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

Giovanni Caria, Nicolas Proix, Christian Mougin, Baghdad Ouddane, Net Sopheak

INRAE
Laboratoire d'Analyses des Sols

Giovanni CARIA

Research Engineer
INRAE – Soil Analysis Laboratory - Arras (France)

PhD Student – SMRE Doctoral School – Lille (France)
UMR CNRS 8516 – LASIRE – Lille (France)

PROIX Nicolas (INRAE Arras), MOUGIN Christian (INRAE Versailles),
OUDDANE Baghdad (CNRS Lille), NET Sopheak (CNRS Lille)

INRAE - INSTITUTE

- 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

- 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

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

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

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

- **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. fongicides. 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)

HPLC analytical conditions :

- Column : Acclaim C18 100 mm x 2.1 mm x 2.2 µm
- Column oven : 30°C
- Gradient : H20 / Methanol (90/10) to (10/90) in 20 min
- Flow : 0.200 µl/min
- Injection volume : 5 µL

Mass parameters :

- ESI + Ionisation
- MS and MS/MS

Analysis :

- Identification by individual solutions and screening tool
- External calibration solutions : 0.010 to 400 µg/l

TRIAZINES

Analyte	Formula	m/z	RT [min]	External Corr. Coef.	External calibration range (µg/L)	
Ametryn	$C_9H_{17}N_5S$	228.1277	9.23	0.99968	0.250	400
Atraton	$C_9H_{17}N_5O$	212.1506	7.80	0.99925	0.175	400
Atrazine	$C_8H_{14}ClN_5$	216.1010	8.25	0.99923	0.025	400
Atrazine-desethyl	$C_6H_{10}ClN_5$	188.0697	5.74	0.99427	0.250	400
Atrazine-deisopropyl	$C_5H_8ClN_5$	174.0541	4.74	0.99362	0.875	400
Cyanazine	$C_9H_{13}ClN_6$	241.0963	6.59	0.99913	0.875	400
Desmetryne	$C_8H_{15}N_5S$	172.0651	8.21	0.99762	0.875	400
Methoprotryne	$C_{11}H_{21}N_5OS$	272.1540	9.13	0.99964	0.250	400
Prometryne	$C_{10}H_{19}N_5S$	242.1434	10.13	0.99956	0.100	400
Propazine	$C_9H_{16}ClN_5$	188.0697	9.25	0.99987	0.875	400
Prometon	$C_{10}H_{19}N_5O$	184.1193	8.88	0.99906	0.875	400
Simazine	$C_7H_{12}ClN_5$	202.0854	7.10	0.99979	0.050	400
Terbutylazine	$C_9H_{16}ClN_5$	230.1167	9.45	0.99967	0.175	400

PHENYLUREAS

Analyte	Formula	m/z	RT [min]	External Corr. Coef.	External calibration range (µg/L)	
DCPU	$C_7H_6Cl_2N_2O$	204.9930	8.01	0.99729	1.250	400
DCPMU	$C_8H_8Cl_2N_2O$	219.0087	8.51	0.99982	0.875	400
Diuron	$C_9H_{10}Cl_2N_2O$	233.0243	8.65	0.99957	0.250	400
Fenuron	$C_9H_{12}N_2O$	165.1022	5.13	0.99829	0.250	400
IPPMU	$C_{11}H_{16}N_2O$	193.1335	8.22	0.99809	0.010	400
IPPU	$C_{10}H_{14}N_2O$	179.1179	7.77	0.99924	0.100	400
Isoproturon	$C_{12}H_{18}N_2O$	207.1492	8.39	0.99976	0.175	400
Linuron	$C_9H_{10}Cl_2N_2O_2$	249.0192	9.40	0.99954	0.875	400
Methabenzthiazuron	$C_{10}H_{11}N_3OS$	222.0696	8.36	0.99968	0.025	400
Monolinuron	$C_9H_{11}ClN_2O_2$	215.0580	7.83	0.99976	0.175	400
Monuron	$C_9H_{11}ClN_2O$	199.0633	6.97	0.99943	0.875	400
Neburon	$C_{12}H_{16}Cl_2N_2O$	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)	
Acetochlor	$C_{12}H_{15}ClNO^{1+}$	224.0837	10.41	0.99984	0.250	400
Aclonifen	$C_{12}H_9ClN_2O_3$	265.0374	10.97	0.99488	0.175	400
Boscalid	$C_{18}H_{12}Cl_2N_2O$	343.0399	9.48	0.99902	0.100	400
Clomazone	$C_{12}H_{14}ClNO_2$	240.0786	8.98	0.99968	0.175	400
Epoxiconazole	$C_{17}H_{13}ClFN_3O$	330.0804	10.37	0.99863	0.010	400
Fenpropidin	$C_{19}H_{31}N$	274.2529	8.45	0.99927	0.250	400
Imidacloprid	$C_9H_{10}ClN_5O_2$	256.0596	4.80	0.99964	0.250	400
Metazachlor	$C_{11}H_{13}ClNO^{1+}$	210.0680	8.20	0.99980	0.175	400
Metolachlor	$C_{15}H_{22}ClNO_2$	284.1412	10.44	0.99974	0.250	400
Thiacloprid	$C_{10}H_9ClN_4S$	253.0309	5.63	0.99985	0.175	400
Thiamethoxam	$C_8H_{10}ClN_5O_3S$	292.0266	4.25	0.99629	0.875	400
Phenacetine	$C_{10}H_{13}NO_2$	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	CaCO3 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

