Optimizing a 190+ Pesticides Multiresidue Screening Workflow for the Preparation and Analysis of Produce by LC-MS/MS

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Abstract & Introduction

Pesticides are used ubiquitously to help increase crop yields; however, they can pose risks for public health and pollinators (honeybees). Faster multi-residue screening workflows, which combine easier sample preparation techniques, yield higher recoveries, and lower instrument detection limits in fruits and vegetables, are often sought. Accomplishing these goals increases sample throughput, and reduces costs for laboratories and their clients. To demonstrate the feasibility of developing improved methods, organic celery and other representative matrices were spiked with pesticides down to 10 ppb. Samples were extracted using Restek Q-sep QuEChERS Extraction Salts and cleaned up with complementary dSPE. Each sample was diluted 10x with water prior to analysis. Separations were performed with a Restek Raptor ARC-18 column (100 mm x 2.1 mm, 2.7 µm) on a Shimadzu Nexera UHPLC coupled to a Shimadzu LCMS-8060 for detection (Figure 1). Recovery and precision results from organic celery, spinach, orange, brown rice flour, avocado and honey are shown.

Methods

The chromatogram in Figure 1 is typical of chromatograms obtained throughout this study from various matrices. Back pressures did not exceed 4000 psi when the method conditions outlined in Table 1 were followed. A gradient was used to best separate the LC Multiresidue Pesticide Kit (Restek Cat. # 31971). All samples were in acetonitrile after extraction (10 ppb). To make them amenable to LC analysis, the samples were diluted 10x with water (1 ppb). For matrix effect determination, solvent-based calibration curves and matrix matched calibration curves were compared to each other. For best results, standards be mixed on the same day of each experiment. Matrix matched calibration curves were used for recovery calculations and concentrations.

