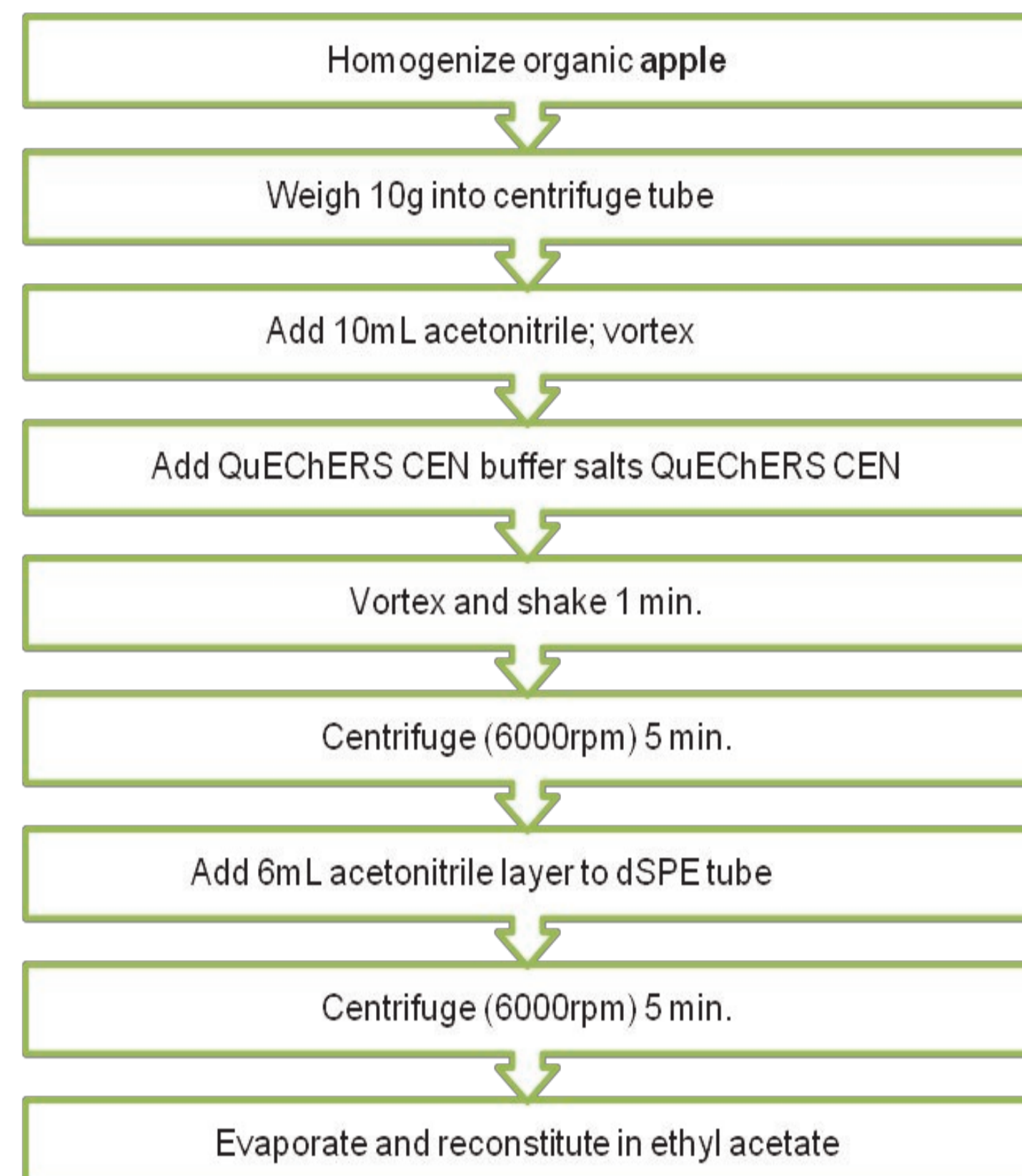


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INTRODUCTION

Pesticide residues remain a high priority on the list of consumer concerns in regards to food safety. A result of this is that laboratories are required to create analytical methods capable of screening the maximum number of compounds using the minimum number of methods, whilst ensuring sample turn around times are met. The majority of countries have established clearly defined regulations relating to pesticide residues, with legislation imposing Maximum Residue Limits (MRLs)¹ for different food commodities. To meet these criteria, laboratories require analytical techniques that are sensitive, accurate and robust. Multiresidue analysis is challenging due to the varying matrix complexity of different food commodities and the requirement for low part per billion (ppb) detection levels to achieve MRL compliance for a diverse range of pesticides. Currently there is in excess of 1000 known pesticides in use and laboratories are continually under pressure to increase the scope of the analytical methods used for routine monitoring purposes. Various technologies are used to meet these challenges, the most common being liquid chromatography (LC) and gas chromatography (GC) coupled to tandem quadrupole mass spectrometry (MS/MS), allowing laboratories to cover a wide range of compounds required by legislation. In this poster we provide example performance data from a new GC-MS/MS system using fruit commodities that have been extracted by the QuEChERS CEN method and cleaned up by dispersive SPE, as described in a EURL-FV multiresidue method using QuEChERS for fruits and vegetables².

