MONITORING PLASTICS IN RIVERS AND LAKES

Guidelines for the Harmonization of Methodologies





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Abbreviations and acronyms

µATR-FTIR	micro-Attenuated Total Refection-Fourier Transform Infrared (spectroscopy)
μFTIR	micro-Fourier Transform Infrared (spectroscopy)
ABS	Acrylonitrile butadiene styrene
AI	Artificial intelligence
ATR	Attenuated Total Reflection
AWI	Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research
BFR	Brominated flame retardants
BPA	Bisphenol A
CARS	Coherent Anti-Stokes Raman Scattering
DSC	Differential Scanning Calorimetry
EPS	Expanded polystyrene
EVA	Ethylene vinyl acetate
FPA FTIR	Focal Plane Array (FPA)-based Fourier Transform Infrared (FTIR) Spectroscopy
FTIR	Fourier Transform Infrared (spectroscopy)
FTIR-ATR	Fourier Transform Infrared-Attenuated Total Reflection (spectroscopy)
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectrometry
GPS	Global positioning system
H_2O_2	Hydrogen peroxide
HDI	Human Development Index
HDPE	High-density polyethylene
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ISO	International Organization for Standardization
КОН	Potassium hydroxide
LDPE	Low-density polyethylene
LOEC	Lowest observed effect concentration
MIRS	Mid-infrared spectroscopy
MPSS	Munich Plastic Sediment Separator
MS	Mass spectrometry
MSFD	Marine Strategy Framework Directive
NaOAc	Sodium acetate
NGO	Non-governmental organization
NIRS	Near-infrared spectroscopy
NOAA	United States National Oceanographic and Atmospheric Administration

NOEC	No observed effect concentration
OECD	Organisation for Economic Co-operation and Development
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PAN	Polyacrylonitrile
PBDE	Polybrominated diphenyl ether
PC	Polycarbonate
PCB	Polychlorinated biphenyl
PE	Polyethylene
PES	Polyester
PET	Polyethylene terephthalate
PMA	Polymethyl acrylate
PMMA	Polymethyl methacrylate
PO	Polyolefin
POM	Polyoxymethylene
POP	Persistent organic pollutant
PP	Polypropylene
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PUR	Polyurethane
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
PVOH	Polyvinyl alcohol
Pyr-GC-MS	Pyrolysis-Gas Chromatography-Mass Spectrometry
QR	Quick response code
RPM	Revolutions per minute
SDS	Sodium dodecyl sulphate
SI	International system of units
TED-GC-MS	Thermoextraction-Desorption-Gas Chromatography-Mass Spectrometry
TGA	Thermogravimetric analysis
Tris HCl	Tris (hydroxymethyl) aminomethane hydrochloride
UAV	Unmanned aerial vehicle
UV	Ultraviolet
WWTP	Wastewater treatment plant
ZnCl ₂	Zinc chloride



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Executive summary

More than 8,000 million metric tons of plastics have been made since the beginning of large-scale production in the 1950s. As a consequence of the omnipresence of plastic products, combined with insufficient waste management and handling practices, plastic debris has entered the environment and is present in practically all ecosystems. It has been detected even in remote locations such as mountain lakes and polar sea ice. The most prominent example of widespread plastic contamination of the environment is provided by the world's oceans. Research, societal awareness and actions have long focused on marine plastics.

Based on our current knowledge, the vast majority of marine plastics originate from land-based sources. Hence, the focus of research as well as actions has been expanded to freshwater and terrestrial environments. Rivers have been identified as major pathways for connecting land-sourced plastics with marine environments. Moreover, rivers and other freshwater bodies such as lakes and reservoirs are themselves threatened by plastics contamination in the same way as the marine environment.

Despite its relevance and a growing body of data and knowledge on freshwater plastics, the current understanding of transport processes, loads and impacts is limited, mainly because data are lacking. Most published data on freshwater plastics stem from individual projects which apply different sampling and analysis techniques. This lack of harmonization hampers the comparison and ultimately the synthesis of data.

This report builds on the large body of knowledge and experience gained from marine plastic monitoring. For example, methods of sample processing and instrumental analytics for particle characterization are mostly the same for freshwater and marine systems. Many other aspects require the adaptation of sampling techniques and the design of monitoring programmes according to specific freshwater conditions, such as the typically high content of coarse natural particulate material or the high variability of plastic concentrations in rivers driven by river flow variations.

The report provides methodological guidelines to support monitoring and assessment programmes for plastics in freshwater. It contains the most current procedures for monitoring and analysing plastic content in rivers, lakes, reservoirs and water/wastewater treatment plants.

Recommendations have been developed reflecting stakeholder inputs from a series of workshops, which revealed that developing and developed countries face similar challenges with the implementation of monitoring programmes for plastics in freshwater environments. However, the type and intensity of hurdles to be overcome in setting up monitoring programmes may differ in different countries. The guidelines are designed to assist in the timely development and implementation of freshwater plastic monitoring programmes, tailored to the different starting conditions in the different countries.

Such monitoring programmes are needed in order to prioritize land-based sources, which is a prerequisite for achieving United Nations Sustainable Development Goal 14, Target 14.1 to "prevent and significantly reduce marine pollution of all kinds, particularly from land-based activities, including marine debris and nutrient pollution" by 2025 (https://sdgs.un.org/goals).

1. Introduction

1.1 Purpose

The purpose of this report is to provide guidelines for the assessment of plastic contamination, from macro- to microplastics, in freshwater environments. It provides the most current procedures for monitoring and analysing plastic content in rivers, lakes, reservoirs and water/wastewater treatment plants. In addition, recommendations are made based on a series of workshops for water managers and other stakeholders. A project group, consisting of seven experts in different fields, was created with the direct goal of developing guidelines for plastic monitoring in freshwater. The project group was co-led and funded by the United Nations Environment Programme (UNEP).

This report is intended to reach local, national, intergovernmental and international organizations which are responsible for or have an interest in understanding and/or managing plastic waste within any of the varying freshwater environments. There is also an intention that, by providing a guidance document for monitoring and assessment methods, these procedures will be widely utilized and become a standard protocol. Such harmonization would allow monitoring programmes and subsequent results to be easily compared, leading to a growing database of knowledge and understanding of plastic waste in freshwater. Proper actions, mandates and laws could then be developed to assist national authorities and regional groups.

1.2 Plastic contamination in freshwater environments

One reason these guidelines are important is that most plastic debris research is currently focused on the oceans (Blettler *et al.* 2018). Consequently, the available sampling techniques and protocols have been developed for marine systems. They can possibly be applied in freshwater environments but may need adaptation to freshwater conditions including the fast-moving waters of rivers and streams, a higher sediment content, different biota and a higher incidence of micro- and nanoplastics, to name a few. The differences between freshwater and marine systems are mostly limited to sampling techniques. Many freshwater-specific factors affect sampling procedures more than the actual (laboratory) analysis, which tends to be similar to the analysis of seawater samples.

1.2.1 From oceans to land

To address the widespread and increasing problem of plastic contamination, most attention and research thus far have been directed to marine ecosystems. However, when investigating the origin of plastic debris in the oceans it is widely assumed that 80 per cent of this debris comes from land-based sources although this is currently poorly supported by data (Andrady 2011, Jambeck *et al.* 2015). The amount of land-based plastic entering the oceans each year has been estimated to be ~ 9 million metric tons (Jambeck *et al.* 2015), with one of the major pathways being riverine export at about 2 million metric tons per year (Lebreton *et al.* 2017; Schmidt, Krauth and Wagner 2017). This kind of estimate is subject to large uncertainties since observation networks for monitoring plastic in freshwaters are small and sporadic, with heterogeneous methodologies. Yet current knowledge about plastic contamination in freshwater suggests that this contamination is as widespread as in the marine environment.

1.2.2 Macro- and microplastics

Microplastics, specifically defined in Chapter 3, have gained considerable attention since the pioneering study by Thompson *et al.* (2004). In freshwater, microplastics are typically far more abundant (particle count per volume) than larger debris. In terms of mass concentrations (mass per volume), data from river studies suggest that microplastics and larger items broadly contribute equally to the total mass concentration (Schmidt, Krauth and Wagner 2017). Thus, monitoring programmes should ideally capture the entire size spectrum of plastic particles.

1.2.3 Reservoirs and lakes

Damming of rivers may significantly alter downstream transport of plastic debris (Lebreton *et al.* 2017). This is particularly significant for large rivers (average discharge above 1,000 m³ s⁻¹), of which 46.7 per cent are affected by damming. In addition to the role of reservoirs in intercepting downstream plastic transport, those used for fisheries/aquaculture or drinking water abstraction are susceptible to the impacts of plastic contamination.

1.2.4 Wastewater treatment plants

Wastewater treatment plant (WWTP) effluents are considered a steady pathway for microplastic particles in rivers (Kay *et al.* 2018), notwithstanding that a considerable fraction of the plastic in raw sewage is typically retained during the treatment process. Reported removal efficiencies range between 72 per cent (Leslie *et al.* 2017) and 99 per cent (Talvitie *et al.* 2017). The majority of observed removal rates are above 95 per cent (Murphy *et al.* 2016; Lares *et al.* 2018; Simon *et al.* 2018). If sewage sludge is later applied as fertilizer, plastic particles retained during the sewage treatment process can be re-released. Raw sewage which enters river networks through combined sewer overflows during intense rain or through sewers generally not connected to a WWTP contains plastic debris which is not restricted to microplastics.

1.2.5 Drinking water

Microplastics have been detected in tap water and bottled water. However, lack of standardization of microplastics sampling and analysis results in large differences among different studies (Koelmans *et al.* 2019). For a risk assessment, improved reproducibility and comparability of results are needed.

1.2.6 Freshwater plastic monitoring – learning from marine plastic monitoring and new challenges

Monitoring methods for freshwater can benefit from the large body of knowledge and experience gained from marine plastic monitoring. For example, methods of sample processing and instrumental analytics for physical and chemical particle characterization are the same for freshwater and marine systems. However, other aspects require adaptation to specific freshwater conditions. One example is the typically higher content of coarse natural particulate material such as wood, leaves or seeds, and fine particles such as microalgae or clay minerals compared to the marine environment. Thus, sample preparation and analysis must be designed to handle the large non-plastic particle fraction in freshwater samples.

In the open oceans the challenge for representative monitoring lies mainly in the large area to be monitored. In rivers, concentrations of particulate material often depend on discharges. There is a tendency for concentrations to increase due to first flush effects and the addition and mobilization of more material as discharge increases. Generally, sedimentation and resuspension of particles are important processes in freshwater bodies (Kooi *et al.* 2018). Monitoring programmes must be designed to adequately capture variations in plastic concentrations in freshwater systems. Moreover, monitoring must properly support the identification and quantification of point and diffuse sources of plastics in freshwater in order to prioritize intervention measures.

1.3 Organisation and use of the report

This report provides a series of guidelines, methods and recommendations to support the development, design and implementation of monitoring and assessment programmes for freshwater plastic contamination. The report is organized in 12 chapters. Chapter 1 covers background information as well as the need and the relevance of such a guideline. Chapter 2 discusses the scope of this document. Definitions and terminology in the context of plastic in the environment, are presented in Chapter 3. The general guidelines on how to develop a freshwater plastic monitoring programme are provided in Chapter 4. That Chapter also provides a scoring scheme of the sampling and observation methods covering the cost of the equipment for observation, sampling and analysis, the infrastructure to run and maintain the equipment, the efforts for installing the equipment, and requirements in terms of skilled female and male personnel which guides the reader towards the appropriate selection of methods based on available resources. Technical information about sampling and analysis methods is provided in Chapters 5, 6 and 7. The methods in Chapter 5 include sampling in a stricter sense (where material is taken for further analysis) and observation methods which rely on visual counting of plastic particles or items. Chapter 6 focuses on preparatory issues after sampling, and Chapter 7 gives an overview of state-of-the-art analysis methods. Chapters 4-7 are recommended for readers who wish to technically implement a monitoring programme and decide on the optimal sampling and analysis methods. These chapters are organised to start with the simple and inexpensive methods.

