

Evaluation of Cleanup, Dilution, and Workflow Techniques for Pesticide Residue Analysis by LC-MS/MS

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Challenge of Residue Analysis in Difficult Matrices

- Co-extracted materials
 - Matrix effects (suppression / enhancement) will complicate accurate quantitation of target compounds
 - Can cause issues with sample introduction systems
 - MS/MS source contamination

Potential Solutions

- Reduction in initial sample amount
 - Will have a negative impact on LOQ if calibration range is not adjusted
- Dilution of sample extract
 - Effect of dilution is not always linear, a 10x dilution can result in greater than 10x reduction in background matrix levels
 - Works well for large multi-residue methods
- Use of d-SPE cleanups
 - Can target specific matrix interferences

Difficult Matrices

Boswellia Powder (anti-inflammatory)

Olive Powder

Spirulina (blue green algae)

Experimental

Evaluate cleanup and dilution schemes for matrix removal

- 3 matrices
- 4 different cleanup / dilution schemes
- 140 compounds

Pesticide recovery trends for each technique

Experimental

QuEChERS Extraction (AOAC 2007.01)

- 5g sample hydrated with 17mL water for 30 minutes
- 15mL extraction solvent

d-SPE cleanup Fatty Samples d-SPE (5982-5122)

- 50mg PSA
- 50mg C18EC
- 150mg MgSO₄

Experimental

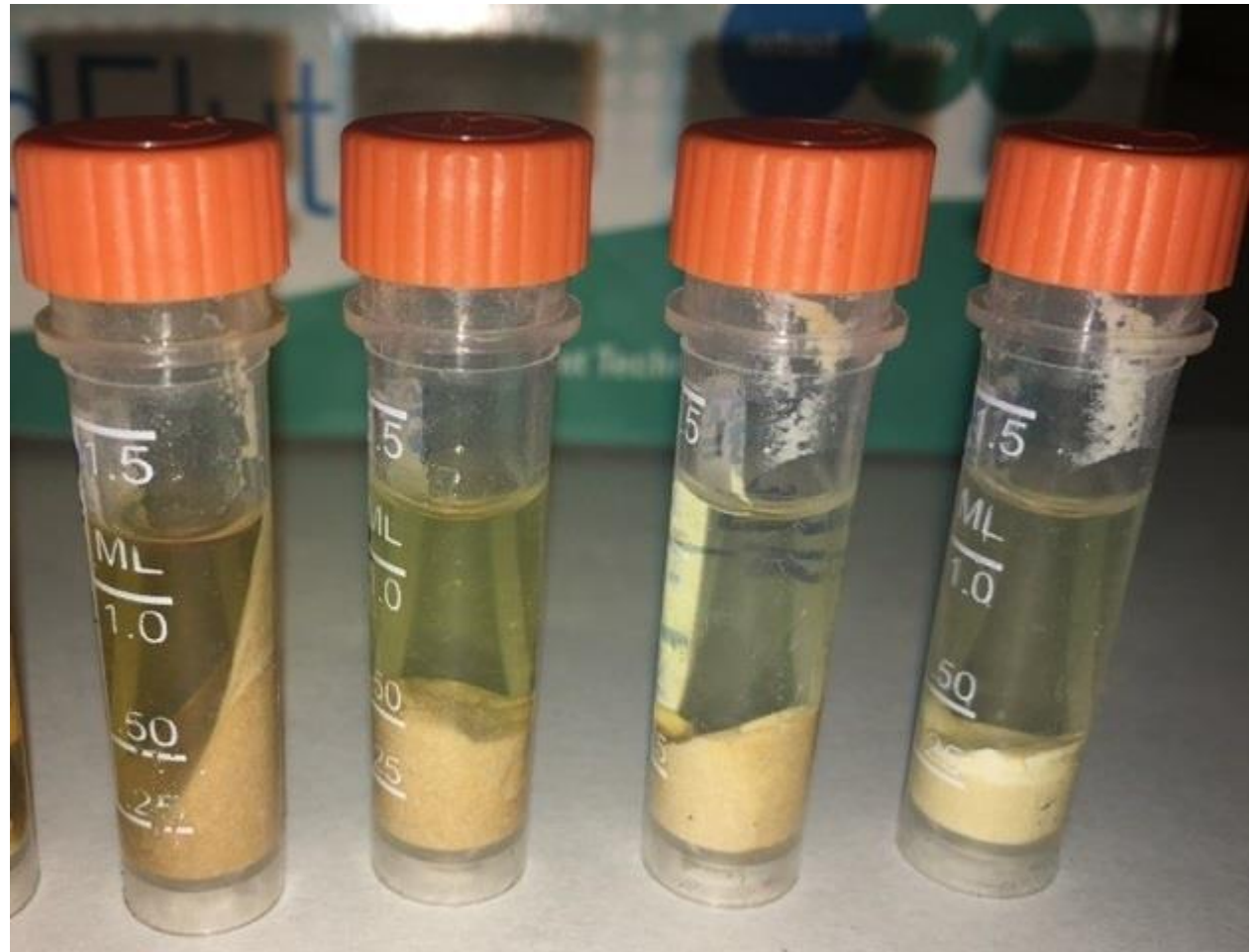
Cleanup and dilution schemes

- 1 - no dilution, 20x dilution post cleanup
- 2 - 2x dilution pre-cleanup : 10x dilution post cleanup
- 3 - 4x dilution pre-cleanup : 5x dilution post cleanup
- 4 - 10x dilution pre-cleanup : 2x post cleanup