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.

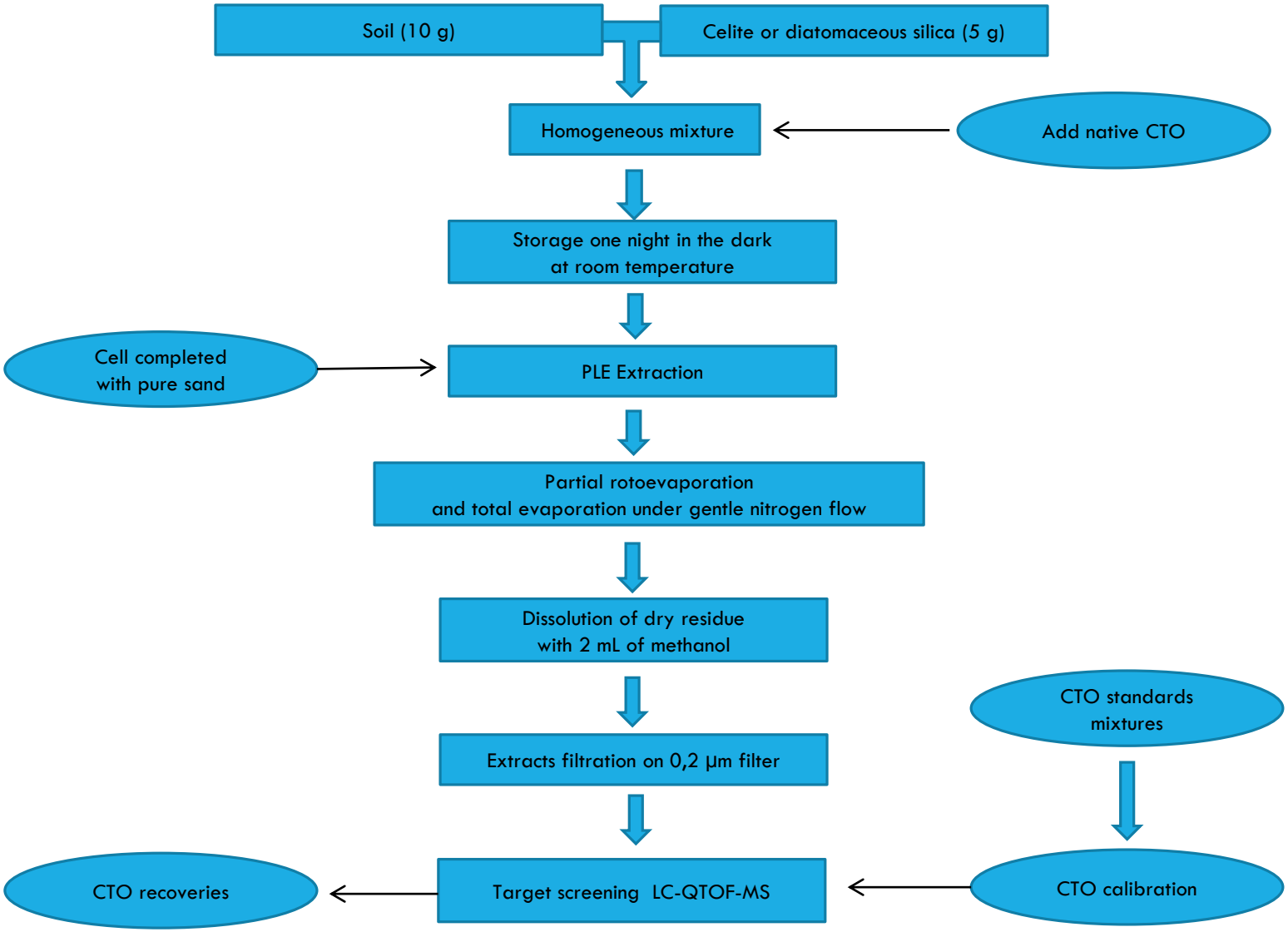
Ease of implementation of extractions.