METHODS



Samples of organic apple were extracted using the QuEChERS method as shown in Figure 1. Raisin samples were first rehydrated with LCMS grade water and then the equivalent to 5 g of sample was taken for extraction. Supernatant from the QuEChERS extracts were then cleaned up using dispersive solid phase extraction (d.SPE) tubes which contained 25 mg of primary secondary amine (PSA) sorbent and 150 mg MgSO₄ per 1 mL of sample extract. Samples were then evaporated and reconstituted in ethyl acetate and post spiked with the pesticide mix and analysed using the gas chromatography, mass spectrometry method highlighted below.

Gas chromatography

GC Oven: Agilent 7890
 Column: Rtx-5MS, 30 m x 0.25 mm x 0.25 µm
 Oven Programme: 91°C (hold 1.0 min) to 330°C at 8.5°C/min and hold for 5 min, run time 34.12 min
 Carrier Gas: Helium, flow rate 1.4 mL/min
 Inlet Temperature: 320°C
 Injection Volume: 1 µL
 Inlet Mode: Pulsed Splitless
 Liner: Gooseneck splitless liner (RESTEK) 4 mm x 6.5 x 78.5



Mass Spectrometry

MS System: Xevo TQ-GC
 Ionisation Mode: EI Positive
 Electron Energy: 70 eV
 Source Voltage: 3.0 V
 Source Temperature: 250°C
 Transfer Line Temperature: 320°C
 MS1/MS2 Resolution: 1.5 Da/0.75 Da
 Gain: 1.0
 Acquisition: MRMs generated by Quanpedia database (Figure 3.)

RESULTS AND DISCUSSION

Figure 1: Summary of QuEChERS extraction procedure utilised for organic apple.

