Chromatographic analyses of pesticide residues in Food Safety Laboratory

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GENERAL ACTIVITIES OF THE LAB: TESTING OF PESTICIDE RESIDUES

- Statutory – participation in scientific and R&D projects
- Official – cooperation with the Ministry of Agriculture and Rural Development and the Plant Health and Seed Inspection since 2002
  - monitoring of correct use of PPPs on the national level
- FVO audits in the above mentioned field in 2013, 2015 and 2017
- Commercial (IPR, GLOBALGAP, HACCP, export)
- Tests complying with GLP (plant protection products to be registered) for the Ministry of Agriculture and Rural Development and the EU
- Evaluation of applications for registration of PPPs for the MARD and EFSA

PLAN OF THE LECTURE

1. General info on PPP.

2. Correct sampling for testing.

3. How pesticides are tested

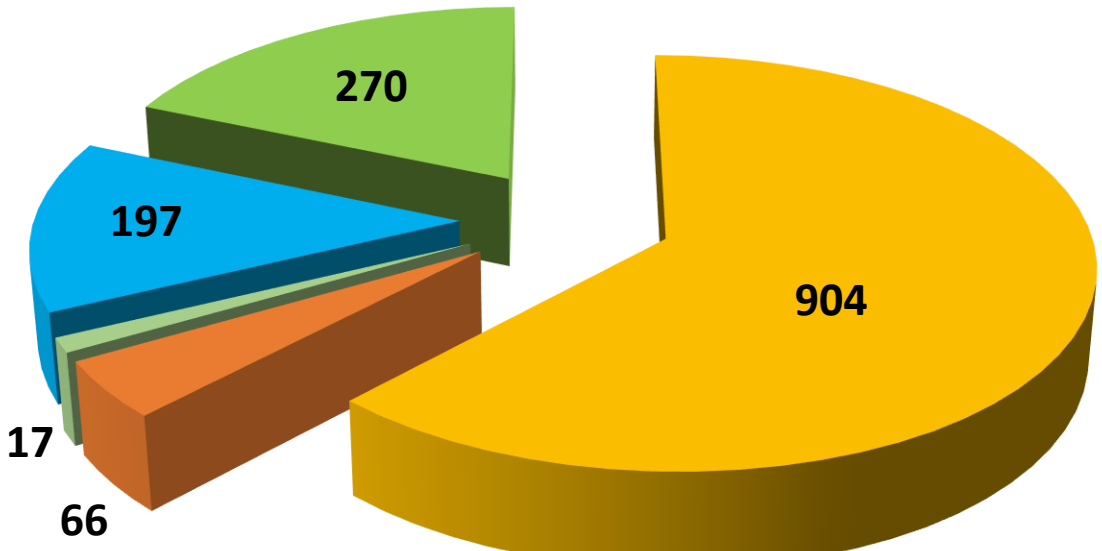
4. Some results on crops, soil and water.

General info on PPP

Number of active substances in PPPs Evaluated by EU and Poland (1454 substances)

(according to the regulation (WE) 396/2005 -11-03-2021)

http://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/

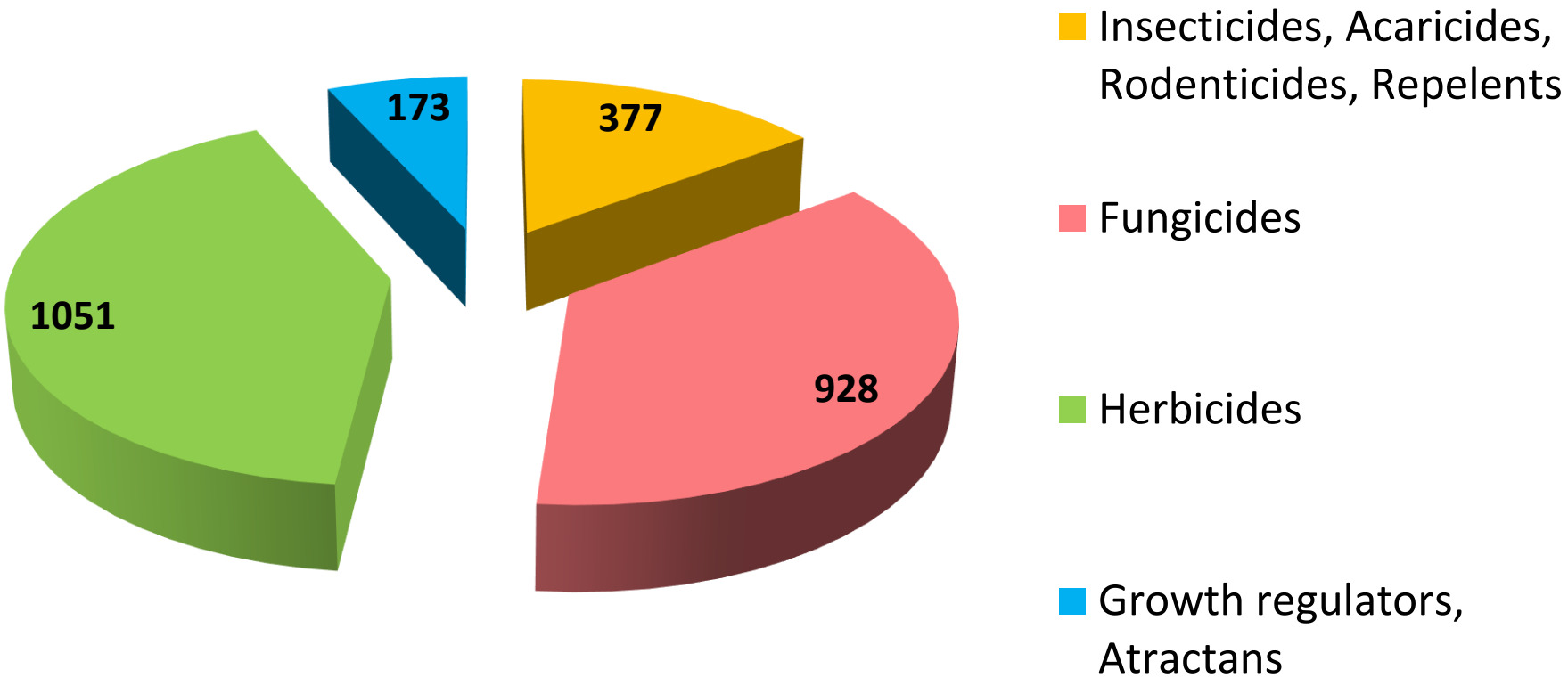


- Not allowed
- During evaluation
- Not evaluated yet
- Allowed in EU and not in Poland
- Allowed in Poland (and in UE)

Number of Plant Protection Products (PPPs) registered in Poland (2529 PPPs)

(according to Ministry of Agriculture register -26-02-2021)

https://bip.minrol.gov.pl/Informacje-Branzowe/Produkcja-Roslinna/Ochrona-Roslin/Rejestr-Srodkow-Ochrony-Roslin



https://www.gov.pl/web/rolnictwo/wyszukiwarka-srodkow-ochrony-roslin---zastosowanie

Wyszukiwarka środków ochrony roślin - zastosowanie

Wyszukiwarka środków ochrony roślin - umożliwia wyszukiwanie środków ochrony roślin po uprawach, agrofagach itp.* Do wyszukiwania należy używać filtrów (pokaż filtry).* Nazwa oznacza nazwę środka ochrony roślin.* Rodzaj oznacza rodzaj środka ochrony roślin (chwastobójczy, insektycyd, fungicyd itd.).* Grupa oznacza grupę roślin (rośliny rolnicze, rośliny sadownicze, rośliny warzywne itd.).* Przy wyszukiwaniu upraw na zastosowania na małoobszarowe, w polu maloobszarowe należy wpisać słowo TAK.

Wpisz czego szukasz

Zwiń filtry

nazwa

Rodzaj

Substancja_czynna

uprawa

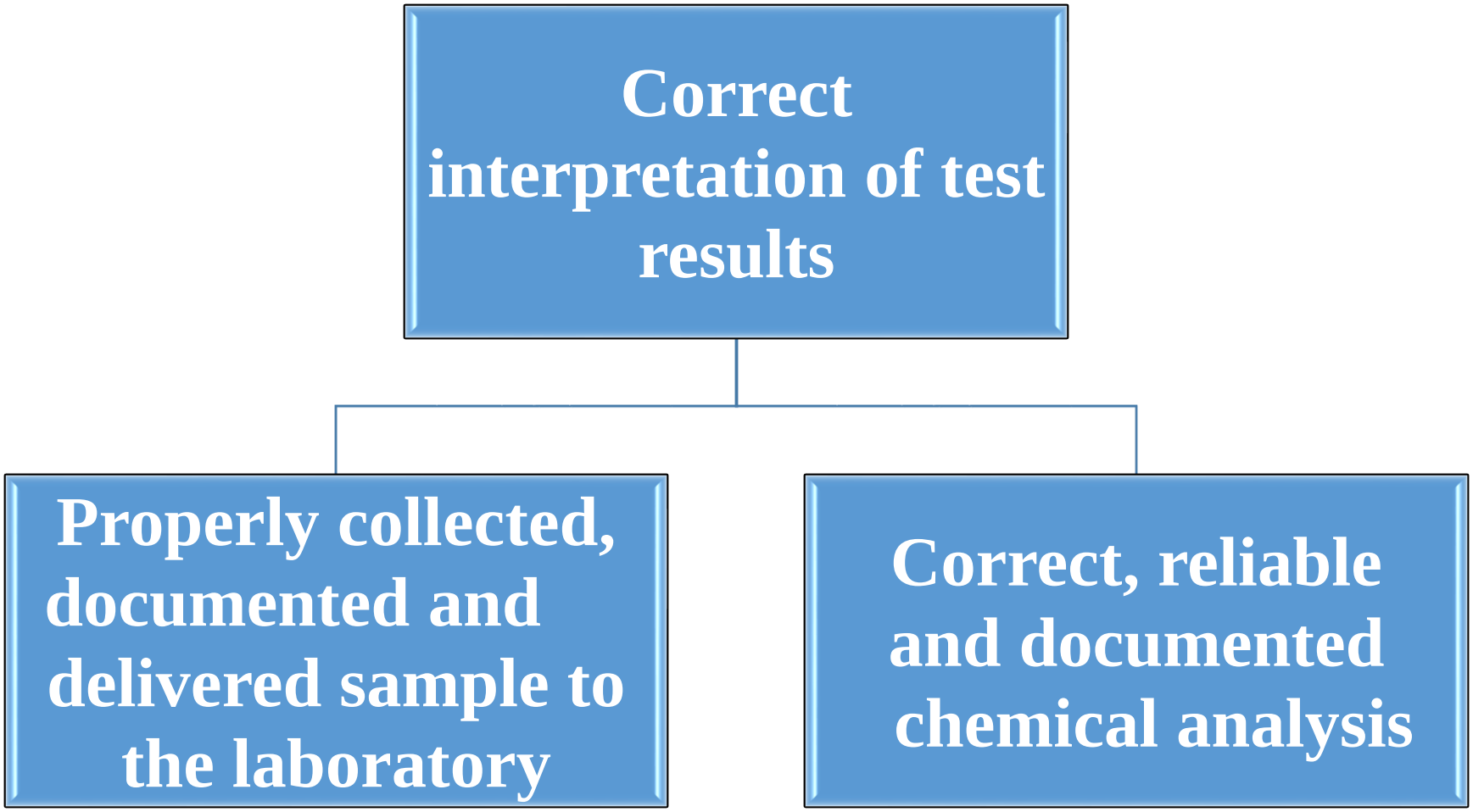
agrofag

nazwa_grupy

maloobszarowe

Liczba elementów: **9217**

Correct sampling for testing

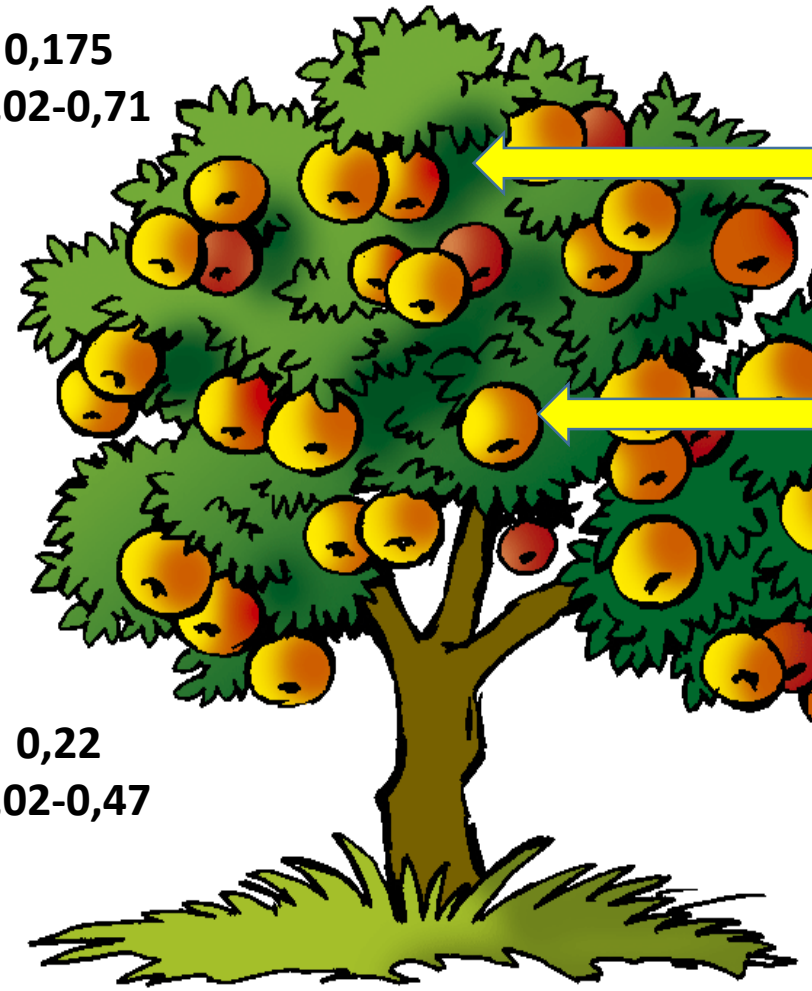

Correct interpretation of test results
Properly collected, documented and delivered sample to the laboratory
Correct, reliable and documented chemical analysis

