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Adam Krantz

August 23, 2019

Office of Resource Conservation and Recovery (Mail Code 2822T)
U.S. Environmental Protection Agency
1200 Pennsylvania Avenue NW
Washington, DC 20460

Submitted Via the Federal eRulemaking Portal: <http://www.regulations.gov>

Re: Comments on EPA's SW-846 Update VII, Phase 2 - Method 8327 for Per- and Polyfluoroalkyl Substances (PFAS) Using External Standard Calibration and Multiple Reaction Monitoring (MRM) Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) (Docket ID EPA-HQ-OLEM-2018-0846)

Dear Ms. Christina Langlois-Miller,

The National Association of Clean Water Agencies (NACWA) appreciates the opportunity to submit comments on the U.S. Environmental Protection Agency's (EPA) updated testing Method 8327 for per- and polyfluoroalkyl substances (PFAS).

NACWA represents the interests of more than 300 public clean water utilities across the country, many of which operate their own testing laboratories, and everyday provide an essential service managing billions of gallons of the nation's wastewater to ensure the protection of public health and the environment.

As our understanding of PFAS matures and the science evolves, it is imperative that the methodologies used to quantify these emerging contaminants be precise and reproducible. Because public wastewater utilities are not sources of PFAS, but rather passive receivers, the cost placed on utility ratepayers for sampling and analysis or any potential regulatory compliance requirements cannot be based on inconsistent, deficient, or unverifiable data.

It is clear from EPA's Statistical Report and the Data Validation Summary that significant errors are present with nearly half of the analytes tested (n=11 of 24), revealing serious issues with reproducibility, response, recovery, stability and chromatography. The imprecisions found for long-chain PFAS compounds, short-chain PFAS compounds, and PFAS precursors all expose problems with this methodology. With the 3,000 plus known PFAS compounds in the environment, public wastewater utilities must have the confidence that their sampling and analysis accurately reflects the true concentrations and are not misrepresented by unacceptable uncertainty. If there is variability in precision across the board for PFAS compounds, as the Statistical Report and Data Validation Summary demonstrates, EPA must reconsider and revise this methodology.

Generally, to date, our analytical techniques of sampling chemicals in the environment have been limited to measuring concentrations at the part per billion level. Now, as analytical techniques and laboratory methodologies have advanced, we are able to measure contaminants, like PFAS, at the part per trillion level. Because we are measuring PFAS at extremely small concentrations, significant concerns remain as to whether laboratories can obtain representative samples that are truly reflective of the population being studied. We cannot begin to have confidence in analytical results until we can verify that sampling equipment, laboratory staff and/or the personnel conducting the sampling are not contaminating samples or having an effect on sample concentrations.

EPA must not move forward with this methodology until there is additional and sufficient scientific confidence and precision to resolve the problems associated with laboratory equipment, contamination, and instrument sensitivity.

Specific Comments on Draft Methodology

NACWA is providing specific comments on the draft methodology it received from its member, the Sanitation Districts of Los Angeles County (LACSD). Staff at LACSD have worked extensively on developing methods for PFAS and consulted with other experts in developing these comments.

As stated above, almost half (11 out of 24) of the target analytes in the method were indicated to have significant issues with reproducibility, response, recovery, stability and chromatography. Analytical methods must not be deemed acceptable if these crucial method do not meet the standards of quality required by the regulatory programs that would use this method. Several analytical chemistry measures are available to mitigate for these issues such as correcting for matrix effects (via isotope dilution or internal standardization) or eliminating steps that could potentially lead to analyte loss (e.g., filtration). Specifically, the following changes to the draft method are recommended to help mitigate these issues:

- **Allow isotope dilution quantitation.** PFAS are analyzed using electrospray ionization mass spectrometry (ESI-MS), which is prone to matrix suppression or enhancement. ESI-MS methods typically employ isotope dilution or internal standardization to correct for these problems. Isotope dilution is considered to be the best method to correct for the matrix interferences that are often encountered in environmental samples and is generally recommended for PFAS quantitation in non-potable water matrices. However, draft Method 8327 relies on external calibrations and therefore runs an unacceptable risk of over or under reporting PFAS concentration values. The draft method requires addition of 19 isotopically-labeled analogues but effectively wastes this expensive requirement by not using isotope-dilution to enhance the precision and accuracy of quantitation.
- **Replace the filtration step with centrifugation.** Section B11.2.4 of the draft method 3512 describes a filtration step of the diluted field samples. PFAS are surface active, and compound loss to the filters is likely, even with a 50% organic co-solvent. This loss may in fact account for the poor reproducibility observed for some compounds during the validation study. In lieu of filtration, centrifugation of samples to separate out the particulates is preferred. This technique also minimizes the plastic waste from disposable syringes and reduces solvent waste (60 mL/sample) generated from the recommended wash steps for reusable syringes (B11.2.6).
- **Potentially eliminate addition of acetic acid.** Section 2.1 indicates that acetic acid is added *“because it improved the sensitivity of some target analytes.”* The method does not specify which compounds are enhanced by the addition of acid, nor the level of signal enhancement. If the increase in sensitivity is negligible (as observed in tests conducted by LACSD), this step can be eliminated since this is one more reagent that requires PFAS screening prior to use.

- **Correct the method text on qualifier transitions for PFHxA.** Section 1.3 lists Perfluorohexanoic acid (PFHxA) as one of the compounds that lack qualifier transitions. PFHxA has two transitions: m/z 313→269 and 313→119, which are listed Table 3.
- **Do not allow for calibrations forced through zero.** Section 11.3.6 indicates that forcing linear and quadratic curves through zero is allowed “*when background PFAS are present to better estimate background concentrations.*” Forcing the curve through zero can potentially bias the results and should not be used to compensate for background PFAS that can easily be mitigated by replacing HPLC tubing with materials made from non-fluorinated polymers (e.g. PEEK) and installing a delay column.
- **Use pipettes for sample collection.** Section 8.1 indicates collection of 5 mL of sample in a 15 mL container but does not specify the procedures for doing so. We recommend providing samplers with pipettes to accurately dispense 5 mL of sample into the container. This prevents under/overflowing of containers and eliminates the gravimetric determination of organic solvent needed to maintain the 50% organic co-solvent requirement (B11.1.1) as well as the adjustment of internal standard/surrogate spikes (B11.2.1). The method also does not specify the number of samples to be collected. We recommend a minimum of four samples which can be used for MS/MSD and re-extraction if needed.
- **Perform dilutions on replicate samples.** Section 11.5.3 recommends dilution of the extracts with 50-50 methanol water with 0.1% acetic acid for samples with PFAS levels exceeding the calibration range. This procedure is problematic because it also dilutes the isotopically labeled analytes already spiked in the samples. We recommend performing dilutions on a replicate sample that has not yet been processed. Sample dilution can be performed by transferring samples to a new container, quantitatively rinsing the original container, diluting with additional solvent, and scaling the internal standard/surrogate spiking volume to maintain the same labeled compound concentration as the calibration standards.
- **Potentially widen the acceptance criteria for surrogate/internal standard recoveries.** Section 9.6.4 recommends preliminary acceptance criteria of 70-130% for the isotopically labeled PFAS analogues. This may not be routinely achievable for complex matrices such as wastewater. In fact, the method indicates surrogate recovery issues with multiple labeled PFAS. We recommend 50-150% as a starting point and statistically-derived limits should remain an option.
- **Add a section that allows for the addition of compounds to the method.** The list of PFAS compounds of interest is continuously changing. Accordingly, the method should include language that allows for the addition of new PFAS compounds. This language is present in draft method 3512 (B1.3) but the analytical method 8327 language is limited to the 24 compounds listed in section 1.0.

Conclusion

NACWA disagrees with EPA’s finding in the Executive Summary that, despite nearly half the samples indicating analytical errors, the method is “generally acceptable.” If an analytical method reveals errors or inconsistencies to this extent – in particular in situations where the method may ultimately be used for determining compliance with the Clean Water Act or another environmental statute – the method must be rejected until it can provide the scientific confidence needed. EPA must, at a minimum, revise the draft methodology based on the above recommendations and propose a new draft method with

sufficient data to qualify performance of the method for public comment before considering approval of its use in regulatory programs.

Thank you for your consideration of these comments. Please contact me at eremmel@nacwa.org or 202/533-1839 with any questions or to discuss further.

Sincerely,

A handwritten signature in cursive script, appearing to read "Emily Rimmel".

Emily Rimmel
Director, Regulatory Affairs