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Name of item reviewed: Microplastics Definition, Analytical Method, Handbook, and Health Effects Guidance Language

Based on my expertise and experience, I am reviewing the findings, assumptions or conclusions I agreed I could review with confidence, including:

- Assumption #1: Significant uncertainties in the occurrence and toxicity of microplastics preclude the development of a narrowly preceptive 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

General Overview

With increasing awareness of the widespread distribution of (micro)plastics in all environmental compartments across the globe, there have been significant increased research efforts to define, measure, monitor and assess risks of this class of emerging pollutants. Academic studies continue to be published in scientific journals at an exponentially increasing rate, and there have been a number of large-scale reviews conducted to assess microplastics (MPs) in water resources, including those for human consumptions (notably; Microplastics in drinking water (World Health Organization) and A scientific perspective on microplastics in Nature and Society (SAPEA)). However, the complexity and heterogeneity of microplastics pollution has hindered the ability to make clear and overarching conclusions because 1) the diversity of MPs complicates risk assessment in terms of variation in polymer composition, associated additives and chemicals, particle size and morphology, and weathering processes, 2) precise definitions of MPs have been proposed by several scientific or regulatory bodies, but there is limited consensus on how to classify materials, 3) challenges of MPs detection, particularly particles < 10 µm) still exist, 4) linking MPs properties with specific hazards remains elusive, and 5) difficulty in comparing published literature continues, as few standardized test materials or methods exist. Taken together, these factors make creating enforceable and consistent regulations challenging. Nevertheless, despite these uncertainties, it is crucial that large-scale and comprehensive efforts to measure, monitor and regulate MPs continue in order to understand the associated impacts and risks MPs pose both to the environment and human health. Importantly, these finding need to be communicated to the public in simple, unambiguous and restrained language to not hyperinflate potential risk but rather provide clear guidance on current state-of-the-art scientific information. In this context, the Microplastics Definition, Analytical Method, Handbook, and Health Effects Guidance Language reviewed here provides a holistic and scientifically based approach to continuously monitor the concentration of MPs in drinking water, which can

serve as a useful baseline study for academics and a necessary component of communication to the general public for reassurance that their drinking water remains clean and safe.

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

In general, I agree with the authors that there are many uncertainties which exist in understanding the risks associated with MPs, some of which stems from the physical and chemical diversity of this class of contaminants. From an analytical standpoint, this can also make quantification more challenging since not only the particle size needs to be considered, but also polymer chemistry, morphology, and extent of weathering. While not directly discussed in this assumption but mentioned in the definition of MPs in the handbook, the presence of plastics added chemicals could also be toxic. However, no further clarification of which chemicals would be targeted (or if it envisioned to potentially monitor them alongside MPs) have been given. The diversity of materials makes overarching statements regarding the concentration of MPs in a given sample and associated risks more challenging, considering each material variant could be classified differently depending on how narrowly each classification was made. Therefore, I can appreciate the intentions behind having as broad a definition of MPs as possible in order to encompass the largest number of potential target materials. However, when a definition becomes too broad, it becomes more difficult to subsequently classify the type(s) of materials contained in each sample, as they could all fit under a broad definition of MPs, which limits the utility of any dataset which is collected. In this context, only one sub-classification appears to have been made (for size, nanoplastics (1 - <100 μm) and large microplastics (100 μm to 2.5 cm), see 3.1.7 in Handbook). Confusingly, this seems to be different to the size distinction listed in section 3.1 of the Handbook, from 1 nm to 5,000 μm .

