

JOINT MONITORING PROGRAM OF PESTICIDE RESIDUES IN HONEY

MRM – COMPOUNDS
PART A



European
Commission

EURL-AO



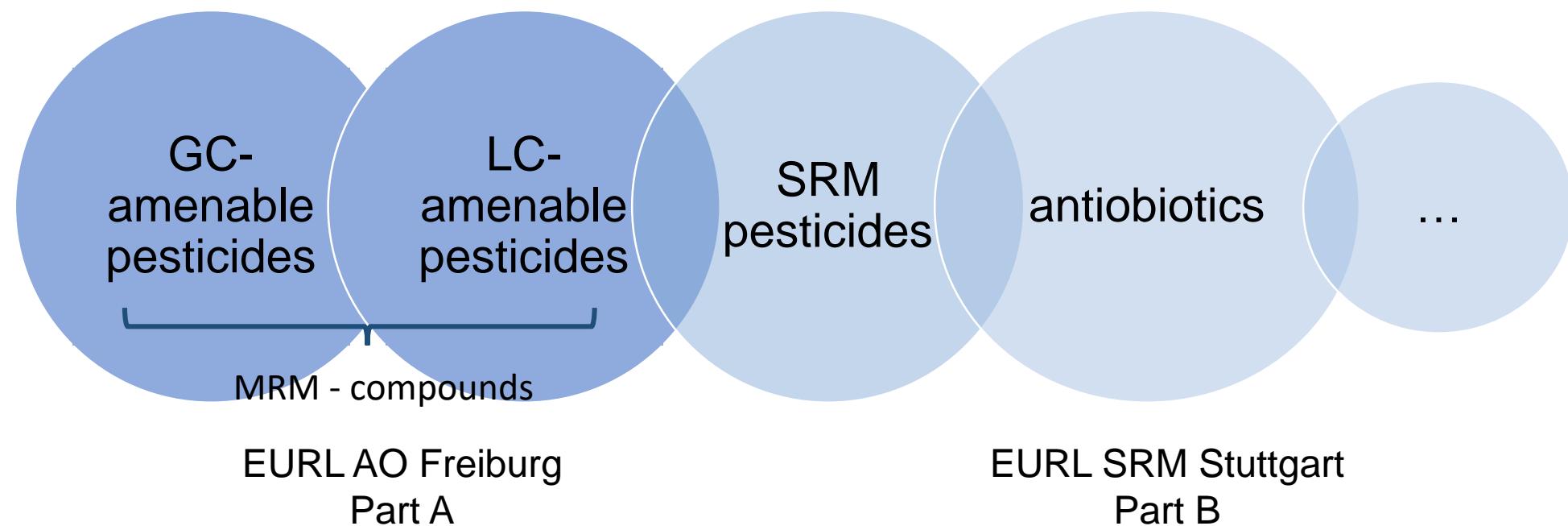
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BACKGROUND INFORMATION

- ✓ overview about the pesticide situation in honey
- ✓ monitoring of the most important commercially available honeys on European market

