DWQI – Cyanotoxin Round Robin Update

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Background

- The overgrowth of photosynthetic microorganisms is known as a harmful algal bloom (HAB)
  - Species that can form HABs include true algae, diatoms, and cyanobacteria
    - There are recreational and drinking water risks associated with HABs, particularly when HABs dominated by cyanobacteria species
    - Cyanobacteria can sometimes produce toxins during bloom events
      - These toxins include microcystin; which has in excess of 200 congeners
      - Detection of microcystin is usually performed using one of two methods:
        - EPA 546 – Enzyme Linked Immunosorbent Assay
        - EPA 544 – LC-MS/MS

Round Robin Project Development

- DWSG requested DSR to evaluate and draft drinking water values for commonly detected cyanotoxins following UCMR-4
  - Toxicologists within DSR developed a draft drinking water value for microcystin of 0.07 µg/L
    - Testing Limitations for commonly used quantification/detection of microcystin
      - EPA 546 MRL – 0.3 µg/L
      - ADDA-OH Kit Detection Limit – 0.1 µg/L
  - Discussions with utilities of the draft number lead to the proposed use of an enhanced sensitivity kit, which was not an approved modification of EPA 546
    - EPA has since allowed this kit as an approved substitution/modification to 546
    - SAES test kit uses different detection chemistry to have a lower detection limit; 0.016 µg/L
- Discussions with DWSG, DSR, and OQA lead to a formal request to DSR for a proposed project to look at the validation of the SAES kit, the lower-level detection limit of microcystin in finished drinking water, and to look at ways to increase testing capacity for either 546 and/or 544

Previously Presented - Round Robin

- Work was only done for microcystin
  - No other analytical concern for the other cyanotoxins in finished water
- EPA Health Advisory – 0.3 µg/L Microcystin - FDW
- DSR Draft Health Advisory Number – 0.07 µg/L - FDW
- EPA 546 MRL – 0.3 µg/L
- ELISA looks at total microcystin; at time when the draft DSR number was first being discussed DEP was made aware of newer detection chemistry which was being used, but had not yet been approved as a certified modification of EPA 546
  - SAES test kit uses different detection chemistry to have a lower detection limit; 0.016 µg/L
  - ADDA-OH (validated for EPA 546) – detection limit is 0.1 µg/L

Previously Reported – Round Robin

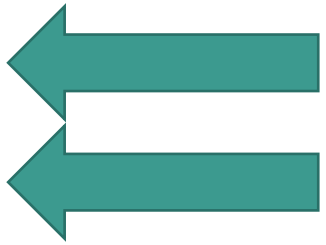
- Objective 1
  - Compare the performance of the SAES kit to ADDA-OH at low levels to measure reliability for precision and accuracy.
    - NJDEP lab was in process of obtaining OQA certification for 546 at the time and has since completed certification.
- Objective 2
  - Send out spiked samples with known concentrations to utilities routinely performing microcystin analysis to see real world recovery and data at low levels
    - A concept like how Abraxis (ELISA kit vendor) performs proficiency testing with known concentrations
- Objective 3
  - Compare the SAES kit at low levels to EPA 544 with spiked finished drinking water to measure sample recovery

Updated Report – Round Robin

- Objective 3 – Method Comparison
  - Based on data obtained from the first two objectives, selected concentrations were chosen and a utility with known blooms in source water, but no known breakthrough in finished drinking water, was asked to provide finished water samples.
    - These water samples were spiked with the following concentrations:
    - 0 µg/L (spiked with deionized water)
    - 0.07 µg/L
    - 0.1 µg/L
    - 0.3 µg/L
  - All samples were run in duplicate with method 546 controls using the SAES kit
  - “Raw” samples were quenched with the appropriate quenching agent/preservative (EPA 546 and 544 require different conditions); then spiked with the concentrations of microcystin and processed according.

Updated Report – Round Robin

	Expected	Reported	Recovered
Sample 1-0.07	0.07 µg/L	0.09 µg/L	128.57%
Sample 2-0.1	0.1 µg/L	0.134 µg/L	134.00%
Sample 3-0.3	0.3 µg/L	0.389 µg/L	129.67%
Sample 1a-Spike	0.07 µg/L	0.079 µg/L	112.86%
Sample 2a-Spike	0.1 µg/L	0.137 µg/L	137.00%
Sample 3a-Spike	0.3 µg/L	0.363 µg/L	121.00%
Sample 0	0	0	N/A



Samples spiked before extraction

Samples spiked after extraction

	Nod-R	MC-YR	MC-RR	MC-LR	MC-LA	MC-LY	MC-LF	
Sample 0	0	0	0	0	0	0	0	ng/L
Sample 1 - 0.07	0	0	0	83	0	0	0	
Sample 2 -0.1	0	0	0	130	0	0	0	
Sample 3 -0.3	0	0	0	390	0	0	0	

micrograms/L	EPA 546	EPA 544	Expected	Difference EPA 546/544	Difference EPA 546/Expected	Difference EPA 544/Expected
0.07	0.09	0.083	0.07	108.43%	128.57%	118.57%
0.1	0.124	0.13	0.1	95.38%	124.00%	130.00%
0.3	0.389	0.39	0.3	99.74%	129.67%	130.00%
0	0	0	0	N/A	N/A	N/A

Conclusions from Round Robin

- From Objective 1 and 2
  - Detection at values less than the MRL are possible with the standardly used kit – ADDA-OH, though consistency and operator training will likely play a big factor in the success of extrapolating below the lowest standard. This would not be a recommended approach based on lab experiences
  - The SAES kit generally reported values “higher” than spike-in at lower levels, this could be due to plotting issues with the curve, biological interference, or any number of factors which affect the way log plotted values show.
- From Objective 3
  - When microcystin is detected at low levels (below 0.3µg/L) with the SAES kit, EPA 544 is in good detection agreement of reporting values with the kit data for detection based on microcystin-LR, which is the most commonly occurring congener produced by cyanobacteria

Questions?

- Thank you to all the utilities who took part in the Round Robin!