Joint Monitoring Program of Pesticide Residues in Honey

Part B: SRM

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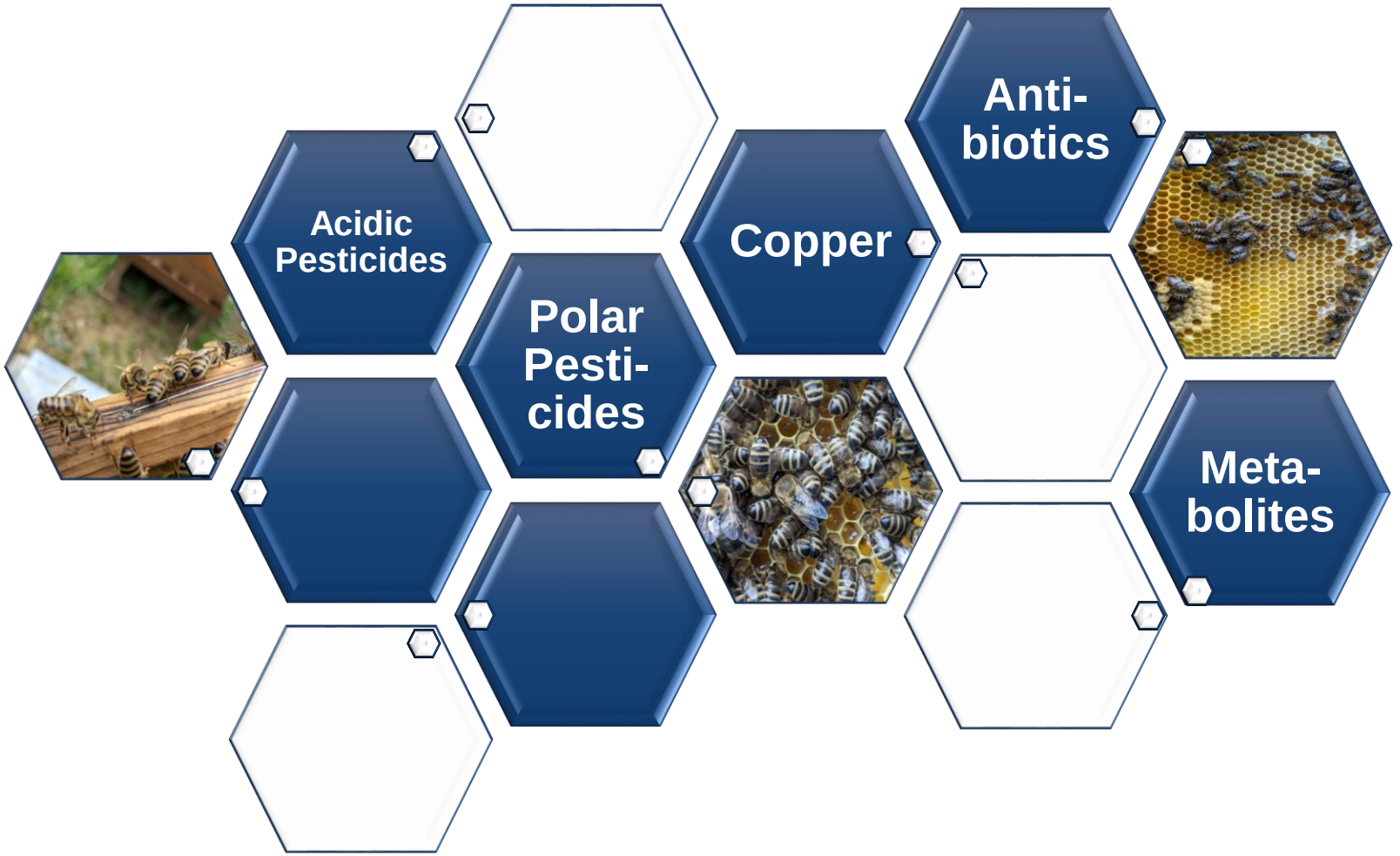
SRM compounds in Honey

MRM

SRM

own picture

SRM Compounds in Honey



own pictures

SRM Compounds in Honey

Polar Pesticides

- ☐ Glyphosate
- ☐ Matrine/Oxymatrine
- ☐ Phosphonic acid
- ☐ Perchlorate
- ☐ Mepiquat
- ☐ Nicotine
- ☐ …

Antibiotics

- ☐ Streptomycin
- ☐ Tetracyclin
- ☐ Enrofloxacin

Acidic Pesticides

- ☐ 2,4-D
- ☐ Haloxyfop
- ☐ Fluazifop

Metabolites

- ☐ 3-phenoxybenzaldehyde
- ☐ 3-phenoxybenzoic acid
- ☐ TCPy

Elements

- ☐ Copper

SRM Compounds in Honey

QuPPe

Polar Pesticides

- Glyphosate
- Matrine/Oxymatrine
- Phosphonic acid
- Perchlorate
- Mepiquat
- Nicotine
- …

Antibiotics

- Streptomycin
- Tetracyclin
- Enrofloxacin

QuEChERS

Acidic Pesticides

- 2,4-D
- Haloxyfop
- Fluazifop

Metabolites

- 3-phenoxybonzaldehyde
- 3-phenoxybenzoic acid
- TCPy

Elemtal analysis

Elements

- Copper

(LC-MS/)MS Measurement

Polar Pesticides

- GPC/Hypercarb:
  ESI negative
- HILIC:
  ESI negative (2)
  ESI positive (2)