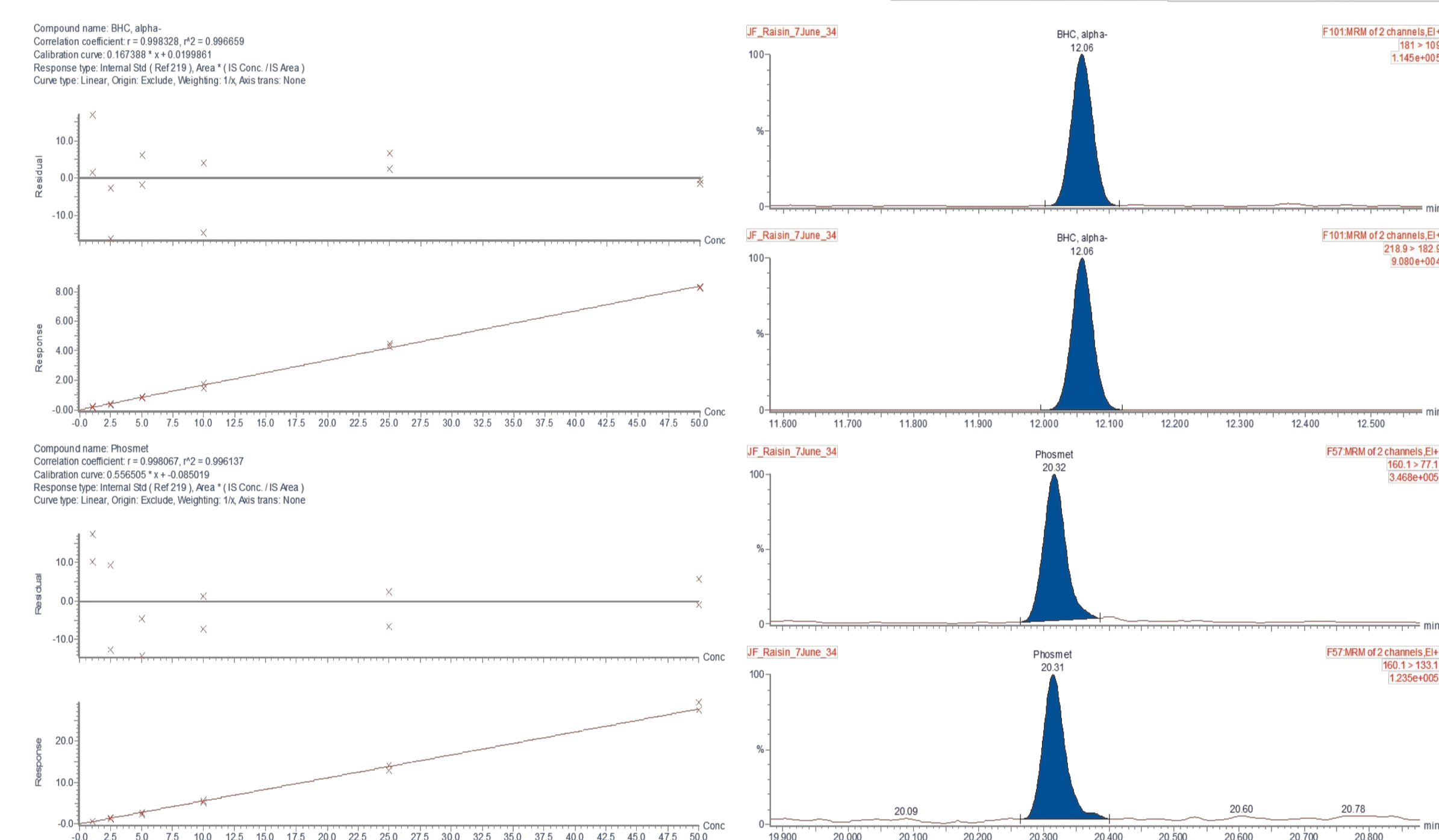


Figure 2. Bracketed matrix matched calibration curves in organic raisin, 0.002 mg/kg - 0.1 mg/kg (1.0 - 50 ng/ml in vial) and example MRM chromatograms (5.0 ng/ml).

