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Riverine Plastic Pollution: Sampling and Analysis Methods

March 2022

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U.S. DEPARTMENT OF ENERGY

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Executive Summary

Riverine plastic pollution has been found in all major U.S. rivers, but the exact amount of plastic being released to the oceans has not been quantified. Field studies conducted in U.S. rivers have used a range of sampling and analysis techniques and rarely measured the mass of the plastic collected. Measurements of riverine plastic pollution are needed to calibrate and validate models used to estimate the U.S. riverine plastic emissions to the oceans.

This report surveys measurement methods used to quantify riverine pollution and current estimates of U.S. riverine plastic pollution from measurements and models. Measurement methods include field sampling and laboratory analysis. Field sampling methods are described for large (macro) and small (micro) plastic particles. Laboratory analysis methods are described for macro and microplastic with an emphasis on the detailed characterization processes of microplastics. Waterborne leachate analysis is also briefly described. Three models are described that estimate plastic pollution based on mismanaged plastic waste in the river catchment basins. The models were validated and calibrated with global data sources. The data sources were predominantly outside of the U.S., where the magnitude and composition of plastic pollution is different than what is found in U.S. rivers.

Comprehensive measurements of riverine plastics are needed not only to characterize the riverine plastic pollution, but also parameterize and validate models of plastic fate and transport. This report also describes five key U.S. rivers that span a range of sizes and environmental conditions that could be sampled to obtain data to support characterization and model development of plastic pollution from rivers to oceans. Sampling and analysis protocol recommendations are made to ensure the highest quality of data are collected in the five rivers.

Acronyms and Abbreviations

DI	DeIonized
EMSL	Environmental Molecular Sciences Laboratory
FTIR	Fourier-Transform InfraRed
RO	Reverse Osmosis
MPW	Mismanaged Plastic Waste
WWTP	Waste Water Treatment Plant
NREL	National Renewable Energy Laboratory
PNNL	Pacific Northwest National Laboratory
WaterPACT	Waterborne Plastics Assessment and Collection Technologies

Acknowledgments

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1.0 Introduction

Plastic usage has been increasing at a rapid rate in the last 50 years. In 2016, the U.S. generated more plastic waste than any other country in the world (Zalasiewicz et al. 2016; Law et al. 2020). The increased usage of plastic has resulted in riverine plastic pollution (Rochman 2018). Riverine plastic pollution is especially concerning where rivers feed water supplies and because rivers are conduits to the ocean where remediation is even more difficult due to dispersion (Koelmans et al. 2019; Eerkes-Medrano et al. 2019). Rivers have become one of the main pathways for plastic pollution to reach the oceans and the mass of plastic released at river mouths worldwide is estimated at 4.8 to 12.7 million metric tons every year (Jambeck et al. 2015). Plastic has been detected in U.S. rivers that discharge into the Pacific Ocean, Atlantic Ocean, Gulf of Mexico, and the Great Lakes, but the total amount of plastic being discharged by U.S. rivers is unknown and the fate and transport in the waterways is not well understood (Blettler et al. 2018). Previous studies report a variety of sampling and analysis procedures and a broad range of pollution values, making it difficult to compare the results and fully assess riverine plastic pollution in the U.S. In order to fully understand riverine plastic pollution in the U.S., we must understand what forms it takes and how to measure it with field sampling and laboratory analysis techniques.

The defining characteristics of plastic pollution are that it is a synthetic solid polymeric matrix, insoluble in water, and can be found either in its original manufactured form or broken down into smaller pieces (Frias and Nash 2019). Plastic pollution is found in a range of sizes and polymer types. Pieces are often characterized by the length of their largest dimension and generalized as either macroplastic, microplastic, or nanoplastic. In reference to their largest dimension, many studies refer to particles $< 1\mu m$ as nanoplastics, plastics $> 1\mu m$ and $< 5mm$ as microplastics, and larger particles as macroplastics. Some studies have an intermediate category between microplastics and macroplastics called mesoplastics, but no standard definition exists (Lippiatt et al. 2013; Hartmann et al. 2019). Broadly, the size of the plastic particle helps describe which animals might ingest it, and the polymer type determines its density and its propensity to sink or float downriver.

Sampling and analysis techniques of plastic pollution vary depending on the size and polymer of the plastic being studied. For example, studies that sample the water surface only detect low density floating plastics and do not detect dense particles that are slowly settling to the river bottom. Studies that sample with nets only collect particles that are larger than the size of the net mesh openings. Grab sampling collects more microplastic particles than net sampling because it captures smaller particles (Barrows et al. 2017; Kapp and Yeatman 2018). Grab sampling studies would therefore estimate larger plastic particle loads than net sampling studies. For these reasons, field studies to quantify riverine plastic pollution need to be carefully designed to ensure they detect the desired size and type of particle. The studies also need to report every detail of the materials used, quality control measures, environmental conditions of the sampling, and laboratory procedures (Cowger et al. 2020).

The Department of Energy is addressing the problem of U.S. riverine plastic pollution with the Waterborne Plastics Resource Assessment and Debris Characterization (WaterPACT) project. The overall objectives of WaterPACT are to: 1) characterize, quantify, model, and valorize the range of waterborne plastics and leachates in U.S. rivers; 2) develop modeling, analysis, and technology tools to reclaim and remediate waterborne plastic debris; 3) leverage existing DOE funded research, such as distribitued generation, blue economy markets, materials characterization, and re-/upcycling; and 4) identify, understand, and reduce environmental and health stressors disproportionally impacting underserved communities. The project will leverage existing Water Power Technologies (WPTO) and Advanced Manufacturing Office (AMO) funded research and be conducted over two phases (FY22-23 and FY24-26).

One of the specific objectives in Phase I of the project is to collect field data and develop numerical models to assess and characterize U.S. riverine plastic pollution. This report reviews field sampling and analysis methods that will be used in the WaterPACT project. It also reviews models currently used to estimate riverine pollution quantities and discusses currently available datasets and gaps. The data gaps and sampling inconsistencies reported here highlight the need for a systematic plastics collection and analysis program. Best practices are also detailed to ensure future field data can be used to parameterize models that describe how much plastic pollution is in U.S. rivers, and its sources, fate and transport from rivers to the oceans.

2.0 Review of Field Sampling Methods

The majority of plastic pollution research studies are conducted in the ocean, but the field sampling techniques are similar to those used in rivers. River studies can be slightly different from ocean studies due to the depths of the water, the velocities of the currents, and the suspended sediment loads. Here we review field sampling methods for macroplastic and microplastic and describe how the methods can be applicable to river studies.

