



Optimization of Total Nitrogen and Total Organic Carbon Analysis using Combustion Methodology

Presenter: Ashley Roberts, Laboratory Manager

Coauthor: Li Zhang, Ph.D., Laboratory Manager

August 2nd, 2023

- HRSD's Central Environmental Laboratory
 - Sustainable Water Initiative for Tomorrow (SWIFT)
- Total Nitrogen (TN)
 - TN Background
 - Calibration by Matrix Matching
- Total Organic Carbon (TOC)
 - Optimization of Sparge Time
 - Usage of Secondary Material

- The CEL Breakdown

- 55 employees
- Analyze regulatory, research and process monitoring for 14 wastewater treatment plants
- Accredited for approximately 350 analytes
- 2022 produced 266,761 results in non-potable water, drinking water, and solid and chemical materials

- SWIFT

- What is it?
 - Advanced treatment process to produce water that meets drinking water standards
 - Replenishment of the Potomac Aquifer

- Implementation of SWIFT has resulted in 30% increase workload
 - Drinking water in Organics
 - Metals speciation
 - Microbiology

Total Nitrogen (TN) Combustion Optimization

- TN is measured by calculation (sum of TKN, NO_3 & NO_2).
- TKN method
 - labor intensive
 - produce corrosive fumes
 - hazardous waste.



Shimadzu TOC-L Analyzer with TN Module

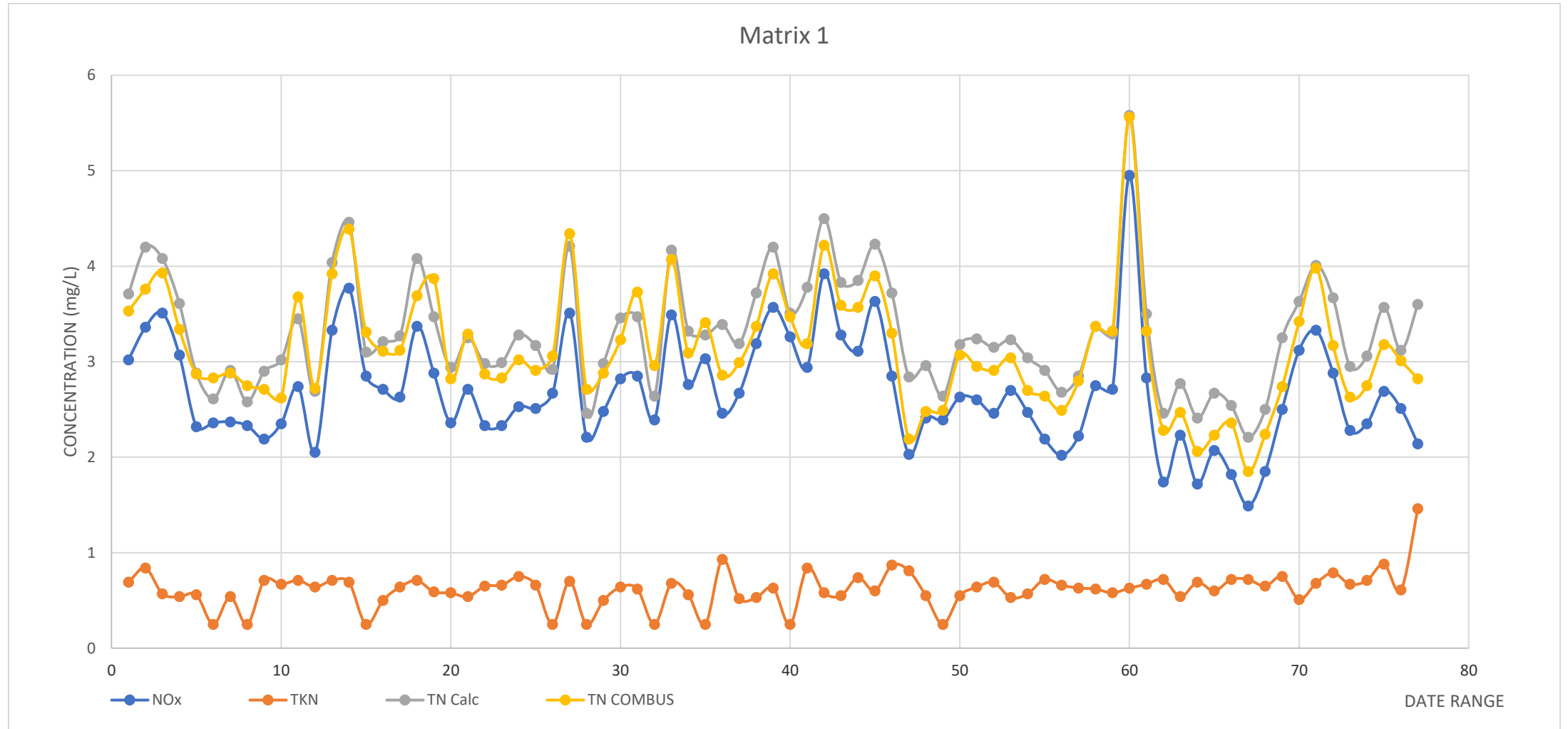
- Began analyzing TN in 2017 in support of SWIFT
- Fast and efficient
- Direct measurement of TN