| Compound Name | Quon MRM Transition | Calibration r ² Apple 1 µg/kg - 50 µg/kg | Calibration r ² Raisin 2 µg/kg - 100 µg/kg |
|-----------------------|---------------------|--|--|
| 2,4-Methoxychlor | 227.1 > 121.1 | 0.998 | 0.999 |
| 2-Phenylphenol | 170 > 115 | 0.998 | 0.997 |
| Acetochlor | 223 > 132.1 | 0.998 | 0.997 |
| Aldrin | 262.9 > 192.9 | 0.998 | 0.995 |
| Allidochlor | 132 > 56 | 0.993 | 0.997 |
| BHC, delta- | 181 > 109 | 0.997 | 0.997 |
| BHC, gamma- | 181 > 109 | 0.993 | 0.995 |
| Bromopropylate | 340.8 > 183 | 0.997 | 0.994 |
| Chlorfenson | 175 > 111 | 0.998 | 0.994 |
| Chloroneb | 191 > 113 | 0.995 | 0.995 |
| Chlorthal-dimethyl | 300.9 > 222.9 | 0.999 | 0.997 |
| DDD, o,p'- | 235.1 > 165.1 | 0.998 | 0.998 |
| DDT, o,p'- | 235.1 > 165.1 | 0.998 | 0.997 |
| Endosulfan II | 195 > 125.2 | 0.995 | 0.997 |
| Fenson | 141 > 77.1 | 0.999 | 0.995 |
| Isazophos | 172 > 130 | 0.996 | 0.993 |
| Malathion | 173 > 99 | 0.997 | 0.996 |
| Metolachlor | 162.2 > 133.2 | 0.997 | 0.997 |
| Phosmet | 160.1 > 77.1 | 0.997 | 0.996 |
| Pretilachlor | 162.2 > 132.1 | 0.997 | 0.998 |
| Propachlor | 176 > 57 | 0.998 | 0.998 |
| Pyriproxyfen | 136.1 > 78 | 0.995 | 0.996 |
| Tetrahydrophthalimide | 151.1 > 80.1 | 0.996 | 0.996 |
| Tolclofos-methyl | 265 > 250 | 0.999 | 0.997 |
| Triallate | 268 > 184 | 0.999 | 0.995 |

Table 1. Representative bracketed matrix matched calibration curve r² values in organic apple and raisin.

The use of the Quanpedia database (Figure 3.) which contained all compounds from the RESTEK GCMS mix, with a minimum of two MRM transitions for all compounds, allowed for an analytical method to be quickly established without the need to further optimise compounds.

Calibration was assessed in two matrices and found to be acceptable, to SANTE³ guidelines 11813/2017. Examples of matrix matched calibration curves for organic raisin can be seen in Figure 2. Response was linear for representative compounds over a range of 0.001 to 0.050 mg/kg (R² > 0.993, residuals < 20%) in apple and over a range of 0.002 to 0.100 mg/kg (R² > 0.993, residuals < 20%) in raisin, as shown in Table 1.

Repeatability of the GC-MS/MS method was determined by injecting three QC levels at n=5 of from the matrix matched curves. The accuracy data from raisin and apple can be seen in Figure 4, compounds were within +/- 15% of target levels. %RSD data can be seen in Figure 5, compounds were within RSD <20% at all levels.