Extraction method usable for other environmental solid matrices.

PRESSURIZED-LIQUID EXTRACTION

BUCHI E-916 SPEED-EXTRACTOR

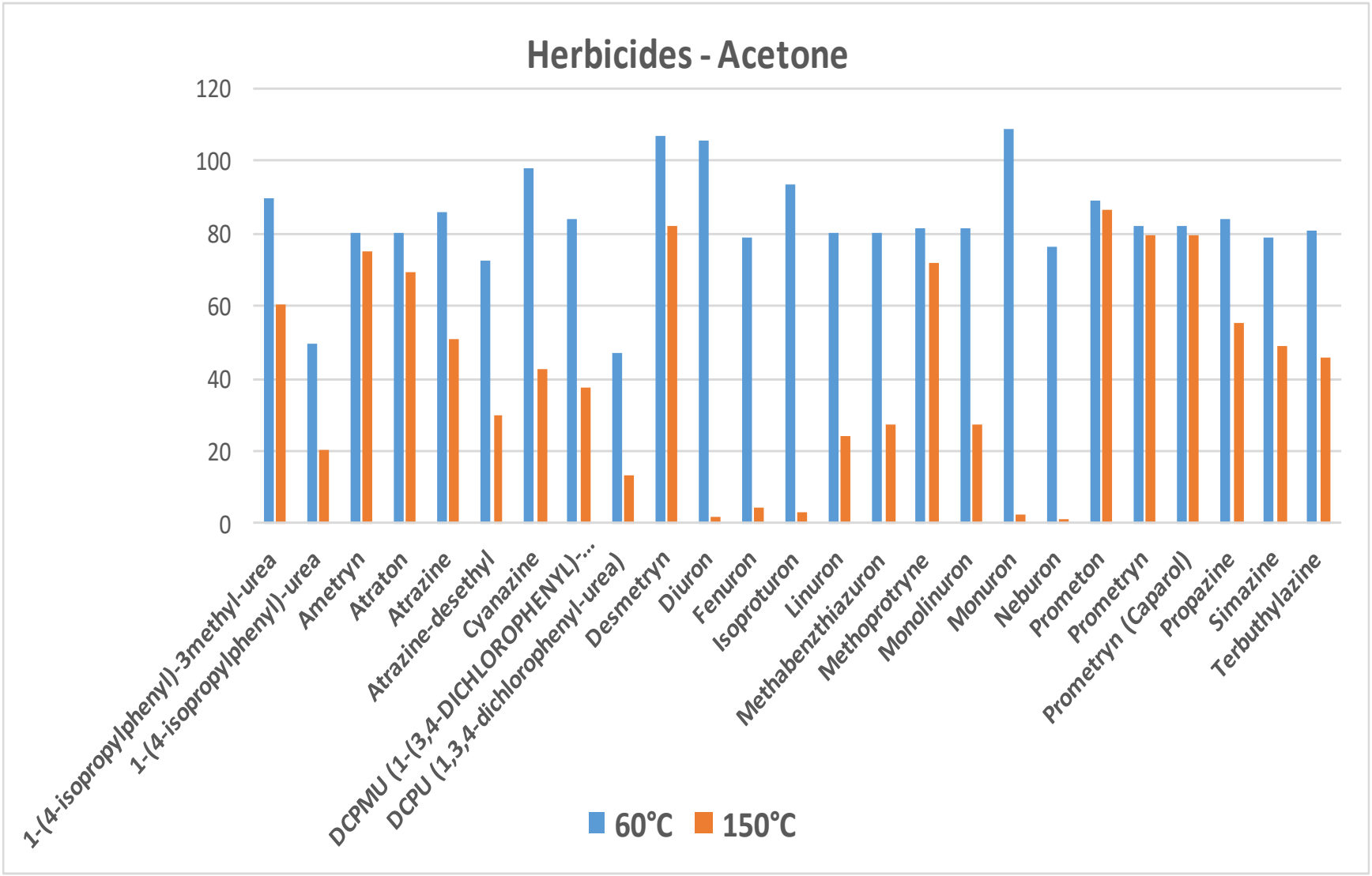
ANALYSIS METHOD