Chapters 8 and 9 review some of the complexities of freshwater plastic contamination (pathways in Chapter 8, and interactions with other forms of pollution in Chapter 9). In Chapter 10 stakeholder positions are discussed and the results of a stakeholder survey and a series of online workshops are presented. This chapter is recommended for readers interested in the social dimensions of freshwater plastic contamination. Chapters 11 and 12 provide a summary of recommendations from multiple perspectives on monitoring (and acting against) plastic contamination in freshwater environments. Readers who are mainly interested in regulation or possible measures against plastic contamination, as well as obstacles to their implementation, may switch to Chapters 10-12 after familiarizing themselves with the terminology.

2. Objectives and scope of the guidelines

The report details the state-of-the-art of monitoring plastic debris of all sizes in freshwater, ranging from whole items to micro-sized fibres and fragments. The information provided is built on existing work and takes into account the most up-to-date studies. For the most part, sampling techniques and monitoring concepts for freshwater environments are not fundamentally different from those applied in marine settings. The report therefore builds on the *Guidelines for the Monitoring and Assessment of Plastic Debris in Marine Environments* by the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) (2019). To avoid redundancies, descriptions of overlapping aspects are brief. At the same time, similarities and differences in plastic inputs, distribution and effects between the marine and freshwater environment are discussed.

The guidelines are intended to be a cornerstone of work towards harmonized methodologies for monitoring and reporting plastic debris in freshwater systems. They will aid the development and implementation of monitoring programmes in rivers, lakes and reservoirs, as well as for wastewater treatment plants. Such monitoring programmes are needed to prioritize land-based sources, which is a prerequisite for achieving United Nations Sustainable Development Goal 14 Target 14.1: "by 2025, prevent and significantly reduce marine pollution of all kinds, particularly from land-based activities, including marine debris and nutrient pollution". A series of recommendations are also made on improved reporting, stakeholder involvement, and expanding data availability.

3. Definitions and terminology

In this report the term "plastic debris" applies to all sizes of plastic particles. Although science and policy use similar terminology, there is no agreed or official text setting out exactly how to categorize plastic debris. Therefore, the terminology used in this report follows that of GESAMP (2019).

Plastic debris

Plastics are synthetic organic polymers with thermoplastic or thermoset properties (synthesized from hydrocarbon or biomass raw materials), elastomers (e.g. butyl rubber), material fibres, monofilament lines, coatings and ropes. Many plastics are produced as a mixture of different polymers and various plasticizers, colorants, stabilizers and other additives. About 80 per cent of plastics production in Europe comprises polyethylene (PE) (both high-density [HDPE] and low density [LDPE]), polypropylene (PP), polyvinyl chloride (PVC), polyurethane (PUR), polystyrene (PS), and polyethylene terephthalate (PET). Packaging represents the dominant market sector for plastics (39.9 per cent), followed by building and construction (19.8 per cent) and automotive (9.9 per cent) (PlasticsEurope 2019).

Size categories

The sizes and shapes of plastic particles are the main properties which should be captured in sampling and analysis procedures. At the same time, sampling procedures must be appropriate for the targeted particle size. Particles less than 5 mm in size are commonly referred to as microplastics, whereas the terms meso-, macro-, and megaplastics are used to describe larger particles (Table 3.1). The sub-categories defining larger plastic particles are not often used in the literature. As a consequence, these guidelines only refer to the categories macro-, micro- and nanoplastics. A recent International Organization for Standardization (ISO) report defines large microplastics as particles 1-5 millimetres (mm) in size. Nanoplastics are generally defined as particles smaller than or equal to 100 nanometres (nm) (Besseling *et al.* 2019). A size threshold of 500 micrometres (µm) is often applied to differentiate between large and small microplastics (e.g. Mintenig *et al.* 2017; Haave *et al.* 2019). When mass-based analysis of microplastics is attempted, it is reasonable to divide the sample into even more size fractions (cut-off at 1,000, 500, 100, 50, 10 and 5 µm; Braun *et al.* 2018). This report provides a rough estimate of average particle mass in each size class.

Morphology categories

The shapes of plastic debris are important indicators of their origin and their state of fragmentation or disintegration. Shape definitions are mainly important in the case of particles less than 1 centimetre (cm) in size. Since larger particles often occur as whole items or larger fragments, it may be possible to categorize them according to their origin (e.g. bottles, bags or straws). For shape categorization of plastic debris in freshwater, the United Nations Environment Programme (UNEP) guidelines for marine litter can be used (Annex III in GESAMP 2019).

As with size categories, there is currently no standardized scheme for different shapes of plastic debris. However, the five shape categories used for marine litter, according to GESAMP 2019, can be readily applied to freshwater environments. These microplastic morphologies are identified as 1) fragments, 2) fibres/filaments, 3) beads/ spheres, 4) films/sheets, and 5) pellets (Table 3.1).

Microplastic characteristics	Classes	Description
	mega	>1m
-	macro	25 mm-1 m
Size	meso	5 mm-25 mm
	micro	< 5 mm
	fragments	irregularly shaped particles, crystals, fluff, powder, granules, shavings
	fibres	filaments, microfibres, strands, threads
Morphology	beads/spheres	grains, spherical microbeads, microspheres
	films/sheets	polystyrene, expanded polystyrene
	pellets	resin pellets, nurdles, pre-production pellets, nibs

Table 3.1. Commonly used characteristics for categorizing plastic debris (adapted from Lusher et al. 2017)

Colour

Similarly to shape, the colour of particles can provide helpful information about their origin. In a biological context it can also provide information about whether organisms have a feeding preference based on colour. Overall, however, colour is not regarded as a crucial parameter for the categorization of plastic debris (GESAMP 2019; Hartmann *et al.* 2019). If colour is being reported, categories should be based on simple classification schemes such as the 13 categories provided by the ISCC-NBS (Inter-Society Color Council and National Bureau of Standards) system (Table 3.2) to avoid subjective bias. This system allows further allocation to finer sub-categories. Alternatively, the slightly more ambiguous EMODNet (European Marine Observation and Data Network) classification can be applied, which only uses six colour categories (black/grey, blue/green, brown/tan, white/cream, yellow, orange/pink/red) but systematically distinguishes transparent and opaque particles (Galgani *et al.* 2017).

Colour	Abbreviation	Example	Colour	Abbreviation	Example
Pink	Pk		Green	G	
Red	R		Blue	В	
Orange	0		Purple	Р	
Brown	Br		White	Wh	
Yellow	Υ		Gray	Gy	
Olive	OI		Black	Bk	
Yellow green	YG				

Table 3.2. ISCC-NBS colour classification system

Monitoring

Monitoring indicates the intention to measure the current status of an environment or to detect trends in environmental parameters with respect to space or time. These measurements should be performed systematically, using harmonized sampling methods and a consistent data and metadata management procedure.

4. Designing monitoring programmes for freshwater environments

4.1 Transferring from marine systems – similarities and differences between marine and freshwater systems

Research, as well as public interest, have long focused on plastic contamination in oceans and coastal areas. However, there is increasing awareness that a considerable amount of marine plastic contamination originates from land-based sources. Rivers, for example, have been shown to deliver large amounts of plastic debris into the marine environment (Lebreton *et al.* 2017). It can therefore be asserted that freshwater systems are also impacted by plastic contamination, with reservoirs intended for the production of drinking water being particularly susceptible to elevated plastic concentrations.

Plastic debris monitoring in freshwater systems can rely on a large body of expertise gained in marine monitoring programmes. There is already a wealth of experience with sampling techniques, analytical methods, and the design of monitoring programmes in the marine environment. Freshwater plastic debris monitoring should build on this experience and adapt techniques, concepts and protocols to meet specific needs. In many cases, methods and protocols for the characterization of plastic debris can be directly transferred from marine to freshwater applications. This is relevant for classification schemes (size and morphology), particle counting methods, and the chemical characterization of contaminant particles by polymer type. At the beginning of an assessment, it should be defined whether the primary focus is quantification of plastic hotspots, sources, sinks and flows in a catchment, or the assessment of possible risks and effects in freshwater ecological communities (Figure 4.1). It is highly recommended to measure the dimensions of particles when

Figure 4.1. Types of plastic-related assessments in freshwater environments. *Light grey elements are considered less important for the specific purpose. "Macroplastic" includes mega- and mesoplastic (see table 3.1). "Shoreline" includes riverbanks as well as lake shorelines as there is no uniformly accepted term. NOEC: no observed effect concentration; LOEC: lowest observed effect concentration. Graph: Katrin Wendt-Potthoff and Tim van Emmerik*



microscope-based methods are used, so that a rough estimate of polymer mass can be derived in addition to plastic particle concentration.

Monitoring of the marine environment includes shorelines, the water surface and column, and seafloor sediments. Each of these compartments can be sampled using a specific method. Freshwater environments are more diverse, and sampling strategies have to be adapted to conditions at the specific site. A large river, for instance, requires a different sampling design than a small stream. While sampling of large rivers can be conducted from a vessel and may require several monitoring points along the cross-section, a small stream can be sampled from the bank or by wading. A major step prior to laboratory analysis of microplastic particles is sample preparation, mostly to remove organic material. Typically, in freshwater environments such as rivers and lakes the content of particulate organic material (e.g. leaves, branches) is higher than in the marine environment. In rivers and lakes this material is freshly received from the banks while in the marine environment it is typically already broken down. A general scheme of how to develop a monitoring programme, from identifying the objectives aligned with available resources to its implementation, is shown in Figure 4.2.

4.2 Developing a monitoring programme – how to start?

The majority of the world's rivers remain ungauged with respect to plastic contamination. To date, no regularly operating plastic monitoring programmes exist. To further complicate matters, there is no general "off the shelf" solution for establishing a monitoring programme. Developing and implementing an environmental monitoring programme generally comprises three phases: a development phase, a design phase and an implementation phase (Fig. 4.2). These phases are the same for plastics as for any other substance of concern. The development phase identifies the objectives or research questions and aligns these with the available resources. Getting the monitoring started has the highest priority. For example, in rivers floating, macroplastics can be observed from bridges and manually counted, involving citizen scientists without the need for extensive preparation, a laboratory or costly sampling equipment. The objectives of a project can be many and varied, so a "one size fits all" recommendation does not exist. Figure 4.2 shows some typical examples, although there are many more.

The second phase - the design phase – specifies the compartments, the sampling locations and frequencies, as well as the sampling and analysis techniques. However, for the second phase there is no blueprint that can be easily applied at every location. A few, key guiding principles should generally be considered:

- If possible, plastic monitoring should be integrated into existing monitoring programmes. This allows
 using already available metadata (e.g. river discharge, typical fish populations) and an efficient use of
 resources (travel cost). If available, existing regional plastic assessments (e.g. see https://wedocs.unep.org/
 handle/20.500.11822/33519) should also be considered for maximum consistency of information.
- 2) Plastic concentrations and plastic loads can be highly variable over time. This time variation can provide useful information on the mechanisms of plastic transport. For instance, in rivers, increasing concentrations with increasing river discharge can be an indication of remobilization of material already present in the river channel. Thus, it is generally recommended to focus on relatively frequent and long-term monitoring at fewer locations rather than measuring sporadically at many locations.
- 3) Generally, simpler and cost-effective methods should be preferred in order to be able to capture more data rather than fewer samples for advanced and costly analysis. In general, the effort required to monitor plastics increases with decreasing particle size. Thus, if appropriate, a monitoring programme should be designed starting from macroplastics (Figure 4.3).