Field sampling methods are typically designed to answer a specific science question and the methods used may not be transferable to another study with a different science question. For example, studies that are investigating plastic consumption by fish only analyze plastic found inside of fish instead of in the water around the fish (Phillips and Bonner 2015). Many river studies only sample the surface water and then assumptions are made about the concentration profile to obtain total river estimates. The concentration profile can be vertically uniform or increase with depth and is usually only discussed in the context of microplastics although macroplastics may also be transported below the surface. When the concentration profile is vertically uniform, the plastic is transported as wash load. When the concentration profile increases with depth, the plastic is transported as settling suspended load and when most of the plastic is transported along the bed, it is considered as bed load (Cowger et al. 2021). Plastic being transported as settling suspended load or bed load are not detected by surface sampling. The specific gravity of a plastic particle determines if it will float or sink. Plastic particles with a specific gravity below one will float, but biofouling may change their buoyancy (Andrady 2011). Plastic particles with a specific gravity above one should sink but they may sink slowly if they are small and suspended by river turbulence. Table 1 lists common polymers, their applications, and the specific gravity of each polymer (Kershaw et al. 2019).

Most field sampling has been done by scientific researchers, but there are exceptions. The van Emmerik et al. (2020) study had volunteers report macroplastics with an app and the Barrows et al. (2018) study had volunteers collect jar samples to measure microplastics. Kershaw et al. (2019) provides guidelines for citizen science monitoring programs.

Table 1. Common polymers, applications, and specific gravity. Data from Kershaw et al. (2019).

Polymer	Common applications	Specific gravity
Polystyrene	Coolers, floats, cups	0.02-0.64
Polypropylene	Rope, bottle caps, gear, strapping	0.90-0.92
Polyethylene	Plastic bags, storage containers	0.91-0.95
Styrene-butadiene (SBR)	Car tires	0.94
Polystyrene	Utensils, containers	1.04-1.09
Polyamide or Nylon	Fishing nets, rope	1.13-1.15
Polyacrylonitrile (acrylic)	Textiles	1.18
Polyvinyl chloride	Thin films, drainage pipes, containers	1.16-1.30
Polymethylacrylate	Windows (acrylic glass)	1.17-1.20
Polyurethane	Rigid and flexible foams for insulation and furnishings	1.20
Cellulose Acetate	Cigarette filters	1.22-1.24
Poly(ethylene terephthalate)(PET)	Bottles, strapping	1.34-1.39
Polyester resin + glass fibre	Textiles, boats	>1.35
Rayon	Textiles, sanitary products	1.50
Polytetrafluoroethylene (PTFE)	Teflon, insulating plastics	2.2

2.1 Macroplastic

Macroplastics are either counted using visible observations or collected with booms and nets (Moore et al. 2011; Carson et al. 2013; Baldwin et al. 2016; Lindquist 2016; González-Fernández and Hanke 2017; van Emmerik et al. 2018; Meijer et al. 2021). Visible observations can be conducted by people or by cameras and analyzed with image processing algorithms (van Lieshout et al. 2020). Only surface floating plastics are counted with visible observations and the plastics are not collected for chemical composition or mass analysis. Booms only collect surface floating macroplastics and don't provide any information about macroplastics that are in the water column or on the river bottom. Nets are most often used at the surface but are also sometimes used for sampling below the surface (Moore et al. 2011; Baldwin et al. 2016).

2.2 Microplastic

Microplastic samples are collected as either bulk samples with jars or as volume reduced samples with nets or pumps (Hidalgo-Ruz et al. 2012). Nets are the most common method followed by jars and then pumps. There are advantages and disadvantages to the different collection methods (Barrows et al. 2017). Pump sampling filters can clog, but more frequent sampling remedies this problem (Kershaw et al. 2019). Nets are often made of plastic and contamination can occur due to imperfect cleaning between sample collections (Green et al. 2018). The mesh size of the nets and the volume of water sampled by the jars or nets varies between studies. Some studies only sample at the surface, whereas others sample at multiple depths. Nets can only capture particles larger than their mesh size. Jar samples capture every size of particle, which means the sample analysis is only limited by the laboratory detection methods. The smaller sizes of microplastics are important because particles smaller than 150 μm are biologically relevant, such as particles from tires (Covernton et al. 2019). The size constraints on the net sampling method mean the number of particles per volume of water could be lower than in jar samples because some small particles fit through the net holes (Green et al. 2018). Nets also sample higher volumes of water than jars, and therefore the measurements have less uncertainty and higher signal to noise ratios (Green et al. 2018; Hung et al. 2021). Jar sampling often only samples one or two liters of water, which can result in many samples with a concentration level of zero. Microplastics may be present in the sampled river, but not at a concentration level high enough to be detected by jar sampling. One example of that is a citizen science study in U.S. rivers and streams where almost half of the samples did not contain microplastics (Figure 1) (Barrows et al. 2017, 2018). A measurement value of zero shows that no microplastics were found in a single jar sample, but it does not confirm that microplastics don't exist in those rivers or streams. Combining jar sampling with net sampling provides a more complete understanding of the microplastic pollution problem by capturing all sizes of particles and sampling enough water to raise the signal to noise ratio (Tamminga et al. 2019).