Total dilution factor of 20x for all injections

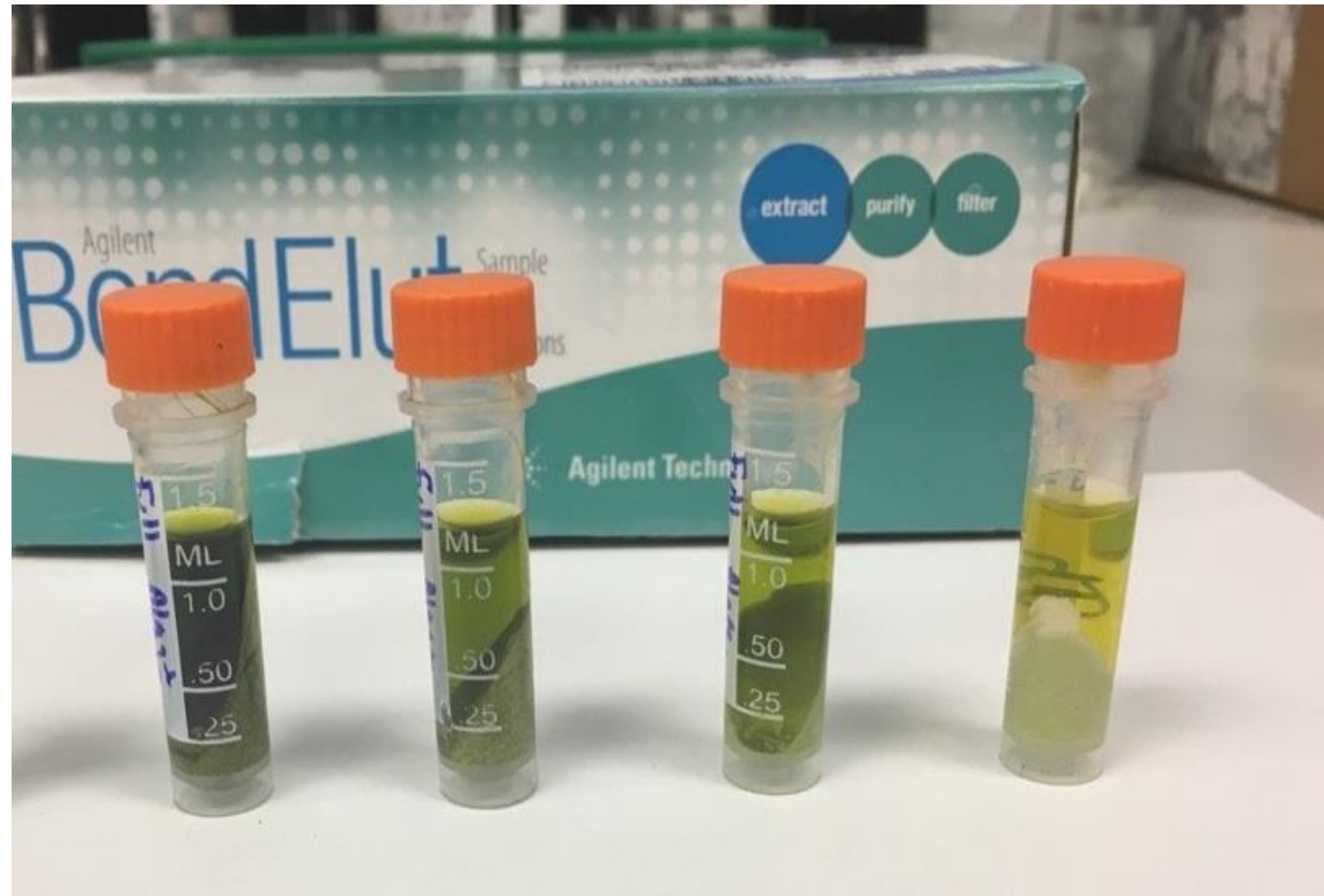
Olive Powder

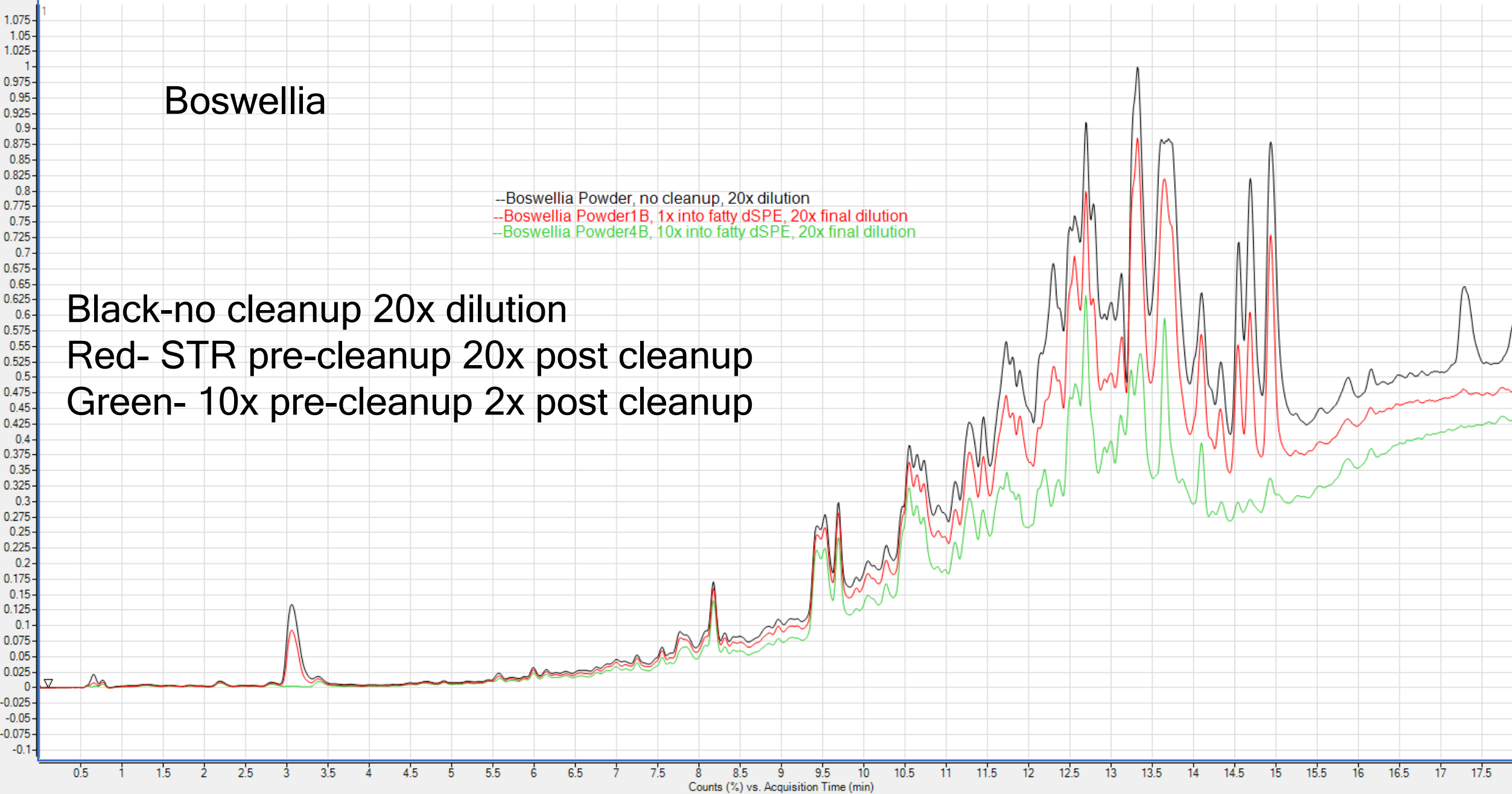
- no dilution
- 2x dilution
- 4x dilution
- 10x dilution

