September 26, 2019

Annalisa Kihara, PE  
Supervising Water Resources Control Engineer  
Division of Water Quality  
California Water Resources Control Board  
1001 I St.  
Sacramento, CA 95814

Subject: CASA Recommendations for Phase 3 of PFAS Investigation

Dear Ms. Kihara:

On behalf of the California Association of Sanitation Agencies (CASA), thank you for the opportunity to submit our input about the focus of Phase 3 of your investigation of PFAS around the state. We understand that Phase 3 will focus on sampling at facilities that include publicly owned treatment works (POTWs). CASA represents more than 120 public agencies that engage in wastewater collection, treatment, recycling, biosolids management, and resource recovery. Our agencies are committed to the protection of the environment and public health and assisting the State Water Board in its investigations related to PFAS.

Through the focused, targeted and phased strategy suggested below, we believe the State Water Board will be able to answer its research questions in a timely manner while still taking into consideration current data collection initiatives and pending research. This strategy only focuses on the POTW aspects of Phase 3 and does not address how the State Water Board should pursue other potential entities, such as industries that discharge to POTWs. Specifically for POTWs, we recommend that the State Water Board roll out Phase 3 in two stages:

1. First, the State Water Board should initiate a more selective and limited inquiry to address specific items described below, which will allow the completion of pending research and investigations that may provide critical information to guide the subsequent stage.

2. Second, as appropriate, extend the investigation to additional facilities, once there are approved analytical methods and better informed research questions based on contours of affected areas derived from incoming data. At this point, the State Water Board also could begin gathering biosolids information, after approved analytical methods and controls are available.

As described in greater detail below, we suggest that the first stage of Phase 3 target only wastewater facilities serving areas where significant PFAS detections are likely or known to occur or exist. This can be demonstrated through existing data from the State Water Board’s Phase 1 data gathering, and potentially, industrial use data showing where there have been PFAS detections. This strategy would allow the State Water Board to focus on wastewater treatment facilities in areas that may be of concern based on the Phase 1 data, and it maintains a closer nexus to the pathway and underlying focus of these investigations: exposure through drinking water. CASA also strongly supports source control as an effective mitigation strategy where appropriate. While broad or indiscriminate pretreatment requirements would be premature and may not provide a significant reduction in PFAS environmental contamination, as the investigation and research findings ascertain the significant dischargers of PFAS, CASA will communicate with our members regarding the need for additional pretreatment or other controls at specified sources when feasible. Stage 1 could also include collecting data from POTWs that already are gathering/have gathered this data, with the caveat that such data may overstate the presence of PFAS due to the lack of approved methods and should only be viewed through that lens.
We recommend postponing the second stage of Phase 3 until approved and reliable analytical methods are available. Ideally all investigations would be timed to coincide with availability of approved and reliable analytical methods. We understand, however, the State Water Board may decide there is a short term need to identify and potentially address areas where data have already indicated a higher potential for the presence of PFAS. Should the State Water Board proceed in advance of reliable analytical methods, all data and information gathered using unapproved methods should be appropriately caveated and the State Water Board should acknowledge the potential for misstating the presence or levels of PFAS in wastewater streams.

Most importantly, in designing Phase 3, the State Water Board should identify what specific questions this data-gathering effort is intended to answer, what functions the PFAS data it will gather from wastewater facilities will serve, and what benefits will be obtained. For investigative orders such as those being utilized here, a reasonable relationship must exist between the need and benefit of the report generated from the investigation and the burden and costs to undertake complying and producing the technical or monitoring program report.

**Background Information on PFAS and Wastewater**

Although the State Water Board is likely aware of these foundational considerations, we believe it is important to contextualize the presence of PFAS as it relates to wastewater agencies. We appreciate your keeping these points in mind when developing recommendations for the investigation of wastewater treatment facilities.

1. **POTWs are Receivers of PFAS, Not Producers.** Wastewater treatment facilities and processes do not utilize PFAS, nor are we “sources” of PFAS. Rather, wastewater treatment facilities are “receivers” of these ubiquitous chemicals which are used by manufacturers and consumers, and our facilities merely convey and attempt to manage the traces of PFAS that are used in daily life by our society. That is, PFAS in effluent or biosolids is simply a function of influent we receive from different sites and sources.

2. **Distinguish Contaminated Sites from Background Levels.** There is a significant difference in PFAS concentrations at producer and heavy user contaminated sites versus background levels in groundwater and surface water. For example, sites found near manufacturers of PFAS can have levels of contamination at 100,000 to 500,000 parts per trillion (ppt), whereas, the new notification levels and prospective response levels being discussed for drinking water systems range from 5 – 40 ppt. This is a small fraction of the concentrations found at highly contaminated sites, and it is more effective to limit exposure through identifying and remediating contaminated sites, heavy “sources,” and manufacturing/commercial use of PFAS.

