

# Evaluation of matrix effects in pesticide multi-residue methods by mapping natural components using LC-HRMS

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## INTRODUCTION

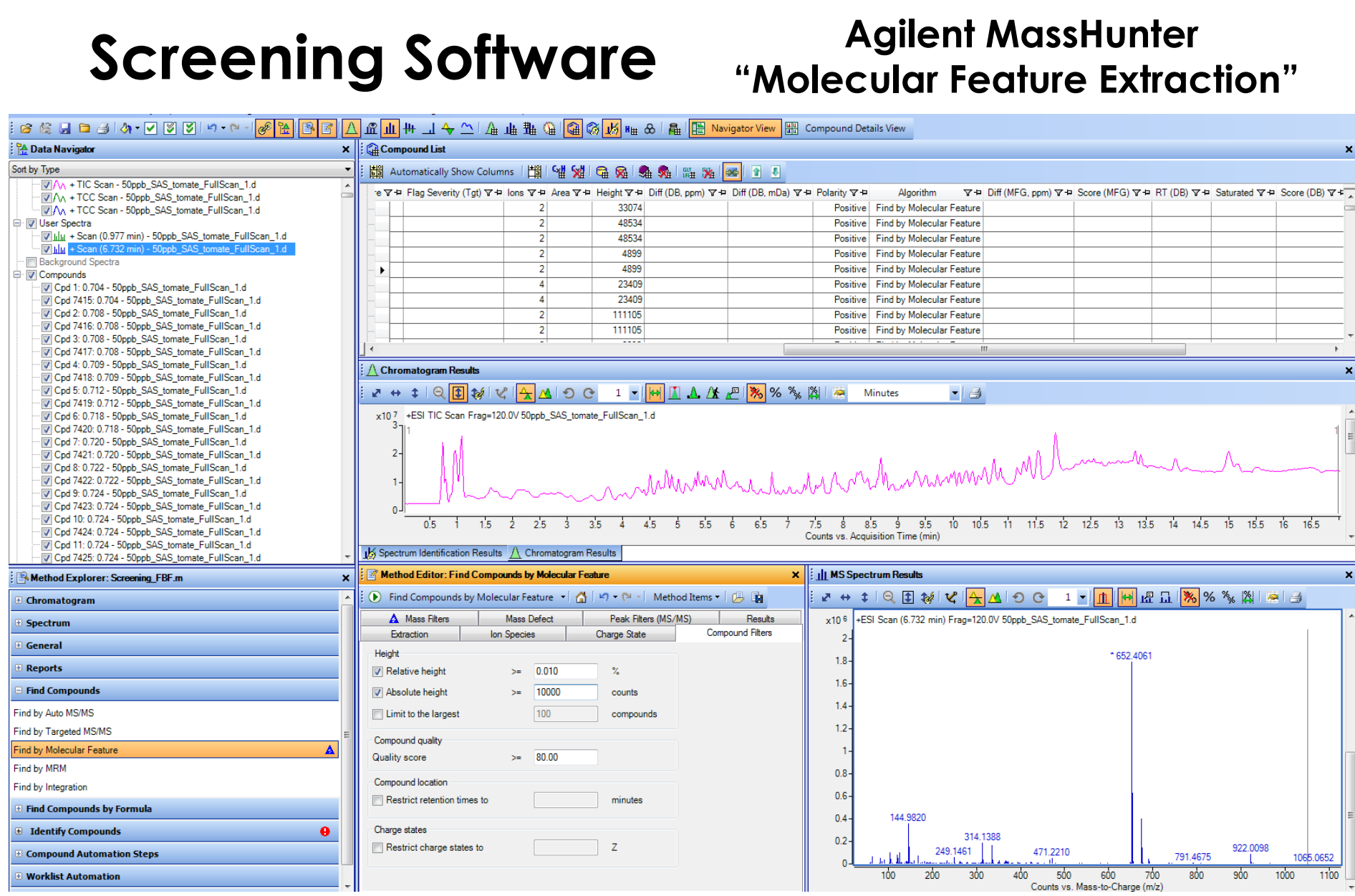
The presence of matrix effects is one of the major concerns in food analysis. Its presence affects the analyte signal and can lead to errors in the quantification and the detection of the analytes. In this work the relation between matrix suppression and co-extracted matrix components has been investigated. Twenty three different commodities were extracted by various extraction Multi-residue Methods –MRM–, mapping their natural compounds by retention time and accurate mass. Mapping them allows to evaluate the benefit in using one specific method or what can be the main natural compounds that can interact with the target analytes.