The position of the apple on the tree and the residue of phosphamidon

Position on the tree	**High Outsite**	**High Insite**	**Middle Outsite**	**Middle Insite**	**Low Outsite**
Avarage [mg/kg]	**0,175**	**0,05**	**0,265**	**0,09**	**0,22**
Min. [mg/kg]	**0,02**	**0,01**	**0,07**	**0,03**	**0,02**
Max. [mg/kg]	**0,71**	**0,09**	**0,47**	**0,14**	**0,47**

A.Ambus. Food Additives and Contaminants, 2000, vol. 17, no.7, 519-537

The position of the apple on the tree and the residue of phosphamidon [mg/kg]



Dependence of phosphamidon residues on the size of the test sample

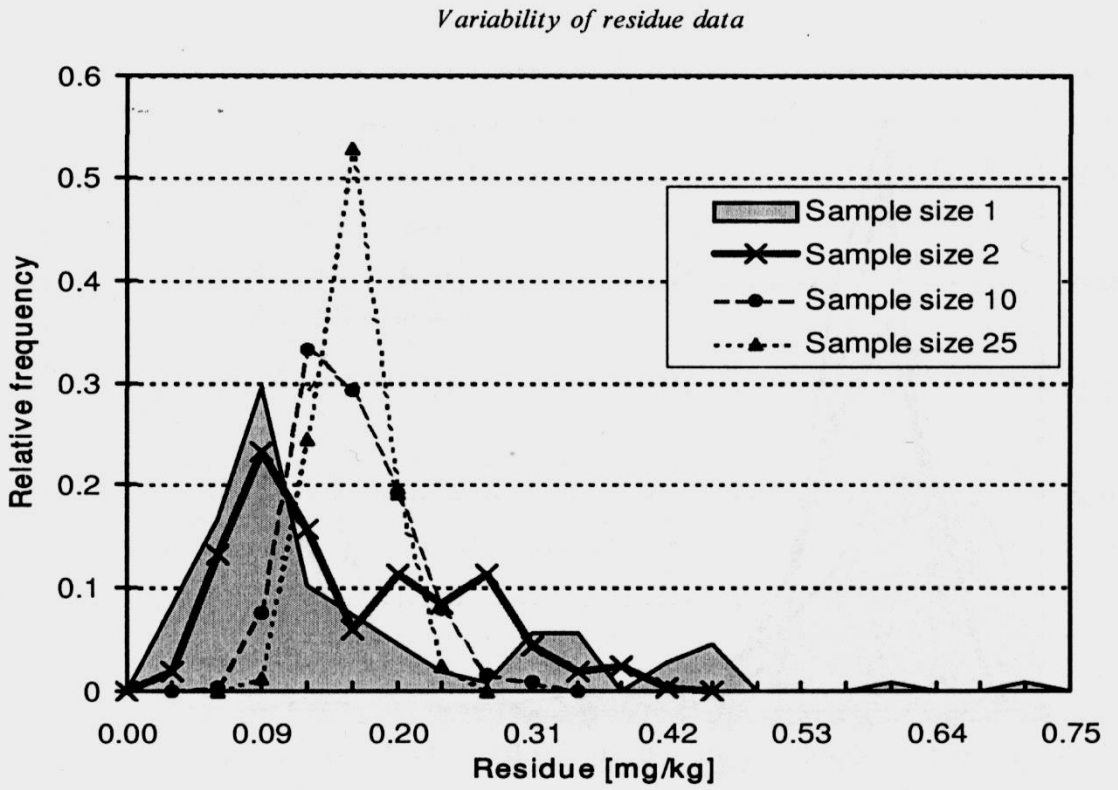


Figure 2. Distribution of phosphamidon residues in apples 6 days after treatment.

A.Ambus. Food Additives and Contaminants, 2000, vol. 17, no.7, 519-537

Legal standards regarding the method of sampling

- **COMMISSION DIRECTIVE 2002/63/EC of 11 July 2002 establishing Community methods of sampling for the official control of pesticide residues in and on products of plant and animal origin and repealing Directive 79/700/EEC**

- **Rozporządzenie Ministra Zdrowia z dnia 17 października 2007r. „w sprawie pobierania próbek żywności w celu oznaczania pozostałości pestycydów” (Dz.U. 07.207.1502) - Reg. of Ministry of Health**

- **Rozporządzenie MRiRW z dn. 16 grudnia 2013 r. „w sprawie pobierania próbek roślin, produktów roślinnych lub przedmiotów do badań na obecność pozostałości środków ochrony roślin” (Dz.U. 2013 poz. 1549) – Reg. of MARD**

The Polish Committee for Standardization standards regarding the method of sampling

- **PN-78/R-04011 – Plant material and soil. Sampling for the quantitative determination of pesticide residues**
- **PN-69/R-75021 – Fresh fruit. Quality testing.**
- **PN-71/R-75356 – Fresh vegetables. Quality testing.**

description of primary samples and minimum size of laboratory samples (COMMISSION DIRECTIVE 2002/63/EC)

Commodity classification	Examples	Nature of primary sample to be taken	Minimum size of each laboratory sample
Small sized fresh products units generally < 25 g	Berries, peas, olives	Whole units, or packages, or units taken with a sampling device	1 kg
Medium sized fresh products, units generally 25 to 250 g	Apples, oranges	Whole unit	1 kg (at least 10 units)
Large sized fresh products, units generally > 250 g	Cabbages, cucumbers, grapes (bunches)	Whole unit	2 kg (at least 5 units)

How pesticides are tested

Steps of the analytical method

Initial sample preparation
- cooling, comminution, grinding

Extraction of pesticides from a sample

Purification of the extract from undesirable substances

Qualitative and quantitative analysis using GC- & LC-MS/MS

Guidance document on analytical quality control and method validation procedures for pesticide residues and analysis in food and feed.

EUROPEAN COMMISSION
DIRECTORATE GENERAL FOR HEALTH AND FOOD SAFETY

Safety of the Food Chain
Pesticides and Biocides

SANTE/11813/2017
21 – 22 November 2017 rev.0

Guidance document on analytical quality control and method validation procedures for pesticide residues and analysis in food and feed.

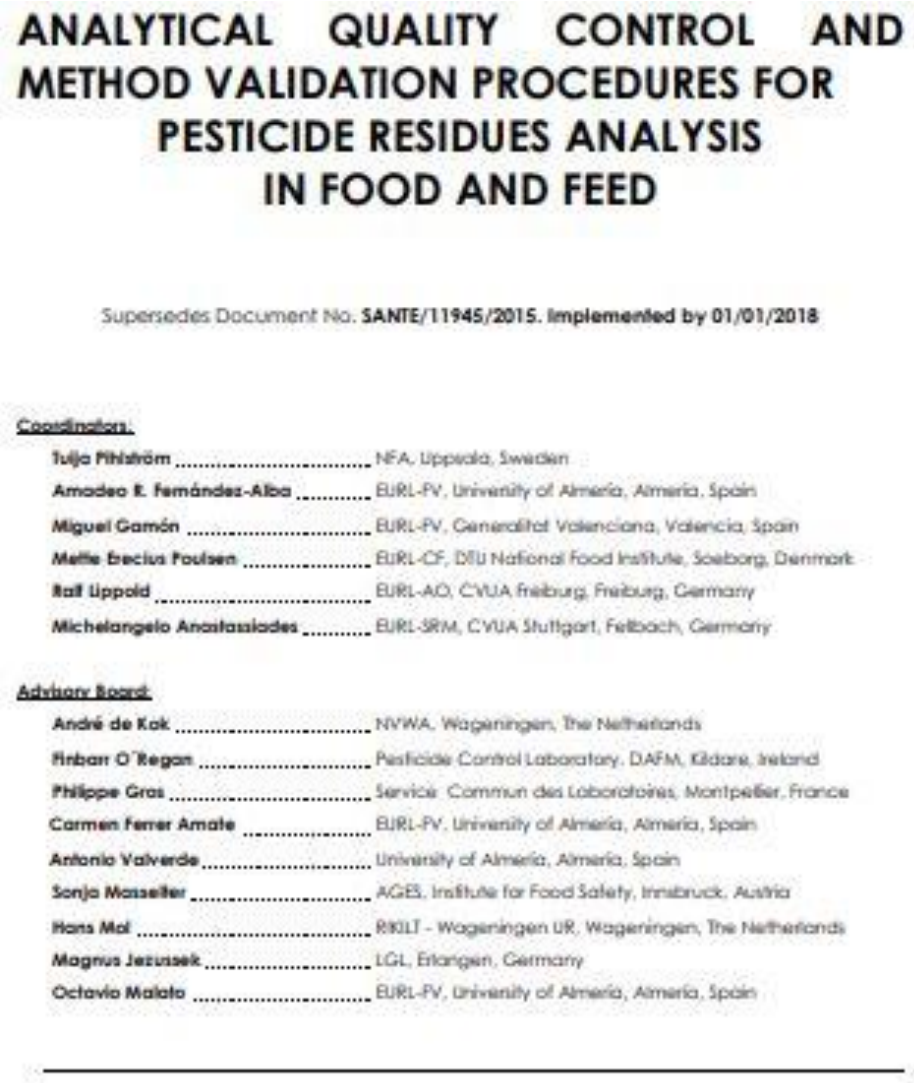
SANTE/11813/2017

Supercedes

SANTE/11945/2015
Implemented by 01/01/2018

This document has been conceived as a technical guideline of the Commission Services. It does not represent the official position of the Commission. It does not intend to produce legally binding effects.

Only the European Court of Justice has jurisdiction to give preliminary rulings concerning the validity and interpretation of acts of the institutions of the EU pursuant to Article 267 of the Treaty.



ANALYTICAL QUALITY CONTROL AND METHOD VALIDATION PROCEDURES FOR PESTICIDE RESIDUES ANALYSIS IN FOOD AND FEED

Supersedes Document No. **SANTE/11945/2015. Implemented by 01/01/2018**

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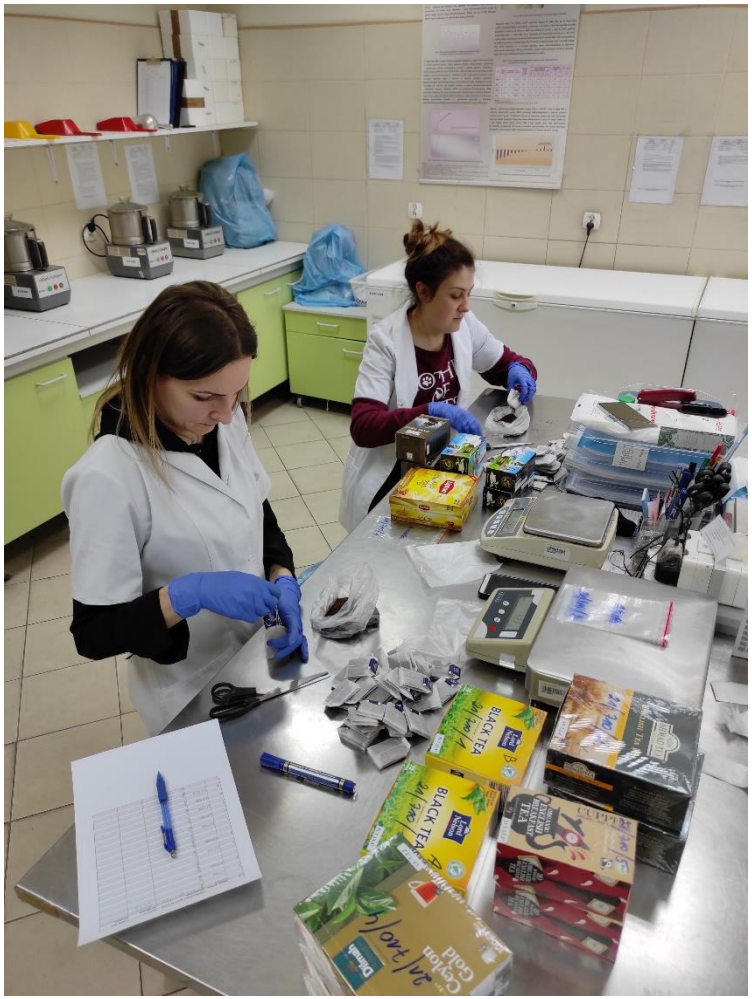
Receipt of samples to the laboratory

