# News on SRMs

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EURL-SRM

Joint EURL Workshop
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# LAB-PRIORITIES

1st MRM-Compound
2nd MRM-Compound
3rd MRM-Compound
4th MRM-Compound
5th MRM-Compound

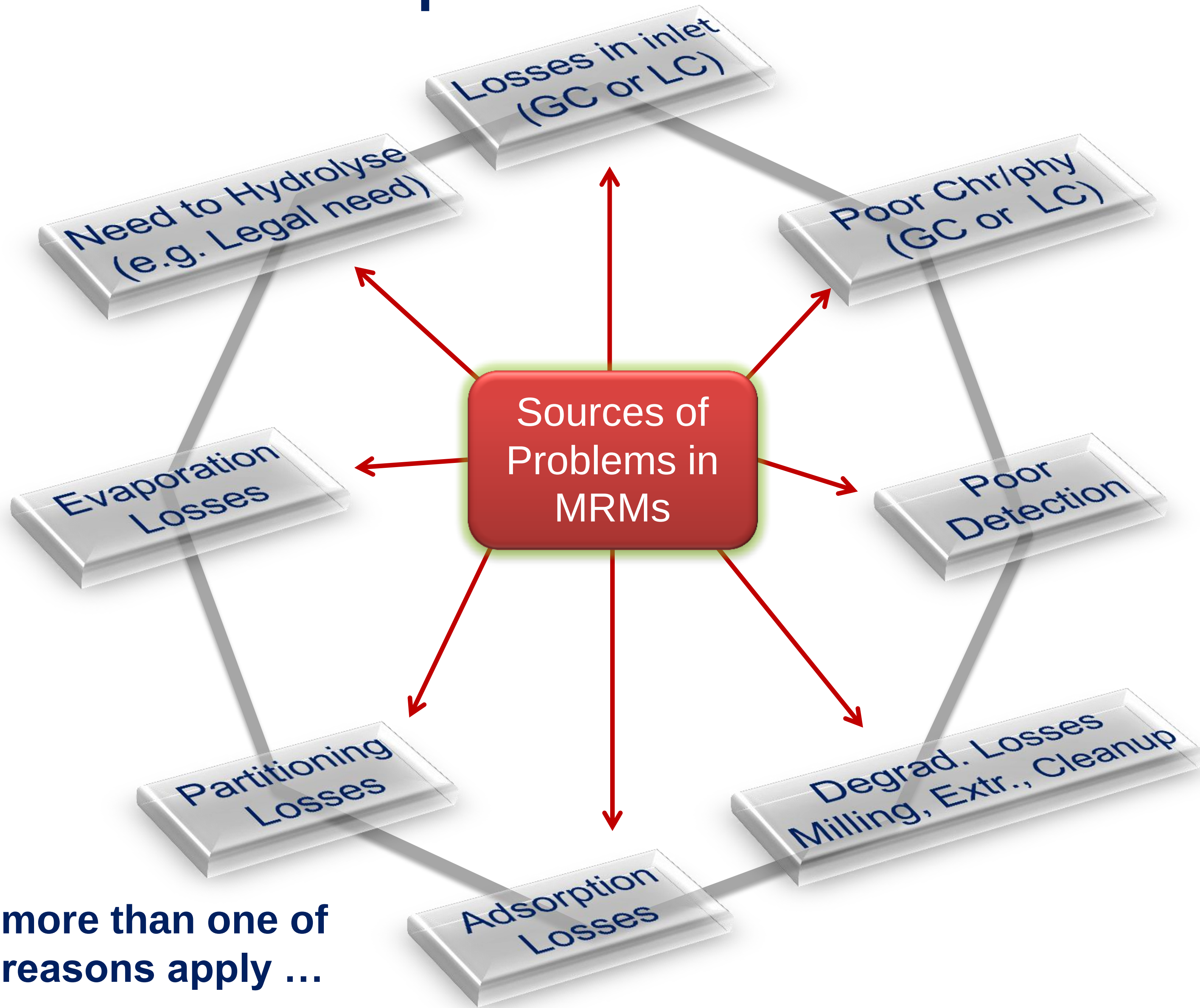
⋮

96th ~~SRM-Compound~~ (shift ↓ to 136th)
97th SRM-Compound (maybe)

**SRM-compounds are not very popular ...**

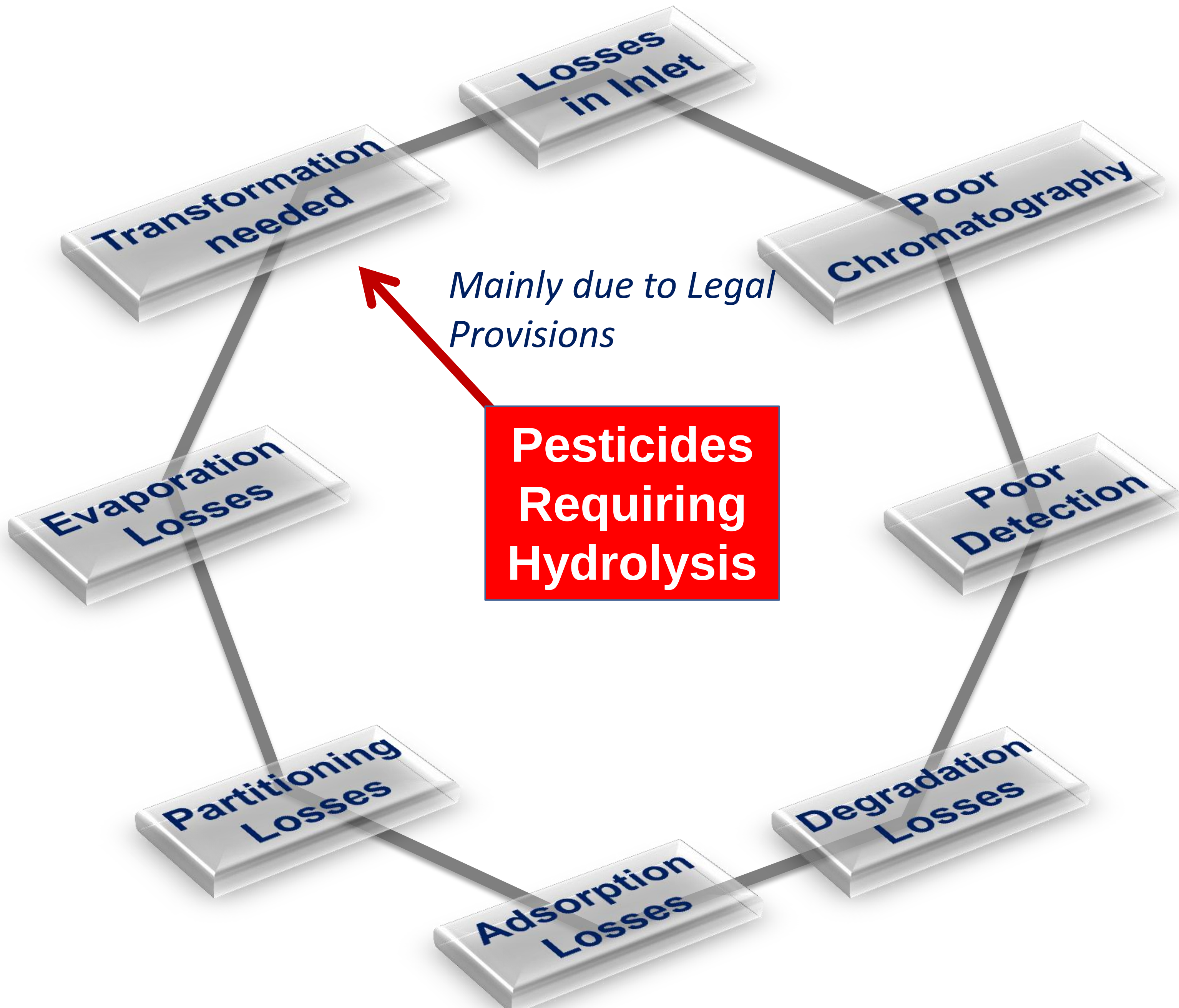
**Let’s take**
**a closer look**
**at the SRM pesticides**

# What makes a compound non-amenable to MRMs?




**Often more than one of these reasons apply …**

# What makes a compound non-amenable to MRMs?



# Some Residue Definitions requiring Hydrolysis

Parent often MRM-amenable!

| Compound | Residue definition |
|---|---|
| **Amitraz** | amitraz including the metabolites contyaining the 2,4 -dimethylaniline moity expressed as amitraz |
| **Cycloxydim** | including degradation and reaction products which can be determined as 3-(3-thianyl)glutaric acid S-dioxide (BH 517-TGSO2) and/or 3-hydroxy-3-(3-thianyl)glutaric acid S-dioxide (BH 517-5-OH-TGSO2) or methyl esters thereof, calculated in total as cycloxydim |
| **Dinocap** | sum of dinocap isomers and their corresponding phenols expressed as dinocap |
| **Diuron** | Diuron including all components containing 3,4- dichloraniline moiety expressed as 3,4-dichloraniline |
| **Flufenacet** | sum of all compounds containing the N fluorophenyl-N-isopropyl moiety expressed as flufenacet equivalent |
| **Prochloraz** | sum of prochloraz and its metabolites containing the 2,4,6-Trichlorophenol moiety expressed as prochloraz |
| **Pyridate** | sum of pyridate, its hydrolysis product CL 9673 (6-chloro-4-hydroxy-3-phenylpyridazin) and hydrolysable conjugates of CL 9673 expressed as pyridate |
| **Vinclozolin** | sum of vinclozolin and all metabolites containing the **3,5-dichloraniniline moiety**, expressed as vinclozolin |

**MAIN STRATEGY:**

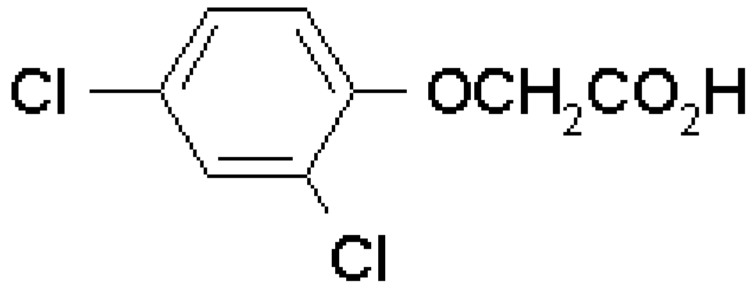
Modify residue definitions to only include major MRM-amenable components

# Some Residue Definitions concerning acidic pesticides

| Compound | Residue definition | Free Acids | Acids released via hydrolysis | |
|---|---|---|---|---|
| | | | Esters | Conjug. |
| **2,4-D** | 2,4-D (sum of 2,4-D and its **esters** expressed as 2,4-D) | X | X | |
| **2,4-DB** | Sum of 2,4-DB, its salts, its **esters** and its **conjugates**, expressed as 2,4-DB | X | X | X |
| **Cyhalofop** | sum of **cyhalofop butyl** and its free acids | X | X | |
| **Fluazifop** | **Fluazifop-P-butyl** (fluazifop acid (free and **conjugate**)) | X | (X) | X |
| **Fluroxypyr** | Fluroxypyr including its **esters** expressed as fluroxypyr | X | X | |
| **Haloxyfop** | Haloxyfop-R **methyl ester**, haloxyfop-R and **conjugates** of haloxyfop-R expressed as haloxyfop-R | X | (X) | X |
| **Ioxynil** | Sum of Ioxynil, its salts and its **esters**, expressed as ioxynil | X | X | |
| **MCPA / MCPB** | MCPA, MCPB including their salts, **esters** and **conjugates** expressed as MCPA | X | X | X |
| **Prohexadione** | Prohexadione (acid) and its salts expressed as prohexadione-calcium | X | | |

# Pesticides requiring a hydrolysis step

## 2,4-D




- Selective systemic herbicide
- Control of broad leaved weed
- Plant growth regulator used to prevent premature fruit drop
- Formulations include free acid, salts, esters
- May form conjugates (covalent binding to matrix components)

→ hydrolysis step needed
if residue definition includes conjugates and/or esters

# QuEChERS combined with Alkaline Hydrolysis

- Previous approach Hydrolysis by adding base directly to sample
- New approach: Hydrolysis after ACN-addition (first extraction step)
- Efficient hydrolysis of esters

**Weigh 10 g of Frozen Sample**

**Add 10 mL Acetonitrile + NaOH**

**Shake for 30 min at 40°C**

**Neutralize with $H_2SO_4$ + shake**

**Add ISTD-Solution**

Shake

**Add 4 g $MgSO_4$ / 1 g NaCl / Citrate Buffer**

Shake and Centrifuge

**Analysis of acidic pesticides by LC-MS/MS**

optionally:

Cleanup aliquot via Freeze-out

Collaboration with German NRL-SRM and BfR (interlab. Validation planned)

# Excellent hydrolysis of esters with new approach

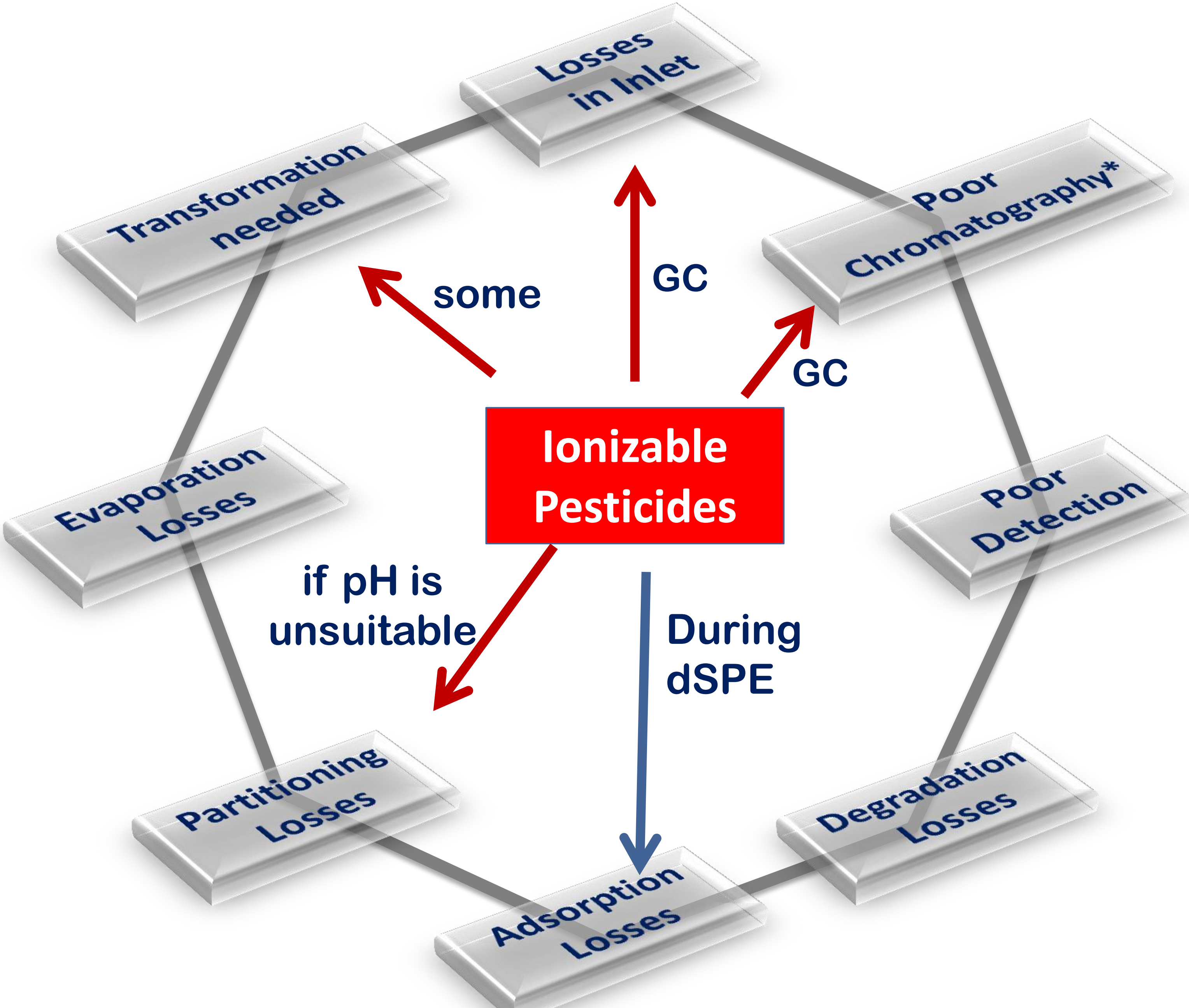
| Remaining Esters after AH (%) | 30 Min , 40°C | 60 Min , 40°C | 30 Min , 80°C | 30 Min , 40°C | 60 Min , 40°C | 30 Min , 80°C |
|---|---|---|---|---|---|---|
| | Hydrolysis before ACN-Addition | | | Hydrolysis **during extraction** | | |
| **2,4-DP-ethyl-hexyl** | 104 | 65 | 11 | **0** | **6** | **4** |
| **Cyhalofop-butyl** | 20 | 10 | 0 | **0** | **0** | **0** |
| **Diclofop methyl** | 15 | 7 | 2 | **2** | **1** | **1** |
| **Fluazifop-(P)-butyl** | 22 | 12 | 0 | **0** | **0** | **0** |
| **Fluroxypyr-1-meptyl** | 70 | 29 | 3 | **0** | **0** | **0** |
| **Haloxyfop-ethoxyethyl** | 11 | 6 | 0 | **0** | **0** | **0** |
| **MCPA butoxyethyl** | 3 | 2 | 0 | **0** | **0** | **0** |
| **Mecoprop-1-octyl** | 110 | 70 | 12 | **0** | **0** | **0** |

Matrix: Cucumber Level: 0,2ppm

# Impact of AH on results of acidic pesticides (real samples)

| Sample Name | Compound | Conc. using QuEChERS [mg/kg] | Conc. using QuEChERS w. AH (30 Min, 40°C) [mg/kg] | Ratio (QuEChERS = 100%) |
|---|---|---|---|---|
| **DRIED SAMPLES** | | | | |
| **Beans, dry 1** | **Fluazifop** | 0,053 | 0,067 | **125** |
| **Beans, dry 2** | **Haloxyfop** | 1,133 | 1,120 | 99 |
| **Lentils, dry (green)** | **2,4-D** | 0,078 | 0,077 | 99 |
| **Lentils, dry (red)** | **Haloxyfop** | 0,128 | 0,149 | 116 |
| **Peas, dry (yellow) 1** | **2,4-D** | 0,107 | 0,104 | 97 |
| **Peas, dry (yellow) 2** | **Fluazifop** | 0,362 | 0,482 | **133** |
| **Soya, dry** | **Fluazifop** | 0.43 | 0.52 | **120** |
| **Tomatoes dried** | **Fluazifop** | 0,036 | 0,041 | 113 |
| **Oranges, dried 1** | **2,4-D** | 0,138 | 0,294 | **213** |
| **Oranges, dried 2** | **2,4-D** | 0.015 | 0.029 | **180** |
| **Canola 1** | **2,4-D** | 0,006 | 0,020 | **356** |
| **Canola 1** | **Fluazifop** | 0,490 | 0,494 | 101 |
| **Tea** | **2,4-D** | 0.015 | 0.014 | 91 |
| **Wheat 1** | **2,4-D** | 0,075 | 0,068 | 91 |
| **Wheat 2** | **2,4-D** | 0,164 | 0,212 | **129** |
| **Oregano** | **Fluazifop** | 0,096 | 0,551 | **574** |
| **Aubergine** | **4-CPA** | 0.027 | 0.032 | 120 |
| **FRESH SAMPLES** | | | | |
| **Grapefruit** | **2,4-D** | 0.06 | 0.410 | **536** |
| **Lime** | **2,4-D** | 0.050 | 0.055 | 109 |
| **Lime** | **2,4-D** | 0.398 | 0.657 | **165** |
| **Orange 1** | **2,4-D** | 0.074 | 0.092 | **124** |
| **Orange 2** | **2,4-D** | 0.088 | 0.135 | **253** |
| **Orange 3** | **2,4-D** | 0.158 | 0.393 | **248** |
| **Beans** | **Fluazifop** | 0,359 | 0,401 | 112 |

