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**A new, simple, efficient and robust multi-residue method based on pressurized-liquid extraction of agricultural soils to analyze pesticides by liquid chromatography coupled with a high-resolution quadrupole time-of-flight mass spectrometer**

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## ➤ INRAE - INSTITUTE

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- Creation in 2020 from two scientific and technologic public institutes :
  - INRA, a French national institute of research for agronomy created in 1946
  - IRSTEA, a French national institute of research for environment created in 1971
- 6 major themes :
  - Climate change and risks
  - Agroecology
  - Biodiversity
  - Food, overall health
  - Bioeconomics
  - Society and territories
- Some informations :
  - 8,400 public officials
  - 3,100 private contract agents
  - 18 research centers
  - 14 research department
  - 268 research, service and experimental units

# ➤ INRAE - SOIL ANALYSIS LABORATORY

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## ➤ Organization :

- Service unit for researchers from INRAE and other institutes,
- AgroEcoSystem Department and Hauts de France Research Center,
- 22 public officials with 5 engineers and 17 technicians,
- Approval for soil analysis by agriculture minister,
- Accreditation for soil analysis by COFRAC N°1-1380.

## ➤ Missions :

- Evaluation of soil fertility parameters,
- Control of their possible degree of pollution,
- Assessment of the impact of waste recycling in agriculture.

## ➤ Analytical platform :

- Preparation and agronomic characterization of soils,
- Spectroscopic techniques for metallic elements analysis,
- Chromatographic techniques for organic compounds analysis.

## ➤ Research activity :

- Development and metrological improvement of analysis methods,
- Improved method functionality.

## ➤ RESEARCH PROJECT

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Development of targeted and non-targeted screening methods for trace organic compounds in soils using high performance liquid chromatography coupled with a high resolution and time-of-flight mass spectrometer.

## ➤ SCIENTIFIC INTERESTS OF THE PROJECT

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Contribute to the diagnosis of the Environment state (Soils) and to the monitoring of its evolution.

Develop targeted and non-targeted screening methods in order to acquire comprehensive data on CTO in soils.

Innovate the methodological approach to determine the comprehensive content of soils in polluting or natural CTO, ideally from a single analysis of soil extract.

## ➤ PROJECT'S OBJECTIVES

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Develop a CTO analysis method by LC-QTOF-MS.

Select and acquire CTO of different chemical families susceptible to be found in soils.

Select and prepare soils of different nature to lead performance studies of selected CTO.

Select a CTO extraction technique for soils and define its optimal configuration.

## ➤ STUDIED CTO

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### ➤ **Triazines** (herbicides)

- Ametryn, Atraton, desethyl-Atrazine, deisopropyl-Atrazine, Atrazine, Cyanazine, Desmetryne, Methoprotryne, Prometryne, Prometon, Propazine, Simazine, Terbutylazine.

### ➤ **Phenylureas** (herbicides)

- Diuron, DCPU, DCPMU, Isoproturon, IPPU, IPPMU, Fenuron, Linuron, Methabenzthiazuron, Monuron, Monolinuron, Neburon.

### ➤ **Emerging pesticides** (herbicides. fungicides. insecticides)

- Acetochlore, Aclonifen, Boscalide, Clomazone, Epoxiconazole, Fenpropidine, Imidaclopride, Metazachlore, Metolachlore, Thiaclopride.



# ➤ LC-QTOF-MS SYSTEM



LC Thermofisher Ultimate 3000 / QTOF MS Bruker Impact II

## ➤ CTO ANALYSIS (LC-QTOF-MS)

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HPLC analytical conditions :

- Column : Acclaim C18 100 mm x 2.1 mm x 2.2  $\mu\text{m}$
- Column oven : 30°C
- Gradient : H<sub>2</sub>O / Methanol (90/10) to (10/90) in 20 min
- Flow : 0.200  $\mu\text{l}/\text{min}$
- Injection volume : 5  $\mu\text{L}$

Mass parameters :

- ESI + Ionisation
- MS and MS/MS

Analysis :

- Identification by individual solutions and screening tool
- External calibration solutions : 0.010 to 400  $\mu\text{g}/\text{l}$

# ▶ TRIAZINES

Analyte	Formula	m/z	RT [min]	External Corr. Coef.	External calibration range (µg/L)	
<b>Ametryn</b>	C <sub>9</sub> H <sub>17</sub> N <sub>5</sub> S	228.1277	9.23	0.99968	0.250	400
<b>Atraton</b>	C <sub>9</sub> H <sub>17</sub> N <sub>5</sub> O	212.1506	7.80	0.99925	0.175	400
<b>Atrazine</b>	C <sub>8</sub> H <sub>14</sub> ClN <sub>5</sub>	216.1010	8.25	0.99923	0.025	400
<b>Atrazine-desethyl</b>	C <sub>6</sub> H <sub>10</sub> ClN <sub>5</sub>	188.0697	5.74	0.99427	0.250	400
<b>Atrazine-deisopropyl</b>	C <sub>5</sub> H <sub>8</sub> ClN <sub>5</sub>	174.0541	4.74	0.99362	0.875	400
<b>Cyanazine</b>	C <sub>9</sub> H <sub>13</sub> ClN <sub>6</sub>	241.0963	6.59	0.99913	0.875	400
<b>Desmetryne</b>	C <sub>8</sub> H <sub>15</sub> N <sub>5</sub> S	172.0651	8.21	0.99762	0.875	400
<b>Methoprotryne</b>	C <sub>11</sub> H <sub>21</sub> N <sub>5</sub> OS	272.1540	9.13	0.99964	0.250	400
<b>Prometryne</b>	C <sub>10</sub> H <sub>19</sub> N <sub>5</sub> S	242.1434	10.13	0.99956	0.100	400
<b>Propazine</b>	C <sub>9</sub> H <sub>16</sub> ClN <sub>5</sub>	188.0697	9.25	0.99987	0.875	400
<b>Prometon</b>	C <sub>10</sub> H <sub>19</sub> N <sub>5</sub> O	184.1193	8.88	0.99906	0.875	400
<b>Simazine</b>	C <sub>7</sub> H <sub>12</sub> ClN <sub>5</sub>	202.0854	7.10	0.99979	0.050	400
<b>Terbutylazine</b>	C <sub>9</sub> H <sub>16</sub> ClN <sub>5</sub>	230.1167	9.45	0.99967	0.175	400