Figure 4.2. Steps and considerations for developing and implementing a plastics monitoring programme

Develop the monitoring programme							
Identify objectives	Available resources						
 Typical examples: Quantify export from river catchments Quantify abundance of plastic in river systems, lakes, or biota Abundance of specific items for policy-making Quantify removal efficiencies in wastewater treatment facilities Exposure of aquatic life to microplastic 	 Gender-balanced pool of skilled personnel for sampling (simple) and lab analysis (complex) Sampling equipment Laboratory facilities IT infrastructure for automated monitoring 						
Design the monitoring programme	Design the monitoring programme						
Compartments and location	Temporal resolutions						
 Compartments and location Compartments: Water surface, water column, sediments, shorelines, biota 	 Temporal resolutions Frequency should be adapted to the variability of the system Regular monitoring interval 						

Particle size

- Adjust the size classes considered to the objectives and the available resources for sampling and analysis
- Smaller particle sizes are typically associated with higher sampling and analysis efforts

Analysis methods

- Select observation and sampling methods according to the compartments and size classes
- Select analysis methods according to the monitoring objective and resources, e.g., for particle counts it may be necessary to identify the polymer type

Implement the monitoring programme

Establish, evaluate, refine

- Apply established sampling and analysis protocols
- Establish locations and a workflow of sampling and analysis
- Conduct the monitoring as planned for an initial period (e.g. one year)
- · Collect the required meta data
- Evaluate the data, refine design of the monitoring if needed

Analysis methods

- Data sharing will add value to the data, making data available to the public is highly recommended
- Comply with metadata standards

Figure 4.3. Visualization of the hierarchical design of monitoring programmes, starting from simpler methods and large particles (macroplastic) towards smaller particles and a more advanced analysis



The third phase is implementation. It is recommended to start with a pilot phase with a limited number of locations to test the workflows and the selected techniques. A pilot phase will help to evaluate whether the monitoring design is appropriate. Almost as important (see Section 11.5.2 Metadata) is the collection of metadata which make it possible to put the plastic data in context. Note that a final monitoring strategy can comprise several components with varying spatiotemporal scales, for example, (1) long-term monitoring focused on seasonal dynamics, and (2) targeted intensive monitoring efforts of limited duration focused on diurnal dynamics or quantifying the response to hydrological events.

4.3 Choosing the optimal methods

The choice of sampling and observation methods should optimally fit the objectives of the monitoring programme and the available resources. Table 4.1 provides a scoring scheme of the sampling and observation methods covered in this report in terms of the cost of the equipment for observation, sampling and analysis, the infrastructure to run and maintain the equipment (e.g. instrumental analytical methods require adequate laboratories facilities to be operated), the efforts required for installing the equipment in the field or the lab and the requirements in terms of skilled female and male personnel who conduct the monitoring and analysis. We recommend starting monitoring by selecting methods with low scores, with a monitoring programme that will keep the start-up costs low.

Table 4.1. Scoring scheme for the sampling and observation methods covered in this report

Cost of the equipment for observation, sampling and analysis, the infrastructure to run and maintain the equipment, the efforts required for installing the equipment, and requirements in terms of skilled female and male personnel

		upment cost	astructure	ff training level	tallation effort	1Low1.5Low-Medium2Medium2.5Medium - High	
		Equ	Infr	Sta	Inst	B 3 High	
Micro							
Sampling							
River Water Surface	Drift net	1.5	2	2	2.5	Driftnet installation in larger rivers (e.g.	
	Pump and Filtration	2	2	2.5	2.5	may require more effort and equipment than sampling smaller, wadable rivers	
River Water Column	Drift net	1.5	2	2	2.5	Basically the same equipment as for water surface sampling	
	Pump and Filtration	2	2	2.5	2.5		
River sediment	Grab sampling	1.5	1	1	1		
Shorelines (Lake + River)	Grab sampling	1	1	1	1		
Lake surface	Trawl net and vessel	2	2.5	2.5	2	Additional effort if the same vessel is used at various lakes, must be transported	
	Pump and Filtration mounted on vessel	3	2.5	2.5	2		
Lake water column	Trawl net and vessel	2	2	2	2.5	Depending on the depth of the lake	
	Pump and Filtration mounted on vessel	3	2.5	2.5	2.5	additional equipment might be needed to lower the trawl or the pumping hose to the required depths	
Biota	Collect from drift nets, trawls, catching with nets	1.5	2	2.5	2.5	Requires skilled staff	
	Electro fishing	1.5	2	2.5	2.5	Additional equipment needed, requires skilled staff	
Analysis							
Microscopy		2.5	2	2	2.5		
Microscopy and spec	troscopy (FTIR, Raman)	3	3	3	3	Requires high-end analytical labs	
Alternative instrumen (e.g. Pyro-GC/MS)	tal analytical methods	3	3	3	3		
	Meso						
Sampling							
River Water Surface	Drift net	1.5	2	2	2.5		
	Pump and Filtration	2	2	2.5	2.5		
River Water Column	Drift net	1.5	2	2	2.5		
	Pump and Filtration	2	2	2.5	2.5		
River sediment	Grab sampling	1.5	1	1	1		
Shorelines (Lake + River)	Grab sampling	1	1	1	1		

		Equipment cost	Infrastructure	Staff training level	Installation effort	1Low1.5Low-Medium2Medium2.5Medium - High3High
Lake surface	Trawl net and vessel	2	2.5	2.5	2	
	Pump and Filtration mounted on vessel	3	2.5	2.5	2	
Lake water column	Trawl net and vessel	2	2	2	2.5	
	Pump and Filtration mounted on vessel	3	2.5	2.5	2.5	
Biota	Collect or Catching with nets/electro-fishing	1.5	2	2.5	2.5	Mesoplastics will be ingested only by larger organisms where the particles are in the size range of their typical food food. Requires skilled staff.
Analysis						
Visual observation		1	1	2	1	
Spectroscopy (FTIR, F	Raman)	3	3	3	3	For polymer identification
	Macro					
Sampling						
River Water Surface	Visual counting	1	1	1.5	1	
	Camera automated camera counting	2.5	2.5	2.5	2	Bridge mounted or via UAV
	Drift net	1.5	2	2	2.5	
River Water Column	Drift net	1.5	2	2	2.5	
River sediment	Grab sampling	1.5	1	1	1	
Shorelines (Lake + River)	Grab sampling	1	1	1	1	
Lake surface	Trawl net and vessel	2	2.5	2.5	2	
Lake water column	Trawl net and vessel	2	2.5	2.5	2	
Biota	Collect or catch with nets/electro-fishing					Only very large organisms will contain macroplatics, it will be challenging to sample these
Analysis						
Visual observation		1	1	2	1	
Spectroscopy (FTIR, Raman)			3	3	3	For polymer identification

4.4 Precautions against sample contamination

When sampling or processing samples of microplastics, precautions should be taken against sample contamination. Microplastics have been detected almost everywhere. They can be transported through the air (Bergmann *et al.* 2019) or released from clothing during normal wear, among other sources. The smaller the plastic particle size one wishes to detect, the more critical are the procedures to avoid (or at least trace) contamination.

Initially, anyone involved in sampling should take these protective measures:

- U Wear clothing made of natural fibres during sampling where possible;
- □ Use cotton lab coats during laboratory work;
- □ Use nitrile gloves and change them frequently.

Furthermore, the materials and reagents for microplastic research should be chosen and treated carefully:

- Avoid plastic equipment during sample handling and switch to metals (stainless steel, aluminium) or glassware instead. If this is not possible, use polymers that are not widely found in the environment, e.g. polytetrafluoroethylene (PTFE) or fluorinated ethylene propylene (FEP). (Cost should be considered, as rarer plastics tend be more expensive). The use of non-plastic containers also prevents chemical contamination by plastic-associated substances (see Chapter 9). If plastic containers have to be used, a piece of aluminium foil may be placed between the vessel and the lid to avoid abrasion. Keep samples of the plastic materials you use in order to be able to identify their spectra later.
- □ Clean vials or equipment with filtered water or ethanol and adapt the filter type to the desired microplastics detection level (e.g. use at least 0.45 µm filters to detect particles down to a size of 1 µm). Reagents used to treat samples also have to be filtered.
- Keep sampling devices, sample containers and reagent vessels closed as much as possible. If possible, handle samples and reagents on a clean bench. The installation of air cleaners, such as portable dust boxes, is also advisable.

Current research shows that completely preventing any contamination is practically impossible (e.g. Koelmans *et al.* 2019). Contamination by small fibres is common. If contamination is never detected, the sampling procedure is likely not working properly. It is therefore recommended to run procedural blanks to trace how much and where contamination occurs. This means the whole sampling and extraction procedure is imitated without a real sample. In the case of large water samples, filtered drinking water or ultrapure water can be used as a surrogate. In the field, glass fibre filters can be attached to the sampling equipment or containers and can be analysed later for airborne particles.

During sample handling in the lab, empty containers can be opened and treated with reagents in the same manner as those containing samples. In the end, whether the contaminating particles can be distinguished from the real sample particles by microscopy and/or spectroscopic methods has to be evaluated. If they cannot, their concentrations have to be subtracted from the particle concentrations in the samples. If they can be distinguished, a more specific procedure may be applied. In any case, concentrations and types of contamination must be documented and possible sources should be identified.

5. Sampling and observation

This chapter provides guidance on sampling the three key matrices of freshwater environments: water, sediments and biota. Water consists of the water surface and the water column of lakes and rivers. The discussion of sediments focuses on lake and riverbed sediments. This includes sampling from the shorelines of lakes and rivers. Because they are easily accessible, lake and river shorelines often benefit from clean-up actions. Relevant data can be used for monitoring and linked to citizen science projects. The biota to be sampled comprise invertebrates, fish and birds. As freshwater is a major drinking water resource, the report includes sampling of drinking water and wastewater. Guidance is provided for sampling wastewater along the treatment process from raw sewage sludge to the final effluent from wastewater treatment plants.

Depending on the sampled water body and the intended spectrum of particle sizes, the volume of water necessary to obtain a representative sample will vary. The general solids content is crucial. Table 5.1 suggests appropriate sample sizes for the quantification of small microplastics (1 to approximately 50 µm).

Solids content	Very high	High	Low	Very low
Filterable substances including plankton (mg/L)	> 500	100-500	1-100	< 1
Examples	wastewater treatment plant intake	street drainage	wastewater treatment plant effluent, surface waters	groundwater, mineral water, drinking water
Recommended sample volume for particles 1-50 µm	5 mL	500 mL	1L	500 L

Table 5.1. Recommended volumes for water samples of different solids content (adapted from Braun et al. 2018)

The analysis of larger particles, or mass-based analysis of plastic polymers, generally require larger sample volumes. As an example, 500-1,000 litres (L) should be filtered for mass-based analysis of plastic particles 10-100 μ m in size from freshwater reservoirs.

5.1 Sampling of rivers

5.1.1 Water surface and water column

5.1.1.1 Macroplastics

Various methods have been developed in recent years to monitor macroplastics on the surface of the water or in the water column. Three main categories of monitoring strategies can be identified: sampling methods (Hohenblum *et al*, 2015; van Emmerik *et al*. 2018), tracking methods (Tramoy *et al*. 2020), and visual observation methods (González-Fernández and Hanke, 2017; van Emmerik *et al*. 2018). Here several examples are provided for each category, and how their application may be optimized is discussed.

5.1.1.2 Sampling methods

Macroplastic debris sampling is a straightforward and intuitive monitoring strategy. Often nets are used to collect riverine litter, which is subsequently analysed in the field or the lab. To date, most assessments have focused on sampling floating plastics or plastics in the upper 1.5 m of the water column. Sampling can have two main goals: debris is collected to analyse composition, polymer type, item type, size and mass distribution; or sampling

is carried out to determine the plastic concentration at given points in space and time. Plastic concentration C_n (kg/m³) can be calculated using:

$$C_P = \frac{M_P}{V}$$

$V = Q \cdot t = A_n \cdot u \cdot t$

with collected plastic mass M_p (kg), sampled water volume V (m³), river discharge at sampling net Q (m³/s), sampling net opening A_n (m²), flow velocity u (m/s) and sampling duration t (s). The variables that should be considered in designing a sampling-based monitoring strategy for surface and water column sampling are discussed below.