# What makes a compound non-amenable to MRMs?



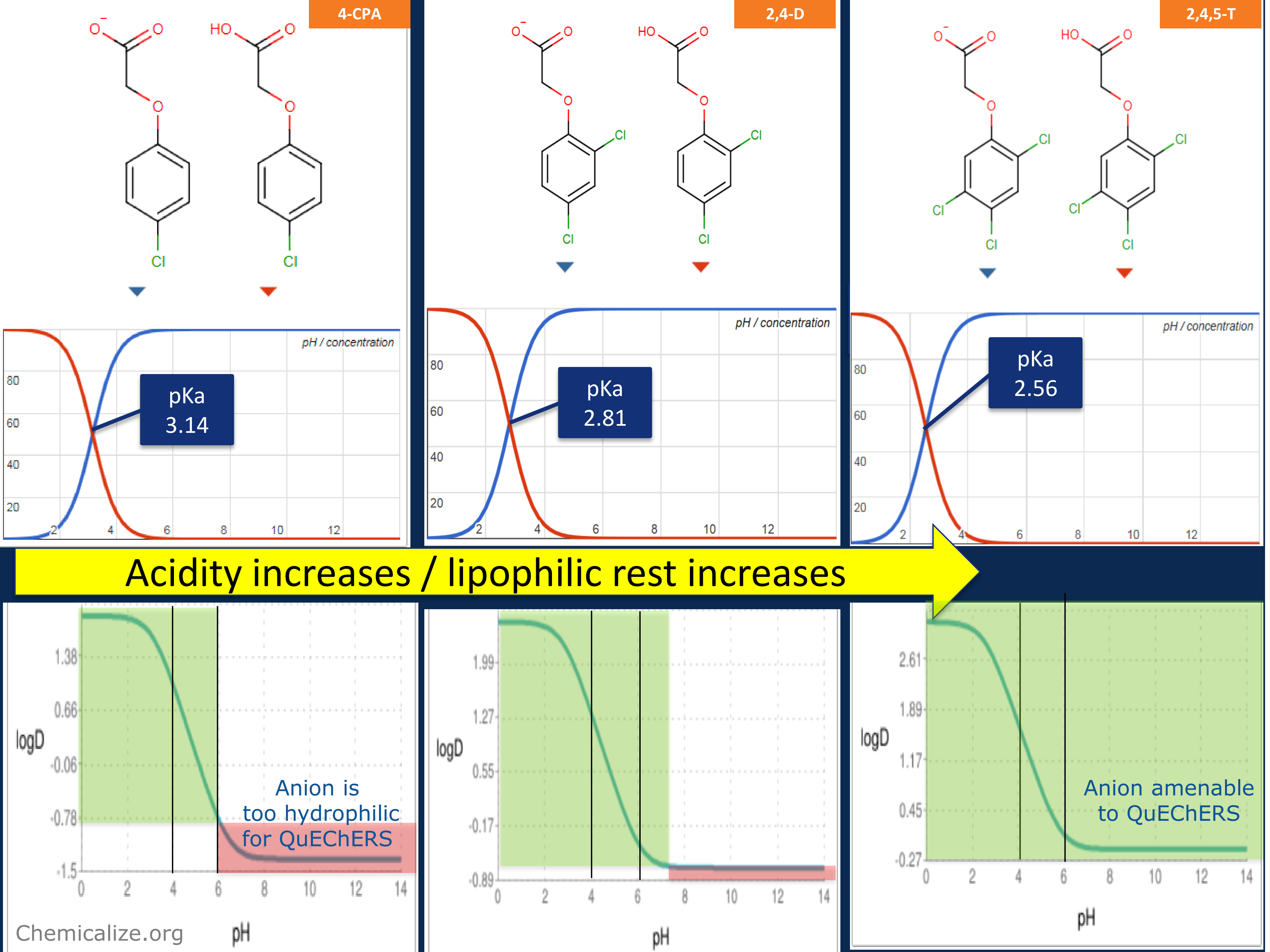
# Pesticides with pH-dependend polarity:

pH-range of agricultural samples: ~2.5 – 7

ACIDS: **HX** — High pH → / ← Low pH — **$X^-$** Ionic form

BASES: **$BH^+$** Ionic form — High pH → / ← Low pH — **B**

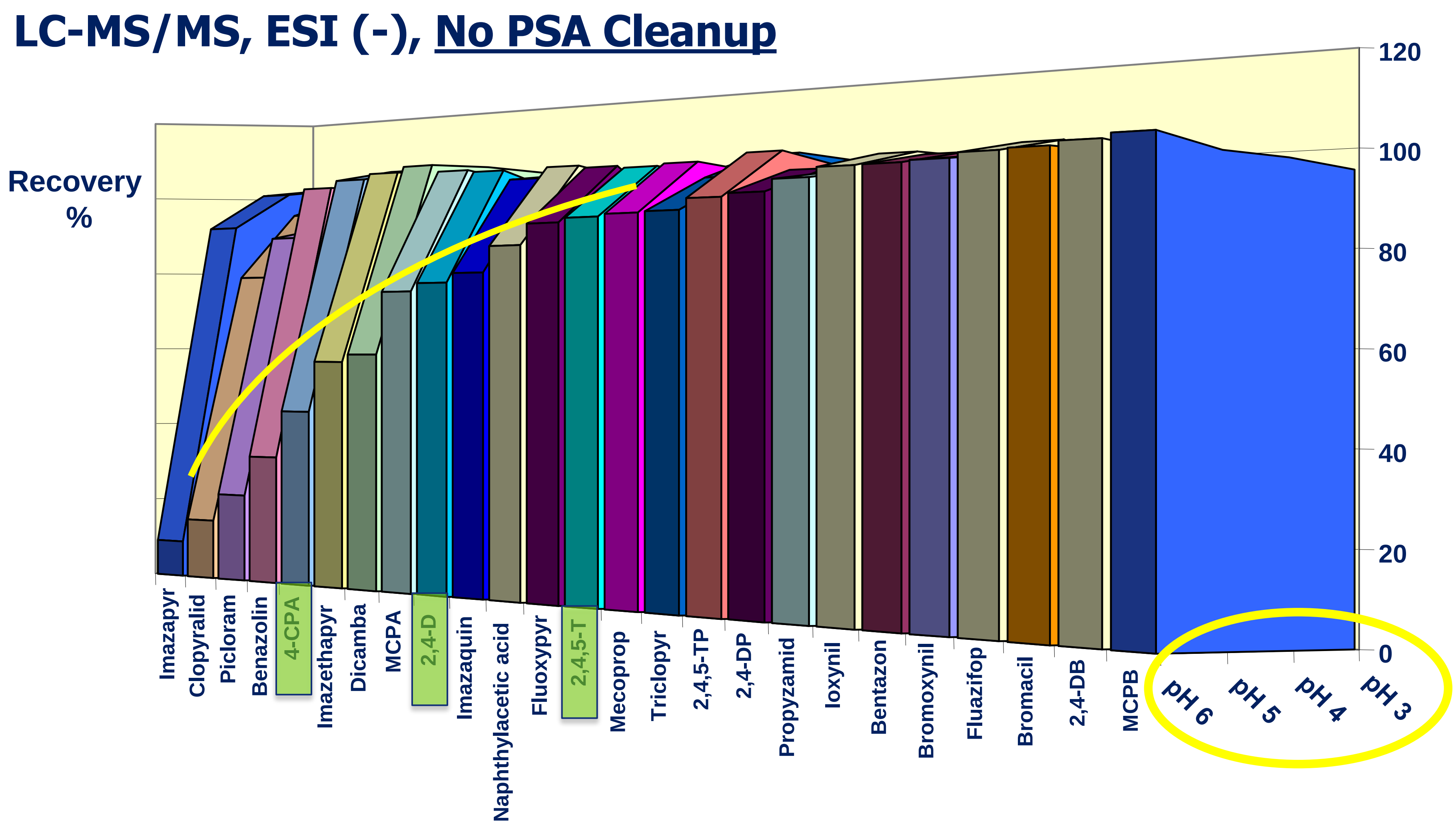
**Ionic form is much more polar!!**



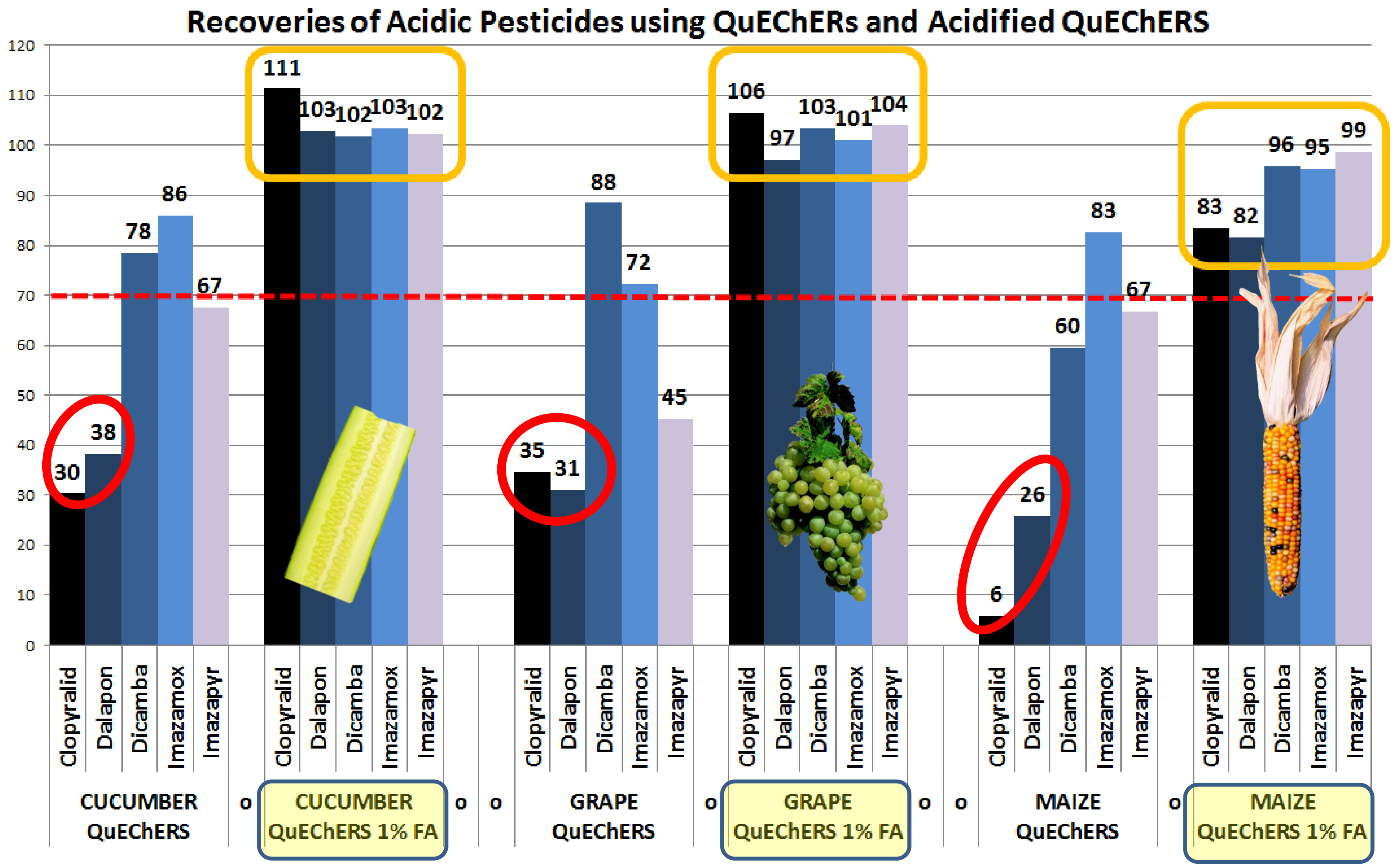
4-CPA
2,4-D
2,4,5-T
pH / concentration
pKa 3.14
pKa 2.81
pKa 2.56
Acidity increases / lipophilic rest increases
logD
pH
Anion is too hydrophilic for QuEChERS
Anion amenable to QuEChERS
Chemicalize.org

# Acidic pesticides – influence of pH on recovery

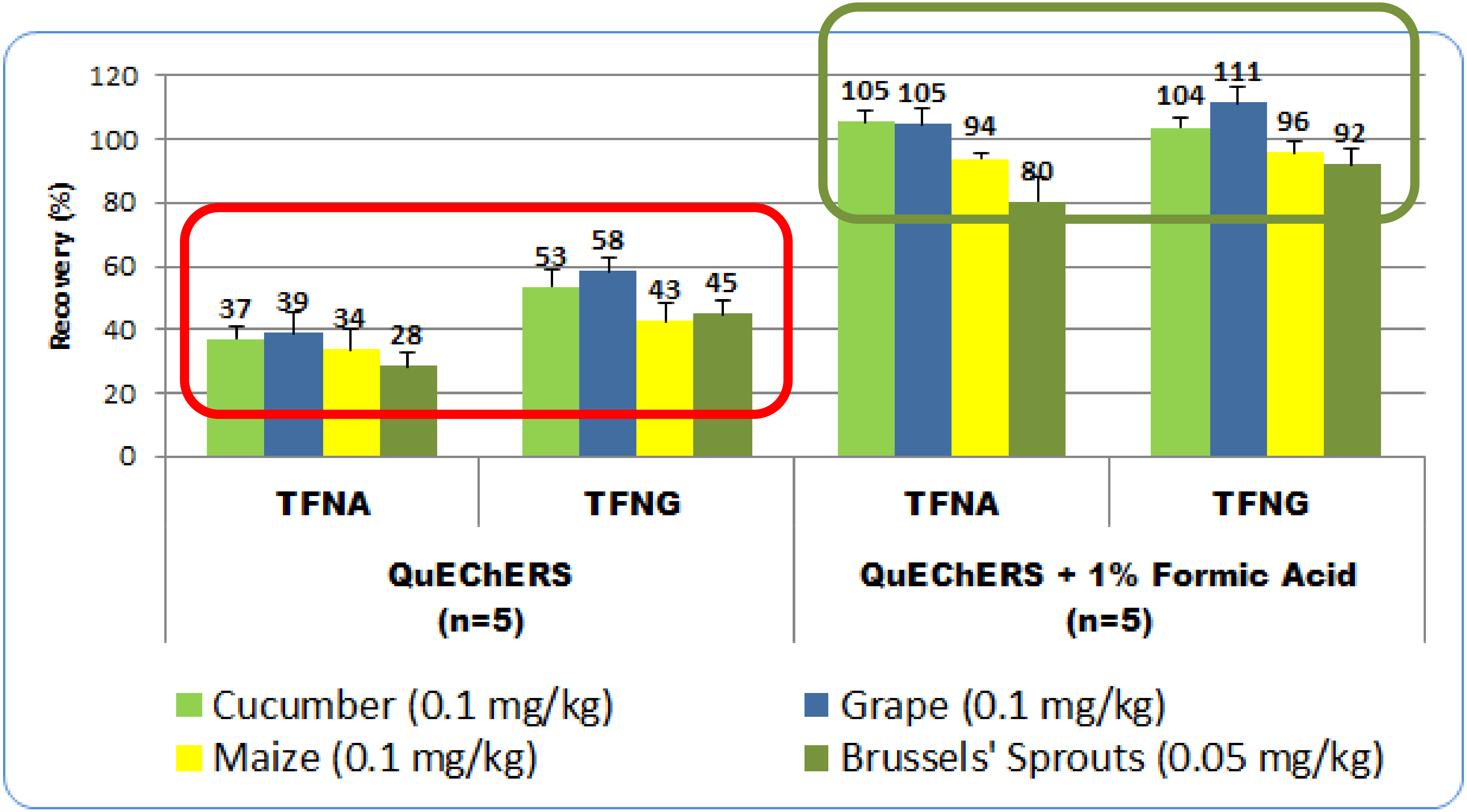
## Original QuEChERS (no buffer used)



# Other examples …



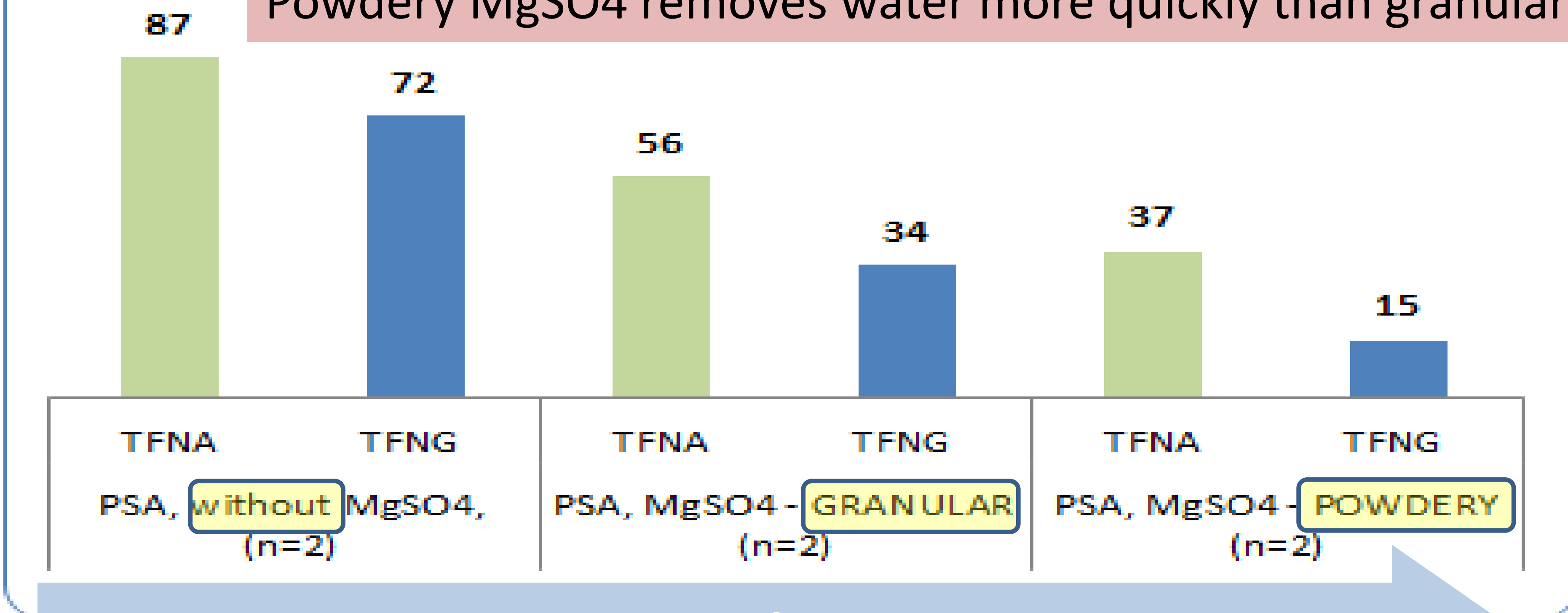
# Impact of pH on TFNA and TFNG recoveries



# Losses during dSPE cleanup with PSA

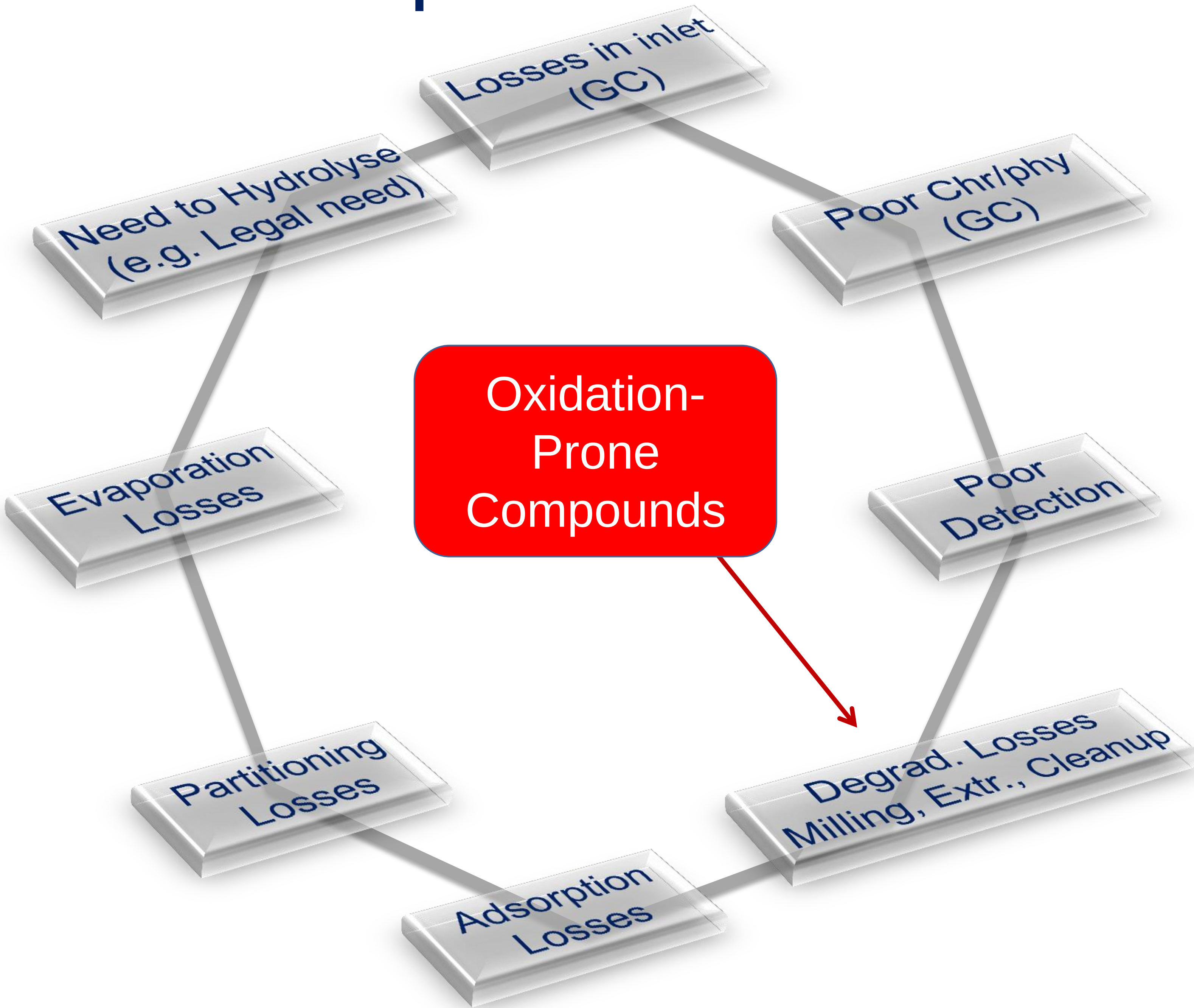
Spiked raw extract ► dSPE-Cleanup with PSA and with or w/o MgSO4

Water Content in extracts influences acid removal
Powdery MgSO4 removes water more quickly than granular

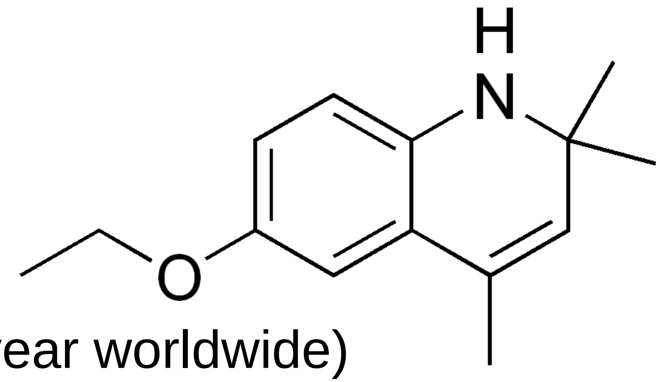



Water content ▼/PSA Activity ▲
Acid Removal ability▲ / Cleanup-Effect ▲/ Recoveries ▼

# What makes a compound non-amenable to MRMs?



# Usage of Ethoxyquin (EQ)



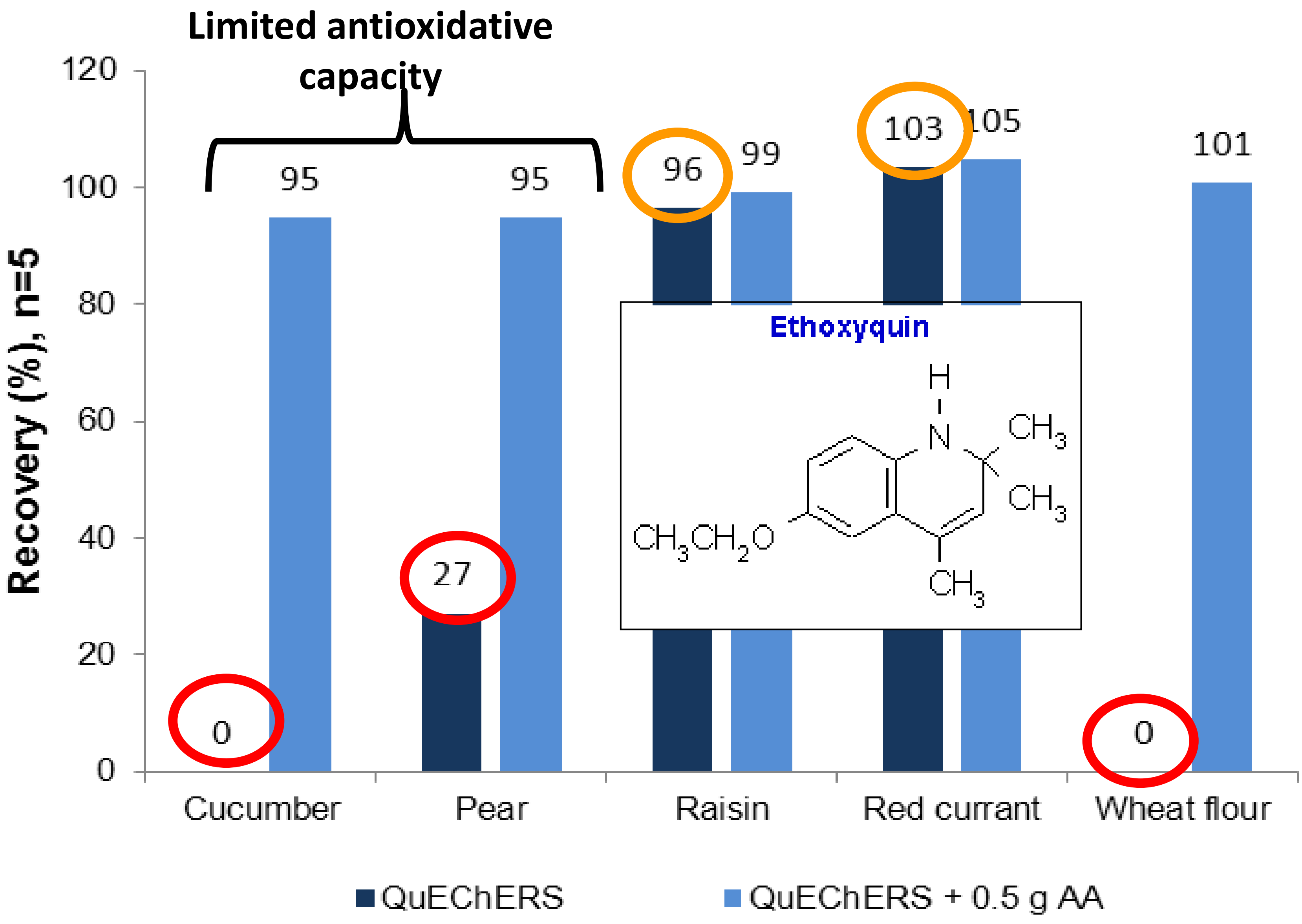
- Against storage scald for apples and pears
- Antioxidant in feed (E 324) and cereals
- Antioxidant in fish meal and fish feed (2000 t per year worldwide)
- USA: Additive for chicken feed, to achieve intense colour of egg york
- Antioxidant for pepper, chili powder, curcuma (preservation of color)
- Additive for cosmetics and medical devices