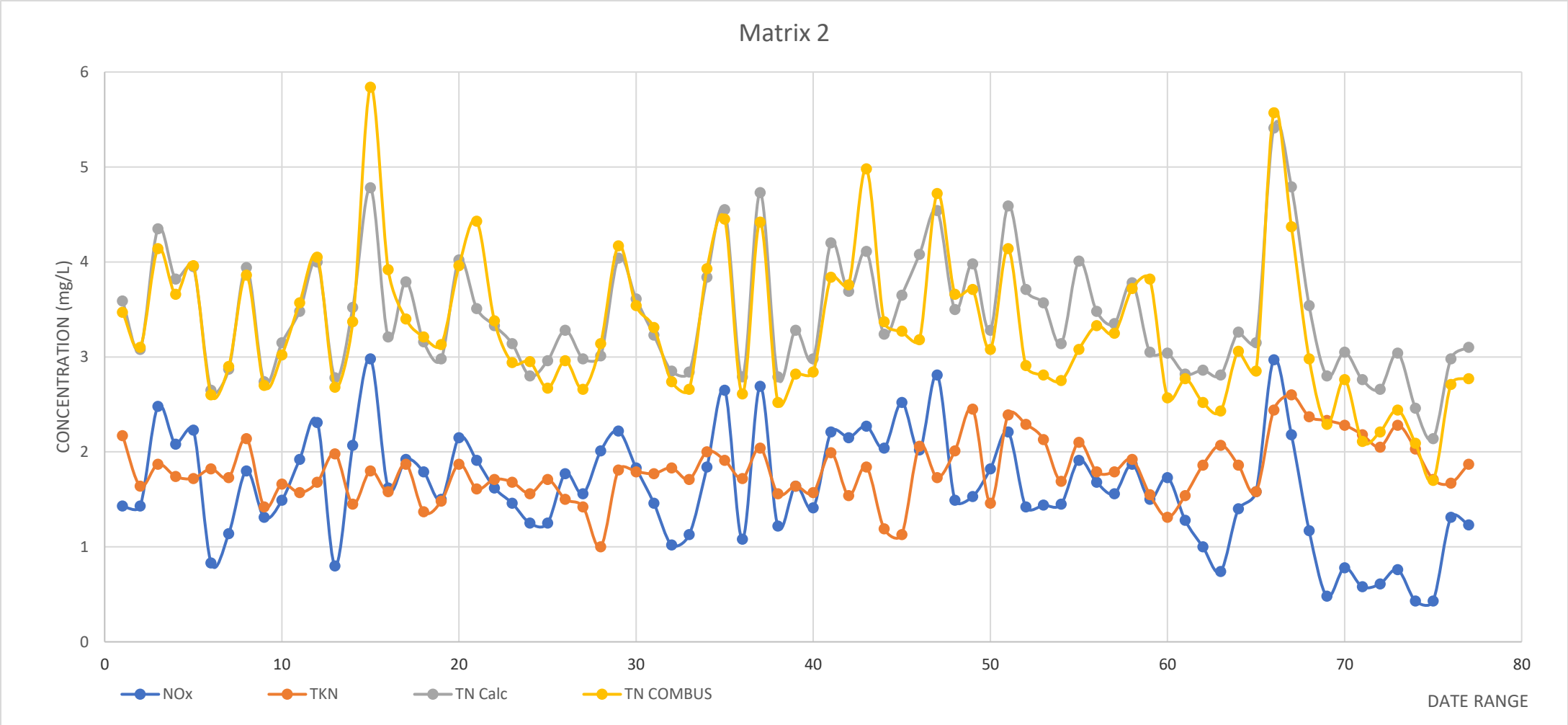
- Initially calibrated with NO₃ only standard
- Noticed variance of some sample sites
- ASTM D8083-16 method published in 2016
 - Utilized a mixed calibration standard of NO₃ and NH₃
- Based on previous NO₃ only curve, saw a decrease in peak areas (at the higher end of our curve) and slope using a mixed calibration curve
- NH₃ possibly has a lower efficiency or behaves differently