Deployment method

Sampling nets can be deployed using various methods, including boats (Sadri and Thompson 2014), lifting cranes on bridges (Moore, Lattin and Zellers 2011; Hohenblum et al. 2015), direct deployment from riverbanks (Moore, Lattin and Zellers 2011) and direct deployment from bridges (Rech et al. 2014; van Emmerik et al. 2018; van Emmerik et al. 2019c). In smaller, shallow rivers and streams nets can be deployed manually by wading (Baldwin et al. 2016). Direct deployment from riverbanks and bridges is done using relatively small and lightweight nets that can be handled by one or two persons. The advantages include rapid and flexible deployment, as no additional equipment or machinery is required. However, these deployment methods strongly depend on the availability of safe deployment sites on bridges or accessible riverbanks (Rech et al. 2015). The sampling volume and mass are also limited by the maximum load those handling the nets can handle, which is generally in the order of several kilograms for flow velocities around 1 m per second. Deployment from riverbanks has the additional disadvantage that only a limited part of the crosssection can be sampled. As the horizontal distribution of plastic transport can vary considerably (e.g. van Emmerik et al. 2018), this may result in unrepresentative samples. Net sampling from bridges has been done using nets with multiple layers, also in order to sample at deeper layers of the water column (van Emmerik et al. 2019a; van Emmerik et al. 2019b). However, the forces on the sampling net can become difficult to manage in the case of increased flow velocities, which may lead to poor execution of sampling protocols. Manual deployment of nets by wading into a river allows exact positioning with respect to depth and along the cross-section. In wadable rivers, nets can easily be deployed and remain unsupervised for some time if they are fixed at the riverbed by an anchor (Figure 5.1).

Figure 5.1. Examples of the use of sampling nets in a wadable river (*left, Baldwin et al. 2016*) and from the bank and a crane (right, Moore, Lattin and Zellers 2011)



A way to overcome this problem is to deploy sampling nets using boats or cranes. Assessments of plastic transport in rivers in Los Angeles (United States) (Moore, Lattin and Zellers 2011) and in the Danube (Austria) (Hohenblum *et al.* 2015) used cranes to deploy sampling nets from bridges (Figure 5.2). With such equipment the maximum load imposed by collected debris mass and flow velocity can be considerably heavier than in the case of direct deployment. In both these examples that was the case Moore, Lattin and Zellers (2011) assessed the increase in plastic transport in response to torrential rain events in the Los Angeles basin. Hohenblum *et al.* (2015) deployed a three-layered netting system to collect plastic debris at the surface, in the middle of the water column, and right above the riverbed. For such assessments deployment with cranes is absolutely necessary. The disadvantages include the need for additional equipment and space on bridges or riverbanks.

Sampling from boats is the most common plastic sampling method in the open ocean. Several assessments have deployed nets using boats in rivers across continental Europe (van der Wal *et al.* 2015) and in the United Kingdom (Sadri and Thompson 2014). The greatest advantage of using boats is that one can sample at any safe location on a river without being limited to suitable bridges. In contrast to other methods, this allows plastic sampling in estuaries (e.g. Sadri and Thompson 2014), which may shed light on actual plastic emissions from rivers into the ocean. Sampling can be carried out by transecting the river longitudinally, in cross-section or in a figure-eight shape (van der Wal *et al.* 2015), or by maintaining the same location during the sampling (stationary sampling). The latter yields similar results as bridge-deployed sampling. In contrast to the marine environment (Kukulka *et al.* 2012), boat sampling in rivers has not been widely applied to date. Lenaker *et al.* (2019) successfully used boat sampling from multiple depths of the water column in rivers and lakes.

Figure 5.2. Sampling a large river (the Danube) by crane from a bridge. *An array of nets is positioned to sample the water surface and the water columns simultaneously (Hohenblum et al. 2015).*



Miscellaneous sampling methods have been applied to collect plastic debris in rivers. Morritt *et al.* (2014) investigated plastic transport at deeper layers in the water column of the Thames in the United Kingdom by deploying fish fykes just above the riverbed. No results from similar assessments have been reported to date. Riverine plastic debris that accumulated at dedicated infrastructure, for example in the Seine in France (Gasperi *et al.* 2014) and at Jones Falls in the United States (Lindquist 2016), has been collected. For these assessments no additional infrastructure was required. However, locations where plastic could be sampled were limited.

Net dimensions

Net dimensions are crucial variables that influence results. This includes the height and depth of the frame, how deeply the frame is submerged, net length and net mesh size. Height and depth determine the sampling area of the net, which in turn determines the maximum size of the debris that can be sampled. Choosing a net opening is always a balance between sample size and the effort required to operate the net. Generally, macroplastic sampling nets tend not to exceed 1 m in height or width. Examples of nets used include $1.0 \times 0.5 \text{ m}^2$ (Saigon, Viet Nam; van Emmerik *et al.* 2018), $0.67 \times 0.5 \text{ m}^2$ (Jakarta waterways, Indonesia; van Emmerik *et al.* 2019a), $0.6 \times 0.3 \text{ m}^2$ and $0.6 \times 0.6 \text{ m}$ (the Danube, Austria; Hohenblum *et al.* 2015), $0.5 \times 0.15 \text{ m}^2$ (the River Tamar, United Kingdom; Sadri and Thompson 2014), $0.27 \times 0.105 \text{ m}^2$ (Chilean rivers; Rech *et al.* 2014).

The size distributions of collected debris can give additional insight into the net opening size that may be most appropriate given the scope of the assessment. Deployment depth, and the depth to which the frame is submerged, also influence the sampling results. More submerged plastic can be sampled when nets are installed at greater depths. However, in some cases it is crucial to allow some space between the water surface and the top of the net. In rivers with large amounts of floating plastics such as polyethylene terephthalate (PET) bottles and expanded polystyrene (EPS) foams, a net that is too deep will be unable to capture them.

Net length determines the drag force on the net and the maximum debris collection capacity. For rivers with high plastic concentrations and/or high flow velocities (e.g. the Jakarta rivers; van Emmerik *et al.* 2019a) it is recommended to use smaller nets in case they are deployed from bridges without additional equipment. This implies that the duration of sampling should be shorter, as the maximum capacity will be reached more quickly. Longer nets are advised when sampling duration is longer and when, for example, cranes or a larger number of people are available to retrieve the nets.

Mesh size influences the lower size limit of items that can be collected. Smaller mesh sizes determine the force on the sampling net. During periods of increased flow velocity, a too small mesh size can result in a backwater curve in front of the net opening. Debris may then be diverted away from the net, while the sample retrieved becomes less representative of the actual riverine debris concentration and composition. Mesh sizes used for macroplastic debris reported in the literature range between 300 µm (Sadri and Thompson 2014) and 4 cm (van Emmerik *et al.* 2018). Choosing the best mesh size, as in the case of other variables, is an iterative process. The more size distribution statistics are collected for a specific river, the better the mesh size can be selected. Harmonization of the mesh sizes used is recommended, although there are often practical reasons to select another size. It is most important that the mesh size used is clearly reported, so that the results and size distribution can be interpreted consistently.

🗅 Depth

Most macroplastic monitoring efforts focus on floating and suspended plastic debris in the upper 1.5 m of the water column. Data on (and understanding of) the vertical distribution of plastic debris are lacking. The distribution of plastic in the water column is related to the buoyancy, shape and degree of degradation of the plastic, river morphological characteristics and the hydrological regime. However, it remains difficult to predict the vertical profile of plastic debris for a given river without in situ data. Plastic debris at lower layers may make up a considerable share of total plastic transport. Morritt *et al.* (2014) collected plastic just above the riverbed, but no reference measurements were made at the surface. One of the few efforts to quantify a profile along the water column demonstrated that 66-79 per cent of total plastic transport may be below a depth of 1.5 m (Hohenblum *et al.* 2015). Recently, sampling of plastic in the upper 1.3 m showed that in the upper layer the clear majority (88 per cent) was transported in the upper 0.5 m (van Emmerik *et al.* 2019a). Sampling at deeper layers requires more costly and labour-intensive methods.

Deployment location

Choosing a deployment location depends on the question that an assessment or monitoring effort is focused on. To date, the focus has mainly been on estimating plastic transport for a given river cross-section or plastic emissions from a river into an ocean. For river export into the oceans the optimal deployment location should be as close to the river mouth as possible. As estuaries are wider towards the river mouth, suitable infrastructure for plastic sampling close to the mouth is often lacking. For example, in the Saigon River the suitable measurement location closest to the river mouth was still 70 km away (van Emmerik *et al.* 2018). Other methods to monitor plastic emissions (e.g. boat-based sampling, drones) are therefore likely to be more suitable. Note that estuaries are subject to complex flow dynamics, as they are influenced by both the tide and the freshwater discharge. Flow velocity and direction may change on hourly timescales, which in turn influence plastic transport and export into the ocean. Monitoring at the river mouth gives the best estimate of actual export to the sea. However, these can only be made in a meaningful way if the complex dynamics are taken into account, for example through high-frequency monitoring during targeted time periods. In rivers with deltas, it is hardly feasible to design a representative monitoring programme. It is recommended to select a location upstream of the deltaic section of the river.

For bridge-based net sampling, it is recommended to find bridges with a sidewalk separated from motorized traffic. Determining a sampling location across the width of the river depends on the purpose of sampling. It can either be done to obtain debris statistics such as material (organic, plastic, other), polymer type, mass and size distribution, or to quantify the cross-sectional variation of plastic debris concentration. If sampling is mainly carried out to obtain bulk statistics, the location with the highest plastic concentration can be sampled. To measure the cross-sectional variation, other variables determine the number of sampling locations, such as variation in flow velocity, navigational activity (if it is unsafe to sample in the navigation route), sampling duration and available workforce.

□ Sampling duration and frequency

Macroplastic debris transport can exhibit large temporal variations on seasonal, daily and subdaily scales. Appropriate sampling duration and frequency may be chosen depending on the purpose of the assessment.

Typical deployment durations vary between minutes (Moore et al. 2011) and 24 hours (Wagner et al. 2019), but depend on the mode of operation. If sampling is done manually, deployment durations are generally in the order of minutes to hours. For longer deployment, set-ups are recommended that can be operated without continuous supervision, for example by using litter traps or fixed nets. The deployment duration of nets depends on the debris loading of both plastics and other components, such as organic material and suspended sediment. Deployment times must be sufficiently long to capture material, but must be short enough to avoid full clogging or blocking of the net opening. Rapid clogging of nets or filters in rivers with high organic material loads or high suspended sediment loads may prevent these types of sampling techniques. In such cases visual counting might be more appropriate. In general, deployment times will need to be adjusted for each individual sampling location and potentially for individual samplings in rivers with high load variations. The sampling frequency is determined by the objectives of the monitoring programme and the available resources. It is recommended to take samples under different flow conditions as plastic loads can depend on river dynamics, which can be variable at different time scales. Close to the river mouth, the flow dynamics are influenced by both freshwater discharge and the tide. Depending on their relative contributions, this may lead to changes in flow velocity and direction multiple times per day. Other river systems, such as intermittent streams are not always easy to forecast, may show large variations across seasons. In extreme cases, rivers may run dry for several months. Both examples emphasize the importance of taking into account river flow dynamics in the design of a river plastic monitoring strategy. As river flow dynamics, such as hourly tidal dynamics or the exact onset date of a first flush in intermittent stream, are not always easy to forecast, this should be anticipated in river plastic monitoring. In the case of strong hourly variations, it is recommended to plan several high frequency sampling sessions, for example, hourly measurements during a full tidal cycle. For intermittent streams, a strategy could combine standard weekly or monthly measurements, combined with flexible measurements based on the rainfall and discharge forecasts. Note that measurements of zero plastic flow (due either to no plastics or to no river discharge) are also valuable data that gives important insights in the plastic transport dynamics of that very river system.

□ Sample analysis protocol

Once the sample is collected, it can be analysed in the field or in the lab. If one is interested in general riverine debris characteristics, it is recommended to separate the sample into organic material, plastic litter and remaining debris. Depending on the extent of the assessment, the remaining debris can then be separated into additional classes, but that is beyond the scope of this report. Plastic litter can be categorized through advanced analysis such as Raman spectrometry (which can determine the exact plastic polymer type) or the use of lookup tables. Advanced analysis is difficult to perform in the field and equipment is expensive. There are several methods for simplified analysis.