Antibiotics

- HILIC
- C18

Acidic Pesticides

- C18:
  ESI negative

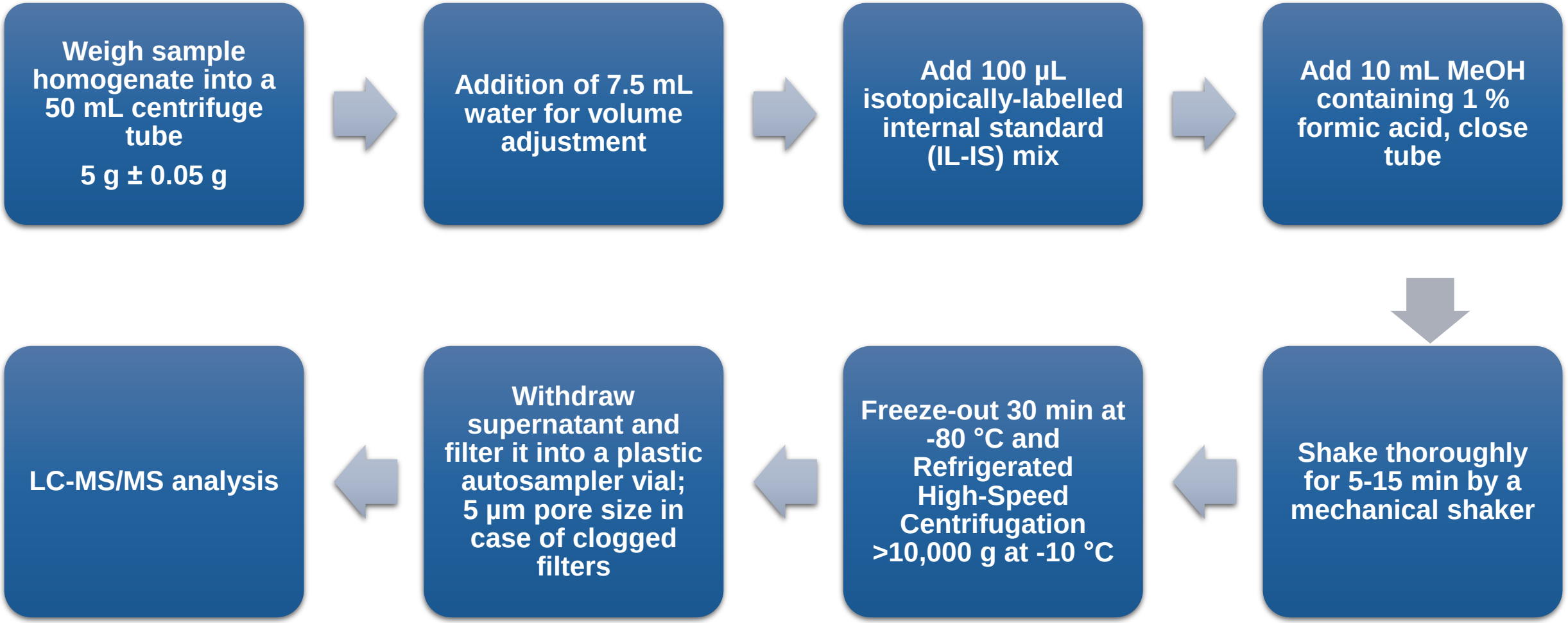
Metabolites

- C18 LC-MS/MS and ToF:
  ESI negative
  ESI positive

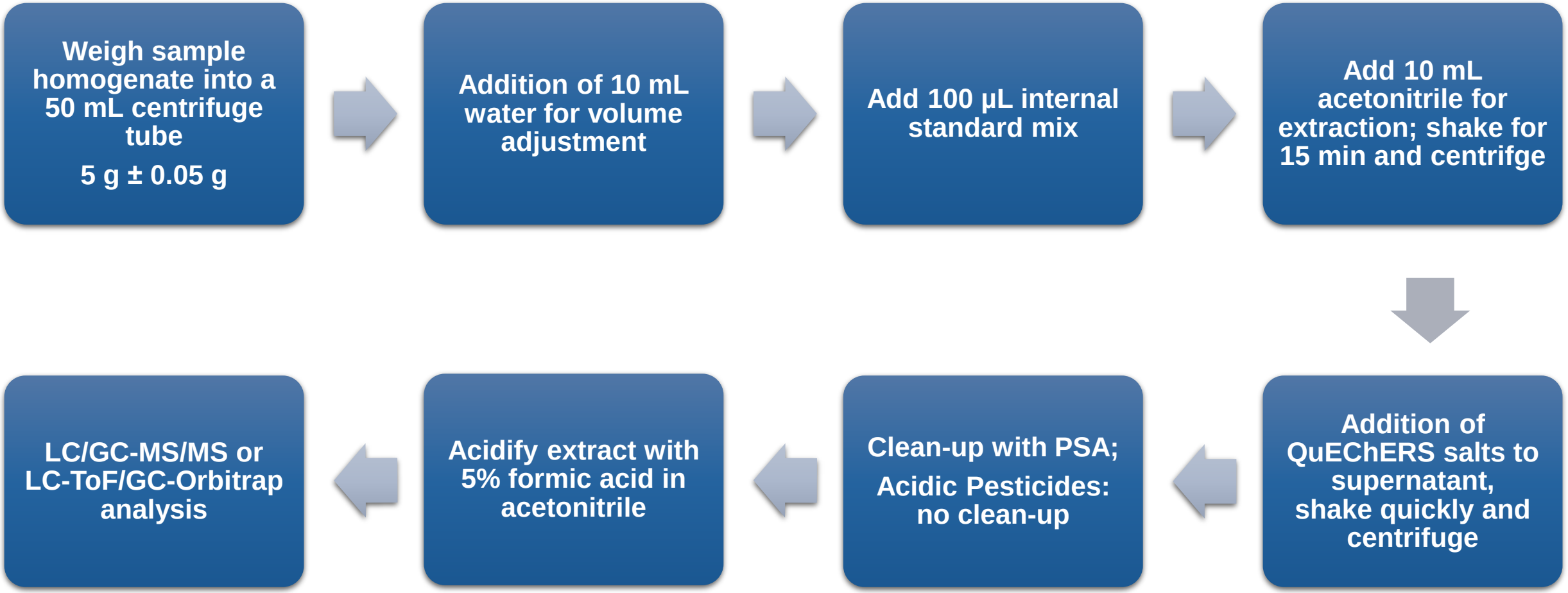
Elements

- ICP-MS

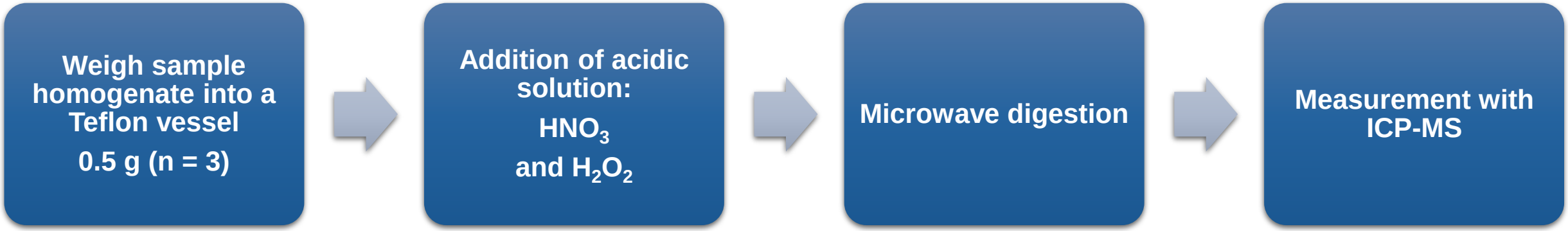
Extraction: QuPPe for Honey



Extraction: QuEChERS for Honey



Sample preparation for ICP-MS



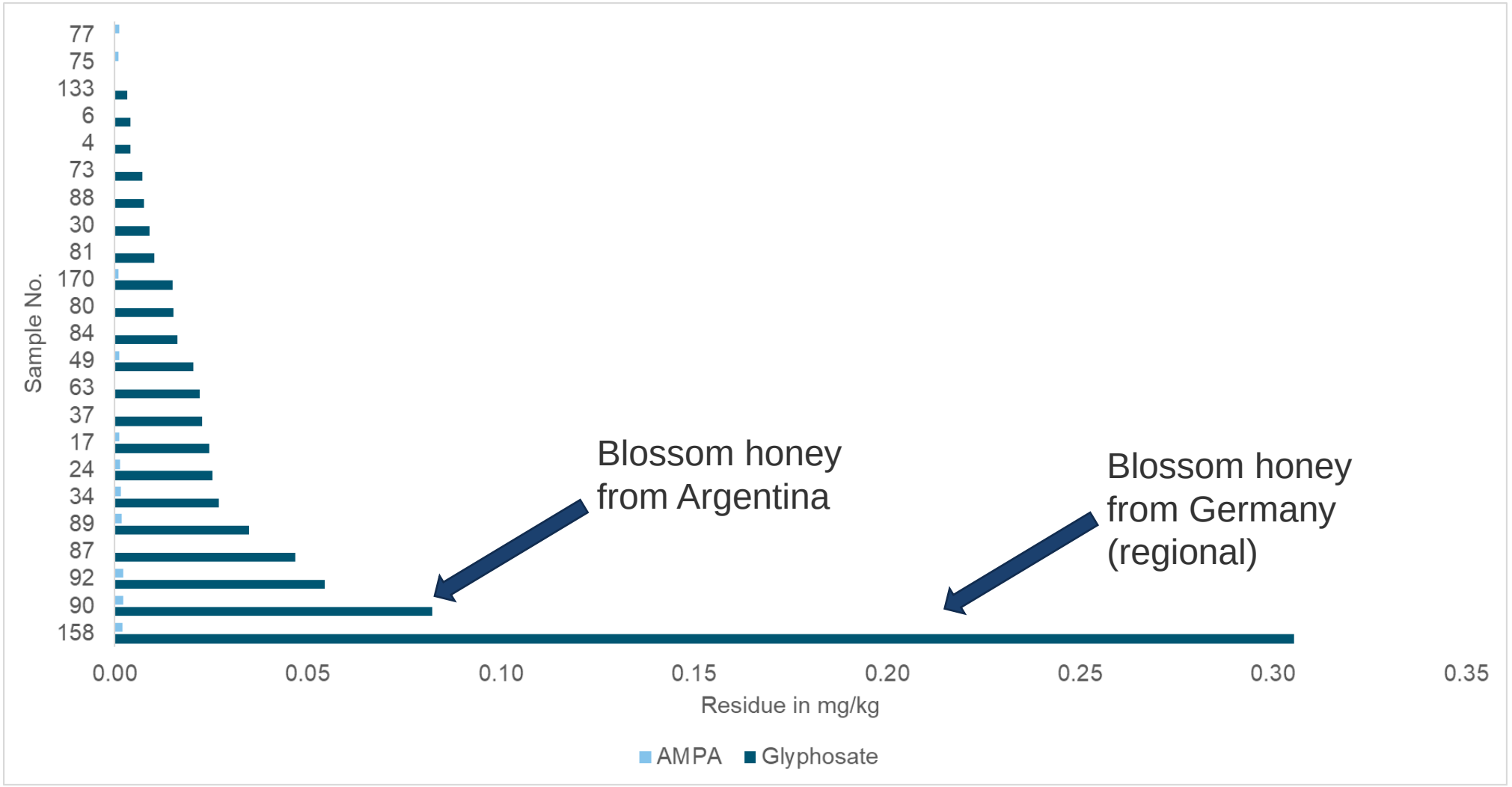
Results

Polar Pesticides and Metabolites ESI negative Pt. 1/4

	Glyphosate	AMPA	Fosetyl	HEPA
Number of findings (in % of all)	21 **(13 %)** (9 EU, 11 non EU)	11 **(7 %)**	5 **(3 %)**	7 **(4 %)** (3 CR, 2 MX, 1 MX/NC 1 BR)
Number of findings > LSVL (in % of all)	11 **(7 % of all)**	0	1 **(0.6 %of all)**	7 **(4 % of all)**
LSVL in mg/kg	0.02	0.005	0.02	0.02
Median > LSVL in mg/kg	0.027	-	-	0.108
Maximum result in mg/kg	0.31 (DE)	-	0.02 (IT)	0.51 (CR)
MRL in mg/kg	0.05	-	0.5	-
Number > MRL	**2**	-	0	**-**

Additionally analyzed compounds, but with no results (LSVLs in mg/kg):
Ammeline (0.02), ethephon (0.02), glufosinate (0.02), MPPA (0.02), N-acetyl-glufosinate (0.02), N-acetyl-glyphosate (0.02), maleic hydrazide (0.02), diethyl phosphate (0.01), dimethyl thiophosphate (0.01), diethyl thiophosphate (0.01), diethyl dithiophosphate (0.01), dimethyl dithiophosphate (0.01)

Correlation between glyphosate and AMPA findings



Polar Pesticides and Metabolites ESI negative Pt. 2/4

	Dimethyl phosphate	Dimethoat-O-desmethyl	Ammelide
Number of findings (in % of all)	3 **(2 %)**	5 **(3 %)**	17 **(11 %)**
Number of findings > LSVL (in % of all)	2 **(1 % of all)**	0	2 **(1 % of all)**
LSVL in mg/kg	0.01	0.005	0.02
Median > LSVL in mg/kg	0.041	-	0.023
Maximum result in mg/kg	0.07 (MX)	-	0.023 (PT)
MRL in mg/kg	-	-	-
Number > MRL	-	-	-

Additionally analyzed compounds, but with no results (LSVLs in mg/kg):
Ammeline (0.02), ethephon (0.02), glufosinate (0.02), MPPA (0.02), N-acetyl-glufosinate (0.02), N-acetyl-glyphosate (0.02), maleic hydrazide (0.02), diethyl phosphate (0.01), dimethyl thiophosphate (0.01), diethyl thiophosphate (0.01), diethyl dithiophosphate (0.01), dimethyl dithiophosphate (0.01)

Polar Pesticides and Metabolites ESI negative Pt. 3/4 - ***Frequently detected***

	Chlorate	Perchlorate	Phosphonic acid
Number of findings (in % of all)	77 **(41 %)** (41 EU, 7 blend, 29 non EU)	149 (**93 %**) (71 EU, 10 blend, 68 non EU)	161 (**100 %**)
Number of findings > LSVL (in % of all)	8 **(5% of all)**	80 **(50% of all)**	12 **(7% of all)**
LSVL in mg/kg	0.01	0.001	0.05
Median > LSVL in mg/kg	0.017	0.003	0.146
Maximum result in mg/kg	0.07 (CN)	0.03 (CN)	1.6 (AU, Manuka)
Median of positives (incl. 'semiquantitatives')	0.003	0.003	0.010
MRL in mg/kg	0.05		0.5 (fosetyl)
> MRL	**1**		**1**

due to high background

Polar Pesticides and Metabolites ESI negative Pt. 4/4 - *Frequently detected*

	Bromide	Cyanuric acid	Trifluoroacetic acid
Number of findings (in % of all)	157 **(98 %)** (74 EU, 11 blend, 72 non EU)	147 **(91 %)** (76 EU, 11 blend, 60 non EU)	135 **(84 %)** (69 EU, 11 blend, 55 non EU)
Number of findings > LSVL (in % of all)	61 **(38 % of all)**	94 **(58 % of all)**	68 **(42 % of all)**
LSVL in mg/kg	0.05	0.02	0.05
Median > LSVL in mg/kg	0.452	0.036	0.100
Maximum result in mg/kg	2.8 (BR)	0.23 (MX)	0.76 (MX)
Median of positives (incl. 'semiquantitatives')	0.414	0.036	0.063
MRL in mg/kg	**0.05**	-	-
Number > MRL	**142**	-	-