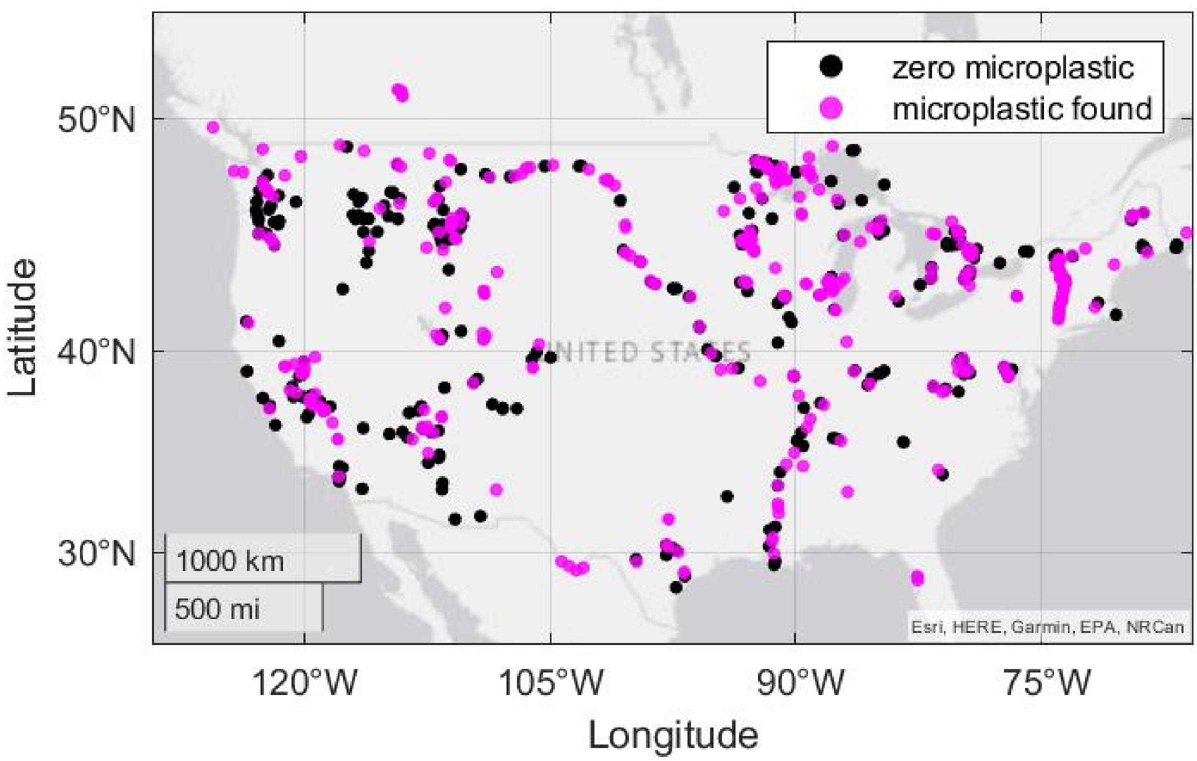

Figure 1. Map of citizen science jar sampling sites (data from https://www.adventurescientists.org/).

3.0 Review of Laboratory Analysis Methods

Laboratory analysis of riverine samples aims to quantify the number, size, shape, weight, and polymer type of the particles collected. Here we review laboratory analysis methods for macroplastic and microplastic, and briefly discuss water analysis for leachates.

3.1 Macroplastic

Post-collection analysis of macroplastic samples can include counting and weighing the plastic bottles, polystyrene containers, and plastic bags (Carson et al. 2013; Lindquist 2016). This can be carried out in the field instead of shipping the samples to a laboratory. In some studies it is impractical to wash and weigh every piece of macroplastic, so items of a given type are counted and the estimated mass of the total is based on the mass of one item (Kershaw et al. 2019). The polymer type can be determined by reading the number on the bottom of the container, comparing the characteristics to known characteristics of commonly used polymers, or a sample can be taken to the laboratory for Fourier-transform infrared (FTIR) or Raman spectroscopy analysis.

3.2 Microplastic

Laboratory analyses of microplastics are composed of multiple steps to separate the particles from organic material, weigh the sample, count the particles, document the particle size fractions and morphology, and determine the polymer composition (Hidalgo-Ruz et al. 2012). During laboratory analysis of the sample, care must be taken to mitigate contamination, and negative and positive controls must be used as quality control measures of the laboratory analysis procedures. Following specific reporting guidelines can increase the reproducibility and comparability of the results (Cowger et al. 2020).

3.2.1 Sample Treatment

The first step in sample treatment is to separate the plastic from other materials in the sample. This can be done by visual inspection under a microscope, density separation, or matrix digestion (Primpke et al. 2020a). Under a microscope, a particle can be compared to a set of visual guidelines that would identify it as plastic, touched with a hot needle to test for melting, or dyed with Red Nile dye (Andrady 2011). Visual inspection can overestimate the number of plastic particles if non-plastic particles are incorrectly identified as plastic. Spectroscopy can be combined with visual inspection to verify the chemical composition of unidentifiable particles (Kroon et al. 2018). Density separation utilizes density differences to separate plastic particles from other sample constituents. Table 2 lists four commonly used solutions for density separation of microplastics, their densities, and studies in which they were used. Matrix digestion separates out plastic particles by digesting organic matter in the sample. Table 3 lists four digestion methods, their advantages and disadvantages, and studies that used the methods (Kershaw et al. 2019). Once the microplastic particles are isolated they can be weighed, photographed, and examined for their physical and chemical characteristics.

Table 2. Commonly used solutions for density separation of microplastics. Data from Kershaw et al. (2019).

Salt	Density (g cm^{-3})	Reference
Sodium Chloride (NaCl)	1.2	Hidalgo-Ruz et al. (2012)
Sodium Polytungstate (PST)	1.4	Hidalgo-Ruz et al. (2012)
Sodium Iodide (NaI)	1.6	Claessens et al. (2013)
Zinc Chloride (ZnCl2)	1.7	Imhof et al. (2012)
	1.6	Zobkov and Esiukova (2017)

Table 3. Digestion methods and their advantages and disadvantages. Data from Kershaw et al. (2019).

Digestion	Advantages	Disadvantages	Reference
Oxidative	Inexpensive	Needs temperature control	Masura et al. (2015)
		Several applications	
Acid	Rapid (24 h)	Can attach some polymers	Claessens et al. (2013)
Alkaline	Effective	Damages cellulose acetate	Dehaut et al. (2016)
	Minimal damage to most polymers		
Enzymatic	Effective	Time-consuming (days)	Löder et al. (2017)
	Minimal damage to most polymers		

3.2.2 Physical Characterization

Physical characterization determines the shape of the microplastic particle. It can be done with either the naked eye or a microscope (Figure 2). Microplastic samples are examined and described by morphological descriptors. Five common morphological descriptors and their characteristics are listed in Table 4 (Kershaw et al. 2019). Fragments can be particles that have broken off of larger pieces of litter. Foam deforms easily under pressure and can be partly elastic. Film can have smooth or angular edges and line has a length that is much longer than its width. A pellet is harder than a sphere of foam. Once the microplastic particles have been grouped by their morphology, they are often counted and the degree of weathering is noted.