# PHENYLUREAS

Analyte	Formula	m/z	RT [min]	External Corr. Coef.	External calibration range (µg/L)	
<b>DCPU</b>	C <sub>7</sub> H <sub>6</sub> Cl <sub>2</sub> N <sub>2</sub> O	204.9930	8.01	0.99729	1.250	400
<b>DCPMU</b>	C <sub>8</sub> H <sub>8</sub> Cl <sub>2</sub> N <sub>2</sub> O	219.0087	8.51	0.99982	0.875	400
<b>Diuron</b>	C <sub>9</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O	233.0243	8.65	0.99957	0.250	400
<b>Fenuron</b>	C <sub>9</sub> H <sub>12</sub> N <sub>2</sub> O	165.1022	5.13	0.99829	0.250	400
<b>IPPMU</b>	C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O	193.1335	8.22	0.99809	0.010	400
<b>IPPU</b>	C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> O	179.1179	7.77	0.99924	0.100	400
<b>Isoproturon</b>	C <sub>12</sub> H <sub>18</sub> N <sub>2</sub> O	207.1492	8.39	0.99976	0.175	400
<b>Linuron</b>	C <sub>9</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	249.0192	9.40	0.99954	0.875	400
<b>Methabenzthiazuron</b>	C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> OS	222.0696	8.36	0.99968	0.025	400
<b>Monolinuron</b>	C <sub>9</sub> H <sub>11</sub> ClN <sub>2</sub> O <sub>2</sub>	215.0580	7.83	0.99976	0.175	400
<b>Monuron</b>	C <sub>9</sub> H <sub>11</sub> ClN <sub>2</sub> O	199.0633	6.97	0.99943	0.875	400
<b>Neburon</b>	C <sub>12</sub> H <sub>16</sub> Cl <sub>2</sub> N <sub>2</sub> O	275.0712	10.79	0.99979	0.250	400

# EMERGING PESTICIDES

Analyte	Formula	m/z	RT [min]	External Corr. Coef.	External calibration range (µg/L)	
<b>Acetochlor</b>	C <sub>12</sub> H <sub>15</sub> ClNO <sup>1+</sup>	224.0837	10.41	0.99984	0.250	400
<b>Aclonifen</b>	C <sub>12</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>3</sub>	265.0374	10.97	0.99488	0.175	400
<b>Boscalid</b>	C <sub>18</sub> H <sub>12</sub> Cl <sub>2</sub> N <sub>2</sub> O	343.0399	9.48	0.99902	0.100	400
<b>Clomazone</b>	C <sub>12</sub> H <sub>14</sub> ClNO <sub>2</sub>	240.0786	8.98	0.99968	0.175	400
<b>Epoxiconazole</b>	C <sub>17</sub> H <sub>13</sub> ClFN <sub>3</sub> O	330.0804	10.37	0.99863	0.010	400
<b>Fenpropidin</b>	C <sub>19</sub> H <sub>31</sub> N	274.2529	8.45	0.99927	0.250	400
<b>Imidacloprid</b>	C <sub>9</sub> H <sub>10</sub> ClN <sub>5</sub> O <sub>2</sub>	256.0596	4.80	0.99964	0.250	400
<b>Metazachlor</b>	C <sub>11</sub> H <sub>13</sub> ClNO <sup>1+</sup>	210.0680	8.20	0.99980	0.175	400
<b>Metolachlor</b>	C <sub>15</sub> H <sub>22</sub> ClNO <sub>2</sub>	284.1412	10.44	0.99974	0.250	400
<b>Thiacloprid</b>	C <sub>10</sub> H <sub>9</sub> ClN <sub>4</sub> S	253.0309	5.63	0.99985	0.175	400
<b>Thiamethoxam</b>	C <sub>8</sub> H <sub>10</sub> ClN <sub>5</sub> O <sub>3</sub> S	292.0266	4.25	0.99629	0.875	400
<b>Phenacetine</b>	C <sub>10</sub> H <sub>13</sub> NO <sub>2</sub>	180.1019	6.07	0.99897	12.500	400

# SOILS NATURE

Origin	Nature	Clays g/kg	Fine silts g/kg	Coarse silts g/kg	Fine sands g/kg	Coarse sands g/kg	TOC g/kg	Total N g/kg	CaCO <sub>3</sub> g/kg	pH
Lievin	Loessic silt	205	255	457	74	9	22	1.5	1	6.6
Airon-Saint-Vaast	Sandy deposits redistributed on glacis	111	109	200	341	239	12	1.2	16	8
Dompierre-sur-Helpe	Silty alluvium	380	321	268	22	9	38	4.0	< 1	5.5
Steenwerck	Alluvium of the Lys plain	312	260	293	102	33	13	1.4	< 1	7.5
Marcq-en-Ostrevent	Loess	194	236	446	112	12	12	1.2	3	7.9

## ➤ EXTRACTION MODE REQUIREMENTS

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Extraction likely to be total.