The OSPAR method (OSPAR 2010) includes a list with standard categories of items that can be used to categorize sampled debris. The advantage of this method is that it is standardized, which allows easy comparison with data from other rivers or sampling efforts. The OSPAR methodology has recently been adapted for freshwater by *Schone Rivieren* (Clean Rivers; see annex 3). An even simpler method proposed by van Emmerik *et al.* (2018) categorizes sampled plastic into seven categories (PET, PS, EPS, PP/PE-soft, PP/PE-hard, Multilayer, Other) based on a lookup table. The advantages include easy application, first order estimation of the polymer type, and a limited number of categories. A disadvantage is that items may be categorized wrongly. Once categorized, the mass and item count of each category can be measured. Note that when the mass is determined directly after retrieval, it equals the wet mass. For the dry mass it is recommended to dry the plastic items for at least 24 hours at 70 degrees, or to sun dry them for at least 72 hours.

Factor	Description	
Deployment method	Deployment of sampling equipment (e.g. nets) from boats, bridges or other means	
Net dimensions	Height and width of the sampling net	
Mesh size	Mesh size of the net used for sampling	
Depth	Vertical section in the water column where samples are taken	
Deployment location	Location along the river and the cross-section of the river	
Sampling duration	Total time to collect the sample	
Sampling frequency	Frequency of taken samples	
Sample analysis	Protocol used to separate, process and analyse the sample	

Table 5.2. Factors to consider in sampling macroplastics

Tracking methods

Tracking the travel paths of plastic items is a common monitoring method which is often unreported. There are two main categories: active tracking using a global positioning system (GPS), and passive tracking by releasing marked items that can be reported once retrieved. Active tracking is an accurate method of following plastic debris in river systems. GPS trackers can be placed in typical macroplastic items such as water bottles (e.g. Tramoy *et al.* 2019). Additional mass can be added to decrease the tracker's buoyancy and ensure that it is submerged just below the water surface. The energy demand of GPS trackers depends on the data-sending frequency. Some trackers can enter sleep mode when no movement is registered. With such settings, trackers may last multiple months. A GPS tracker should not be submerged too deeply, as it will then not be able to send signals.

Since GPS trackers are easily lost or stolen, using them can be costly. Some researchers mark typical macroplastic items that can be tracked passively. For example, Ivar do Sul *et al.* (2014) used painted plastic items to quantify the retention time of plastic debris in mangrove forests. Others have placed QR codes or contact information on plastic items. If citizens or professionals find these items, the location can be reported. Tracking plastic items can provide insights into the travel paths and times of plastic debris in river systems. However, it does not allow quantification of plastic concentrations or plastic transport at given points in space or time.

Visual observation methods

As most macroplastic observations to date have been carried out using varying methods, the Riverine and Marine floating macro litter Monitoring and Modelling of Environmental Loading (RIMMEL) project has aimed to harmonize riverine plastic litter data collection (Gonzalez *et al.* 2016; González-Fernández and Hanke 2017). Rather than sampling or tracking the plastic, plastic litter transport can be quantified through visual observations from bridges. Using the same protocol in each river, consistent observations of floating plastic litter can be made in terms of time and space. An example is a recent synthesis of visual observation data for over 20 rivers in Asia and Europe (van Calcar and van Emmerik 2019). The cross-section of a river is divided into sections, depending on the amount of plastic, measurement duration and river width. For each of these sections the number of plastic items observed during a given period is counted. This can then be normalized over time and space to arrive at a plastic transport profile over the river width and total plastic transport in items per unit of time (generally items per hour). River characteristics and bridges vary greatly. For each location, an exact protocol should be optimized. The aspects that should be considered are discussed below. Note that visual observations can be combined with physical sampling, for example to convert the measured transport in items per unit of time to actual mass transport (van Emmerik *et al.* 2018).

Measurement location

Similar to plastic sampling, the nature of the assessment determines the optimal measurement location. For transport it is recommended to find a bridge close to the river mouth. In larger rivers, bridges close to the mouth are often not safe to work on due to their height or traffic intensity. The distance between the bridge and the water surface determines the minimum observable plastic item size. From experience, items larger than 1 cm can be observed at heights of around 10-14 m (van Emmerik *et al.* 2018). If smaller items should also be observed, or when only bridges a greater distance above the water surface are available, using binoculars is recommended. The height and width of the bridge also influence the width of the section that can be observed comfortably. Experience shows that a width equal to the observation height generally works well.

Visual observation methods are highly flexible in terms of discharge conditions and flow velocities as they only require optical contact to the water surface. While using sampling nets may not be feasible during high flows with high flow velocities and high debris loads, visual observations provided the observer is in a safe location can still be performed.

□ Site preparation

Preparing the measurement location includes dividing the bridge into sections, choosing the side on which to take measurements, and determining the sampling duration. Division of the bridge into sections depends on the number of people taking part in the sampling, the sampling frequency and the required spatial coverage. Having more sections allows better estimation of the cross-sectional transport profile, which may be important for optimizing waste reduction strategies. If only total plastic transport is important, fewer sections can be identified. Some examples of applications include the Saigon River (10 sections, 15 m wide, 60 per cent coverage; van Emmerik *et al.* 2018), the Jakarta waterways (four to 10 sections, 5 m wide, 100 per cent coverage; van Emmerik *et al.* 2019a), the Rhône (one sub-section, 60 per cent coverage; Castro-Jiménez *et al.* 2019), and the Seine (three sections, 30-40 m wide, 100 per cent coverage; van Emmerik *et al.* 2019c).

Box A. Example of macroplastic monitoring in the Saigon River, Vietnam

The Saigon River is probably one of Vietnam's most plastic emitting rivers (Lebreton *et al.* 2017). To further characterize plastic transport in this river, a monitoring programme was initiated in March 2018 (van Emmerik *et al.* 2018). The goals of that effort were to determine 1) plastic mass transport, 2) distribution over the cross-section, and 3) plastic polymer composition. Monitoring was carried out using a combination of visual counting and net sampling from bridges. Visual counting was done hourly at 12 locations across the river's width (Figure A.1).

Sampling was performed continuously at two locations (Figure A.1). Visual counting yielded the distribution of plastic transport over the river width, as well as plastic transport in items per hour. Through sampling the average mass per plastic item was determined, which was in turn combined with visual counting results to estimate plastic mass transport. The samples were separated into polystyrene (PS), polyolefins (PO), polyethylene terephthalate (PET) and mixed/unknown.

The cross-sectional plastic transport profiles changed considerably between hourly observations (Figure A.2). At ebb tide the highest transport was observed on one side of the river; at flood tide it was observed on the other side. Quantifying the distribution of plastic transport across the river's width is crucial to optimize contamination prevention and reduction strategies. Based on sampling, an average plastic item mass of 3.6 grams was determined, resulting in an average net plastic transport of 0.2-0.3 metric tons per day in March 2018. Further analysis revealed that most plastic items were polystyrene foam fragments and food container fragments (Figure A.3). The third most abundant category was plastic bags.

Figure A.1. Overview of the measurement location and observation points across the bridge (reproduced from van Emmerik et al. 2018, Creative Commons Attribution 4.0, CC BY 4.0)



Figure A.2. Variation of plastic transport profiles (items/minute) during one day. Colours indicate different hours *(reproduced from van Emmerik et al. 2018, Creative Commons Attribution 4.0, CC BY 4.0)*



Figure A.3. Item categories and polymer types based on 614 analysed plastic items

(reproduced from van Emmerik et al. 2018, Creative Commons Attribution 4.0, CC BY 4.0)



This example demonstrates that a relatively modest monitoring campaign can yield invaluable insights into spatiotemporal variations in plastic transport, the order of magnitude of net transport, and item categories and polymer types. These insights are crucial if plastic sources, sinks and pathways are to be identified.

□ Sampling duration and frequency

Sampling duration and frequency depend on the variation in flow velocity and sections across a river's width. For rivers with considerable variation in flow velocity, such as those in tidal zones, it is recommended to take measurements at least once per hour. The duration of each measurement should at the most be equal to one

hour divided by the number of sections. The magnitude of plastic transport also influences optimal sampling duration. For rivers with more than 1,000 items per hour, it is recommended to measure one or two minutes per section. For rivers with less than 100 items per hour, it is recommended to measure at least 15 minutes per section.

Counting protocol

In addition to counting the total number of plastic items per unit of time, trained observers can count items in specific plastic classes. This generally works well if two observers can measure at the same time. One observer reports the plastic types (e.g. OSPAR *Schone Rivieren* or seven categories from van Emmerik *et al.* 2018) (Annexes 1 and 2) and the other reports the overall observation. For higher plastic transport rates (> 1,000 items per hour) this method becomes more strenuous and the likelihood of unobserved items increases. In that case it is recommend to count only the total number of plastic items. Additional measurements can be performed on a smaller sub-section to determine the count per selected category.

Automated monitoring

Scaling up visual observations may be facilitated through the use of automated monitoring rather than manual counting by observers from bridges. For example, tools have recently been developed that use Unmanned Aerial Vehicles (UAVs) for beach litter monitoring (Martin *et al.* 2018). Geraeds *et al.* (2019) presented a monitoring protocol for macroplastics monitoring using UAVs for rivers. It was demonstrated that variations in time and space can be well quantified from UAV-based camera imagery. Further research will focus on the use of UAVs for long-term data collection of plastic litter in river systems. Another promising way forward is the use of cameras for automated plastic monitoring. Kylili *et al.* (2019) developed a deep learning-based approach to identify floating plastic debris in marine environments. For river systems such an approach would offer an unprecedented opportunity to collect long-term time series of plastic transport. A recent proof-of-concept study demonstrated the added value of camera-based automated monitoring of river plastics in Jakarta rivers (van Lieshout *et al.* 2020). A precision of almost 70 per cent was obtained. Furthermore, the results suggest that the number of plastic transport, camera-based monitoring may therefore be more reliable.

5.1.1.2 Micro- and mesoplastics

Macroplastics can be monitored by sampling and/or by tracking and imaging methods. The latter can typically not be applied to micro- and mesoplastics, which must be monitored by sampling. Micro- and mesoplastics are often sampled concurrently by net sampling. Monitoring that specifically aims at these smaller fractions may make use of specifically adapted net design. Compared with marine studies, smaller manta trawls or neuston catamarans are used. Most studies apply nets with mesh sizes of around 300 µm. Samples are typically large, so that with a 30 cm manta trawl, 20-50 m³ of water can be sampled in 10-30 minutes. However, it has been found that using finer nets will detect more particles, especially fibres, although sample volumes will necessarily be lower with such an approach. Larger sampling volumes can be achieved by pump and filtration sampling, where water is pumped through a series of filters of decreasing mesh size (e.g. Bannick *et al.* 2019; see also Chapter 5.2.1.2)

Studies targeting very small particles in rivers or streams are rare so far, but one catchment-wide assessment using 1 litre bottles combined with 0.45 µm filtration has been published (Barrows *et al.* 2018). That assessment included major contributions from trained citizens. This strategy should be developed further to obtain a better perspective on spatial and temporal distributions of microplastics in rivers.

In contrast to macroplastics, monitoring microplastic transport in situ is much more difficult. Current estimates are based, to a large extent, on theoretical considerations. The lateral and vertical structure of large rivers generally needs to be taken into account, which requires a modification of existing sampling equipment in order to sample different depths at the same time (Liedermann *et al.* 2018). Liedermann *et al.* (2018) also revealed a slight tendency of near-bank microplastic accumulation.

5.1.2 River sediments

The consequence of temporal variations in flow is that the extension of shore sediments, as well as the depth of the water above riverbed sediments, can be variable. Floods may decrease microplastic concentrations on a catchment scale (Hurley *et al.* 2018). Therefore, the previous hydrological situation has to be known when judging microplastic concentrations in river sediments. River sediment deposits are much less stable than those in lake sediments. Sampling of undisturbed sediments cannot be achieved in most cases, and sediment thickness cannot be related to sedimentation time. No standard methodology for obtaining layered sediments from riverbeds has been established. Riverbed samples are therefore sampled by using metal spoons (as for shore samples) or different grab samplers, usually covering the top 10-15 cm of sediment. These samples are large enough (in the kilogram range) to obtain meaningful microplastic concentrations.

