Review on

Microplastics in Drinking Water Policy Handbook

by

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1. Objectives and Scope

This review was prepared in response to the invitation letter issue by the California State Water Resources Control Board and dated of February 02, 2022, which requested the *"External Scientific Peer Review of the Scientific Basis of Microplastics Definition, Analytical Method, Monitoring & Reporting Order, and Health Effects Guidance Language"*, as shown in Appendix 01 and Appendix 02 of the present document. According to the invitation letter, the review should *"take into account both the scientific basis for the proposed rule and the intended application or implementation of that science in the context of the proposed rule."*.

As recommended in the invitation letter, it must be clear that I am providing this review based on my previous experience and expertise in the fields of *Chemical Engineering*, *Polymerization Reaction Engineering*, *Characterization of Polymer Materials* and *Statistical Methods*, particularly in regard with the following conclusions and assumptions:

- Assumption #1: Significant uncertainties in the occurrence and toxicity of microplastics preclude the development of a narrowly prescriptive definition;
- Conclusion #1: Adopted Definition is Sufficiently Health-Protective and Appropriate with Respect to Scientific Uncertainties;
- Conclusion #2: Standardized Analytical Methods (Methods) Considered for Adoption are Fit for Purpose for Assessing Microplastics Contamination in Source Waters Used for Drinking Water;
- Conclusion #3 Proposed Microplastics in Drinking Water Policy Handbook (Handbook) is an Appropriate and Sound Approach with Respect to Occurrence and Hazard Knowledge and Gaps and Consideration of Available Resources.

2. Assumption #1

According to Assumption#1, *"Few studies are available regarding human exposure and health hazards of plastic particles, and significant data gaps remain. Plastic particles are a diverse contaminant suite and may be differentiated by a variety of criteria such as substance, state at a given*

temperature and pressure (e.g., solid at room temperature and standard pressure), dimensions, shape and structure (morphology), and color (Rochman 2019). The influence of these parameters in the environmental fate, transport, and human health impacts of microplastics are not fully understood. Due to these uncertainties, reliable assessments of risks to humans are not possible (Noventa et al 2021; Coffin et al. submitted).”

This reviewer fully agrees with Assumption#1. Besides the many consistent and reliable arguments that are presented in the reference papers, it must also be considered that living tissues have developed and lived in presence of nano- and microparticles since ever, as inorganic and organic nano- and microparticles of all sorts are naturally suspended in the air and in aqueous bodies due to uncontrolled natural processes (Sherrell and Boyle, 1992; Wallace, 2000; Gauthier *et al.*, 2001; Shapiro and Galperin, 2005; Ghio, 2011; Guchi, 2015). Therefore, it is not possible to unequivocally and equally associate harmful health effects for all sorts of nano- and microparticles of different compositions, structures, shapes, dimensions, among other characteristics, without assuming that all nano- or microparticles are potentially and equally dangerous to humans, which seems to be absurd.

It must be clear that the new and significant threats posed by anthropomorphic nano- and microplastic materials are not exactly their characteristic dimensions and shapes or the fact that they are suspended in the natural fluids, but their new compositions and possible new and unknown synergetic chemical and biological interactions when in contact with the living tissues. Consequently, different particles (or materials) can potentially exert very distinct effects on the human body and human cells metabolism, and one should not assume that they all offer the same potential risks to human health.

3. Conclusion #1

According to Conclusion #1, *“Health and Safety Code section 116350 et seq., California Safe Drinking Water Act requires the State Water Board to administer provisions related to drinking water to protect public health. To prioritize the protection of public health in light of significant scientific uncertainties, the adopted definition of ’Microplastics in Drinking Water’ was defined broadly, and with as few exclusions as possible, to ensure that policies, regulations, and standardized methodologies based on the definition capture a wide diversity of plastic particle types (Coffin 2020; Coffin et. al 2021). Furthermore, while technological limitations in the measurement of plastic particles were considered to be informative to the definition, such limitations are likely transient and serve only as a rough guide for prospective technical and economic feasibility of sampling and monitoring. While there is currently no widely recognized definition (Hartmann et al. 2019), attempts were made to harmonize with additional regulatory bodies (Coffin 2020) with the understanding that this definition may be used by additional parties, and outside the intended scope of drinking water.”*

As described by Coffin (2020) and in the draft version of the Policy Handbook, *"'Microplastics in Drinking Water' are defined as solid polymeric materials to which chemical additives or other substances may have been added, which are particles which have at least three dimensions that are greater than 1nm and less than 5,000 micrometers (µm). Polymers that are derived in nature that have not been chemically modified (other than by hydrolysis) are excluded."* In this reviewer's opinion, this definition seems appropriate for the purposes of the current law, as clearly defended by Coffin (2020). Besides, it is in accordance with most scientific reports, as also supported by Hartmann *et al.* (2019), Coffin (2020) and Coffin *et al.* (2021).