Possible variation of extraction parameters.

Automation of extraction.

Repeatability and Reproducibility of extractions.

Reduced extraction volumes of organic solvents.

Short duration for extraction.

Ease of implementation of extractions.

Extraction method usable for other environmental solid matrices.

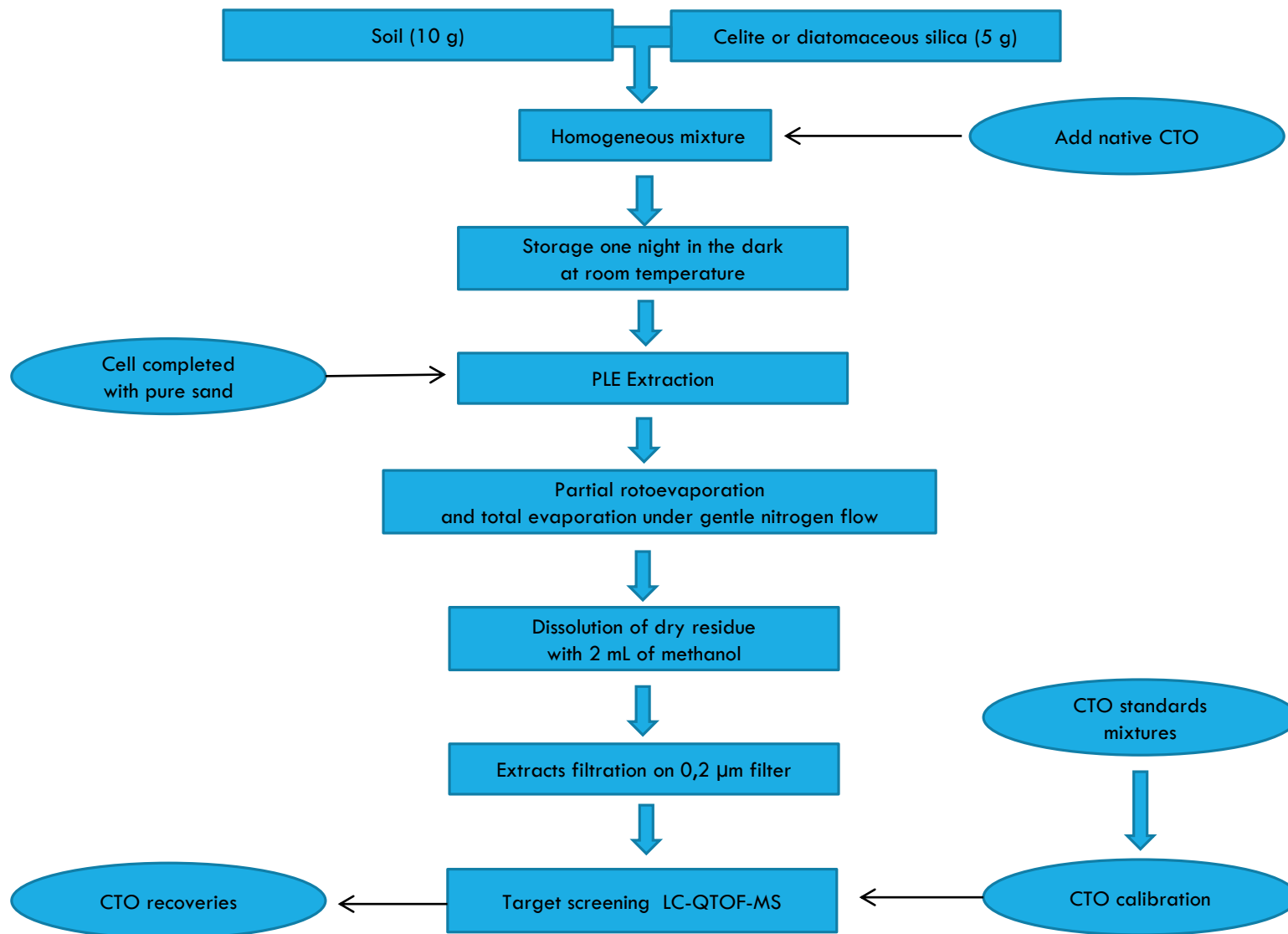
# ➤ PRESSURIZED-LIQUID EXTRACTION



BUCHI E-916 SPEED-EXTRACTOR



# ANALYSIS METHOD



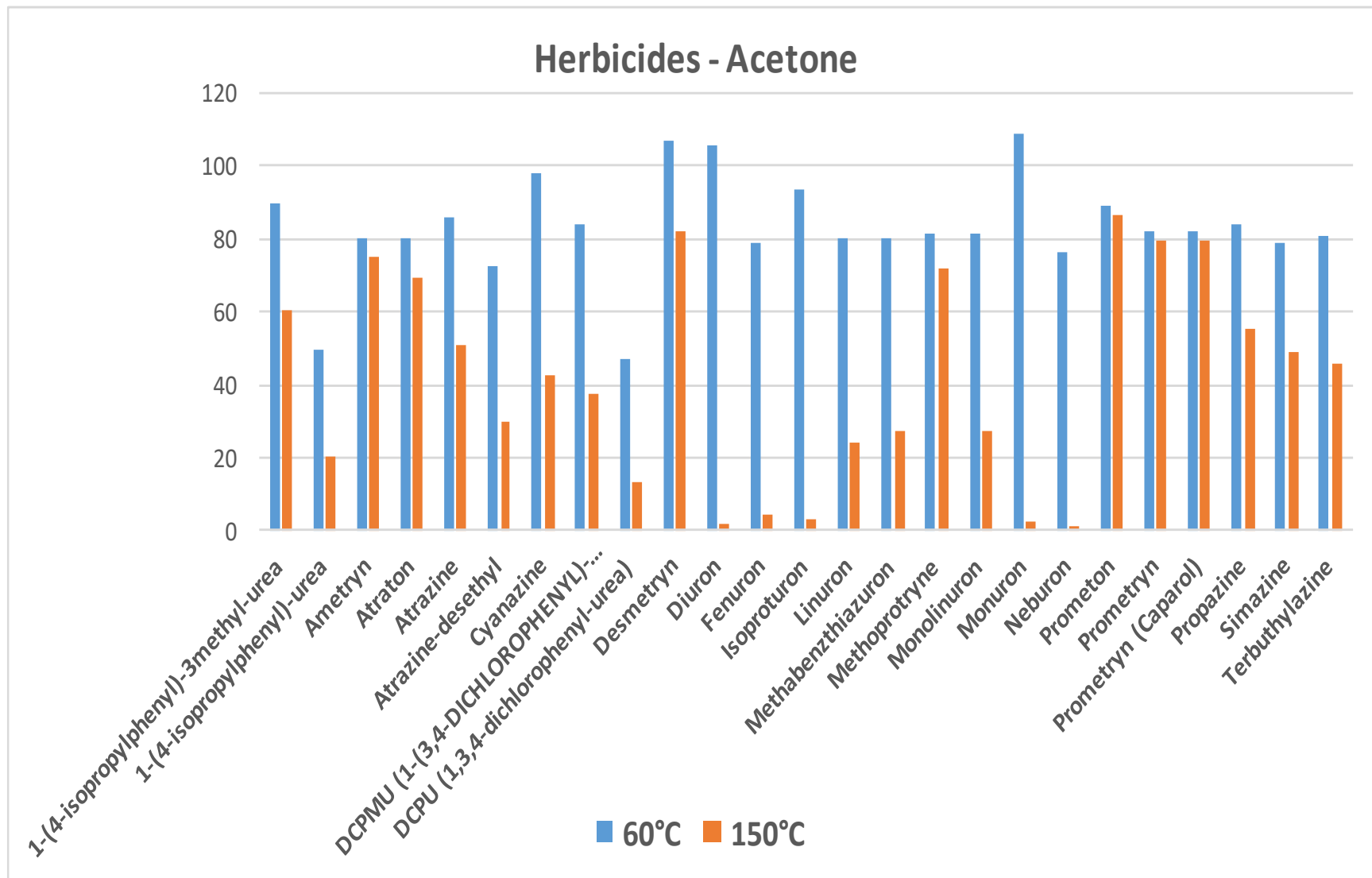