In this section, peer reviewers were asked to 1) assess the appropriateness of the State Water Boards definition of MPs, in particular the adopted definition of substance, state and dimensions criteria. In particular, the definition's substance criteria does appear to be reflective of the scientific consensus of plastic, that is, anthropogenic polymeric materials. While I do not necessarily suggest changing the accepted definition, for the context of this review and Handbook I would recommend:

1. Clarifying the (apparent) discrepancies in size as mentioned above.
2. More clearly stating the different specific categories of MPs which will be measured/reported. Here, size is mentioned but further sub-classifications for shape could also be included, such as morphology (e.g. at least, to differentiate between fragments and fibers). Furthermore, a list of target polymers could also be mentioned, so that one could assess the scope of polymers which are under

the purview of study here. Finally, the definition makes a distinction for particles with a composition of polymer content greater or equal to 1% by mass. It is not clear if these distinctions will also be reported in the final evaluation of MPs in drinking water or not.

3. Taken together, the reader questions if further sub-classifications from point 2 will be specifically reported, or if all particles measured which fall under the definition of MP will be reported collectively. To some extent, this overarching and all-encompassing definition may make further risk assessment more difficult if/when particles of a certain polymer/size/morphology/composition are shown to be more hazardous than others. Therefore, further sub-classifications may be advantageous to be measured, where possible, to aid in future hazard guidance.
4. While I can appreciate that some of these aspects are covered to some extent in Conclusion #2 more associated with analytical methods, having the definition of sub-classifications (if using) in the section for definitions would be advantageous.
5. While chemical additives are generally mentioned in the definition, again it should be stated if the associated chemicals will be measured in the plastics (or not), and what limitations this poses when evaluating the associated risks of MPs found in drinking water.

Conclusion #2: Standardized Analytical Methods (Methods) Considered for Adoption are Fit for Purpose for Assessing Microplastics Contamination in Source Waters Used for Drinking Water

As stated by the authors, one major hurdle in comparability between studies for MPs quantification is the lack of standardized materials (i.e. MPs controls) and harmonized methods. Furthermore, the authors have considered several practical aspects which will be necessary to move harmonization beyond academic research laboratories to make them applicable to measurements conducted on a more routine monitoring basis. This includes equipment availability, personnel hours and cost. Therefore, I find the three aspects which the methods were benchmarked against very appropriate, with 1) accuracy of the method(s), 2) repeatability/reproducibility within and among laboratories and 3) resources necessary to perform the method(s). In particular, developing a laboratory accreditation process and requiring the laboratories to be accredited in order to analyze the samples for MPs in this context is very welcome and important.

As the target for the use of this protocol is specifically for drinking water, testing the applicability of methods (either in the Study Core or Study Augmentations) was not necessary, but presumably this was conducted to have a broader understanding of the methods beyond the context of drinking water assessment, and does not change the validity of the findings for the methods selected specifically for drinking water in the context of the water quality surveys in California.

In this section, peer reviewers were asked to evaluate the standard operating procedures (SOP) for draft methods developed by SCWRP (Wong 2021a, Wong 2021b) with respect

to quality assurance and quality control criteria, as well as the (yet unpublished) inter-laboratory validation (De Frond et al.). Additionally, reviewers were requested to assess sub-sampling methods (De Frond et al., unpublished) and chemical identification for MPs (De Frond et al., unpublished). In particular, the interlaboratory comparison using standardized methods for extraction and measurements is a welcome addition to the literature and such a comparison is needed to guide the current recommendations and workflow of this MPs in drinking water monitoring work. In my review, I have considered the general SOP for methods, sub-sampling methods, and interlaboratory comparisons, but do not focus on the appropriateness of the method(s) for chemical identification for MPs since this is beyond my personal expertise.

A few points need further clarification, which ideally should be included in the next iteration of the document which is reviewed here:

1. Wong 2021a states that the method is applicable for particles down to 50 μm in diameter, but the current document to review states that 20 μm are the smallest MP target size, even though 10 μm are anticipated to be most frequent. While De Frond 2021 has assessed smaller particles, the method has not been validated for these smaller size fractions as part of Wong 2021a or Wong 2021b, which are specifically used as support materials for the Handbook. De Frond et al. showed that an excellent average recovery and chemical identification was achieved for particles greater than 50 μm in size, and therefore it is unclear on what basis the limit of 20 μm was chosen for the smallest particles was for this proposed protocol.
 - a. De Frond et al. (interlaboratory study) references Primpke et al 2020, and suggests that FTIR and Raman are capable of measuring particles down to 25 μm and 1 μm respectively. However, there does not seem to be a distinction in the workflow presented here about what the limit of detection (LOD) is for the respective techniques, and they are grouped together to have an LOD of 20 μm . This may need to be made clearer, about when and how to assess particles of different sizes.
2. Minimizing contamination and blanks procedures seem acceptable, as well as the anticipated number of samples to be processed by one technician/scientist per working day.
3. In a practical context, something that is somewhat unclear is sample collection and handling, i.e. will specific samples be collected for MPs analysis, or will standard controls which measure other water quality metrics be sub-sampled for MPs analysis?
4. The Wong reports state that the methods can be done independent of the total volume of water collected. However, it should be indicated the total sample volume of water intended to be collected in the context of monitoring and/or if this volume would change depending on sampling location, sampling plant, etc. or to achieve a given number of MPs in the sample to 1) have sufficient statistics and 2) ensure that the measured MPs are above the levels of the blanks (i.e. above the limit of quantification).
5. In the Wong reports, MPs are filtered and subsampled to measure “representative” particles with IR or Raman. However, even though 30 particles are selected as a

subsample and this should be done “at random”, it still seems there could be potential for bias, especially with very heterogeneous samples. Perhaps it could be helpful to make it required that a minimum of 3 sub-samples were collected and analyzed (should there be such high MPs concentrations from any given sample), and then all three values are reported to also assess the variation in sub-samples. In particular, the subsampling approach on which this work is based (De Frond et al. sub-sampling study), the researchers used an *in-silico* approach to come to these conclusions, with only a limited data set (13 studies), none of which were from drinking water. Moreover, this study suggested a minimum of 73 particles be used to capture the heterogeneity of MPs in the sample when considering chemical identification (Figure 4), and only when assessing relative abundance of material types, fewer particles could be analyzed (35 MPs). Furthermore, the authors suggest that approximately 60% of particles may need to be analyzed for a representative sub-sampling. It is therefore unclear why 30 MPs is suggested in this current document to review.

6. Overall, the suggested methodology should also be tested physically before being adopted. It does not seem adequate to base sub-sampling strategies only through *in-silico* approaches, since laboratory staff may inadvertently introduce biases when choosing particles to sub-sample.
7. In the quality assurance section(s) of the Wong reports, recovery efficiency between 50% -150% is considered acceptable. However, this seems to be quite a large variance, and it would be better if here tighter controls were implemented to reduce uncertainty in the context of MPs in drinking water for this monitoring study.
8. The results from De Frond et al. (unpublished, interlaboratory study) are very interesting and telling. Even for particles which are within the “easily” measurable size fraction ($> 20\mu\text{m}$), a large fraction of the MPs recovery was outside the target range for recovery, with many laboratories reporting higher or lower recovery values (Figure 1). The authors state that particle counts were underestimated by 24% overall, yet with 92% recovery for particles over $50\mu\text{m}$. However, given the spread of recoveries reported (Figure 1), this average value seems to be a bit misleading, since many values were actually much higher than 100% recovery.
9. The blanks were also quite contaminated (average of 91 MPs particles), which may be particularly worrying considering the presumed low concentration of MPs in drinking water. It is therefore unclear if the SOP is appropriate to reduce contamination sufficiently.

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 Research

The plan to monitor and report the quantities of MPs in drinking water proposed by the California State Water Board is timely and important. This will be the first large scale, continuous, long-term monitoring effort of MPs in any context, and will provide valuable information for academic researchers, technical experts in water treatment facilities and

the general public. As there is so little reliable information about current MPs concentrations in potable water, this effort will provide much needed knowledge and reassurance that citizens are consuming clean water, or bring attention to the fact that water treatment practices need to be amended to reduce the number of MPs in potable water. This effort provides one arm of a risk assessment (i.e. assessing exposure, but not hazard), since to date there are no health-based guidances on a “safe” amount of MPs to consume. This is because there are many data gaps in understanding health related hazards of MPs. Collectively, as no systematic and harmonized monitoring effort has been required by any government in the world to assess MPs in drinking water, this effort again shows that California is at the forefront of promoting both environmental research and a precautionary approach to limiting human exposure to anthropogenic contaminants.

