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CONSIDERATIONS FOR MONITORING MICROPLASTICS IN THE NON-TIDAL POTOMAC RIVER

INTERSTATE COMMISSION ON THE POTOMAC RIVER BASIN

CONSIDERATIONS FOR MONITORING MICROPLASTICS IN THE NON-TIDAL POTOMAC RIVER

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Christina C. Davis

Interstate Commission on the Potomac River Basin
30 West Gude Drive
Suite 450
Rockville, MD 20850

www.potomacriver.org
info@icprb.org

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Disclaimer:

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UNITS AND ABBREVIATIONS

PET-PEST	polyethylene terephthalate-polyester
PP	polypropylene
PU	polyurethane
PE	polyethylene
PVC	polyvinyl chloride
µm	micrometers
mm	millimeters
EDC	endocrine-disrupting compound
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyl
DDT	dichlorodiphenyltrichloroethane
ARB	antibiotic-resistant bacteria
WTP	water treatment plant
WWTP	wastewater treatment plant
ICPRB	Interstate Commission on the Potomac River Basin
L	liters
ASTM	American Society for Testing and Materials
SOP	Standard Operating Procedure
MAG	microplastics-analysis-grade
PCTE	polycarbonate track etch
FB	field blank
IR	infrared spectroscopy
FTIR	Fourier Transform IR
LDIR	Laser Direct IR
O-PTIR	Optical-Photothermal IR
GCMS	gas chromatography-mass spectrometry
ELAP	Environmental Laboratory Accreditation Program

1.0 INTRODUCTION

1.1 Definition of Microplastics

Microplastics are of particular interest due to their size and associated threats to human and ecological health. Microplastics may be 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 1 nm 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.* (California State Water Resources Control Board, 2022, p. 3)

Microplastics in natural systems may be classified according to origin—as either *primary* or *secondary*.

While microplastics are still considered emerging contaminants, a growing body of scientific literature and journalistic articles raises concerns about the impacts of microplastics on human health. Ongoing research is aimed at understanding and quantifying the sources of microplastics to the environment, fate and transport, and impacts on human health and ecosystems.

1.2 Objective

Given the prevalence and associated health risks of microplastics in the environment, the State of California established a 2018 statutory requirement for the State Water Resources Control Board to adopt a microplastic definition, adopt a standard methodology for testing drinking water, and require four years of testing and reporting of microplastics in drinking water (California State Water Resources Control Board, 2022, pp. 2-3). Although there are currently no similar mandates in other states or at the federal level, multiple scientific and policy agencies in the Chesapeake Bay watershed are addressing plastics and microplastics through various initiatives and research.

The Interstate Commission on the Potomac River Basin's (ICPRB's) 2022 Clean Water Act Section 106 Potomac Basin Water Quality Improvement grant included a Task 3 activity to "assist water suppliers in VA, MD, and DC in developing microplastic sampling and analysis methodologies and conduct field sample collection." This white paper, which explores the feasibility of a microplastic monitoring program in the non-tidal Potomac basin, represents the output for this activity. Section 2 describes considerations for collecting and processing samples for microplastics analysis. Section 3 provides a brief explanation of analytical methods and quality control recommendations for the detection, quantification, and identification of microplastics. Since microplastics are an emerging contaminant, field sample collection was not feasible in 2022. Standard methods for sampling and analysis are still evolving, and ICPRB found that qualified analytical services were not readily available. However, with the adoption of California's standard analytical methodologies in May 2022, we anticipate that laboratory services will become more accurate, available, and cost-effective in the future. Section 4 summarizes the results of this feasibility assessment and outlines the recommended steps to design and execute a microplastics monitoring plan for the non-tidal Potomac River.

2.0 SAMPLING METHODS

Sampling for microplastics in surface water generally involves two steps: collecting the microplastic material and processing the material for transport and analysis by a laboratory. An effective sampling plan must include adequate controls to identify and quantify microplastic contamination that may occur during sampling and transport.

2.1 Sample Collection and Processing

ASTM Standard D8332-20 describes practices for collecting water samples "to determine the presence, count, polymer type, and physical characteristics of microplastic particles and fibers" (ASTM, 2020). The method entails passing water through a series of stacked stainless-steel sieves and then collecting the particles retained on each sieve for analysis. ASTM recommends sieve mesh sizes of 20 μm, 150 μm, 500 μm, and 5000 μm.

