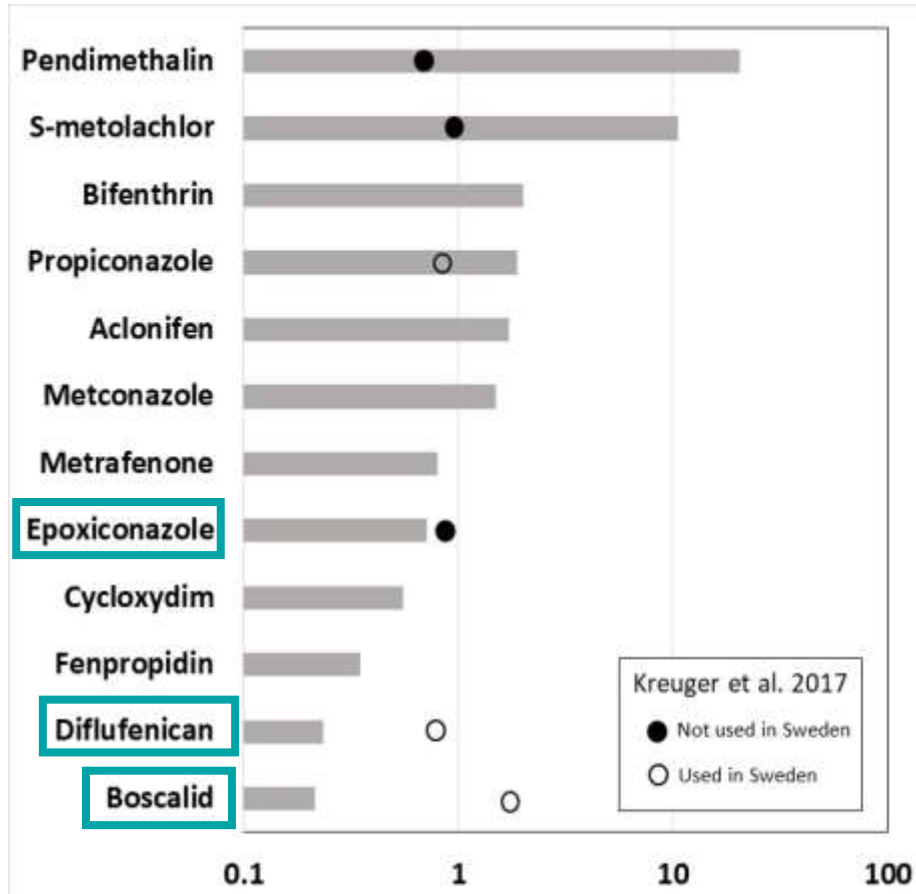
Cumulated wet deposition and consequences on soil contamination

Soil contamination
Compounds also found by Pelosi et al. (2021) in top 5 cm soil of untreated aeras (grasslands and hedrows) of the ZAPVS in 2016

⇒ Wet deposition ≈ 1% to 2.4% of soil concentration (no degradation, no infiltration)

⇒ Spray drift, dry deposition and run-off to be added

⇒ Modelling required



Bars: Cumulated wet deposition ($\mu g \cdot m^{-2}$) from March to November 2018 in ZAPVS;
Dots: wet deposition/year from Kreuger et al. (2017) from April to October in 2012 to 2015 in Sweden