- Lower slope = higher results
- Higher slope = lower results
- How does the matrix of the calibration standards impact accuracy of sample results?
- Began using two calibration curves
- How do we determine which calibration to use?
 - Mixed calibration for samples containing “equal parts” NO_x and TKN
 - NO_3 calibration for samples containing mostly NO_x

Calibrated by NO₃ Curve



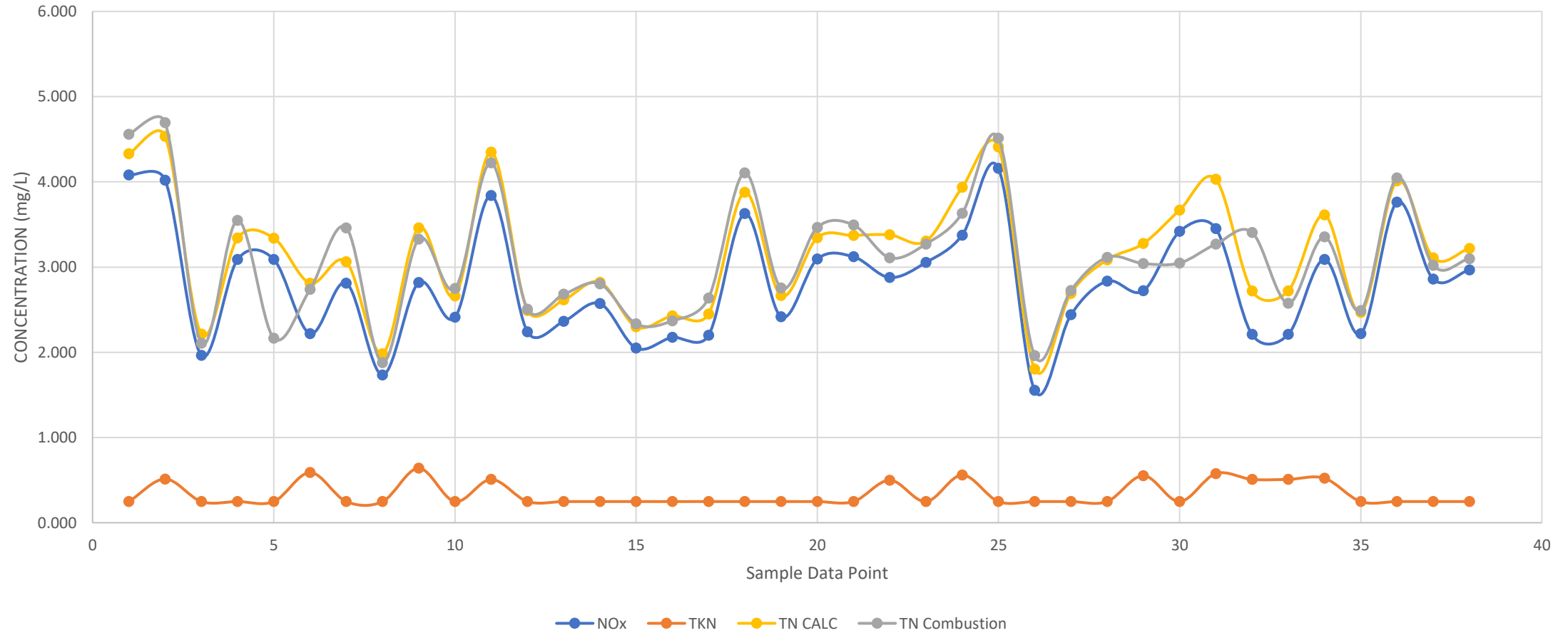
Calibrated by Mixed Curve



- By matrix matching calibration curves to samples, there was an improvement in data comparability between TN by Calculation and TN Combustion.