ASTM Standard D8332-20 includes procedural variations for expected suspended solids content (i.e., low, medium, or high suspended solids) and flow regime (i.e., pressurized or non-pressurized flow). Surface water sampling assumes "low to medium" suspended solids. For non-pressurized sample collection directly from the water body, ASTM D8332-20 recommends pumping 1500 L through stainless-steel tubing across the sieve stack as shown in the schematic (reprinted as Figure 1). Calculating and reporting microplastic particle counts per unit volume of water requires accurate measurement and reporting of the water volume passed across the sieve stack.

Figure 1. Water sampling apparatus for non-pressurized systems from ASTM Standard D8332-20 (reprinted from ASTM, 2020)

Although collection methods are beyond the scope of the California State Water Resources Control Board's standard operating procedures (SOPs) for extracting and measuring microplastics in drinking water (Wong and Coffin, 2022a; Wong and Coffin, 2022b), California's SOPs recommend that sample collection methods comply with ASTM Standard D8332-20. Alternatively, these SOPs allow samples to be collected as smaller volume grab samples (< 20 L). Sieve mesh sizes of 20 μm, 212 μm, and 500 μm are recommended by the California SOP, whereas ASTM Standard D8332-20 recommends sieve mesh sizes of 20 μm, 150 μm, 500 μm, and 5000 μm. Grab samples collected according to the California SOPs are to be sieved and processed in the same manner as pumped samples.

A third method that was employed to collect microplastic samples from the Raritan River and Raritan Bay involved dragging plankton nets with mesh sizes of 80 μm and 150 μm behind a boat during periods of low, moderate, and high discharge (Bailey et al., 2021). In this study, the water volume that passed through the net was measured with a flow meter in the net or calculated using boat speed, time, and the net dimensions. The researchers rinsed the nets with deionized water and separated the particles using sieves with mesh sizes of 250 μm, 500 μm, and 2000 μm, discarding the material retained on the 2000 μm sieve.

Regardless of which collection method is employed—inline pumping, grab sampling, or net dragging—collected water samples should be passed through a stack of stainless sieves to separate microplastics and other particles (Table 1). Per ASTM Standard D8332-20, the sieves should be placed in a 5-gal metal container with either a spigot or holes drilled in the container bottom to allow water that has passed through the final sieve to flow out. Upon completion of the sieving step, each sieve should be rinsed with a minimal volume of deionized or microplastics-analysis-grade (MAG) water, and the suspended material should be transferred to a glass storage container with a non-plastic lid (ASTM, 2020; Wong and Coffin, 2022a; Wong and Coffin, 2022b). The California State Water Resources Control Board SOP defines MAG water as "high-purity water filtered through a filter with pore-size 1 μm or smaller (of any appropriate material; glass fiber filters are suitable) and used as reagent water and to rinse apparatus" (Wong and Coffin, 2022a; Wong and Coffin, 2022b).

Table 1. Summary of collection methods and sieve mesh sizes for microplastic sampling

Sample Collection Method	Reference(s)	Sieve Mesh Sizes (μm)
Inline pumping (1500 L)	ASTM Standard D8332-20 (ASTM, 2020)	5000 500 150 20
Inline pumping (1500 L), or Grab sampling (<20 L)	California SOPs (Wong and Coffin, 2022a; Wong and Coffin, 2022b)	500 212 20
Net dragging	Bailey et al., 2021	2000 500 250

ASTM Standard D8332-20 states that samples should be transported and stored at 4 ± 2°C (ASTM, 2020). California's SOPs allow samples to be shipped at room temperature, though shipping and storage at 6°C is preferred (Wong and Coffin, 2022a; Wong and Coffin, 2022b). Samples should not be frozen or exposed to direct sunlight or bright light.

2.2 Quality Control

Koelmans et al.'s (2019) review and evaluation of fifty microplastic studies yielded recommendations for various aspects of microplastic sampling, including sample volumes, collection methods, and controls (Table 2).