**Non authorized in EU**

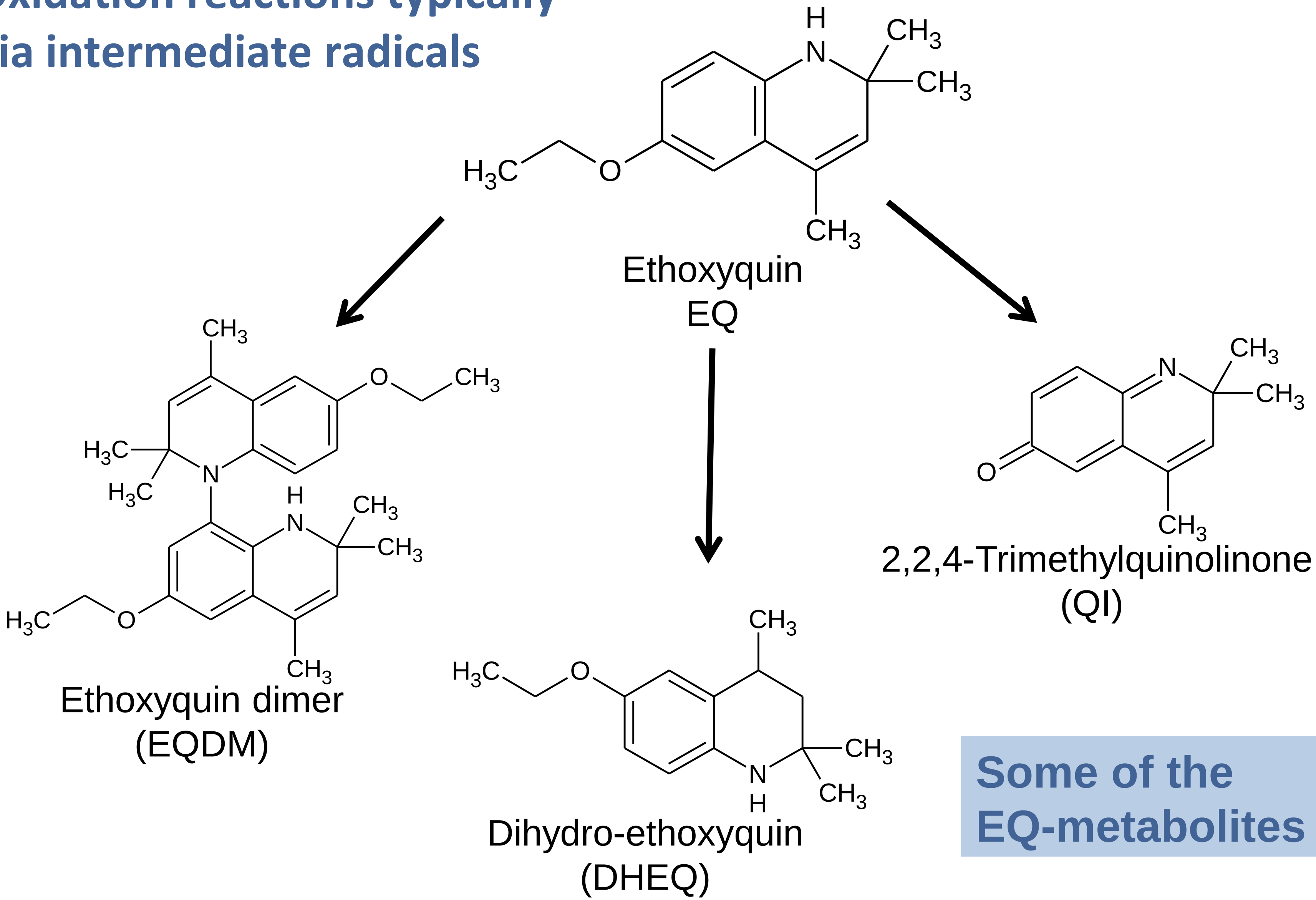
since Sept. 2011

(grace period ended Sept. 2012 )

# Losses of EQ during extraction



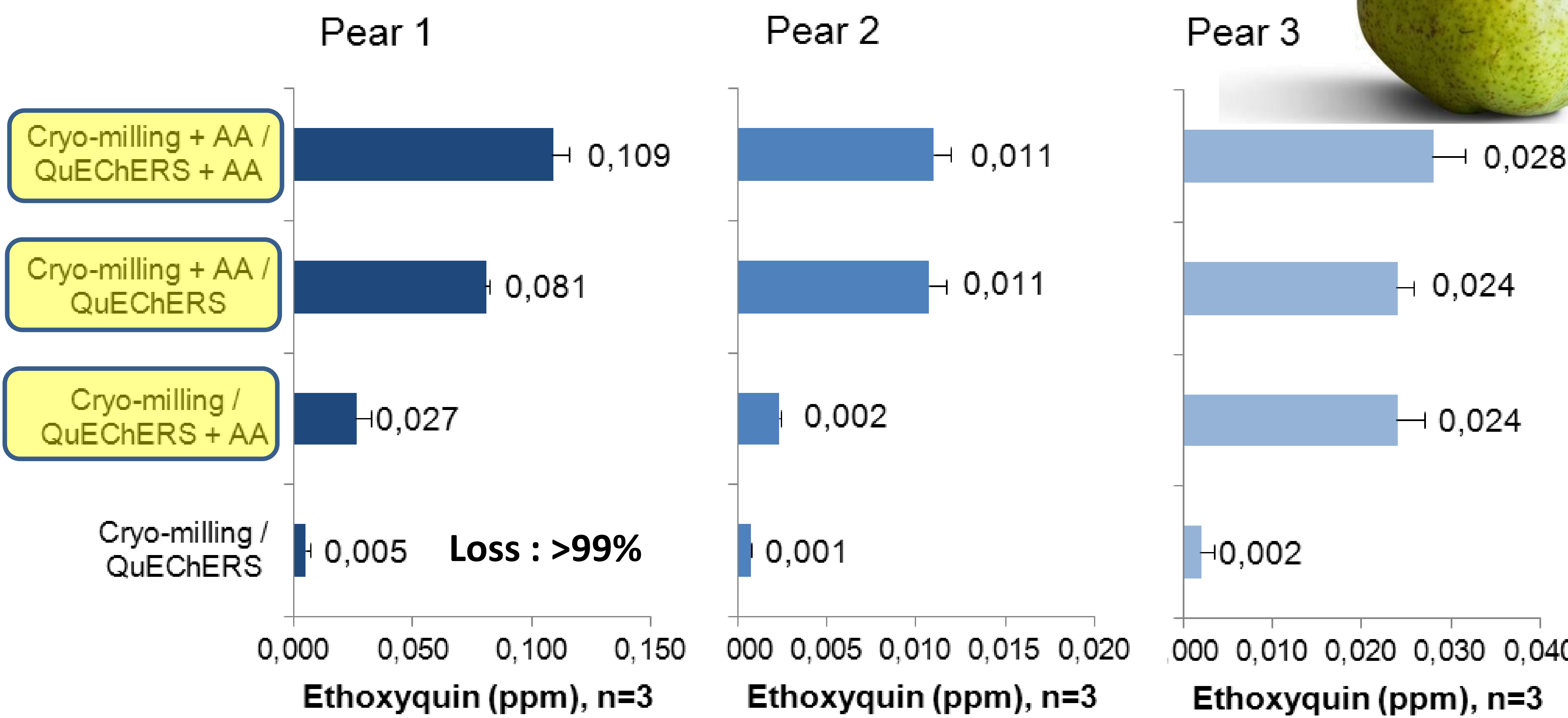
# Oxidation reactions typically via intermediate radicals




**Some of the EQ-metabolites**

# Ethoxyquin losses also
# … during Sample Processing

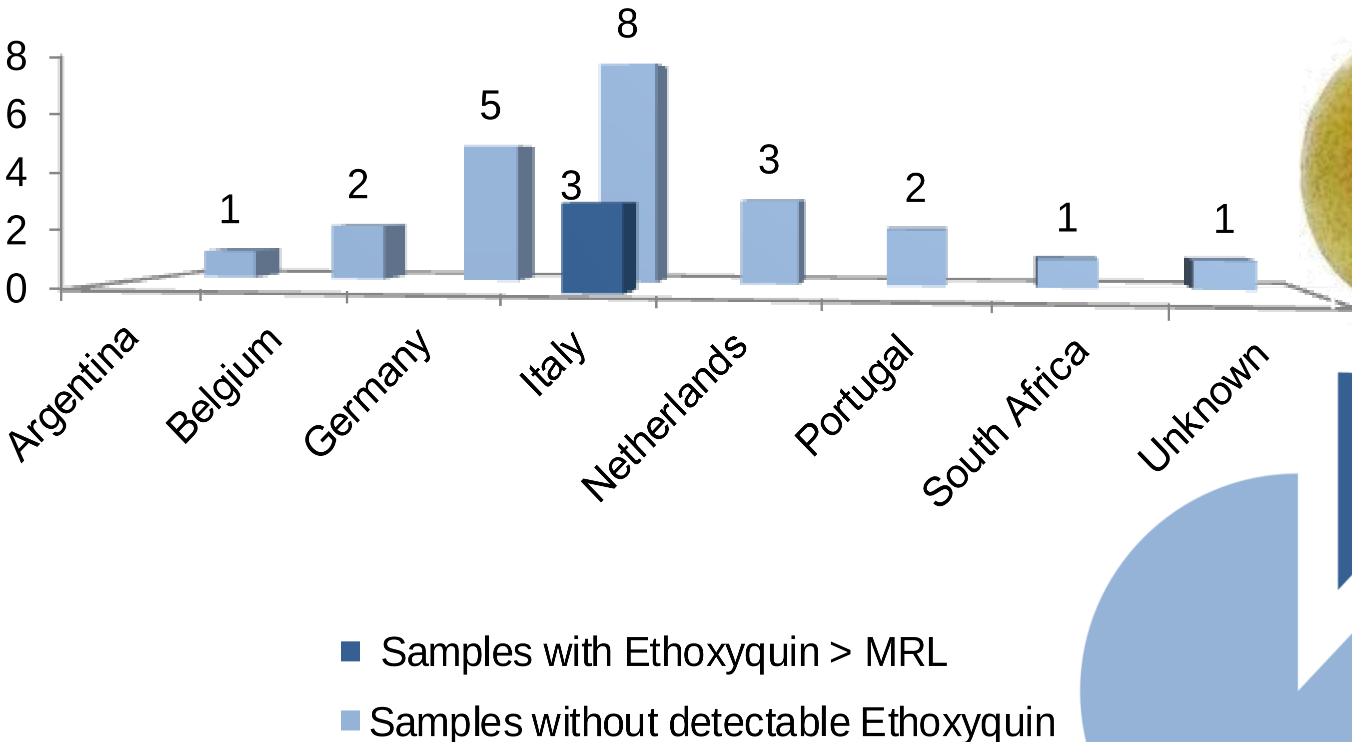
## Pears w. incurred EQ (real samples of US-origin)

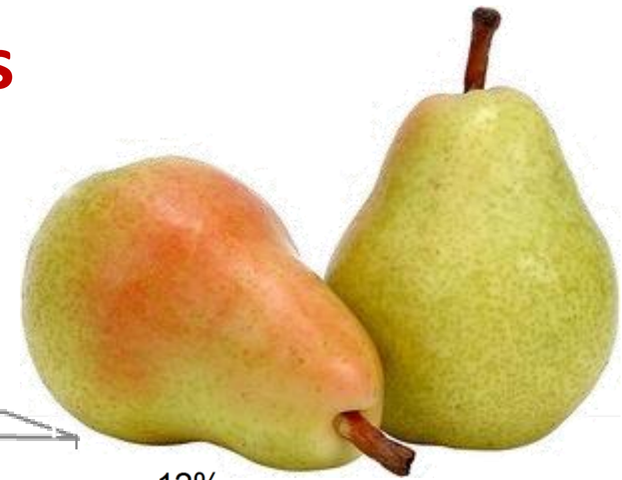


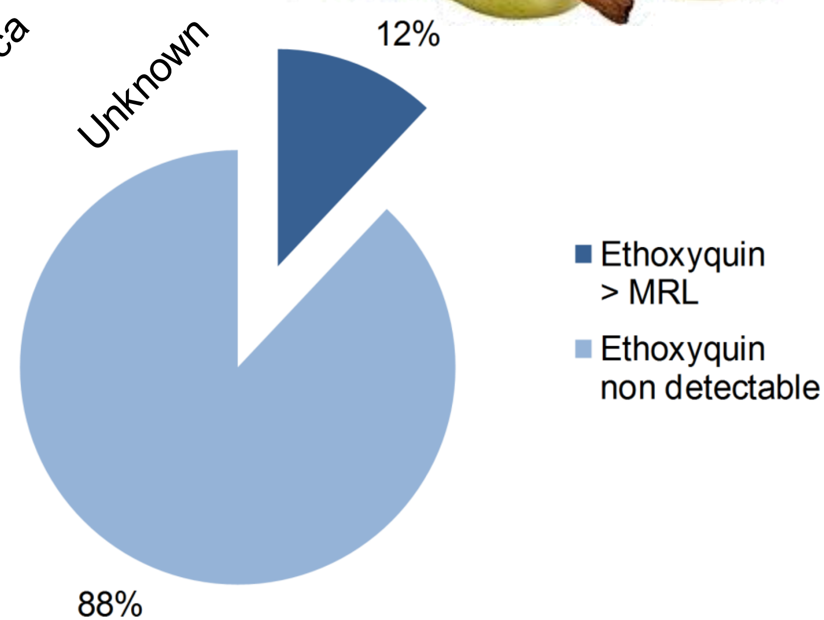

**<u>AA-Additions</u>**:

During milling: 1g /100 g ; for Extraction: 0.3 g /10 g

# Ethoxyquin Results in Routine Analysis



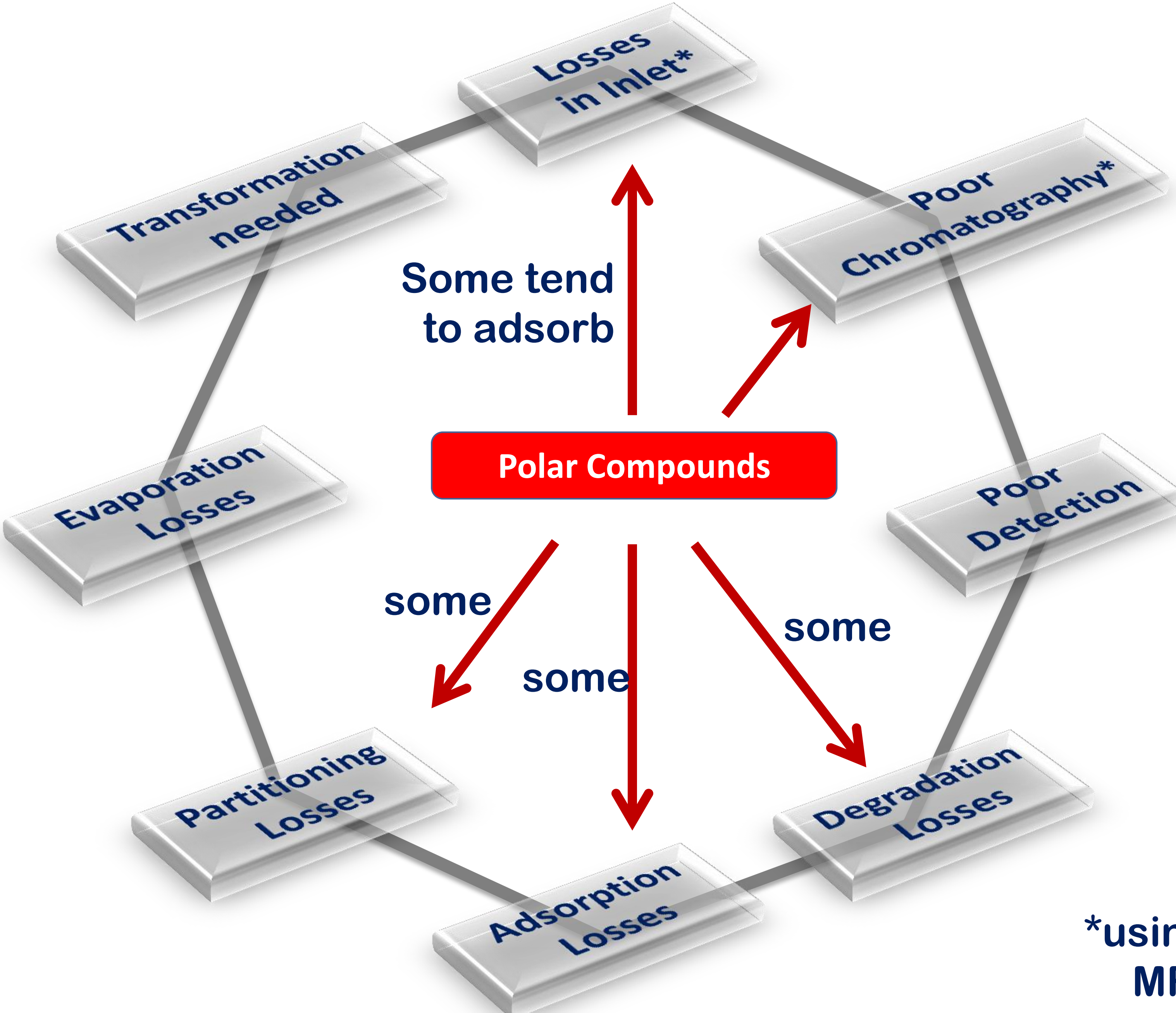



**26 samples analyzed**

► **All cryogenically processed w. AA-addition during milling**

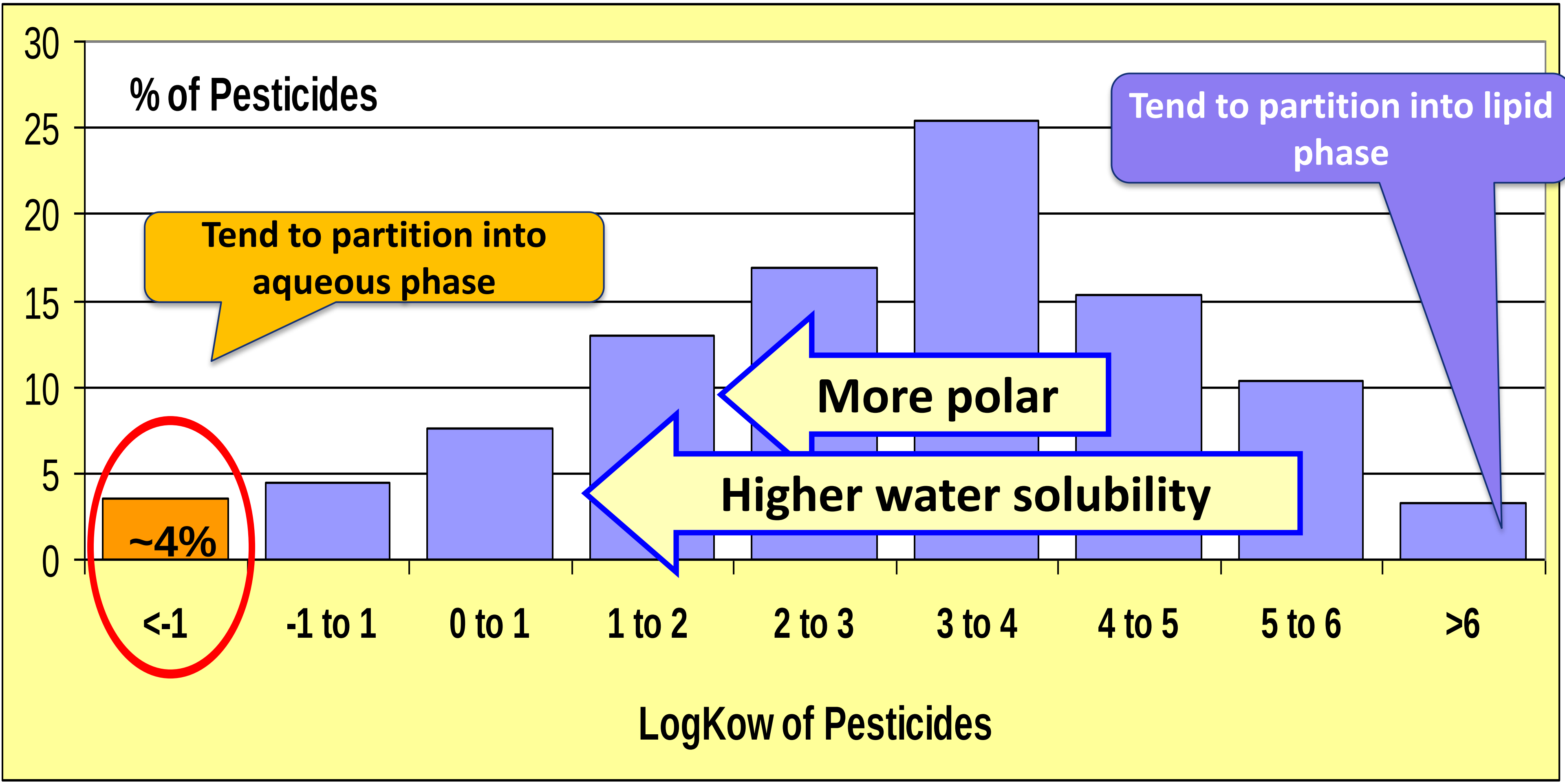
► **3 Italian pears >MRL (also illegal use)**

# What makes a compound non-amenable to MRMs?



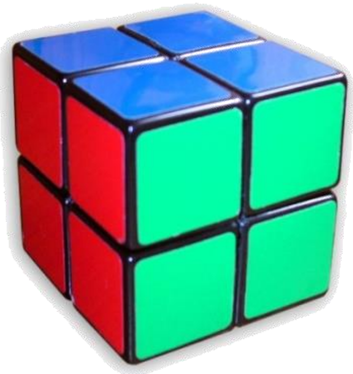

*using standard MRM settings

# Pesticide overview...



# QuPPe: Quick Polar Pesticides Method

[kju:b]



European Commission

EURL-SRM

EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

## Quick Method for the Analysis of numerous Highly Polar Pesticides in Foods of Plant Origin via LC-MS/MS involving Simultaneous Extraction with Methanol (QuPPe-Method)

- Version 8.1 (March 2015, Document History, see page **56**)

**Authors:** M. Anastassiades; D. I. Kolberg; E. Eichhorn; A. Benkenstein; S. Lukačević; D. Mack; C. Wildgrube; I. Sigalov; D. Dörk; A. Barth

**Note:** Changes from V7 to V8 are highlighted in yellow and changes from V8 to 8.1 are highlighted in turkuaz

### 1. Scope and Short Description

A method is described for the residue analysis of very polar, non-QuEChERS-amenable, pesticides in foods of plant origin such as fruits (including dried fruits), vegetables, cereals and processed products thereof as well as honey.