Despite the previous considerations, the present reviewer would like to highlight two additional points. The first point regards the implicit definition of polymer as a carbon chain, as it becomes clear in Table 1 presented by Coffin (2020). However, the technical definition of *polymer* is indeed much wider and can also include inorganic chains, such as the ones named generically as *geopolymers* (Majidi, 2013; Cong and Cheng, 2021). As a matter of fact, there are many incentives to include geopolymers explicitly in the proposed definition, as these materials can be produced synthetically and are frequently based on metal atoms that can interact with human cells and present cell toxicity, including silicon, aluminum, titanium and zirconium. Particularly, geopolymers have been widely used for manufacture of different types of glasses and cements. It can be true, though, that it may be difficult to monitor synthetically produced geopolymers, although monitoring of metal concentrations in drinking water constitutes an important variable for water quality control. If the law is intended to focus specifically on monitoring and control of carbon chains, perhaps this should be stated explicitly.

The second point regards the definition of liquid, which has been proposed in the form: *'"Liquid' means a substance or mixture which (i) at 50 degrees Celsius (˚C) has a vapor pressure less than or equal to 300 kPa; (ii) is not completely gaseous at 20 ˚C and at a standard pressure of 101.3 kPa; and (iii) which has a melting point or initial melting point of 20 ˚C or less at a standard pressure of 101.3 kPa."* Although the proposed definition is in accordance with UNECE (2013), the fact is that it can be inappropriate for quality control of drinking water. First of all, the definition is somewhat ambiguous, as: (i) a substance presenting a vapor pressure of 300 kPa at 50 ºC is 25 times more volatile than water; (ii) it is difficult to comprehend what *"completely gaseous"* mean; (iii) many polymer materials are amorphous, do not present a melting point and present very low glass transition temperatures. Besides, polymer particles that are suspended in water are likely to be swollen and contain high amounts of water, turning the proposed definition even more ambiguous. For these reasons, this reviewer believes that this definition of *"solid state"* might rely on unambiguous rheological properties; for instance, defining as *"solid"* the particles that present viscosities that are much higher than the viscosity of water (for example, the viscosity of honey is 10,000 time higher than the viscosity of water) or that do not flow under a specified shear stress.

4. Conclusion #2

According to Conclusion #2, *"Characterizing microplastics contamination is technically and logistically challenging. A commonly utilized tool - light microscopy - allows quantification of larger particles but loses effectiveness as the size range decreases from millimeters to microns (Primpke et al. 2020). This is of particular importance to drinking water, as the majority of microplastics found are smaller than 10 microns (Novotna et al. 2019), and human health effects are not anticipated to occur for particles larger than this size (Wright and Kelly, 2017). Furthermore, self-contamination of samples is difficult to control, and measurements of microplastics can be easily confounded by other non-plastic materials, such as paper and natural plant material, that can be present in the same size ranges (Scopetani, et al. 2020). Spectroscopic techniques, including Raman and infrared, can accurately quantify the number and shape of microplastic morphologies and distinguish polymer types (Primpke et al. 2020). Despite these methods showing great potential, few standardization efforts have been attempted to date, and no harmonized method has received widespread use (Primpke et al. 2020)."*

The present reviewer fully agrees with the ideas described in the previous paragraph. However, it is necessary to acknowledge that this is a fast-evolving field of knowledge and that other techniques are also evolving rapidly and present great potential for identification of microplastics, such as nuclear magnetic resonance (NMR) (Peez *et al*., 2019, 2022), possibly in combination with other analytical techniques.