## ➤ EXPERIMENT PLAN

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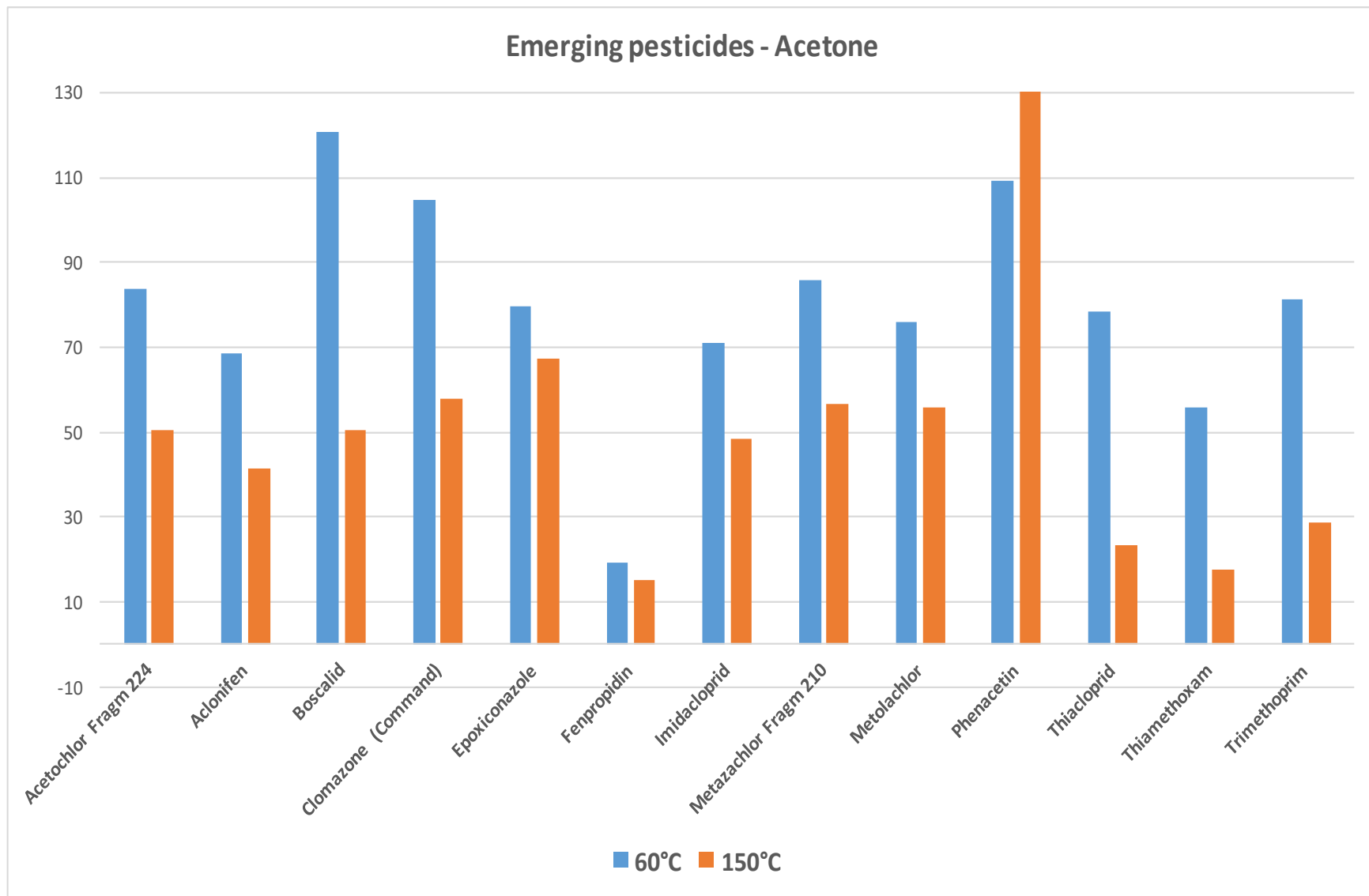
- Soils study
  - 5 soils of the North region of France
  - spiked soils to 40 µg/kg
- PLE parameters
  - 2 temperatures : 60 and 150 °C
  - 2 pressions : 100 and 150 Bar
  - 2 and 3 cycles of 5 minutes
  - 2 organic solvents : Acetone and Methanol
- Analysis
  - 16 trials for each soil (total of 80 analyzes)
- LC-QTOF MS (ESI+) – external calibration