Residues are extracted from the test portion following water adjustment and the addition of acidified methanol. The mixture is centrifuged, filtered and directly analyzed by LC-MS/MS. Various options for the simultaneous LC-MS/MS analysis of different combinations of pesticides are provided. Quantification is in most cases performed with the help of isotopically labeled analogues of the target analytes, which are used as internal standards (ILISs). So far available, these ILISs are added directly to the test portion at the begin-

# LC-MS/MS Analysis of QuPPe Extracts

## QuPPe Version 8.1 –LC-MS/MS-Aproaches

| | M 1.1 | M 1.2 | M 1.3 | M 1.4 | M 2 |
|---|---|---|---|---|---|
| **ESI-mode** | **Neg.** | **Neg.** | **Neg.** | Neg. | **Neg.** |
| **Separation principle** | **Anion Exchange** | **Anion Exchange** | **Carbon** | **Carbon** | **HILIC** |
| **Column type** | **AS-11** | **AS11-HC** | **Hypercarb** | **Hypercarb** | **Obelisc-R** |
| **Ethephon** | ✓ | ✓ | ✓ | NEW | |
| **HEPA** | ✓ | ✓ | ✓ | | |
| **Glufosinate** | ✓ | ✓ | ✓ | | |
| **N-Acetyl-Glufosinate** | ✓ | ✓ | ✓ | | |
| **MPPA** | ✓ | ✓ | ✓ | | |
| **Glyphosate** | ✓ | ✓ | ✓ | | |
| **AMPA** | ✓ | ✓ | ✓ | | |
| **Phosphonic acid** | ✓ | ✓ | ✓ | ✓ | |
| **N-Acetyl-AMPA** | | ✓ | ✓ | | |
| **Fosetyl-Al** | | ✓ | ✓ | | ✓ |
| **Maleic hydazide** | | | ✓ | | ✓ |
| **Perchlorate** | | | ✓ | ✓ | ✓ |
| **Chlorate** | | | ✓ | ✓ | |
| **Bialaphos** | | | ✓ | | |
| **Cyanuric acid** | | | ✓ | | |

# LC-MS/MS Analysis of QuPPe Extracts

## QuPPe Version 8.1 –LC-MS/MS-Aproaches

| | M 3 | M 4.1 | M 4.2 | M 5 | M 6 | M 7 | M8 |
|---|---|---|---|---|---|---|---|
| ESI-mode | Pos. | Pos. | Pos. | Pos. | Pos. | Pos. | Pos. |
| Separation principle | HILIC | HILIC | HILIC | HILIC | HILIC | HILIC | Carbon |
| Column type | Obelisc-R | Obelisc-R | BEH-Amide | PFP | Obelisc-R | Trinity P1 | Hypercarb |
| Amitrole | ✓ | | ✓ | | | | |
| ETU | ✓ | | ✓ | ✓ | | | |
| PTU | ✓ | | ✓ | ✓ | | | |
| Cyromazin | ✓ | ✓ | ✓ | | | | |
| Trimesium | ✓ | ✓ | ✓ | | | | |
| Daminozide | ✓ | ✓ | ✓ | | | | |
| Chlormequat | ✓ | ✓ | ✓ | ✓ | | | |
| Mepiquat | ✓ | ✓ | ✓ | ✓ | | | |
| Difenzoquat | ✓ | ✓ | ✓ | ✓ | | | |
| Propamocarb | ✓ | ✓ | ✓ | | | | |
| Melamine | | ✓ | ✓ | | | | |
| Diquat | | ✓ | | | | | |
| Paraquat | | ✓ | | | | | |
| N,N-Dimethylhydrazine | | ✓ | | | | | |
| Nereistoxine | | ✓ | ✓ | | | | |
| Streptomycin | | | | | ✓ | | |
| Kasugamycin | | | | | ✓ | | |
| Morpholin | | (✓) | (✓) | | | ✓ | |
| Diethanolamine | | (✓) | (✓) | | | ✓ | |
| Triethanolamine | | (✓) | (✓) | | | ✓ | |
| 1,2,4-Triazole | | (✓) | | | | | ✓ |
| Triazole Alanine | | (✓) | | | | | ✓ |
| Triazole acetic acid | | (✓) | | | | | ✓ |
| Triazole lactic acid | | | | | | | ✓ |

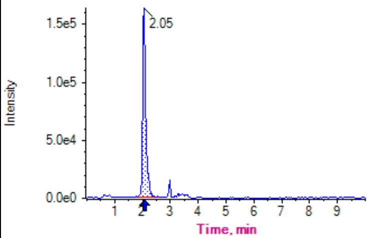
# QuPPe 4.2 (BEH-Amide column)

NEW

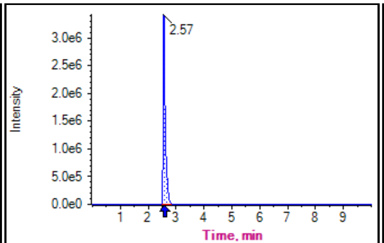
| Instrument parameters | Conditions |
|---|---|
| Ionisation mode | ESI pos |
| Column/temperature | BEH Amide 2.1 x 100mm 1.7 µm (P/N: 186004801); 40°C |
| Pre-filters | e.g. Supelco column saver 2.0 µm Filter |
| Pre-column | BEH Amide 1.7 µm (P/N: 186004799) |
| Eluent A | 50 mmol $NH_4$-formate in water (adjust to pH 3 with formic acid)<br>**Use brown glass !** |
| Eluent B | Acetonitrile |
| Gradient | see table below |
| Injection volume | 2 µL |

Gradient:

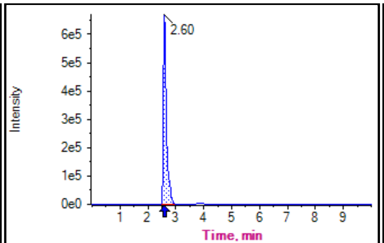
| %A | Flow [mL/min] | Time [min] |
|---|---|---|
| 3 | 0.5 | 0 |
| 3 | 0.5 | 0.5 |
| 30 | 0.5 | 4.0 |
| 60 | 0.5 | 5.0 |
| 60 | 0.5 | 6.0 |
| 3 | 0.5 | 6.1 |
| 3 | 0.5 | 10 |



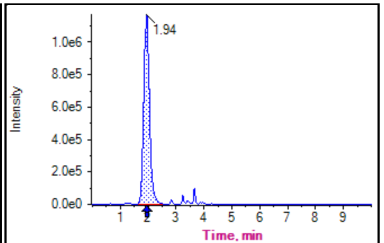
Amitrol 85/43 T



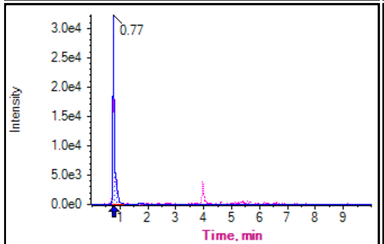
CCC 122/58 T



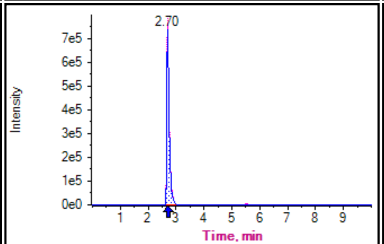
Cyromazin 167/68 T



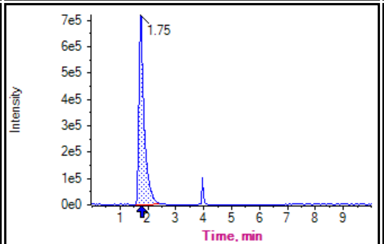
Daminozid 161/143 T



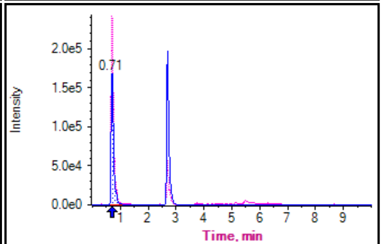
ETU 103/60 T



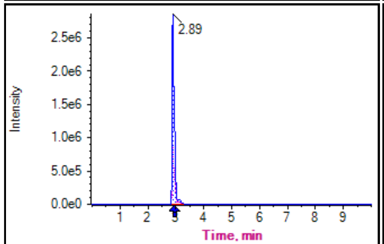
Mepiquat 114/98 T



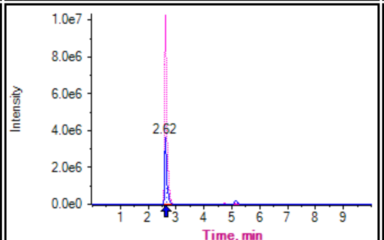
Nereistoxin 150/105 T



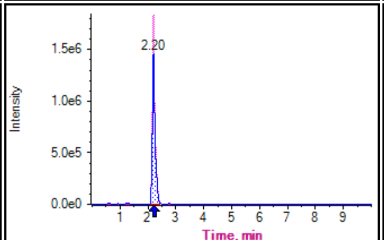
PTU 117/60 T



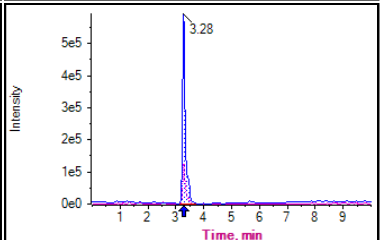
Trimethylsulfonium 77/62 T



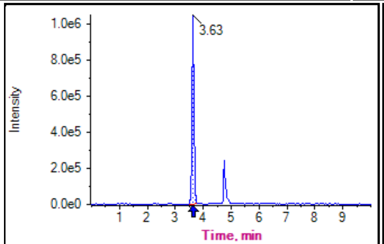
Propamocarb 189/144 T



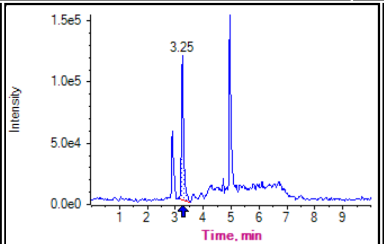
Difenzoquat (metilsulfate) 249/77 T



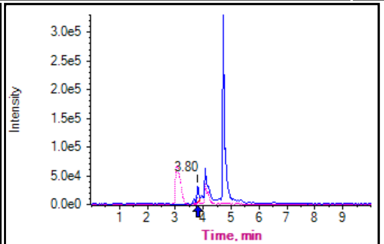
Melamine 127/85 T



Triethanolamine 150/132 T



Morpholine 88/70 T



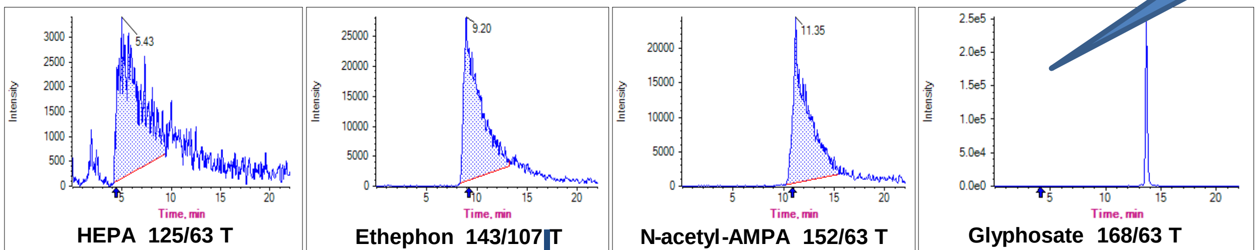
Diethanolamin 106/88 T

# QuPPe 4.2 (BEH-Amide column)

# QuPPe 3.1 (Hypercarb column)

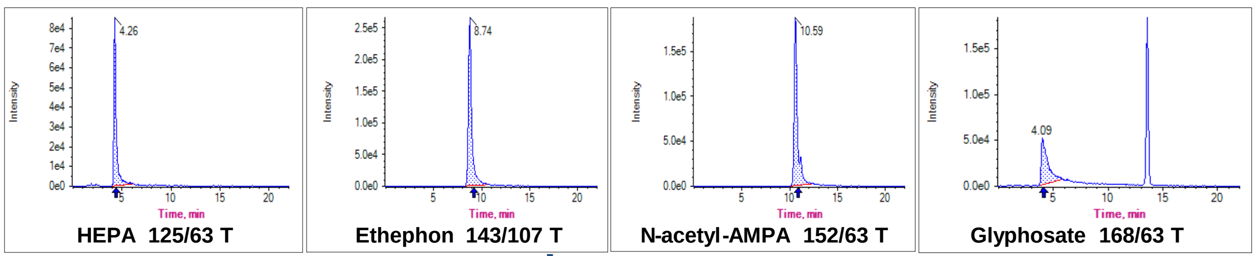
absent

0.1 mg/mL

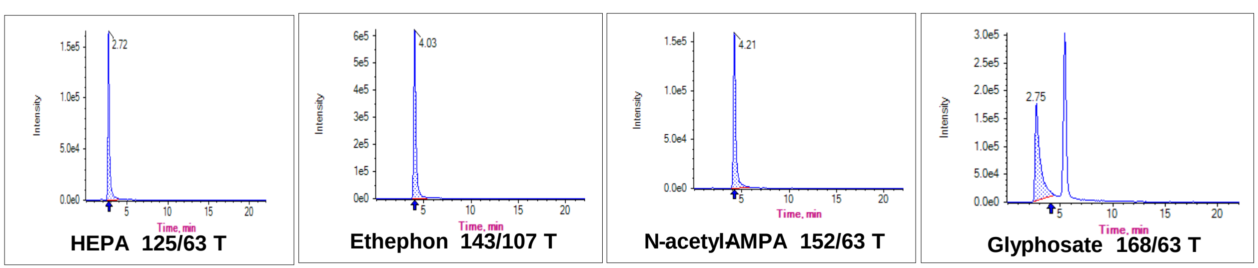



**New column:**
**in MeOH**

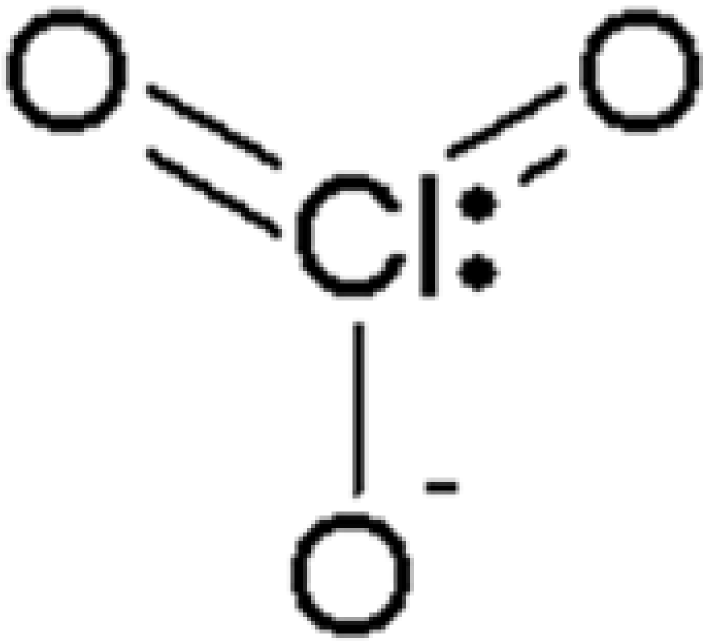
**Primed w. SPINACH EXTRACT (10 inj.)**



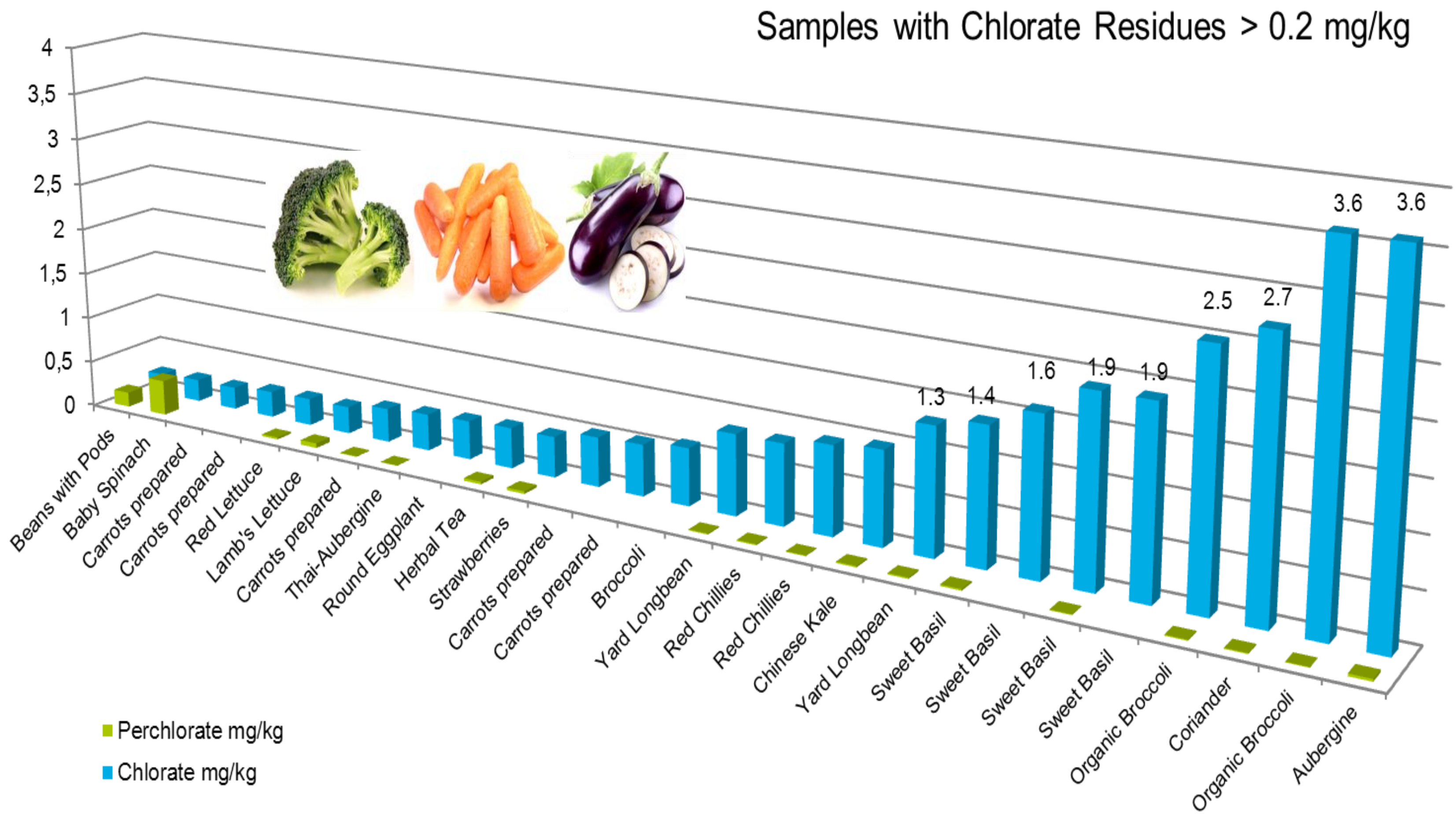

**After several days of routine use (injection of various commodities)**



# Chlorate



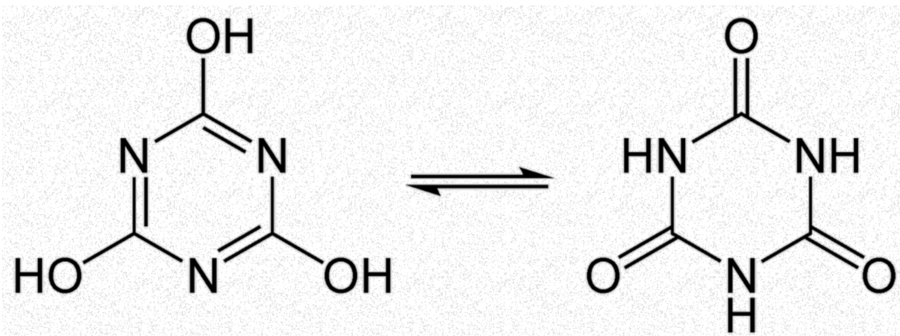
# Little correlation between chlorate / perchlorate



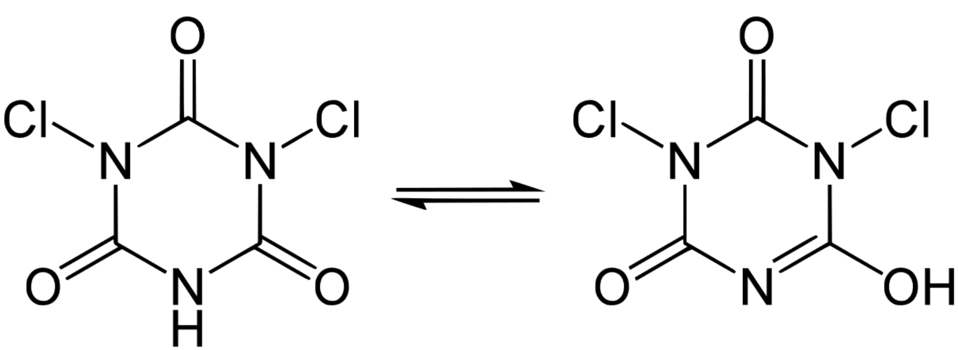
# Question?