Table 2. Recommendations for microplastic sampling methods from Koelmans et al. (2019)

Aspect	Recommendations
Sample volume	• Minimum 500 L
Sample collection	• Pre-rinse containers with filtered water in lab • Minimize use of plastic sampling materials • Avoid synthetic clothing fibers • Avoid volunteer/citizen sampling due to higher error rates
Negative controls	• Collect replicated ($n \geq 3$) procedural blanks
Positive controls	• Analyze replicated ($n \geq 3$) positive controls covering targeted size class and polymer types • Correct reported counts for positive controls if results are low, but reproducible

Adherence to the California SOPs requires the use of both trip blanks and field blanks as negative controls. Wong and Coffin (2022a; 2022b) define these blanks as follows:

- **Trip Blank** – A sample of MAG water of a similar volume as test samples, taken from the laboratory to the sampling site and returned without having been exposed to sampling procedures and the environment outside of the lab. The trip blank is to assess contamination introduced during shipping and storage only and must be present for each set of field samples from a sample collection period.
- **Field blank (FB)** – An aliquot of MAG water that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FB is to determine if method analytes or other interferences are introduced into the samples during shipment and collection. At least one FB must be sent out for each sampling event and analyzed with the samples from the analysis batch. The volume of the FB must be similar to that of actual samples collected and processed by this method. FBs differ from trip blanks in that the FB evaluates contamination during both shipment and collection, while the trip blank only accounts for contamination during shipment

Trip blanks are not to be opened in the field, but must remain sealed until analysis. In contrast, FBs are to accompany sample containers from the laboratory to the field and back to the laboratory. FBs are to be opened for the duration of each sampling event (Wong and Coffin, 2022a; Wong and Coffin, 2022b).

3.0 ANALYTICAL METHODS

3.1 Methods

The two California SOPs for extraction and measurement of microplastic particles from drinking water were developed based on peer-reviewed literature and an international method evaluation study conducted by the Southern California Coastal Water Research Project Authority (SCCWRP) (Wong and Coffin, 2022a; Wong and Coffin, 2022b; Coffin, 2021). Both methods pair visual microscopy for particle counts with spectroscopic methods for chemical identification of particles.

If the samples are not passed through a stainless-steel sieve stack in the field, the SOPs involve sieving followed by vacuum filtration in the laboratory. If sieving was completed in the field, only vacuum filtration is carried out in the laboratory. The filtration step isolates particles on a 20-µm and an optional 1-µm polycarbonate track etch (PCTE) membrane filter (Figure 2).