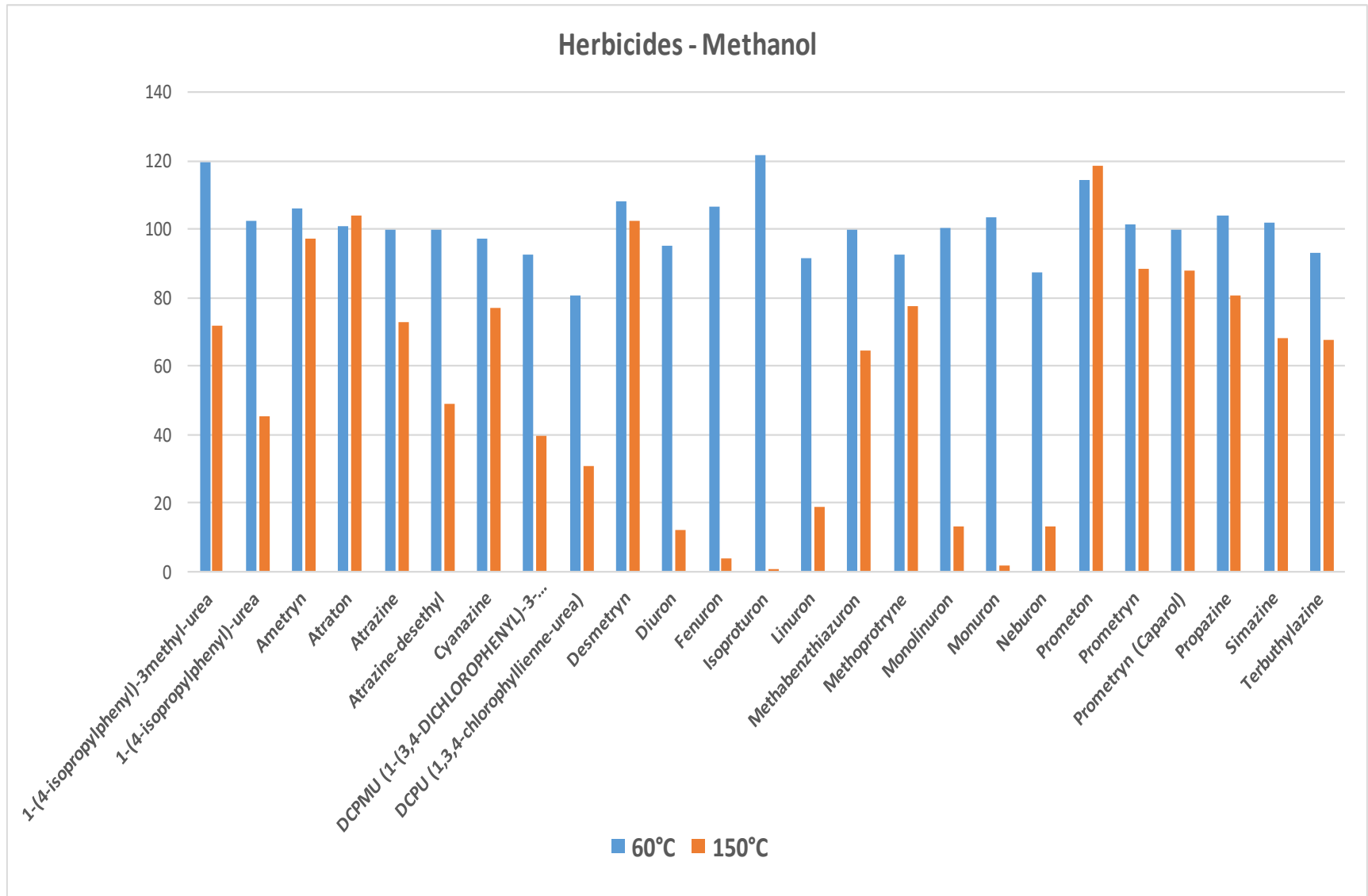
# HERBICIDES RECOVERY - ACETONE



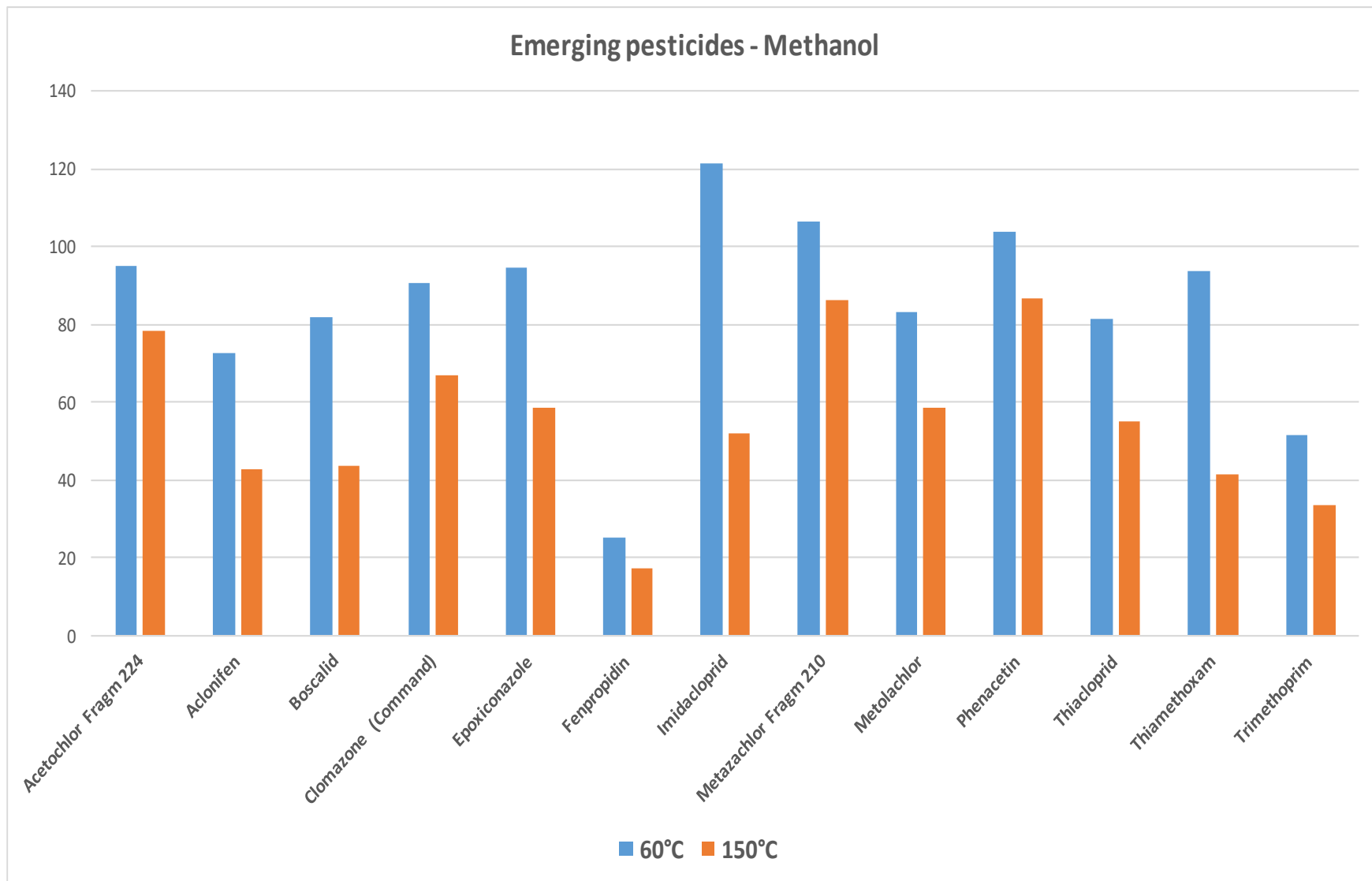