## Is there correlation between Chlorate and Cyanuric acid?

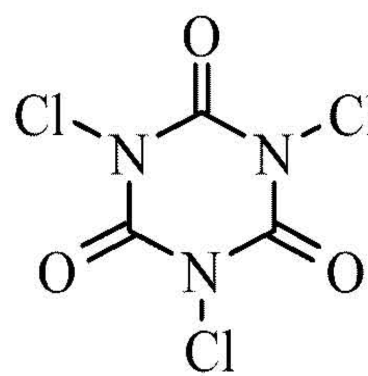
**Cyanuric acid is used as chlorine stabilizer in waters (swimming pools).**
**Binds chlorine and releases it slowly, extends depletion time.**




Cyanuric acid and Isocyanuric acid

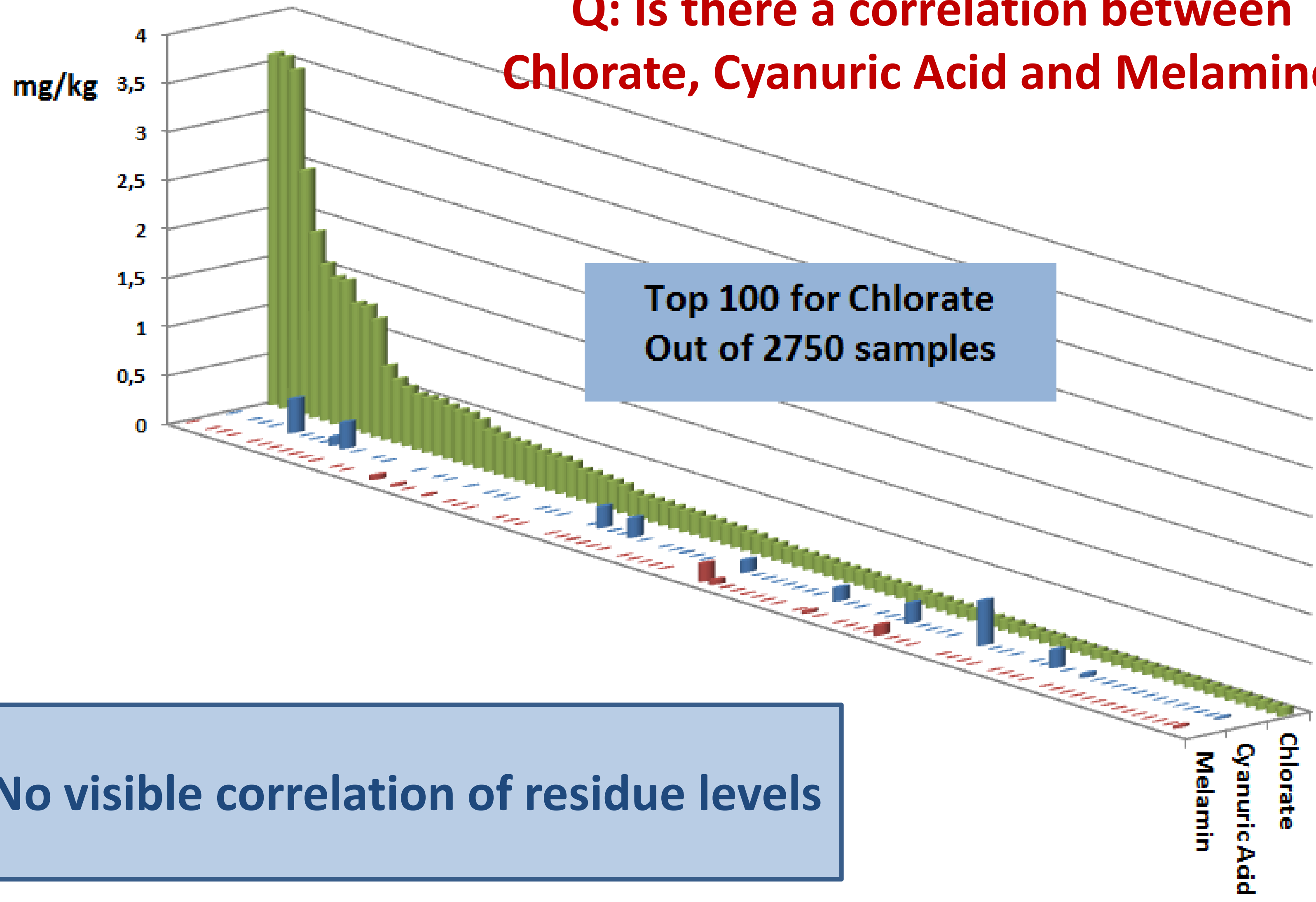



Dichloroisocyanuric acid



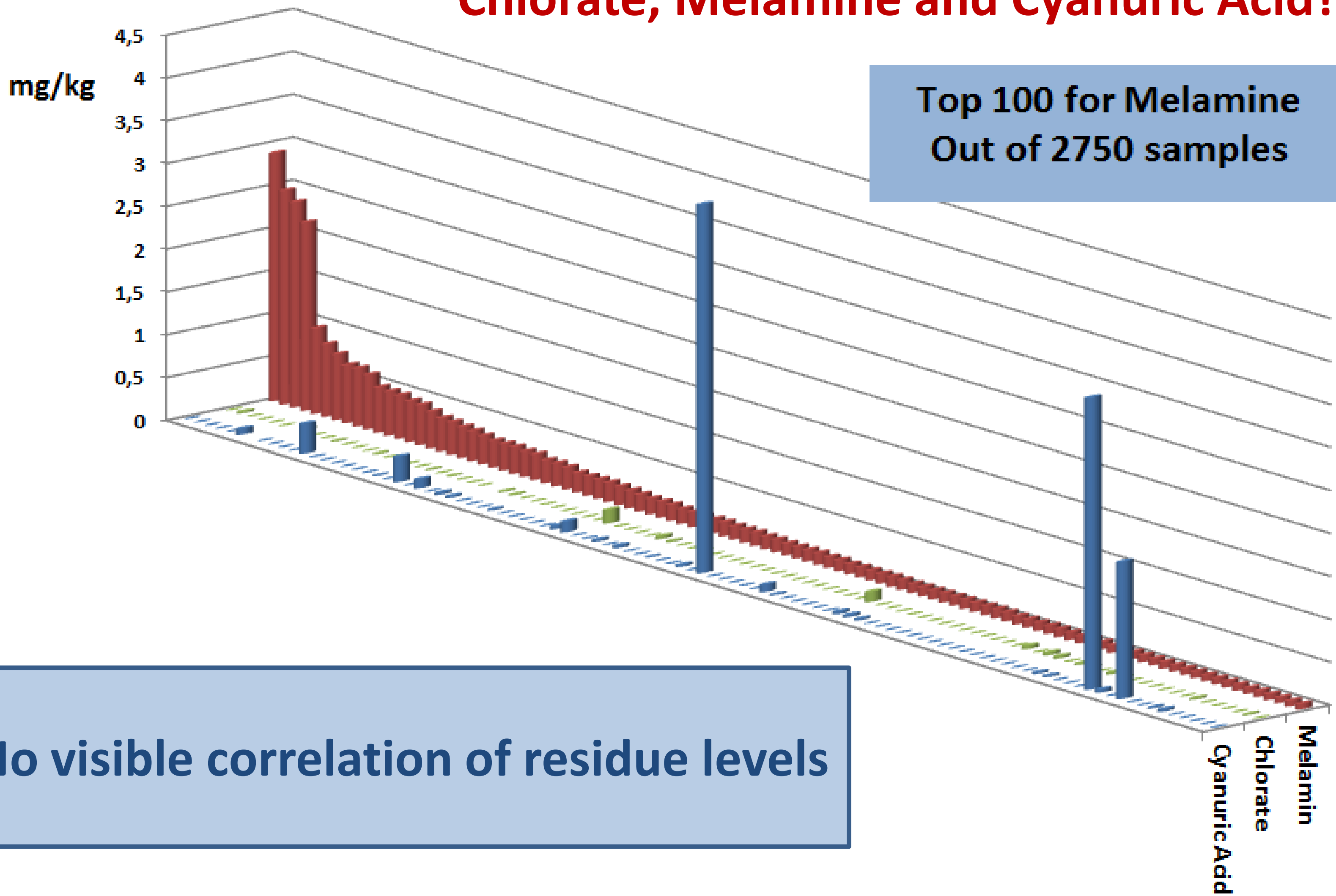

Trichloroisocyanurate

# Q: Is there a correlation between Chlorate, Cyanuric Acid and Melamine?




**No visible correlation of residue levels**

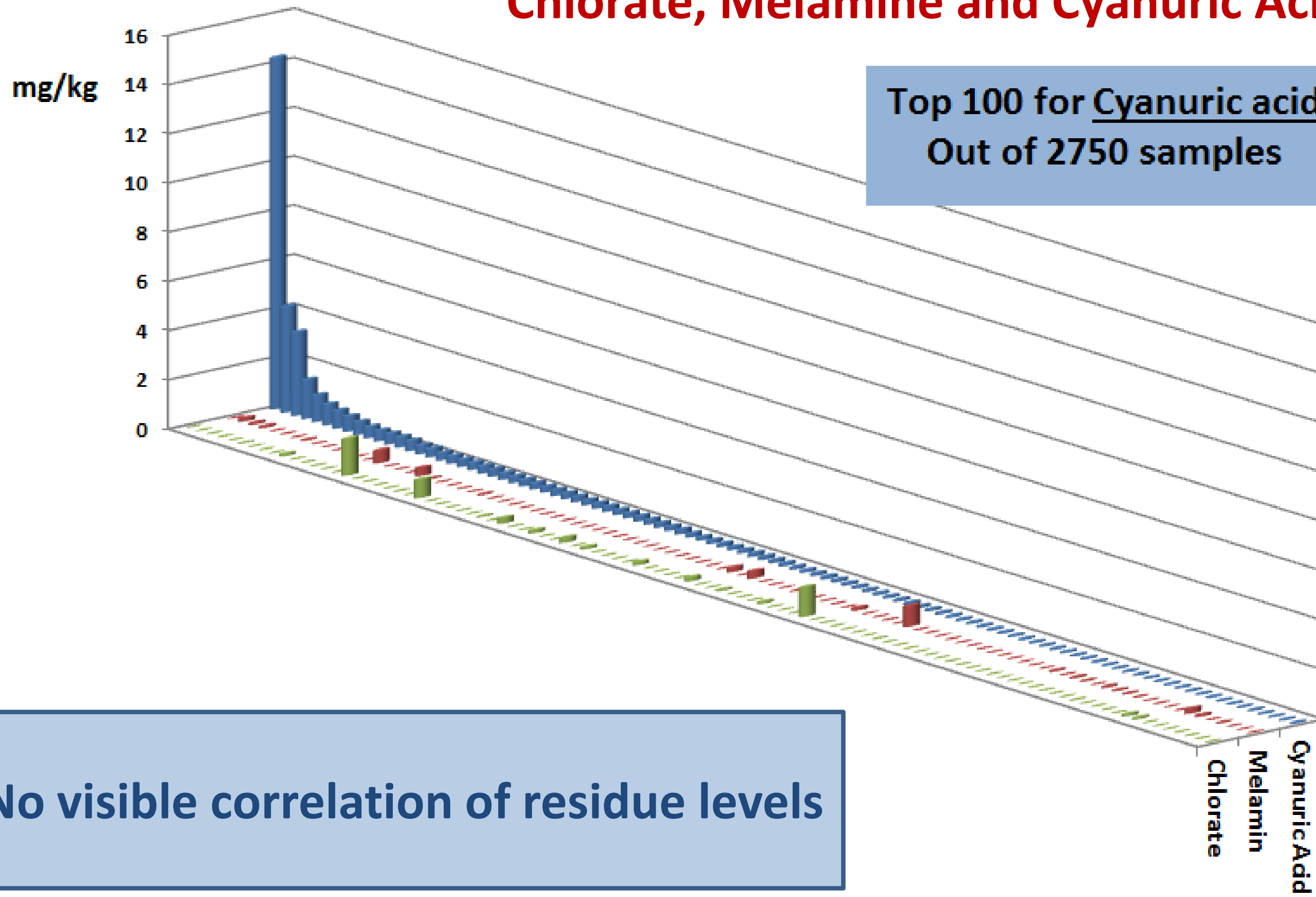
# Q: Is there a correlation between Chlorate, Melamine and Cyanuric Acid?




Top 100 for Melamine
Out of 2750 samples

**No visible correlation of residue levels**

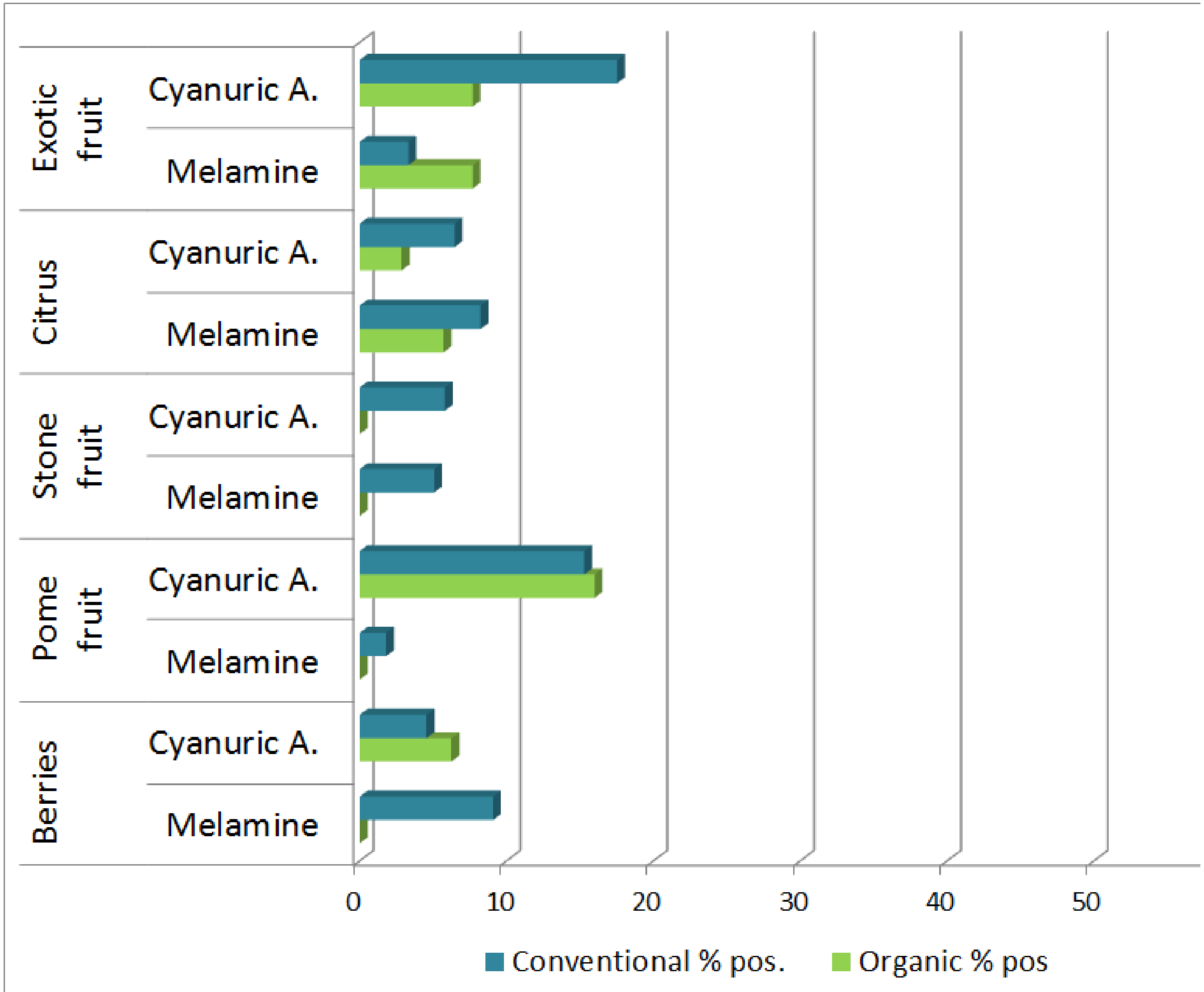
# Q: Is there a correlation between Chlorate, Melamine and Cyanuric Acid?



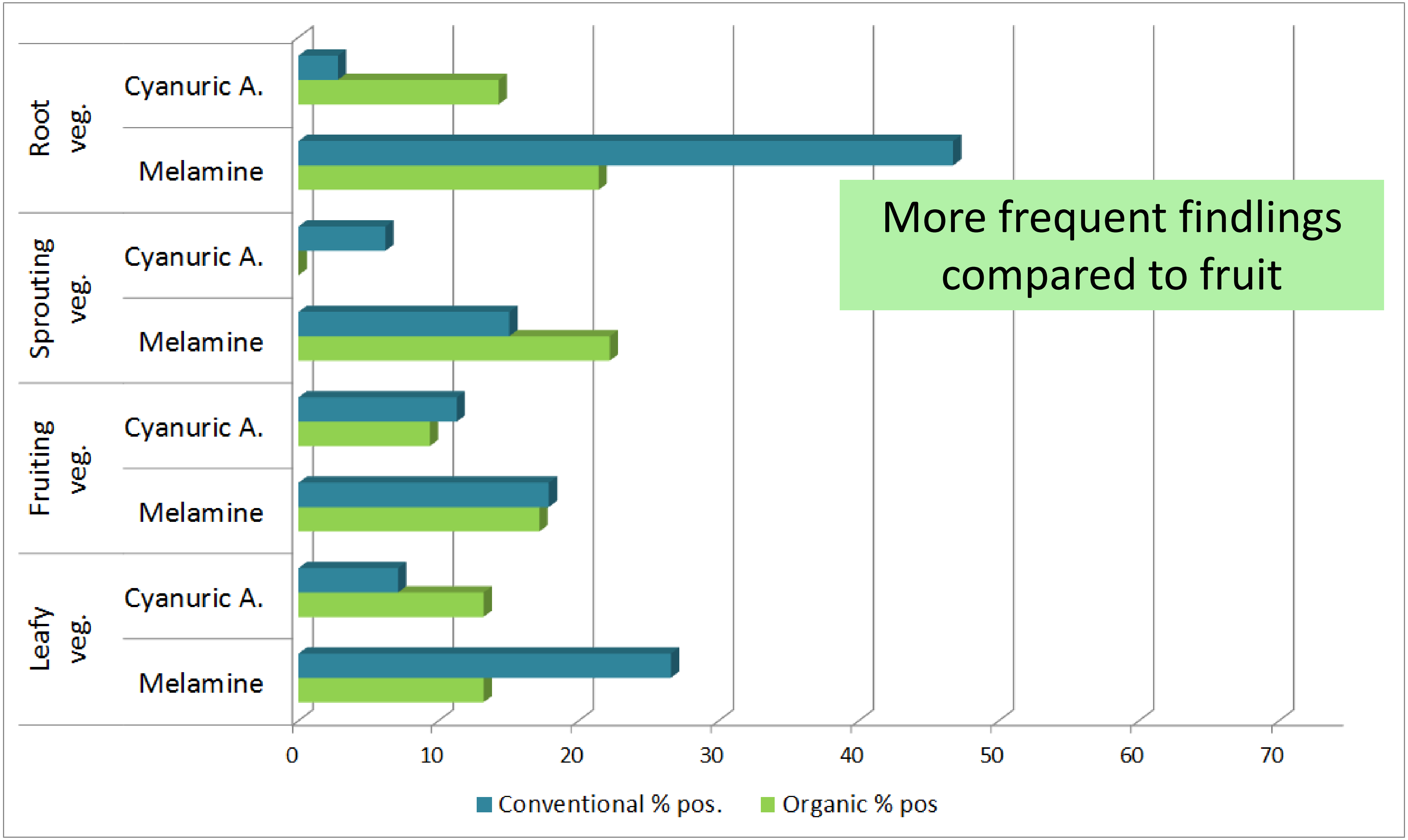

Top 100 for Cyanuric acid
Out of 2750 samples

**No visible correlation of residue levels**

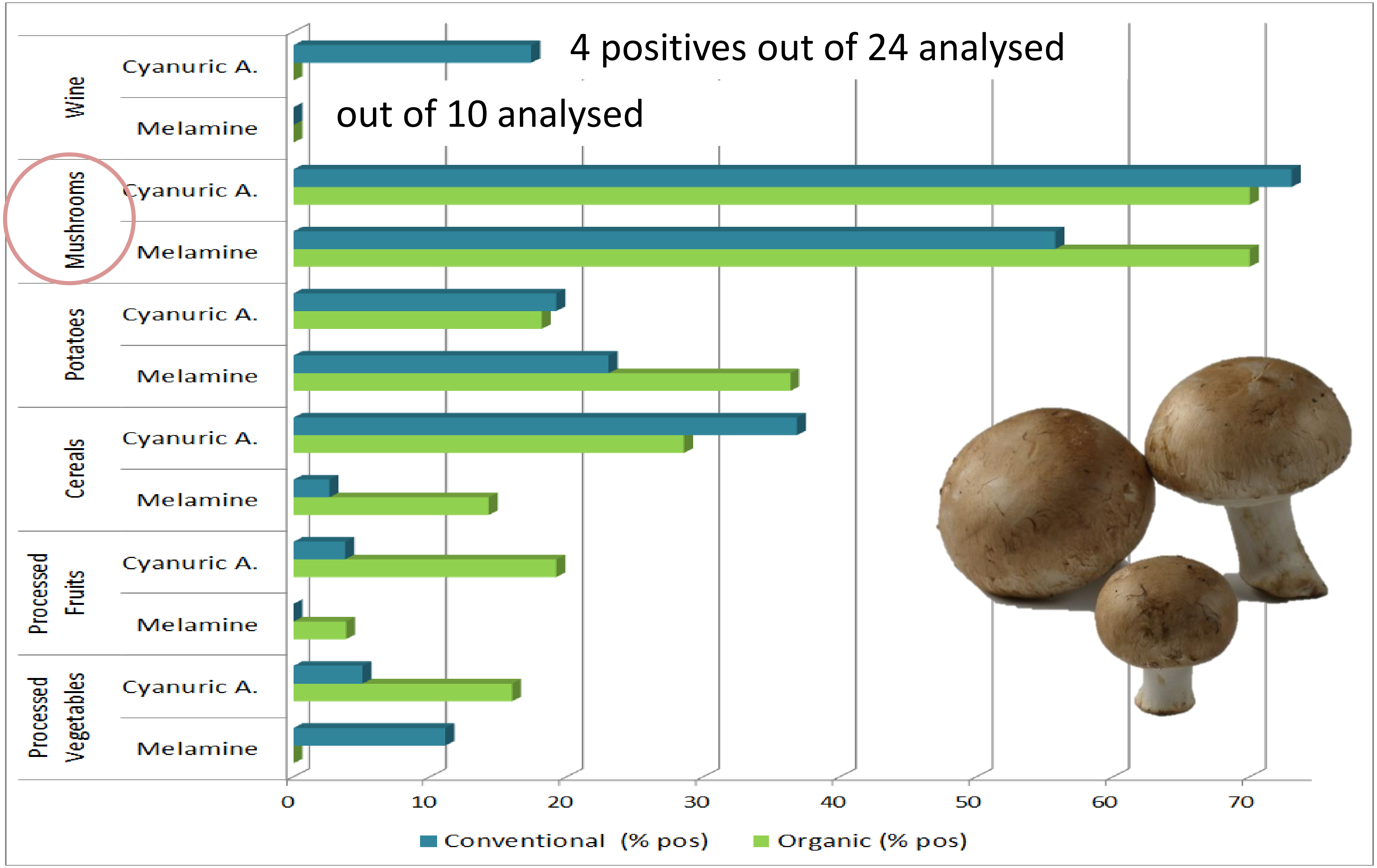
# Residues of Cyanuric acid and Melamine (Fruits)