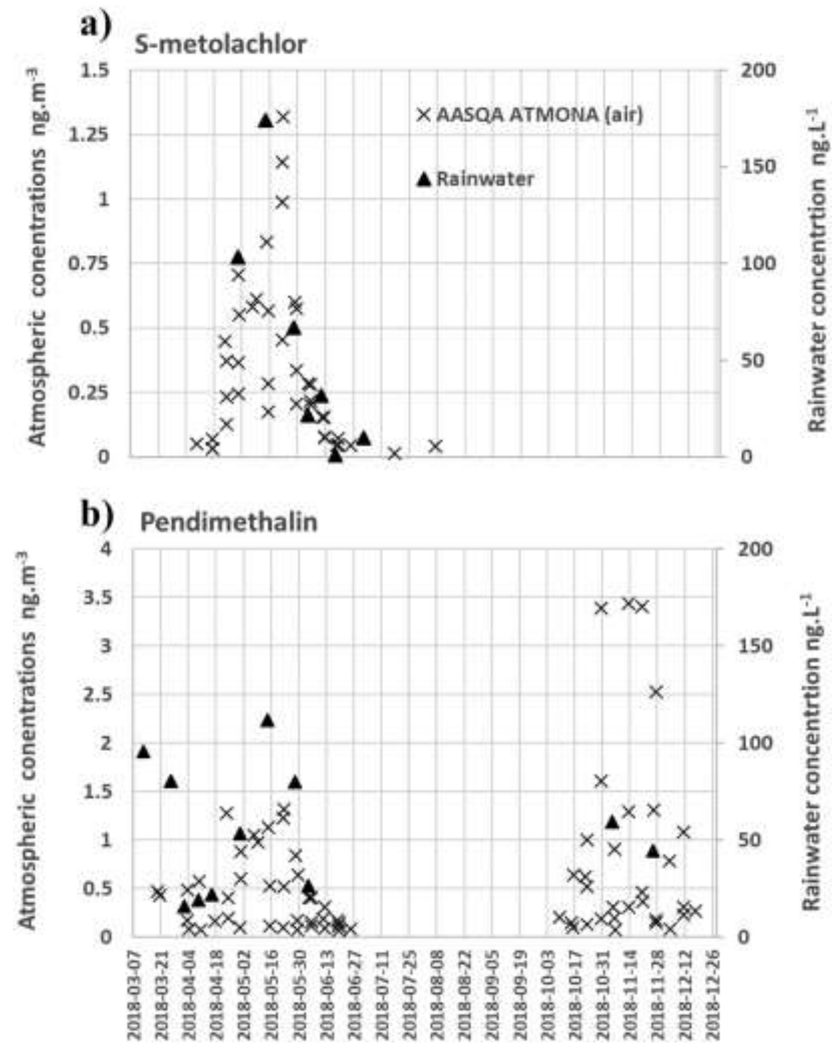
Results

Comparison with regional monitoring data from national association

Air concentration in ng.m^{-3}

	This study	AASQA ATMONA
Fenpropidin (min)	0.01	0.19
(max)	0.50	0.22
S-metolachlor (min)	0.31	0.34
(max)	1.08	1.32
Pendimethalin (min)	1.21	0.17
(max)	22.44	1.32

Good correlation between the seasonal variations in pesticide concentrations measured in the rainwater and atmosphere



Conclusion

(**+) sensitive and robust method** (comparison with available regional data)

possibility of quantifying air/water concentrations with a single analytical pipeline

=> reduces uncertainties and allows calculation of air/water ratio (provided that air and water samplings are synchronised)

(+) **easily deployable air sampling system** (mobile and electricity-free)

increase in the number of sampling sites at the landscape level

(-) **but human intervention**

Areas of improvement and perpectives:

continue the estimation of air/water concentration ratios => parameterisations

quantify the gas/particulate phases partitioning

get more information on farming practices => comparison of contamination according to pesticide use - conventional vs organic

develop models to integrate the exposure of non-target ecosystems or populations

=> these results show the need to follow up / develop measurement networks to study the contamination of air and rainwater

Thank you for your attention

For additional information:
Décuq C. et al., 2022. A multiresidue analytical method on air and rainwater for assessing pesticide atmospheric contamination in untreated areas. Science of The Total Environment 823, 153582. https://doi.org/10.1016/j.scitotenv.2022.153582