Moreover, Conclusion #2 informs the reader that *"The State Water Board contracted with the Southern California Coastal Water Research Project (SCCWRP) to develop standard operating protocols for assessments of microplastics in drinking water using Raman and infrared spectroscopy and evaluate their performance through an interlaboratory validation study (de Frond et al. submitted). The Southern California Coastal Water Research Project assessed the following aspects in the interlaboratory validation study: 1) accuracy of the method, 2) repeatability/reproducibility within and among laboratories, and 3) resources necessary to perform the methods (i.e. people, equipment, time and consumables)."*

The present reviewer agrees that this has been a very positive and much needed action.

Additionally, Conclusion #2 states that *"Recognizing that microplastics measurement techniques and instrumentation are rapidly evolving, and that myriad innovations exist and are yet un-validated, SCCWRP's study plan involved two components: 1) Study Core focused on assessing accuracy, reproducibility and cost for five analytical methods in four frequently-encountered matrices (clean water, dirty water, sediment, and tissue). Multiple laboratories from throughout the world performed these methods using a series of standard operating procedures; and 2) Study Augmentations in which smaller sub-study elements in which individual laboratories investigated how novel methods, or small permutations of the core study standard operating protocols, affect method*

performance (SCCWRP Microplastic Measurement Methods Evaluation Study 2020). The Study Augmentations leveraged the Study Core by using the same samples, as well as custom samples as applicable, to examine method variations. Five analytical methods were performed in the Study Core for drinking water samples by a minimum of 6 and a maximum of 22 independent laboratories, including stereoscopy, stereoscopy with dye staining, Fourier-transform infrared spectroscopy, Raman spectroscopy, and pyrolysis-GC/MS (SCCWRP Microplastic Measurement Methods Evaluation Study 2020). Participating laboratories were sent blind identical samples created by a single laboratory that contained representative types of plastic particles varying in sizes, colors and morphologies as well as non-plastic materials intended to serve as false-positive controls (de Frond et al. submitted). Data received from participating laboratories were evaluated both quantitatively and qualitatively according to several sets of quality assurance quality control criteria developed specifically for microplastics (Brander et al. 2020; Koelmans et al. 2019) in addition to United States Environmental Protection Agency criteria for the evaluation of drinking water method performance for standardization purposes (Wendelken 2015), and criteria for interlaboratory validation of methods (Standard Methods 2019)."

Finally, Conclusion #2 requests that *"Peer reviewers should evaluate the standard operating procedures for draft methods developed by SCCWRP (Wong 2021a; Wong 2021b) with respect to their quality assurance and quality criteria reporting requirements and methods in light of challenges specific to microplastics. Peer reviewers are encouraged to refer to the manuscript which describes the findings of the inter-laboratory validation study as well as additional manuscripts detailing subsampling protocols for chemical verification and details regarding performance for spectroscopic methods evaluated in the study to evaluate the draft standard operating procedures. Note that these manuscripts are undergoing peer review with the respective journals to which they have been submitted and should be considered confidential and subject to change in response to journal reviewer comments."*

First of all, Conclusion #2 is largely supported by documents provided by SCCWRP (which describes the proposed interlaboratory validation study) and De Frond *et al.* (which describe the most important obtained results). The document provided by SCCWRP describes the proposed experimental plan and presents detailed experimental protocols for analyses of microplastics through a number of promising techniques, including stereoscopy, die staining stereoscopy, Fourier transform infrared spectroscopy, Raman spectroscopy and combined pyrolysis-GCMS (coupled gas chromatography mass spectrometry). As described by De Frond et al., the techniques were selected based on previously available experience of researchers who work in the field, as extensively documented in published scientific literature.

As we go through the documents provided by De Frond *et al.*, we learn that the proposed interlaboratory validation study was indeed performed and that *"FTIR and Raman spectroscopy accurately identified microplastics by polymer type for 95% and 91% of particles analyzed, respectively*". Although De Frond *et al.* explicitly state that *"The full dataset is publicly available to download via SCCWRP: (webpage link)."*, this reviewer was unable to find and download the

data set without help (which has not been solicited, though). Therefore, it is important to highlight that this reviewer is somewhat obliged to rely on the qualitative and quantitative assessment of the available data reported by De Frond *et al*. Moreover, although documentation regarding the use of Raman and FTIR spectroscopic techniques seems rather complete, very little information has been provided about the performances obtained with the other alternative techniques, suggesting that the obtained performances were much worse in these cases.