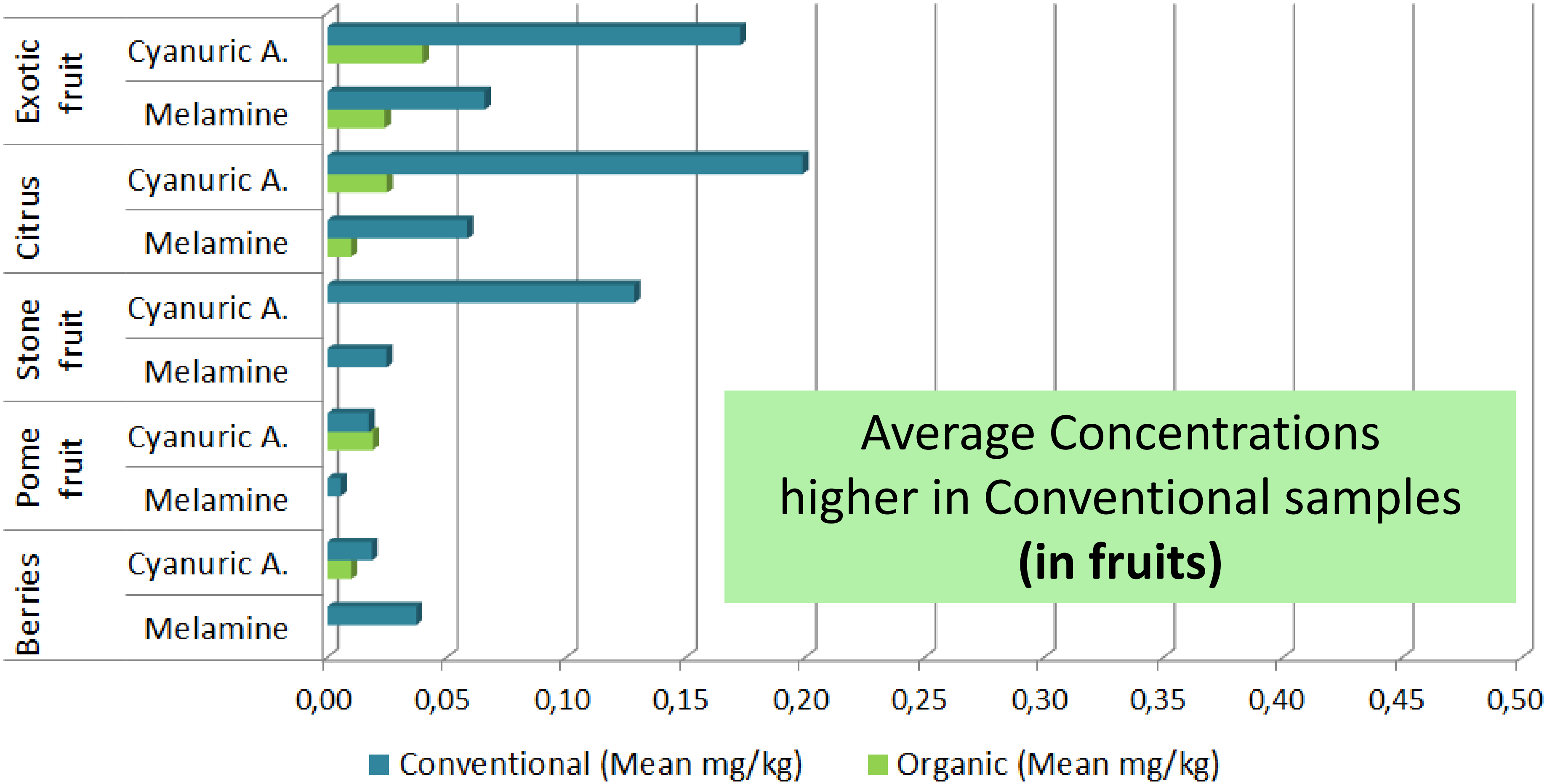
# Residues of Cyanuric acid and Melamine (Vegetables)



# Residues of Cyanuric acid and Melamine (other)

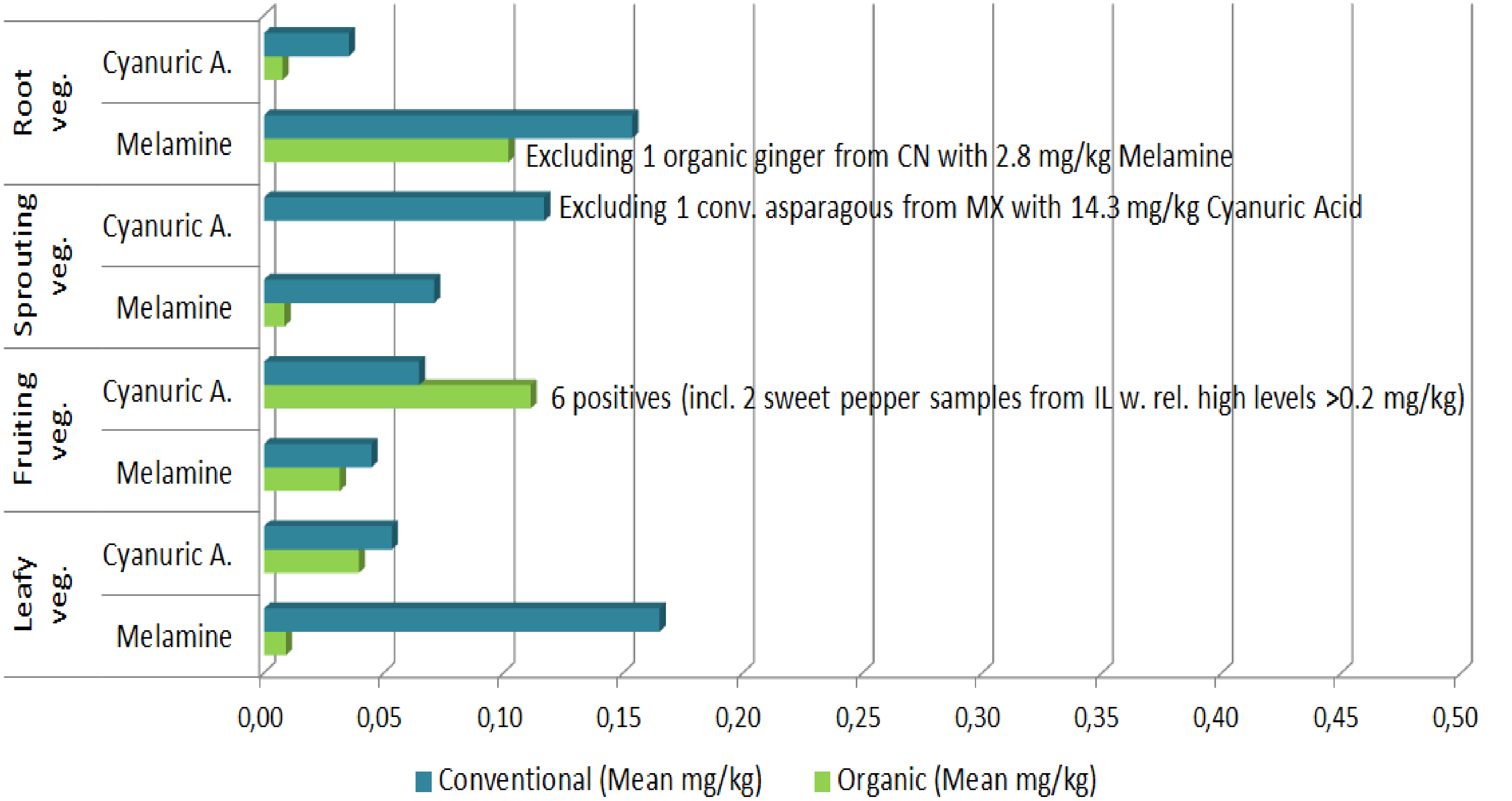


# Residues of Cyanuric acid and Melamine (Fruit)

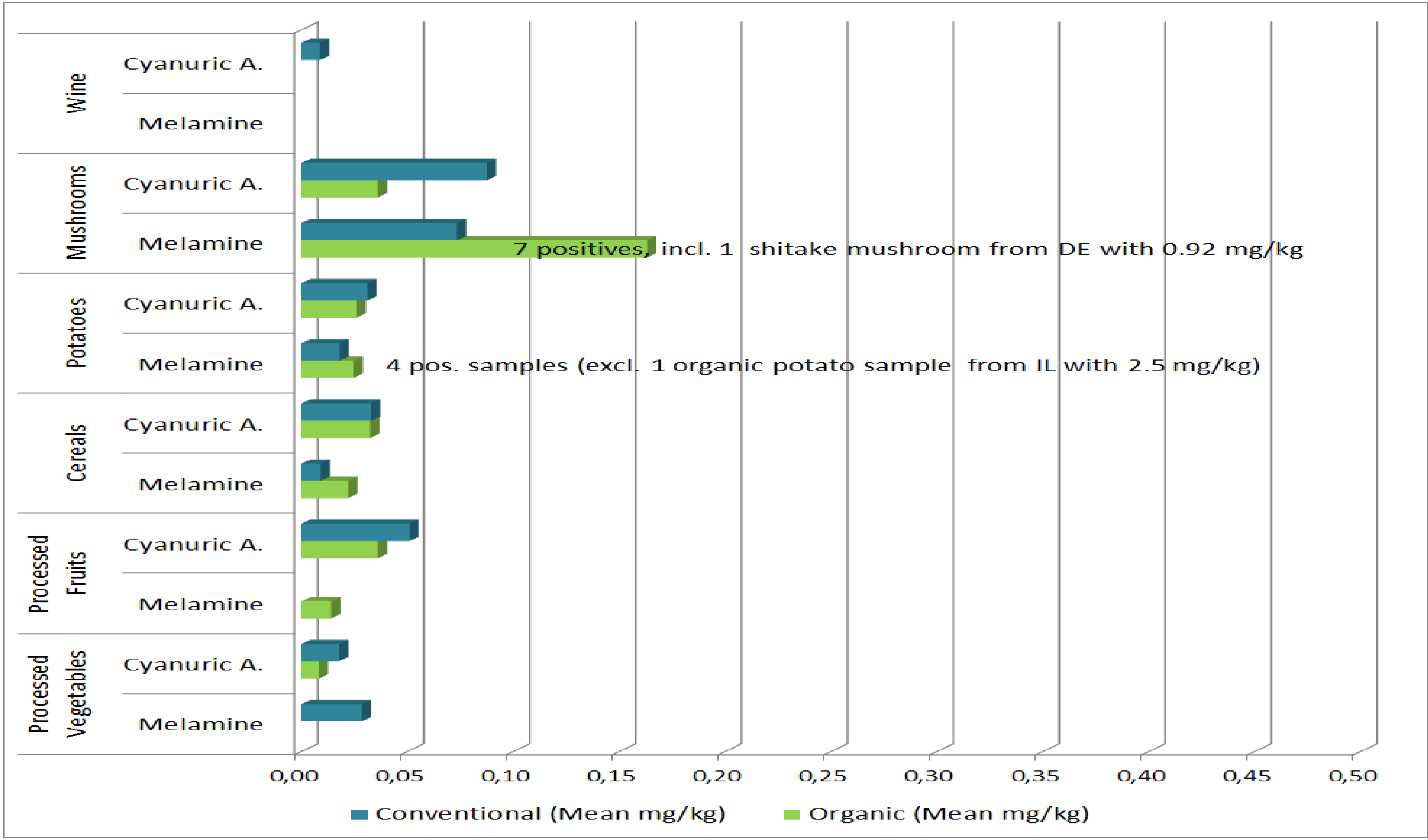



Average Concentrations higher in Conventional samples **(in fruits)**

# Residues of Cyanuric acid and Melamine (Veg.)



# Residues of Cyanuric acid and Melamine (other)

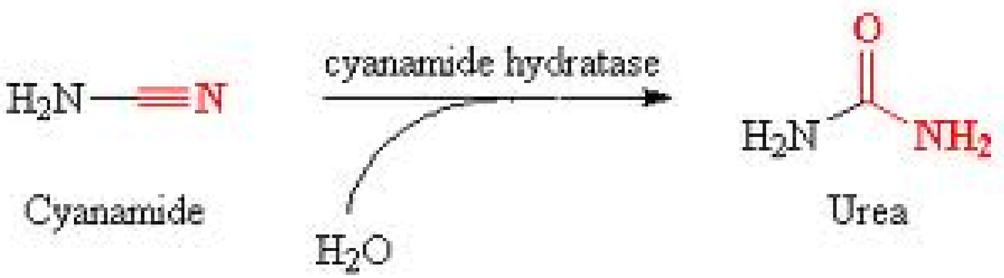


# Question?

## Is there correlation btw Cyanuric A. /Melamine and fertilizers?

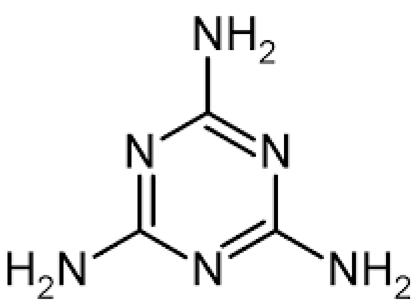
**Cyanamide and Calcium cyanamide ($CaCN_2$ ) used as fertilizers**

**Cyanamide hydrolyzes to urea**




**At high pH /temperature it condensates …**

- Dimer: **Dicyandiamide** (nitrification inhibitor)
- Trimer: **Melamine** .



Melamine

# Residues of Pesticides /Contaminants in Fertilizers (mg/kg)

| # | Melamine | Cyanuric acid | Diethanol-amine | Triethanol-amine | 1,2,4-Triazole | Triazole-Alanine | Triazole Acetic acid | Triazole lactic acid | Chlorate | Perchlorate |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 0,07 | 80 | 0 | | | | | | 0,51 |
| 2 | | 0,09 | 23 | 0 | | | | | 21 | 37 |
| 3 | 0,091 | | | 0,42 | | | | | | |
| 4 | | | | | | | | | | |
| 5 | 1,7 | 2,4 | Calcium Cyanamide type | | | | | 0,04 | | |
| 6 | 0,39 | 2,7 | 0,04 | 0,05 | | | | | | |
| 7 | | | | 0,02 | | | | | | |
| 8 | | | 13 | | | | | | 27 | 14 |
| 9 | | | 0,95 | 0,04 | | | | | | |
| 10 | 7,3 | 0,09 | 0,60 | | | | | | | |
| 11 | | | 11 | | | | | | 15 | 20 |
| 12 | | 41 | 0,03 | | | 0,2 | 0,9 | | | |
| 13 | 0,06 | | 0,34 | 0,12 | | | | | | |
| 14 | 0,02 | | | 0,05 | | | | | | |
| 15 | | | | | | | | | | |
| 16 | | 0,09 | | 16,3 | | | | | 8 | 11 |
| 17 | | | | | | | | | | |
| 18 | 5,9 | 2,1 | Calcium Cyanamide type | | | | | 0,03 | | |
| 19 | | | 0,58 | 0,03 | | | | | | |

# Residues of Diethanolamine and Triethanolamine in Fruit (2014)

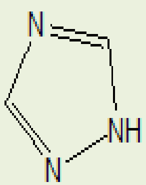
| | | Diethanolamine (DEA) (mg/kg) | | | | Triethanolamine (TEA) (mg/kg) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | No. Samples | Positive | Ave. | Min. | Max. | Positive | Ave. | Min. | Max. |
| **Berries** | 197 | 5 | 0.03 | 0.02 | 0.04 | 11 | 0.06 | 0.02 | 0.20 |
| **Pome fruit** | 78 | | | | | 1 | 0.06 | 0.03 | 0.10 |
| **Stone fruit** | 99 | 1 | 0.06 | 0.06 | 0.06 | 8 | 0.14 | 0.02 | 0.48 |
| **Citrus fruit** | 76 | 2 | 0.25 | 0.03 | 0.46 | 3 | 0.24 | 0.03 | 0.62 |
| **Exotic fruit** | 98 | 5 | 0.15 | 0.02 | 0.52 | 9 | 0.09 | 0.02 | 0.30 |

**Morpholine, DEA, TEA**: used in wax emulsions for fruit treatment (NOT in EU)
**DEA and TEA** : contained in pesticide formulations (also in EU)

**Residue finding of Morpholine (2014)**
7 x pos. (6x stone fruit, 1x citrus fruit). Max 0.07 mg/kg.
(in the past more findings and higher levels (Citrus, apples, mango …)
► industry has reacted

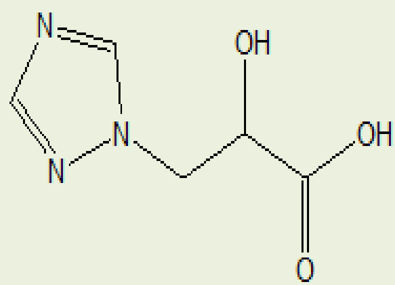
# Triazole Derivative Metabolites TDMs

In Plants

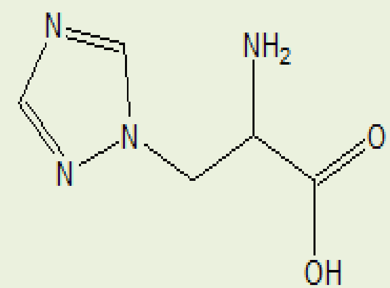


1,2,4-Triazole (TRZ)

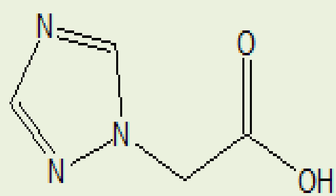
Soil + (Plants)



Triazole lactic acid (TLA)

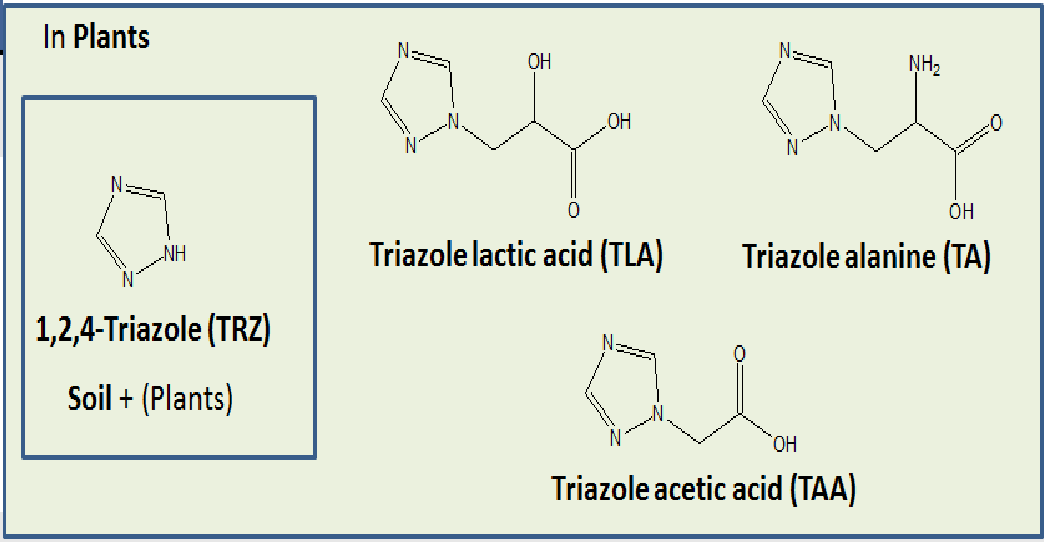


Triazole alanine (TA)



Triazole acetic acid (TAA)

# Triazole Derivative Metabolites (TDMs) – Short Overview




## USE/OCCURANCE:

Metabolites of Triazole fungicides (widely used)