PROJECT

- samples were analysed by EURL AO and EURL SRM



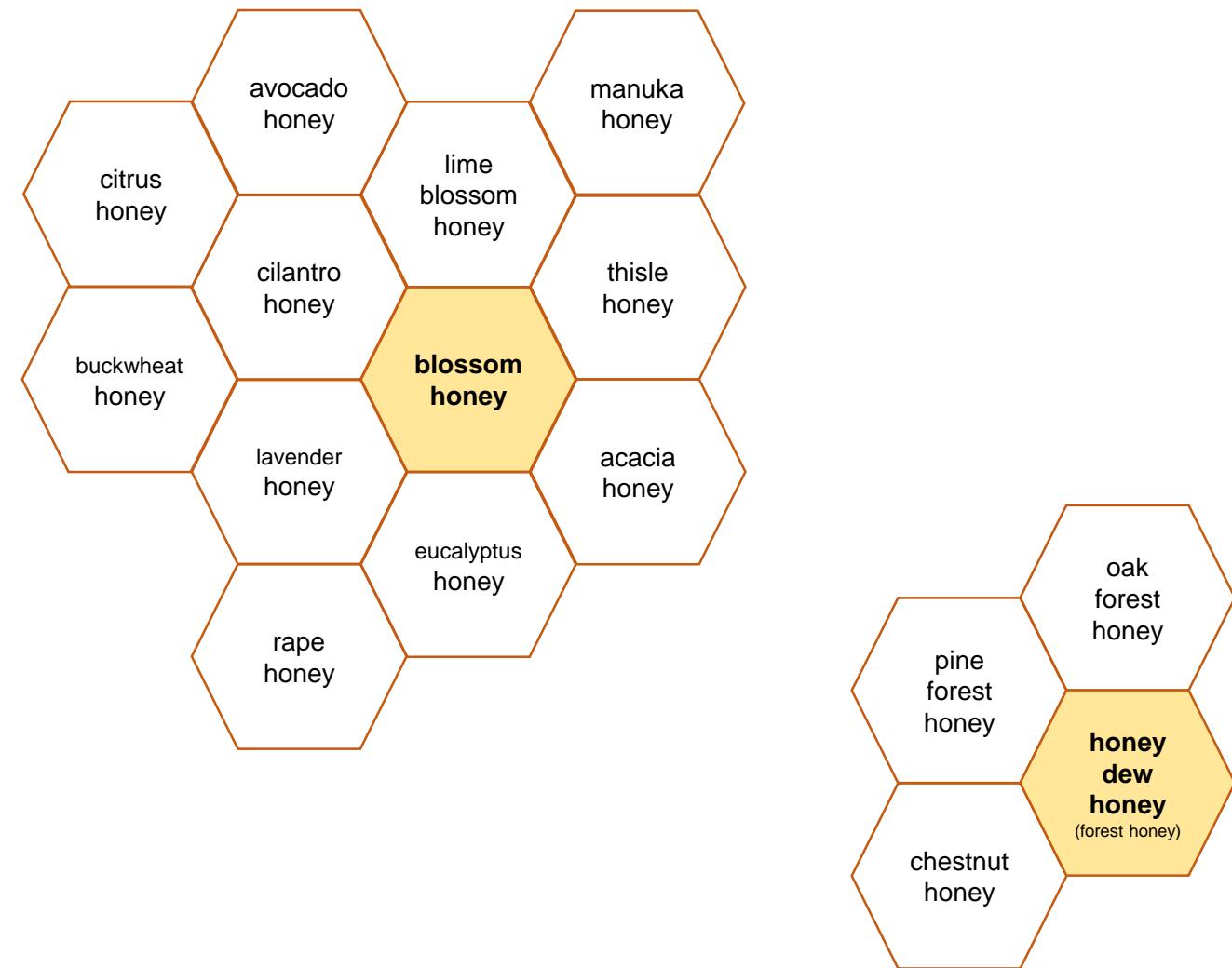
SAMPLING

- 173 honey samples
 - 74 from EU countries
 - 74 from non-EU countries
 - 12 EU/non-EU blends
 - 3 not specifies EU countries
 - 9 not specified non-EU countries
 - 1 unspecified origin

SAMPLING

- 173 honey samples
 - 11 organic samples
- different types
 - blossom honey
 - forest honey
 - blends of different types

honey type	number
blossom honey	93
forest honey	12
unknown	68



VALIDATION

- validation according to SANTE/11312/2021
- six different sample types included:
 - blossom honey
 - forrest honey
 - fir honey
 - summer blossom honey
 - coffee blossom honey
 - forest blossom honey
- samples spiked at different concentration levels:
 - 0.5 µg/kg, 1 µg/kg, 5 µg/kg, 10 µg/kg, 20 µg/kg (GC)
 - 1 µg/kg, 5 µg/kg, 10 µg/kg (LC)

VALIDATION

- validation of GC-Orbitrap-MS and LC-Q-TOF based screening method for
 > 600 pesticides and metabolites

#	CAS	Analyte	#	CAS	Analyte
1	3896061	Acequinocyl	117	3805167	Heptachlorepoxyde, cis- (Isomer B)
2	3845091	Acetochlor	118	3805168	Heptachlorepoxyde, trans- (Isomer A)
3	3860017	Acrinathrin	119	3805035	Hexachlorobenzene
4	3845001	Alachlor	120	3832024	Hexazinone (Velpar)
5	3805002	Aldrin	121	3835173	IN-F7321 [bis-(4-fluorophenyl)methyl]silanol
6	3860006	Allethrin	122	3810051	Iodofenphos
7	3845002	Allidochlor	123	3895019	Iprodione
8	3895005	Anthraquinone (9,10-Anthracenedione)	124	3811069	Isazophos
9	3832005	Atrazine	125	3811101	Isocarbophos
10	3812001	Azinphos-ethyl	126	3805082	Isodrin
11	3812002	Azinphos-methyl	127	3841011	Isopropalin
12	V3895158	Benalaxy-M	128	3833005	Lenacil
13	3841001	Benfluralin	129	3811535	Leptophos
14	3805091	Bifenoxy	130	3830013	Linuron
15	3860014	Bifenthrin	131	3812015	Malathion
16	3600142	Biphenyl	132	3807034	Metalaxylyl
17	3810562	Bromfenovinfos-methyl	133	3845066	Metazachlor
18	3810561	Bromfenovinfos	134	3811063	Methacrifos
19	3805174	Bromocyclen	135	3812017	Methidathion
20	3811002	Bromofos-ethyl	136	V3805226	Methoxychlor, 2,4-