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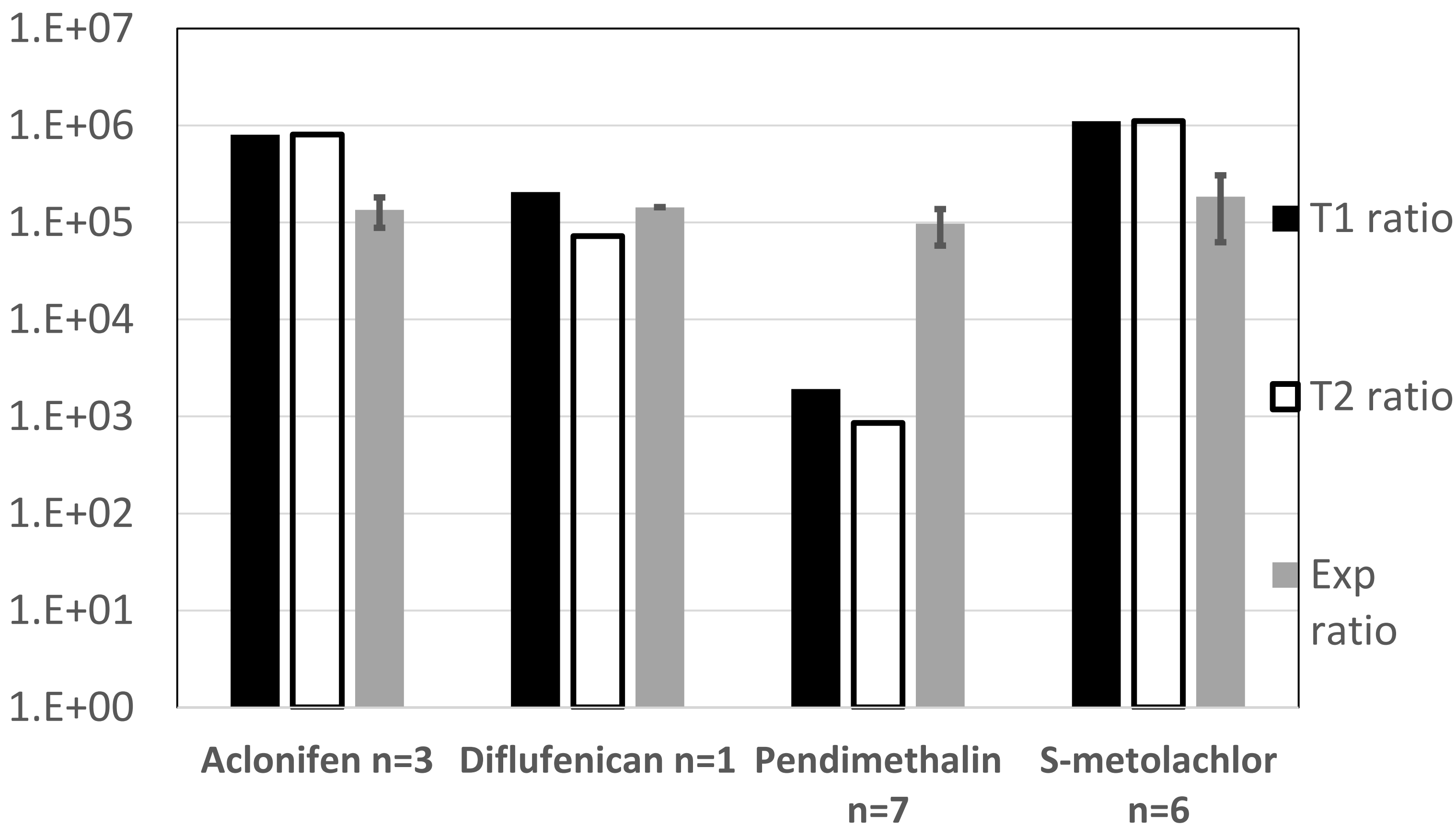
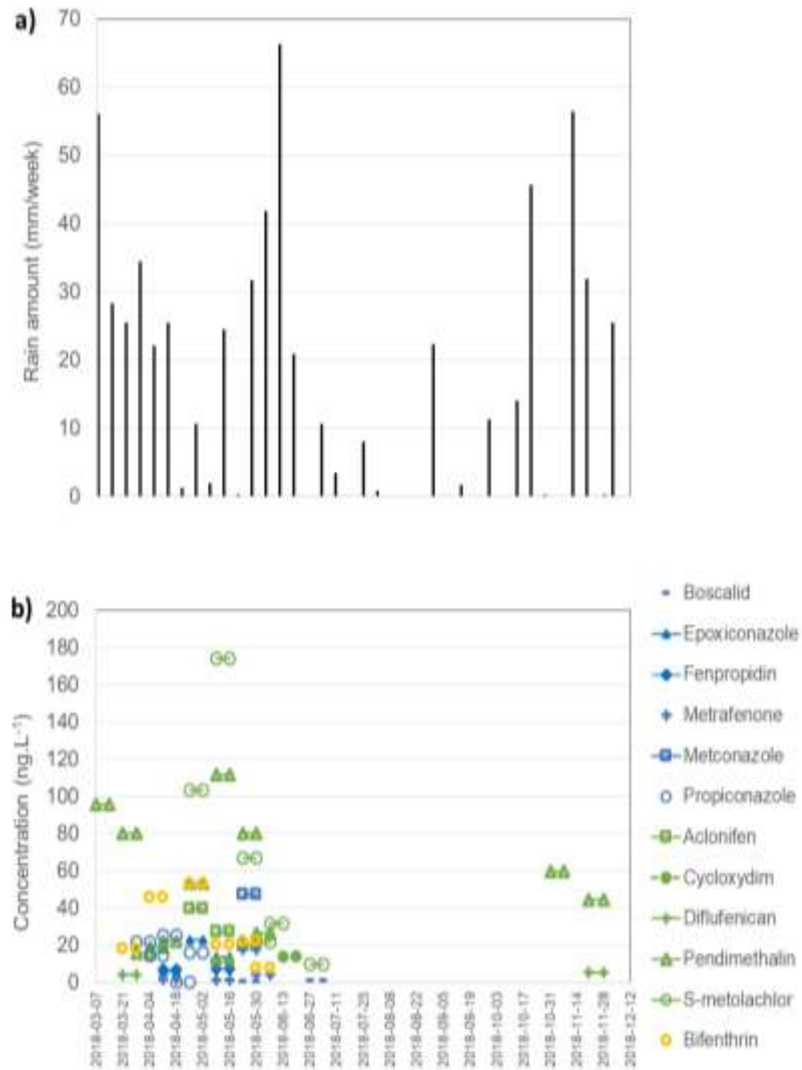
Rescape project (founded by ONEMA, Research call ECOPHYTO « Pesticides » 2014
PING project (founded by the Metaprogram INRAE SMaCH 2017) SMaCH PING
ZAPVS (Zone Atelier Plaine & Val de Sèvres, CNRS-CEBC, Beauvoir sur Niort) and JL Gautier
Atmo Nouvelle Aquitaine (AASQA) and A. Hulin