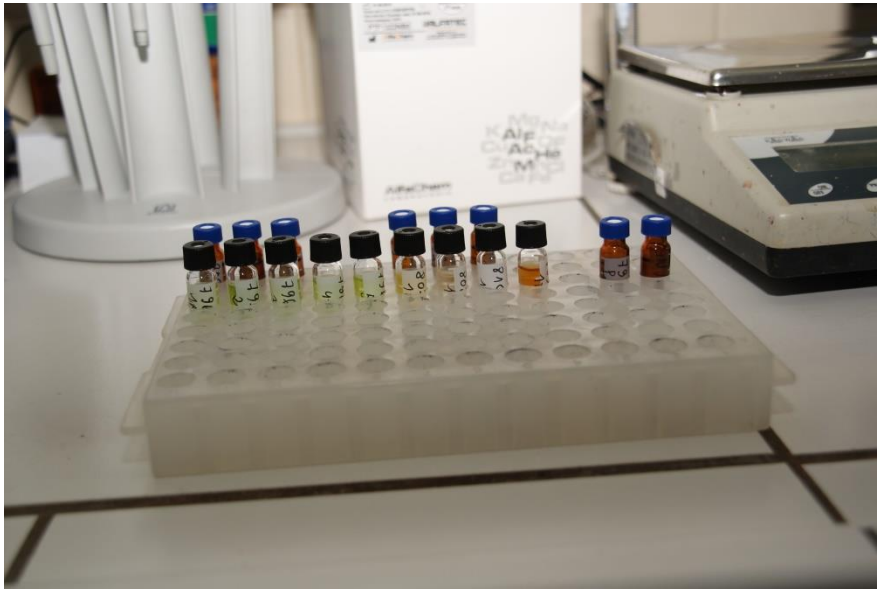
Case study – tea bags



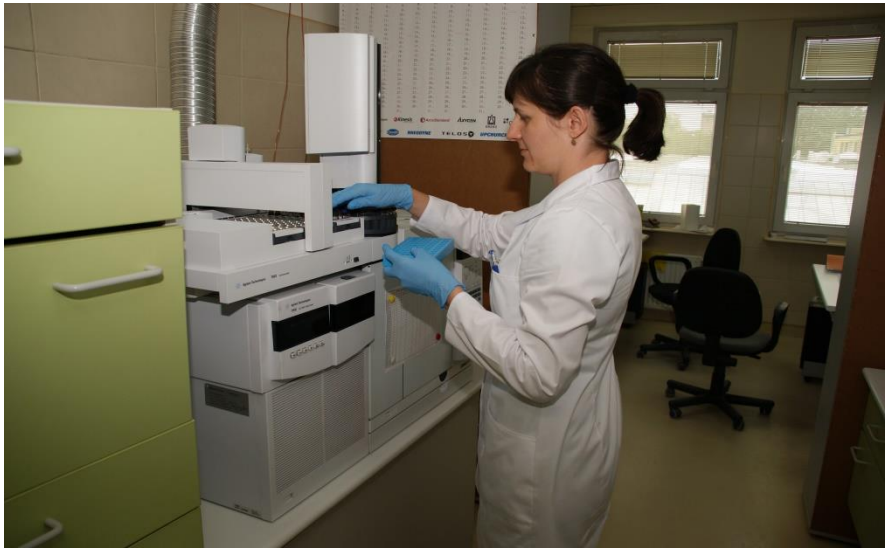
The grinding process of samples

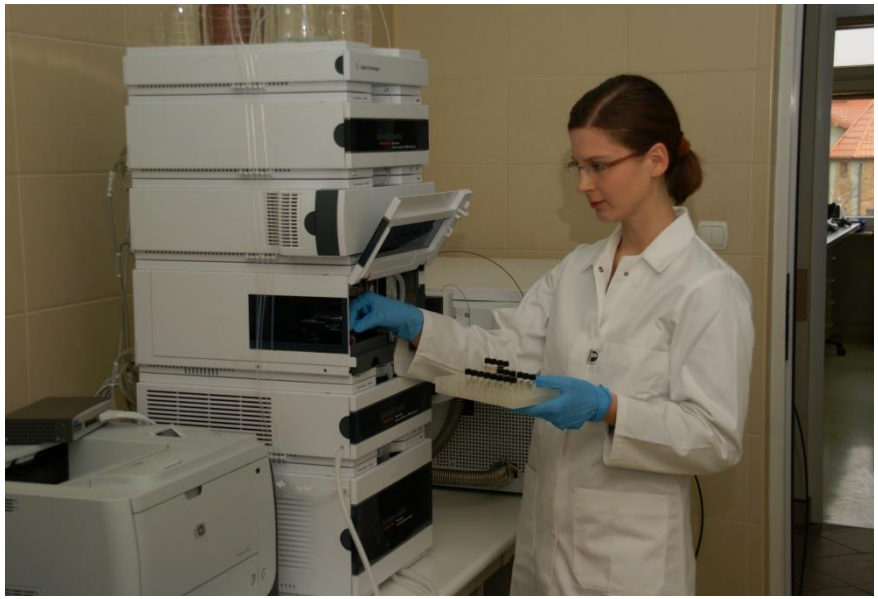
Sample storage

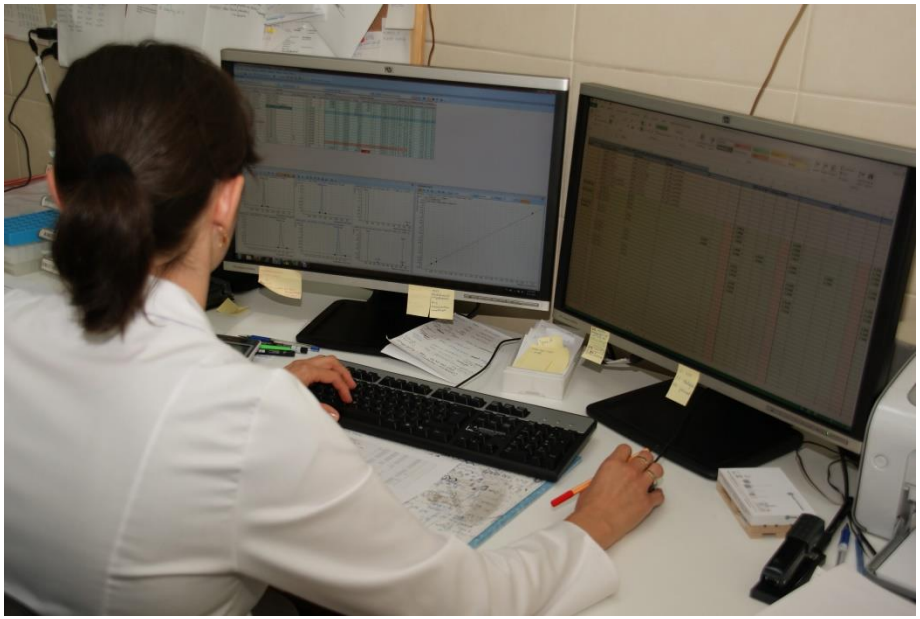
Extration of pesticides



Chromatographic Analysis

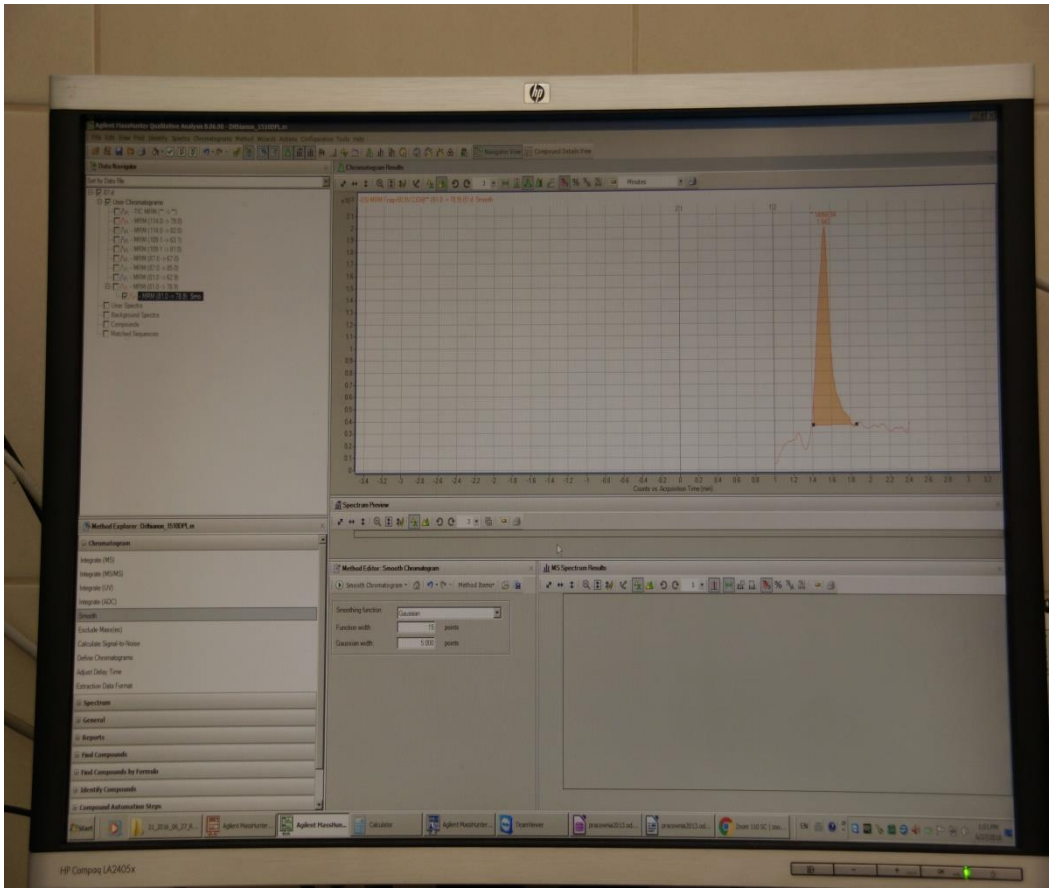


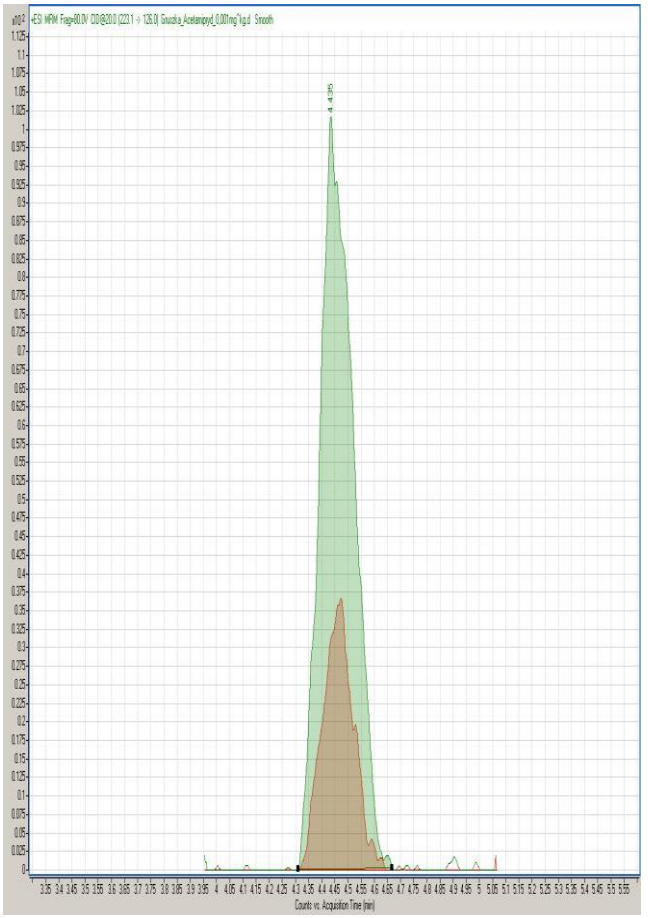




An example of analytical capabilities

Chromatographic peak represented 1 µg/kg of Acetamiprid obtained by LC-MS/MS system