METHODS

SweEt-AO



- weight in 5 g
- 5ml water, shaking 10 min,
- 10 ml cyclohexane/ethylacetat, shaking 10min
- 5 g Na₂SO₄, 0.2 g PSA; Shake (15 min); centrifuge (5 min at 3200 g)
- supernatant: 2 g Na₂SO₄, shaking 10 min, centrifuge (10 min at 3200 g)

- 5 ml extract GPC
- evaporate to 5 ml
- wash over in 25 ml pear shaped flask
- concentrated down to a residual drop and taken up in 0.5 ml of ethyl acetate

- 100 µl extract with 3 µl APs in Vial for measurement



QuEChERS

- weight in 5 g
- 100 µL internal standard;
- shake and wait for 10 min
- add 10 mL H₂O shake for 10 min
- add 10 mL ACN shake for 10 min

- addition of extraction salts: 4 g MgSO₄ + 1 g NaCl + 1 g trisodium citrate x 2 H₂O + 0.5 g disodium citrate x 6 H₂O
→ shaking for 10 min, centrifuge for 5 min
- transfer aliquote of 6 mL of supernatant in a vial containing 150 mg PSA and 900 mg MgSO₄
→ shake 10 min; centrifuge 5 min

- tranfer aliquote into a vial for LC-TOF measurement



RESULTS

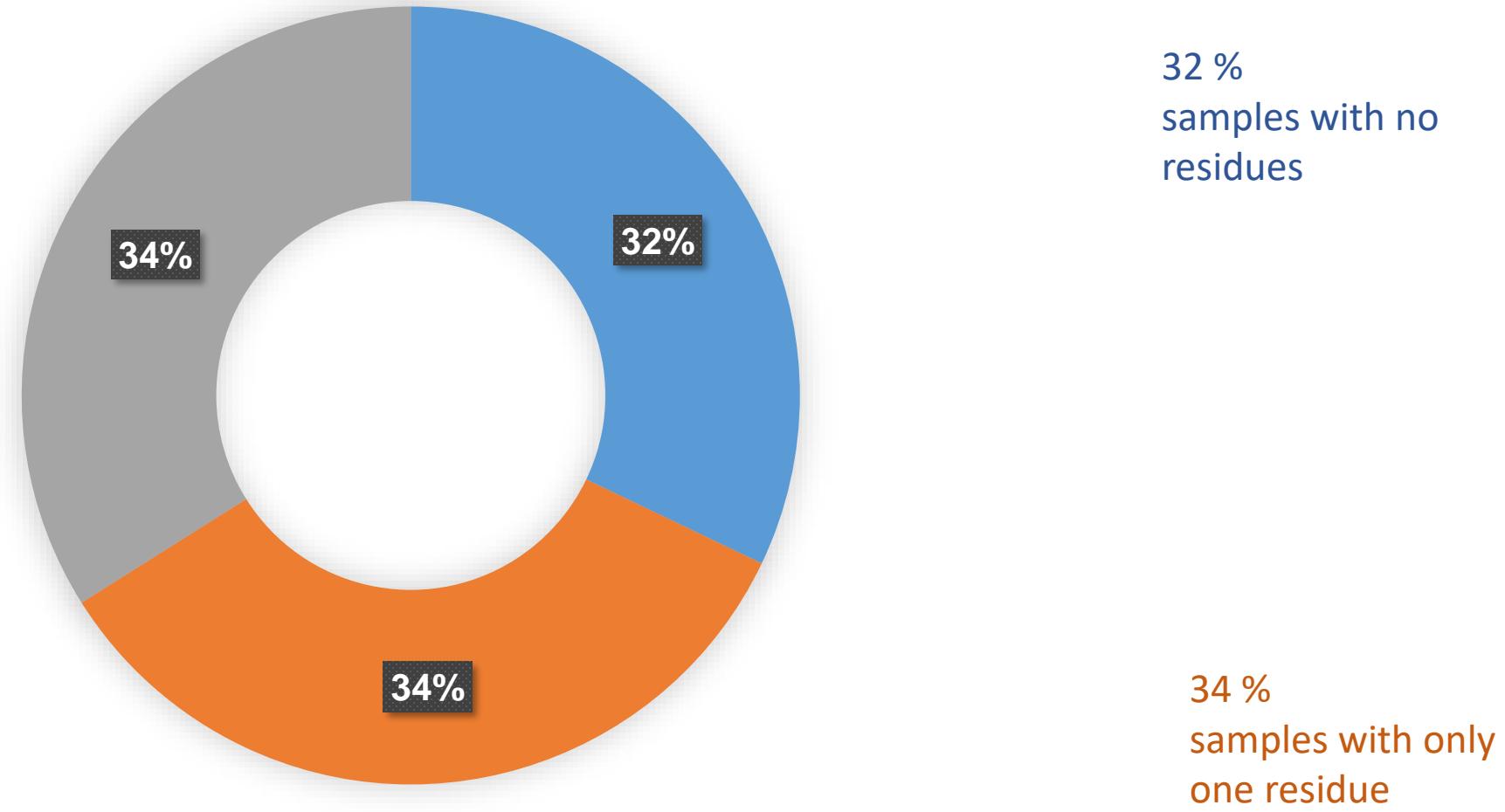


Diagram 1: Distribution of pesticide residues of the total samples

RESULTS – GC

FREQUENCY OF THE RESIDUES

- in total, 8 different residues were quantified
- most findings of **DMF (N-(2,4)-dimethylphenyl)formamide)** and **coumaphos**
- Residue findings below the MRL-values

reporting range: 0.5 – 71.4 µg/kg

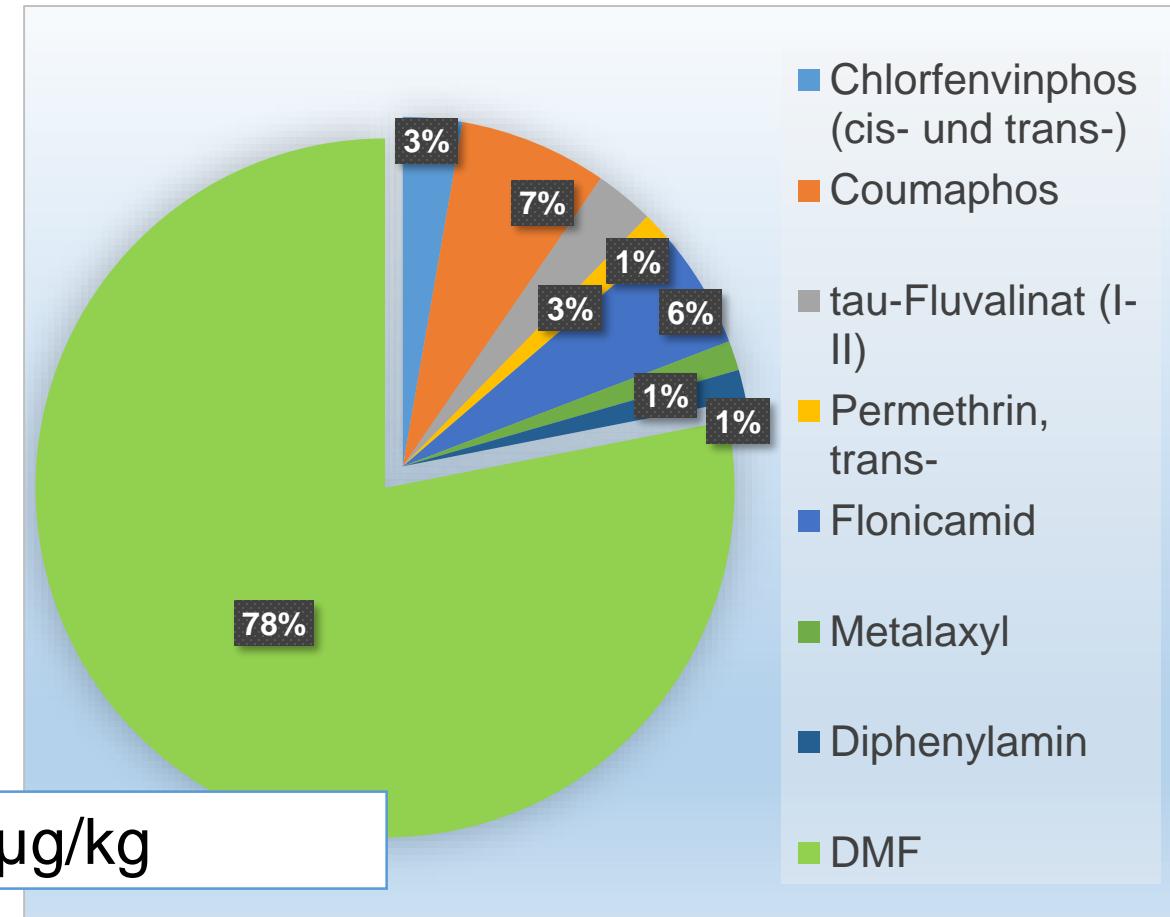


Diagram 2: Distribution of GC-amenable pesticide residues of the total samples

RESULTS – LC

FREQUENCY OF THE RESIDUES

- in total, 10 different residues were quantified
- most findings are **coumaphos** and **N-(2,4-Dimethylphenyl)-N-methylformamide (DMPF)**
- residue findings below the MRL-values