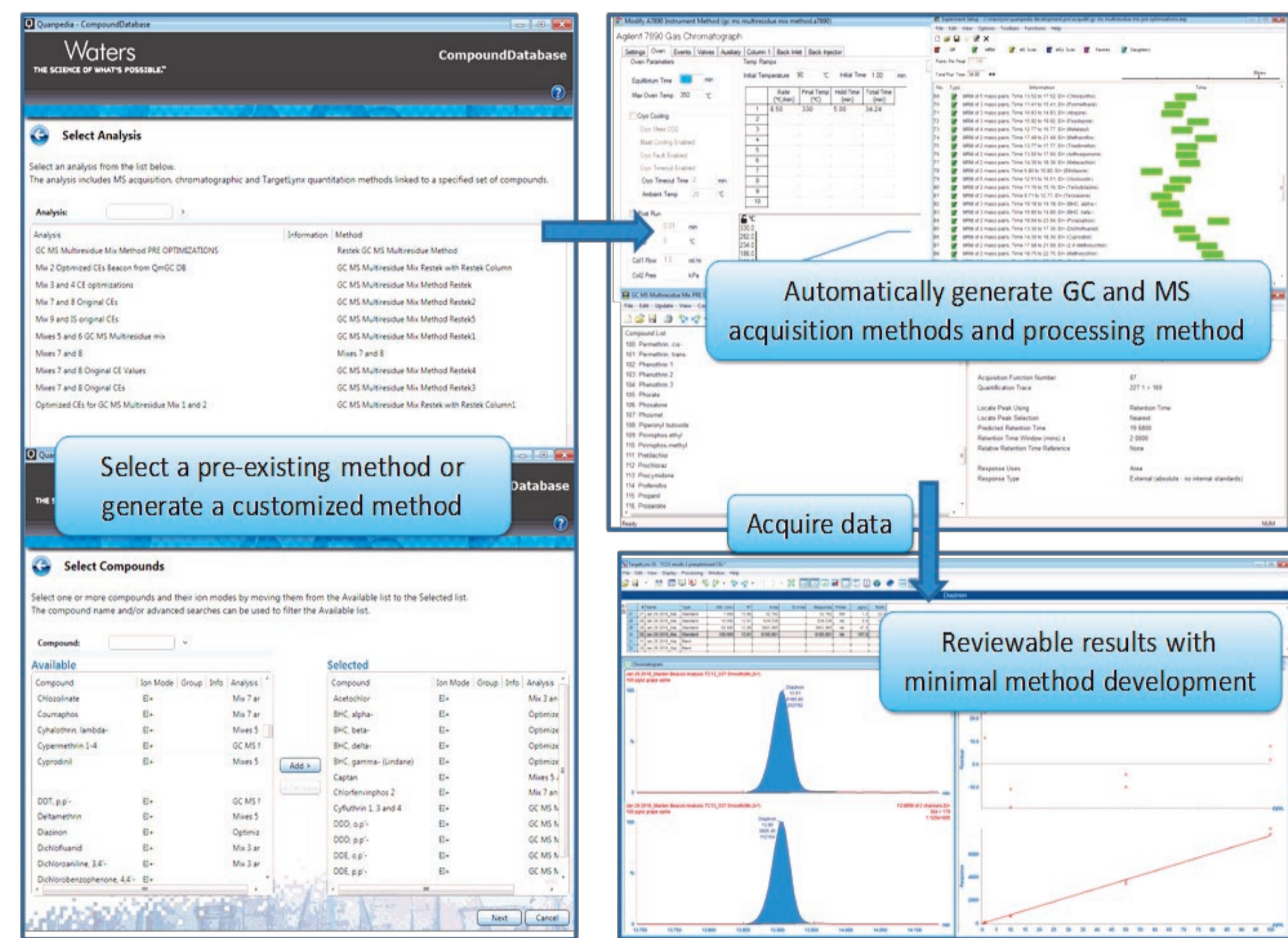


Figure 3. Example workflow using Quanpedia to generate a new pesticide multiresidue analysis and Targetlynx XS processing method for routine analysis.