# EMERGING PESTICIDES RECOVERY - ACETONE



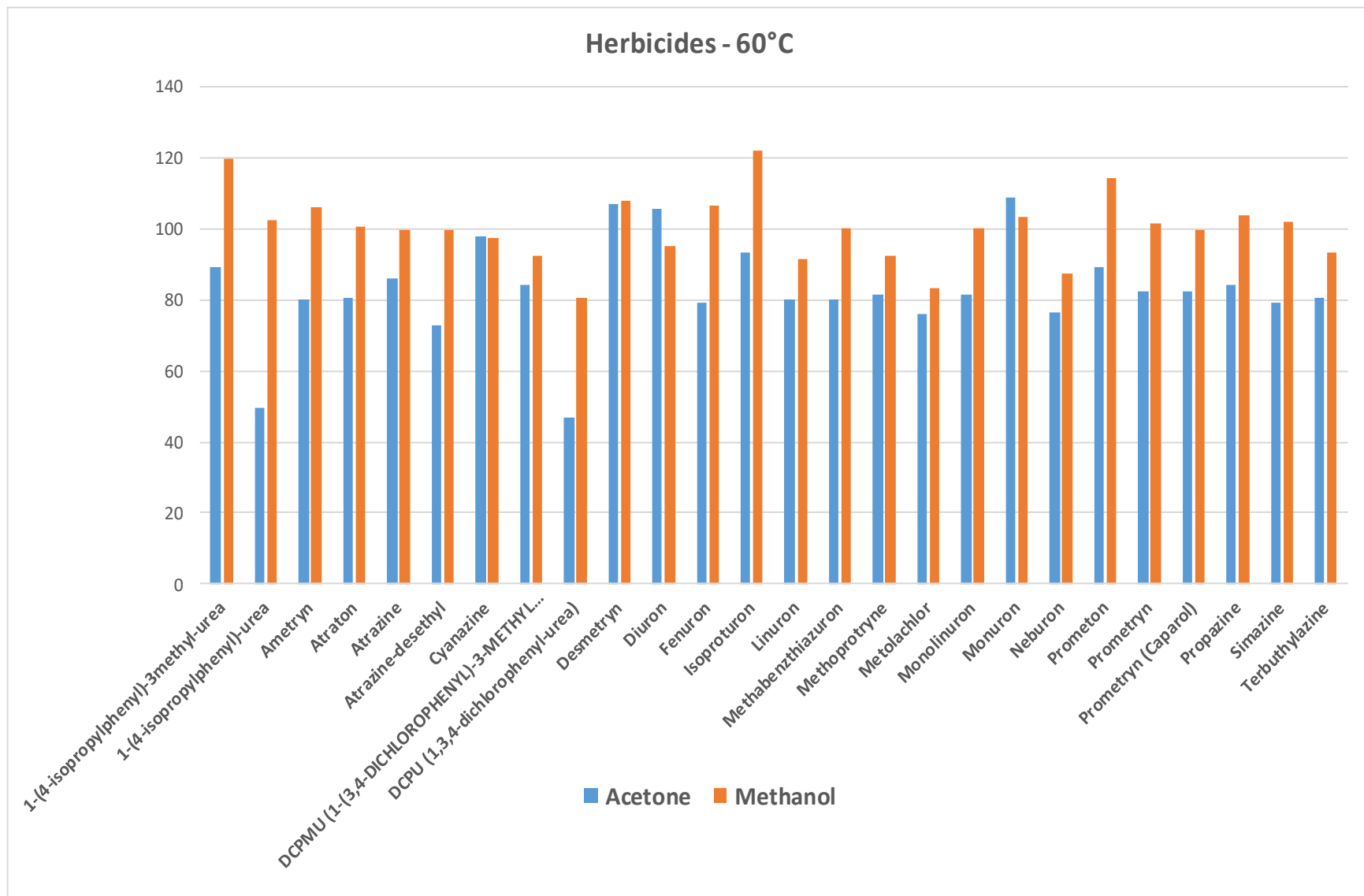