De Frond et al,'s main findings can be summarized shortly in the form:

- Particle counts were under-reported by almost all laboratories, particularly in the size range below 50 μm;
- Both Raman and FTIR spectroscopy are appropriate to identify microplastic and natural particles;
- Laboratory contamination was frequent;
- Particle subsampling for chemical identification through Raman and FTIR analyses caused bias, which was higher for smaller particles.

Based on De Frond *et al.*'s main findings, it can be concluded that much effort has yet to be done for development of unequivocal and unambiguous techniques for monitoring of polymer microplastics present in drinking water, for the following reasons:

- It can be said that current particle counting procedures are likely to underestimate the presence of microparticles in drinking water;
- It can also be said that microplastics identification techniques are likely to provide biased compositions of plastics contamination of drinking water;
- Data reported by different laboratories presented high variability, indicating that extensive training and harmonization of experimental protocols are still needed, which must be considered by legislators and proposed standard methods (which should make extensive use of blind standard samples for monitoring of local contamination and measuring biases);
- Cross interlaboratory validation studies must still be performed with real (and possibly more complex) drinking water samples, instead of using synthetic samples with known composition.

Therefore, based on De Frond *et al*.'s findings, it seems correct to consider that current methods and techniques can provide qualitative signals (and warnings or alarms) for monitoring and control of drinking water, but not quantitative measures that can be used for absolute control of the drinking water quality.

The previous discussions are important to define the technological scenario where the standard procedures described by Wong (2021a, 2021b) are inserted: "*determination of microplastics greater than 50 (20) μm in size in treated drinking water using visual microscopy for particle counts, and Infrared (Raman) spectroscopy for chemical identification of counted particles"*. One must observe that Wong does not intend to describe a general quantitative method for microparticles counting and characterization, but to harmonize methodological aspects of the procedures described by De Frond *et al*., so that Wong's proposals

are subject to all previously described constraints. Bearing this important piece of information in mind, we provide some additional remarks below:

- filter papers are potential sources of natural and synthetic polymer particles and fibers; as the use of filter papers are recommended in many parts of the two documents, additional technical specification should be provided;
- the use of glove boxes might be considered for preparation of particle counting samples and comparative particle contamination analyses;
- a similarity index (such as the correlation between two sets of spectral data) might be proposed to describe quantitatively how similar the obtained spectral data and the stored reference spectral data are, as reference spectra stored in software libraries are used for purposes of polymer identification;
- the two papers might be combined into a single document, given the significant large amount of repetition and overlap between the two manuscripts;
- as thoroughly described in the references, overall, both proposed procedures follow the best recommended practices in the field.

5. Conclusion #3

According to Conclusion #3, *"Health and Safety Code section 116350 et seq. requires the State Water Board to administer provisions related to drinking water to protect public health. Furthermore, Health and Safety Code section 116376 et seq., requires the State Water Board to develop requirements for four years of testing and reporting of microplastics in drinking water which may be conducted through the adoption of a policy handbook that is not subject to the administrative procedure act. Based on the cost and availability of laboratories to conduct monitoring using the standardized method (see Assumption 2), and the determination of health effects by the expert panel facilitated by SCCWRP (see Assumption 4), a draft Microplastics in Drinking Water Policy Handbook (Handbook) has been developed to set forth requirements for conducting monitoring and reporting of microplastics in source waters used for drinking water and treated drinking waters for four years."*

The present reviewer fully supports the described initiative and declare that had access to the *"Drinking Water Policy Handbook"* for preparation and submission of this peer review.

Moreover, according to Conclusion #3, *"Microplastics are known to occur at a wide range of concentrations in drinking water (approximately 1 x 10^{-4} to 100 particles/L) (Koelmans et al. 2019). Microplastics are typically not found in groundwater, and if so, have only been found at extremely low levels on the order of 1 x 10^{-4} particles/L (Mintenig et al. 2019). Furthermore, removal of microplastics by treatment type varies dramatically. Conventional treatment using coagulation-flocculation removes between approximately 40 and 70% of microplastics, with greater removal from more advanced treatment techniques, (typical removal rates of 80-88%) (Pivokonsky et al. 2020). Microplastics originating from the deterioration of polymeric distribution systems (polyvinyl*

chloride, polypropylene, polyethylene) has been observed, albeit at low levels (Mintenig et al. 2019; Kirstein et al. 2020), however significant data gaps remain for understanding contributions from distribution systems."