Matrix 3 with NO₃ Curve

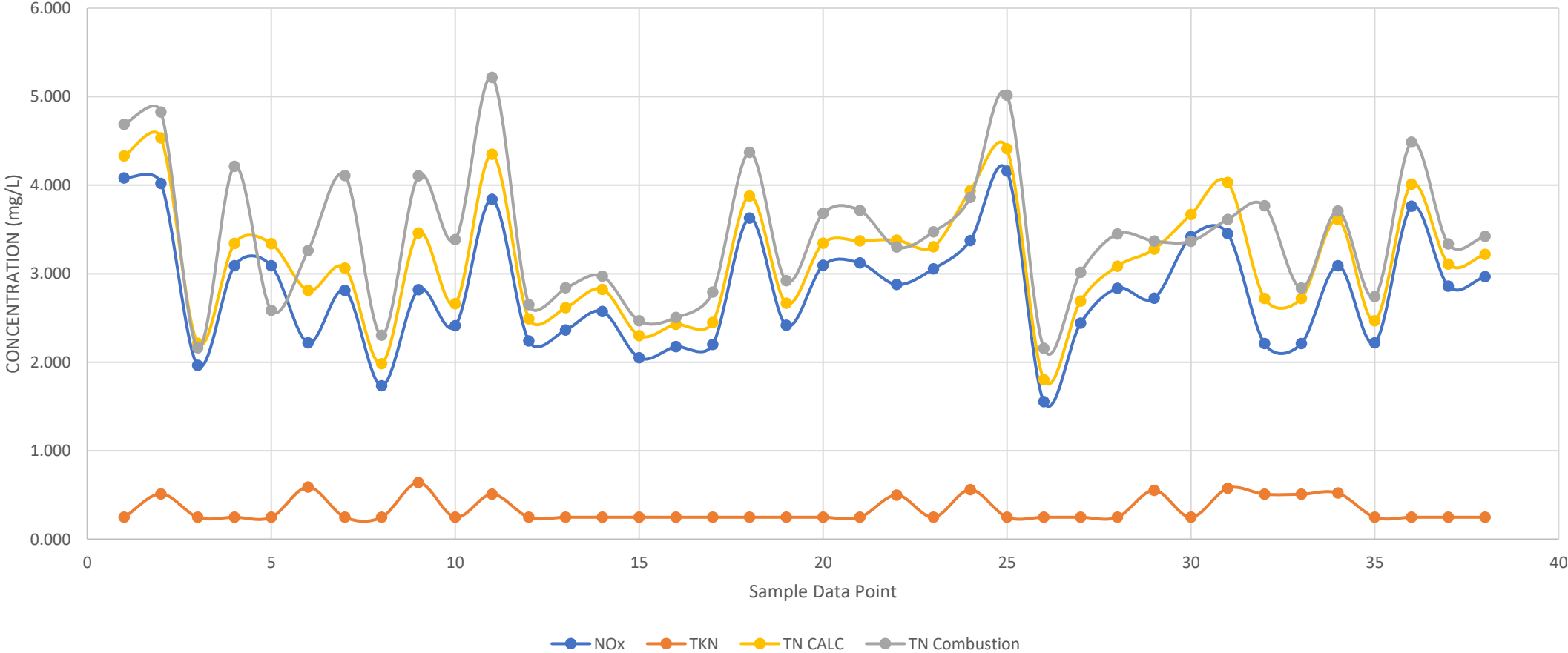
Matrix 3



What if we used a Mixed Curve?

Matrix 3 with Mixed Curve

Matrix 3



- In order to minimize the difference between TN by calculation and TN by combustion, various calibration types are needed to fully capture TN composition based on sample matrix.