Polar Pesticides ESI positive Pt. 1/3

	Melamine	Nicotine	Trimesium
Number of findings (in % of all)	60 **(37 %)** (36 EU, 6 blend, 18 non EU)	**37 (23 %)** (15 EU, 2 blend, 20 non EU)	16 **(10 %)** (8 EU, 2 blend, 6 non EU)
Number of findings > LSVL (in % of all)	28 **(17% of all)**	2 **(1% of all)**	1 **(0.6% of all)**
LSVL in mg/kg	0.005	0.01	0.002
Median > LSVL in mg/kg	0.015	0.015	-
Maximum result in mg/kg	0.11 (ES)	0.020 (IN)	0.004 (MX)
MRL in mg/kg	-	0.05	-
Number > MRL	-	-	-

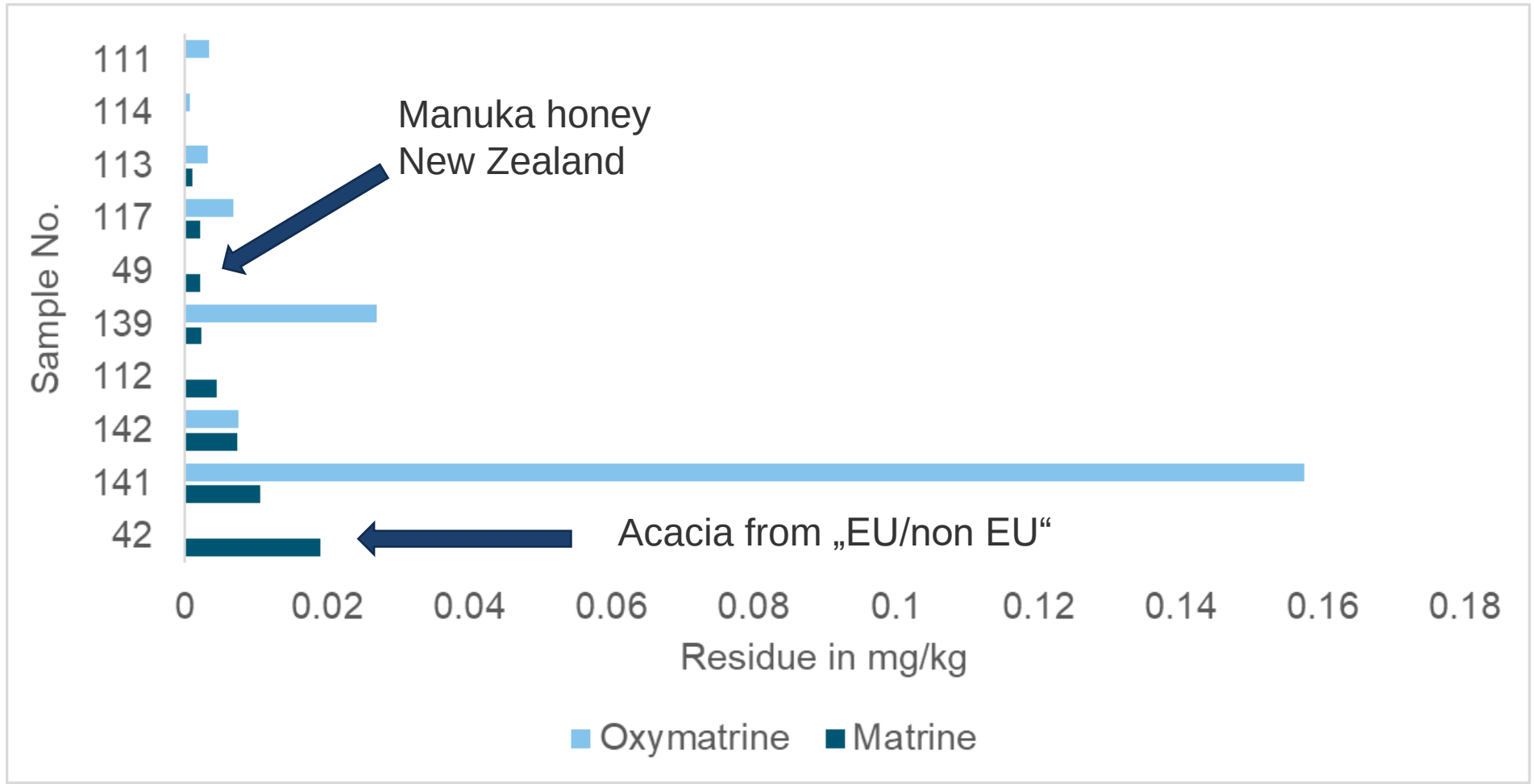
Additionally analyzed compounds, but with no results (LSVLs in mg/kg):
Aminocyclopyrachlor (0.05), amitrole (0.02), cyromazine (0.02), ETU (0.05), PTU (0.05), triazole alanine (0.05), difenzoquat (0.02), mepiquat-OH (0.02), nereistoxin (0.02), propamocarb (0.02), propamocarb-N-desmethyl (0.02), propamocarb-N-oxide (0.02), ametoctradin-metabolite M650F04 (0.02 est. LOQ), AHMP (0.02 est. LOQ)

Polar Pesticides ESI positive Pt. 2/3

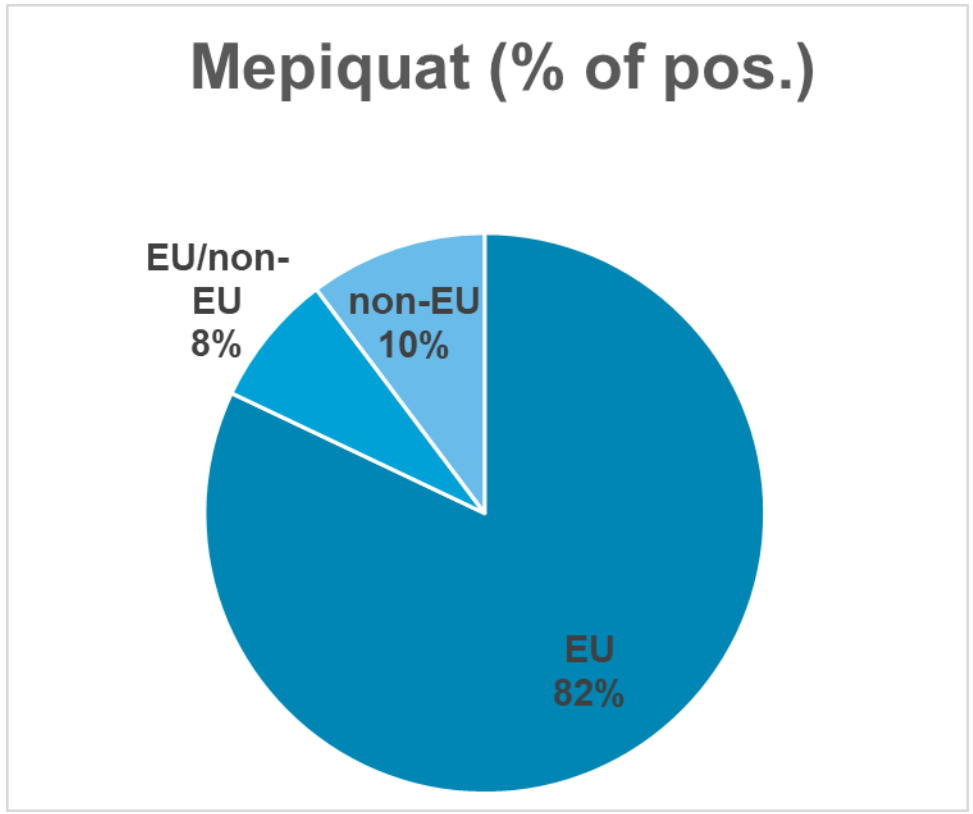
	Matrine	Oxymatrine	Mepiquat	Chlormequat
Number of findings (in % of all)	8 **(5 %)** (6 CN, 1 NZ, 1 unknown)	7 **(4 %)** (all CN)	39 **(24 %)** (32 EU, 3 blend, 4 non EU)	3 **(2 %)**
Number of findings > LSVL (in % of all)	3 **(2 % of all)**	4 **(3 % of all)**	8 **(5 % of all)**	3 **(2 % of all)**
LSVL in mg/kg	0.005	0.005	0.002	0.002
Median > LSVL in mg/kg	0.011	0.017	0.005	0.002
Maximum result in mg/kg	0.019 (EU/non EU)	0.16 (CN)	0.007 (IT, AU)	0.005 (HU)
MRL in mg/kg	0.01 (default)	0.01 (default)	0.05	0.05
Number > MRL	**2**	**2**	-	-