5.2 Sampling of lakes and reservoirs

There are a number of factors to take into consideration when planning a sampling study. The following is a general list of lake characteristics which can impact the likelihood that (microplastic) particles will settle, undergo sedimentation, or be transported through the freshwater system:

- □ shape and depth;
- □ zoning (vertical and horizontal);
- □ land use (with respect to potential plastic sources);
- □ stratification (as a function of season/temperature);
- □ wind direction;
- □ ultraviolet (UV) exposure (weathering);
- D biological processes (bioturbation or gas bubble formation).

5.2.1 Water surface and water column

5.2.1.1 Selection of sampling sites

The deepest point of a lake is generally considered representative in lakes with a simple (close to circular) shape and in small lakes. Large lakes, especially those with a complex morphometry (dendritic shoreline or more than one basin), need several sampling points. Inflows may be a major source of plastics in lakes (Vaughan, Turner
and Rose 2017). If possible, these inflows should be directly sampled in addition to lake water sampling. Cities or villages have been shown to cause locally elevated concentrations of plastics (Mihai 2018). Therefore, it has to be decided first whether typical or representative concentrations are needed, and whether the effect of point sources will be considered. If macroplastics are to be sampled, the shorelines will be especially interesting (see Chapter 5.3).

Reservoirs possess horizontal zoning, namely 1) a more riverine part with measurable flow and a large fraction of allochthonous matter, 2) an intermediate zone, and 3) a lacustrine zone near the dam where flow is close to zero and autochthonous production dominates (Uhlmann *et al.* 2011), (Figure 5.3). Ideally, these three zones should be sampled to determine whether there is a gradient in microplastics concentration. Many reservoirs possess pre-dams, built to keep sediments and nutrients from reaching the main dam. The water in these pre-dams should be sampled for microplastics to determine whether they could be effective in microplastics reduction. Lake modelling can be helpful in predicting transport routes and hotspots of plastic particle contamination.





5.2.1.2 Sampling technology

In large lakes, samples representing large parts of the near-surface water can be obtained using manta trawls or neuston nets. However, their mesh size (typically 300-390 μ m; Hidalgo-Ruz *et al.* 2012) limits the detection of microplastic particles. Plankton nets have finer mesh sizes (down to 100 μ m for oceanographic nets) and can be used for horizontal or vertical sampling (Figure 5.4). Vertical sampling integrates over depth at a given location. The standard mesh size for a limnological plankton net targeting phytoplankton is 55 μ m, while even finer nets are available. Plankton nets are suitable for medium volumes of water. The selection of mesh size always entails a trade-off between the lower cut-off of particle sizes and the risk of clogging due the presence of suspended sediment and organic material such as plankton and leaves. **Figure 5.4. Limnological plankton nets.** *Left: small net with 55 µm mesh size and a metal cod end; middle: large net; right: cod end of the large net.*



Photographs: Yvonne Rosenlöcher, UFZ

Pumping technology as applied to wastewater effluents (Mintenig *et al.* 2017) is suitable for surface water, which particularly means the top 0.5 m. An improved encapsulated version of this device has been developed by Lenz and Labrenz (2018). With it, small particles > 10 μ m can be trapped in a stainless steel cartridge and a few hundred litres of water can be filtered from surface waters unless there are severe cyanobacterial blooms. Instead of performing size fractionation after processing the material from the stainless steel cartridge, for lake water it has been found practical to combine the pumping apparatus on-site with prefiltration through 500 μ m and 100 μ m stainless steel sieves. In this case, large containers for temporary storage of pre-filtered water are needed (e.g. a stainless steel barrel with a lid) (Figure 5.5).

Figure 5.5. Pumping device and stainless steel barrels on a rubber boat for reservoir sampling.



Photograph: UFZ

Glass fibre filters can be attached to the outside of the barrels to check for possible airborne contamination. Generally, electricity (e.g. provided by a diesel generator) has to be available for pumping. A stable boat which can hold the equipment and at least two people is also required. If water from deeper parts of a lake or reservoir are to be sampled, submersible pumps have to be used (e.g. Setälä *et al.* 2016). However, as microplastic concentrations tend to decrease with water depth in marine settings (GESAMP 2019) and this decrease is expected to be similar in lakes, the surface layer should be sampled first to obtain an impression of the prevailing microplastic contamination. A recent study demonstrates that the concentration of irregular particles decreased with depth in a lake, while the distribution of fibres did not show a vertical pattern (Tamminga and Fischer 2020). This means that the specific density of the respective polymer might be less important for fibres, and extrapolation from a few samples to the entire water column will need different algorithms for irregular particles and fibres.

Sieving or filtering samples ex situ is generally not suitable for lakes or reservoirs, as a minimum of hundreds of litres of water are needed for reliable quantification of microplastics (Braun *et al.* 2018). However, if specific information about small microplastic fibres is desired, a combination of Niskin bottle sampling with microfiltration (0.45 µm; Whitaker *et al.* 2019) can be applied. This should be used in combination with high-volume techniques whose purpose is to obtain information about larger particles.

5.2.1.3 Sample processing in the field

While single macroplastic particles mainly need to be measured and documented, and safely stored if later polymer or biota analysis will be attempted (see Chapter 7), samples of microplastics from nets and sieves need to be processed on-site. Since material in nets and sieves must not dry, it should be covered during transport (e.g. on a boat carrying it to the lake shore), especially in hot or windy weather. The contents of the net or sieve are then flushed to a sample vessel with filtered water. Glass vessels are preferable to minimize contamination (see Chapter 4.2). Analytical sieves need to be treated gently so that they retain their specified mesh size, and plankton samples tend to be sticky. It is crucial to allow enough time and water to perform several collection and rinsing steps for a sieve (Figure 5.6). The final volume of the sample should be kept small. If biota will be analysed using the same material, the final sample should be preserved or cooled.

Figure 5.6. Fractions > 500 μm (left) and > 100-500 μm (right) from the water in a dam. *Note the large amount of phototrophs (greenish mass).*



Photograph: UFZ

Pump samples in cartridges should be left in the cartridges until they are processed in the lab. They should not be blown dry, as drying will impede their retrieval. Open fittings must be closed (e.g. with aluminium foil and parafilm) to avoid drying and contamination. Cooling is also recommended because of the microbial biomass in the sample material.

If an analysis of organic contaminants from the material is desired, samples have to be stored and transported either cooled (4°C) or frozen.

Whether density separation should be included in the sample preparation depends on the amount of other particles in the water samples (see Chapter 6).

5.2.2 Lake sediments

Lake sediments can be considered an archive of material inputs from the catchment. Concentrations of plastics in lake sediments can be expected to vary much less in time than water-based concentrations. Therefore, a high temporal resolution of sampling is not necessary. Similar to water sampling, the mode of sampling is determined by lake morphometry and hydrology. Sampling frequency can be guided by the sedimentation rate (the higher this is, the more sampling dates and the greater the sediment depth to be considered) or by certain events (e.g. storms, floods, major land use changes in the catchment). The number of necessary sampling sites is determined by lake morphometry and hydrology. A bathymetric map is helpful. If this is not available, transects of depth measurements can provide necessary information about lake bottom structure.

Sediment samples from soft sediments without large debris or vegetation can be obtained using rod-operated or cable-operated Ekman grabs. These grabs typically extract the top 15 cm and provide a large amount of sample in a single step. A disadvantage is that the sediment surface is disturbed and the exact depth of the grab cannot be determined. Alternatively, gravity coring can be used for sediment sampling. Gravity corrers come in various diameters, with cores typically 6 cm or 9 cm wide. Depending on sediment structure and compaction, cores up to 40 cm long can be obtained with an almost undisturbed sediment surface. It is recommended to take three cores per site to determine possible variation. Sediments can be divided into defined layers with simple mechanical devices available from the corer manufacturer (Figure 5.7).

The disadvantages of gravity coring are the relatively smaller volume of samples in the top 15 cm, and the fact that liners used for coring are typically made of clear plastic polymers such as polyvinyl chloride (PVC). Therefore, scraping with spoons, etc. has to be avoided when retrieving the sediment from the liner, and scratched old liners should not be used for sediment microplastic sampling.

Sediment subsamples should be placed in containers. If plastic cannot be avoided, new containers should be used and aluminium foil should be placed between the container and its lid to avoid abrasion. Cooling or freezing until processing in the lab (Chapter 6) is recommended.

In summary, lakes and reservoirs have both vertical and horizontal zoning, which must be addressed during sampling efforts. Density stratification and, consequently, mixing of inflows may vary with the annual cycle. For horizontal plastic concentrations in surface water, it is important to ascertain the main and prevailing wind direction. From ocean studies it is known that a large fraction of plastics floats on the surface and that concentrations decrease with depth (Choy *et al.* 2019). This pattern is apparently less uniform in freshwater

Figure 5.7. Mechanical devices to cut sediment cores into defined layers. *Maximum resolution is 5 mm. The plexiglass liner is 9 cm in diameter.*



Photograph: UFZ

(Lenaker *et al.* 2019, Tamminga and Fischer 2020). Moreover, there is plastic in sediments, so that some material must sink through the water column and be deposited in the sediments.

From a catchment perspective, lakes or reservoirs can be regarded as sinks of microplastics. Whether permanent burial can be achieved depends on the likelihood and frequency of resuspension, as well as on biological processes such as bioturbation and gas bubble formation. With respect to reservoirs, which have not often been studied so far, sedimentation of microplastic particles is currently regarded as mainly a transient phenomenon (Watkins *et al.* 2019). Ideally, sampling of shores should be combined with water and sediment sampling, which has not often been the case in studies available until now.

5.3 Sampling of lake shores and riverbanks

Shorelines of aquatic ecosystems are (temporary) accumulation zones for plastic litter. Quantifying shoreline plastic litter yields insights into the sources, sinks and pathways of plastic contamination through river catchments. Both the deposition and mobilization of plastic debris on shores depend on water level and flow velocity. Understanding the dynamics of shoreline plastics can help to identify potential sources of additional plastic contamination (remobilized shoreline plastics) in response to extreme events such as floods. Riverbanks have been monitored extensively around the world. Several examples are given here of monitoring strategies and their respective results. For quantification on riverbanks, data are often collected using a citizen science-based approach. Several such efforts are compared. A more detailed overview of available riverbank monitoring methods can be found in Vriend *et al.* (2020). Lake shores are less well studied. Available studies are used to discuss the role of lake shores in plastic mobilization through catchments, and some examples of reported monitoring efforts are given.

Riverbank and lake shore sampling methodologies are often based on the OSPAR *Guidelines for Monitoring Marine Litter on Beaches* (OSPAR Commission 2010). The OSPAR method consists of two types of sample units: 1) a section parallel to the water, 100 m wide from the dunes to the water's edge, where all litter items are registered; and 2) a section (parallel to the water) 1,000 m wide from the dunes to the water's edge, where all items > 50 cm are registered. An OSPAR survey is conducted four times per year. All beaches are monitored within the same two-week timeframe. Sampling is carried out one hour after the maximum daily water level. Especially in coastal sections of river systems, water levels can be influenced by tidal dynamics. This is less important for river sections with small or negligible water level variations. The sampled items are 1) picked up, 2) marked on a standardized datasheet, and 3) removed. Sampling locations are chosen based on the absence of any previous cleaning activities. Note that the standardized list of items that can be marked includes other litter categories in addition to plastics, such as metal and glass (see the Annexes).

Stichting De Noordzee adapted the beach OSPAR method for the *Schone Rivieren* (Clean Rivers) project to monitor riverbank plastics along Dutch rivers (van Emmerik *et al.* 2020). Surveys have two parts: a 100 m survey and a detailed survey. For the 100 m survey a trajectory parallel to the water is selected, from the water's edge to the highest visible waterline or riparian vegetation. Surveyors walk along strips 1-3 m wide parallel to the water and pick up all the litter they see from walking height (i.e. not on their knees). All the litter picked up is identified and marked using the same item categories as the beach OSPAR. For the detailed survey, a sample of 50 cm x 50 cm of the litter layer is taken at the high waterline. No sample is taken of the soil. The sample is taken away by the surveyor and all granulates are counted. Both surveys are conducted twice a year (autumn and spring), but there is no standardized timeframe during which the measurements should be carried out. All measurements are performed by citizen scientists trained by Stichting De Noordzee.