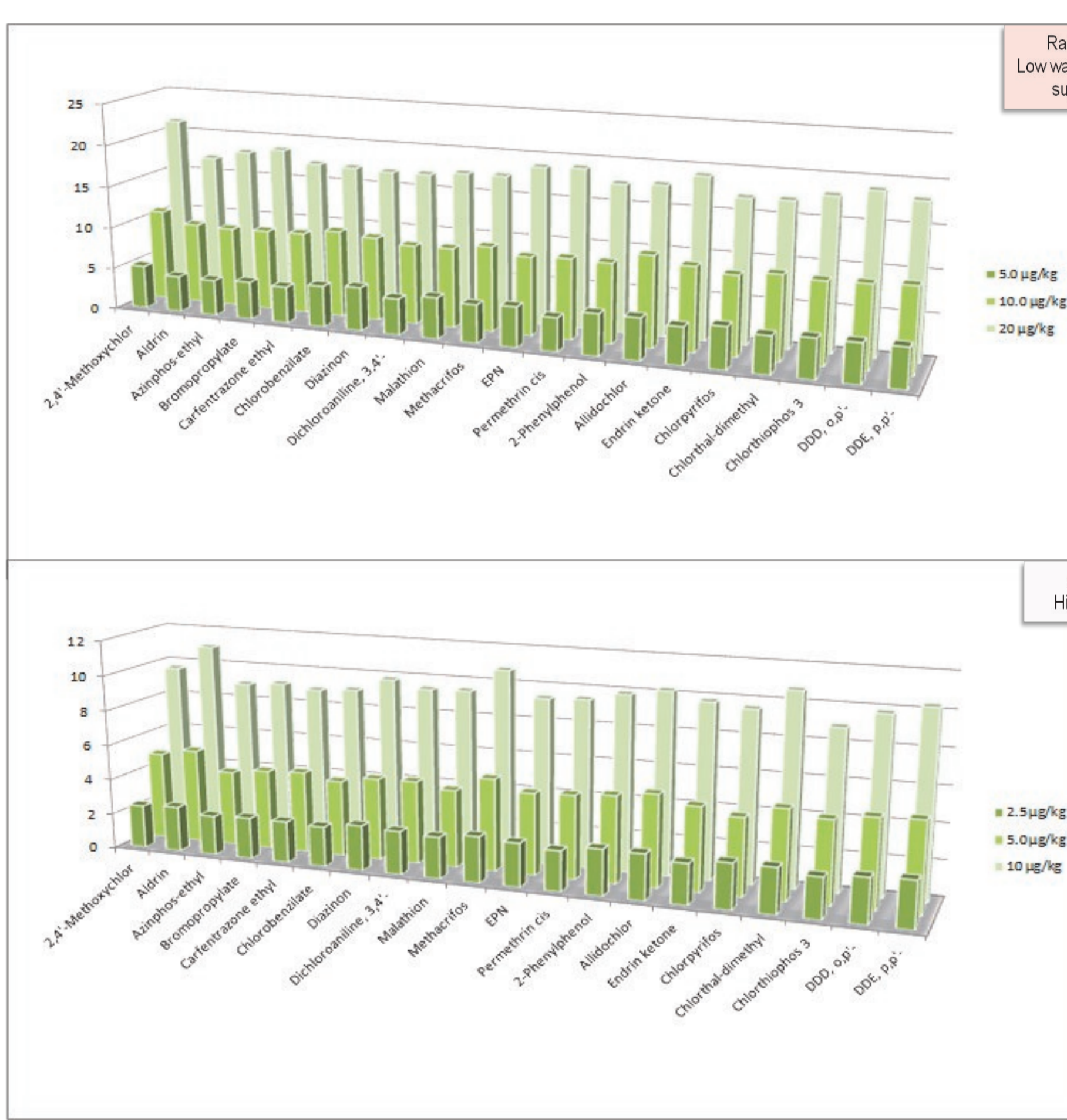


Figure 4. Calculated mean concentration values (n=5) of three QC levels of example pesticides in raisin and apple