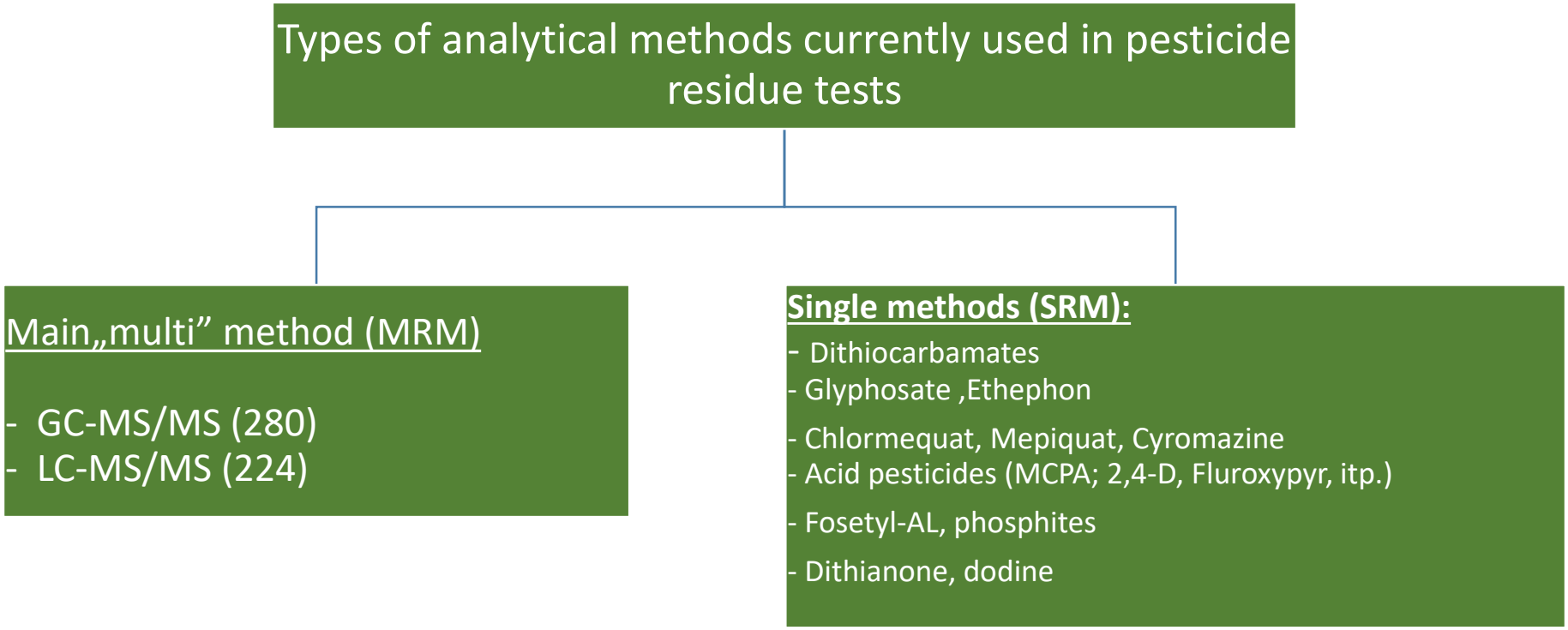




Critical points in the lab

- Reception / registration of samples
- The process of comminution / grinding samples
- Storage conditions of samples
- The process of extraction of pesticides
- Supervision of analytical standards
- Supervision of the chromatograph and detectors
- Correct selection of matrices for standardization
- Correct reading of results and interpretation

Types of analytical methods currently used in pesticide residue tests



PROFICIENCY TESTS – final approval

- EU Proficiency Test on Pesticide Residues in Fruit and Vegetables , CRL-MRM, University of Almeria, Spain;
  (class A obtained)

- EU Pesticide Residues in Cereals using Multi and Single Residue Methods. – CRL Cereals and Feedingstuff, National Food Institute, Danish Technical University
  (class A obtained)

- CRL Single Residue Methods, CVUA Stuttgart, Germany.
  (class A obtained)

- EU Pesticides Residues in Food of Animal Origin, CRL CVUA Freiburg, Germany
  (class A obtained) – honey, eggs

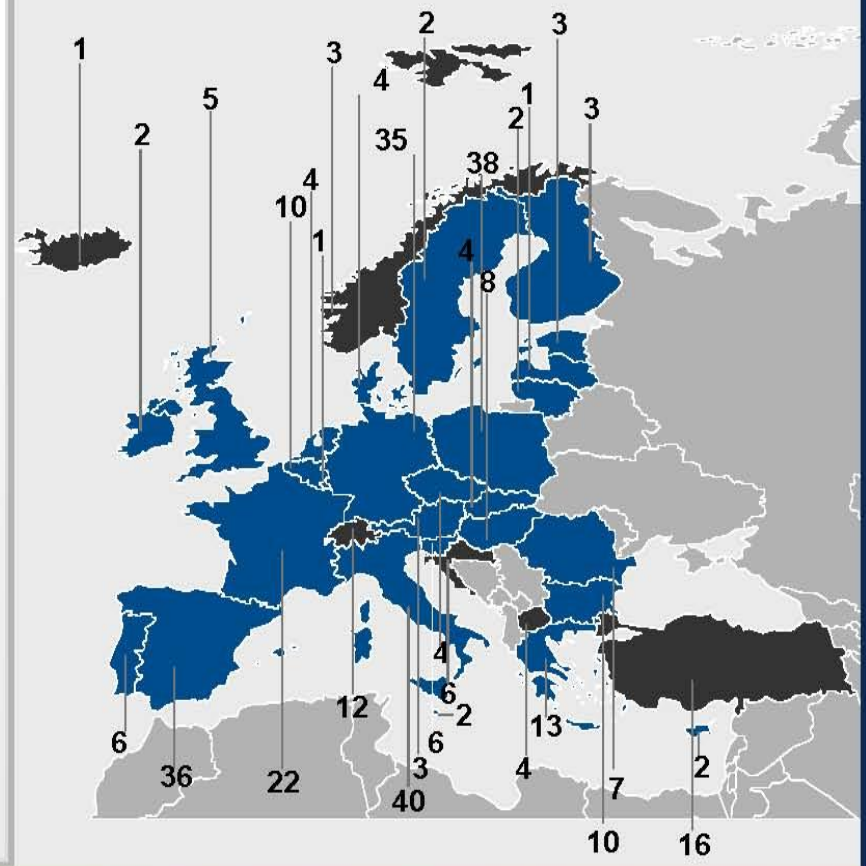
- Sigma-Aldrich PT Pesticides in soil, Proficiency Test LPTP14-S4
  (fully positive result) - soil

EU Lab-Network - Overview

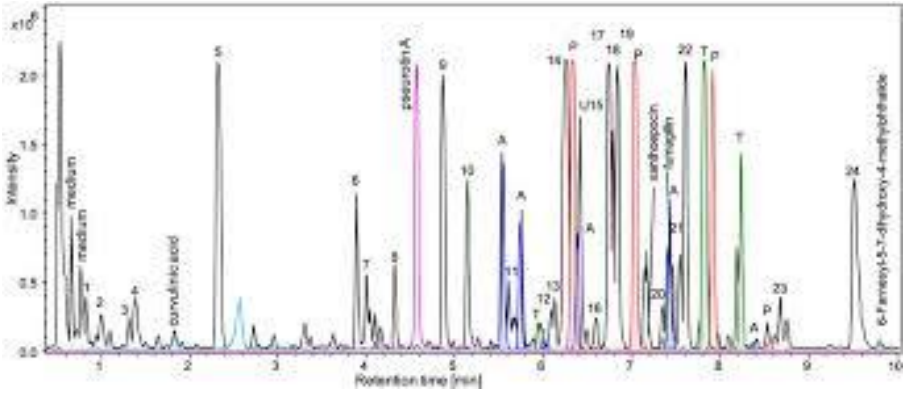
Official Labs for Pesticide Residues

- **315 official labs in network:**
  - **273 EU-labs**
  - **16 EFTA-labs**
  - **26 EU-candidate labs**
- **Most of the data from surveys imported in EURL DataPool**
- **Users of EURL DataPool can update the data by themselves!**

Number of labs per country



Some results on crops, soil and water.



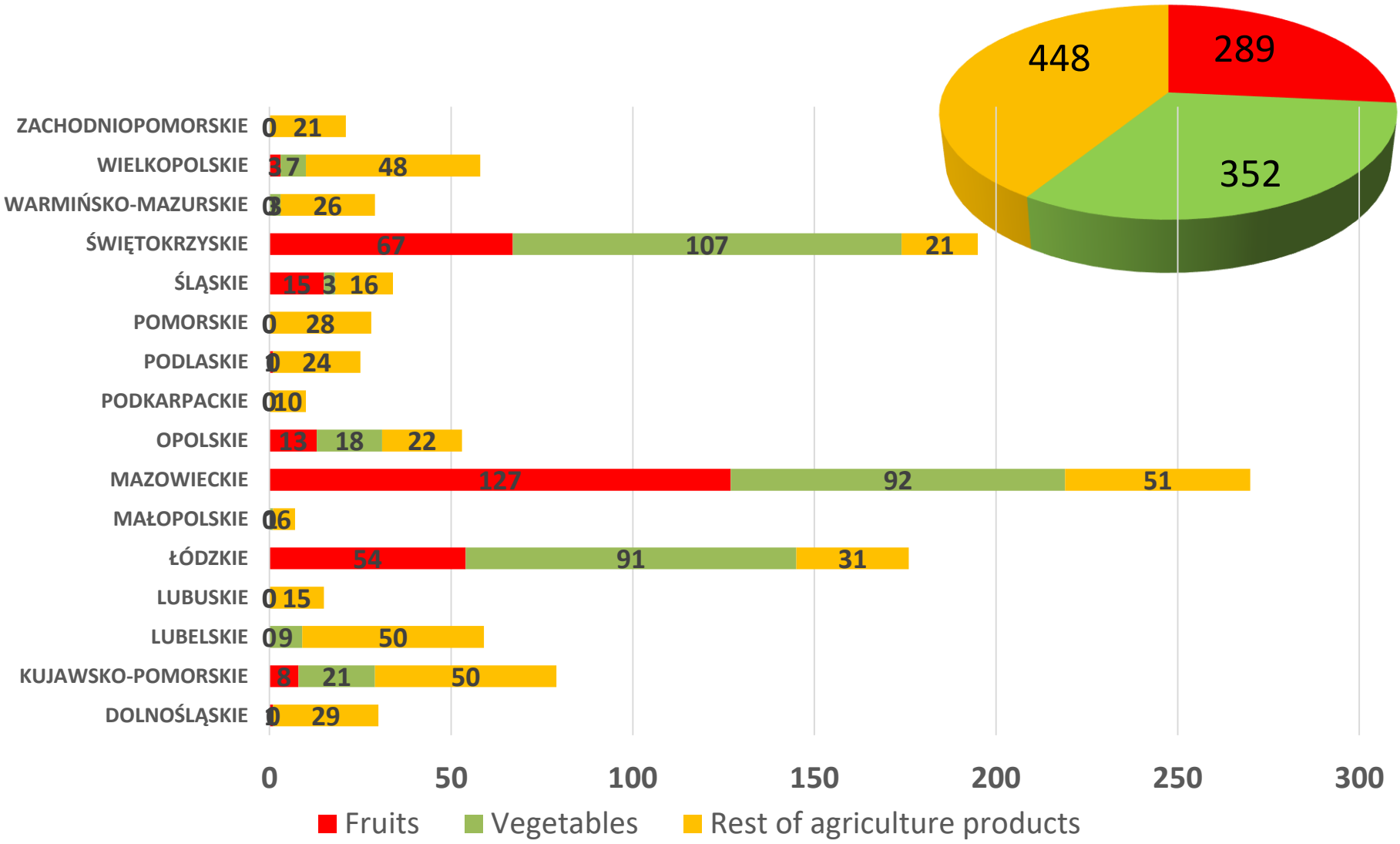
TEST METHODOLOGY

- Test period: May – December
- Samples were collected by employees of 16 Regional Inspectorates of Plant Health and Seed Inspection and sent to the Food Safety Lab
- Fruit, vegetables and crops were collected from harvests and warehouses at farms
- Reports were sent to Regional Inspectorates of Plant Health and Seed Inspection. Alerts were issued in case of:
  - MRL excessed by over 100% (RASFF report);
  - detection of residues of unwanted pesticides in certain plant products (information in test reports)
  - Interactive cooperation with regional branches of the Main Inspectorate of Plant Health and Seed Inspection with reference to detected residues

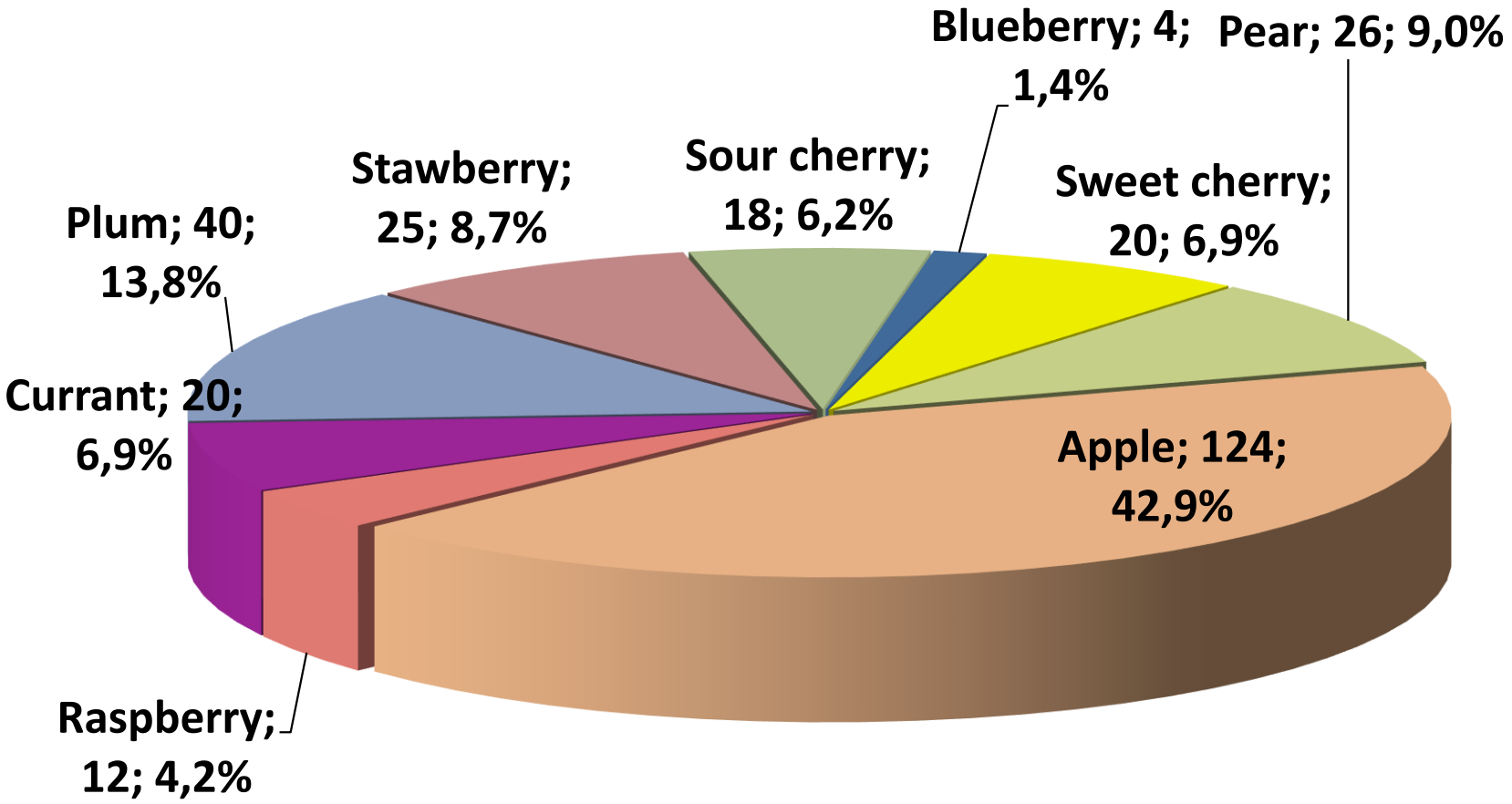
LEGAL BASIS OF TEST RESULT INTERPRETATION

- Regulation of the European Commission and the Council no. 396/2005 as amended
- Plant Protection Products Register in the MARD
- Current labels of the Plant Protection Products