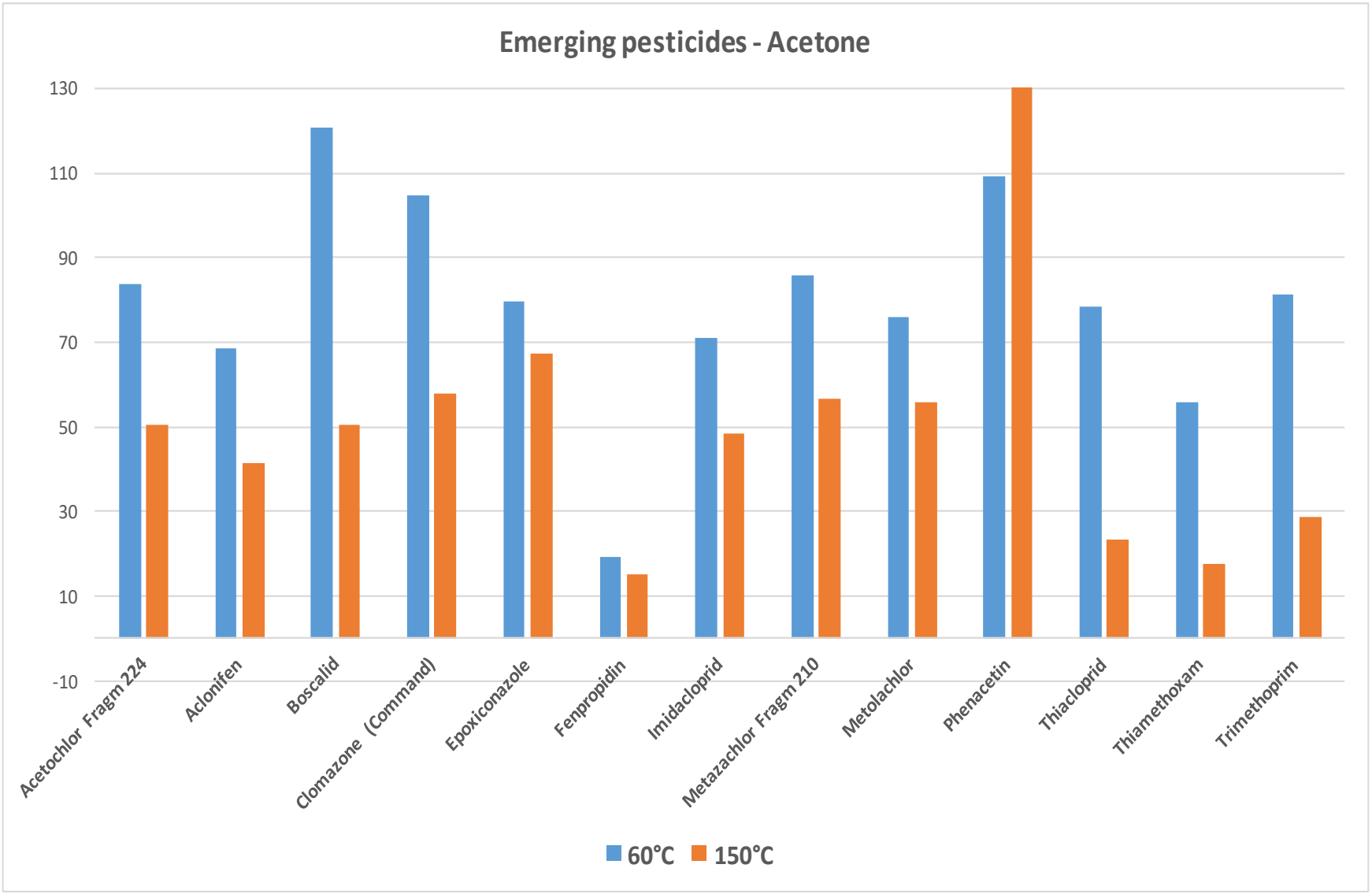
EXPERIMENT PLAN

- 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

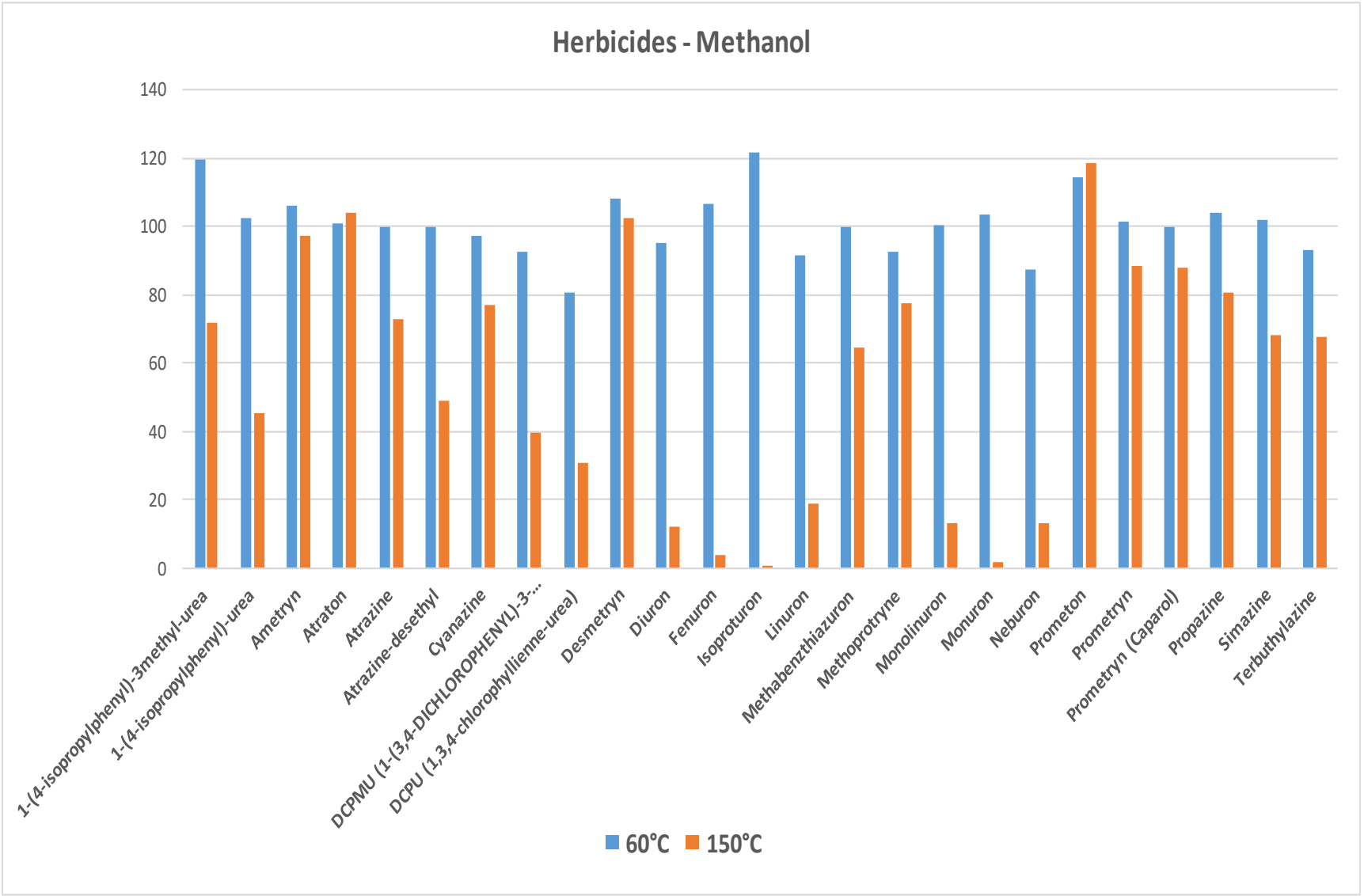
HERBICIDES RECOVERY - ACETONE