reporting range: 1.0 – 38.4 µg/kg

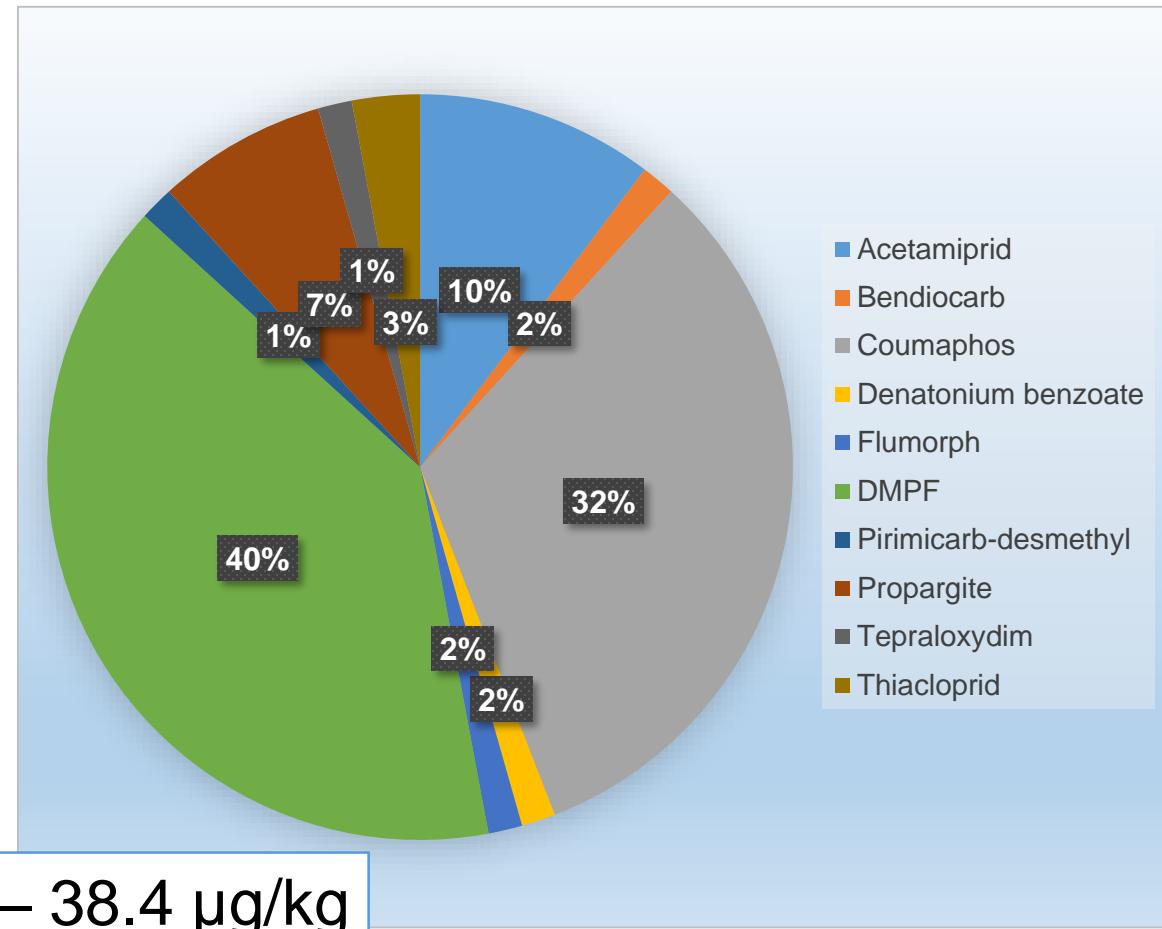