Figure 1: LC Multiresidue Pesticide Mix Extracted from Brown Rice Flour

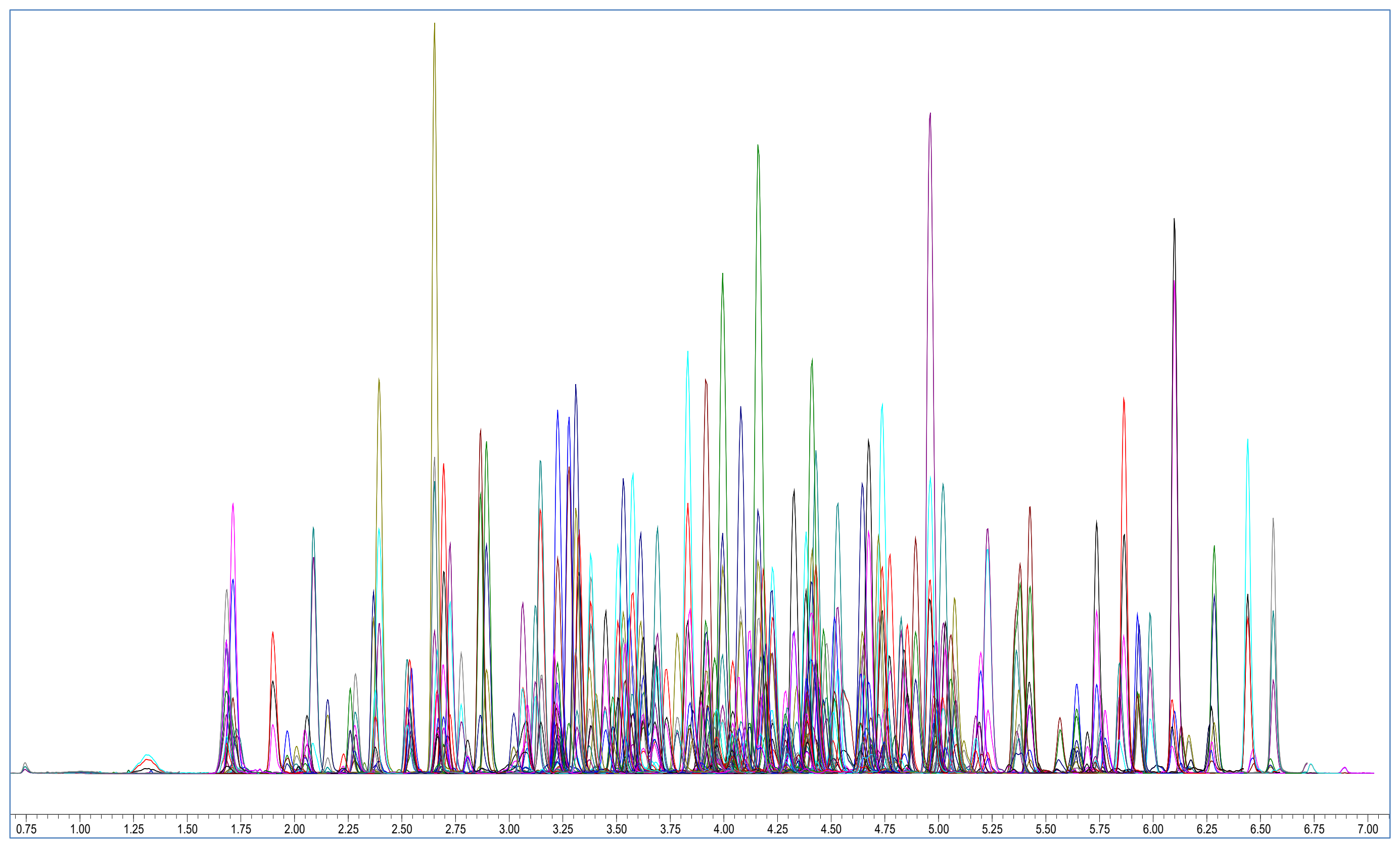


Table 1: Method Conditions for Pesticide Recovery

Column:	Raptor ARC-18 2.7 µm, 100 mm x 2.1 mm (Cat. # 9314A12)	
EXP Guard:	Raptor ARC-18 2.7 µm, 5 mm x 2.1 mm (Cat. # 9314A0252)	
Inline Filter:	UltraShield UHPLC PreColumn Filter (Cat. # 25811)	
Instrument:	UHPLC MS/MS	
Mobile Phase A:	2 mM NH_4 Formate + 0.2% Formic Acid in H_2O	
Mobile Phase B:	2 mM NH_4 Formate + 0.2% Formic Acid in Methanol	
Gradient:	Time (min)	%B
	0.00	5
	2.00	60
	4.00	75
	6.00	100
	7.50	100
	7.51	5
	9.50	5
Flow Rate:	0.4 mL/min	
Column Temp.:	50 °C	
Ion Mode:	ESI+/ESI-	
Diluent:	90:10 Water:Matrix matched acetonitrile	
Injection Volume:	5 µL	

Sample Preparation

A variety of foods were chosen to cover a broad spectrum of commodity compositions (Figure 2).

- Homogenized where necessary.
- Exceptions to QuEChERS methods were needed for some matrices.
  - Orange Peel (5g), 7.5 g Water
  - Brown Rice Flour (10 g), 10 g Water
  - Honey (5g), Water 10 g
- QuEChERS and dSPE used as described in Table 2

Recoveries of pesticides were successful (Figure 3) and had good linearity (Figure 4) with the exception of whole orange. In this case, matrix effects (Figure 5) and quantitation were poor. To simplify the analysis, the peel and fruit of the orange were analyzed separately. The fruit could be analyzed with no added water, whereas the peel was treated as a dried fruit. This improved matrix effect recoveries and calibration.