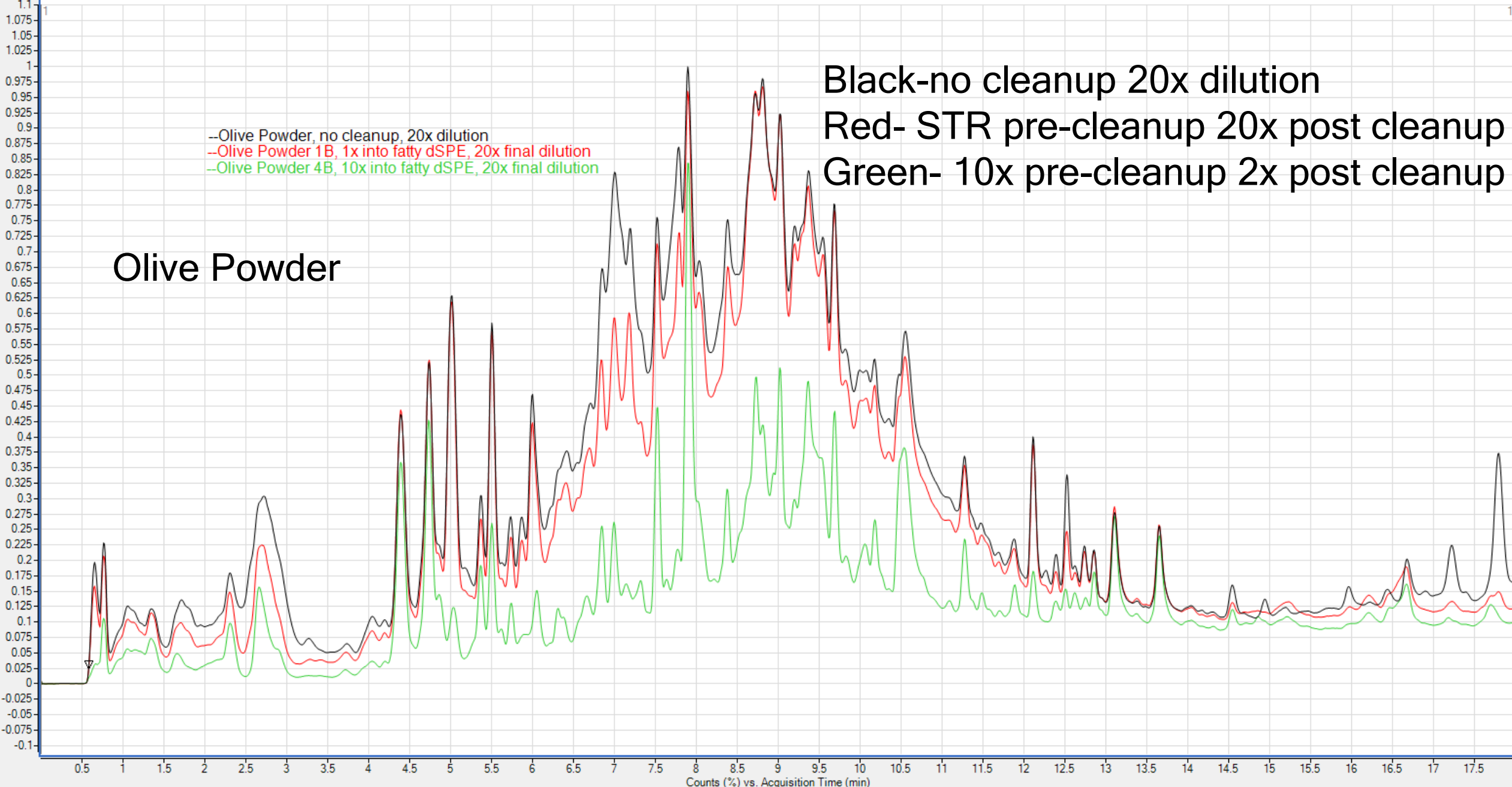


Spirulina

- no dilution
- 2x dilution
- 4x dilution
- 10x dilution



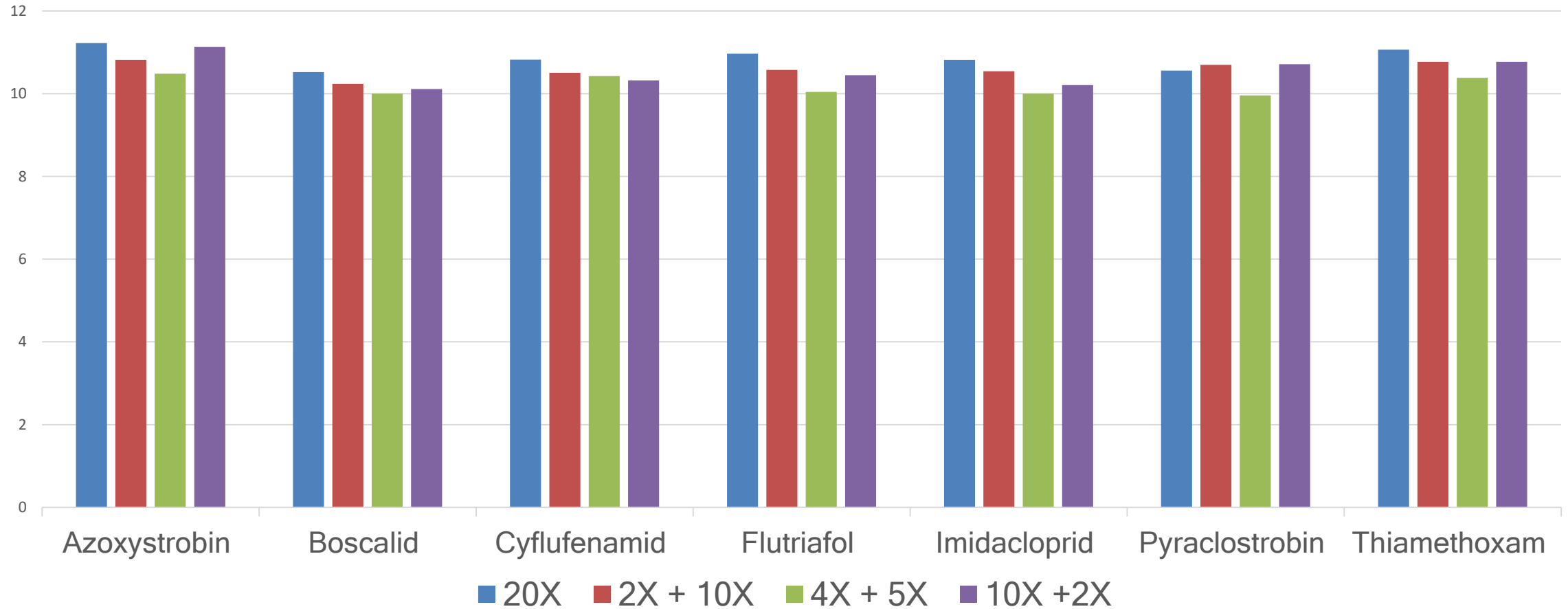