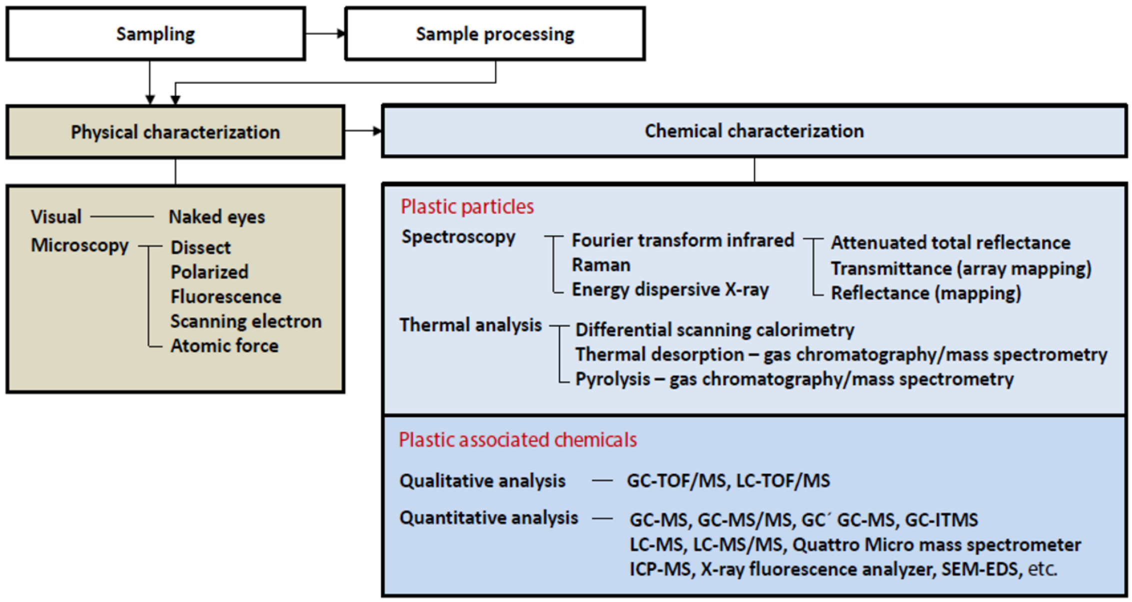

Figure 2. Physical and chemical characterization methods. Reproduced from Kershaw et al. (2019).

Table 4. Morphological descriptors of microplastic particles. Data from Kershaw et al. (2019).

Field description	Alternative descriptor	Characteristics
Fragment	Granule, flake	Irregular shaped hard particles
Foam	EPS, PUR	Near-spherical or granular particle
Film	Sheet	Flat and flexible
Line	Fiber, filament, strand	Long fibrous material
Pellet	Resin bead, Mermaids' tears	Hard spherical or granular shape

3.2.3 Chemical Characterization

Chemical characterization is necessary to determine the polymer composition of plastic particles (Cabernard et al. 2018; Kershaw et al. 2019; Primpke et al. 2020a). Microplastic characterization methods are shown in Figure 2 and the most common methods are listed in table 5 along with their advantages and disadvantages. Characterization analysis procedures usually examines one particle at a time but semi-automated detection equipment and software has been developed (Primpke et al. 2020b). If the particles are being examined one at a time, then a random subset can be analyzed (Song et al. 2015). The different methods of counting and characterizing particles can produce different counts of the number of particles per liter of water. When comparing microscope counting to FTIR counting, microscope counting showed more fibers and fewer fragments than FTIR counting (Song et al. 2015). When comparing FTIR to Raman spectroscopy, Raman spectroscopy identified more microplastic particles than FTIR spectroscopy (Cabernard et al. 2018). The difference was most apparent for particle sizes

$<= 500\mu m$, but the analysis times were four times higher. The type of chemical characterization used in a study depends on the size of the particle the study wants to detect, the number of particles that need to be analyzed, and the funding and time available for analysis.

Table 5. Microplastic characterization methods, advantages, and disadvantages. Data from Kershaw et al. (2019).

Identification	Advantages	Disadvantages
Microscopy	Simple	No chemical characterization
	Low cost	High possibility of false positives
	Color and morphological information	Subjective in interpretation
		High possibility of missing small particles
Microscopy + FTIR	No false positives	Expensive equipment
	Reduction in false negatives	Laborious and time-consuming
	Non-destructive	Requires expertise in spectral interpretation
	Detection limit 20μm particles	Removal of organic material is a prerequisite
		Particles must be transferred to a metal plate
Microscopy + Raman	No false positives	Expensive equipment
	Reduction in false negatives	Laborious and time-consuming
	Non-destructive	Requires expertise in spectral interpretation
	Detection limit 1μm particles	Removal of organic material is a prerequisite
	Non-destructive analysis	Interference by pigments
	Non-contact analysis	Risk of laser damage to particles
		Exact focusing required
Semi-automated spectroscopy	No manual particle selection error	No visual image data on single particles
	High automation potential	Production of a large volume of data
	In principle no false negatives	Long post-processing time
		Requires expertise in spectral interpretation
		Requires removal of interfering particles
		Expensive instrument

3.3 Leachates

Leachates are chemicals that have leached from solid plastic into water. Laboratory analysis of jarred river water samples can reveal if any leachates are present. The chemical composition of plastic leachates in rivers may vary due to the amount and type of solid plastic in the water and the salinity and pH of the river water (Gunaalan et al. 2020).

4.0 Review of Plastic Pollution in U.S. Rivers

Plastic pollution has been found in high discharge and low discharge U.S. rivers, but the exact amount that is being transported to the oceans has not been quantified. Several global studies have derived equations for the amount of plastic released at the coasts in terms of the mismanaged plastic waste in the river catchment area. While those equations were derived with data from worldwide rivers, they can be used to estimate the magnitude of U.S. riverine plastic pollution from local estimates of mismanaged plastic waste. The plastic pollution estimates vary dramatically and therefore field studies are needed to calibrate the equations for U.S. conditions. The local field studies of macroplastic and microplastic that have been conducted so far of U.S. rivers used a variety of sampling and analysis methods that were suited to specific research questions. In order to better quantify the amount of plastic pollution U.S. rivers are releasing into the ocean, local field studies need to be conducted with sampling and laboratory analysis procedures developed with that goal in mind. The data from the local field studies will be used to initialize future models, which will estimate plastic discharge to the oceans.

4.1 Estimates of Plastic Pollution From Mismanaged Waste

Riverine plastic pollution is often estimated by assuming it is correlated with mismanaged plastic waste (MPW) generated in the catchment area (Schmidt et al. 2017; Lebreton et al. 2017; Meijer et al. 2021). Field measurements of the mass of plastic in rivers are used to calculate constants in the equations. The field data used in these three studies were collected in rivers all over the world and did not have consistent field or laboratory sampling methods. Some field measurements measured macroplastic and others measured microplastic, and none used complementary laboratory cross-validation. After fitting the equation to the field data, this relationship can be used to estimate plastic emissions from any river into oceans anywhere in the world based on an estimate of MPW for that river.