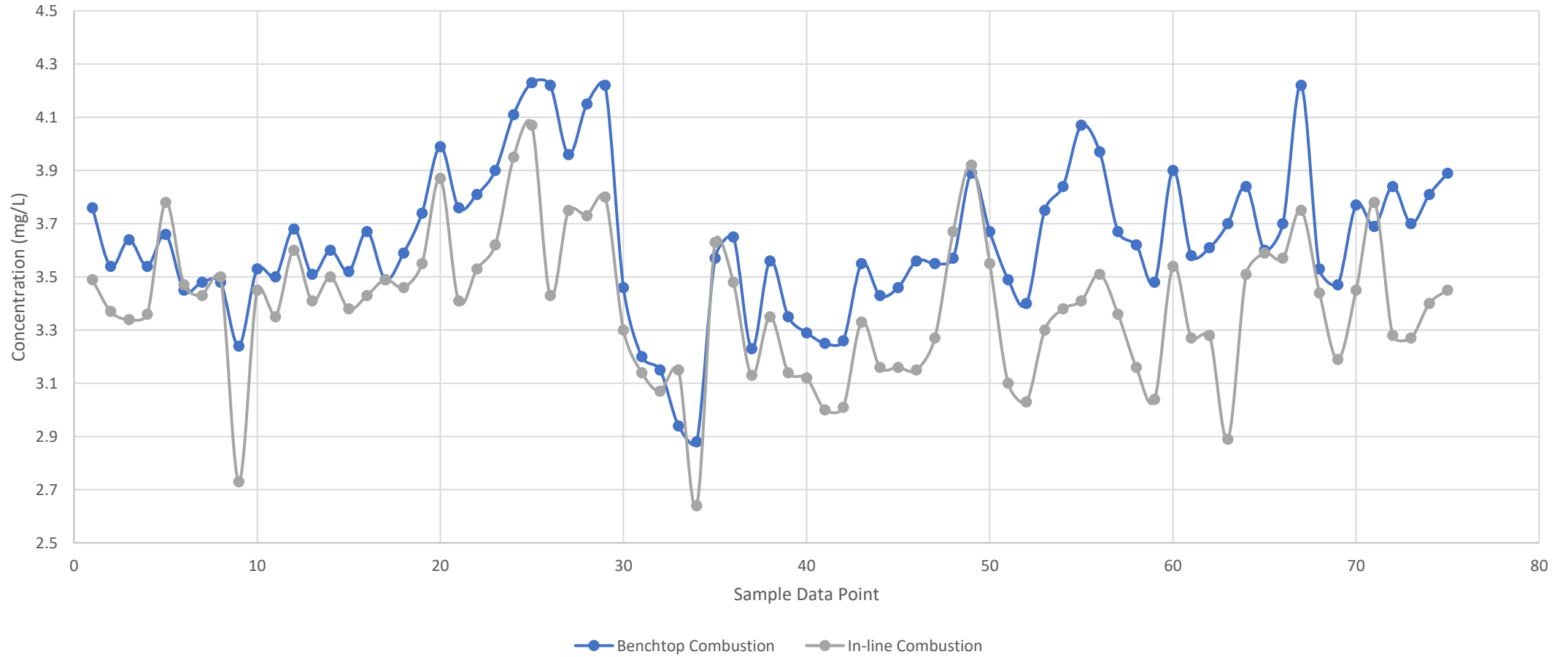
Total Organic Carbon (TOC) Combustion Optimization

- TOC is a critical non-specific indicator of water cleanliness
 - Natural Organic Matter
 - Amino acids, humic acids, fulvic acid
 - Human Waste
 - Synthetic Matter
 - Detergents, pesticides, fertilizers
- Sample results show the amount of organic carbon present, not what organic carbon compounds are present

- TOC is used to make key decisions at our SWIFT Research Center
- Need fast, highly reliable results
- 5-TOC analyzers at HRSD (2-in-line combustion analyzers, 2-benchtop combustion analyzers, & 1-persulfate analyzer)
- The goal is to have acceptable precision between all analyzers in use (10%)
- Must ensure that analyzers are performing optimally

- 3 TOC analyzers in house (designated for specific purpose)
- Data agreed between The SWIFT Research Center in-line analyzer and lab combustion analyzer
- Around August of 2020, the primary laboratory instrument lost sensitivity and required detector replacement
- Began exclusively using a persulfate analyzer

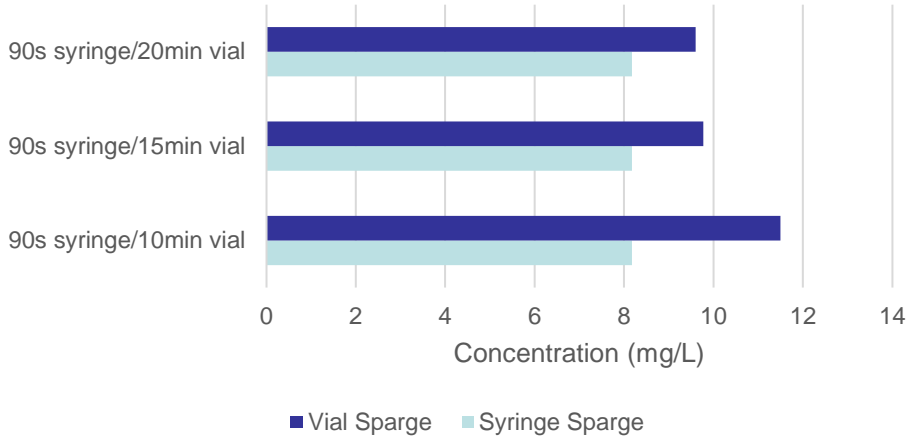
Data Comparison of Benchtop Combustion vs In-line Combustion