Figure 2: Representative Matrices

Figure 3: Percent Recoveries and Statistics

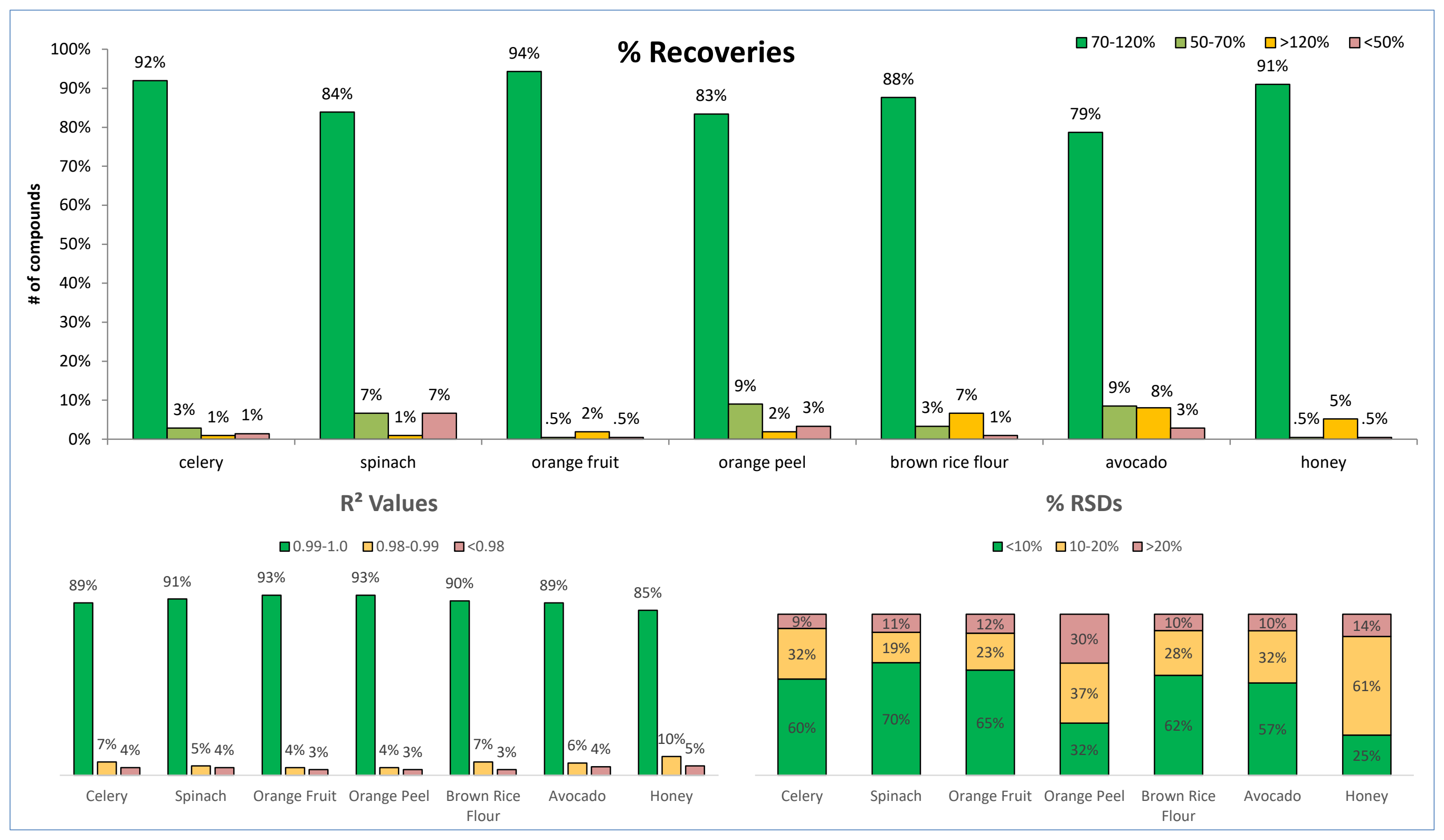


Table 2: QuEChERS and dSPE Conditions

	QuEChERS Salts	Cat. #	dSPE Method	Cat. #	PSA (mg)	C18 (mg)	GCB (mg)
Celery	AOAC 2007.01	25852	EN 15662	26218	25		7.5
Spinach	AOAC 2007.01	25852	AOAC 2007.01	26123	50	--	50
Orange	AOAC 2007.01	25852	AOAC 2007.01	26124	50	--	--
Brown Rice Flour	Original Unbuffered	25848	AOAC 2007.01	26125	50	50	--
Avocado	Original Unbuffered	25848	AOAC 2007.01	26125	50	50	--
Honey	EN 15662	25850	AOAC 2007.01	26124	50	--	--