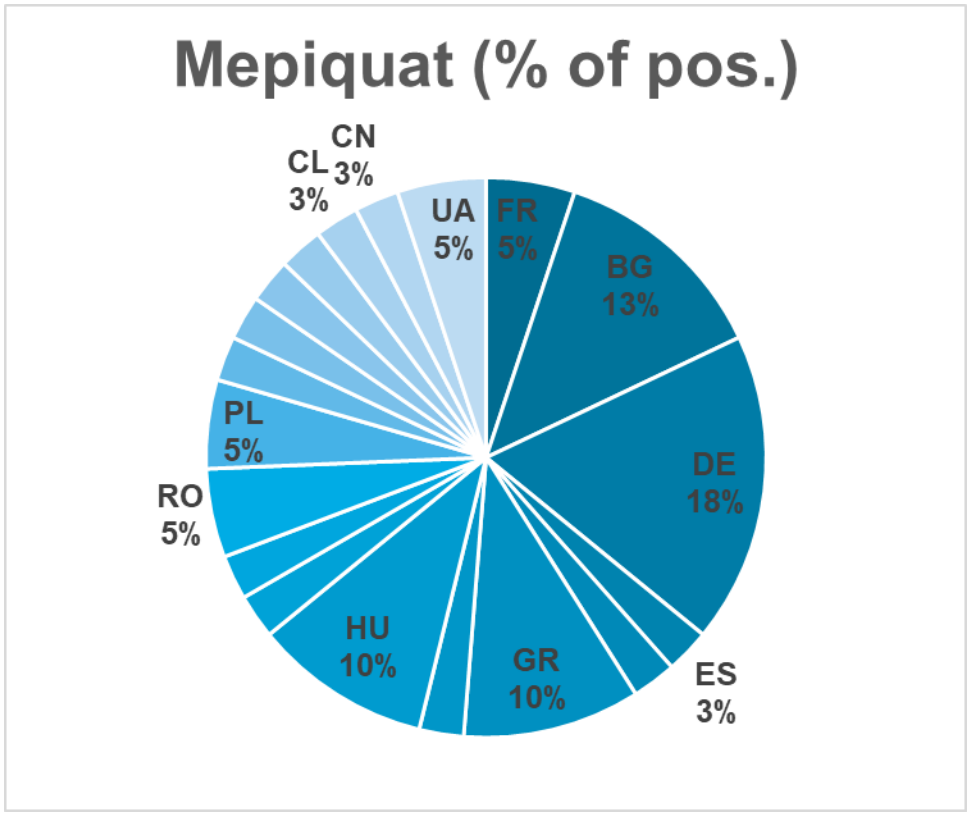
Additionally analyzed compounds, but with no results (LSVLs in mg/kg):
Aminocyclopyrachlor (0.05), amitrole (0.02), cyromazine (0.02), ETU (0.05), PTU (0.05), triazole alanine (0.05), difenzoquat (0.02), mepiquat-OH (0.02), nereistoxin (0.02), propamocarb (0.02), propamocarb-N-desmethyl (0.02), propamocarb-N-oxide (0.02), ametoctradin-metabolite M650F04 (0.02 est. LOQ), AHMP (0.02 est. LOQ)

Correlation between matrine and oxymatrine findings



Polar Pesticides ESI positive – *Details on Origin of Mepiquat results*





Polar Pesticides ESI positive Pt. 3/3

	Triazole acetic acid	Triazole lactic acid	Morpholine	Daminozide
Number of findings (in % of all)	18 **(11 %)** (12 EU, 6 non EU)	1 **(0.6 %)**	1 **(0.6 %)**	1 **(0.6 %)**
Number of findings > LSVL (in % of all)	4 **(3 % of all)**	0	1 **(0.6 % of all)**	0
LSVL in mg/kg	0.02	0.02	0.02	0.02
Median > LSVL in mg/kg	0.023	-	-	-
Maximum result in mg/kg	0.029 (HU)	-	0.02 (IN, VN)	-
MRL in mg/kg	-	-	-	0.06
Number > MRL	-	-	-	0

Additionally analyzed compounds, but with no results (LSVLs in mg/kg):
Aminocyclopyrachlor (0.05), amitrole (0.02), cyromazine (0.02), ETU (0.05), PTU (0.05), triazole alanine (0.05), difenzoquat (0.02), mepiquat-OH (0.02), nereistoxin (0.02), propamocarb (0.02), propamocarb-N-desmethyl (0.02), propamocarb-N-oxide (0.02), ametoctradin-metabolite M650F04 (0.02 est. LOQ), AHMP (0.02 est. LOQ)

Antibiotics (ESI positive) Pt. 1/2

	Ciprofloxacin* (C18 phase)	Enrofloxacin* (C18 phase)	Tetracycline (C18 phase)	epi-Tetracycline (C18 phase)	Flumequin* (C18 phase)
Number of findings (in % of all)	4 **(5%)** (all non EU)	1 **(1 %)**	4 **(3 %)**	3 **(2 %)**	1 **(0.6 %)**
Number of findings > est. LOQ (in % of all)	3 **(4 % of all)**	1 **(1 % of all)**	1 **(0.6 % of all)**	1 **(0.6 % of all)**	1 **(1 % of all)**
est. LOQ in mg/kg	0.001	0.002	0.01	0.005	0.001
Median > est. LOQ in mg/kg	0.011	-	-	-	-
Maximum result in mg/kg	0.017 (IR)	2.5 (IR)	0.02 (BG)	0.005 (BG)	0.004 (IR)

*in 81 samples, measured in 2023

Additionally analyzed compounds, but with no results (est. LOQs in mg/kg):
Ampicillin (0.004 est), epi-oxytetracylclin (0.02 est), oxytetracyclin (0.002 est), kasugamycin (0.05 est), norfloxacin (0.004 est), oxolinic acid (0.002 est), roxythromycin (0.001 est), sarafloxacin (0.004 est), spectinomycin (0.05 est), tylosin (0.01 est), validamycin (0.02 est)

Antibiotics (ESI positive) Pt. 2/2

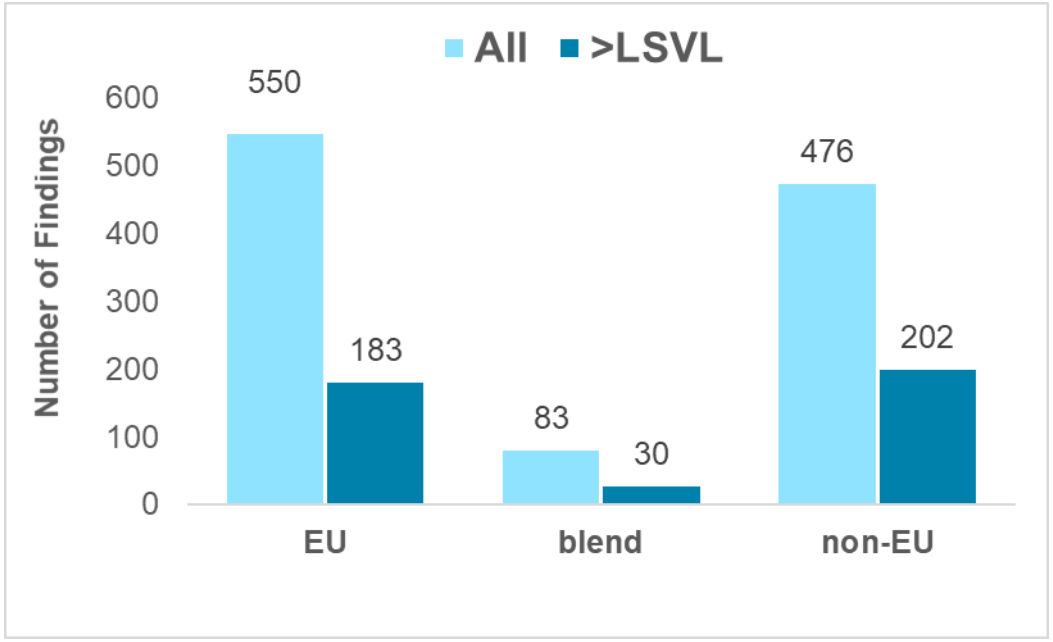
	Streptomycin (HILIC)	Dihydrostreptomycin (HILIC)
Number of findings (in % of all)	1 **(0.6 %)**	9 **(6 %)**
Number of findings > est. LOQ (in % of all)	0	8 **(5 % of all)**
est. LOQ in mg/kg	0.008	0.004
Median > est. LOQ in mg/kg	-	0.016
Maximum result in mg/kg	0.005 semi-quantitative (IR)	0.63 (IR)

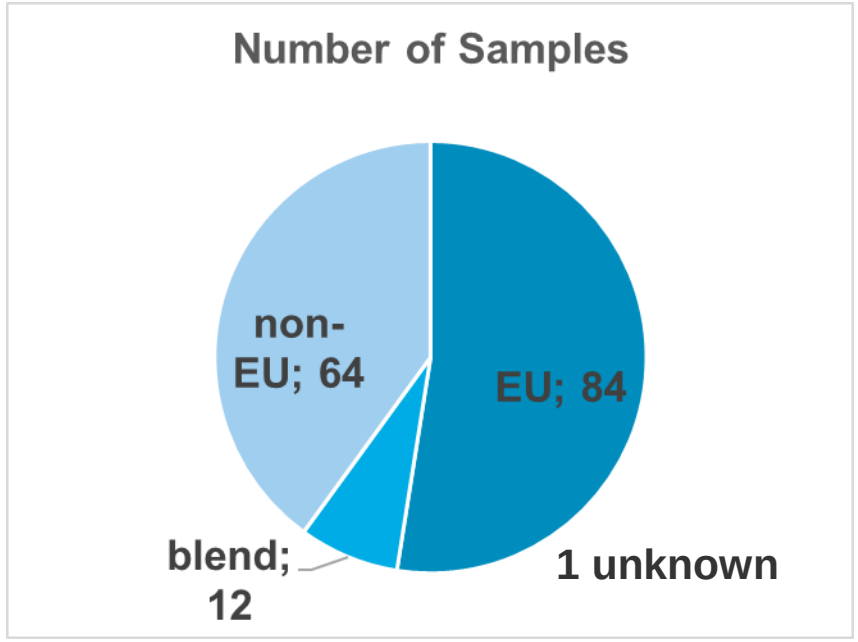
Additionally analyzed compounds, but with no results (est. LOQs in mg/kg):
Ampicillin (0.004 est), epi-oxytetracylclin (0.02 est), oxytetracyclin (0.002 est), kasugamycin (0.05 est), norfloxacin (0.004 est), oxolinic acid (0.002 est), roxythromycin (0.001 est), sarafloxacin (0.004 est), spectinomycin (0.05 est), tylosin (0.01 est), validamycin (0.02 est)

Polar Pesticides – Samples with multiple residues

	# 5	# 92	# 112	# 6	# 9	# 75	# 83	# 133	# 157
Number of findings	**12**	**12**	**11**	**10**	**10**	**10**	**10**	**10**	**10**
Type	Honeydew Honey	un-known	unknown	Blossom	Blossom	Blossom	Honeydew Honey	unknown	Blossom
Origin	**BG**	**BR**	**CN**	**GR**	**TR**	**GR**	**ES**	**HU**	**DE**
Compounds:	**Findings of frequently detected compounds excluded: Chlorate, perchlorate, bromide, cyanuric acid, phosphonic acid, TFA.**								
Mepiquat	✓			✓		✓		✓	✓
Trimesium	✓						✓		✓
Melamine	✓	✓	✓	✓		✓	✓	✓	
Nicotine		✓	✓	✓	✓	✓	✓		✓
Matrine			✓						
ABs	✓ (3 diff.comp.)		✓ (2 diff.comp.)		✓ (2 diff.comp.)				
Glyphosate		✓		✓				✓	
AMPA		✓				✓			
Other		2						1	1