Consequently, the present reviewer fully understands the current concerns related to the possible presence of suspended microplastics in drinking water and the need to monitor and control the quality of this fundamental resource.

Additionally, Conclusion #3 states that *"Microplastics occurrence in water varies across temporal scales, and obtaining a representative sample requires the extraction of high volumes of water (1,000 L suggested as minimum) (Koelmans et al 2019). Sampling using in-line filtration methods reduces background contamination from atmospheric deposition and allows for high-volume extraction (Yuan et al 2022). Standardized sampling methods for microplastics in low- and high-turbidity waters have been promulgated and suggest extraction of high volumes of water (ASTM 2021). The proposed Handbook would require the use of the ASTM D883-20 method for collection of water samples, and analysis using infrared or Raman spectroscopy per SCCWRP methods (Draft Policy Handbook; Wong 2021a; Wong 2021b)."*

At this point, it is important to observe that the *"Drinking Water Policy Handbook"* proposes the combined use of the ASTM D883-20 method for water sampling and of FTIR and Raman spectroscopy for identification of suspended microplastics. Nevertheless, the use of FTIR and Raman spectroscopy for microplastics identification has been analyzed in the previous section of this review (Conclusion #2), which is now concentrated on aspects of water sampling, as described by the *Handbook* and the ASTM D883-20 standard.

Then, Conclusion #3 explains that *"In recognition of the emerging nature of microplastics and the potentially challenging effects (economically, technically, etc.) ordering a designated water system to conduct monitoring may have on the water system and community served, the draft Handbook proposes an iterative monitoring plan to minimize the unnecessary use of resources while obtaining necessary occurrence and exposure information to allow for more reliable characterizations of risk. During the first phase of monitoring which will last two years, wholesale water providers and raw water conveyance systems producing greater than 10,000 million gallons per day and water systems serving over 100,000 people will receive the majority of monitoring orders, and will have the option of proposing consolidated sampling sites representative of source waters for drinking water. Based on the findings from the interlaboratory validation study (De Frond et al submitted) microplastics larger than 20 microns in length will be required for monitoring during the first phase as the majority of laboratories could not reliably quantify smaller particles using the standardized protocols. During the second phase which will also last two years, additional source sampling sites may be chosen, and sites with high concentrations of microplastics as determined in the first phase will require monitoring at a location post-treatment. The State Water Board anticipates that some qualified laboratories will be able to reliably characterize microplastics that pass-through treatment as small as 1 to 5 microns in length and will be able to test these laboratories' performance using proficiency*

testing samples. The State Water Board is working with the National Institute of Standards and Technology to develop microplastics proficiency testing samples."

Therefore, some aspects of the water sampling plan are presented in an introductory manner, for posterior and more involving discussions.

Finally, Conclusion #3 requests that *"Peer reviewers should review the proposed monitoring frequencies, rationale regarding the selection of sampling locations, sampling protocol, selection of required analytical methods, and selection of required rapid and inexpensive (also referred to as "surrogate") monitoring methods detailed in the Handbook with consideration for the protection of public health in light of the anticipated and unknown health effects, and the overall scientific underpinnings of the prescribed sampling, extraction, and analysis methods."*

In order to make the discussion clearer, the review is split into smaller subsections, which are dedicated to distinct subjects.

5.1. Monitoring Phases

According to the *Handbook*, *"State Water Board will employ a two-phase iterative approach for monitoring microplastics to obtain sufficient information to estimate risk through exposure via drinking water. Each step will last two (2) years, with a six (6) month interim period to allow for State Water Board staff to assess results from the first phase and plan the second phase of monitoring accordingly."*

This reviewer completely agrees with the proposal.

Additionally, the *Handbook* states that *"For both phases, the State Water Board will issue orders to water systems and/or wholesaler providers to monitor microplastics in source waters and/or treated drinking water. In Phase I, monitoring will focus on characterizing occurrence in source waters used for drinking for microplastics larger than 20 micrometers in length. Phase II monitoring will be directed towards characterizing occurrence in treated drinking water for microplastics both smaller than, and larger than 20 micrometers in length."*

This reviewer completely agrees with the proposal, but obviously assumes that the *State Water Board* will advise providers on how to execute the monitoring plan in order to harmonize the implemented procedures. Although this seems obvious, this has not been explicitly declared in the *Handbook* (despite the many references to demands that will be included in the monitoring orders, as described in pages #11-12 of the *Handbook*).