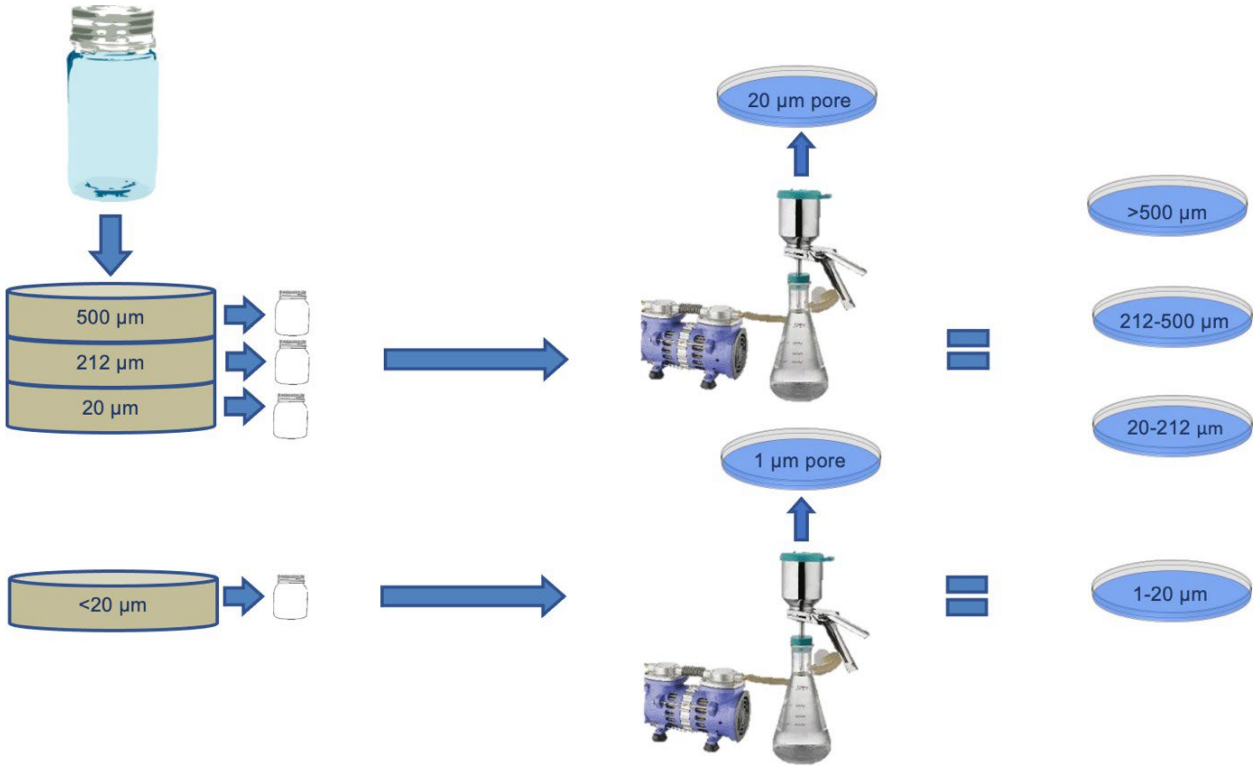

Figure 2. California SOP flow diagram schematic of filtration procedure with a 20-µm sieve (reprinted from Wong and Coffin, 2022a; Wong and Coffin, 2022b)

For surface water and wastewater samples, Koelmans et al. (2019) recommends digestion of samples to eliminate interferences from biogenic organics.

3.1.1 Visual Microscopy

Wong and Coffin (2022a; 2022b) provide procedures for counting and visually characterizing microplastic particles by stereomicroscopy. Color and morphology keys are reprinted in Appendix A.

3.1.2 Infrared Spectroscopy

Per Wong and Coffin (2022a), infrared (IR) "spectroscopy can include, but is not limited to, Fourier Transform IR (FTIR), Laser Direct Infrared (LDIR) Imaging, Optical-Photothermal IR (O-PTIR), and other techniques capable of measuring microplastic particles as small as 50 µm." Upon completion of the microscopic examination, a representative set of particle subsamples is identified by IR spectroscopy. The California SOP directs the analyst to apply the proportion of confirmed microplastic particles to the total particle counts from microscopy to estimate the number of microplastic particles per liter of water (Wong and Coffin, 2022a).

3.1.3 Raman Spectroscopy

The California SOP for Raman spectroscopy (Wong and Coffin, 2022b) establishes a procedure for identifying microplastics as small as 20 µm. Similar to the method for IR spectroscopy, representative subsamples of particles identified by visual microscopy are analyzed by Raman spectroscopy. The proportion of confirmed microplastic particles is applied to the total particle counts from microscopy to estimate the number of microplastic particles per liter of water (Wong and Coffin, 2022b).

3.2 Quality Control

Koelmans et al.'s (2019) evaluation of fifty microplastic studies yielded recommendations for laboratory methods (Table 3) in addition to the recommendations for sampling methods (Table 2).

Table 3. Recommendations for microplastic analysis methods from Koelmans et al. (2019)

Aspect	Recommendations
Laboratory conditions	• Pre-rinse and clean all materials and surfaces • Avoid synthetic clothing fibers • Handle samples in laminar flow cabinet or clean air lab
Negative controls	• Analyze replicated ($n \geq 3$) procedural blanks • Correct reported particle counts with results from blanks
Positive controls	• Analyze replicated ($n \geq 3$) positive controls covering targeted size class and polymer types • Correct reported counts for positive controls if results are low, but reproducible
Sample treatment	• Digestion recommended for surface water samples • Limit exposure to H_2O_2 to 48 h • Limit digestion temperature to $\leq$ 50 °C
Polymer identification	• Confirm with (micro)FTIR or Raman spectroscopy, pyrolysis-GCMS or TCA-GCMS • Analyze minimum number of particles or minimum percentage of filter

In addition to the guidance provided by Koelmans et al. (2019), the California SOPs include detailed requirements for laboratory quality, including an Initial Demonstration of Capability (IDC) and ongoing quality control requirements (Wong and Coffin, 2022a; Wong and Coffin, 2022b). California's Environmental Laboratory Accreditation Program (ELAP) is offering accreditation for microplastic analysis in accordance with the SOPs.

4.0 SUMMARY AND RECOMMENDATIONS

Microplastics are ubiquitous in the environment and have been detected in air, water, soil, and in living organisms around the Earth. Yet, microplastics are still considered emerging contaminants, and methods for sampling and analysis are evolving. Currently, there are limited laboratories with sufficient expertise and analytical capability for measuring microplastics with accuracy and precision. Thus, the challenge to establishing a microplastics monitoring program for the non-tidal Potomac River lies not with whether microplastics are present in the river, but with whether a commercial or academic laboratory can be identified and contracted to analyze samples in accordance with project constraints.