## EXPERIMENTAL SECTION: SAMPLE TREATMENT AND LC-TOF-MS ANALYSIS

**SAMPLE TREATMENT**  
Extraction of blank matrices  
**Citrate buffered QUEChERS** <sup>1,2</sup>  
↓  
Blank extract  
↓  
Spiked with 80 pesticides 100 µg/L  
  
\* Modified QUEChERS  
1. CaCl<sub>2</sub> addition in clean-up (0.2 g sample/ml)  
2. Additional step of SPE with ZrO<sub>2</sub>

**LC-QTOF-MS**  
  
**Operational conditions**  
Full-scan ESI (+) mode  
Nebulizer: 40psi  
Gas Temp : 400°C  
Cap. Voltage: 4000 V.  
Frag. Voltage: 90 V

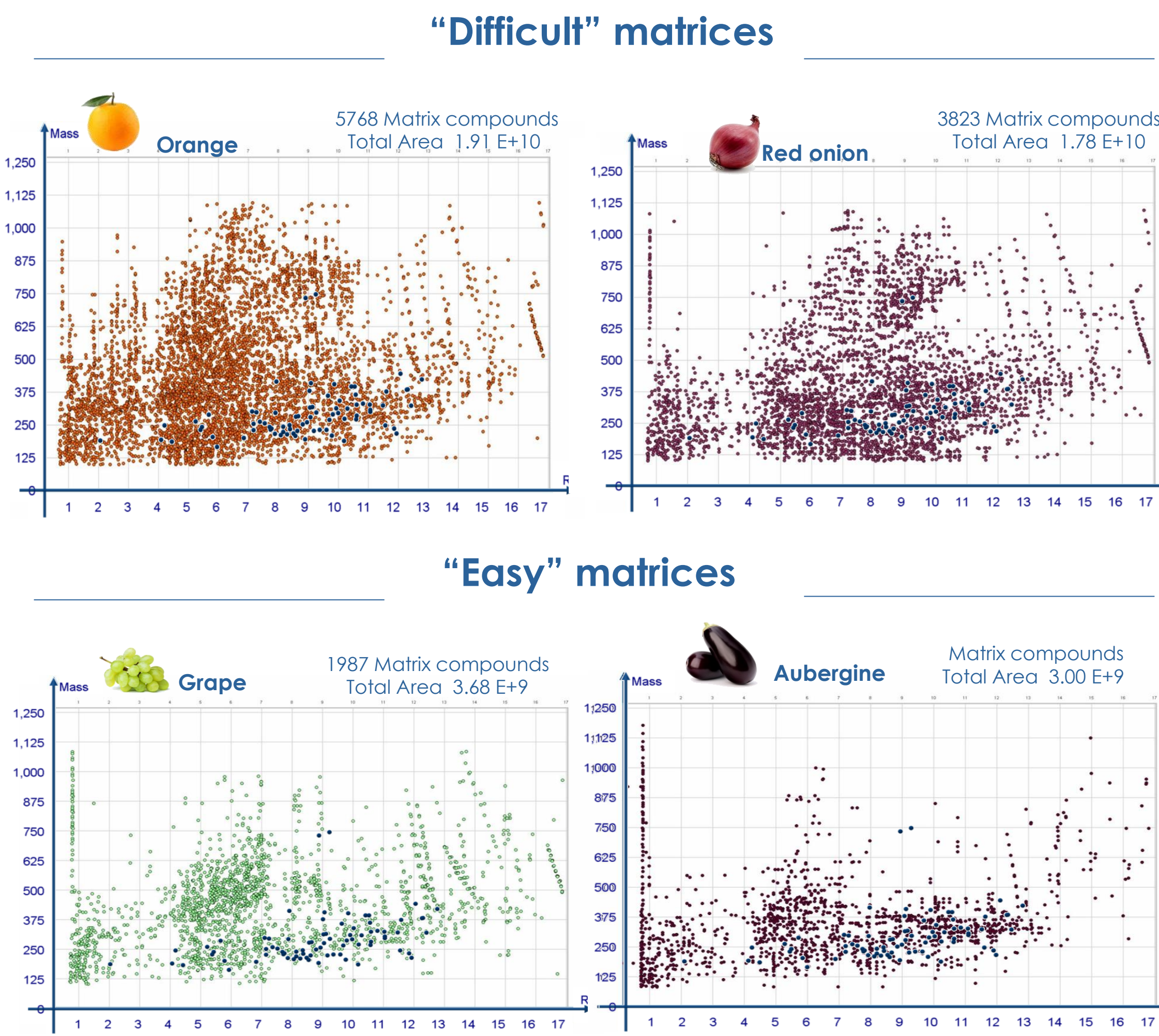
**Chromatography** Agilent 1200 HPLC system  
Column: XDB-C18 Agilent. 50mm x 4.6 mm (1.8 µm)  
  