5.2. Public Water System Selection

According to the *Handbook*, *"Due to significant uncertainties regarding risks of microplastics through drinking water and the costs to reliably monitor microplastics, an adapted version of the UCMR will be utilized to minimize*

impacts to water systems, while obtaining sufficient data to estimate general occurrence and potential human exposure through drinking water. Accordingly, in the first phase of monitoring, a representative sample of water sources will be required to monitor, with a focus on characterizing sources which serve the greatest number of consumers. Wholesale water providers and raw water conveyance systems producing greater than 10,000 MGD and water systems serving over 100,000 people will receive the majority of monitoring orders in Phase I. The State Water Board will evaluate findings from Phase I to determine sampling locations for Phase II."

This reviewer understands and completely agrees with the proposal.

5.3. Techniques

According to the *Handbook*, *"Water systems selected to monitor during Phase I will test for microplastics occurring in drinking water that are larger than 20 µm in length. Monitoring for microplastics shorter than 20 µm in length is strongly encouraged. Monitoring will be limited to source waters only. The potential surrogate techniques listed as being 'required' in Attachment A will be required for monitoring."*

As already discussed in the previous section, based on De Frond *et al*.'s findings, it seems correct to consider that current methods and techniques can provide qualitative signals (and warnings or alarms) for monitoring and control of drinking water, but not quantitative measures that can be used for absolute control of the drinking water quality. In spite of that, this constitutes the best art of the moment and can provide relevant information about the extent of the microplastics problem in drinking water streams.

Although the limitation of Phase I to source waters only is understandable, the fact is that the determination of microplastics concentrations in treated drinking water streams will probably be much more difficult than in source waters. From this perspective, it seems reasonably conservative to include at least some treated water samples in Phase I to evaluate preliminarily whether the proposed procedures will demand adjustments for Phase II (for example, demanding additional sampling times and volumes). Besides, these preliminary samples will also provide some actual microplastics removal efficiencies that might be useful for design of sampling plans for Phase II.

Finally, this reviewer does not oppose the evaluation of the surrogate techniques listed in Attachment A, but is quite skeptical about the quality of the obtainable results. In this reviewer's opinion, the proposed surrogate techniques are also sensitive to the presence of particles and contaminants other than microplastics and, therefore, unless significant correlations are present among the analyzed features (which would be surprising, as the sources of different particles and contaminants are different), surrogate techniques may only provide local empirical correlations that can be useless and not transportable for future monitoring plans and control schemes. For these reasons, I believe that the proposed surrogate analyses should be performed but that obtained data should be analyzed carefully, if possible, with the support of biological activity data

(revealing increased carbon contents due to microbiological control problems) and of total suspended inorganic contents (revealing problems with the filtration and settling unit operations).

5.4. Sampling Points

According to the *Handbook*, *"Water systems, in cooperation with other agencies or water suppliers, may develop and submit a plan to the State Water Board that identifies sampling site(s) for water that is shared by multiple treatment plants and is representative of water that is further treated and distributed to consumers. To make this demonstration, a system shall submit information to the State Water Board regarding the location and distribution of each sampling site, and water quality information for each sampling site. The State Water Board will use this information to determine whether the source waters produce water used by multiple treatment plants. Upon approval of a submitted plan by the State Water Board, water systems shall monitor at the identified sampling site(s). Monitoring conducted through an approved plan may be used to satisfy monitoring requirements upon approval by the State Water Board."*

This reviewer understands and completely agrees with the proposal.

5.5. Water Sampling

According to the *Handbook*, *"Unless specified otherwise in a monitoring order, systems shall utilize the standardized protocol for collecting water samples for microplastics promulgated by ASTM International: "ASTM D8332-20: Standard Practice for Collection of Water Samples with High, Medium, or Low Suspended Solids for Identification and Quantification of Microplastic Particles and Fibers."*

This reviewer understands and completely agrees with the proposal.