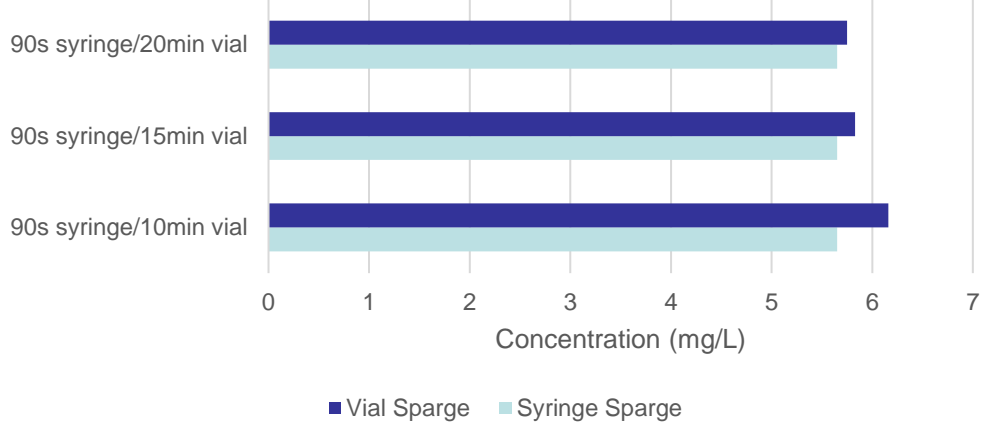
- Worked directly with manufacturer to improve performance and agreement between lab and SWIFT in-line analyzers
- Matched lab analyzer conditions to in-line analyzer
 - Key difference was sparging in the syringe vs vial
- Syringe sparging produced a noticeable difference
- Ran data comparisons between vial sparge and syringe sparge at 4 different sampling points (matrices)