**Mobile phase:**  
AcN (A) (5% water, 0.1% formic acid) and MilliQ Water (B) (0.1 % formic acid)  
10% (A) isocratic t=1 min, then to 100 % (A) in 10 min and maintained for 6 min, Flow rate of 0.6 mL/min.



## RESULTS

| Commodity groups                         | Matrix               | N° of co-extracted compounds |                          |                     | TIC (Counts) | % of Pesticides with High (>50%) Medium (20-50%) and Low Signal Suppression (<20%) |        |     |
|------------------------------------------|----------------------|------------------------------|--------------------------|---------------------|--------------|------------------------------------------------------------------------------------|--------|-----|
|                                          |                      | Retention Time: 0-17min      | Retention Time: 7-13 min | MW>500 RT: 7-13 min |              | High                                                                               | Medium | Low |
| High water content                       | Papaya               | 1270                         | 214                      | 38 (18%)            | 3.70E+09     | --                                                                                 | --     | --  |
|                                          | Aubergine            | 1400                         | 573                      | 36 (6%)             | 3.00E+09     | --                                                                                 | --     | --  |
|                                          | Plum                 | 2008                         | 260                      | 51 (20%)            | 3.12E+09     | --                                                                                 | --     | --  |
|                                          | Lettuce              | 1586                         | 625                      | 208 (33%)           | 3.70E+09     | --                                                                                 | --     | --  |
|                                          | Tomato (Kumato type) | 2155                         | 668                      | 147 (22%)           | 4.18E+09     | 0                                                                                  | 10     | 90  |
|                                          | Tomato (Cherry type) | 2833                         | 746                      | 201 (27%)           | 5.63E+09     | 0                                                                                  | 16     | 84  |
|                                          | Pear                 | 2919                         | 708                      | 173 (24%)           | 3.64E+09     | --                                                                                 | --     | --  |
|                                          | Apple                | 3047                         | 726                      | 270 (37%)           | 4.25E+09     | --                                                                                 | --     | --  |
|                                          | Mango                | 2649                         | 765                      | 199 (26%)           | 3.77E+09     | --                                                                                 | --     | --  |
|                                          | Pepper               | 3419                         | 919                      | 329 (36%)           | 5.51E+09     | 0                                                                                  | 23     | 78  |
|                                          | Green bean           | 2398                         | 913                      | 88 (10%)            | 3.92E+09     | --                                                                                 | --     | --  |
|                                          | Asparagus            | 2277                         | 1053                     | 174 (17%)           | 3.33E+09     | --                                                                                 | --     | --  |
|                                          | Cucumber             | 2258                         | 1068                     | 181 (17%)           | 5.73E+09     | --                                                                                 | --     | --  |
|                                          | Cauliflower          | 2560                         | 1101                     | 160 (15%)           | 3.66E+09     | --                                                                                 | --     | --  |
|                                          | Zucchini             | 3115                         | 1466                     | 510 (35%)           | 5.78E+09     | 6                                                                                  | 25     | 69  |
| High acid content and high water content | Broccoli             | 3397                         | 1666                     | 359 (22%)           | 4.58E+09     | --                                                                                 | --     | --  |
|                                          | Onion (white type)   | 2925                         | 1656                     | 543 (33%)           | 1.05E+10     | 18                                                                                 | 34     | 49  |
|                                          | Onion (red type)     | 3823                         | 2113                     | 765 (36%)           | 1.78E+10     | 56                                                                                 | 33     | 11  |
|                                          | Leek                 | 4381                         | 2155                     | 382 (18%)           | 8.10E+9      | --                                                                                 | --     | --  |
|                                          | Grape (red type)     | 1930                         | 492                      | 134 (27%)           | 3.92E+09     | --                                                                                 | --     | --  |
|                                          | Grape (white type)   | 1987                         | 599                      | 213 (36%)           | 3.68E+09     | --                                                                                 | --     | --  |
|                                          | Grapefruit           | 5064                         | 1933                     | 999 (52%)           | 7.20E+09     | --                                                                                 | --     | --  |
|                                          | Orange               | 5768                         | 2072                     | 879 (42%)           | 1.91E+10     | 55                                                                                 | 33     | 13  |
|                                          | Mandarin             | 6060                         | 2738                     | 1345 (49%)          | 1.57E+10     | --                                                                                 | --     | --  |
|                                          | Chamomile            | 3784                         | 1770                     | 282 (16%)           | 1.36E+10     | --                                                                                 | --     | --  |
| Difficult or unique commodities          | Black tea            | 4910                         | 1828                     | 402 (22%)           | 1.18E+10     | --                                                                                 | --     | --  |
|                                          | Green tea            | 5793                         | 2019                     | 726 (36%)           | 1.32E+10     | --                                                                                 | --     | --  |
|                                          | Red tea              | 4504                         | 1753                     | 497 (28%)           | 1.18E+10     | --                                                                                 | --     | --  |