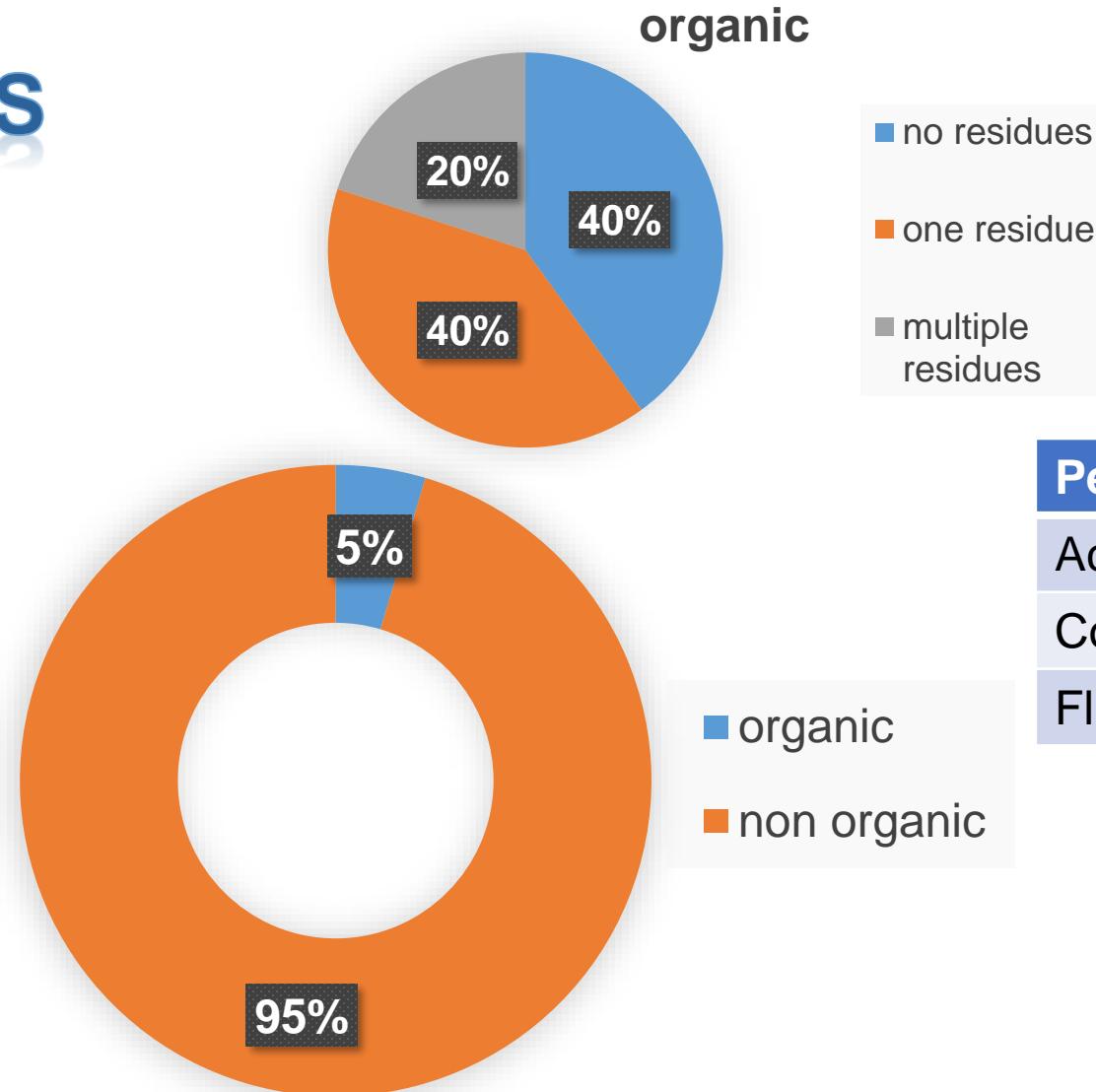