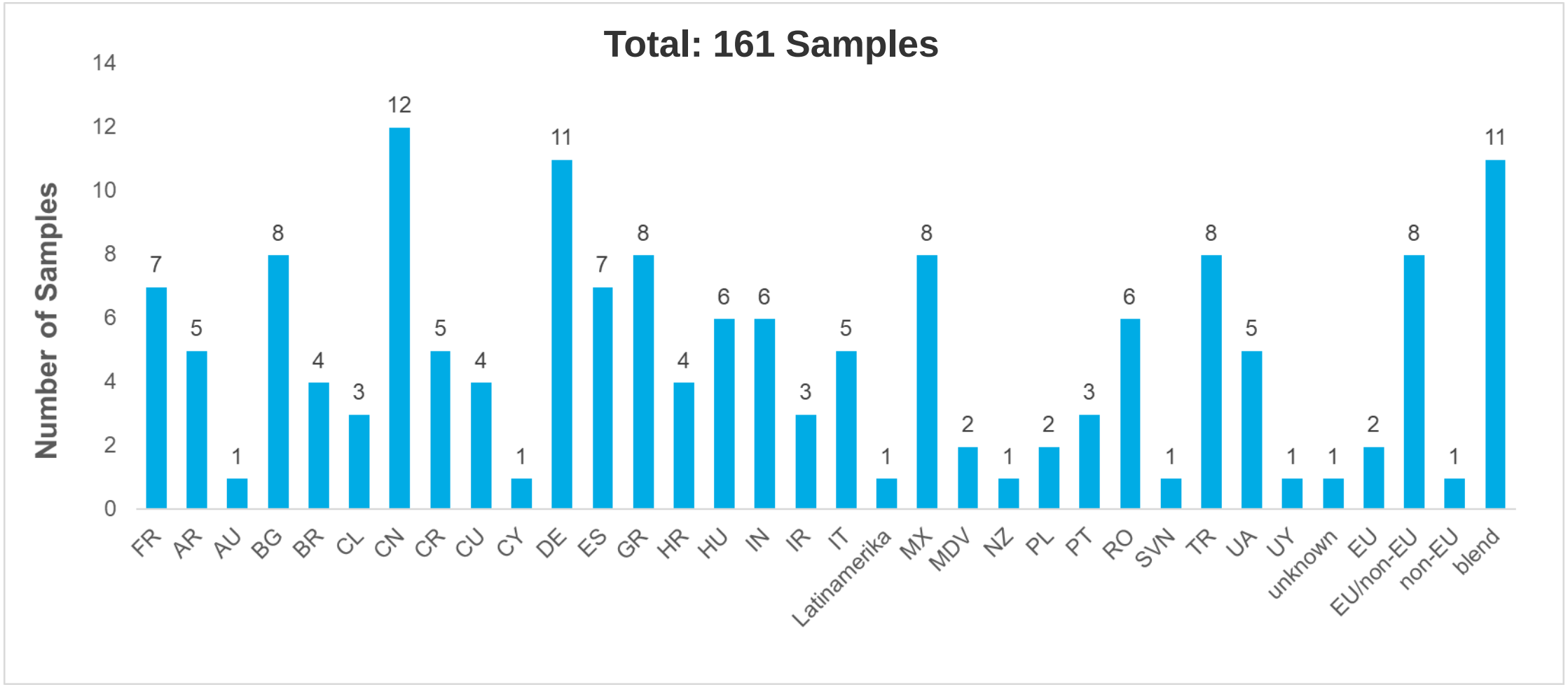
Polar Pesticides: Origin – Most and least findings Pt. 1/2



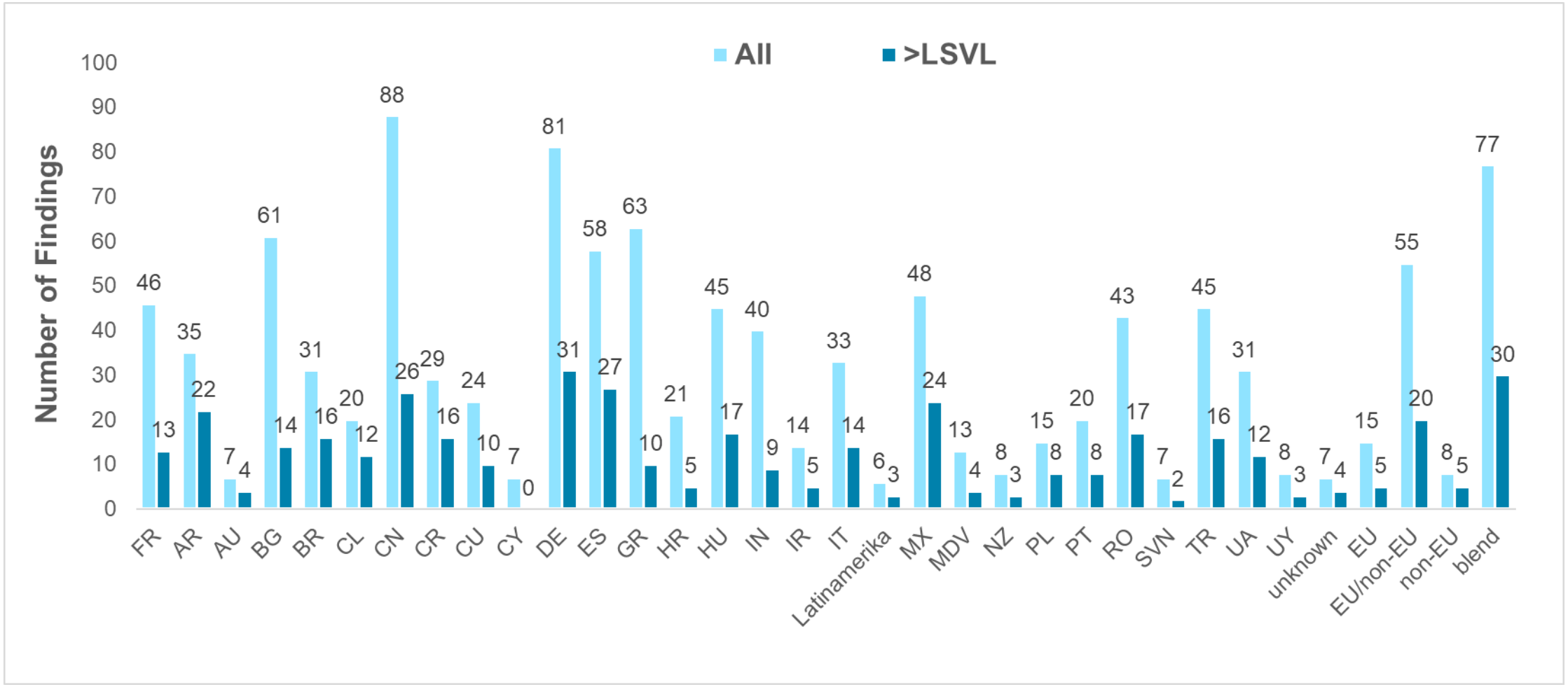


Total: 161 Samples

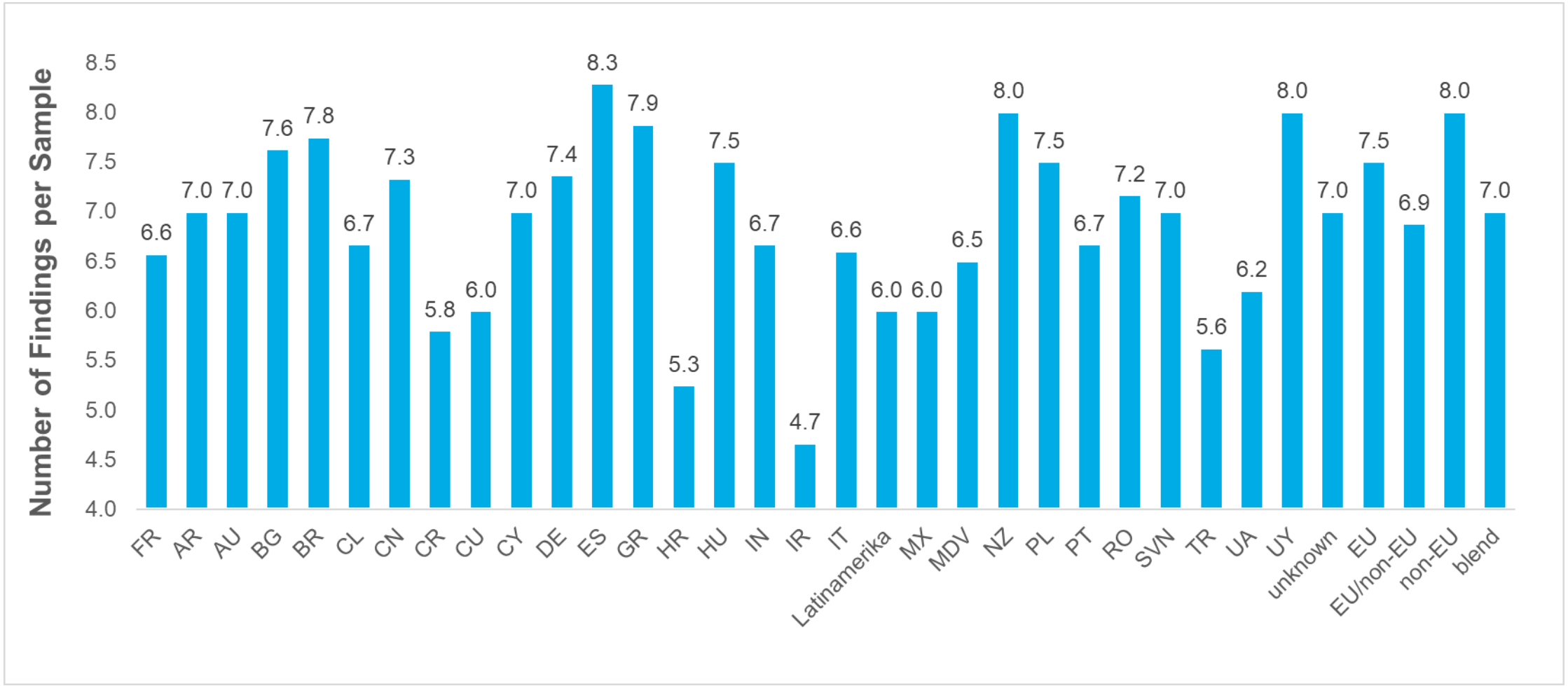
Polar Pesticides: Origin – Most and least findings Pt. 2/2