Schmidt et al. (2017) estimated riverine plastic pollution by assuming a relationship with MPW and two fit constants: b_0 and b_1. The plastic load, M_{out} was calculated with the equation

$$log_{10}(M_{out}) = b_0 + b_1 log_{10}(M_{mpw}) \tag{1}$$

The dataset used to determine b_0 and b_1 was composed of 240 samples from 79 sites in 57 rivers worldwide. The three U.S. studies that were included in the fit data were the Moore et al. (2011) micro and macroplastics study in California, the Carson et al. (2013) macroplastics study in Hawaii, and the Baldwin et al. (2016) micro and macroplastics study in 29 Great Lakes tributaries. The Schmidt et al. (2017) fit was conducted three different ways to obtain three sets of coefficients. The fits were conducted with macroplastic studies data, with microplastic studies data (Model 1), and with only microplastic studies data where macroplastic data were also available (Model 2). Once the coefficients were determined from the fits, the mass of plastic pollution from other rivers was estimated using equation 1 and an estimate of MPW in the river catchment area. Maps of the estimations for 30 most polluted U.S. rivers are shown in Figure 3 and Table 6. Note all three methods predict the Mississippi River as having the largest plastic pollution load of all U.S. rivers. The total estimates of U.S. riverine pollution using the macroplastic data, microplastic data (Model 1), and microplastic data (Model 2) are 860, 144, and 245 tons/year respectively.

Table 6. 30 Most Polluted U.S. Rivers (Schmidt et al. 2017)

River	Outlet	Catchment (1000 km^2)	Population (M)	MPW (tons y^{-1})	Macro (tons y^{-1})	Micro M1 (tons y^{-1})	Micro M2 (tons y^{-1})
Mississippi	Gulf of Mexico	3183	76.7	187183	127	572	84
St. Lawrence	G. St. Lawrence	848	51.5	87812	44	153	26
Rio Grande	Gulf of Mexico	475	10.6	41388	15	41	8
Colorado	Gulf of California	621	8.5	21236	6	13	3
Delaware	Atlantic	29	7.5	18397	5	10	2
Columbia	Pacific	653	7.3	16912	4	9	2
Trinity	Gulf of Mexico	46	6.2	15086	4	7	2
Sacramento	San Fran. Bay	124	6.0	14755	4	7	2
Los Angeles	Pacific	2	5.0	12302	3	5	1
Mobile	Gulf of Mexico	112	4.4	10635	2	4	1
Hudson	Atlantic	35	4.3	10608	2	4	1
Susquehanna	Chesapeake Bay	71	4.0	9877	2	3	1
Santa Ana	Pacific	6	3.9	9431	2	3	1
Apalachicola	Gulf of Mexico	51	3.7	9067	2	3	1
Santee	Atlantic	40	3.6	8845	2	3	1
St. John's	Atlantic	25	3.4	8318	2	2	1
Potomac	Chesapeake Bay	30	2.8	6871	1	2	1
Altamaha	Atlantic	37	2.7	6548	1	2	0
Brazos	Gulf of Mexico	109	2.6	6268	1	2	0
Peedee	Atlantic	41	2.5	5986	1	1	0
Verde	Pacific	18	1.3	5827	1	1	0
Connecticut	Atlantic	29	2.3	5574	1	1	0
Guadalupe	Gulf of Mexico	27	2.2	5246	1	1	0
Merrimack	Atlantic	13	2.0	4931	1	1	0
Cape Fear	Atlantic	23	1.9	4642	1	1	0
Colorado	Gulf of Mexico	107	1.1	4553	1	1	0
Tijuana	Pacific	4	1.7	4479	1	1	0
Duwamish	Puget Sound	2	1.6	4079	1	1	0
Neches	Gulf of Mexico	54	0.8	3930	1	1	0
Blanco	Gulf of Mexico	6	1.3	3655	1	1	0