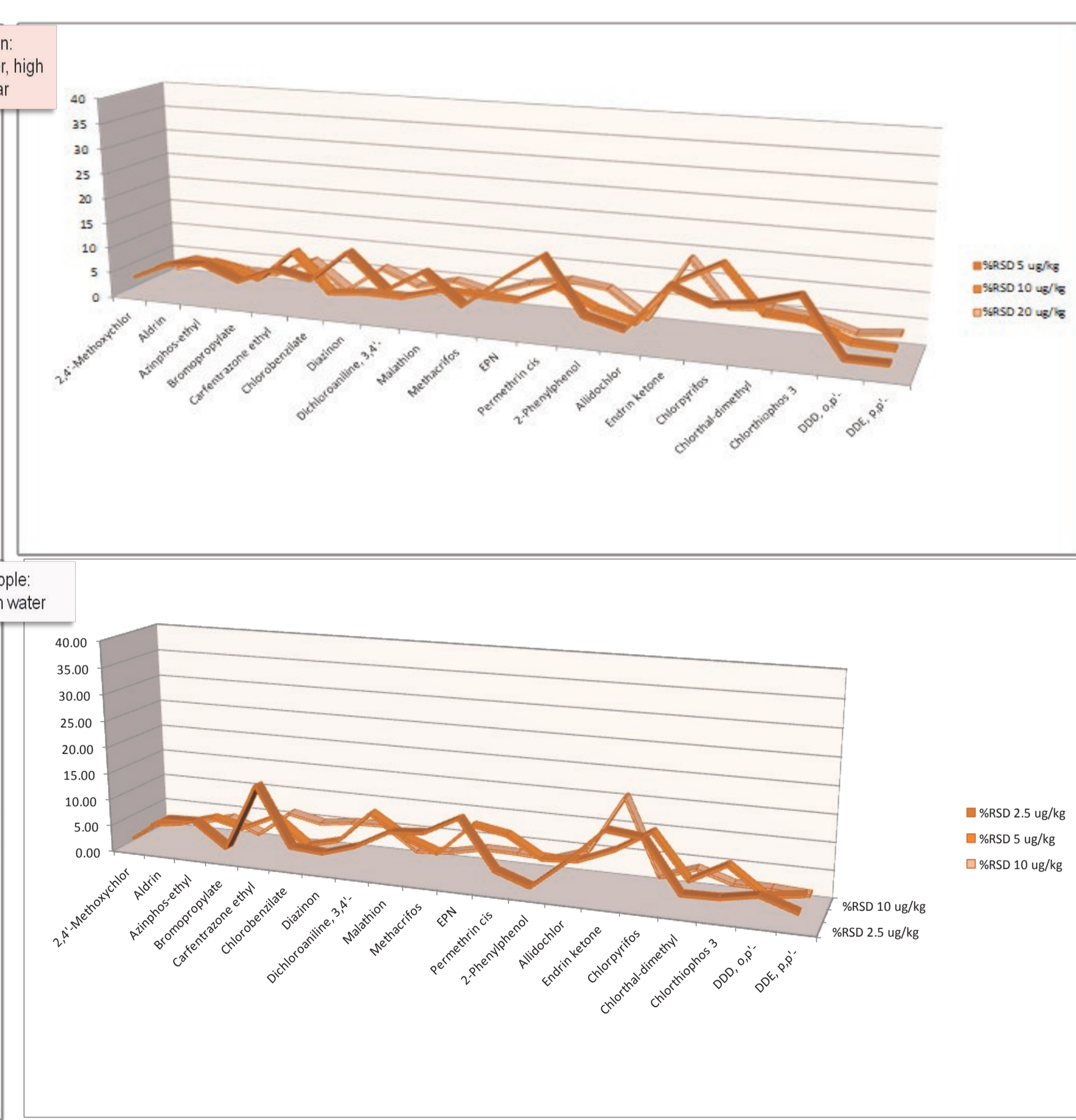


Figure 5. %RSD (n=5) for calculated concentrations of three QC levels of example pesticides in raisin and apple

CONCLUSIONS

- The use of the Quanpedia database allowed establishment of a multiresidue analytical method and processing method, with minimal user interaction required.
- Excellent linearity was obtained from 0.001 mg/kg to 0.050 mg/kg for apple and from 0.002 mg/kg to 0.100 mg/kg raisins, taking into account that only 5 g of raisin was used for the extraction.
- Acceptable repeatability was found at three matrix QC levels for the two commodities, with %RSD <20% and mean concentrations within +/- 15% of the target concentration highlighted for example compounds.
- The Xevo TQ-GC gave excellent performance in terms of sensitivity and repeatability, illustrating its fit for purpose performance for routine pesticide residue laboratories.

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MORE INFORMATION

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