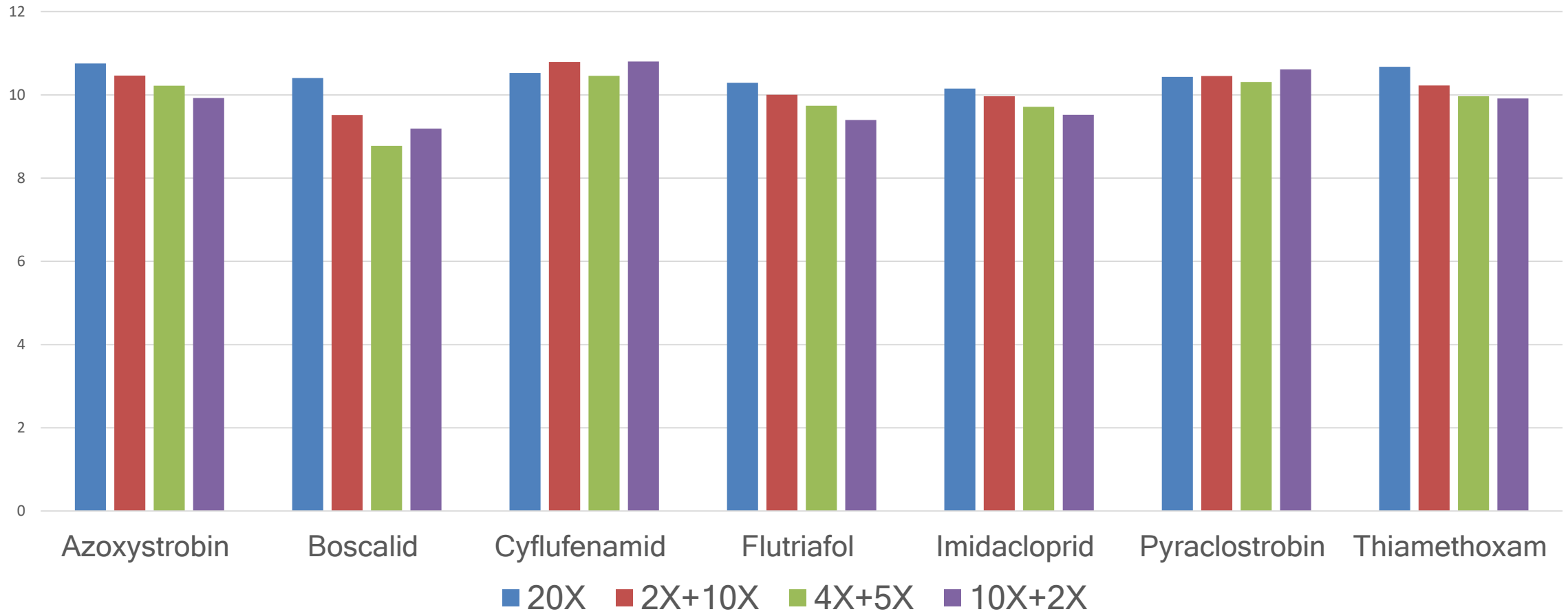
Black-no cleanup 20x dilution
Red- STR pre-cleanup 20x post cleanup
Green- 10x pre-cleanup 2x post cleanup