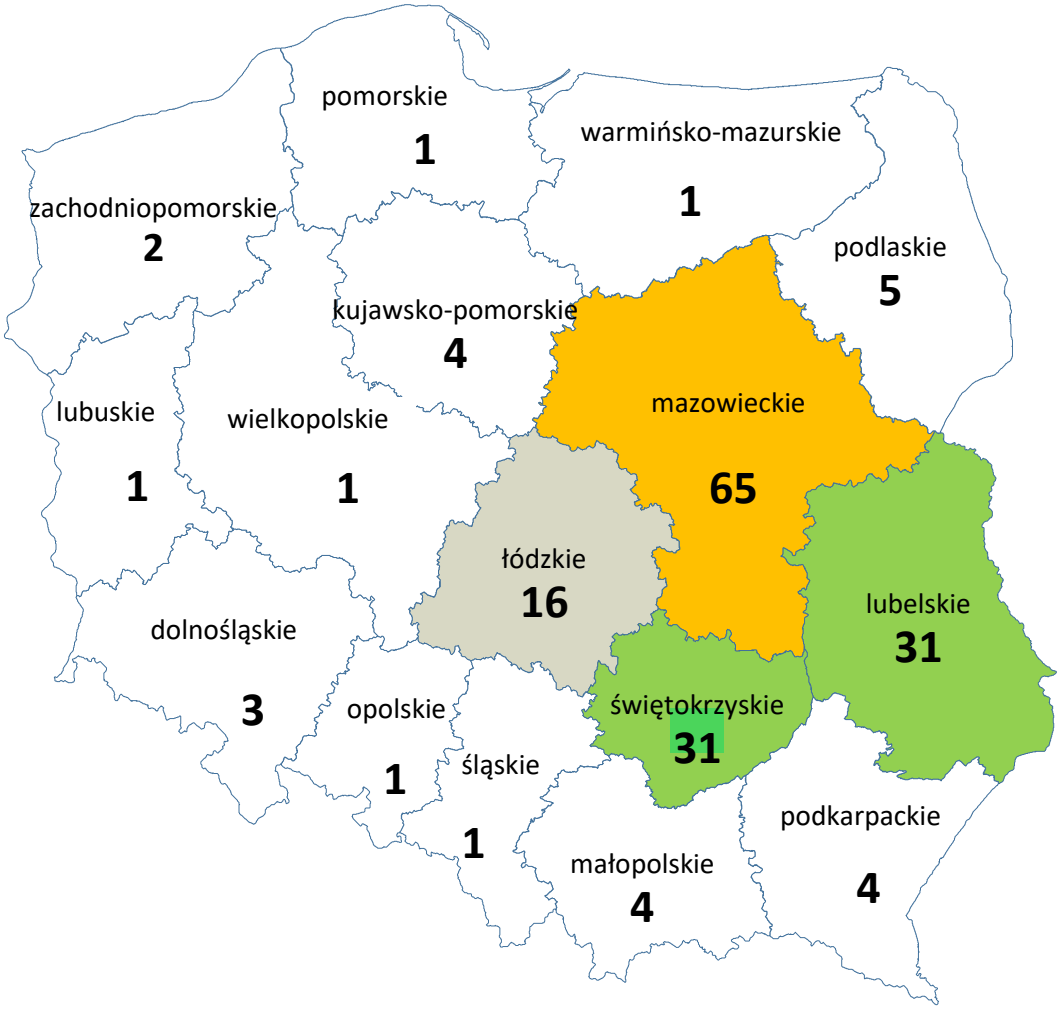
Samples provided by PIORIN (Plant Health and Seed Inspection) - 1089



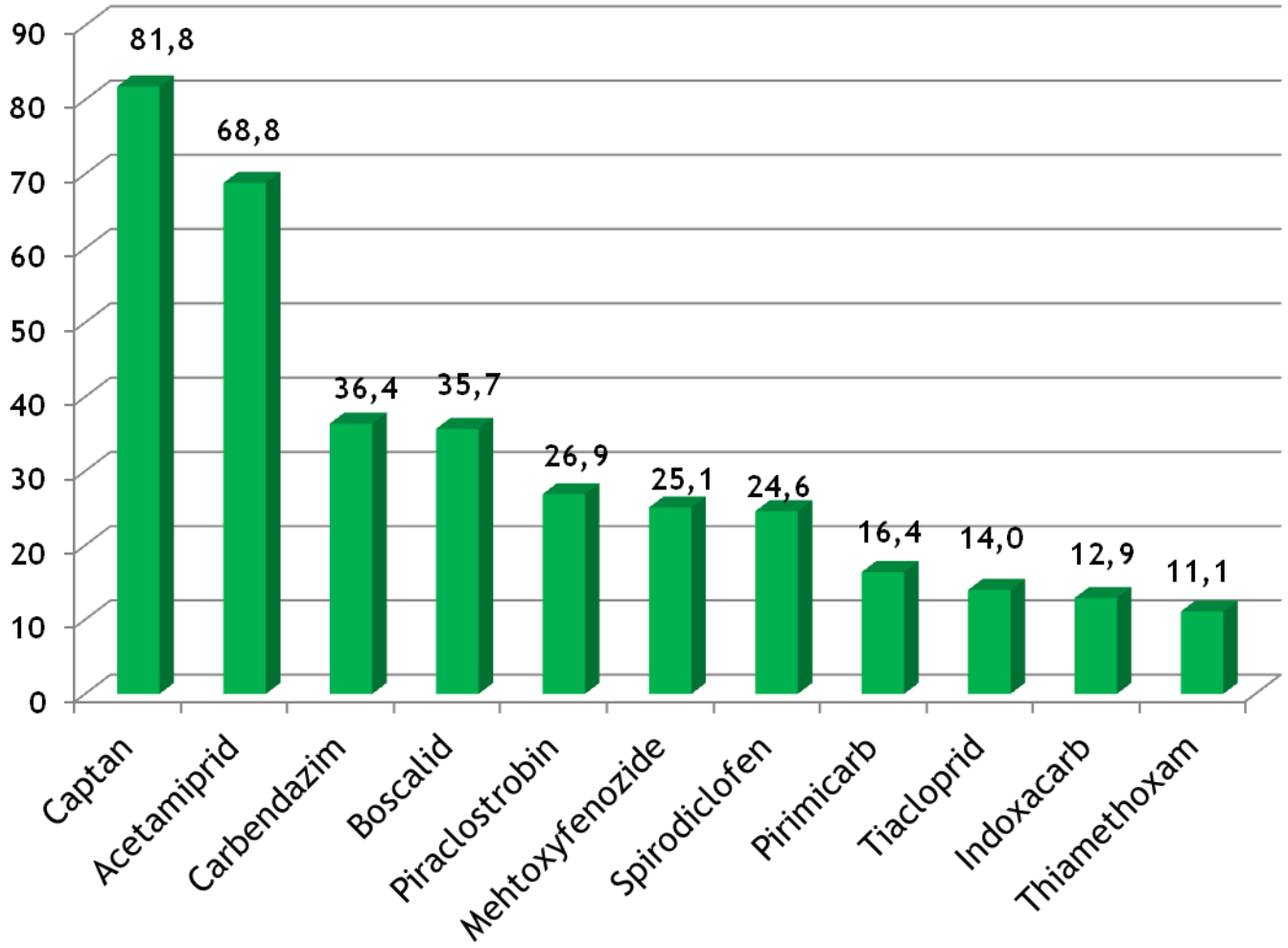
289 samples of fruits (9 species)



APPLE SAMPLING (171 SAMPLES)

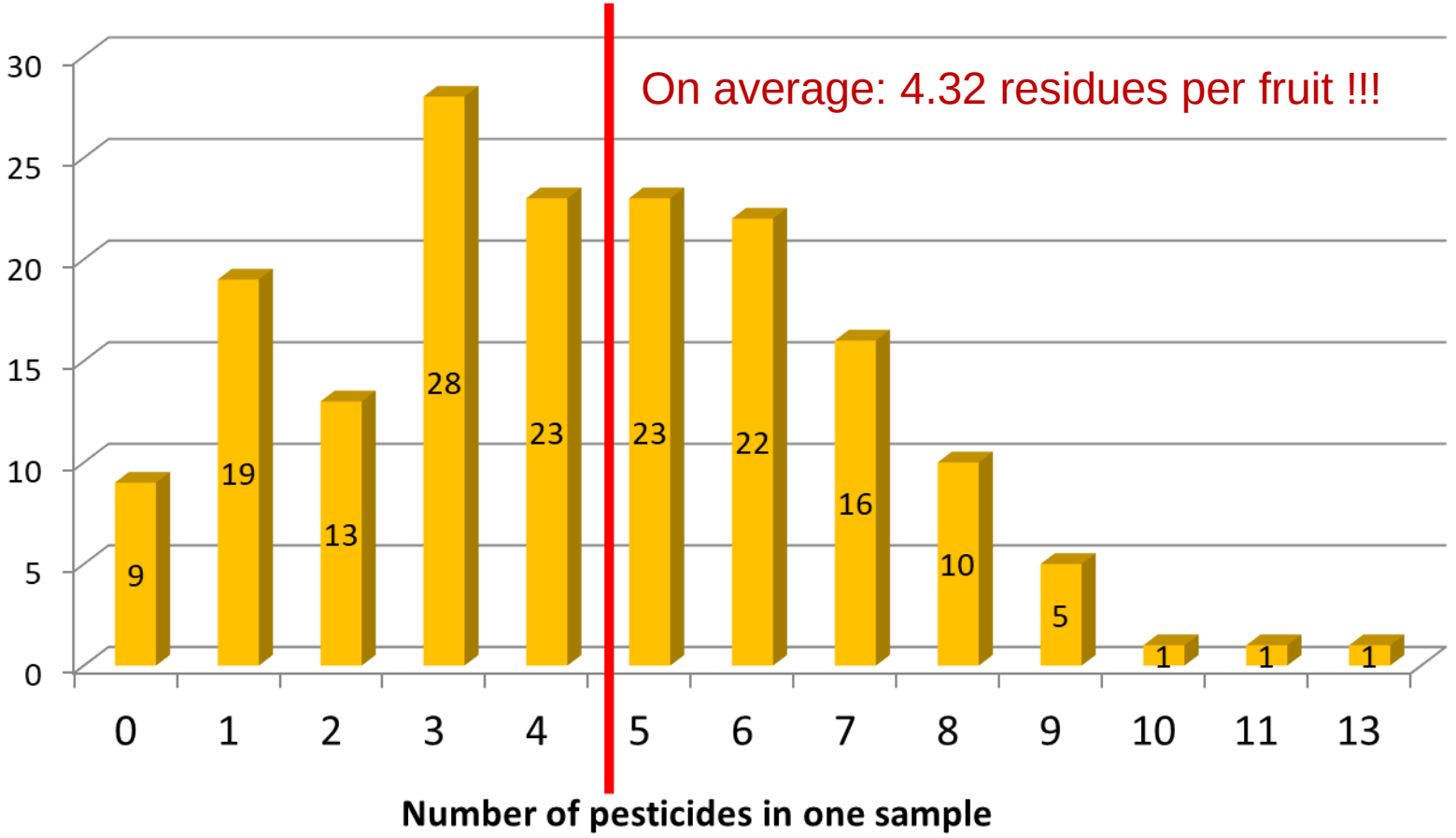


Most commonly detected pesticides in apple (correctly used)