1,2,4 Triazole nitrification inhibitor in fertilizers

## TOXICITY:

**1,2,4-triazole** most toxic one (ADI 0.2 mg/kg BW; ARfD 0.3 mg/kg bw)

**TLA + TA + TAA** rapidly excreted (ADI 1 mg/kg BW; ARfD unnecessary)

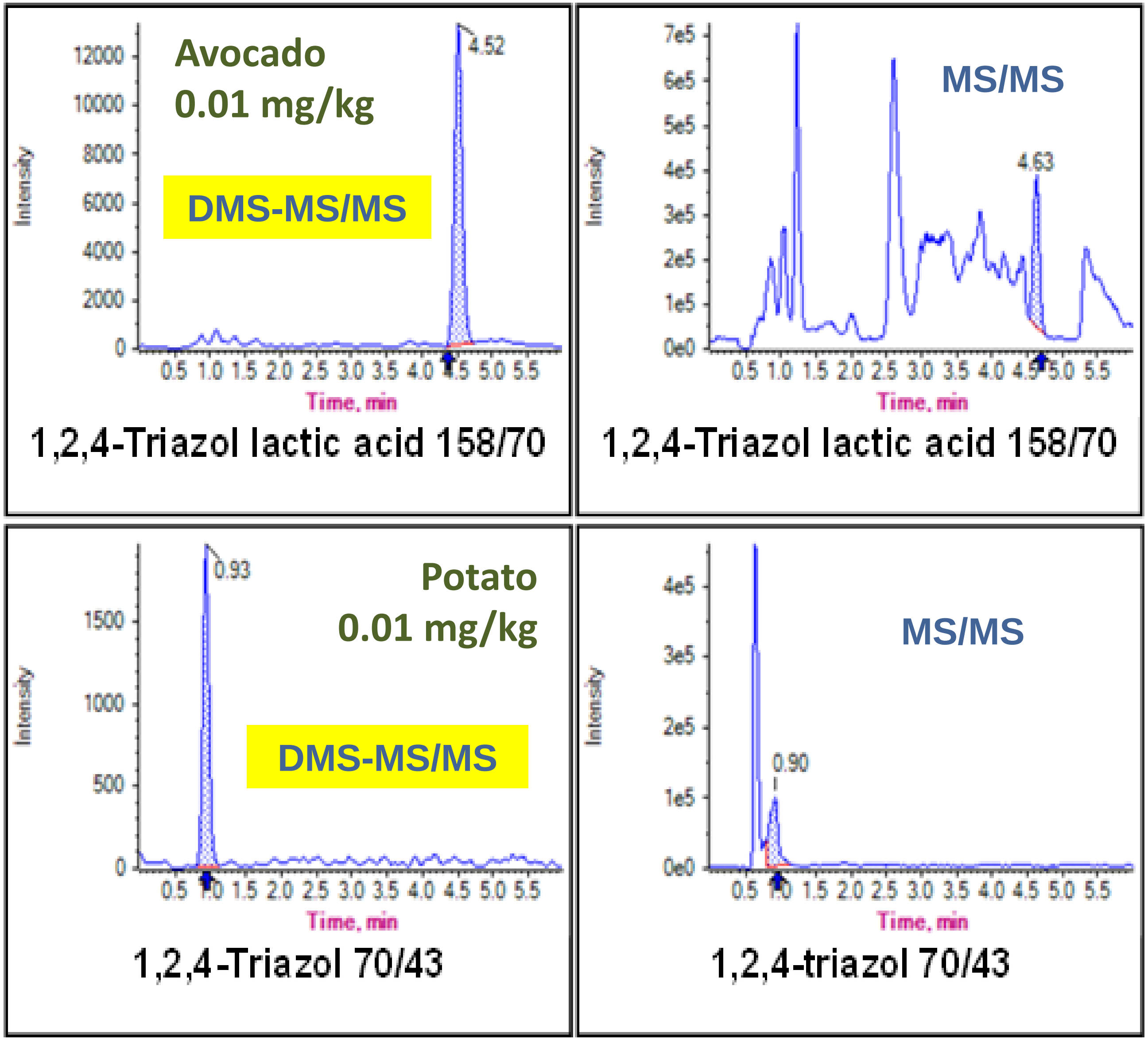
## LEGAL ASPECTS

**Not yet part of RD;**

**EFSA requested information about background levels**

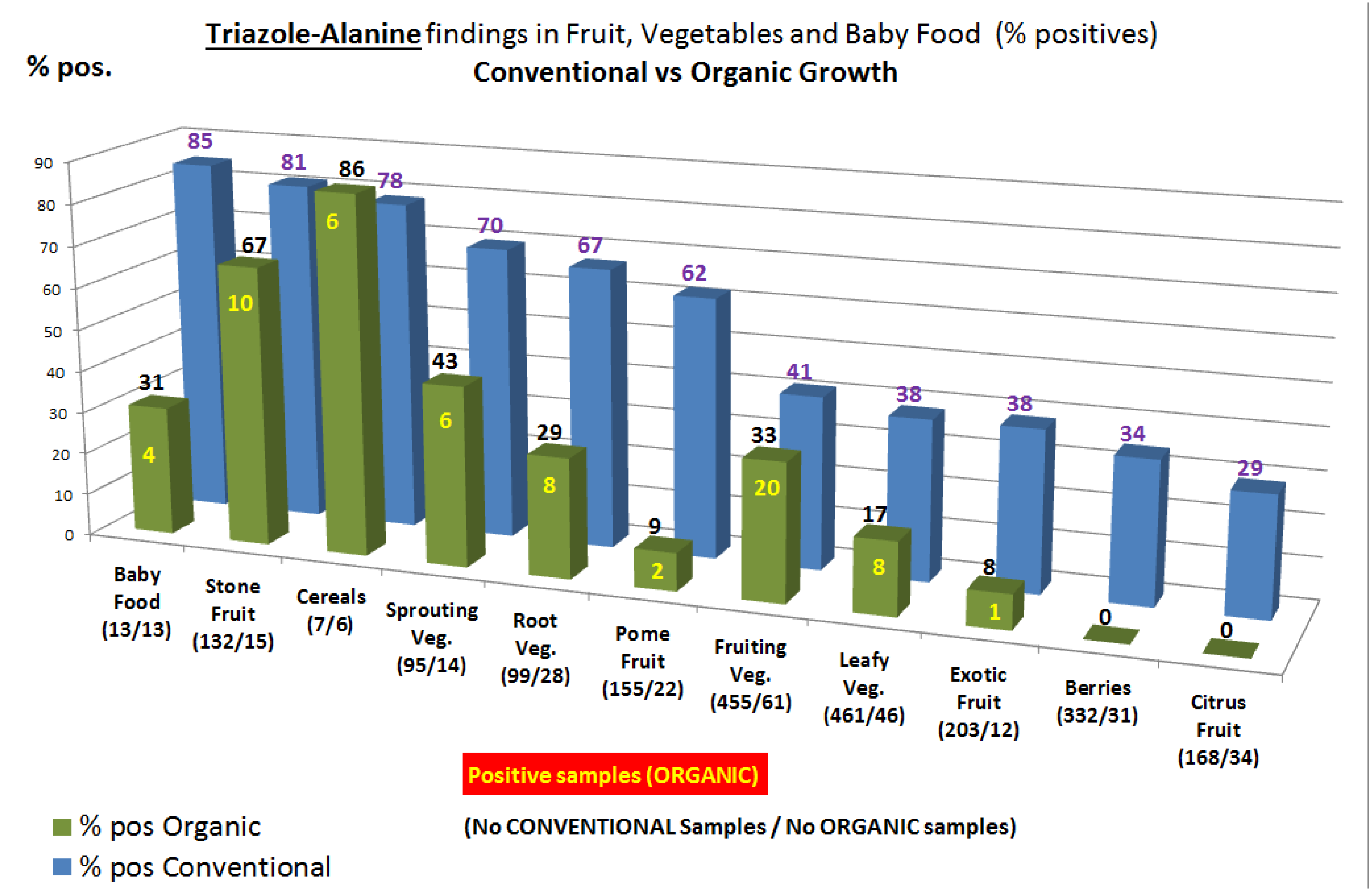
**Task Force by manufacturers of Triazole fung. : Triazole Derivative Metabolite Group (TDMG)**

## QuPPe M8 with Differential Mobility Spectrometry (DMS),

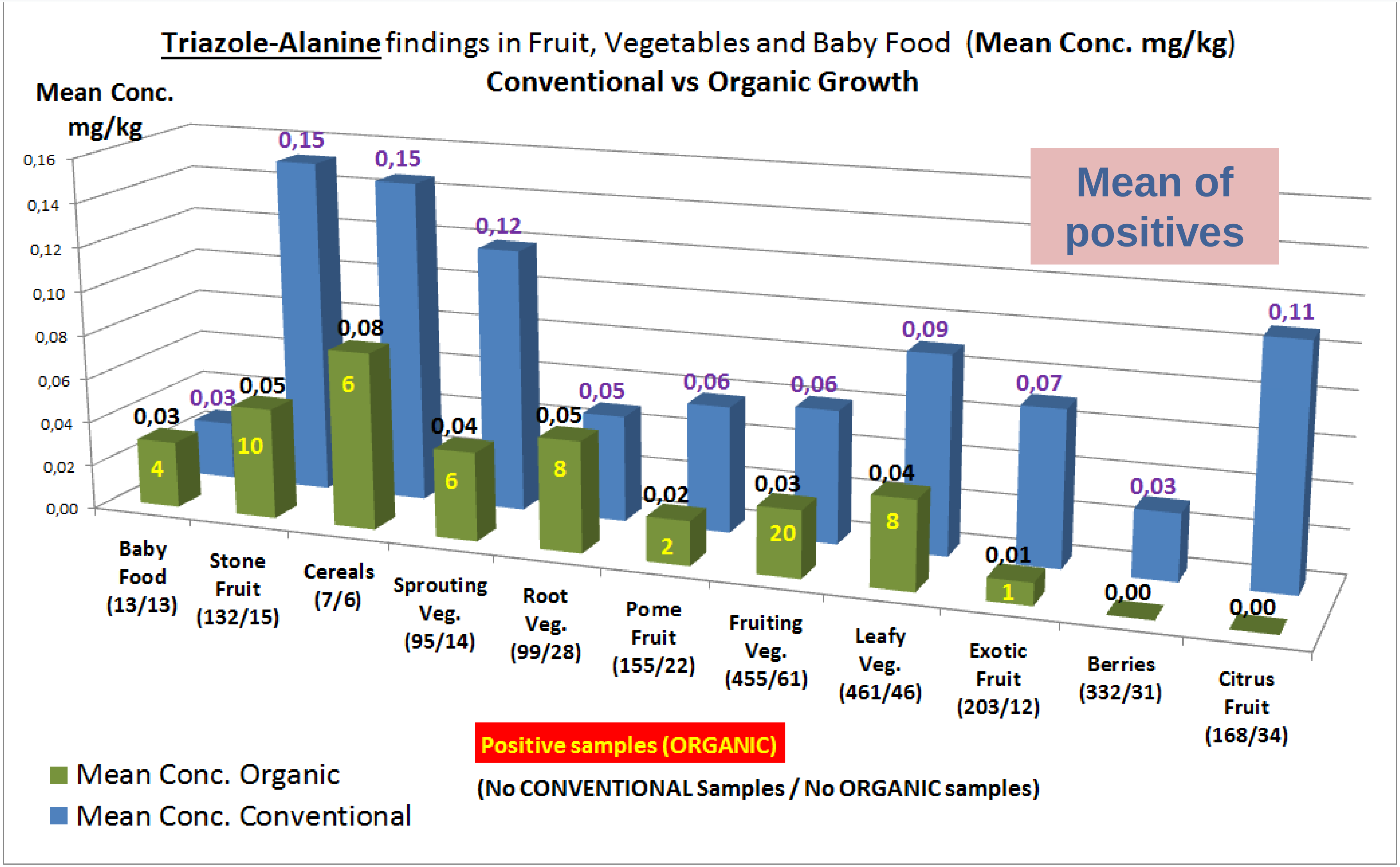
# TDM – Findings in Samples ("Pilot Monitoring")

| Compound | No. of samples | No. of positive samples (>0.01 mg/kg) | % pos. | Minimum level (mg/kg) | Maximum level (mg/kg) | Mean of pos. samples (mg/kg) |
|---|---|---|---|---|---|---|
| **Conventional samples** | | | | | | |
| 1,2,4-Triazole | 2468 | 17 | **0.7** | 0.005 | 0.035 | **0.015** |
| Triazole alanine | 2479 | 1138 | **45.9** | 0.005 | 1.4 | **0.084** |
| Triazole acetic acid | 2472 | 263 | **10.6** | 0.005 | 0.79 | **0.049** |
| Triazole lactic acid | 1398 | 338 | **24.2** | 0.005 | 0.78 | **0.052** |
| **Organic Samples** | | | | | | |
| 1,2,4-Triazole | 384 | 4 | **1.0** | 0.007 | 0.028 | **0.015** |
| Triazole alanine | 385 | 100 | **26.0** | 0.008 | 1.1 | **0.057** |
| Triazole acetic acid | 384 | 28 | **7.3** | 0.004 | 1 | **0.078** |
| Triazole lactic acid | 185 | 20 | **10.8** | 0.01 | 0.059 | **0.023** |




## More frequent findings in conventional crops

## Note: Total No. of positive organic samples was small !!




# Higher levels in conventional crops

## Note: Total No. of positive organic samples was small !!

EURL-SRM

EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

# Quick Method for the Analysis of numerous Highly Polar Pesticides in Foods of Plant Origin via LC-MS/MS involving Simultaneous Extraction with Methanol (QuPPe-Method)

Version 9 (XX 2015, Document History, see page 57)

**Authors:** M. Anastassiades; D. I. Kolberg; E. Eichhorn; A. Benkenstein; S. Lukačević; D. Mack; C. Wildgrube; I. Sigalov; D. Dörk; A. Barth

**Note:** Changes from V8 to V8.1 are highlighted in turquoise and changes from V8.1 to 9 are highlighted in yellow

## Content

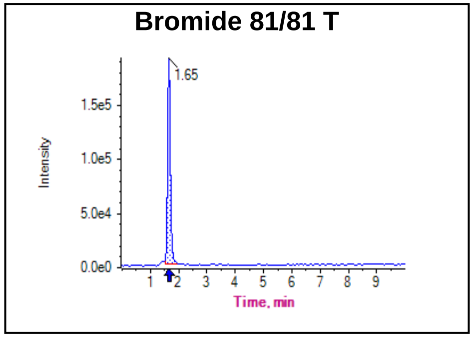


Coming up: QuPPe 9

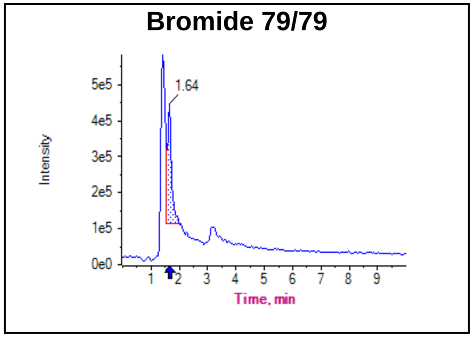
# Coming up: Inclusion of bromide into QuPPe (for screening)

1st step: Method 1.4 "PerChloPhos" (routinely 5-fold dilution)
2nd step: Re-inject following 50-fold dilution (eliminate matrix effects)
3rd step: in case of violations re-analysis with GC-method

81/81 Target




79/79 Qualifier

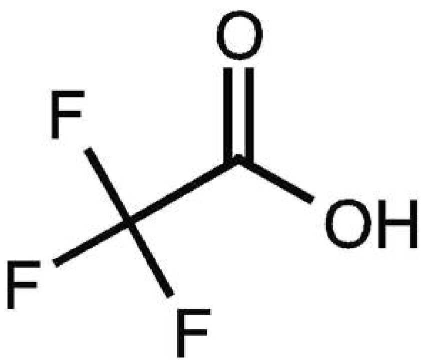



| Commodity | Spiking Level (mg/kg) | Recovery ((n=5),%) | Variation Coefficient (%) |
|---|---|---|---|
| Cauliflower | 5 | 108 | 5.5 |
| Currant | 5 | 110 | 3.7 |

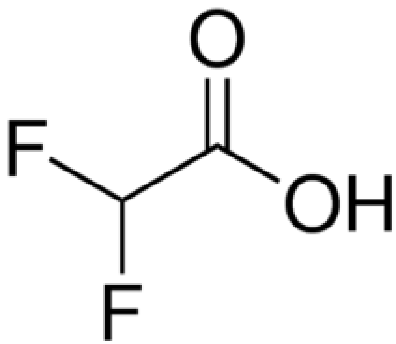
# Coming up: Inclusion of bromide into QuPPe (for screening)

| Commodity | LC-MS/MS (mg/kg) | GC-ECD after derivat. (mg/kg) |
|---|---|---|
| Lettuce | 48,5 | 47,6 |
| Lettuce | 32,3 | 28,1 |
| Thyme | 31,1 | 27,1 |
| Tomatoes | 20,4 | 18,3 |
| Selleriac | 17,1 | 17,5 |
| Parsley | 14,1 | 16,3 |
| Dill | 15,5 | 15,7 |
| Selleriac | 14,0 | 14,9 |
| Eggplant | 13,8 | 12,6 |
| Radish | 10,8 | 11 |
| Rucola | 9,0 | 10,4 |

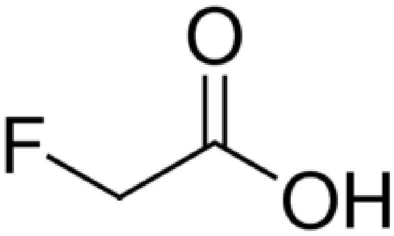
# Coming up: New active substances




**TFA**



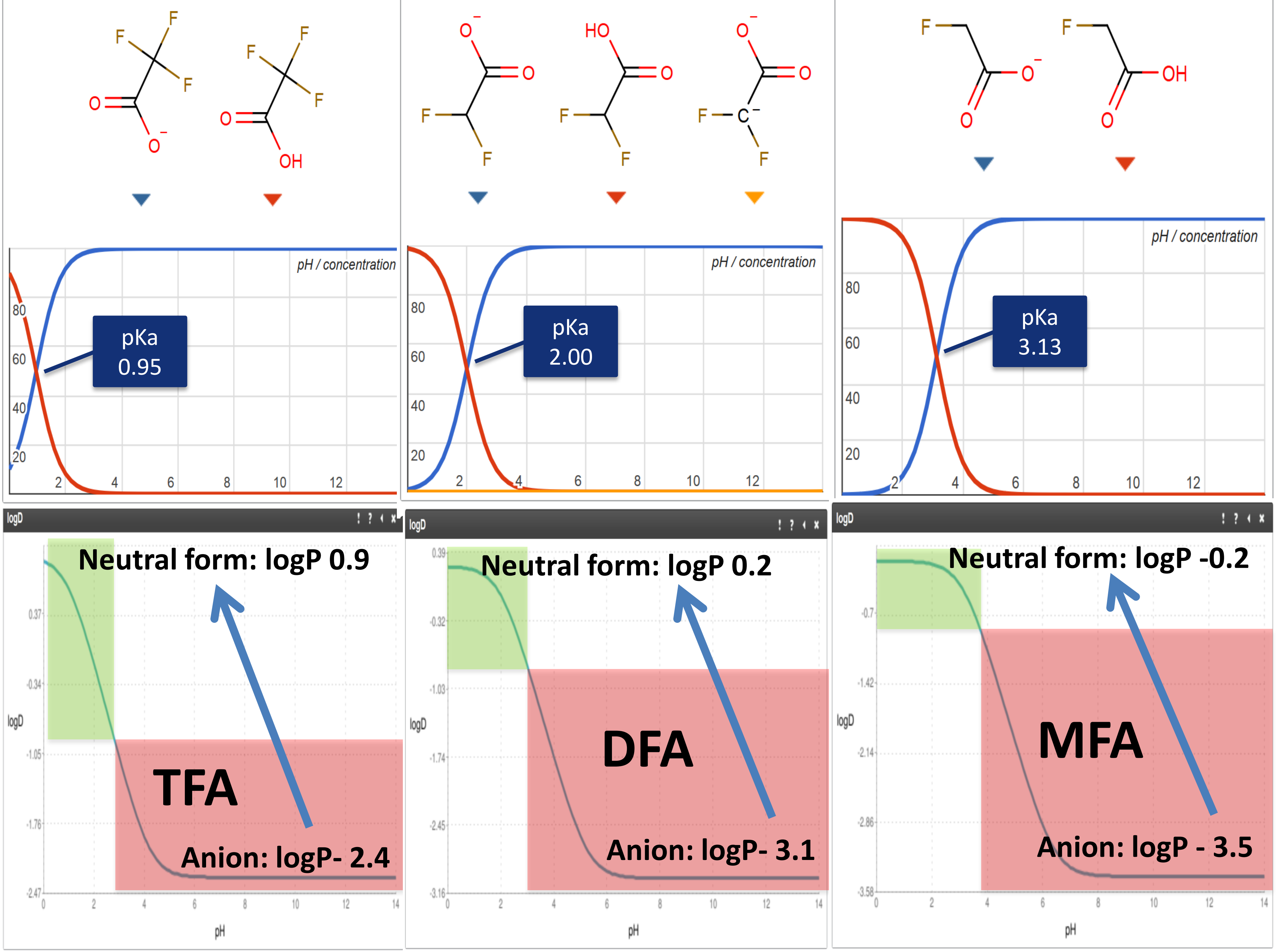

**DFA**




**MFA**

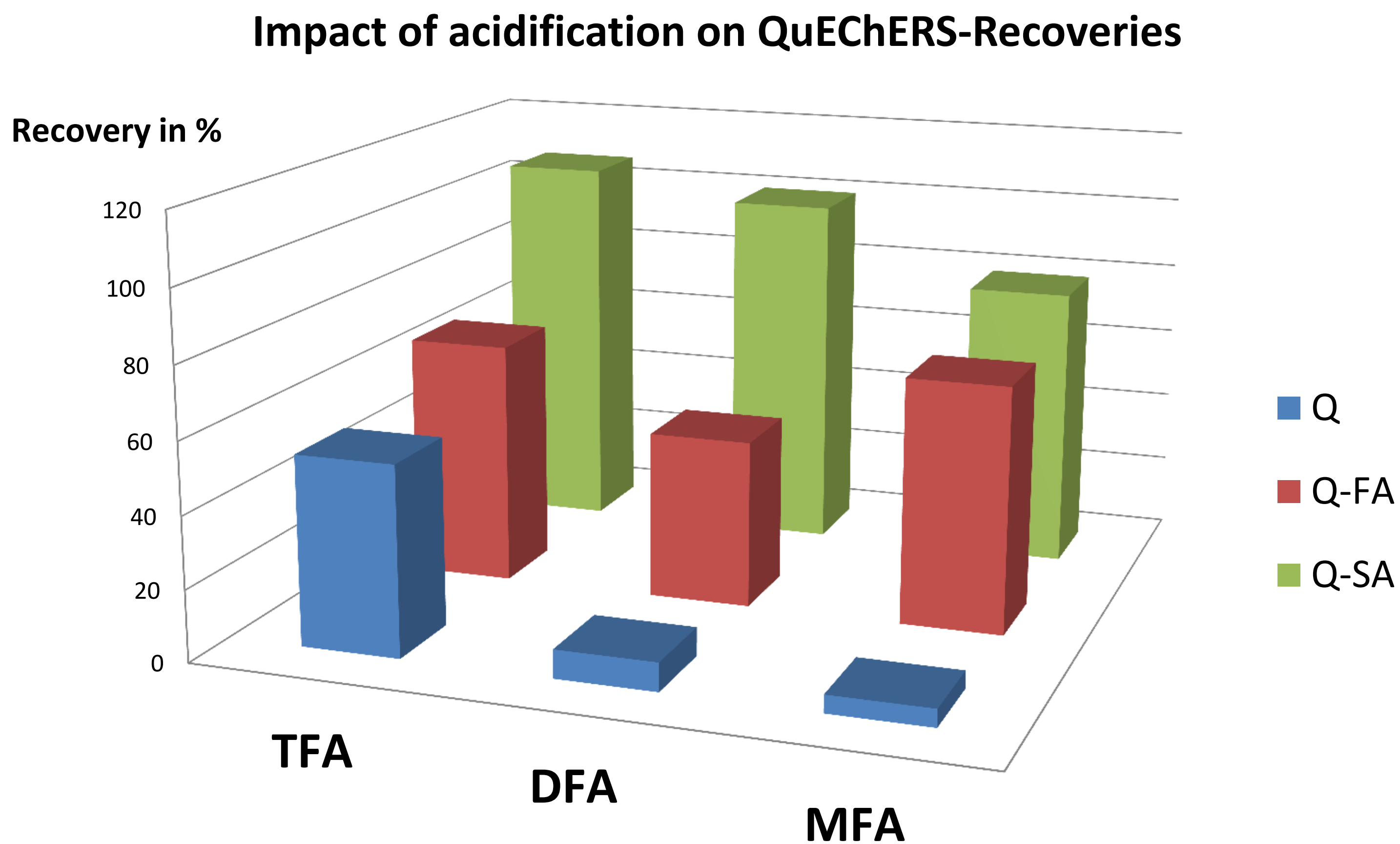
**Why?**
**TFA**: metabolite of several pesticides. e.g. Flumetraline (NAS), EFSA considers need for MRLs
**DFA:** is metabolite of Flupyradifurone (NAS), EFSA considers need for MRLs

**MFA:** Blackmail incidence in New Zealand (baby food),
Also rodenticide,
also naturally in "poison peas„ and other plants (Australia, Brazil, and Africa)


pH / concentration
pKa 0.95
pKa 2.00
pKa 3.13
logD
pH
Neutral form: logP 0.9
Neutral form: logP 0.2
Neutral form: logP -0.2
TFA
DFA
MFA
Anion: logP- 2.4
Anion: logP- 3.1
Anion: logP - 3.5

# Coming up: TFA, DFA, MFA

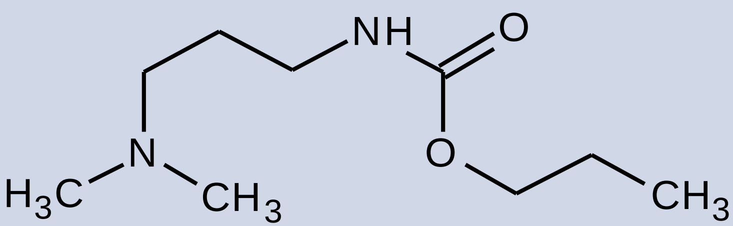
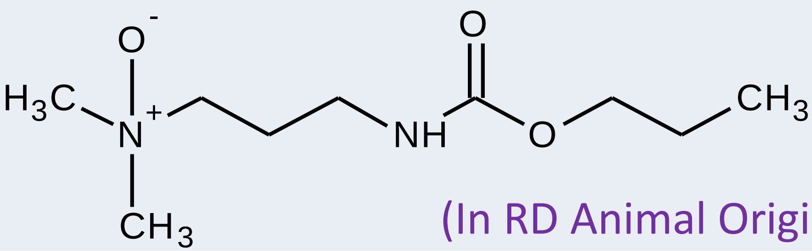
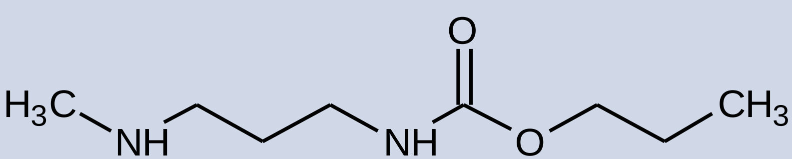
Q = QuEChERS, citrate buffered
Q-FA = QuEChERS w. 1% formic acid
Q-SA = QuEChERS w. sulfuric acid




**Whats Next?**

- Further develop and validate method
- Analyze market samples to asess residue situation

# Coming up: Propamocarb-N-oxide, Propamocarb-N-desmethyl

| Name |
|---|
| **Propamocarb**  |
| **Propamocarb-N-oxide**  (In RD Animal Origin) |
| **Propamocarb-N-desmethyl**  (In RD Poultry) |

How come?
Metabolites are included in the RD for food of animal origin

Within the frame of Art 12 work we started checking analytical behavior

Both metabolites are amenable to QuEChERS and QuPPe

**Propamocarb-N-oxide,**
**Propamocarb-N-desmethyl**

What about
residues in
Food of Plant Origin ?