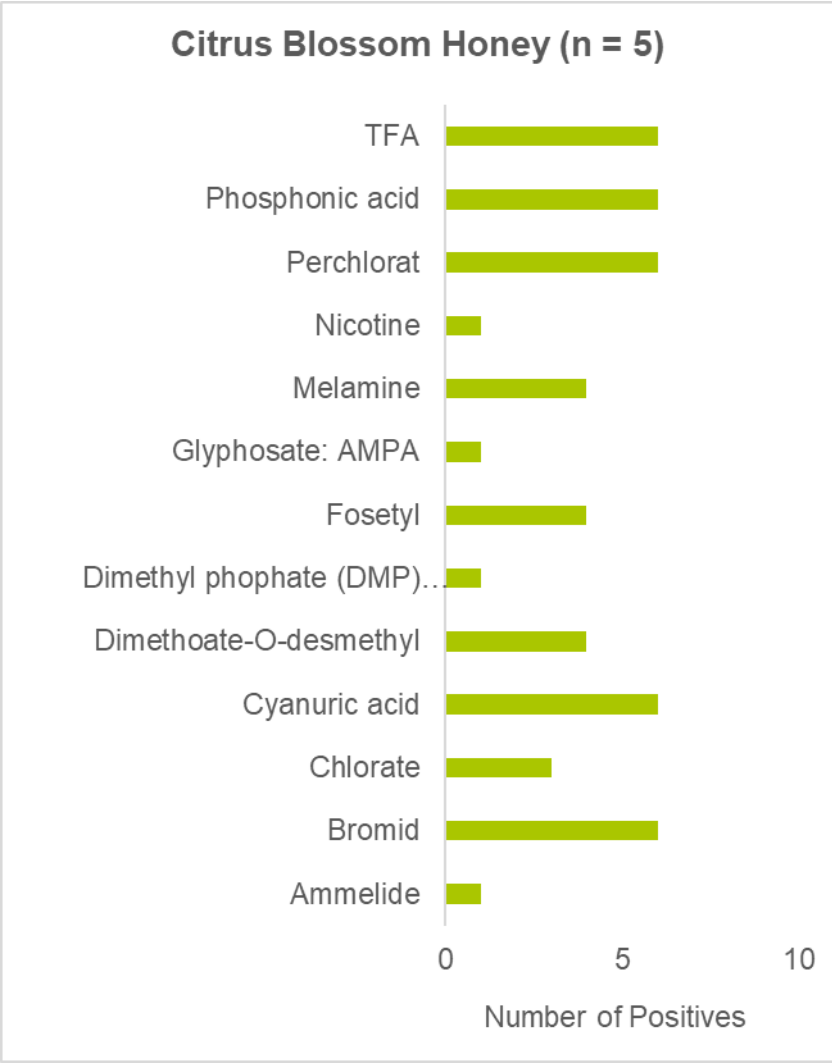
Polar Pesticides: Origin – Most and least findings Pt. 2/2

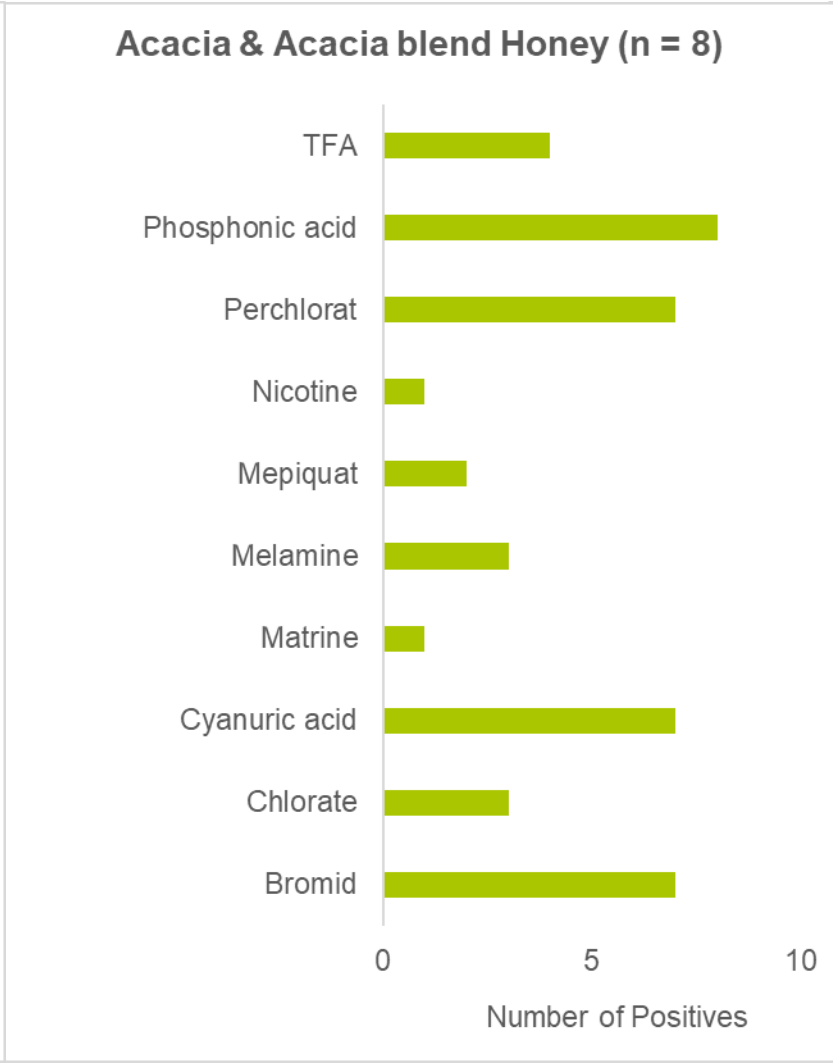


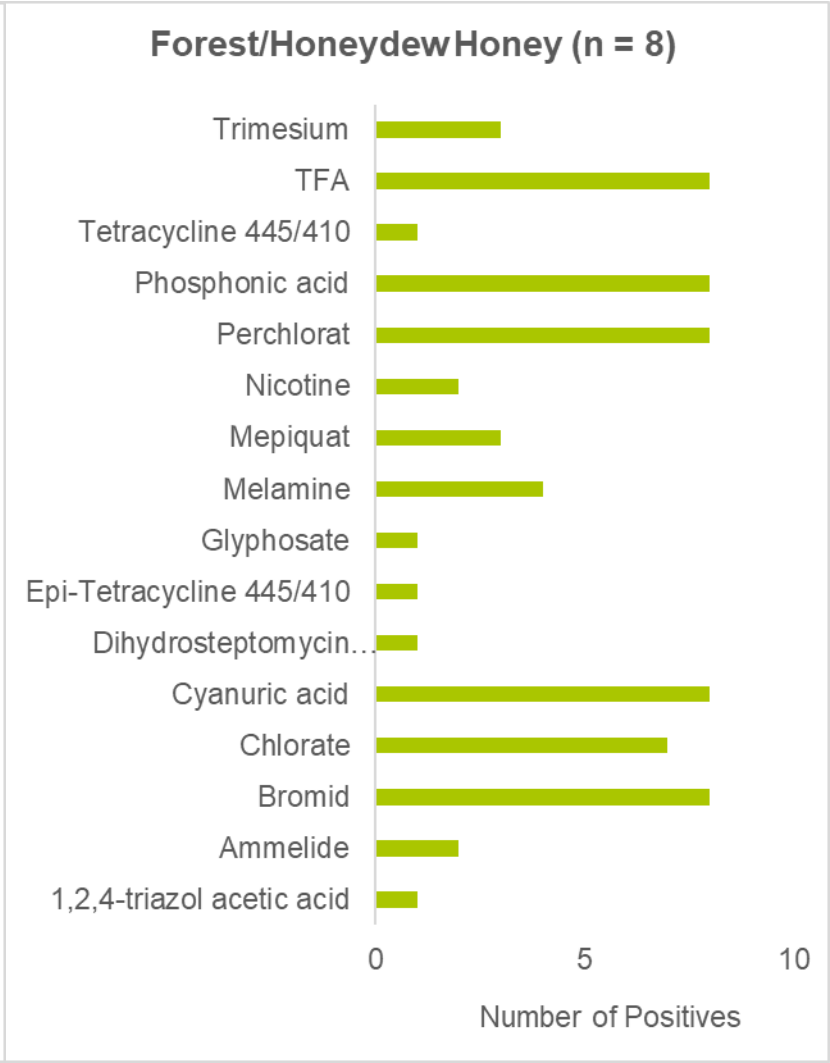
Polar Pesticides: Origin – Most and least findings Pt. 2/2