### Mapping of Co-extracted matrix compounds-Pesticides

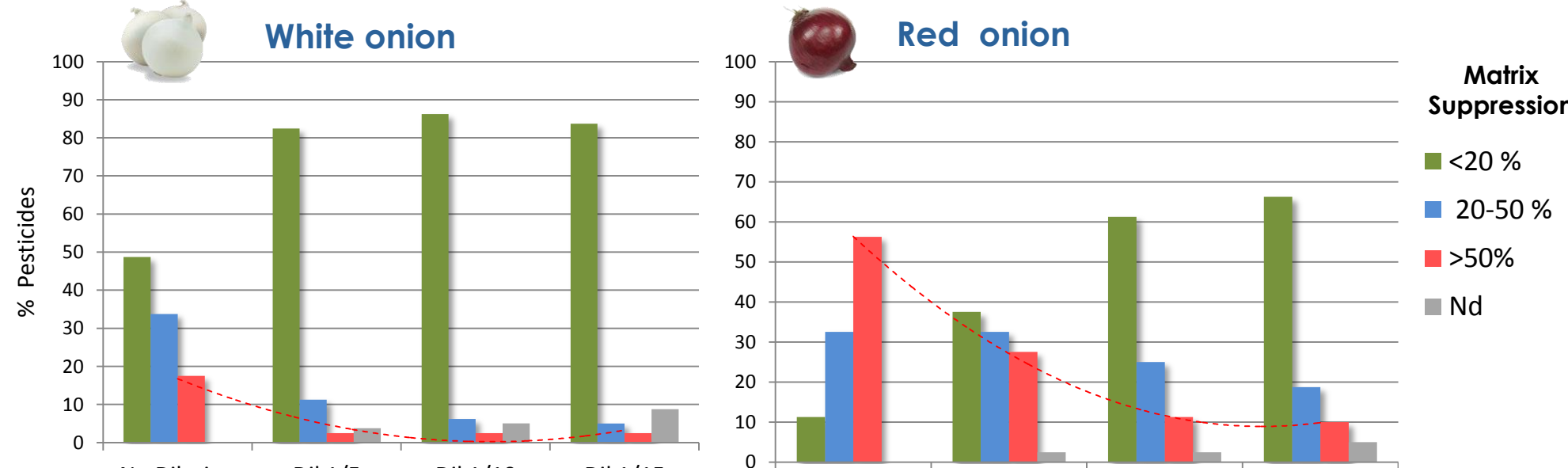


### Signal suppression, number and concentration of co-eluting matrix compounds. Orange matrix (0.2 g sample/ml)

| Pesticide     | Mass     | Rt (min) | Suppression | N° of co-eluting matrix compounds (± 0.05 min) | Σ Compounds signal height of co-eluting compounds (counts) |
|---------------|----------|----------|-------------|------------------------------------------------|------------------------------------------------------------|
| Cinazulfuron  | 413.1005 | 8.09     | -6          | 63                                             | 3E+06                                                      |
| Propoxur      | 209.1052 | 8.23     | 0           | 44                                             | 4E+06                                                      |
| Carbofuran    | 221.1046 | 8.32     | 0           | 34                                             | 3E+06                                                      |
| Isoproturon   | 206.1419 | 8.73     | -88         | 84                                             | 2E+07                                                      |
| Metolachl     | 279.1465 | 8.74     | -74         | 84                                             | 2E+07                                                      |
| Ofurea        | 281.0819 | 8.84     | 1           | 39                                             | 2E+06                                                      |
| Heptenophos   | 250.0162 | 8.97     | -8          | 65                                             | 7E+06                                                      |
| Isoproturb    | 194.1176 | 9.01     | -100        | 94                                             | 2E+07                                                      |
| Flazasulfuron | 407.0511 | 9.22     | -93         | 83                                             | 2E+07                                                      |
| Metazachlor   | 277.0982 | 9.25     | -83         | 93                                             | 3E+07                                                      |
| Bupirimate    | 316.1563 | 9.27     | -83         | 125                                            | 4E+07                                                      |
| Triadimenol   | 295.1082 | 9.42     | -18         | 45                                             | 9E+06                                                      |
| Promecarb     | 207.1259 | 9.95     | -15         | 42                                             | 3E+06                                                      |
| Axoxystrobin  | 403.1162 | 10.03    | -4          | 29                                             | 5E+06                                                      |

All pesticides with high suppression present an elevated number of co-eluting species (> 75), some of them very concentrated (sum of height signal ≥ 2e7)