# First Findings

## Propamocarb-N-oxide, Propamocarb-N-desmethyl

| Commodity | Country of origin | Propamocarb-N-desmethyl mg/ kg | Propamocarb-N-oxid mg/ kg | Propamocarb mg/ kg |
|---|---|---|---|---|
| Brussels sprout | Netherlands | 0,013 | 0,22 | 0,30 |
| Brussels sprout | Netherlands | 0,012 | 0,15 | 0,19 |
| Brussels sprout | Netherlands | 0,009 | 0,14 | 0,18 |
| Spinach | Spain | 0,19 | 0,10 | 8,2 |
| Brussels sprout | Netherlands | 0,003 | 0,088 | 0,056 |
| Lettuce | Italy | 0,061 | 0,075 | 4,5 |
| Lettuce | Belgium | 0,046 | 0,067 | 4,2 |
| Lettuce | Italy | 0,031 | 0,067 | 3,0 |
| Cauliflower, frozen | unknown | 0,001 | 0,062 | 0,010 |
| Cucumber | Spain | 0,005 | 0,055 | 0,34 |
| Cauliflower | France | n.n. | 0,050 | 0,009 |
| Cucumber | Netherlands | n.n. | 0,049 | 0,26 |
| Cucumber | Spain | 0,005 | 0,043 | 0,38 |
| Cucumber | Spain | 0,005 | 0,037 | 0,30 |
| Cucumber | Spain | 0,002 | 0,025 | 0,28 |
| Lettuce | Italy | 0,010 | 0,021 | 0,82 |
| Cucumber | Germany | 0,002 | 0,021 | 0,068 |
| Lollo rosso | France | 0,041 | 0,019 | 2,5 |
| Radish | unknown | 0,009 | 0,019 | 2,4 |
| Potatoes | Germany | 0,005 | 0,019 | 0,012 |
| Lettuce | France | 0,015 | 0,017 | 0,95 |
| Lettuce | Germany | 0,011 | 0,016 | 1,7 |
| Cucumber | Germany | n.n. | 0,014 | 0,040 |
| Potatoes | Germany | 0,003 | 0,011 | 0,009 |
| Potatoes | Germany | 0,001 | 0,011 | 0,004 |
| Melons | Italy | 0,002 | 0,010 | 0,030 |
| Cauliflower, frozen | unknown | n.n. | 0,010 | 0,002 |

First Findings

| Commodity | Country of origin | Propamocarb-N-desmethyl mg/ kg | Propamocarb-N-oxid mg/ kg | Propamocarb mg/ kg |
|---|---|---|---|---|
| Brussels sprout | Netherlands | 0,013 | 0,22 | 0,30 |
| Brussels sprout | Netherlands | 0,012 | 0,15 | 0,19 |
| Brussels sprout | Netherlands | 0,009 | 0,14 | 0,18 |
| Spinach | Spain | 0,19 | 0,10 | 8,2 |
| Brussels sprout | Netherlands | 0,003 | 0,088 | 0,056 |
| Lettuce | Italy | 0,061 | 0,075 | 4,5 |
| Lettuce | Belgium | 0,046 | 0,067 | 4,2 |
| Lettuce | Italy | 0,031 | 0,067 | 3,0 |
| Cauliflower, frozen | unknown | 0,001 | 0,062 | 0,010 |
| Cucumber | Spain | 0,005 | 0,055 | 0,34 |
| Cauliflower | France | n.n. | 0,050 | 0,009 |
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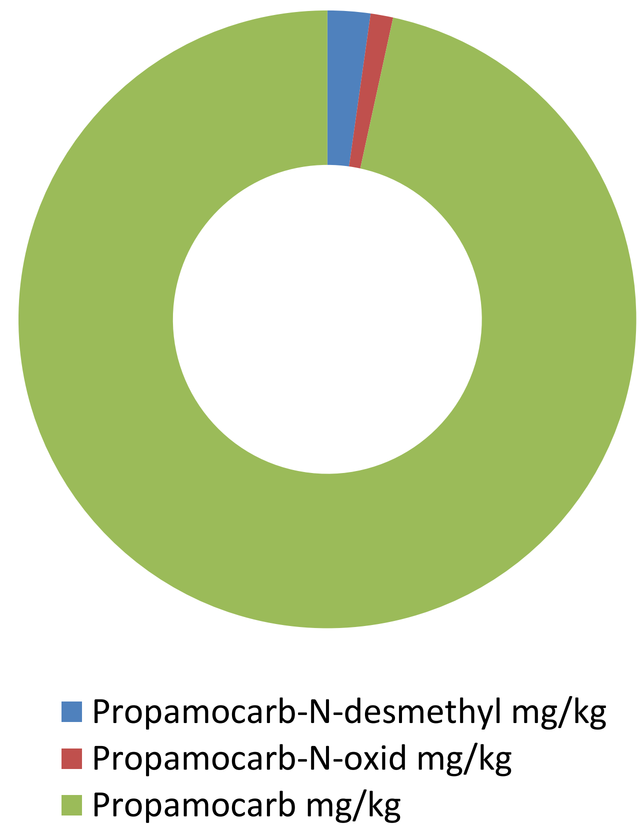

First Findings

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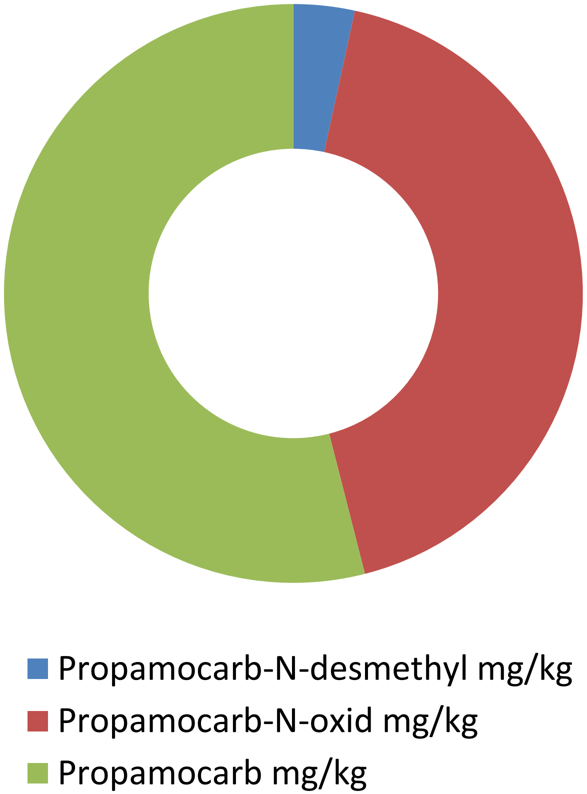
## Propamocarb-N-oxide, Propamocarb-N-desmethyl



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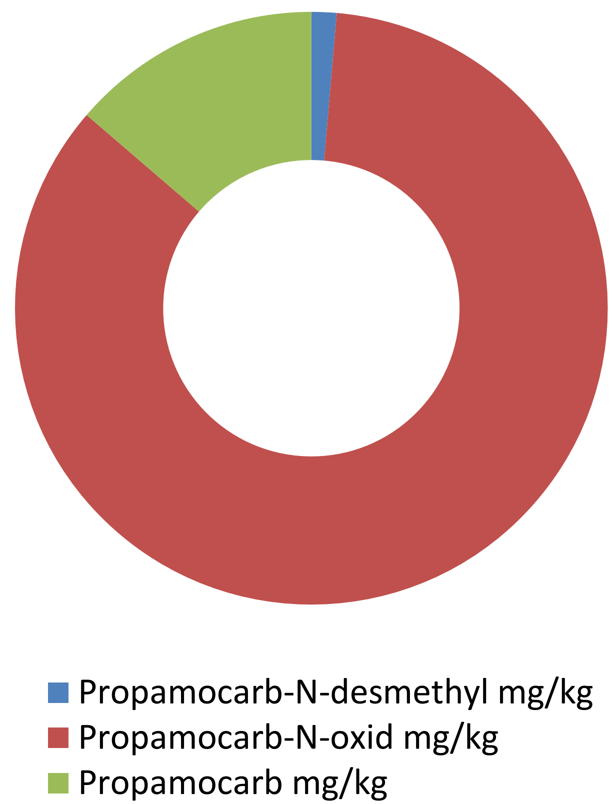
**Propamocarb-N-oxide, Propamocarb-N-desmethyl**



# First Findings

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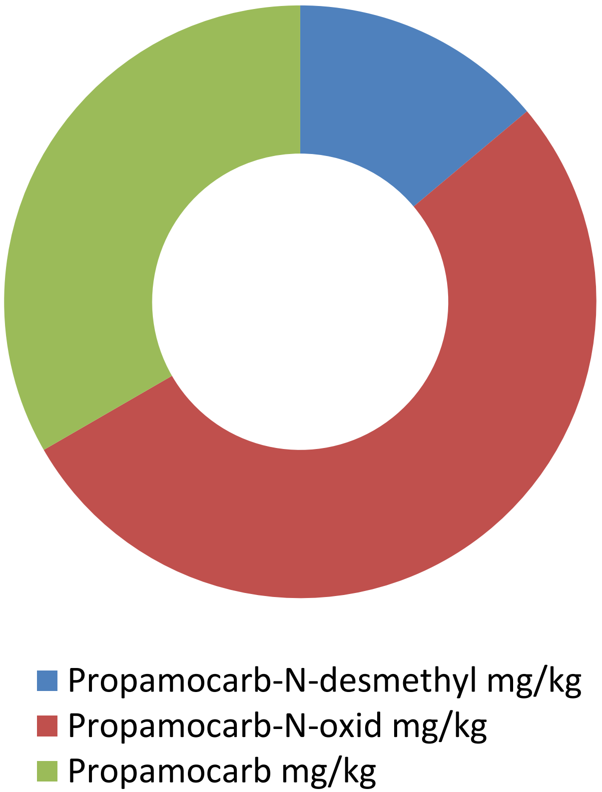
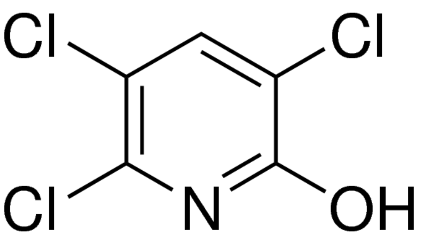
## Propamocarb-N-oxide, Propamocarb-N-desmethyl



# Coming up: Trichloropyridinole, TCPy




pKa: 8.9
Very weak acid

Metabolite of

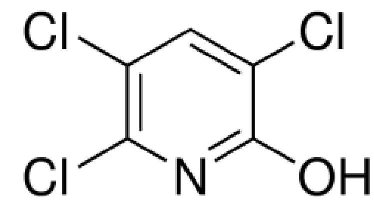
- Chlorpyrifos,
- Chlorpyrifos-methyl
- Triclopyr

Extraction method: QuEChERS without PSA cleanup,
Recovery 100%
Determination: LC-MS/MS: API neg.

First Findings

# Coming up: Trichloropyridinole, TCPy

| Commodity | Country of Origin | TCPy mg/kg | Chlorpyrifos mg/kg | Chlorpyrifos-methyl mg/kg | Triclopyr mg/kg |
|---|---|---|---|---|---|
| Raisin | Turkey | 0,048 | 0,006 | n.n. | n.n. |
| Marjoram | unknown | 0,040 | 0,016 | n.n. | n.n. |
| Grapes | Italy | 0,039 | n.n. | 0,002 | n.n. |
| Grape Juice | unknown | 0,031 | n.n. | n.n. | n.n. |
| Tomato | Spain | 0,026 | n.n. | 0,056 | n.n. |
| Grape Juice | unknown | 0,025 | n.n. | n.n. | n.n. |
| Melons | France | 0,024 | n.n. | n.b. | n.n. |
| Raisin | Turkey | 0,019 | 0,004 | n.n. | n.n. |
| Grape Juice | unknown | 0,018 | n.n. | n.n. | n.n. |
| Raisin | Cyprus | 0,016 | n.n. | n.n. | n.n. |
| Tomato sauce | unknown | 0,013 | n.n. | n.n. | n.n. |
| Grapes | Egypt | 0,012 | 0,008 | n.n. | n.n. |
| Grapes | Italy | 0,011 | n.n. | n.b. | n.n. |
| Ginger | China | 0,008 | n.n. | n.n. | n.n. |
| Apple sauce | unknown | 0,006 | n.n. | n.n. | n.n. |
| Apple sauce | unknown | 0,005 | 0,002 | n.n. | n.n. |
| Plums, dried | Germany | 0,004 | n.n. | n.n. | n.n. |
| Raisin | unknown | 0,004 | n.n. | n.n. | n.n. |
| Grapes | Greece | 0,003 | n.n. | n.b. | n.n. |



# Pos. findings of SRM-compounds in Veggies (2014) CVUAS

| Pesticides and Metabolites | No. of findings | mg/kg | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | <0,01 | 0.01 -<0,05 | 0,05 -<0,2 | 0,2 – <1 | 1 - <5 | 5- <20 | >20 | Max. |
| Fosetyl-(mainly phosphonic A.) | 203 | | 3 | 34 | 60 | 59 | 37 | 10 | 153 |
| Chlorate | 150 | 39 | 74 | 22 | 10 | 5 | | | 3,6 |
| Propamocarb | 98 | 41 | 25 | 14 | 10 | 6 | 1 | 1 | 28,4 |
| Bromide (FEW SAMPLES) | 37 | | | | | 29 | 8 | | 12,4 |
| Propamocarb-N-oxide | 20 | 12 | 4 | 4 | | | | | 0,088 |
| Pymetrozine | 16 | 14 | 2 | | | | | | 0,025 |
| Chlorothalonil | 15 | 7 | 4 | 3 | | 1 | | | 1 |
| Propamocarb-N-desmethyl | 14 | 12 | 2 | | | | | | 0,046 |
| Cyromazine | 12 | 6 | 5 | 1 | | | | | 0,075 |
| 2,4-D | 8 | 6 | 2 | | | | | | 0,016 |
| Folpet | 6 | 4 | 2 | | | | | | 0,02 |
| BAC | 5 | | 3 | 1 | | | | | 0,33 |
| Dodine | 5 | 4 | 1 | | | | | | 0,014 |
| ETU | 5 | 3 | 1 | 1 | | | | | 0,11 |
| Prochloraz, sum | 5 | 4 | 1 | | | | | | 0,023 |
| Clopyralid | 4 | 3 | | 1 | | | | | 0,064 |
| DDAC | 4 | | 3 | | 1 | | | | 0,65 |
| Dithiocarbamates (FEW SAMPLES) | 4 | | | | 1 | 3 | | | 2,3 |
| Maleic hydrazide | 4 | | | | | 1 | 3 | | 8,4 |
| 4-CPA | 3 | 2 | 1 | | | | | | 0,028 |
| Daminozide | 2 | 1 | 1 | | | | | | 0,025 |
| Ethephon | 2 | | | 1 | | 1 | | | 1,3 |
| MCPP | 2 | 1 | 1 | | | | | | 0,011 |
| Nereistoxin | 2 | 1 | 1 | | | | | | 0,016 |
| PTU | 2 | 1 | 1 | | | | | | 0,017 |
| Bromoxynil | 1 | 1 | | | | | | | 0.008 |
| Dicamba | 1 | 1 | | | | | | | 0.018 |
| HEPA, ethephon metabolite | 1 | | | | 1 | | | | 0,35 |
| Nicotine (FEW SAMPLES) | 1 | | | | 1 | | | | 0,61 |
| Trimethylsulfonium cation | 1 | | 1 | | | | | | 0,012 |

**813 samples conventionally grown fresh Vegetables**

# Positive findings of SRM-compounds in Fruits (2014) CVUAS

| Pesticides and Metabolites | No. of Findings | mg/kg | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | <0,01 | 0.01 -<0,05 | 0,05 -<0,2 | 0,2 – <1 | 1 - <5 | 5- <20 | >20 | Max. |
| Fosetyl (mainly phosphonic A.) | 412 | | 14 | 60 | 104 | 120 | 97 | 17 | 82 |
| Captan | 83 | 21 | 29 | 16 | 15 | 2 | | | 4.8 |
| Chlorate | 70 | 16 | 48 | 4 | 2 | | | | 0.65 |
| Dithianon | 67 | 18 | 20 | 26 | 3 | | | | 0.37 |
| Prochloraz, Sum | 44 | 9 | 8 | 11 | 11 | 5 | | | 2.4 |
| Dodine | 40 | 31 | 4 | 3 | 2 | | | | 0.28 |
| Folpet | 38 | 29 | 6 | 3 | | | | | 0.088 |
| 2,4-D | 35 | 18 | 8 | 9 | | | | | 0.16 |
| Gibberellic acid | 26 | 7 | 14 | 4 | 1 | | | | 0.25 |
| Ethephon | 19 | 1 | 10 | 6 | 2 | | | | 0.43 |
| Dithiocarbamates (FEW SAMPLES) | 15 | | | 7 | 8 | | | | 0.67 |
| Fenbutatin oxide | 14 | 5 | 3 | 2 | 4 | | | | 0.33 |
| Chlormequat | 11 | 5 | 5 | 1 | | | | | 0.067 |
| HEPA | 8 | | 4 | 4 | | | | | 0.085 |
| MCPA | 7 | 7 | | | | | | | 0.003 |
| Morpholine | 6 | | 2 | 4 | | | | | 0.071 |
| BAC | 5 | 4 | | 1 | | | | | 0.067 |
| Bromide (FEW SAMPLES) | 5 | | | | | 4 | 1 | | 9.3 |
| CGA 304075, Met. Cyprodinil | 5 | 2 | 1 | 2 | | | | | 0.19 |
| Chlorothalonil | 5 | 1 | 1 | 2 | 1 | | | | 0.2 |
| Trimethylsulfonium-Cation | 5 | 2 | 3 | | | | | | 0.031 |
| Fluazifop, free acid | 4 | 3 | 1 | | | | | | 0.011 |
| Nereistoxine | 3 | 1 | 1 | 1 | | | | | 0.075 |
| Triclopyr | 3 | 3 | | | | | | | 0.008 |
| DDAC | 2 | | 2 | | | | | | 0.015 |
| ETU | 2 | 1 | | 1 | | | | | 0.071 |
| Prohexadione | 2 | 1 | 1 | | | | | | 0.018 |
| Dinocap | 1 | | 1 | | | | | | 0.046 |
| Ethoxyquin | 1 | 1 | | | | | | | 0.005 |
| Glufosinate, Sum | 1 | | 1 | | | | | | 0.011 |
| Glyphosate | 1 | | | 1 | | | | | 0.083 |
| Meptyldinocap | 1 | | | | 1 | | | | 0.97 |
| Propamocarb-N-desmethyl | 1 | 1 | | | | | | | 0.005 |
| PTU | 1 | 1 | | | | | | | 0.005 |

**749 samples conventionally grown fresh fruit**

# MRL-exceedances SRM-compounds in Veggies (CVUAS 2014)

| Substance | Vegetables in which MRL exceedances occurred (country of origin) |
|---|---|
| 4-CPA | Aubergine (Turkey) |
| Acephate | Green Beans, (Kenia) |
| Amitraz, sum | Chilli peppers (Malaysia) **Analyzed by MRM (via metab. DMF, DMPF)** |
| BAC | Carrot (Spain); Chilli peppers (Malaysia); Spinach (Portugal); Basil (Malaysia) |
| Chlorate | Sweet Peppers (Morocco, Spain 2x, Israel 2x, Hungary); Zucchini (Spain 2x, Italy, Germany); Parsley (Unknown 2x, Germany 2x); Green Beans (Spain 2x, Cambodia, Morocco 2x, Kenia, Germany); Basil (Cambodia, Germany 6x, Malaysia 2x); Dill leaves (Italy, Germany); Broccoli (Spain 3x); Melon (Honduras 2x); Asparagus (Peru); Lemon grass (Thailand); Chervil (Germany); Tomato (Unknown, Morocco 3x, Turkey, Belgium 4x, France, Germany 3x, Netherlands, Spain 3x); Rucola (Italy 2x); Endive (Italy 2x, Germany); Melon/Honeydew melon (Costa Rica); Aubergine (Spain, Thailand, Malaysia, Netherlands, France, Turkey, Belgium); Savoy Cabbage (Italy); Celeriac (Germany); Spinach (Spain, Unknown, Italy 2x); Radish (Italy, Unknown); Cucumber (Germany 4x, Netherlands); Iceberg Lettuce (Spain); Peas with pod (Spain, Simbabwe, Peru); Celery (Spain); Oakleaf Lettuce (Spain 2x, Germany); Lambs Lettuce (Germany 4x); Lettuce (Germany, Italy); Coriander (Cambodia, Germany) |
| Daminozide | Tomato (Germany) |
| DDAC | Kohlrabi (Italy); Basil (Malaysia); Cucumber (Netherlands); Green Beans (Kenia) |
| Ethephon | Chilli peppers (Turkey) |
| Flonicamid, sum | Sweet Peppers (Turkey) |
| Fosetyl-aluminium | Spinach (Italy); Basil (Germany 2x); Celeriac (Germany); Chinese cabbage (Germany) |
| Nicotine | Chives (Kenia) |

# MRL-Exceedances of SRM-compounds in Fruits (CVUAS 2014)

| Substance | Vegetables in which MRL exceedances occurred (country of origin) |
|---|---|
| Chlorate | Strawberry (Spain 8x); Blackberry (Germany); White table grape (Egypt, South Africa); Cranberry (unknown, USA); Huckleberry; Blueberry (Chile); Pear (Belgium, Italy 3x, Portugal, South Africa 3x); Peach (Chile); Plum (South Africa 6x); Nectarine (Chile); Sweet cherry (Argentina, Chile, Spain 3x, Turkey); Avocado (Chile); Lemon (Spain 2x); Grapefruit (Israel); Lime (Brazil); Pomelo (China); Pineapple (Costa Rica 6x, Ghana); Mango (unknown); Pitahaya (Vietnam 2x) |
| DDAC | Lemon (Argentina) |
| Dodin | Apricot (Turkey) |
| Ethephon | Kumquat (unknown) |
| Folpet | Red table grape (Germany); White table grape (Germany 2x) |
| Fosetyl, Sum | Blackberry (Spain); Nectarine (Chile 2x, Spain); Sweet cherry (Chile); Avocado (South Africa); Mango (Brazil); Kiwi (Italy 2x) |
| Propamocarb | Strawberry (Egypt) |

# Thanks !

European Commission

EURL-SRM

www.eurl-pesticides.eu