Polar Pesticides: Type – Findings



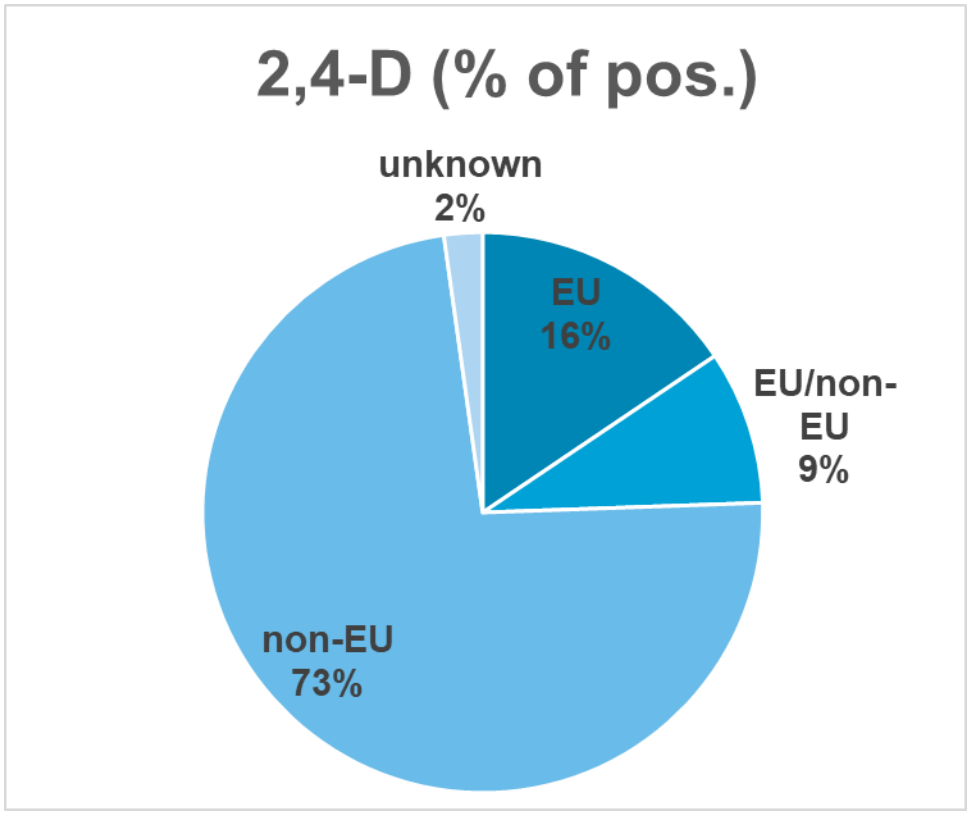


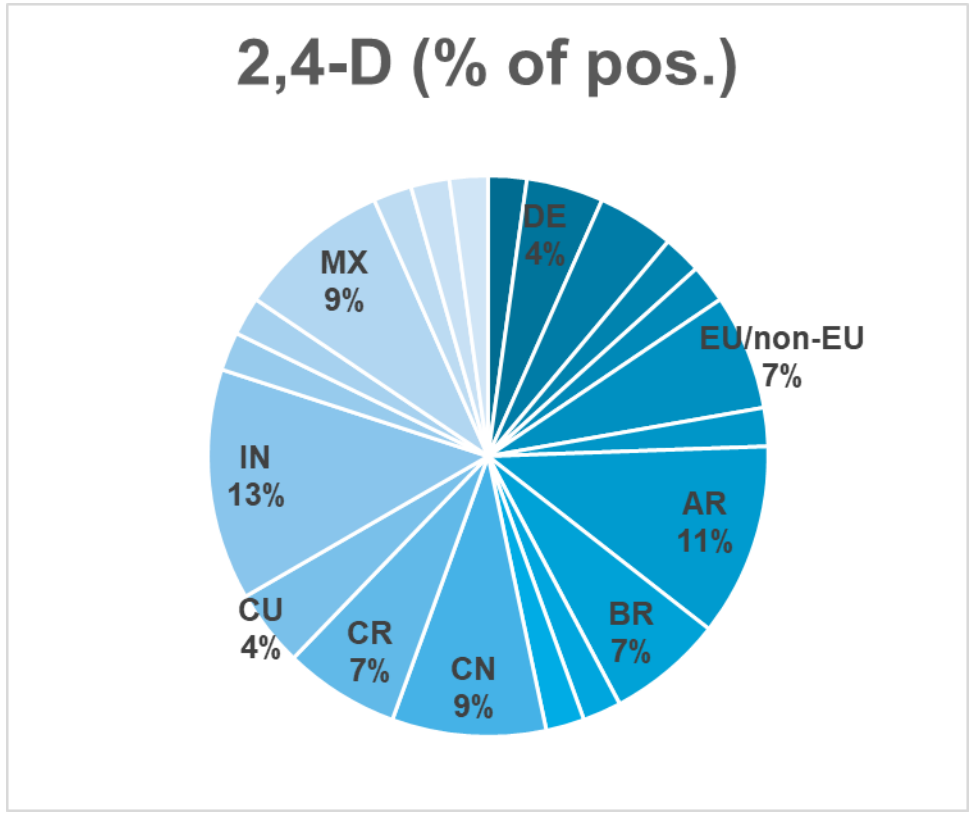


Acidic Pesticides Pt. 1/2

	2,4-D	4-Chlorobenzoic acid	Fluazifop	Haloxyfop	MCPA
Number of findings (in % of all)	45 (28 %)	17 (11 %)	16 (10 %)	2 (1 %)	4 (5 %)
Number of findings > LSVL (in % of all)	13 **(8 % of all)**	0	4 **(3 % of all)**	0	0
LSVL in mg/kg	0.002	0.002	0.002	0.002	0.002
Median > LSVL in mg/kg	0.003	-	0.003	-	-
Maximum result in mg/kg	0.01 (IN)	0.001 semiquantitative (IN)	0.007 (RO)	0.001 semiquantitative (CN)	0.002 semiquantitative (DE)
MRL in mg/kg	0.05	-	0.05	0.05	-
Number > MRL	0	-	0	0	-

Acidic Pesticides – *Details on Origin of 2,4-D results*





Acidic Pesticides Pt. 2/2

	Imazapyr	Pentachloro-phenol	Quizalofop	Trinexapac
Number of findings (in % of all)	1 **(0.6 %)**	2 **(1 %)**	1 **(0.6 %)**	1 **(0.6 %)**
Number of findings > LSVL (in % of all)	0	1 **(0.6 % of all)**	0	1 **(0.6 % of all)**
LSVL in mg/kg	0.005	0.002	0.002	0.002
Median > LSVL in mg/kg	-	-	-	-
Maximum result in mg/kg	0.001 semiquantitative (AR)	0.002 semiquantitative (FR)	traces	0.013 (CR)
MRL in mg/kg	0.05	-	0.05	0.05
Number > MRL	0	-	0	0

Other compounds

	Thymol	DEET	BAC-C14	DDAC-C10
Number of findings (in % of all)	13 **(8 %)**	19 **(12 %)**	1 **(0.6 %)**	3 **(2 %)**
Number of findings > LSVL (in % of all)	13 **(8 % of all)**	0	1 **(0.6 % of all)**	2 **(1 % of all)**
LSVL in mg/kg	0.005	0.002	0.01	0.01
Median > LSVL in mg/kg	0.024	-	-	-
Maximum result in mg/kg	0.12 (CR)	traces	0.01 (IN, VN)	0.02 (ES, GR)
MRL in mg/kg	-	-	0.1	0.1
Number > MRL	-	-	0	0

Metabolites Pt. 1

	3-Phenoxy-benzaldehyde	3,5,6-Trichlor-2-pyridinol	Acetamiprid Metabolite: IM-2-1	Coumaphos alcohol	Coumaphos oxon	Fluvalinate anilino acid
Number of findings (in % of all)	1 **(0.6 %)**	2 **(1 %)**	8 **(5 %)**	2 **(1 %)**	2 **(1 %)**	7 **(4 %)**
Number of findings > LSVL (in % of all)	0	0	0	0	1 **(0.6 % of all)**	0
LSVL in mg/kg	0.001	0.002	0.002	0.005	0.002	0.01
Median > LSVL in mg/kg	-	-	-	-	-	-
Maximum result in mg/kg	traces	0.002 semi-quantitative (IT, MX)	traces	0.003 semi-quantitative (HR)	0.003 (HU)	0.005 semi-quantitative (EU/non-EU)