Olive Powder

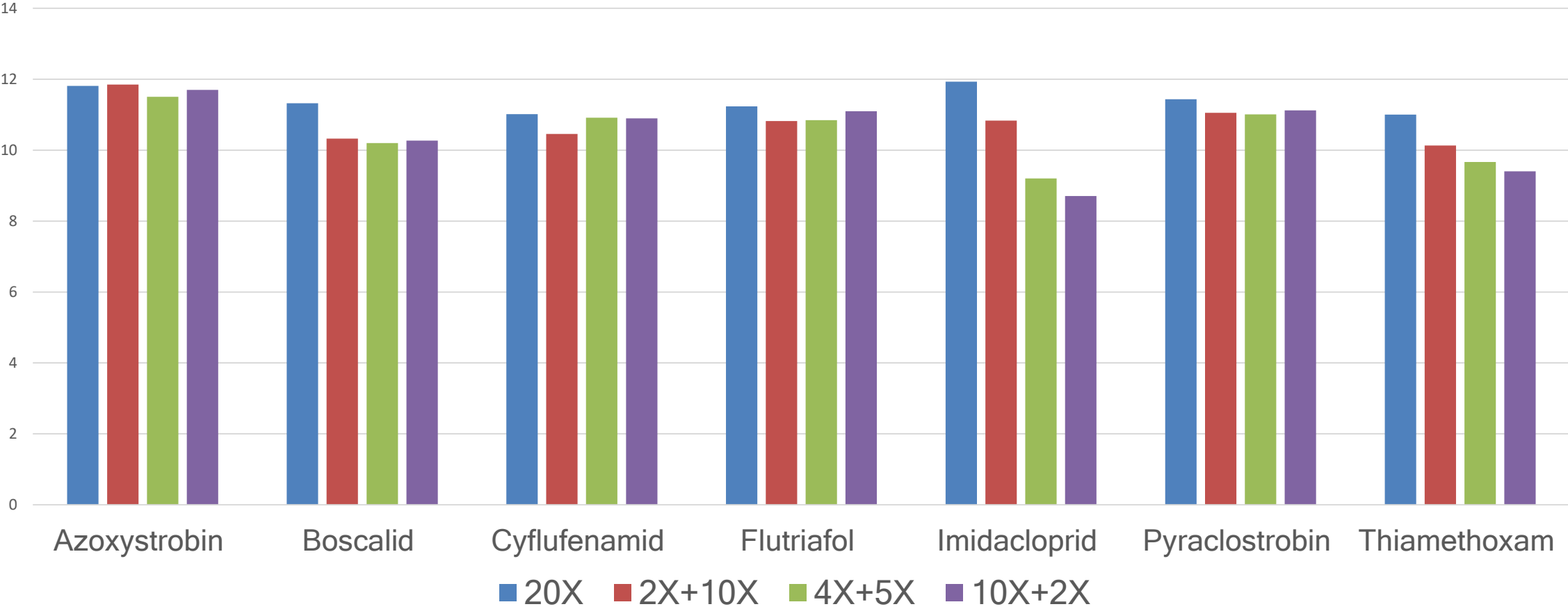
Algae Powder



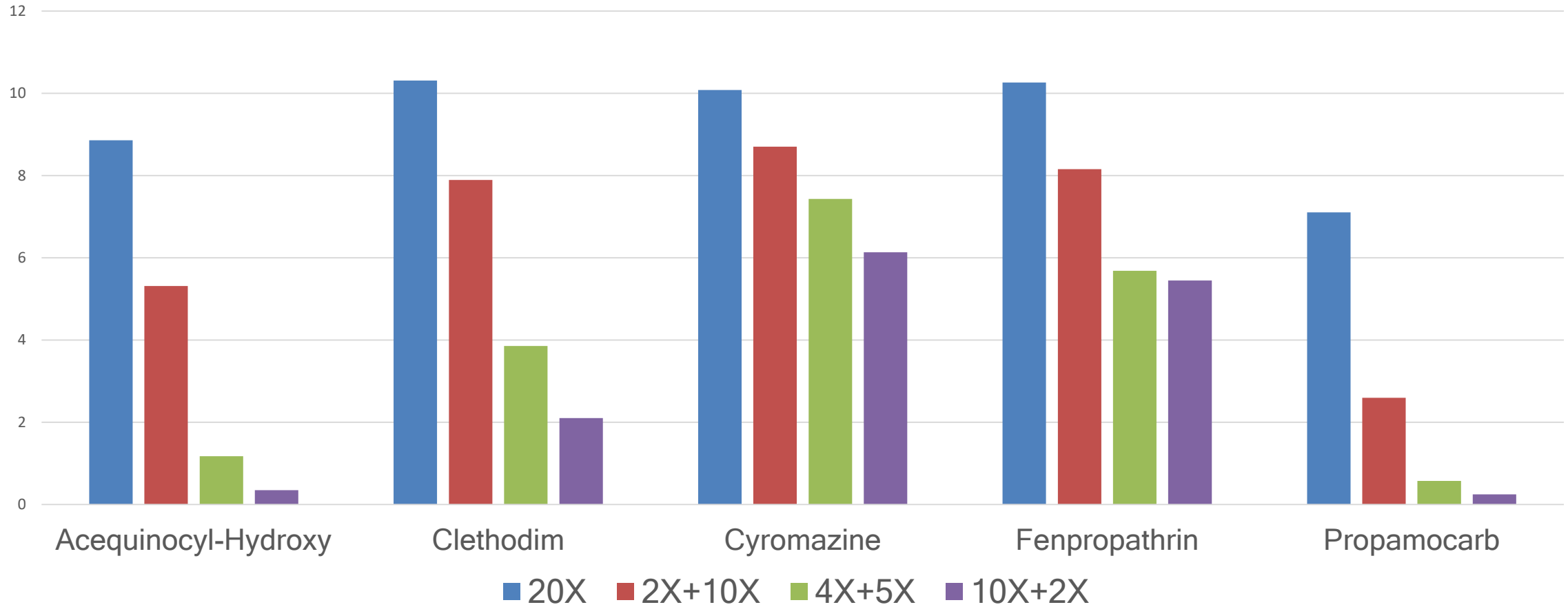
Boswellia



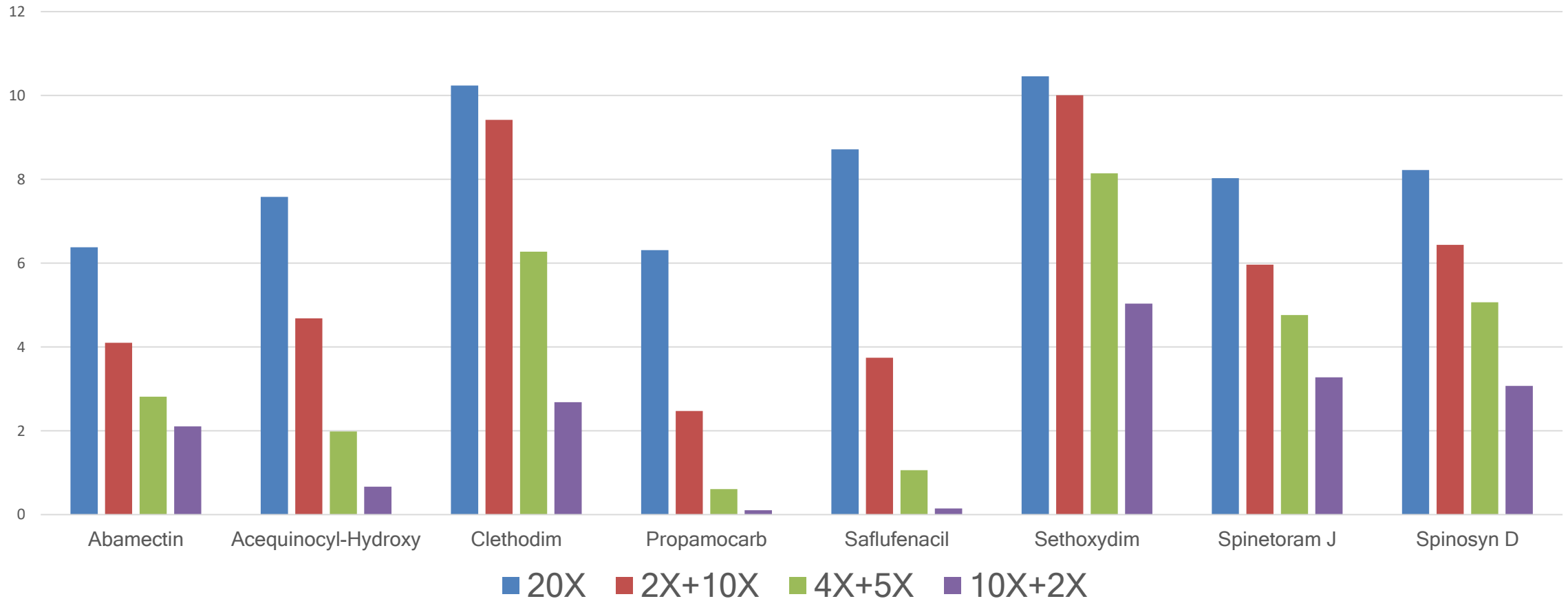
Olive Powder



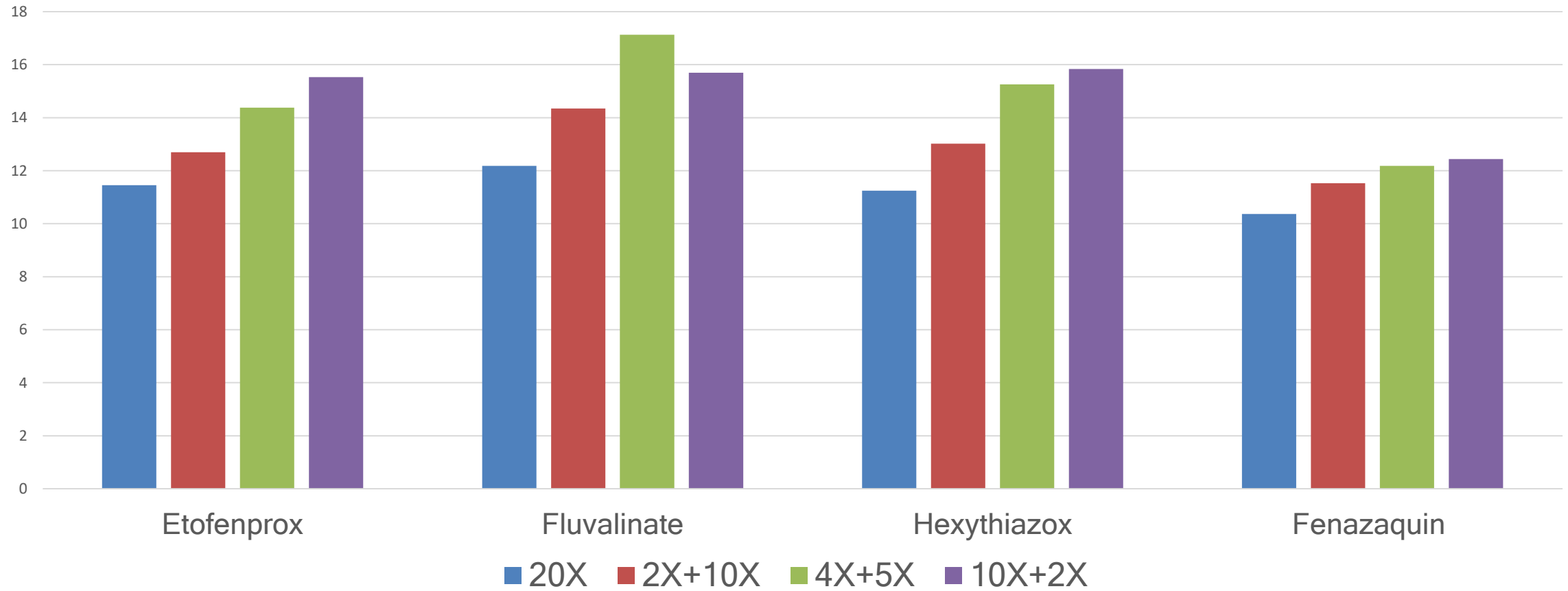
Algae Powder



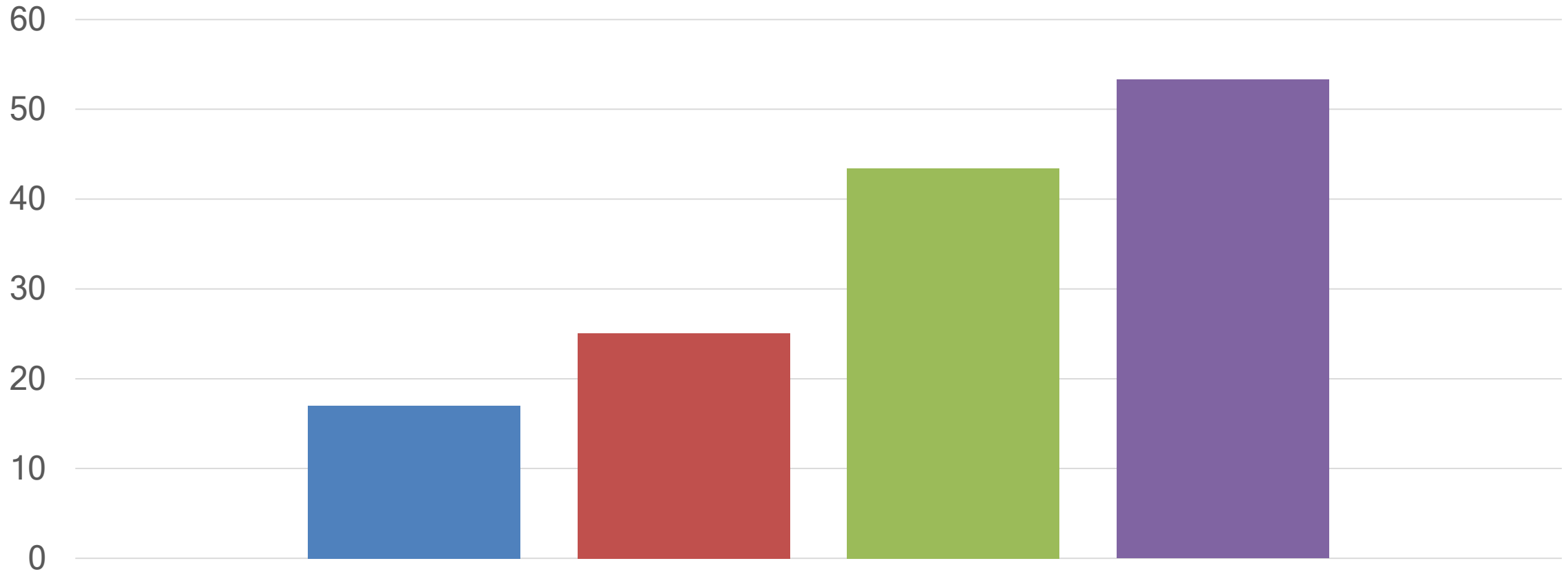
Boswellia