Swiss lake and river shores were monitored by Faure *et al.* (2015). Three shores were sampled per lake, with three replicates per shoreline. For each shoreline, 0.3 m x 0.3 m quadrats were drawn on the drift line. The top 5 cm was sampled, yielding a sampling volume of 4.5 litres. Microplastics were sieved with a 300 μ m sieve and separated into fractions of > 5 mm, > 1 mm and > 300 μ m. Macroplastics and large microplastics were identified visually. Smaller particles were treated to remove organic matter.

In Germany the shores of the Elbe, Weser, Rhine and Danube rivers were monitored during the *Plastikpiraten* (Plastic Pirates) project (Kiessling *et al.* 2019). A stretch of riverbank 20 m x 50 m was identified and separated into three zones: 1) one in daily contact with the river (water line to 5 m away), 2) one in irregular contact with the river (5-15 m away), and (3) one that had no contact with the river (further than 15 m). In each zone a sampling point was set up using a stick and 1.5 m of rope. The rope was used to demarcate a circle. All litter items within the circle were counted and identified. To make identification easier, litter items could be placed on a white cloth. Item classification was simplified compared to the OSPAR method and used seven material categories. Surveys were carried out in the fall and spring.

Klein, Worch and Knepper (2015) analysed microplastics on the shores of the Rhine. A sampling site of 10-15 m parallel to the river was selected, in which 40 random points were chosen. At each point 30 cm² of sediment, 2 cm deep, was scooped up with a metal spoon. All samples were assembled and homogenized to obtain a sample of approximately 3 kg. The sediment was dried, weighed and sieved using different mesh sizes. Samples were subsequently analysed following the Thompson *et al.* (2004) protocol.

One of the few efforts to categorize all plastic size categories was made by Blettler *et al.* (2018). Samples for macro-, meso- and microplastic were collected on the shores of the Paraná River in South America. For

macroplastics, two transects of 50 m x 5 m were identified. All macroplastics were collected and taken to the lab for further analysis. For mesoplastics, three 1 m² quadrats were set out in the macroplastic transects. Collecting and sieving took place in the top 3 cm of the surface using a 5 mm sieve. The litter items were taken to the lab for further analysis. For microplastics the same protocol as Klein, Worch and Knepper (2015) was used.

Most shoreline monitoring efforts involve walking on shores or beaches. Cowger *et al.* (2019) sampled plastic using kayaks. Sampling locations were not selected beforehand, and the only requirement was the absence of previous clean-up activities. Litter items were categorized as tires, metal, recyclables or garbage.

Aspect	Example
Survey method	Transects on shores or sampling from the river/lake, e.g. using kayaks
Transect dimensions	Length and width of transect
Location of transect	Close to water or closer to riparian vegetation
Sampling surface	Total transect, quadrats or circles
Sampling frequency	Single sampling event, annually, semi-annually or quarterly
Plastic size category	Micro-, meso- and/or macroplastics
Categorization	OSPAR item list, material categories, plastic polymer categories
Analysis	In situ analysis (classification, mass, size) or lab analysis
Surveyors	Professionals or citizen scientists

Table 5.3. Considerations for river and lake shore sampling

5.4 Sampling of drinking water

Microplastics in drinking water have a much smaller size distribution. Sampling and detection methods are therefore somewhat specialized. It is clear from drinking water studies thus far that the size distribution is skewed towards the low micrometre range, from 1-10 μ m to > 100 μ m. Likewise, the concentration levels for drinking water are low compared with freshwater or seawater, from 0 to over 4,000 microplastic particles/litre in raw water and around 400 particles L⁻¹ in treated water (Pivokonsky *et al.* 2018). Tap water studied by Kosuth *et al.* (2018) contained 0-61 particles/litre, with an average of 5.45 particles/litre. Of the 539 particles found, the vast majority (98.3 per cent) were identified as fibres. The remainder were identified as fragments (n = 7) or films (n = 2). Fibres varied in length from 0.10 to \pm 5.00 mm, with an average of 0.96 mm (Kosuth *et al.* 2018). Bottled water has also been found to contain microplastics, with 10.4 particles L⁻¹ above 100 μ m and an average of 325 L⁻¹ between 6.5 and 100 μ m (Mason *et al.* 2018). Shape distinction (spheres, fibres, fragments, film, pellets), which has been suggested as a factor in microplastic removal efficacy, could also be a factor in the analysis of detected microplastics, although not all studies thus far observe or account for this. It is likely that ranges in size, concentration and shape are influenced by differing methods of sampling, sample preparation and analysis techniques, attesting to the need for disclosure and for consistent approaches.

To confirm not only the presence of microplastics in drinking water supply, but also the source(s) of contamination, samples should be taken at different stages along the supply chain. A conventional water supply system includes 1) raw water supply (e.g. groundwater, surface water, recovered water or some mix of these), 2) purification (e.g. by a drinking water treatment plant), 3) transport, and 4) final supply to the consumer (e.g. household tap, bottled water). Plastic contamination of drinking water supply can come from various sources, even pipes/fittings and packaging.

Because there are both low concentrations of microplastics and smaller particle sizes in drinking water, a relatively large volume of water should be sampled, as is also suggested for raw freshwater sampling. This can be done by taking multiple small volume samples (e.g. 250 mL) from different sites or a few high-volume samples (e.g. 1,000 litres) from selected sites. The number of sample sites, frequency/randomness of samples, and sources (e.g. raw water, treated water, bottled water) should be considered to ensure that the results are representative. This would entail, for example, a repeated series of sampling over a period of time and/or a series of random sampling. Sampling should also be done at the optimum time of the year, when other conditions may not interfere with the analysis (e.g. in winter, when there are low phytoplankton levels).

The collected sample should be filtered through a series of μ m-scale mesh size filters (studies have used 5-0.2 μ m) for analysis of retained particles. It is recommended to use a series of filters (in descending order based on mesh size) to avoid clogging. Before filters are used, they should be rinsed with laboratory grade water. The choice of filter is important, as some may release fibres and cause sample contamination. Pivokonsky *et al.* (2018) used polytetrafluoroethylene (PTFE) membrane filters, while Mintenig *et al.* (2019) used stainless steel filters. The retentate is then dried and prepared for analysis. Filtered materials should also be treated for any remaining particulates such as precipitates and other particles.

The small amount of literature on sampling microplastic contamination in drinking water refers to the use of Fourier-Transform Infrared (FTIR) microscopy to determine microplastic content. Although this technique is the one most commonly used, it cannot detect particles smaller than 20 µm. To detect smaller sizes, Schymanski *et al.* (2018) and Pivokonsky *et al.* (2018) used micro-Raman spectroscopy.

Mintenig *et al.* (2019) warn that when working with samples expected to have low concentrations of microplastics, such as drinking water, it is especially important to avoid contaminating the samples (see also Chapter 4.2). Measures would include not opening samples outside the laboratory, wearing clothing made only of natural fibres in the laboratory, rinsing all equipment with laboratory grade water, and isolating filter units. The anti-contamination procedures proposed by Schymanksi *et al.* (2018) also include a laminar flow workbench and periodic checks throughout the analysis (before/after comparisons). In addition, they recommend maintaining control (blank) samples alongside the laboratory sample, to be analysed in parallel. This would account for any contamination. It appears from the literature that contamination by fibres is a recurring problem, but that clean air conditions could mitigate this problem.

5.5 Sampling at wastewater treatment plants

Raw sewage and stormwater contain plastic debris over a wide range of sizes. A substantial fraction of plastic particles (95-99 per cent) in raw wastewater is retained during the treatment process (Carr, Liu and Tesoro 2016; Mason *et al.* 2016; Murphy *et al.* 2016; Ziajahromi, Neale and Leusch 2016; Mintenig *et al.* 2017). Retention is dependent on particle size. While larger particles are unlikely to remain in treated wastewater, smaller ones such as fibres can be released with the final effluent into the aquatic environment. The retention of plastic particles in wastewater treatment plants implies that particles accumulate in the sewage sludge. If this sludge is used as fertilizer, the retained plastic particles are released back into the environment.

The goal of monitoring plastics in wastewater treatment plants is often to quantify the efficiency of plastic particle removal along the treatment steps and among different treatment technologies. To date, comparison of data on the fate of plastic in wastewater treatment plants is hampered by the wide range of sampling and

analysis methods applied. This chapter provides guidance on sampling and analysis techniques, from raw sewage to treated wastewater effluents.

5.5.1 Sampling techniques for treated wastewater, raw sewage and sewage sludge

WWTP sampling requires the application of different methods for raw sewage and sewage sludge, as well as for intermediate and final effluents, because of the vastly different content of solids.

5.5.1.1 Treated wastewater

Often effluents at different treatment stages are sampled by pumping treated wastewater through a series of sieves or filters with different mesh sizes using a submersible pump (e.g. Mintenig *et al.* 2017). Ideally, the most direct method of water sampling should be preferred. More specifically, it is preferable to sample water without pumping. The risk of removing or adding particles during the sampling process is therefore minimized. Sieves mostly range from 10 to 500 μ m, but they vary in different studies. On-site size fractionation by sieve stacks allows sampling of large volumes of water, as only the filtered solids are kept as samples. They are taken to the laboratory for subsequent analysis. The pump must be connected to a flow meter to record the volume of water filtered, which is required in order to calculate concentrations.

Other methods involve grab sampling, whereby samples are taken manually or by an autosampler to achieve monitoring over time (e.g. hourly samples over 24 hours). In this way temporal variations can be observed, and robust average concentrations obtained. Particularly in the final effluent, with low plastic particle concentrations, grab sample volumes may be too small for reliable concentration estimates to be made.

A less common approach has been applied by Carr, Liu and Tesoro (2016), who used a surface skimming device positioned in the stream of the final effluent. Compared with pumps or grab samples, the skimmer can sample a comparably large fraction of the cross-sectional area of the channel. As only a single filter size is used in this set-up, on-site size fractionation is not readily possible.

5.5.1.2 Raw sewage and sewage sludge

There is currently considerable ambiguity about what can be considered raw sewage. Samples have been taken from drained sewage, after primary skimming, or the sewage remaining after skimming. Sampling after primary skimming has typically been performed when the fate of microplastics was the focus. Sampling raw influents prior to skimming also provides information on the large size fraction of influent plastics. Drained sewage, post-treatment sewage sludge and untreated sewage are commonly sampled using grab samples. On-site filtration is often hampered by the high solid fraction content. Reported sampling volumes vary between 1 and 10 litres, which can be considered sufficient in light of the expected high plastic particle concentrations.

5.5.2 On-site sample processing

On-site sample processing involves proper storage and avoidance of cross-contamination. Solid samples acquired through on-site size fractionation can be stored and transported with the filter or sieve itself. The devices should be sealed for transport and storage. Depending on the subsequent analysis, refrigerated storage should be used (e.g. for the analysis of organic contaminants adsorbed to plastic debris). Grab samples are ideally stored in glass containers to avoid cross-contamination. Generally, samples with low concentrations and small particle sizes are more likely to be affected by cross-contamination (see Section 4.2).

5.5.3 Sampling design and recommendations

The sampling design should correspond to the questions to be answered by the monitoring programme. Typical underlying questions could address, for example, plastic particle removal efficiency at the different treatment stages within a WWTP, removal efficiency of plastic particles for different treatment technologies, or plastic particle load release by treated effluents into rivers. Knowing plastic particle concentrations throughout the different treatment stages could also be necessary in order to assess potential interference with biological treatment, which might be sensitive to additives such as flame retardants or plasticizers.