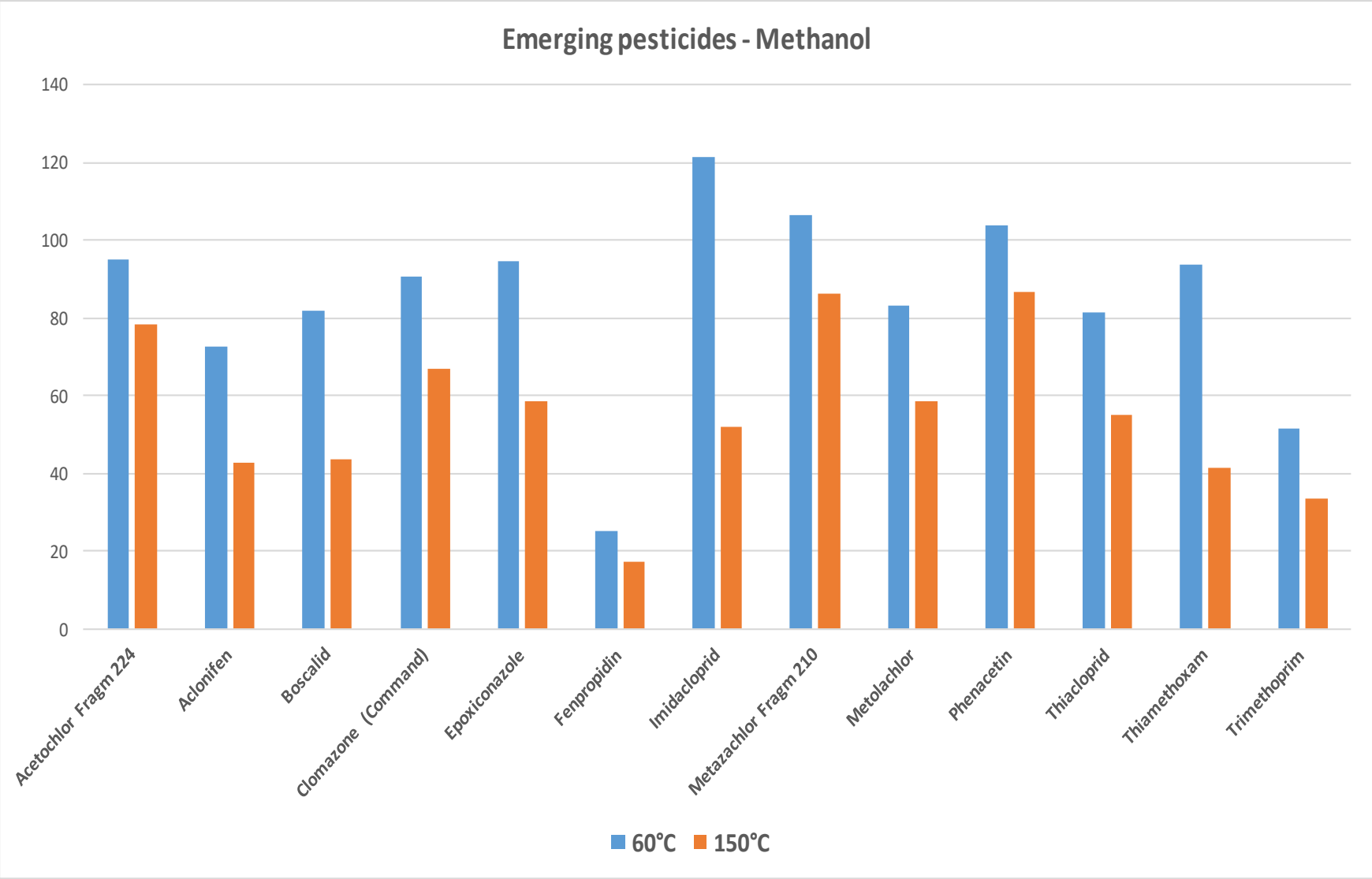
EMERGING PESTICIDES RECOVERY - ACETONE



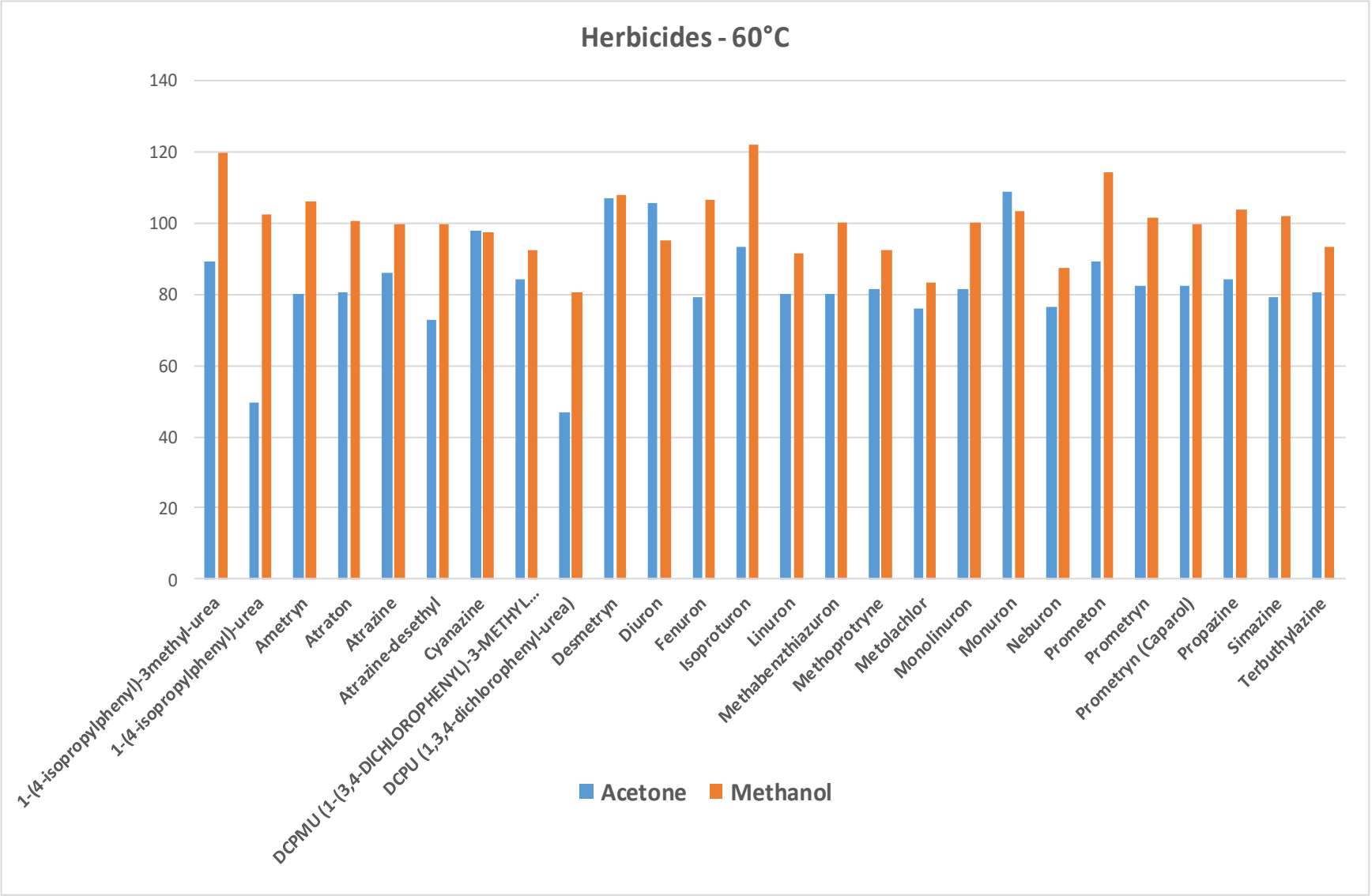
HERBICIDES RECOVERY - METHANOL



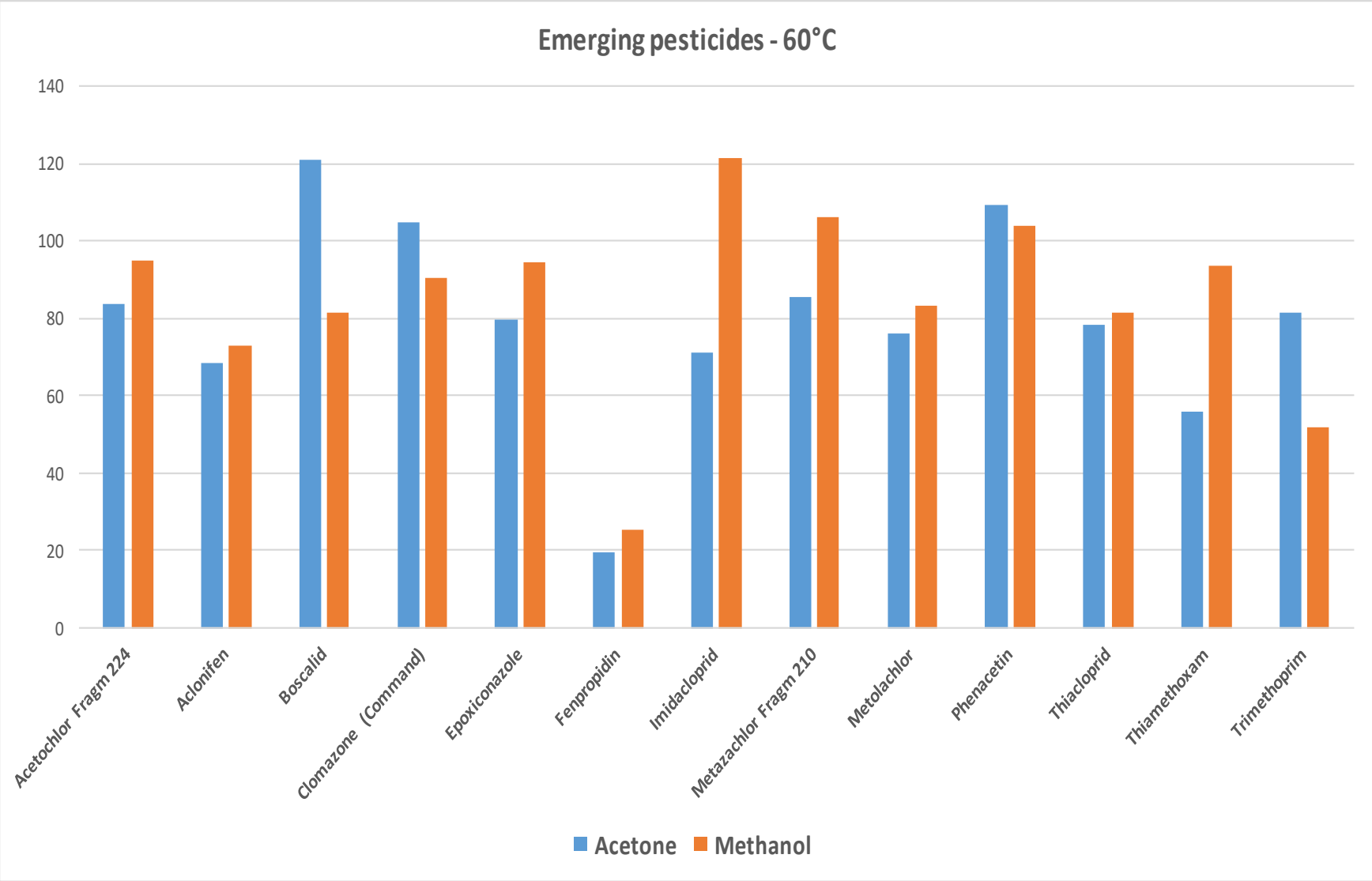
EMERGING PESTICIDES RECOVERY - METHANOL



HERBICIDES RECOVERY – 60°C



EMERGING PESTICIDES RECOVERY – 60°C



OPTIMIZATION OF EXTRACTION T°C

- 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

- 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

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.

Giovanni CARIA. INRAE - Laboratoire d'analyses des sols. Arras
Nicolas PROIX. INRAE - Laboratoire d'analyses des sols. Arras
Christian MOUGIN. INRAE - UMR Ecosys. Versailles / Paris-Saclay
Baghdad OUDDANE. CNRS UMR 8516 - LASIRE. Lille
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