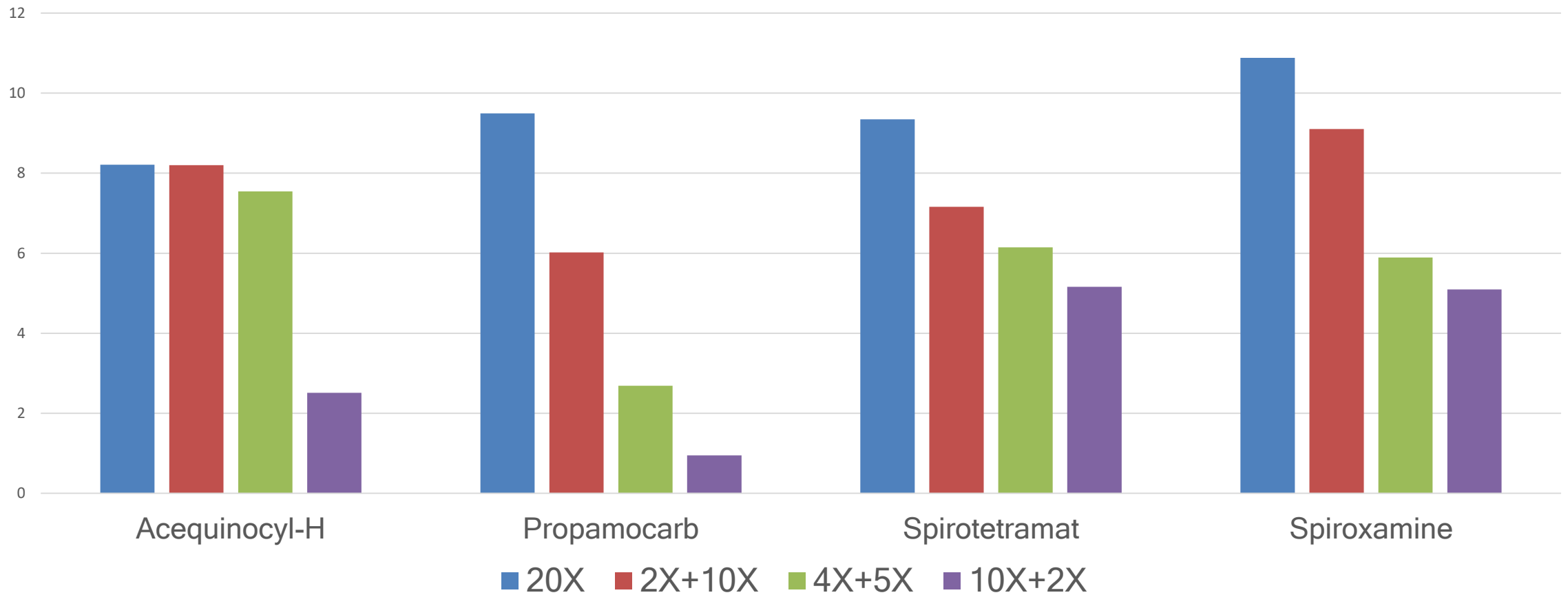
Boswellia



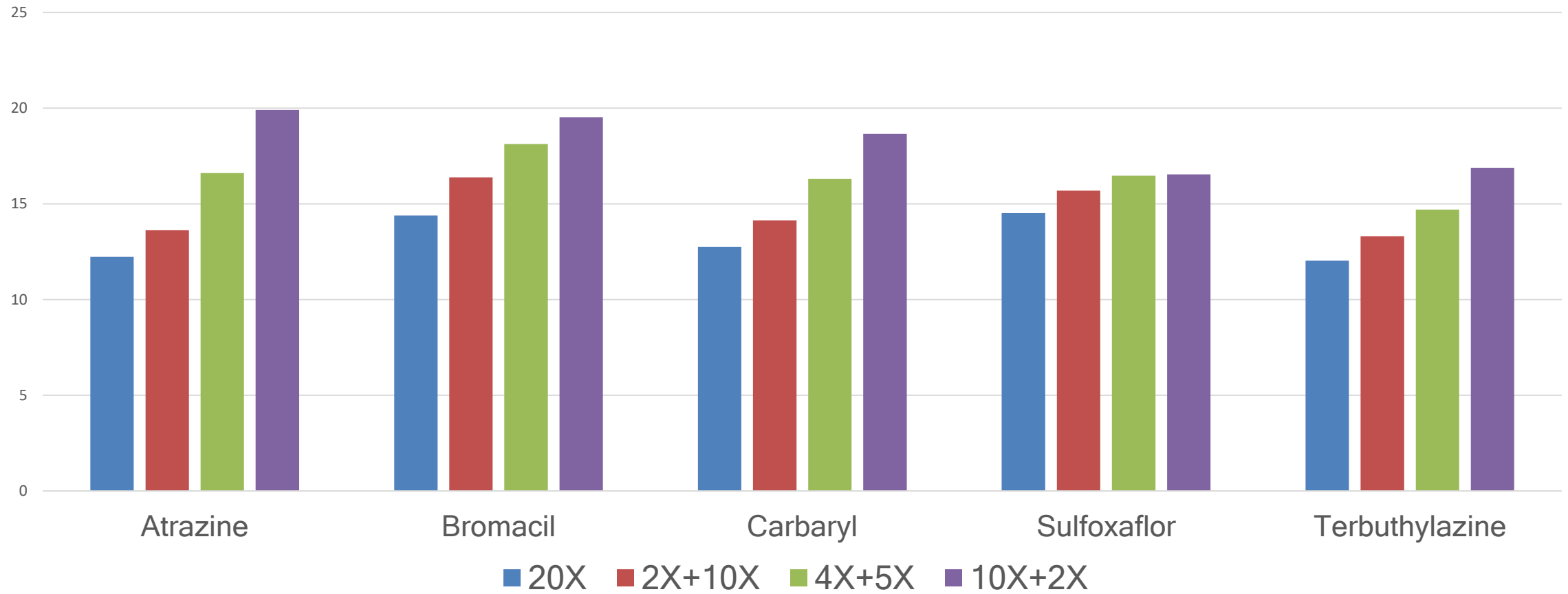
Boswellia - Fenpropantarin



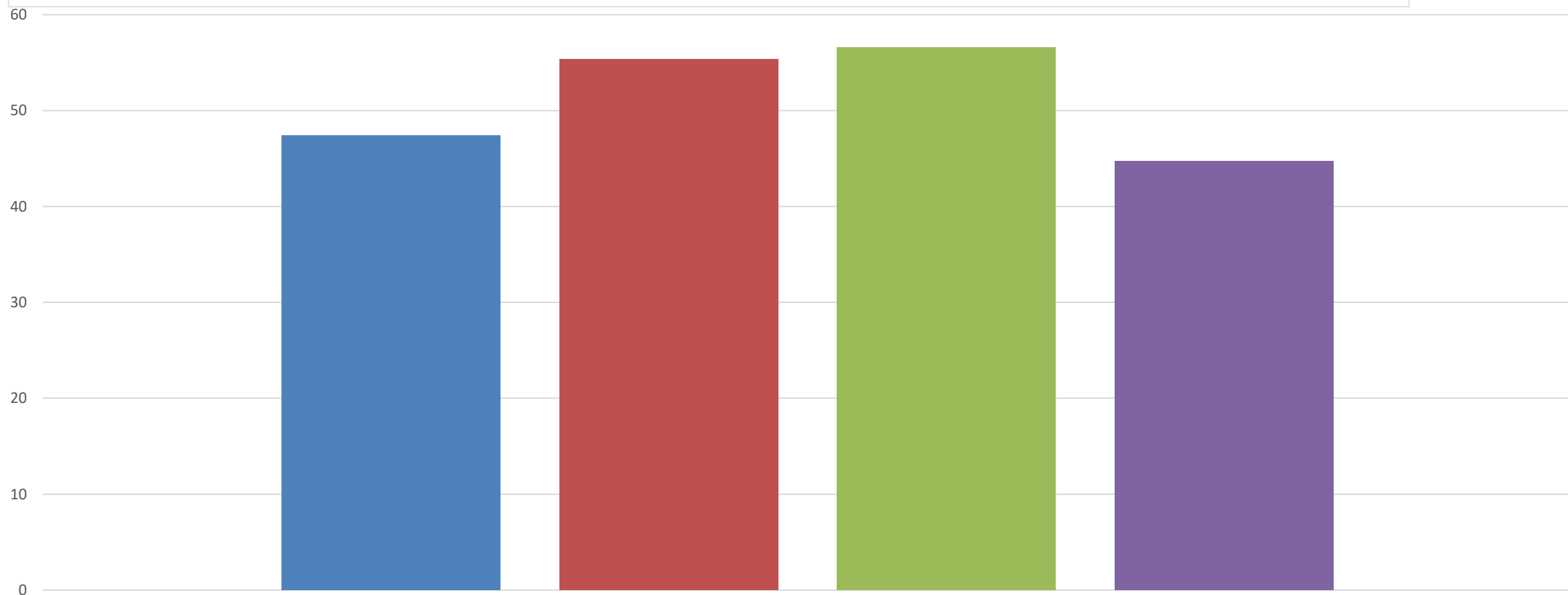
Olive Powder



Olive Powder



Olive Powder - Formentanate-HCl



Takeaways

- Use fullscan data to “see” matrix and evaluate the effectiveness of techniques
- Don’t overlook dilution as a powerful cleanup tool
- All dilutions are not created equal
 - Too **much** matrix on sorbents can negatively impact compound recovery
 - Too **little** matrix on sorbents can negatively impact compound recovery
- Evaluate dilution schemes to measure amount of matrix removed and compound recovery
- Difficult or challenging matrices may have different optimal schemes

Acknowledgements

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Pacific Agricultural Laboratory

Without her expertise this project would not have been possible