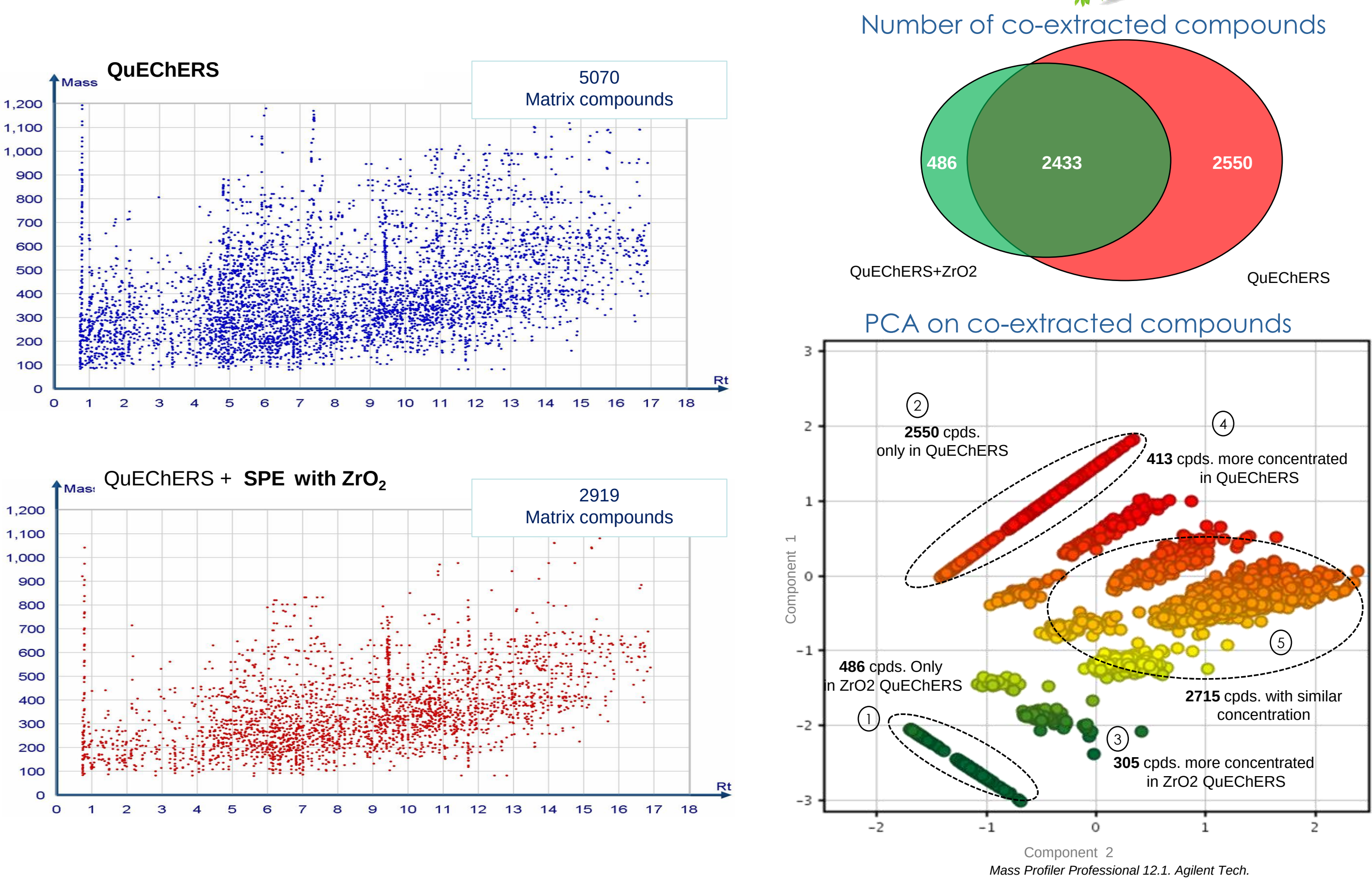
### Dilution to overcome matrix effects



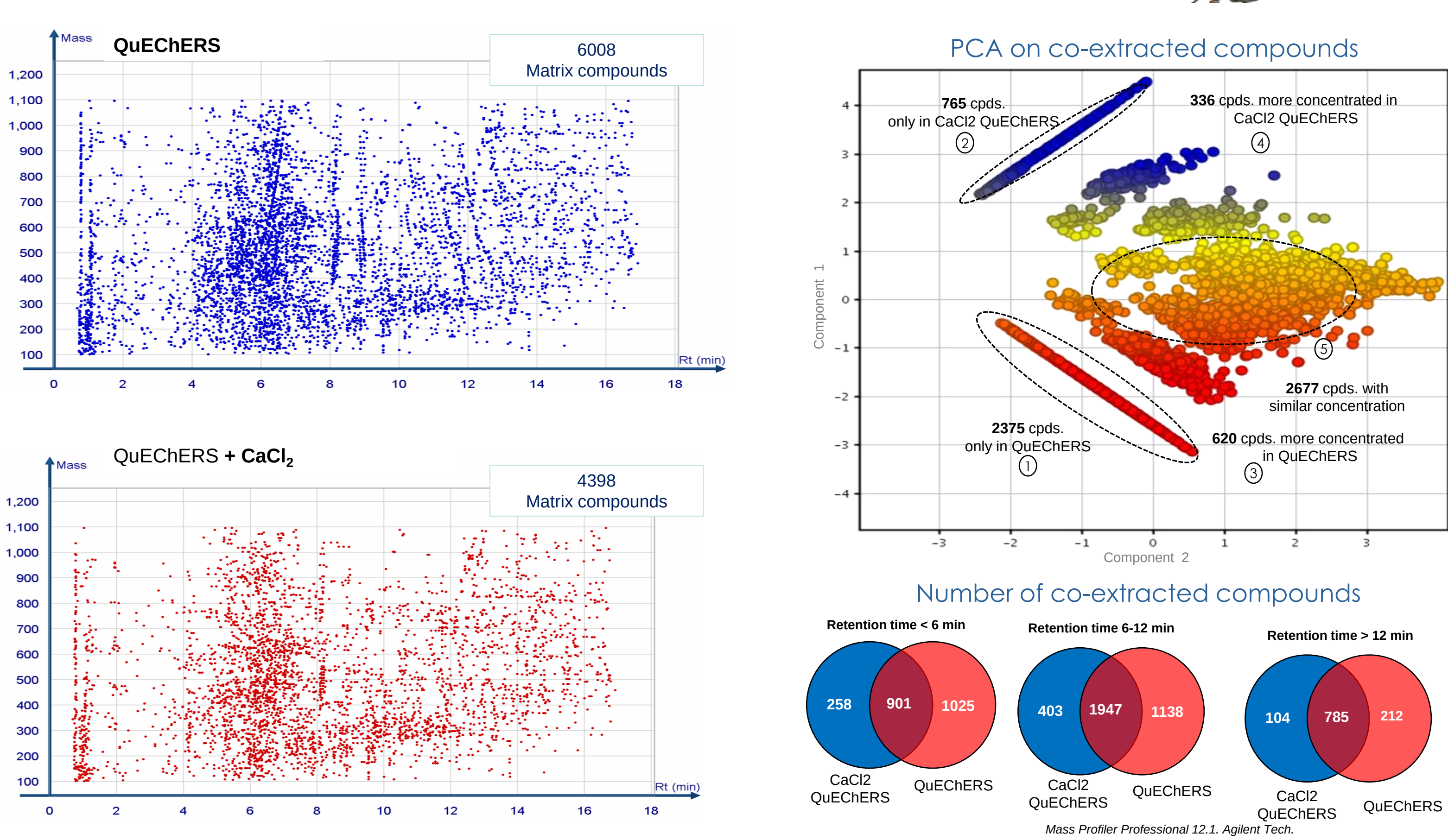
A sample dilution decreases the number of competing molecules and thus the analyte signal increases and matrix effects improved for the majority of pesticides.

## Evaluation of Multi-Residue Extraction Methods

### QUEChERS vs QUEChERS+SPE with ZrO2 in Parsley matrix



### QUEChERS vs QUEChERS+CaCl2 in Green tea matrix



## CONCLUSION

Mapping of matrix components by molecular weight and retention time is a very good approach for assessing matrix difficulty, risk of matrix suppression effects and evaluation of sample preparation methods. The number and distribution of co-extracted compounds, vary much depending on vegetable matrix even those included in the same commodity group according to the AQC SANCO Procedures. “Difficult” matrices providing a high number and concentration of natural components have associated a high suppression. Dilution of the extracts was shown as an effective method to reduce the interfering compounds and to diminish the signal suppression for the majority of the pesticides in all commodities. In tea and parsley matrices the use of CaCl<sub>2</sub> and ZrO<sub>2</sub> respectively, in the clean-up step, showed to be much more efficient removing interfering compounds than the original QUEChERS clean-up.