3. **PFAS Chemicals are Ubiquitous.** PFAS are commonly found in every American household, and in products as diverse as non-stick cookware, furniture, clothing, cosmetics, dental floss, lubricants, paint, carpets, pizza boxes, popcorn bags, and many others. In multiples studies, the mean and median concentration of PFOA in household dust in the United States was found to be between roughly 10,000 and 50,000 ppt, meaning there is significantly more PFOA in the ambient dust in the average home than the current notification levels for drinking water. This is only to note that traces of PFAS found in wastewater effluent or biosolids are likely minor relative to other exposures in the environment. Also, of importance is that PFOA and PFOS are found in every person’s blood stream in the parts per billion range, though those concentrations have decreased by 70% for PFOA and 84% for PFOS between 1999 and 2014, which coincides with the end of the production and phase out of PFOA and PFOS in the United States.\(^1\) This underscores the need for another line of scientific medical inquiry into whether the “forever chemical” nature of PFAS requires bioaccumulation modeling of its health risks, or if a dose-response approach provides a more accurate representation of the harm of exposure. Ultimately, the goal of gathering data is to find ways to address a specific harm, in this case, the potential adverse impacts of PFAS on human health by exposure, so we urge the State Water Board to specify the questions and functions the PFAS data it will gather in Phase 3 will serve at this time and in the future.

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4. **Wastewater Analytical Methods are Still in Development.** As yet, there are no approved analytical methods available for monitoring PFAS in wastewater influent, effluent, or biosolids. The USEPA released method 8327 for non-potable water matrices, which has yet to be finalized, and about which we express concerns below. ASTM has only released single-lab validated methods for non-potable water matrices (D7979) and soil (D7968), but not biosolids. The ASTM methods are only single lab validated, and we are not aware of any commercial labs being able to utilize it. Moreover, the frequently referenced DoD PFAS “method” is actually a set of QC requirements that must be met regardless of the method used. Though the DoD QC requirements serve to improve data quality, their checklist for PFAS does not address things like solid sample preparation techniques, which can be different from lab to lab and create data comparability issues. Attached is an example of just a few of the minor variables in labs that could significantly impact measurement of PFAS, particularly at the trace levels being discussed in the context of drinking water. We are highly concerned that results from any monitoring and investigation using unapproved methods may inaccurately portray the presence of PFAS, or lack interlaboratory comparability. Until such time as those methods are approved, broader investigation and monitoring should be deferred.

5. **Need for PFAS Source Control Program.** Addressing the concentrations of PFAS that may be present in ubiquitous consumer products is critically important, and will require a sustained, multi-year effort to identify target products for chemical substitutions, implement requirements for such substitutions, modify manufacturing processes, and/or modify consumer purchasing decisions. A comprehensive initiative to address the presence of PFAS both in products with high concentrations (e.g. fire-fighting foams) and in widely used products that have low concentrations is essential to any PFAS related actions. Without such a program, focusing on low levels of PFAS in wastewater may drive the need for many facilities to install new treatment processes, which in turn will result in additional residual management challenges (e.g. brine from reverse osmosis), increased energy use in the wastewater sector, and cost shifting compliance to ratepayers rather than placing it on manufacturers. We would welcome the opportunity to work with the Water Boards and other stakeholders to identify products that may be significant sources of PFAS contamination in wastewater and the environment to develop opportunities for reducing PFAS usage.

**Targeted Approach for Monitoring PFAS**

*CASA recommends that the Phase 3 investigation be bifurcated into two stages, the first limited and focused, the second broader once there are more methods available and existing data have been processed and analyzed.*

We recommend a phased investigation to address specific questions rather than casting a wide net at this time. We believe there is a need for additional research before commencing a far reaching and comprehensive investigation of PFAS levels at wastewater treatment plants. Moreover, our members feel it is very important to be on the forefront of protecting public health and the environment and agree that there are many immediate and pressing questions that must be answered to better understand the presence and impact of PFAS. This is especially true when considering the time, effort, and public resources that will have to be expended to comply with such an investigative order.