# HERBICIDES RECOVERY - METHANOL



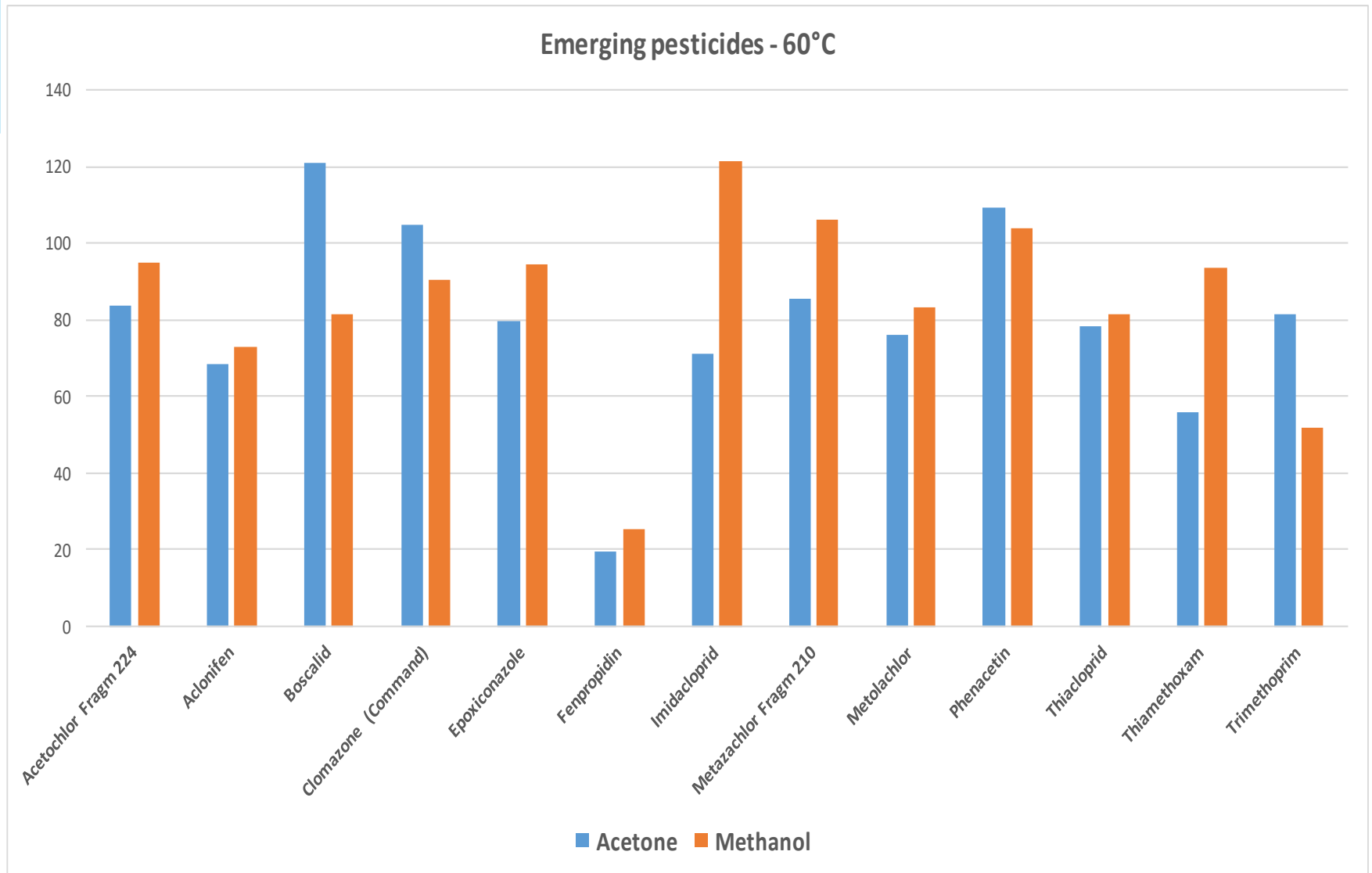
# EMERGING PESTICIDES RECOVERY - METHANOL