5.6. Sampling Frequency

According to the *Handbook*, *"Unless stated otherwise in monitoring orders, samples must be collected on a quarterly basis to assess the temporal variability of microplastics."*

This reviewer thinks that the sampling frequency should be higher, perhaps defined on a monthly or fortnightly basis. Although I can certainly understand that in this case the additional costs can become prohibitive for practical purposes (and, therefore, should be carefully evaluated), the fact is that measurements taken for two years on a quarterly basis will not allow the evaluation of temporal seasonality and variability exactly, but may simply reflect the random variations of microparticles concentrations caused by uncontrolled natural (such as an unusual storm) or anthropomorphic reasons (such as the failure of an industrial effluent treating system). On the other hand, the occurrences of natural and anthropomorphic infrequent events are likely to go unnoticed with such a low sampling frequency.

5.7. Replicates

According to the *Handbook*, *"Public water systems subject to monitoring are highly encouraged to analyze replicate samples collected for microplastics monitoring using one or more surrogate monitoring techniques, if available, and submit surrogate monitoring data to the State Water Board alongside microplastics monitoring results."*

Given the intrinsic limitations of the proposed procedures (as described in the previous section) and the large variability of data reported by distinct laboratories, the sampling plan must necessarily include replicate sampling (at least, triplicates). In this reviewer's opinion, some replicates should be analyzed by distinct laboratories, for purposes of cross validation (that has not been performed with real samples yet) and characterization of statistical uncertainties and variability. Considering that multiple sampling devices will not be available at the sampling points, replicates can be collected during consecutive periods of 24 hours, as recommended by ASTM D8332-20

6. Final Remarks

We sincerely hope that this review will be of use and will contribute with this important initiative supported by the State of California. I will certainly be available for clarifications and additional comments, if needed.

Additional References

- P. Cong and Y. Cheng, Advances in Geopolymer Materials: a Comprehensive Review, Journal of Traffic and Transportation Engineering, 8, 3, 283-314, 2021. (https://doi.org/10.1016/j.jtte.2021.03.004)
- V. Gauthier, B. Barbeau, R. Millete, J.-C. Block and M. Prévost, Suspended Particles in the Drinking Water of Two Distribution Systems, Water Supply, 1, 4, 237-245, 2001. (https://doi.org/10.2166/ws.2001.0089)
- A.J. Ghio, Biological Effects of Utah Valley Ambient Air Particles in Humans: A Review, Journal of Aerosol Medicine, 17, 2, 2011. (https://doi.org/10.1089/0894268041457200)
- E. Guchi, Review on Slow Sand Filtration in Removing Microbial Contamination and Particles from Drinking Water, American Journal of Food and Nutrition, 3,2,47-55, 2015. (http://pubs.sciepub.com/ajfn/3/2/3)
- B. Majidi, Geopolymer Technology, from Fundamentals to Advanced Applications: a Review, 24, 2, 79-87, 2009. (https://doi.org/10.1179/175355509X449355
- N. Peez, T. Rinesch, J. Kolz and W. Imhof, Applicable and Cost-Efficient Microplastic Analysis by Quantitative ^{1}H-NMR Spectroscopy Using Benchtop NMR and NoD Methods, MRC, 60,1 172-183, 2022. (https://doi.org/10.1002/mrc.5210)

- N. Peez, M.-C. Janiska and W. Imhof, The First Application of Quantitative ^{1}H NMR Spectroscopy as a Simple and Fast Method of Identification and Quantification of Microplastic Particles (PE, PET, and PS), Analytical and Bioanalytical Chemistry, 411, 823-833, 2019. (https://doi.org/10.1007/s00216-018-1510-z)
- M. Shapiro and V. Galperin, Air Classification of Solid Particles: a Review, Chemical Engineering and Processing: Process Intensification, 44, 2, 279, 2005. (https://doi.org/10.1016/j.cep.2004.02.022)
- R.M. Sherrell and E.A. Boyle, The Trace Metal Composition of Suspended Particles in the Ocean Water Column near Bermuda, Earth and Planetary Science Letters, 111, 1, 155-174, 1992. (https://doi.org/10.1016/0012-821X(92)90176-V)
- UNECE, Globally Harmonized System of Classification and Labelling of Chemicals (GHS), 5th Ed., United Nations, New York and Geneva, 2013.
- L. Wallace, Correlations of Personal Exposure to Particles with Outdoor Air Measurements: A Review of Recent Studies, Aerosol Science and Technology, 32,1, 15-25, 2000. (https://doi.org/10.1080/027868200303894)