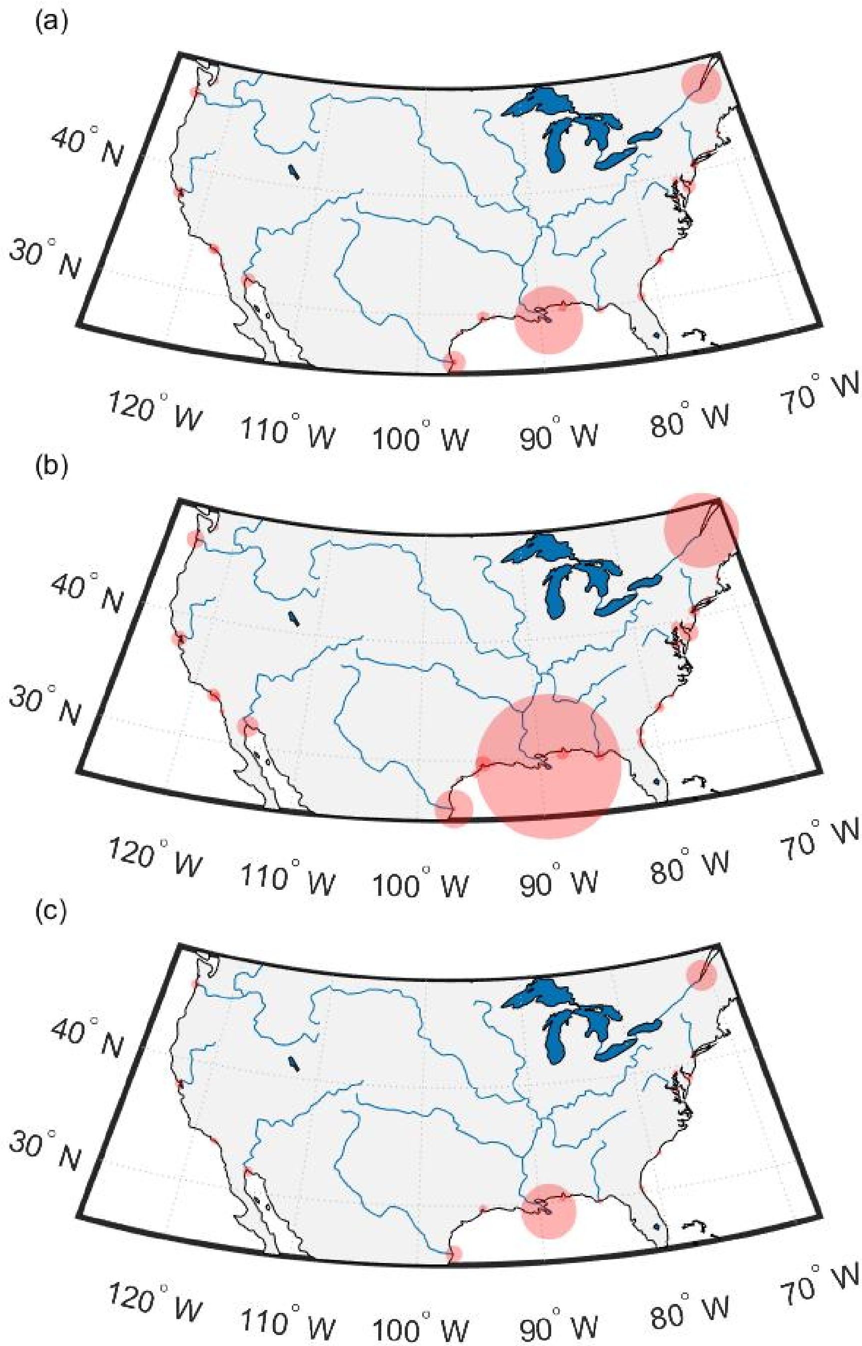

Figure 3. Estimates of plastic emissions from the 30 U.S. rivers that Schmidt et al. (2017) estimated release more than 1 ton per year. The size of the circle corresponds to the size of estimated emission. a) estimate of macroplastic b) estimate of microplastic using Model 1 c) estimate of microplastic using Model 2.

Lebreton et al. (2017) estimated the mass of plastic released at the river outflow based on MPW, but included a catchment runoff parameter. The mass of plastic released at the river outflow, M_{out}, is given as

$$M_{out} = (kM_{mpw}R)^a \tag{2}$$

where M_{mpw} is the mass of MPW produced in the catchment area, R is the average monthly catchment runoff, and k and a are regression-fit parameters. The regression parameters were calculated by fitting a line to data from 13 micro and macroplastic studies that sampled river surface waters worldwide. The studies were conducted by independent research groups, used different sampling methods, and different laboratory analysis methods. Some studies measured only microplastic and others measured both macro and microplastic. The one U.S. study that was used measured the number and mass of microplastic particles found in the Patapsco, Magothy, Rhode, and Corsica rivers of Maryland (Yonkos et al. 2014). Despite the variability in study methods, the $r^2 = 0.93$ for the fit with 30 data points from the 13 rivers.

Meijer et al. (2021) also estimated the mass of plastic released to the ocean based on MPW, but took into consideration the probability that the plastic was mobilized on land, transported across land to a river, or transported down the river to the ocean.

$$M_{out} = \sum M_{mpw} \cdot P(E) \tag{3}$$

where $P(E)$ is the probability that plastic waste discarded on land will be released to the ocean. It is defined as

$$P(E) = P(M \cap R \cap O) = P(M)P(R)P(O) \tag{4}$$

where $P(M)$ is the probability the plastic will be mobilized on land, $P(R)$ is the probability it will be transported from land to a river, and $P(O)$ is the probability it will be transported along the river to the ocean. The probability that plastic will be mobilized on land was calculated as the union probability of a precipitation event, P, and a wind event, W.

$$P(M) = P(P \cup W) = P(P) + P(W) \tag{5}$$

The probability that plastic will be transported from land to a river, P(R), is calculated using the distance to a river and a ”roughness” coefficient derived from the land use classification and average terrain slope. The probability that plastic will be transported along the river and released into the ocean depends on the distance it needs to travel in the river, the river discharge, and the river cross-sectional area. The Meijer et al. (2021) model was calibrated and validated with worldwide macroplastic data. Only one U.S. location was used for the model calibration and no U.S. location was used for validation. The U.S. location used for model calibration was not in a river but in Baltimore’s Inner Harbor (Lindquist 2016).

4.2 Review of U.S. Riverine Macroplastic Collection Studies

Macroplastic pollution has been collected in U.S. rivers by scientific studies or waterway cleanup installations. Two scientific studies used nets and one used booms (Moore et al. 2011; Carson et al. 2013; Baldwin et al. 2016). Net sampling did not yield large quantities of macroplastics due to the small size of the net openings. Baldwin et al. (2016) reported that only 2% of their collected samples were larger than 4.75 mm and they did not report the mass of the samples. Moore et al. (2011) collected 976 plastic particles larger than 4.75 mm over three days of sampling in the Los Angeles River, San Gabriel River, and Coyote Creek. The total mass of the particles larger than 4.75 mm was 141 grams. Booms were used by Carson et al. (2013) to collect debris Hilo, Hawaii. That study collected 380 PET bottles over 205 days. The total mass of the bottles collected was 10.18 kg. The small mass of macroplastics reported in these studies is partly due to the short duration of the collection times and the size of the waterways sampled. Waterway cleanup installations collect plastic for longer time periods and are located where large amounts of debris are found. The Mr. Trashwheel family is a group of waterway cleanup installations that use booms and a water wheel to collect surface debris from waterways (Lindquist 2016). Four trashwheels are in operation in the Baltimore area and plans exist for trashwheels in California and Panama. Mr. Trashwheel collected an estimated 115,985 plastic bottles at one location in 2019 (https://www.mrtrashwheel.com/). This converts to total of 1.18 tons of plastic per year given a weight of 9.25 grams per bottle (https://www.recyclingtoday.com/article/water-bottle-weight-decreases-recycled-content-increases/). A total of greater than one ton per year at only one location indicates the Schmidt et al. (2017) estimate of 127 tons per year of macroplastic exported from U.S. rivers may be close to the actual value.

Both booms and surface nets only intercept plastic that is floating within the top few meters of the water column. This limits their usefulness at quantifying the total plastic emission from U.S. rivers, but the amount of plastic collected on the surface could be considered a lower bound of the total plastic in the river. Booms also intercept anything floating on the surface, which can include large amounts of woody debris. The plastic needs to be separated from the other types of collected debris if the data are to be used in any riverine plastic emission estimates.

4.3 Review of U.S. Riverine Microplastic Collection Studies

Microplastics have been collected by scientific studies and citizen science projects in many U.S. rivers, streams, and waterways over the last ten years. The Adventure Scientist citizen science project found microplastics in streams, rivers, and waterways across the U.S.(Figure 4). Seventeen peer reviewed studies are listed in Table 7 and the states where the studies took place are mapped in Figure 5. Table 7 details if the studies collected microplastics using nets, jars of water, or fish guts. The Martin et al. (2018); Werbowski et al. (2021) studies are not listed as using nets, jars, or fish because they used pumped systems. Table 7 also shows which studies measured at multiple depths, multiple flow regimes, or near waste water treatment plants (WWTP). Several major rivers such as the Mississippi, Columbia, and Hudson have been sampled at one or more locations at least once, but others may not have been been sampled at all. The studies report different metrics quantifying the amount of microplastics. Table 8 shows that most studies counted the number of particles per liter of water. Studies that investigated fish or oysters reported microplastic particle per organism. Very few studies measured the mass of the microplastic pollution, with the exception of Moore et al. (2011) and Yonkos et al. (2014). Moore et al. (2011) reported grams of plastic per cubic meter of water. Similarly, Yonkos et al. (2014) reported grams of plastic per cubic meter of water, but only