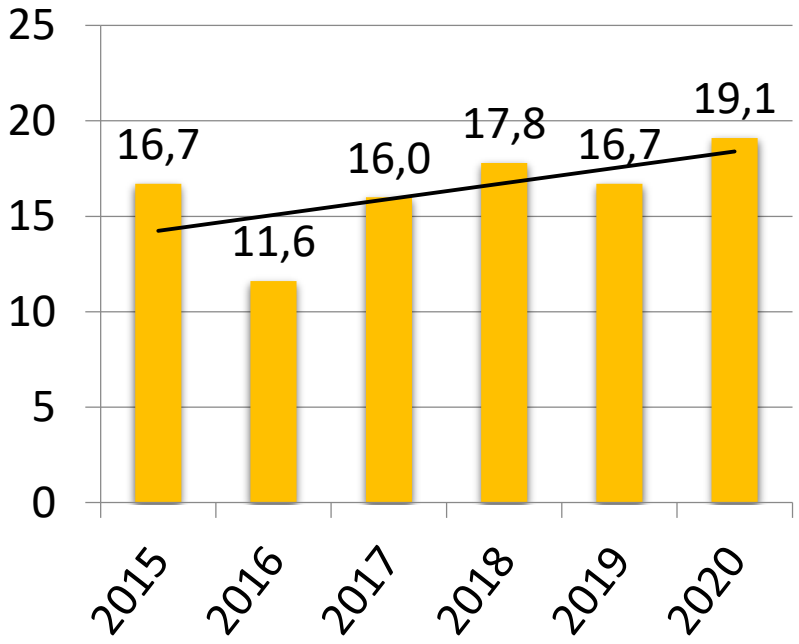
How many pesticides we can find in one apple sample

(samples from 171 orchards)