Evaluation du ratio scavenging

Experimental and theoretical ratios between concentrations in rainwater and in the air, "n" number of rainwater samples, error bars : standard deviation on the various samples



Rain intensity



Analytical conditions

	Air				Water			
	Thermal Desorption efficiency (%)	Calibration R squared y = ax+b	LOQ in ng.m^3	Repeatability in % n=3	Thermal Desorption efficiency (%)	Calibration R squared y= ax^2+bx+c	LOQ ng.L^{-1}	Repeatability in % n=3
Acetochlor	100	0.9998	0.04	13.8	100	0.9981	2.94	2.4
Aclonifen	99.9	0.9985	0.05	3.0	100	0.9984	1.61	0.5
Bifenthrin	99.9	0.9972	0.01	5.4	99.9	0.9854	0.95	8.6
Boscalid	100	0.9997	0.01	3.4	100	0.9965	0.34	4.1
Clomazone	99.8	0.9951	0.09	11.4	99.9	0.9983	2.76	2.6
Cloquintocet-mexyl	100	0.9972	0.02	43.7	100	0.9976	4.85	0.4
Cycloxydim	97.8	0.9968	0.06	9.1	100	0.9971	10.42	9.7
Cypermethrin 1	97.5	0.9934	0.01	7.0	99.4	0.9989	6.49	13.7
Cypermethrin 2	100	0.9974	0.21	4.4	99.5	0.9986	29.41	4.3
Cypermethrin 3	100	0.9799	0.21	4.4	99.4	0.9936	40.00	6.3
Cypermethrin 4	100		0.21	5.5	100	0.9979	38.46	0.6
Cyproconazole 1,2	100	0.9801	0.09	5.0	100	0.9993	18.18	9.1
Deltamethrin	99.6	0.9793	0.17	4.3	98.4	0.9994	7.52	10.8
Diflufenican	100	0.9951	0.01	5.1	100	0.9995	0.50	2.2
Dimethachlor	100	0.9997	0.03	8.8	100	0.9960	2.38	2.0
Epoxiconazole	99.6	0.9893	0.02	6.6	100	0.9998	5.26	4.1
Fenpropidin	100	0.9981	0.02	5.8	100	0.9992	2.13	14.4
lambda-cyhalothrin	100	0.9851	0.06	5.2	100	0.9968	5.41	4.6
Metazachlor	100	0.9987	0.02	5.3	100	0.9954	4.17	0.9
Metconazole	96.9	0.9844	0.04	5.5	100	0.9998	6.10	5.6
Metrafenone	99.8	0.9938	0.02	5.4	99.9	0.9995	1.06	2.7
Napropamide	100	0.9995	0.05	5.0	100	0.9966	2.08	2.7
Pendimethalin	100	0.9986	0.02	18.0	100	0.9995	1.52	2.6
Pirimicarb	100	0.9824	0.04	9.2	100	0.9990	4.13	8.4
Prochloraz	99.7	0.9980	0.14	19.3	100	0.9999	14.71	5.5
Propiconazole 1	99.5	0.9944	0.01	5.9	100	0.9970	3.33	2.5
Propiconazole 2	99.7	0.9879	0.05	4.1	100	1.0000	1.61	3.7
Pyraclostrobin	99.9	0.9825	0.21	34.2	100	0.9987	5.15	14.8
S-metolachlor	100	0.9996	0.01	9.3	100	0.9970	0.96	1.9
Tau-fluvalinate 1	100	0.9992	0.06	6.9	98.1	0.9926	5.43	5.3
Tau-fluvalinate 2	99.8	0.9986	0.06	4.9	98.5	0.9927	4.85	1.8
Thiamethoxam	99.6	0.9994	0.08	13.3	-		-	-

Analytical conditions

	Air	Water
	LOQ in ng.m3	LOQ in ng.L-1
Acetochlor	0.04	2.94
Aclonifen	0.05	1.61
Bifenthrin	0.01	0.95
Boscalid	0.01	0.34
Clomazone	0.09	2.76
Cloquintocet-mexyl	0.02	4.85
Cycloxydim	0.06	10.42
Cypermethrin 1	0.01	6.49
Cypermethrin 2	0.21	29.41
Cypermethrin 3	0.21	40.00
Cypermethrin 4	0.21	38.46
Cyproconazole 1,2	0.09	18.18
Deltamethrin	0.17	7.52
Diflufenican	0.01	0.50
Dimethachlor	0.03	2.38
Epoxiconazole	0.02	5.26
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