Sparge Data Comparison

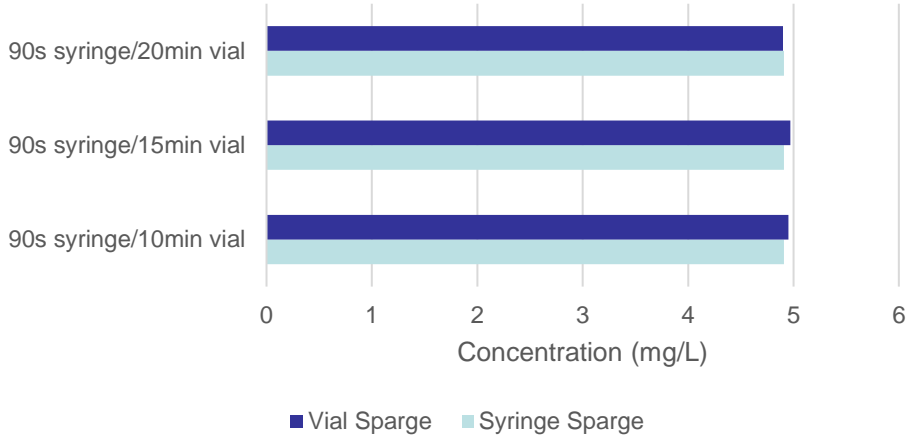
Matrix 1



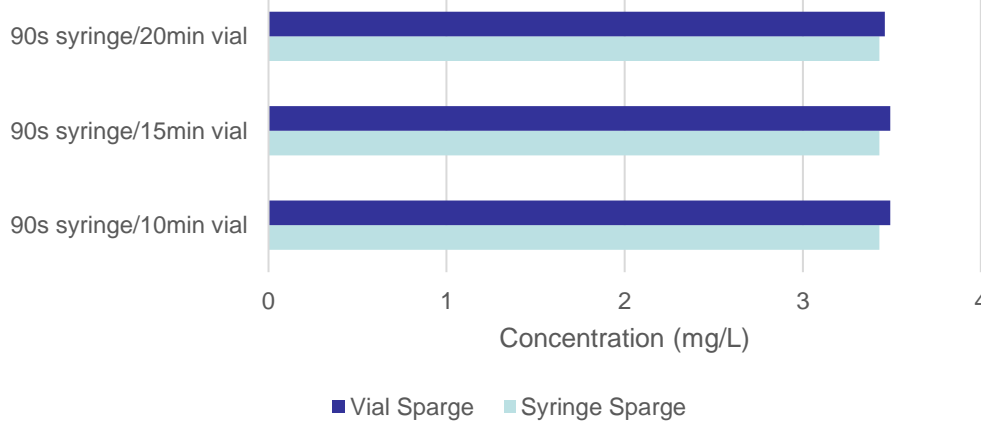
Matrix 2



Matrix 3



Matrix 4



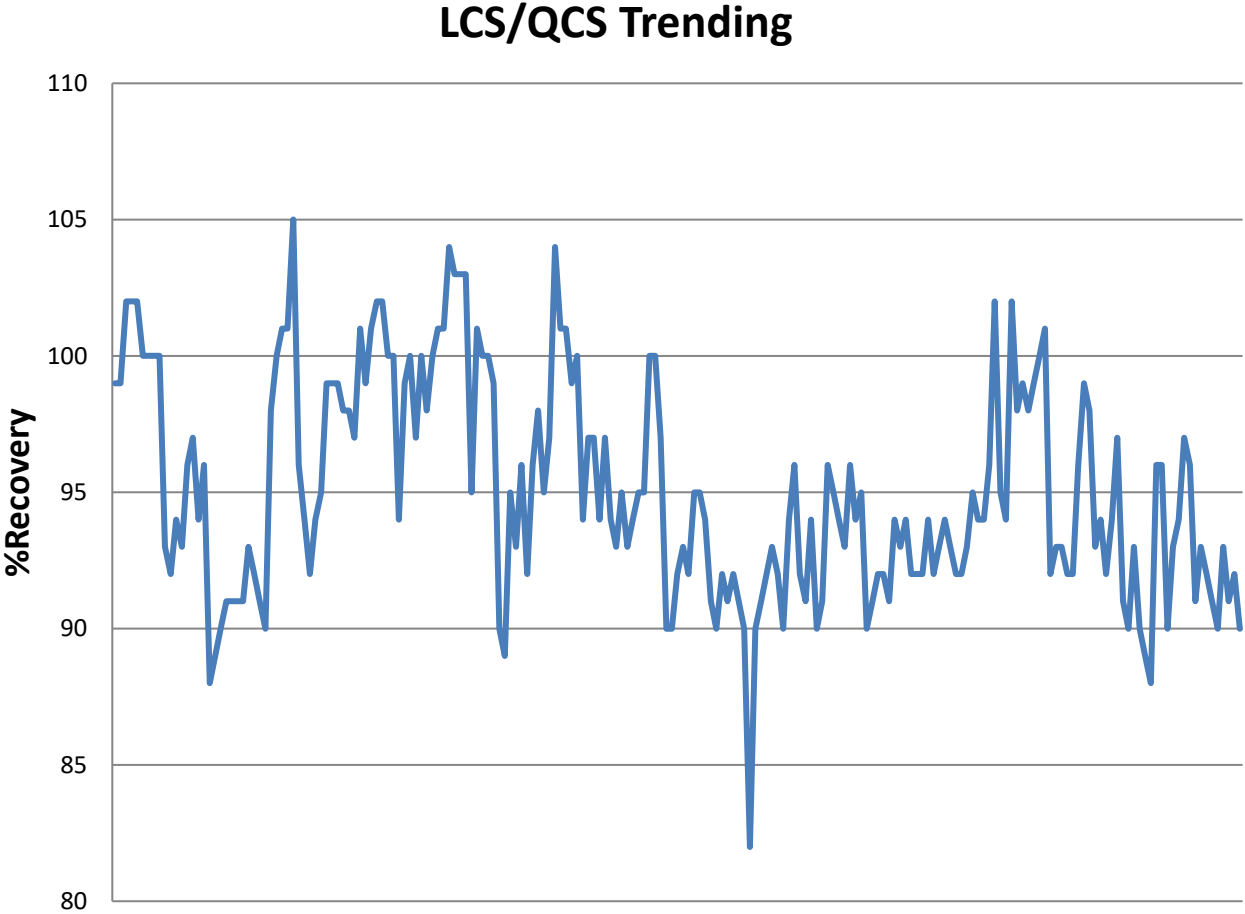
- While the manufacturer's default of a 10-minute vial sparge works great for standards, it is not sufficient for some matrices.
- Some inorganic carbon is retained after 10 minutes, causing higher TOC values
- Difference between lab and in-line analyzer data was minimized to ~5%