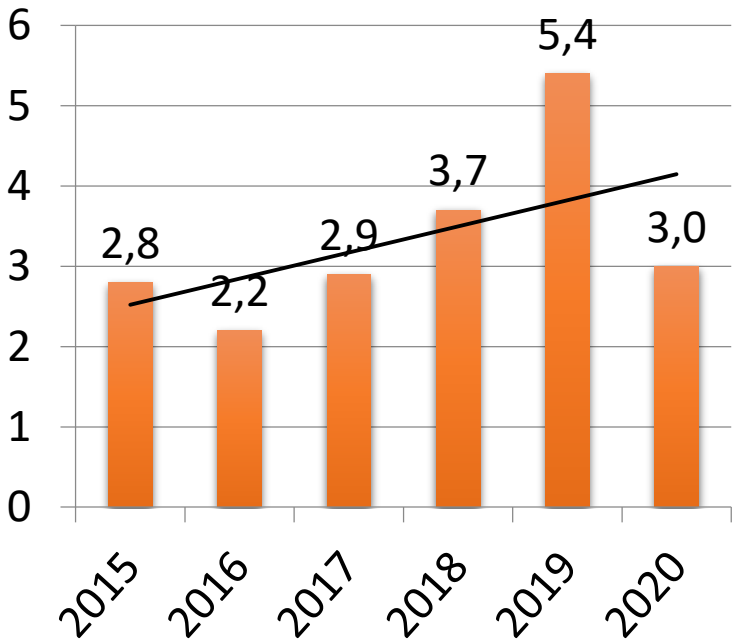


Overall evaluation of all crops

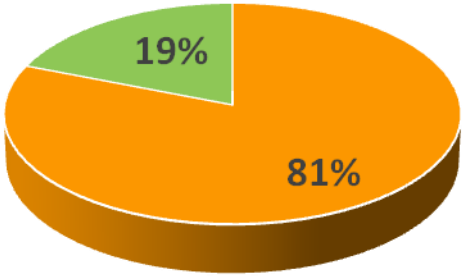
- **Unauthorized use in a given crop**

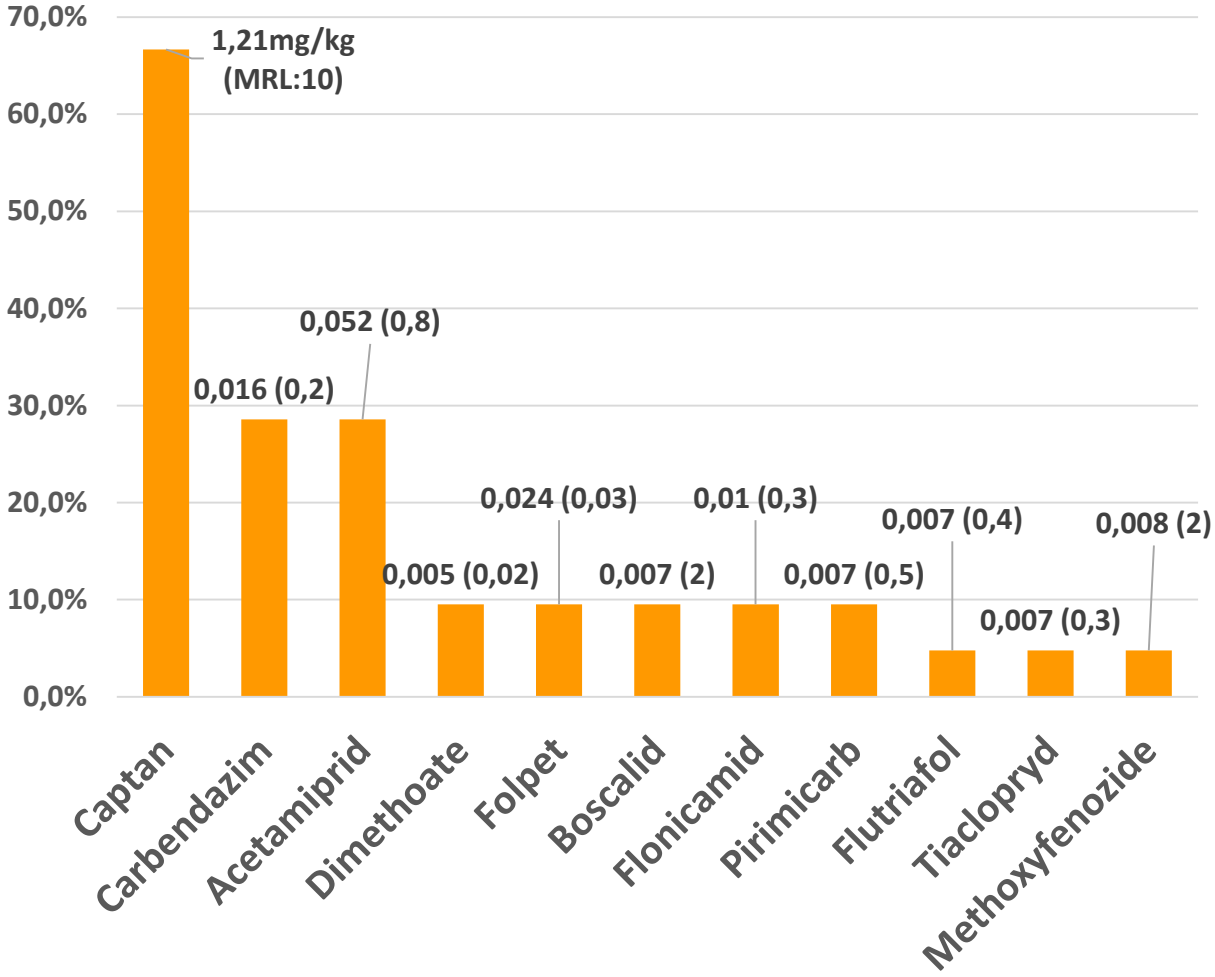


- **MRL vialations**



Pesticide residues in concentrated juice

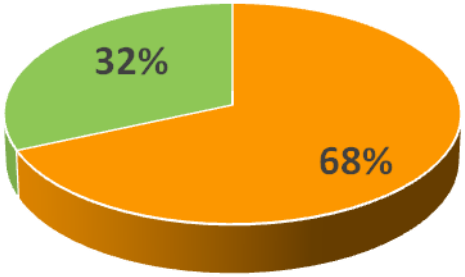




Detected

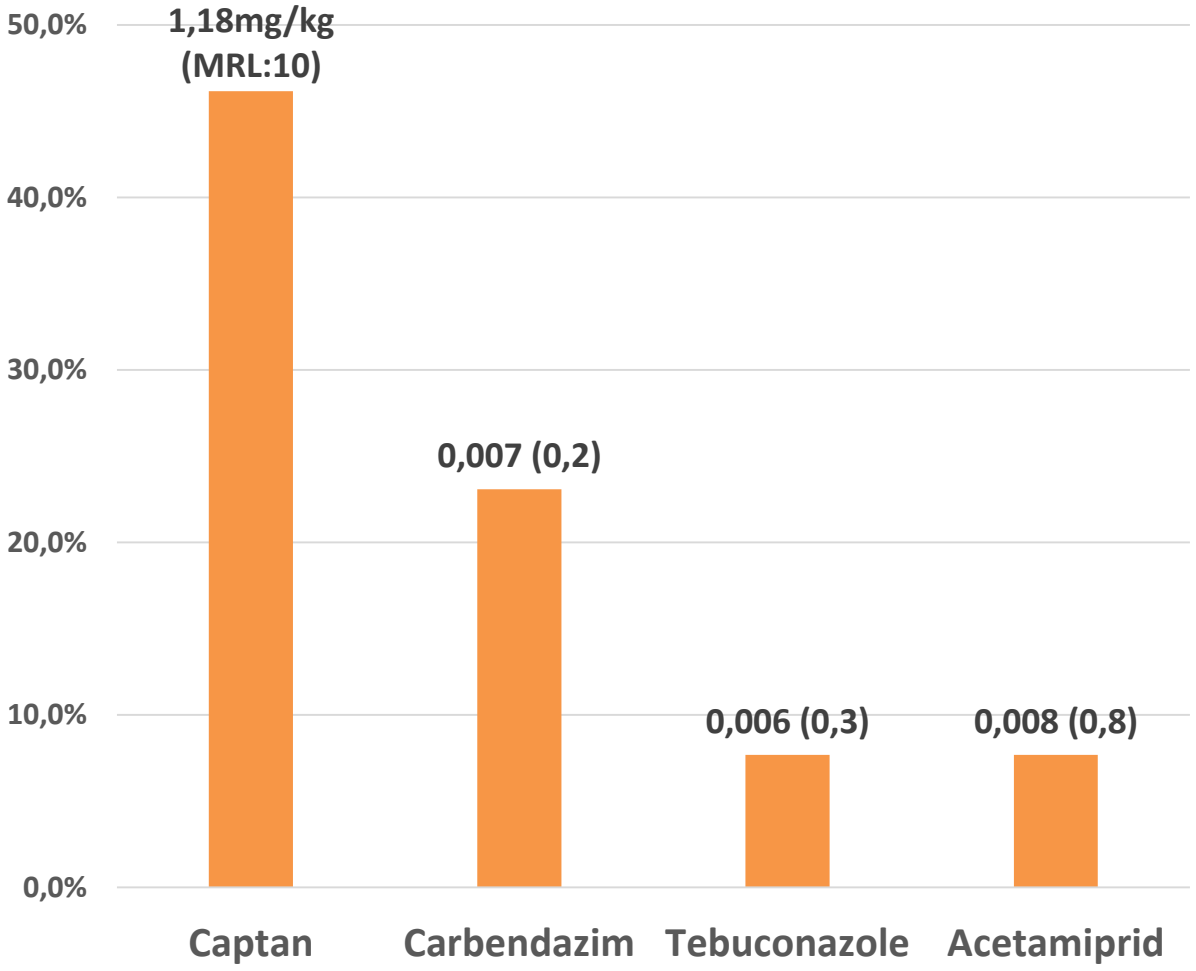
Not detected

Pesticide residues in juice from concentrate

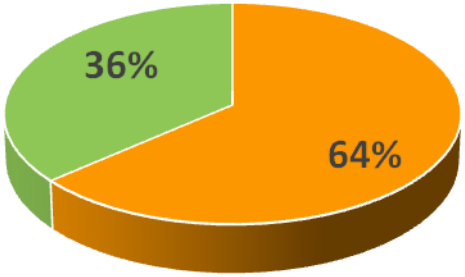


Detected

Not detected

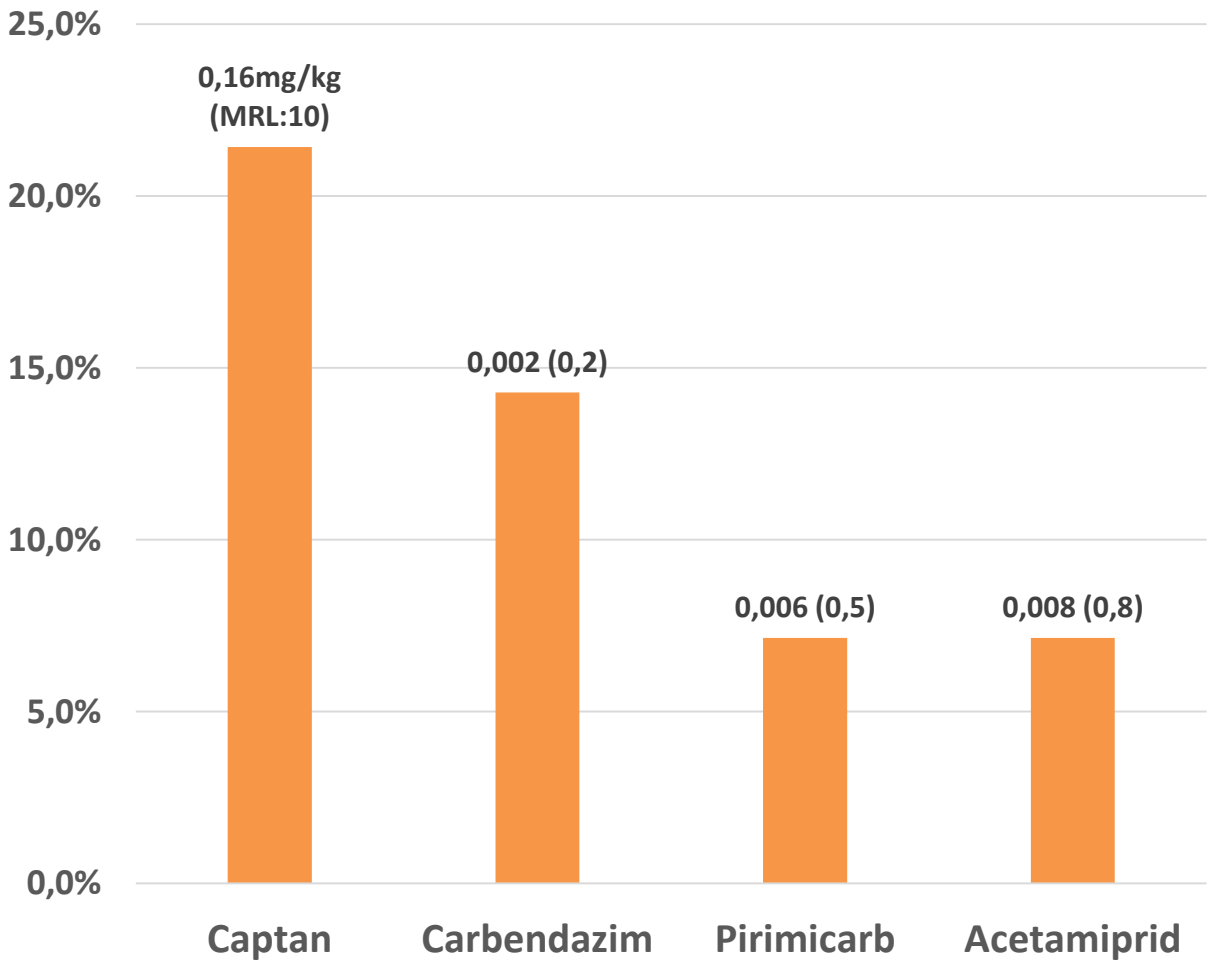


Pesticide resideus in NFC juice



Detected

Not detected



Results of apple pomace tests

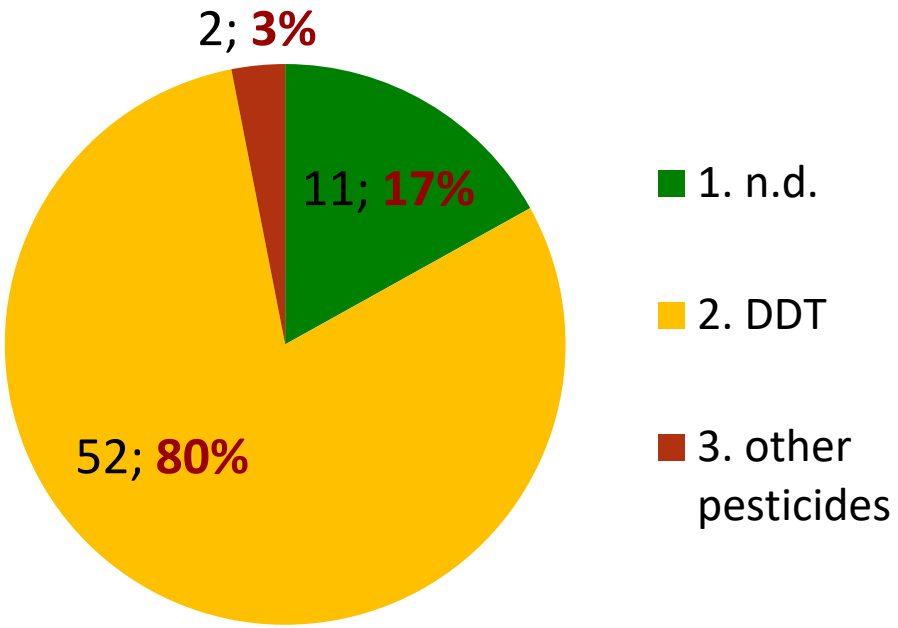
(example of summing up of residues in the product coming from various sources. Concentration 8 times higher than in fresh fruit)

Name	Result [mg/kg]	MRL [mg/kg]	Name	Result [mg/kg]	MRL [mg/kg]
Biphentin	0.038	2.4	Pyraclostrobin	0.96	4
Boskalid	1.91	16	Triadimenol	0.011	1.6
Chloropiryphos	0.082	0.08	Trifloxystrobin	0.13	4
Cypermethrin	0.074	8	Acetamiprid	0.050	6.4
Cyprodinil	0.16	8	Chlorantraniliprole	0.054	4
Difenoconazol	0.042	4	Diflubenzuron	0.034	40
Fenazaquin	0.018	0.8	Fenpyroxymate	0.022	2.4
Fludioxonil	0.12	4	Hexytiazox	0.0082	8
Flusilazole	0.017	0.16	Indoxacarb	0.20	4
Captan	0.69	24	Carbendazim	0.047	1.6
Pyrimethanil	0.021	56	Metoxyphenozide	0.13	16
Pyrimicarb	0.036	16	Pirydaben	0.0013	4
Propargit	0.41	0.08	Spirodiclofen	0.070	4
Propiconazol	0.013	1.2	Tebuconazol	0.011	2.4

Pesticide residues in soil

- Detected pesticides
- Azoxystrobin
- Bifenthrin
- Boscalid
- Bromopropylate
- Chlorpyrifos
- Difenoconazole
- Endosulfan
- Etofumesat
- Flusilazol
- Pendimethalin
- Propargite
- Trifluralin