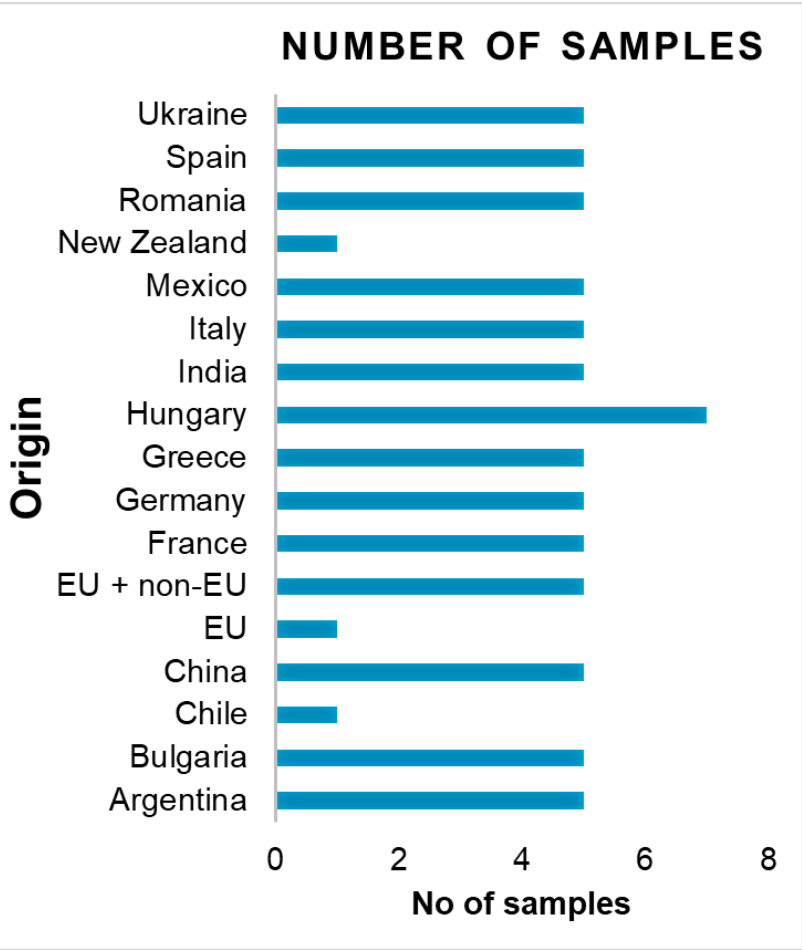
Additional Metabolites

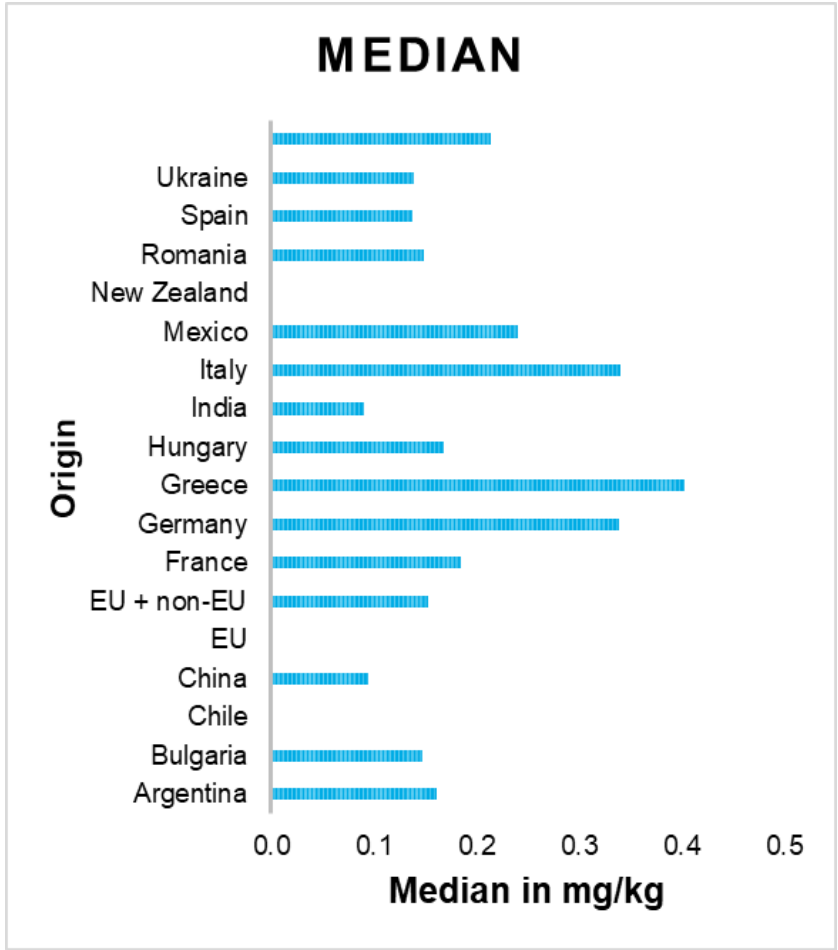
	6-Chloronicotinic acid*	3-Phenoxybenzoic acid*	Azoxystrobin: 2-Hydroxy-benzonitrile*	3-Chloro-5-(trifluoro-methyl) picolinic acid*
Number of findings qualitative/Screening (in % of all)	5 **(6 % of 81)**	3 **(4 % of 81)**	4 **(5 % of 81)**	2 **(3 % of 81)**
estimated LOQ in mg/kg	0.002	0.002	0.005	0.005
Maximum result in mg/kg	0.003 semiquantitative (IT, MX)	traces	0.008 semiquantitative (IT, MX)	traces

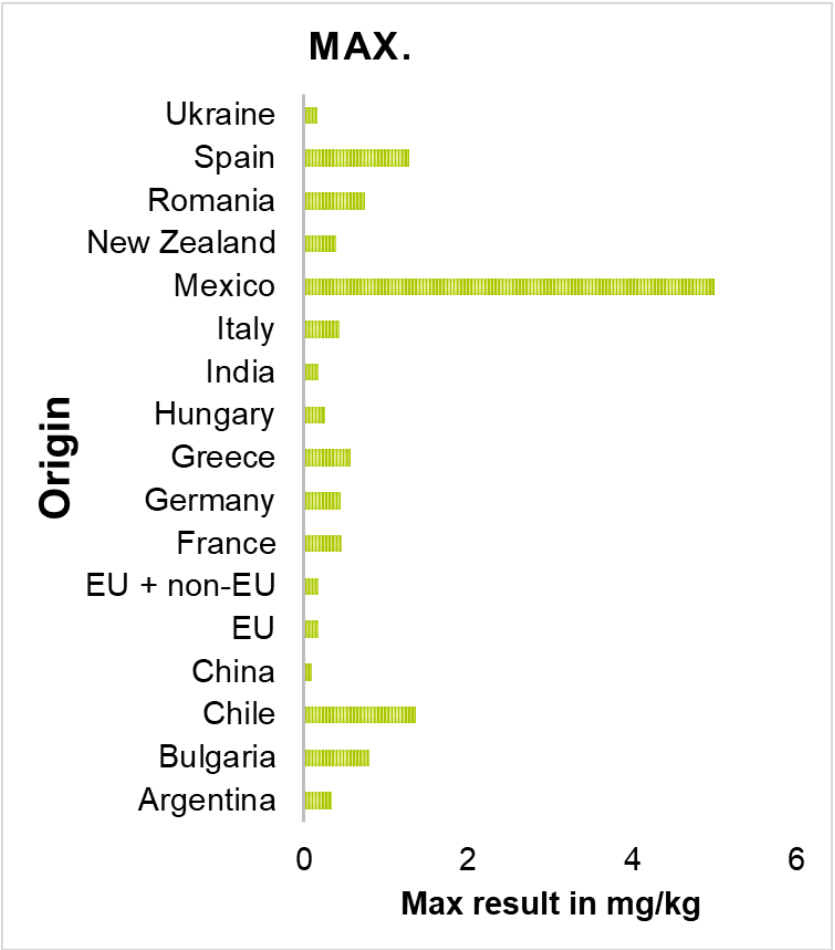
*in 81 samples, measured in 2023

Copper – Results Origin

LOQ: 0.08 mg/kg



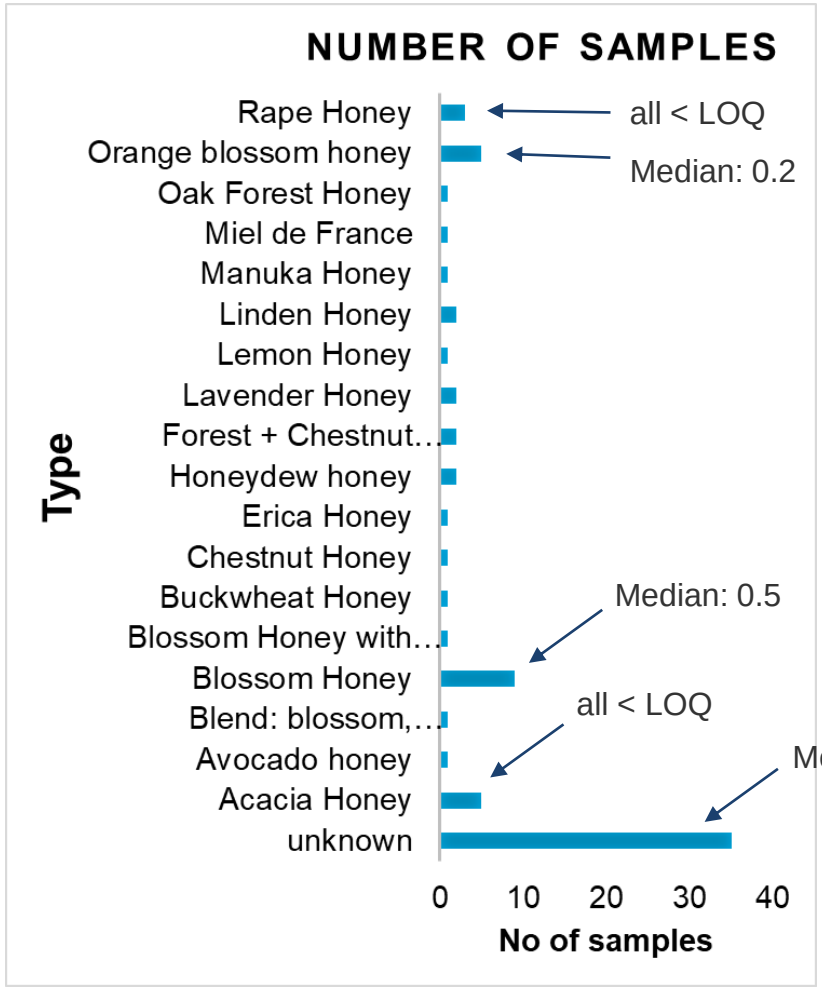


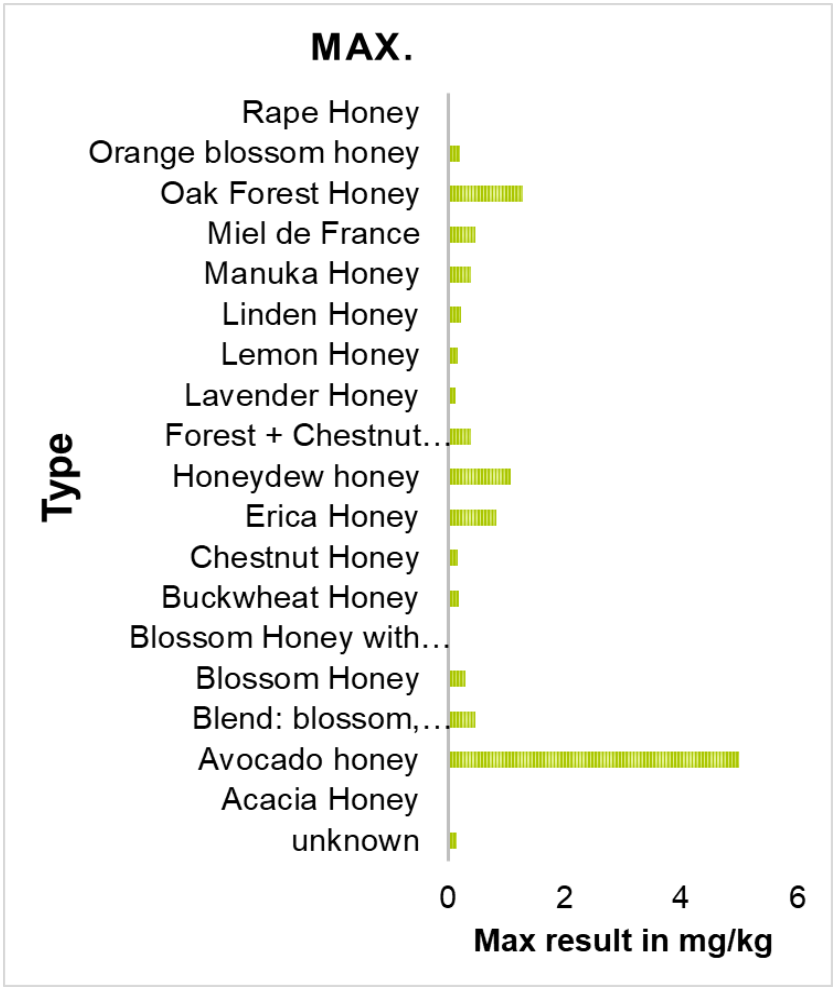


Total: 75 Samples

Copper – Results Type

LOQ: 0.08 mg/kg





Total: 75 Samples

Summary

Polar pesticides – ESI negative

- glyphosate
- some ubiquitous compounds: perchlorate, phosphonic acid, TFA, bromide, cyanuric acid, chlorate

Polar pesticides – ESI positive

- melamine, nicotine, mepiquat

Acidic pesticides and other metabolites

- 2,4-D
- Fluvalinate anilino acid, IM-2-1

MRL violations

- bromide
- matrine, oxymatrine

Copper

- all samples positive

Thank You
for Your Attention

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