As part of this feasibility assessment, three laboratories were contacted for proposals. Quotations provided by Eurofins Eaton Analytical, LLC and EMSL Analytical, Inc. are summarized in Table 4. A third laboratory, Matexcel in Shirley, NY, provided a proposal, but it is excluded from the summary due to method ambiguity and a lack of quality control information contained in the proposal.

Table 4. Commercial laboratory proposals for microplastics analysis

Laboratory	Service(s)	Proposed Cost (September 2022)
Eurofins Eaton Analytical, LLC West Sacramento, CA *Note: Eurofins is pursuing CA ELAP accreditation*	CA SOP-certified Raman analysis of surface water source providing: **Option 1:** Count only, or **Option 2:** Chemical ID, color, morphology, count per each of 4 size fractions	**Option 1:** $1000/sample **Option 2:** $2000/sample
EMSL Analytical, Inc. Cinnaminson, NJ	Count – fluorescence microscopy; ID – Raman spectroscopy **Option 1:** Count only, or **Option 2:** Count and chemical ID based on Raman spectroscopy	**Option 1:** $361/sample **Option 2:** $469/sample

This feasibility assessment has yielded an understanding of the available methods, limitations, costs, and other considerations associated with establishing a microplastics monitoring program for the non-tidal Potomac River. In order to build on current understanding, the following actions are recommended:

1. Continue to monitor peer-reviewed literature and academic research outcomes to track:
   a) improvements to sampling and analytical methods;
   b) improved understanding of the human health risks posed by microplastics in the aquatic environment; and
   c) expected key source inputs of microplastics to the Potomac River (e.g., stormwater, wastewater, etc.).

2. Monitor developments in the California ELAP accreditation process.
3. Continue to communicate with commercial and academic laboratories regarding analytical capabilities.
4. Design a sampling plan that identifies sample sites and optimal sampling frequency.

5.0 REFERENCES

ASTM Standard D8332-20. (2020). *Standard Practice for Collection of Water Samples with High, Medium, or Low Suspended Solids for Identification and Quantification of Microplastics Particles and Fibers*. ASTM International, West Conshohocken, PA. https://www.astm.org/d8332-20.html.

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APPENDIX A. COLOR & MORPHOLOGY KEYS FOR VISUAL IDENTIFICATION OF MICROPLASTIC PARTICLES BY STEROMICROSOPY

Source: Sections 17.1 and 17.2 from Wong and Coffin (2022a; 2022b)

17.1 Color key. This color key is to be used to characterize colors of microplastic particles in samples. All particles described as clear, grey, silver, or white are categorized as white, and all gold, orange, or yellow particles are described as orange.

Color Key	HEX Values	RGB
Black	#000000	rgba(0,0,0,255)
Blue	#add4ee	rgba(173,212,238,255)
	#0ab2f0	rgba(10,178,240,255)
	#0b31d1	rgba(11,49,209,255)
Brown	#ad6800	rgba(173,104,0,255)
	#7f4800	rgba(127,72,0,255)
	#522e06	rgba(82,46,6,255)
Green	#00f727	rgba(0,247,39,255)
	#00a509	rgba(0,165,9,255)
	#005b01	rgba(0,91,1,255)
Multicolor (2+ colors)		
Pink	#fc9cf7	rgba(252,156,247,255)
	#e651d3	rgba(230,81,211,255)
	#c608b1	rgba(198,8,177,255)
PURPLE	#c887fe	rgba(200,135,254,255)
	#b656e4	rgba(182,86,228,255)
	#7d0bc4	rgba(125,11,196,255)
Red	#fd3334	rgba(253,51,52,255)
	#e51c0f	rgba(229,28,15,255)
	#bd0501	rgba(189,5,1,255)
Clear, Grey, Silver, White WHITE	#fcfcfc	rgba(252,252,252,255)
	#c4c4c4	rgba(196,196,196,255)
	#787474	rgba(120,116,116,255)
Gold, Orange, Yellow ORANGE	#ffe501	rgba(255,229,1,255)
	#ffd600	rgba(255,214,0,255)
	#ffc001	rgba(255,192,1,255)

17.2 Morphology Key. This morphology key is to be used to characterize microplastics particles in samples. All foams, films, fragments, or pellets are categorized as fragments, and fibers and fiber bundles are categorized as fibers. See Section 17.3 for examples of these morphologies.

Specific Morphology	Morphology Name to use for Reporting
Foam Film Fragment Pellet	Fragment
Fiber Bundle Fiber	Fiber
Sphere	Sphere
Fragment with rubbery constituency, often black but not always	Rubbery fragment