65 samples of soil

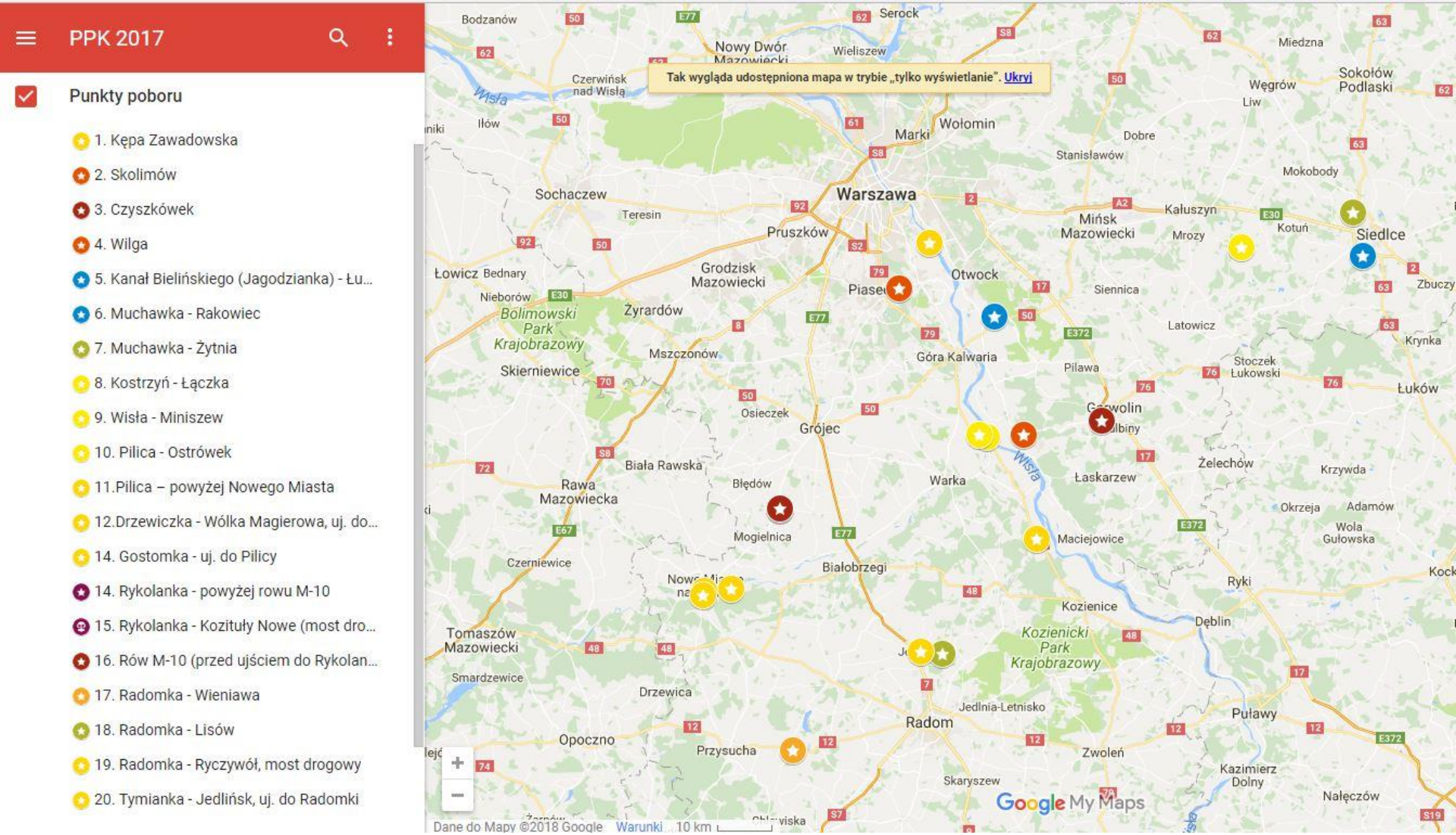


DDT: 0,001 – 0.29 mg/kg avg: 0,015 mg/kg

Scope of the method for water

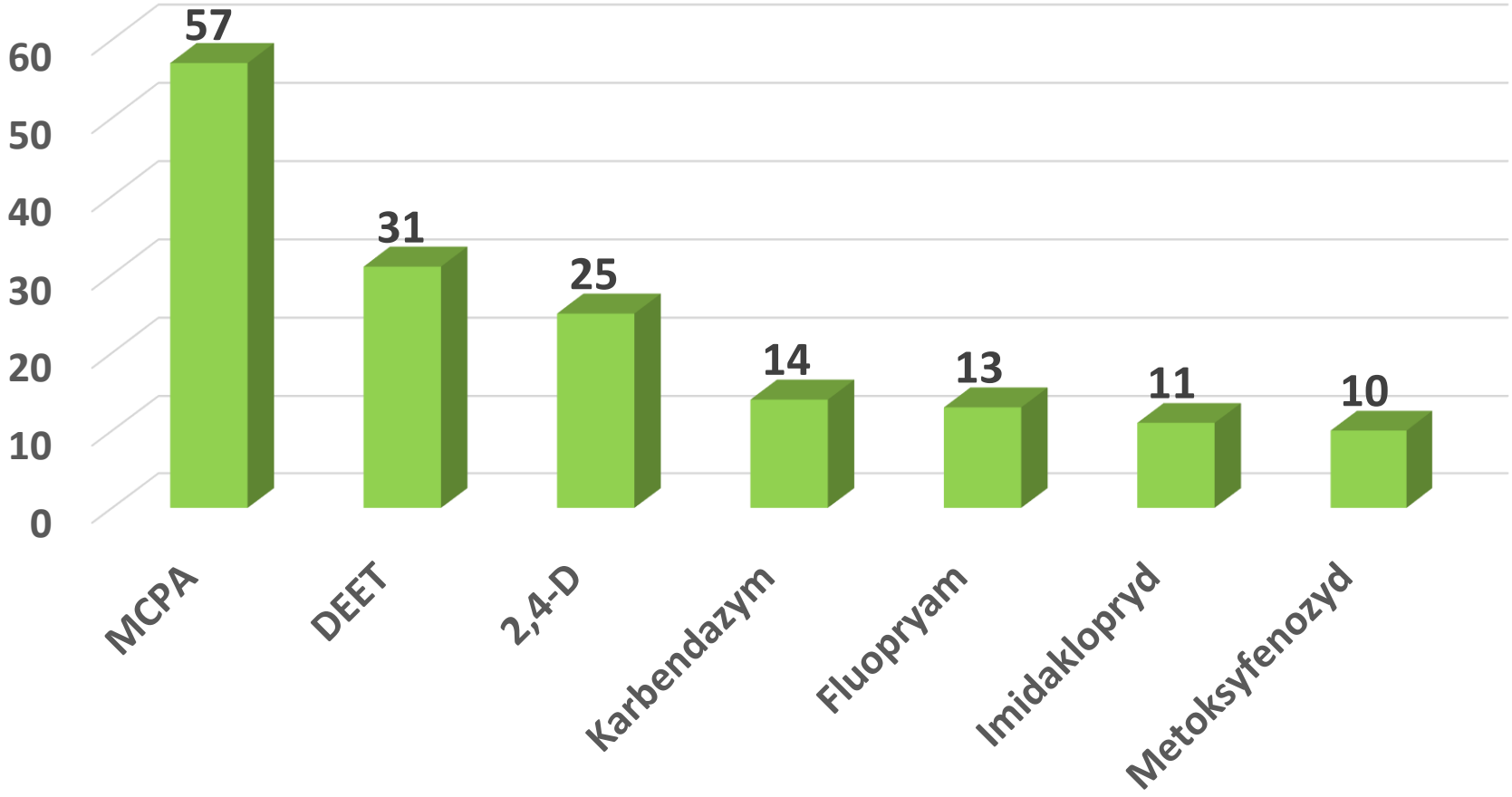
Lp.	Nazwa środka ochrony roślin	DGO µg/l	Lp.	Nazwa środka ochrony roślin	DGO µg/l	Lp.	Nazwa środka ochrony roślin	DGO µg/l
1.	Acetamipryd	0,05	34.	Fentoat	0,05	67.	Metosulam	0,05
2.	Ametoktradyna	0,05	35.	Fluazyfop	0,05	68.	Metrafenon	0,05
3.	Amidosulfuron	0,05	36.	Flufenacet	0,05	69.	Metsulfuron metylu	0,05
4.	Azoksystrobina	0,05	37.	Fluoksastrobina	0,05	70.	Monokrotofos	0,05
5.	Bentazon	0,05	38.	Fluopikolid	0,05	71.	Napropamid	0,05
6.	Bromacyl	0,05	39.	Fluoksypyr	0,05	72.	Oksadiksyl	0,05
7.	Bromoksynil	0,05	40.	Flutolanil	0,05	73.	Oksamyl	0,05
8.	Chizalofop etylowy	0,05	41.	Flutriafol	0,05	74.	Ometoat	0,05
9.	Chloridazon	0,05	42.	Fuberidazol	0,05	75.	Paraokson metylowy	0,05
10.	Chromafenozyd	0,05	43.	Haloksyfop	0,05	76.	Pencykuron	0,05
11.	2,4-D	0,05	44.	Imazalil	0,05	77.	Pinoksaden	0,05
12.	2,4-DB	0,05	45.	Iprowalikarb	0,05	78.	Prokwinazyd	0,05
13.	DEET	0,05	46.	Izoproturon	0,05	79.	Propoksur	0,05
14.	Demeton-S metylowy	0,05	47.	Izopyrazam	0,05	80.	Prosulfokarb	0,05
15.	–sulfon	0,05	48.	Kadusafos	0,05	81.	Siltiofam	0,05
16.	–sulfotlenek	0,05	49.	Karbaryl	0,05	82.	Spiroksamina	0,05
17.	Dichlorprop	0,05	50.	Karbendazym	0,05	83.	Spirotetramat	0,05
18.	Dietofenkarb	0,05	51.	Karbofuran	0,05	84.	Sulfometuron metylowy	0,05
19.	Dimetenamid-P	0,05	52.	Karbofuran-3-hydroksy	0,05	85.	Tebufenozyd	0,05
20.	Dimetoat	0,05	53.	Lenacyl	0,05	86.	Terbufos sulfotlenek	0,05
21.	Etirimol	0,05	54.	Malaokson	0,05	87.	Terbutylazyna	0,05
22.	Fenamidon	0,05	55.	Malation	0,05	88.	Tiabendazol	0,05
23.	Fenamifos	0,05	56.	Mandipropamid	0,01	89.	Tiachlopryd	0,05
24.	–sulfon	0,05	57.	MCPA	0,05	90.	Tiodikarb	0,05
25.	-sulfotlenek	0,05	58.	MCPB	0,05	91.	Tralkoksydym	0,05
26.	Fenobukarb	0,05	59.	Mekoprop	0,05	92.	Zoksamid	0,05
27.	Fenoksaprop-P	0,05	60.	Metalaksyl	0,05			
28.	Fenpropidyna	0,05	61.	Metamidofos	0,05			
29.	Fenpropimorf	0,05	62.	Metiokarb sulfotlenek	0,05			
30.	Fensulfotion	0,05	63.	Metoksuron	0,05			
31.	-sulfon	0,05	64.	Metoksyfenozyd	0,05			
32.	–okson	0,05	65.	Metolachlor-S	0,05			
33.	–sulfon oksonu	0,05	66.	Metomyl	0,05			

Sampling of water
(Inspectorate of Enviromental Protection)

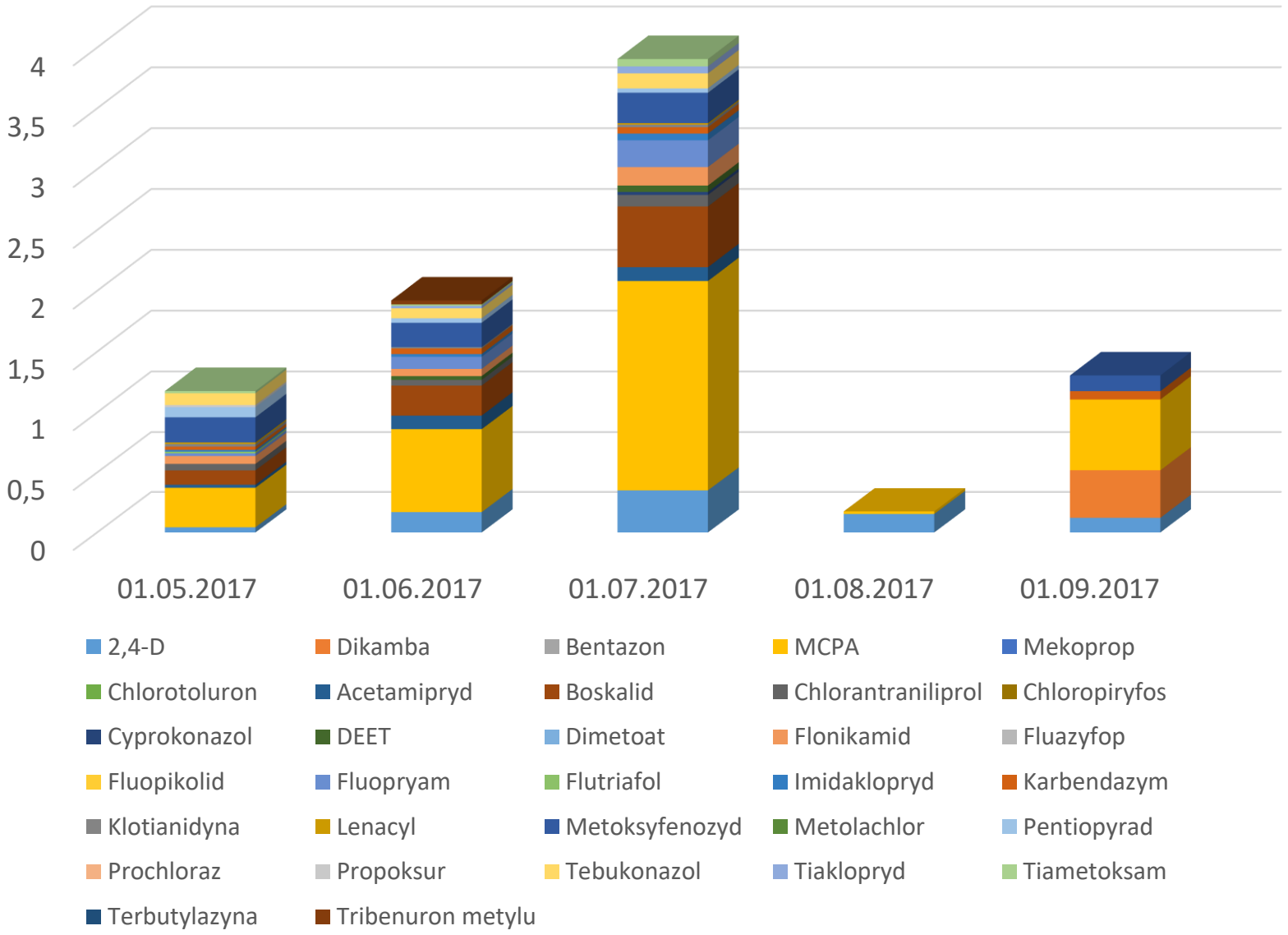


Most often detected pesticides in water

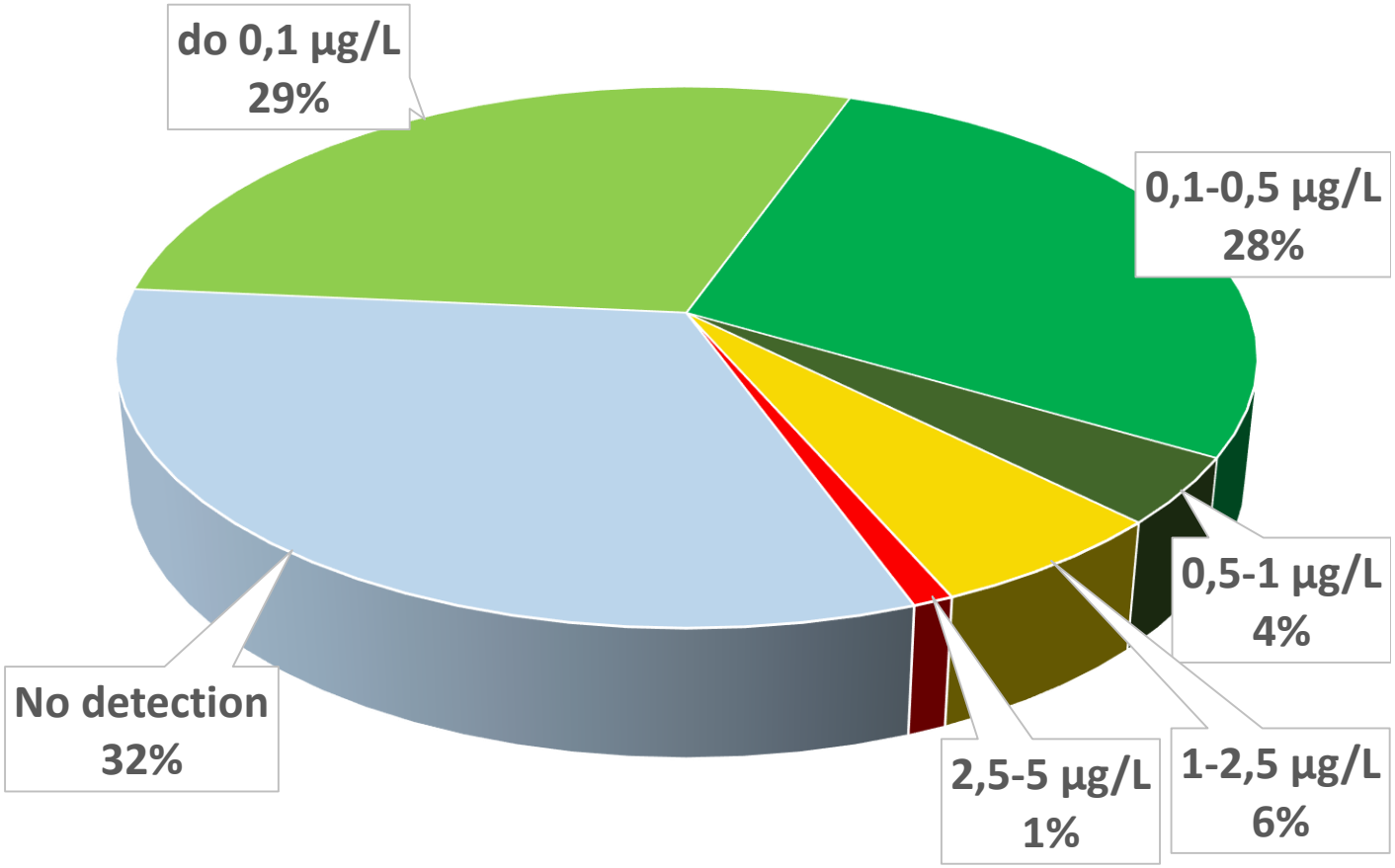
(32 various pesticides)



Results from one sampling point: Rykolanka river



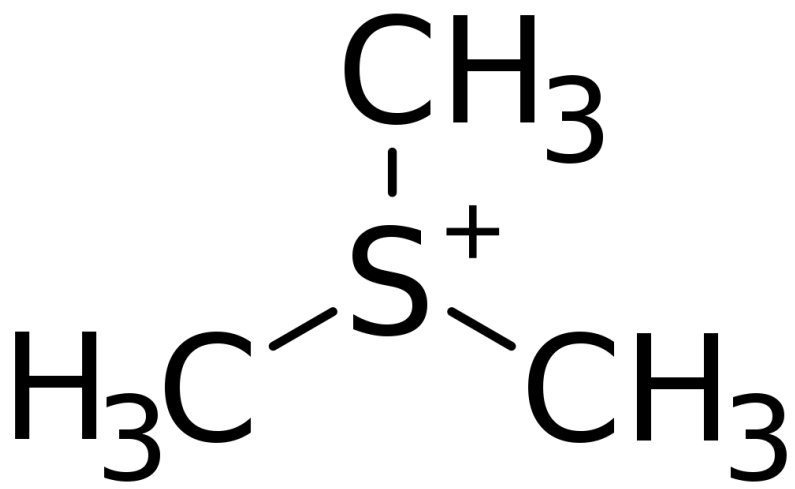
Overall assessment of the samples (100)



The highest value: 3,9 µg/L

Tea bag warning !!!

Trimethyl-Sulphonium cation



- **Resulting from the use of glyphosate (Glyphosate-trimesium)**
- **Not allowed use in EU**
- **MRL for tea: 0,05 mg/kg**

Keep Smile and Be Safe ☺

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THANK YOU FOR ATTENTION!