# HERBICIDES RECOVERY – 60°C



# EMERGING PESTICIDES RECOVERY – 60°C





## ➤ OPTIMIZATION OF EXTRACTION T°C

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- Soils study :
  - 5 soils of the North region of France
  - spiked soils to 40 µg/kg
  
- PLE parameters :
  - temperatures : 60 / 80 / 100 / 120 / 150 °C
  - pression : 150 Bar
  - 2 cycles of 5 minutes
  - organic solvent : Methanol

## SOILS RECOVERY (ESI+) - METHANOL

Pesticides	60°C		80°C		100°C		120°C		150°C	
	Mean (%)	RSD (%)	Mean (%)	RSD (%)	Mean (%)	RSD (%)	Mean (%)	RSD (%)	Mean (%)	RSD (%)
Ametryn	102	3	101	2	105	3	102	5	96	11
Atraton	100	4	103	1	109	4	110	8	107	15
Atrazine	101	6	99	4	100	8	94	11	72	15
Atrazine-desethyl	98	4	102	3	98	8	84	12	43	20
Cyanazine	104	3	105	1	109	3	103	6	73	17
Desmetryn	108	4	117	3	125	4	129	5	106	10
Methoprotryne	93	5	90	3	91	5	88	6	77	11
Prometon	113	3	112	4	121	4	129	5	123	10
Prometryn	100	2	99	1	101	3	97	3	88	11
Propazine	104	4	112	3	114	4	110	8	79	15
Simazine	101	5	102	4	103	7	95	9	62	11
Terbuthylazine	92	5	93	4	92	6	90	8	65	16
IPPMU	119	4	116	3	122	5	121	6	68	8
IPPU	101	4	98	3	101	7	88	11	38	15
DCPMU	92	4	93	7	91	11	77	15	36	20
DCPU	79	9	77	13	73	16	57	18	20	16
Diuron	94	4	95	2	89	6	40	20	0	137

## ➤ SOILS RECOVERY (ESI+) - METHANOL

Pesticides	60°C		80°C		100°C		120°C		150°C	
	Mean (%)	RSD (%)	Mean (%)	RSD (%)	Mean (%)	RSD (%)	Mean (%)	RSD (%)	Mean (%)	RSD (%)
Fenuron	109	4	101	3	91	3	33	22	0	-
Isoproturon	117	8	126	7	120	9	50	22	0	-
Linuron	92	3	86	4	80	7	52	20	8	28
Methabenzthiazuron	98	4	101	3	105	5	101	7	59	12
Monolinuron	96	5	92	1	90	5	64	12	12	24
Monuron	103	4	107	2	100	3	39	18	3	224
Neburon	83	5	82	7	95	17	63	29	0	224
Acetochlor	96	4	104	4	104	5	101	6	80	12
Aclonifen	68	18	74	18	65	21	55	22	35	24
Boscalid	81	14	72	19	67	23	57	26	36	31
Clomazone	93	3	94	3	94	6	86	7	67	15
Epoxiconazole	97	18	101	21	98	25	88	29	59	33
Imidacloprid	120	23	123	20	122	25	98	28	40	30
Metazachlor	104	5	115	3	119	3	117	5	89	11
Metolachlor	86	4	87	4	85	5	82	9	61	13
Thiacloprid	70	23	82	11	84	12	74	18	43	23
Thiamethoxam	87	8	88	8	83	14	64	22	26	33

## ➤ CONCLUSION

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- Optimal pesticides recoveries by pressurized-liquid extraction with Methanol at 80°C, 150 Bars and 2 cycles of 5 min.
- RSD < 21 % and Mean recoveries > 82 % excepted for 3 compounds with Mean recoveries > 72%
- Efficiency of extraction procedure for all types of soils.
- Degradation of organic compounds up to 100°C.
- Extended linearity of external calibration.
- Good sensitivity of LC-QTOF-MS.
- Little or no effect of non-purified extract matrices.

The method developed could be qualified as a **simple, efficient and robust method.**

## ➤ PUBLICATION

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**A new. simple. efficient and robust multi-residue method based on pressurized-liquid extraction of agricultural soils to analyze pesticides by liquid chromatography coupled with a high resolution quadrupole time-of-flight mass spectrometer.**

*International Journal of Environmental Analytical Chemistry.*  
Taylor & Francis. February 2021. pp.1-16.

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Sopheak NET. CNRS UMR 8516 - LASIRE. Lille

<https://www.tandfonline.com/eprint/C2Z7MKCJNXNGDSGZNHYA/full?target=10.1080/03067319.2021.1889531>



INRAE



THANKS  
FOR YOUR TIME  
AND ATTENTION

A large, faint, light-colored outline of the INRAE logo is visible in the background, partially overlapping the text.