In this section, reviewers were asked to respond to 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 monitoring methods in the Handbook, as well as the overall scientific underpinning of the prescribed sampling, extraction and analysis methods therein.

The Handbook provides a complete and good overview of the rationale behind this monitoring campaign. It is appreciated that the State Water Board acknowledges that it is using its monitoring authority carefully to minimize the unnecessary use of resources, but in the case of MPs monitoring described here, I believe this time, money and effort is well placed. Moreover, as several eminent scientists are either working directly at the State Water Board or in collaboration with the State Water Board and the Southern California Coastal Water Research Project in preparing these measures, I feel confident that amendments made to the Policy will be timely and justified when adapted to new and evolving scientific information.

A few aspects may be clarified further:

1. Handbook section 4.2.3 Laboratory Accreditation, and section 4.3.1 Process for Laboratory Accreditation – the authors note that there are no laboratories which have been accredited to measure MPs, and thus it is not clear how the State Water Board will accredit laboratories to perform this work. Will representatives from the State Water Board provide on-site training or tutorial videos? Written text alone seems unlikely to sufficiently explain the intricacies of MPs analysis to technicians/scientists who are new to MPs analysis. Will the laboratories be required to test spiked samples (e.g. similar to the inter-laboratory study performed in De Fond et al) for their accreditation? What are the metrics on which their accreditation be based? Will the laboratories be randomly controlled over the course of the study, or does an initially accreditation remain valid for the entirety of the four year study?
2. Handbook section 5.1 Public Water System Selection – the rationale behind selecting these water systems is justified in that it mostly targets those systems which serve the largest number of people (all large systems serving greater than

10,000 people, all small systems serving between 3,300 – 10,000 people and a representative sample of systems serving fewer than 3,300 people). Systems serving over 100,000 people will receive the majority of monitoring orders in Phase 1. However, focusing solely on the number of people served may not address how/why some facilities have fewer MPs in finished, potable water than others. Therefore, I would suggest collecting additional metadata concerning the water treatment system itself, such as the type(s) of treatment process(es) in place, which may shed light on which systems are most capable of removing MPs from source water. In this context, MPs in source water should also be measured to assess the water treatment plant efficacy – but this is not mentioned strongly enough in the Handbook and the rationale of assessing removal efficiencies is not directly stated.

3. Handbook section 5.2.1.9 – It is suggested that samples should be collected on a quarterly basis, but I'm not sure if this frequency is sufficient to truly assess the temporal variability of MPs either 1) in the source water or 2) potential fluctuations in operational performance of the water treatment systems under study. Keeping in mind the number of study sites and the length of time it takes to analyze individual samples, I can appreciate that this is already a substantial effort. Nevertheless, I would recommend that a select number of water treatment systems be sampled more frequently during Phase 1 to better truly understand temporal frequency of MPs occurrences and efficiency of the treatment plants.
4. Handbook section 5.3 Reporting Requirements – The handbook does not make it clear which specific metrics of the MPs need to be reported, such as particle number, particle size, particle chemistry, particle morphology, etc. More information could be provided here.
5. Handbook section 5.4 – Timeline - The timeline appears appropriate, and it is also good that there is a specific “reflection time” included to make adjustments (if necessary) between Phase 1 and Phase 2.
6. It is difficult to assess the specific sampling locations since this appears to be left up to the various water treatment facilities to make suggestions and then proceed after approval from the State Water Board. While this can make sense in practice, providing some guidance in the Handbook could be warranted.