Using Optional Carbon Sources

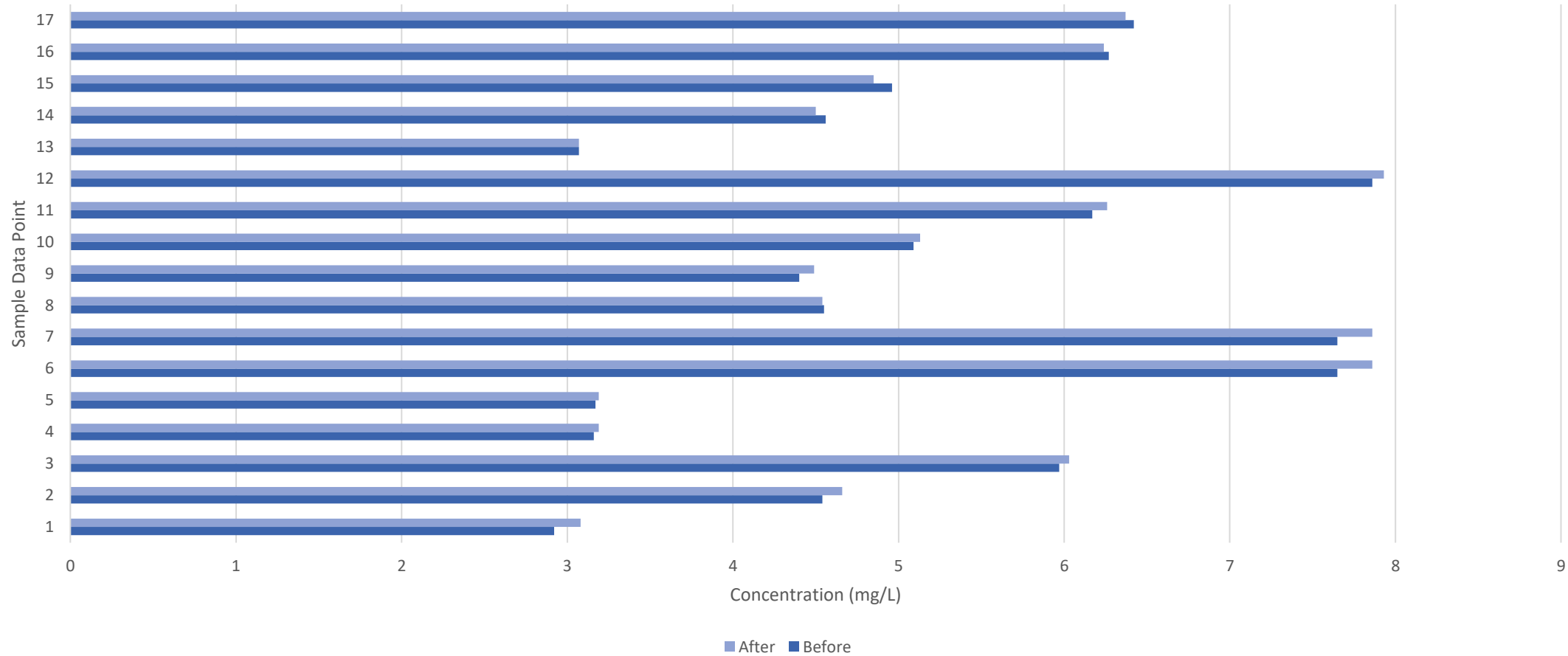
- Traditionally for TOC analysis, KHP is used as the Carbon source in analysis.
- KHP is used in calibration curves
- KHP readily oxidizes during analysis
- Not a good indicator of system issues

- Standard Methods states that LCS must be prepared from a different source of material other than calibration standards
- This could be a different lot or manufacturer
- The persulfate analyzer uses a completely different form of Carbon for verification
- Began using sucrose a secondary verification

- When catalyst conditions are unfavorable, sucrose is not readily oxidized
- Usage of sucrose can show signs of catalyst degradation



Before/After Catalyst Replacement



Conclusion

- Matrix matching sample to calibration is the key to minimize variance in results between TN by calculation and TN Combustion.
- Manufactures settings are a great place to start, however, each lab should optimize their systems for the most reliable data.

Questions?

Thank You

Ashley Roberts

anroberts@hrsd.com

www.hrsd.com/swift