Diagram 3: Distribution of LC-amenable pesticide residues of the total samples

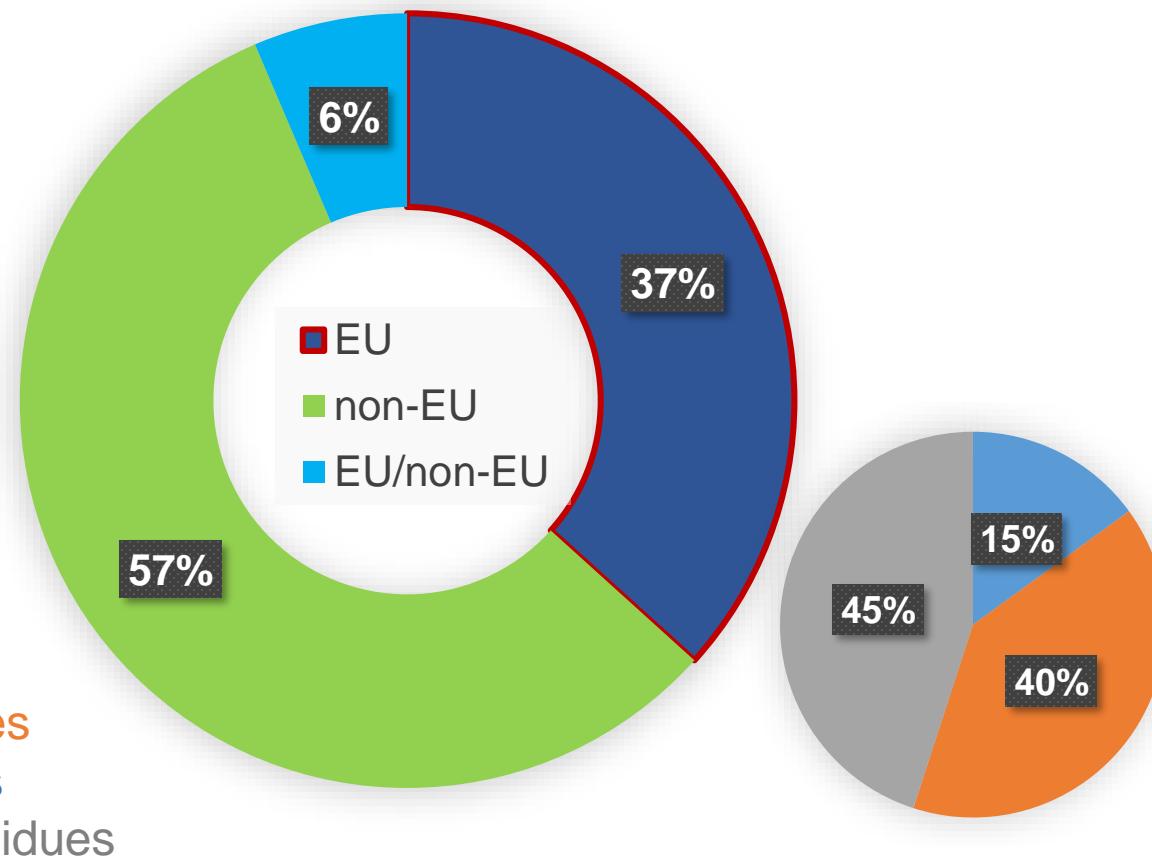
RESULTS



Pesticides	Average ($\mu\text{g}/\text{kg}$)
Acetamiprid	1
Coumaphos	1
Fluvalinate	20

RESULTS

FREQUENCY OF THE RESIDUES



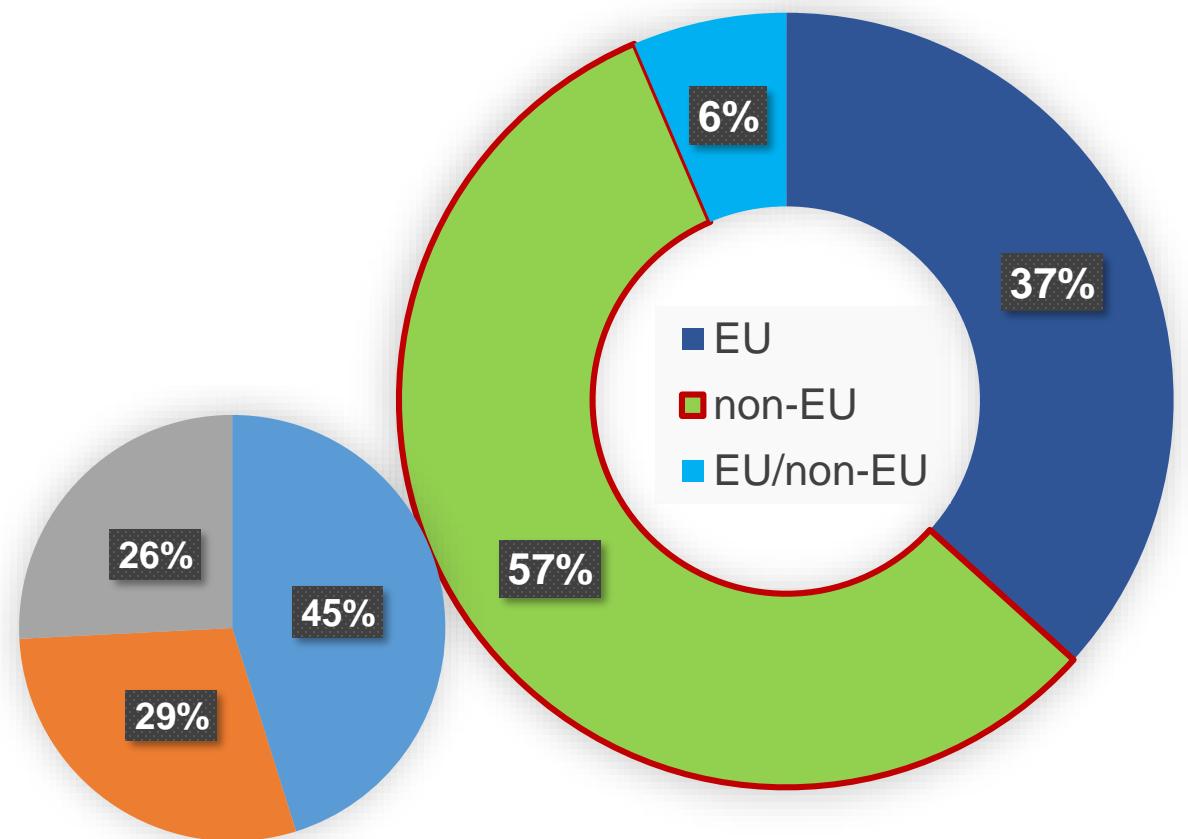
Pesticides	Average (µg/kg)
Chlорfenвiphos	1
Coumaphos	9.5
Fluvalinate	1.5
Tebuconazole	0.8
Flonicamid	1.6
DMF	25
Bendiocarb	4
Acetamiprid	4
DMPF	26