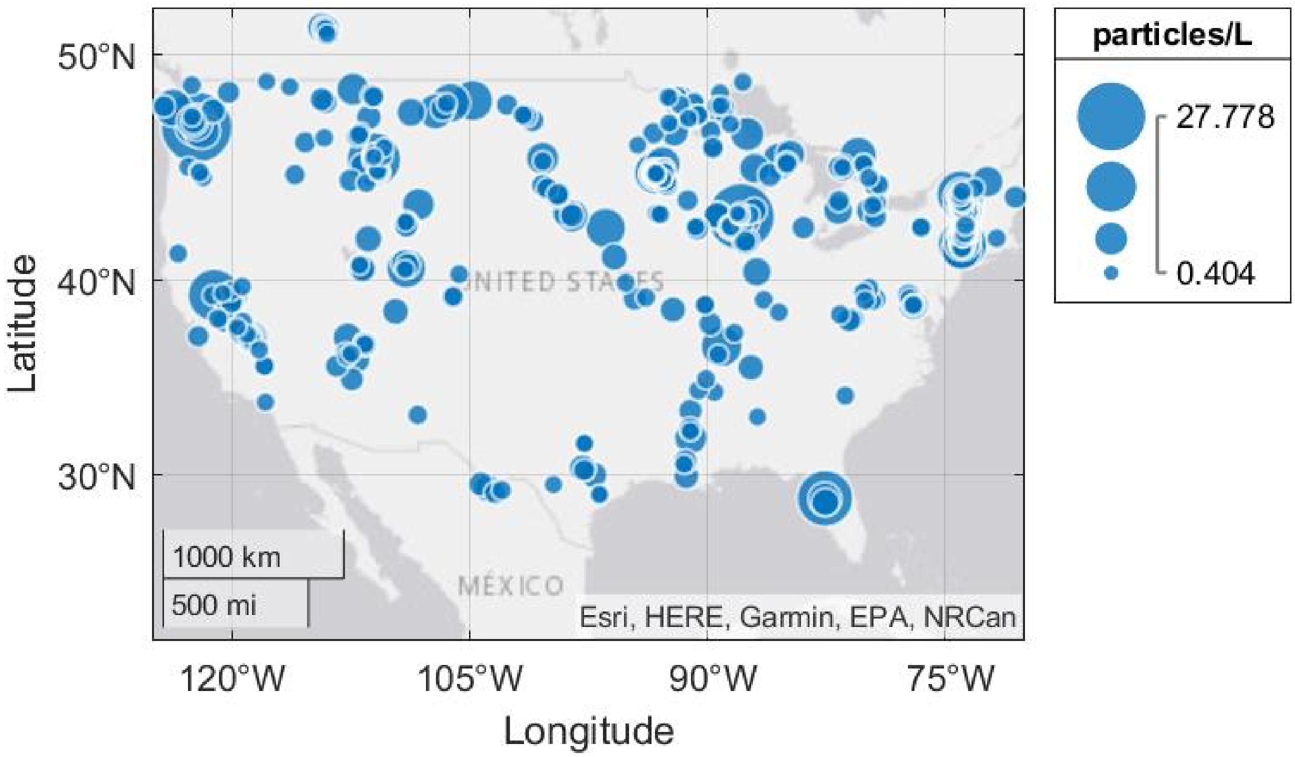

Figure 4. Particle concentration per liter. Data from citizen science jar data collection (https://www.adventurescientists.org/).

collected samples from the surface of the river. Only three studies reported the polymers detected. The Adventure Scientist data (Figure 4) and the peer reviewed scientific studies (Table 7) all indicate microplastic pollution is present in U.S. rivers, but the different sampling schemes, analysis methods, and quantification metrics make it difficult to estimate the total mass of microplastic transported to the oceans along U.S. rivers.

Table 7. U.S. Microplastics Sampling Studies

States	nets	jars	fish	depth	flow	WWTP	reference
CA	x			x	x		Moore et al. (2011)
MD	x				x		Yonkos et al. (2014)
IL	x					x	McCormick et al. (2014)
TX			x				Phillips and Bonner (2015)
MN, WI, IN, MI,OH, NY	x				x	x	Baldwin et al. (2016)
NY		x				x	Miller et al. (2017)
WY, ID, WA, OR	x	x					Kapp and Yeatman (2018)
MT		x					Barrows et al. (2018)
MI, WI		x	x				McNeish et al. (2018)
IL, MO				x			Martin et al. (2018)
WI	x			x			Lenaker et al. (2019)
CA		x					Wiggin and Holland (2019)
LA, IL, TN, AR, MO		x			x		Scircle et al. (2020)
OR	x						Valine et al. (2020)
IL, MO, OH, KY, TN, MS, LA		x			x		Cizdziel (2020)
NY, PA, NJ	x						Baldwin et al. (2021)
CA				x			Werbowski et al. (2021)

Figure 5. Map of major U.S. rivers and states where studies in Table 1 detected microplastics in gray.

Table 8. U.S. Microplastics Sampled Parameters

Study	Number	Mass	Shape	Size	Polymer
Moore et al. (2011)	x	x	x		
Yonkos et al. (2014)	x	x	x	x	
McCormick et al. (2014)	x		x		
Phillips and Bonner (2015)			x		
Baldwin et al. (2016)	x		x		
Miller et al. (2017)	x				
Kapp and Yeatman (2018)	x		x		
Barrows et al. (2018)	x			x	x
McNeish et al. (2018)	x		x		
Martin et al. (2018)	x		x		
Lenaker et al. (2019)	x		x		x
Wiggin and Holland (2019)	x		x		
Scircle et al. (2020)	x			x	
Valine et al. (2020)	x		x		
Cizdziel (2020)	x		x	x	
Baldwin et al. (2021)	x		x		
Werbowski et al. (2021)	x		x		x