**Stage 1: Focusing on What is Currently Known:** CASA recommends the first stage of the State Water Board’s Phase 3 investigation target only: (1) facilities in areas with significant PFAS detections or where PFAS presence is likely or known to occur, demonstrated by using existing data showing where there have been significant detections, including areas such as military bases, fire-fighting training sites, or industrial facilities for chrome plating; (2) POTWs that already are gathering or have gathered PFAS related data (with the caveat that such data may overstate the presence of PFAS due to the lack of approved methods), in order to understand what their monitoring is exhibiting so that later orders can be developed accordingly, and (3) facilities that are actively engaged in groundwater recharge projects, as this demonstrates a potentially closer nexus with drinking water concerns.
Stage 2: Further Investigation Using Approved Methods and Incorporating Research: For the second stage and concurrent with these efforts, there are various methods for effluent, influent, and biosolids being developed, refined, and hopefully becoming more reliable. At such time as those methods are approved, it may be appropriate (depending on data gathered at the initial stage and other scientific research and data that continues to be returned) to broaden the investigation to additional wastewater treatment facilities based on the Stage 1 data. At that time, we may also know more based on completed research – including the presence, transport, and ubiquity of PFAS as well as the effectiveness of different treatment trains – for targeting specific areas or facilities for further investigation. Finally, this stage should consider examining biosolids, with a more targeted focus only in areas that were identified as of concern using data from Stage 1, after analytical methods are finalized.

Methods for Monitoring for PFAS
Without reliable and approved methods in place to monitor and measure for PFAS in influent, effluent, and biosolids, there are major limitations on what can be extrapolated from any data gathered.

An investigation using only a method for effluent or only a method for influent limits how much we can understand about PFAS that are passed through our facilities. This is also true when using a drinking water method for wastewater, such as method 537.1.

This past summer, US EPA sought public comment on a method for effluent, US EPA Method 8327. The comment period closed last month. We previously submitted to you LACSD’s comment letter to US EPA on this method, which is attached hereto. The US DOD issued a statement disapproving of this method and advised it be used only for screening purposes and not “for the collection of definitive data.” Given the draft status of the method, it would be improper to rely on it as part of the State Water Board’s investigation in the coming months. Moreover, requiring laboratory certification for this method would be very challenging. Accordingly, we recommend that the State Water Board consider the unsettled status of this method when determining the scope and immediacy of its Phase 3 orders. A new method using isotopes is currently being validated for future publication that may be more appropriate for wastewater and biosolids – EPA SW-846–8328, or “8328,” which will become a “1600 series” method. Having the benefit of this method and other fully developed ones will enhance the State Water Board’s understanding of levels of PFAS in influent, effluent, and biosolids, and improve the validity and reliability of data.

Special Considerations for PFAS Concentrations in Biosolids
CASA recommends that the State Water Board plan for biosolids testing when analytical methods are approved and there are labs with proven capability to implement them.

Biosolids are an extremely complicated matrix for all analyses, which highlights the compelling need for an approved analytical method for PFAS for biosolids. In the interim, CASA’s members have already been proactive in studying and analyzing the presence of PFAS compounds in biosolids and many are willing to confer and share data they have already gathered with the State Water Board. Given the complexity of the biosolids matrices for analyses, using unapproved methods for PFAS in biosolids raises significant validity and reliability concerns. Moreover, levels in many other types of solids can be comparable or even exceed those found in biosolids. For instance, a recent study sampled soil from the Shasta-Trinity National Forest in Northern California and documented higher concentrations of PFOA than a wastewater agency found in its biosolids. These factors should be considered as the State Water Board decides what types of biosolids sampling to pursue once methods are approved.

3 Ambient levels of PFOS and PFOA in multiple environmental media. Usha K. Vedagiri et al. https://doi.org/10.1002/rem.21548
Treatment Train Considerations
CASA recommends pursuing controlled scientific research on various treatment trains rather than attempting to extrapolate their impact through data gathering using undeveloped methods.

Currently, there are three costly but seemingly effective ways for removing PFAS from drinking water: activated carbon, ion exchange, and reverse osmosis. We understand the State Water Board may be interested in various treatment trains at wastewater facilities and seeks to better understand removal capabilities and how pre-treatment programs impact influent. We recommend performing this analysis and inquiry through scientific and research channels rather than data gathering efforts. Given the aforementioned analytical methods issues, and the inherent uniqueness and variability associated with each influent stream, facility, and treatment train, this would likely be performed best through controlled and dedicated research. CASA has already identified some forthcoming research efforts that could address this issue and fill the data gap, including a Water Research Foundation RFP (#5031) that just recently closed and will examine the occurrence of PFAS compounds in U.S. wastewater treatment plants. There are others ongoing that could be supported by both the State Water Board and the wastewater community. Through a controlled study, a variety of treatment trains and facility sizes could be incorporated into the study design in order to measure their efficacy and provide reliable information about potential removal capabilities.