RESULTS

FREQUENCY OF THE RESIDUES

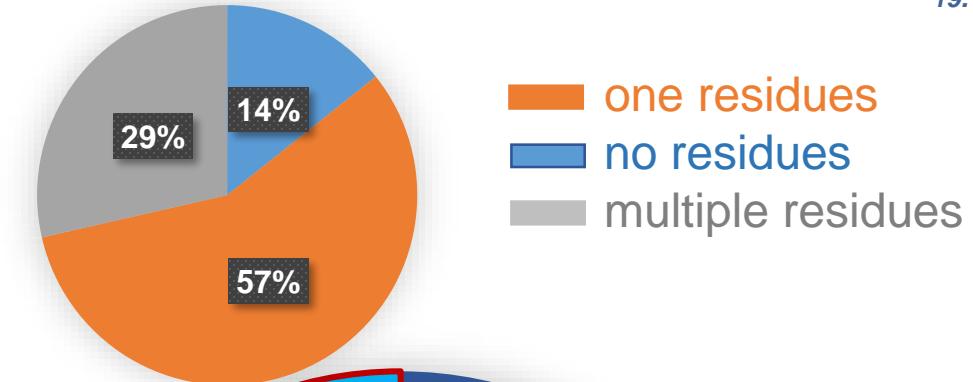
█ one residues
█ no residues
█ multiple residues

Pesticides	Average ($\mu\text{g}/\text{kg}$)
Permethrin	0.6
Coumaphos	6.5
Fluvalinate	2
DMF	11.4
DMPF	20
Acetamiprid	5
Pirimicarb desmethyl	1
Tepraloxidim	3

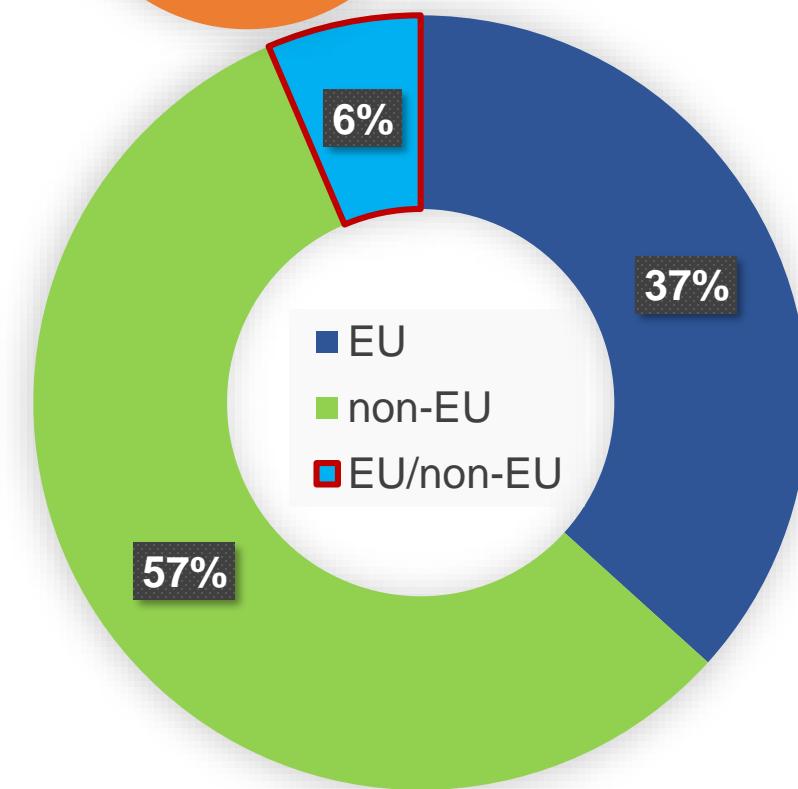


RESULTS

FREQUENCY OF THE RESIDUES



Pesticides	Average ($\mu\text{g}/\text{kg}$)
Flonicamid	0.6
Coumaphos	1
DMF	5.2
Thiacloprid	2



CONCLUSION

- 17 different pesticides and metabolites were quantified
- more pesticide residues were identified below LOQ
- no conspicuities between non-EU and EU countries
- residues below the MRL – values
- most findings on amitraz metabolites



PART B: SRM compounds

Thank You for Your Interest



EURL EUROPEAN
UNION
REFERENCE
LABORATORY



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