5.0 WaterPACT Field Study

The WaterPACT field study will collect data to characterize the riverine plastic pollution and support model development for estimating U.S. riverine pollution. The study will measure the number of particles, mass, and polymer characteristics of plastic pollution, and river hydrodynamics in U.S. rivers. Five rivers have been selected for the initial sampling based on several criteria about their river discharge and the estimated level of plastic pollution. The rivers span the continental U.S., discharging into the Atlantic, Pacific, and Gulf of Mexico, and cover a range of catchment areas and flow periodicity conditions. Table 9 lists the five rivers, their hydroelectric energy capacity, average flow discharge, estimated plastic pollution from Schmidt et al. (2017), the percentage of the total U.S. plastic pollution, population in the watershed, terminus, and the rationale for each river choice. The Mississippi is the largest U.S. river in terms of water discharge, estimated plastic pollution, and population in the watershed. It accounts for an estimated 64% of the total plastic pollution released from U.S. rivers. It was chosen because of the magnitude of its estimated plastic pollution. The Delaware is a much smaller river and is only responsible for an estimated 1% of the total U.S. riverine plastic pollution, but it is one of the top ten most polluted U.S. rivers. It flows through the city of Philadelphia and is the subject of an in depth watershed modeling study that will produce valuable information about flow trajectories. The Sacramento has a higher water discharge than the Delaware but is estimated to emit five less tons of plastic per year due to the size of its watershed population. The Los Angeles is the smallest of the five rivers. It was chosen because of the strong seasonal periodicity of its flow, its high plastic pollution level (Moore et al. 2011), and its heavily engineered concrete structure. The Columbia was chosen because of its infrastructure and dams that may be currently intercepting plastic or could be used in the future as plastic collection sites.

Table 9. Five U.S. Rivers for WaterPACT Sampling (Plastics estimated by Schmidt et al. 2017)

	Mississippi	Delaware	Sacramento	Los Angeles	Columbia	Totals
Energy (GWhr/yr)	764	7	31	<1	52.7	805
Discharge (m^3/s)	13,300	340	797	6	3,592	18,035
Plastics (tons/yr)	699	15	10	8	13	745
% of Total	64	1	1	<1	1	68
Population (,000,000s)	76.7	7.5	6.0	5.0	7.3	102.5
Terminus	Gulf of Mexico	Atlantic	Pacific	Pacific	Pacific	
Rationale	Magnitude	Watershed Study	Planned Project	Periodicity	Infrastructure	

6.0 Conclusions

The rapid increase in plastic production and usage has led to riverine plastic pollution in the U.S. and worldwide. Both macroplastic and microplastic have been found in U.S. rivers in peer-reviewed and citizen science studies. The wide variety of sampling and analysis methods used in the studies hinders comparisons. Very few studies in U.S. rivers have measured the mass of the plastic pollution, which makes it difficult to estimate the mass released to the oceans. Only two studies reported the polymer characteristics of the pollution, which would be useful information for determining the source. Only four studies collected plastic pollution at several depths in the water column. Knowledge of the vertical distribution is needed for future collection plans and for accurate estimates of total riverine plastic pollution.

Global estimates of riverine plastic pollution have been made with models based on estimates of mismanaged plastic waste in river catchment areas. The models were also mostly calibrated and validated with data from other countries where the plastic pollution conditions may be different than in U.S. rivers. Standardized and quality controlled riverine plastic measurements are needed to characterize pollution levels, identify pollution sources, and support model development for estimating the total flux of plastics to the oceans from U.S. rivers. The Department of Energy’s WaterPACT project will collect standardized and quality controlled data in five U.S. rivers that span a range of sizes and environmental conditions. The data from those studies will show where the most pollution is and what type of plastic it is composed of. The data will also be used in future models to estimate the total U.S. flux of plastic to the oceans and aid future developers in site selection for collection.

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Appendix A – Sampling and Analysis Protocol Recommendations

Recommendations are listed here for sampling and analysis protocols that will produce high quality data. Data quality can be assessed with quality assessment criteria. Hermsen et al. (2018); Koelmans et al. (2019) describe criteria that are based on the sampling methods, sample size, sample processing and storage, laboratory preparation, clean air conditions, negative controls, positive controls, sample treatment, and polymer identification.

A.0.1 Fieldwork Contamination Mitigation

Sample contamination can come from many sources such as airborne particles, clothing fibers, or paint chips from the sampling vessel. It can be prevented by the avoidance of synthetic materials during sampling. Researchers can wear natural fiber clothing such as cotton or wool, no watches or bracelets, and sterile exam gloves (Miller et al. 2017; Lenaker et al. 2019). Ropes used to tie equipment to the sampling boat can be made of natural fibers and buckets, spoons, and tweezers can be made of metal (Kershaw et al. 2019). Glass sample jars, metal spoons, metal tweezers, and sieves can be pre-cleaned and stored in foil until they are used. Nets or sieves that will be re-used can be cleaned with DI water and covered with foil between uses (Sutton et al. 2019).

A.0.2 Fieldwork Negative Controls

Negative controls are field blanks that measure the amount of microplastics that might unintentionally contaminate field samples. Before a sampling trawl, a field blank can be collected by flushing 2 L of DI water through the net and into the cod end. The cod end can then be removed and the contents rinsed into a sampling jar identical to those used for sampling (Hung et al. 2021; Miller et al. 2021). During trawl sampling a pre-cleaned sample jar of DI water can be left open to the air to measure the airborne plastic particle load (Valine et al. 2020).

A.0.3 Fieldwork Environmental Conditions

The environmental conditions of the sampling site need to be carefully noted during sample collection (Kershaw et al. 2019). Wind may distribute plastics vertically in the upper water column, which would make a surface measurement underestimate the total concentration (Kukulka et al. 2012). Nearby upstream waste water treatment plants or combined sewer overflow outlets should be documented (Cowger et al. 2020). The depth and flow speed of the river should be recorded along with any known information about flood conditions. Flow speed is needed to calculate how much water flowed through a collection net during deployment and as a parameter for fate and transport models.

A.0.4 Laboratory Contamination Mitigation

Contamination can be avoided by careful control of the laboratory environment. Researchers should wear only natural fiber clothing, cotton lab coats, and sterile gloves. The laboratory work space should be frequently wiped down. All equipment should be washed thoroughly, oven-dried and covered when not in use. Glassware can also be heated in a burnout furnace before use to burn away any microscopic traces of plastic (Kershaw et al. 2019). All materials should be kept in clean air conditions such as a positive pressure laminar flow cabinet or clean room, but a laminar flow hood is preferable to a fume hood (Prata et al. 2021).

A.0.5 Laboratory Negative Controls

A negative control is used to measure how much contamination is being combined with the sample during the laboratory processing. It is a jar that is identical to a sample jar but filled with DI water. The DI water is processed with the same laboratory analysis procedures as the field collected jars.

A.0.6 Laboratory Positive Controls

A positive control is used to verify that the laboratory processing is successfully measuring the correct amount and types of microplastic. It is a jar that is seeded with a known number and composition of microplastics. The positive control jar is processed with the same laboratory analysis procedures as the field collected jars.

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