Calibration

Figure 4: Calibration Curves for Selected Pesticides

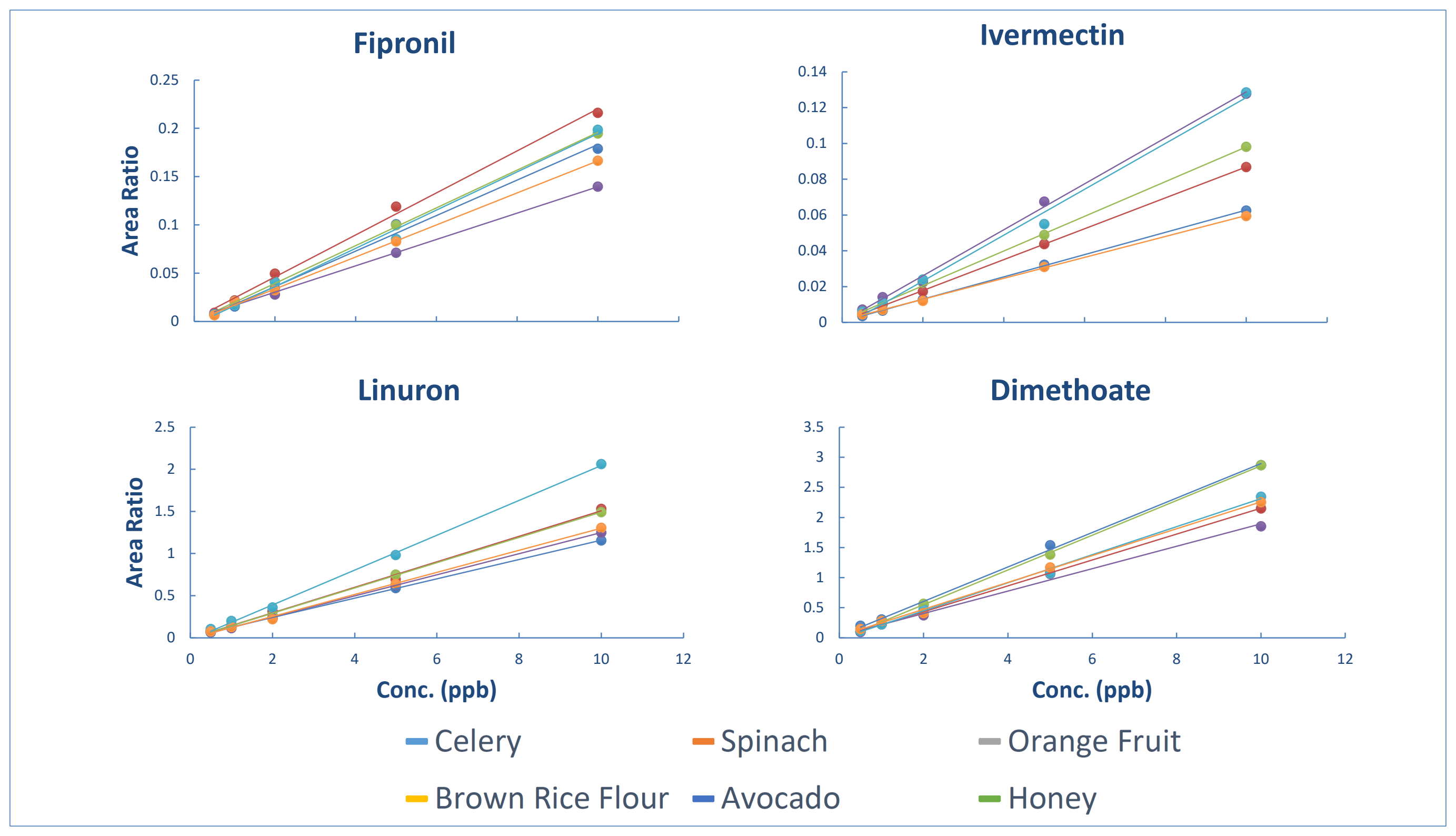
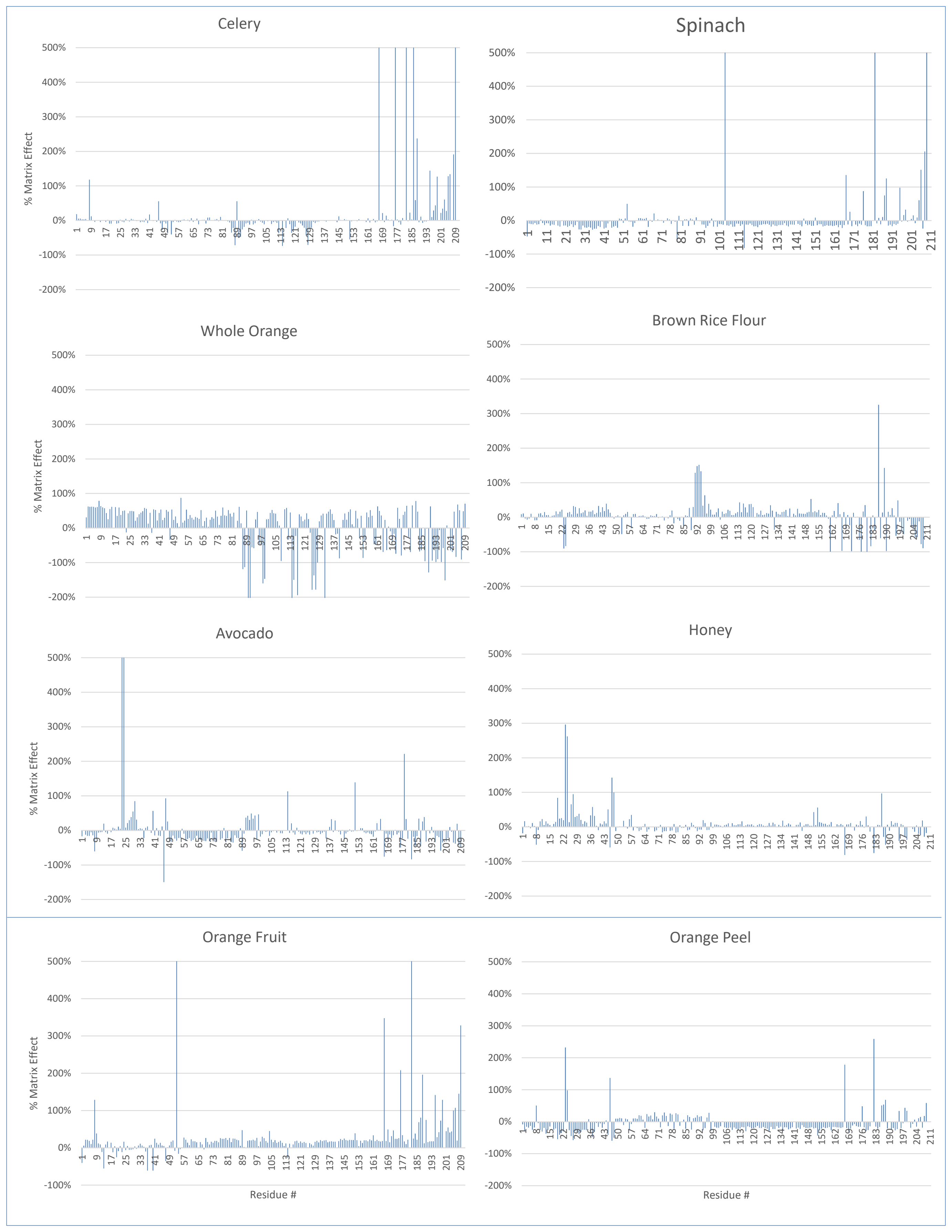


Figure 5: Matrix Effects



Conclusions

Sample preparation is extremely important for effective pesticide extraction, optimal recovery, and consistency. QuEChERS and dSPE functioned as good sample preparation approaches for the matrices used in this study.

- Recoveries were acceptable (70-120%) for 79-94% of the pesticide residues analyzed depending on matrix complexity
- Analyzing the orange in two distinct parts helped to mitigate some matrix effects and improved recoveries
- Separation of the LC Multiresidue Pesticide Kit from matrix was performed in 7 min with Raptor ARC-18
- If adequate LC-MS/MS sensitivity exists, additional sample dilution may improve apparent recoveries by mitigating matrix effects

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