Conclusion
Thank you again for the chance to meet and dialogue on how to undertake Phase 3 of the State Water Board’s investigation. CASA believes the approaches outlined above work best for balancing resources and solidifying our understanding of the presence of PFAS in wastewater influent, effluent, and biosolids. For this purpose, we would like to arrange a follow-up meeting in the first half of October to discuss in more detail questions or responses you may have and to hear an update on the planning for the coming months. Please reach out at your convenience with options that work for your team, and do not hesitate to contact me with any inquiries about the above information.

Sincerely,

Adam Link
Director of Operations

cc: Daniel Newton
    Shahla Farahnak
    Wendy Linck
    Brianna St. Pierre

Attached: List of PFAS Sampling Procedure Challenges
          LACSD Letter on US EPA Method 8327
2. Sampling procedures are challenging

* Deionized water not PFAS free
* Reagents can have PFAS
* Bottles/pipettes can have PFAS
* Extraction instruments have PFAS

Example Procedure Protocols

• Samples for PFAS analysis will be kept in coolers with wet ice. Blue ice is not acceptable for sample storage as it may contain PFAS compounds
• Do not use clothing or boots containing Gore Tex
• Do not use clothing that has been washed with fabric softener
• Do not use clothing chemically-treated for insect resistance or ultraviolet protection
• Do not use water-resistant, waterproof, or stain-treated clothing during PFAS sampling activities
• Do not use Tyvek suits during PFAS sampling activities
• Ensure clothing used during PFAS sampling activities has been washed a minimum of twice
• Do not use personal care products prior to or during PFAS sampling activities; these include but are not limited to insect repellent, sunscreen, makeup, etc.
• Do not use Post-it Notes during PFC sampling activities
• Minimize contact with and use of water-resistant notebooks
• After eating or drinking, always wash hands thoroughly and use new nitrile gloves
Via Electronic Mail
U.S. Environmental Protection Agency
EPA Docket Center, Office of Water Docket
Mail Code 28221T
1200 Pennsylvania Avenue NW
Washington, DC 20460

Attention: Docket ID No. EPA-HQ-OLEM-2018-0846

Comments on U.S. EPA SW-846 Method 8327 for Per- and Polyfluoroalkyl Substances (PFAS)
Docket ID No. EPA-HQ-OLEM-2018-0846

The U.S. Environmental Protection Agency (EPA) recently released SW-846 Method 8327: Per- and Polyfluoroalkyl Substances (PFAS) Using External Standard Calibration and Multiple Reaction Monitoring (MRM) Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), Docket ID No. EPA-HQ-OLEM-2018-0846. The draft method provides for the analysis of 24 PFAS compounds in extracts from both solid and liquid samples and was recently validated by the EPA in reagent water, surface water, groundwater, and wastewater effluent. A Statistical Report and Data Validation Summary were also released for Method 8327, which present the results of the multi-laboratory validation study. The EPA intends that Appendix B of Method 8327, which describes sample preparation procedures for non-potable water, will become standalone Method 3512: Per- and Polyfluoroalkyl Substances (PFAS) in Non-potable Water by Solvent Dilution. The Sanitation Districts of Los Angeles County (Sanitation Districts) appreciate the opportunity to submit comments on the draft method.

The Sanitation Districts are a confederation of 24 special districts, which operate and maintain regional wastewater and solid waste management systems for over 5 million people who reside in 78 cities and unincorporated areas in Los Angeles County, California. The Sanitation Districts operate 11 wastewater treatment and recycling plants and have been a leader for decades in providing recycled water for various beneficial uses, including groundwater recharge. The Sanitation Districts have been monitoring PFAS in wastewater effluent since 2013 and have worked to develop analytical methods and tools to effectively monitor for a suite of the compounds in non-potable aqueous and solid matrices.

After reviewing the draft method documentation, our main concern is that almost half (11 out of 24) of the target analytes in the method were indicated to have issues with reproducibility, response, recovery, stability and chromatography (as indicated in Section 1.0). Analytical methods should not be deemed acceptable if these crucial method parameters are found to be problematic. Several analytical chemistry measures are available to mitigate 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, we recommend the following changes to the draft method:
• **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 the 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 our tests), 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/overfilling 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; 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. Therefore, 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.

Although the draft method has been deemed by the EPA as generally acceptable, it will not generate high quality quantitative data suitable for regulatory reporting and decision making, if followed as written. The method itself acknowledges these limitations. Therefore, we strongly recommend incorporation of the above comments.

Thank you again for this opportunity to provide comments on SW-846 Method 8327 and for careful consideration of these comments. If there are any questions concerning this letter, please feel free to contact the undersigned by telephone at (562) 908-4288 extension 2830 or by email at nmunakata@lacsd.org.

Very truly yours,

Naoko Munakata
Supervising Engineer
Reuse and Compliance Section