As plastic particle concentrations are strongly reduced during treatment from raw sewage to WWTP effluents, it is recommended to use increasing sampling volumes that correspond to the treatment stage. For raw sewage a sample volume of 1-10 litres can be sufficient. On-site filtration allows sampling large volumes of water. Mintenig *et al.* (2017) targeted a sample volume of 1 m³ which was partially reduced for practical reasons (filter clogging). However, to maintain data quality the representativeness of sampled volumes should be ensured. At the least, any deviation from the planned sampling volume must be reported so that the data can be flagged as uncertain. A tendency towards filter clogging generally depends on particle concentrations. Higher concentrations will cause more rapid clogging of the filter or sieve stack. Sampling of final effluents does not necessarily require the application of sieve or filter stacks and can be performed with a single filter size (e.g. 10 μ m). However, consistently using a filter stack provides direct information on size class distribution at the treatment stages and is therefore recommended.

Overall pumping or rinsing of treated wastewater over fractionating filter stacks is recommended for WWTP sampling, as the large sampled volumes ensure representative samples for low microplastic concentrations. Sequential filtering reduces the risk of clogging compared with a single small-sized filter or skimming device. The smallest particle size which can be captured by filtration is limited by the smallest filter size. Stainless steel sieves or cartridge filters are mostly limited to a minimum of 5 μ m. For size fractions smaller than 5 μ m, vacuum filtration and glass microfibre filters with a pore size of ~ 1 μ m should be used.

Ideally, the influent raw sewage is also sampled by similar fractioning. However, coarse skimming prior to pumping is likely needed here. Alternatively, grab samples of raw sewage and sewage sludge can be taken.

5.6 Sampling of freshwater biota

Freshwater biota differ from marine biota not only in their species composition, but also in the abundance and diversity of wider taxonomic groups. Within crustacean zooplankton, cladocerans are important and are the focus of many laboratory studies on microplastics effects (Imhof *et al.* 2017). The most abundant group in benthic meiofauna consists of nematodes (Majdi and Traunspurger 2015). Their study with respect to microplastics effects has been started in laboratory tests (e.g. Fueser *et al.* 2019). However, there are no readily applicable routine methods to study microplastic contents or effects in field-collected samples of these small animals. Larger typical freshwater invertebrates include gammarids, molluscs and insect larvae. The latter are much more abundant and diverse in freshwater than in marine habitats. Conversely, annelids, which are abundant and diverse in marine ecosystems, are only represented by few species in freshwater. Sampling of freshwater biota in situ to obtain information about their microplastic load is not generally practicable. To obtain a representative sample, a large number or mass of organisms is required and, in many cases, specialized analytical procedures

are needed. In addition, not all organisms are suitable to act as bioindicators for plastic contamination. The definition of bioindicator species for freshwater microplastic contamination is just beginning. It is important to consider the size, life history, age and developmental stage of the organism. The life stages of many freshwater organisms have a strong seasonality which needs to be considered. The selected organisms should be typical of the studied ecosystem and fulfil the criteria for good indicator species (Box B, Criteria for good indicator species; adapted from GESAMP 2019).

Box B. Criteria for good indicator species (adapted from GESAMP 2019)

- regional representation (sessile or mobile species within a specific geographic range);
- ethically sound (e.g. non-threatened or not protected, closed seasons respected, opportunistic sampling of dead organisms);
- · abundant in chosen environment;
- already used as bioindicators or biomonitoring species;
- cost of routine sampling/analysis (e.g. sampling simultaneously for other contaminants, merging with other programmes, easily accessible);
- · easy, practical analysis in the laboratory;
- · commercially and ecologically important (e.g. as food source);
- · directly linkable to impact and effects;
- integrated at a source;
- comparable, globally similar species identified worldwide.

If more than one species is to be chosen, the species should cover several ecological niches (pelagic, benthic) and several feeding strategies (e.g. filter feeders, scavengers).

Size

The size of an organism determines possible interactions with different sizes and shapes of plastic litter. The particle size which could potentially be ingested by the organism should be considered in order to judge possible artefacts or surprise findings.

Patterns of activity/life stages

When biota are sampled, diurnal migrations or patterns of activity should be considered as they may affect contact with microplastics and the chance that any ingested microplastics are still present in the gut system. Many zooplankton species migrate vertically to avoid predators, and freshwater fish larvae hide during the day for the same reason (e.g. Lechner *et al.* 2014).

Feeding strategies (categories and examples)

□ Filter feeding and suspension feeding

This feeding strategy is very common in motile and sessile freshwater organisms (e.g. hydropsychid caddisfly larvae). Particles are taken up from the water by pumping through gills or picking up particles during swimming. As this occurs non-selectively, the probability that microplastics will be taken up is great. Highly abundant clams have been shown to be suitable bioindicators for microplastic contamination of lakes and rivers (e.g. Su *et al.* 2018).

Deposit feeding organisms

Deposit feeders dwell on detritus that has settled to the sediment. Examples include oligochaetes like *Tubifex* sp., chironomid and mayfly larvae, and many species of nematodes. Some organisms, such as the Asian clam (*Corbicula fluminea*), combine filter feeding and deposit feeding (Su *et al.* 2018).

Predation and scavenging

Predatory and scavenging organisms may ingest plastic when they mistake it for natural prey or when their prey has ingested microplastics. This may be especially important for freshwater fish, in which the presence of plastic particles is widespread (Pinheiro, Oliveira and Vieira 2017).

Grazing

Feeding by grazing is common among freshwater gastropods and isopods. The organisms scrape microalgae from the surface of the water. In doing so they may take up microplastics adhering to the algae. In addition, they feed on biofilms growing on plastic surfaces. These may differ from biofilms on natural surfaces in the same habitat, thereby influencing feeding activity and the growth of snails (Vosshage *et al.* 2018).

5.6.1 Strategies for monitoring and assessment in biota

Approaches which use samples from commercial suppliers such as fish markets are pragmatic and resourceefficient. As these samples' origin, living conditions and possible depuration phases are unknown, any conclusion about plastic contamination in a specific freshwater system is impossible and results can only be interpreted as related to the species itself. It could be worthwhile to collaborate with local fisheries to obtain more specific fish intestine samples. Organisms which are easily cultured in a lab (e.g. some clams or crustaceans) may be exposed in cages in the freshwater system of interest and later retrieved for microplastic analysis. To facilitate the interpretation of results, water and sediment samples from the same site in the freshwater body should also be taken. In addition to the assessment or monitoring of plastics, typical plastic-associated chemicals are of interest.

5.6.1.1 Invertebrates

Riverine invertebrates have recently been studied for the presence of microplastics. Windsor *et al.* (2019) detected plastic polymers in about 50 per cent of sampled Baetidae, Heptageniidae and Hydropsychidae. A gut clearance period significantly reduced the presence of microplastics, while differences between filter feeders and grazers/detritivores were not significant. The studied organisms are typical for streams and highly relevant in the food web. However, their availability may be limited.

Tubifex worms have been shown to ingest microplastics (Hurley *et al.* 2017). These widely distributed deposit feeders may colonize sediments up to a depth of 10 cm, but can be restricted to the top 2 cm in highly polluted sediments (Lagauzère *et al.* 2009). They have long been known as a suitable genus for sediment toxicity tests (Chapman *et al.* 1999). A recent study showed that they can conveniently be prepared for the analysis of microplastics (Hurley *et al.* 2017). This makes them versatile bioindicator species for sediments even in polluted waters. In addition, *Tubifex tubifex* belongs to the group of species recommended by the Organisation for Economic Co-operation and Development (OECD) for testing bioaccumulation of chemicals in endobenthic animals (OECD 2008).

Another freshwater invertebrate that has been thoroughly tested for microplastic contamination against a background of water and sediment contamination is the Asian clam *Corbicula fluminea* (Su *et al.* 2018). *Corbicula fluminea* is a globally distributed invasive species which inhabits rivers, lakes and estuaries and can reach high densities. It can tolerate a range of contaminants and is easily cultured in the lab. In accordance with Su *et al.* (2018), this species is recommended here as a bioindicator for microplastics in freshwater systems, especially sediments.

Figure 5.8. Typical freshwater biota used for microplastics assessment. *Top: Corbicula fluminea, a group of clams and an individual; bottom: Tubifex sp. (left) and chironomid larva (right). Photographs are not at the same scale.*



Photograph: Mario Brauns, UFZ



Photograph: Sven Bauth, UFZ



https//diptera.info/forum/viewthread.php? thread_id=65255



Thunderclap - Eigenes Werk, CC BY 3,0 https://commons.wikimedia.org/w/index.php?curid=6099484

5.6.1.2 Freshwater fish

Freshwater fish are ecologically important because, among other reasons, they are top predators in freshwater food webs. Their economic importance is less well known, as approximately 94 per cent of freshwater fisheries operate in developing countries (Pinheiro, Oliveira and Vieira 2017). Many of these countries have a considerable plastic litter problem. In contrast to marine studies, plastic in freshwater fish has rarely been studied. To date, it has been detected in 34 species belonging to 10 families worldwide; the percentage of individuals with plastic in their digestive tract ranged from 12 per cent of wild gudgeons (*Gobio gobio*) to 96 per cent of different freshwater species in China (Pinheiro, Oliveira and Vieira 2017). Fish collected at densely urbanized stations had a higher frequency of plastic ingestion. The possible effects of plastic ingestion have not been quantified at the population level. However, plastic ingestion might be a stressor that, added to others, is likely to cause negative effects.

Fibres are the most common plastic morphotypes ingested by fish. Some authors relate the abundance of intestinal plastics to the feeding type and habitat of the species, as demersal fishes tend to show higher plastic abundance than pelagic ones. Relatively little is known about the polymer composition of plastic ingested by freshwater fish, and even less about the possible transfer of plastic-associated contaminants (see Chapter 9) from freshwater fish to human consumers and the associated differentiated gender-related health consequences for women and men (UNEP 2016). In addition to the above-mentioned possible effects of plastic on fish populations, the possibility of biomagnification (enrichment of contaminants along the food chain) is of concern with respect to food security. These two aspects should be studied separately, preferably by choosing a set of reference species based on their previous use in ecotoxicology and their economic importance.

5.6.1.3 Birds

Similar to marine birds, freshwater birds ingest anthropogenic debris, including plastics, as reported for 17 species in Canada (Holland, Mallory and Shutler 2016). Piscivorous birds may ingest plastic with their prey, while dabbling ducks and other surface-feeding birds are likely to take up floating plastic. Plastic ingestion has also been documented for freshwater ducks in Africa; in addition, ducks had microplastic fibres in their feathers (Reynolds and Ryan 2018). The study of bird faeces and feather brushings in that study is a non-destructive and ethically sound approach to sampling plastic contamination in freshwater birds which might be developed into a general biomonitoring method soon. If one is interested in contamination of birds by plastic-associated lipophilic chemicals, sampling of preen gland oil should be carried out. It can serve as a non-destructive assessment or monitoring method for a variety of bird species without stressing or injuring the animals (Teuten *et al.* 2009).

Table 5.4 presents a selection of easily accessible organisms that can be used as bioindicators of plastic contamination and may also be considered for population effects in the field. Plastic-associated effects in the field have not been demonstrated for most of these organisms so far, except the well-known harm caused to birds by plastic objects. However, laboratory studies have produced effects or no-effects outcomes in regard to different endpoints, showing that potential effects can be detected with available methodology. To demonstrate this, some examples are given here. A detailed literature review has not been conducted within the scope of these guidelines. The work of de Sá *et al.* (2018) is recommended for further reading.

One should be aware that depending on the experimental set-up, the type of plastic and the investigated endpoints, studies using the same organism can reveal effects or no effects (Besseling *et al.* 2019). No effects of microplastic ingestion appear to have been detected in *Tubifex* sp. (Redondo-Hasselerharm *et al.* 2018), while chironomids and *Corbicula fluminea* have exhibited various physiological reactions (Oliveira *et al.* 2018; Ziajahromi *et al.* 2018). Some studies of freshwater fish have revealed little or no physiological effects (Malinich *et al.* 2018), while others have demonstrated clear negative outcomes of plastic exposure (Jovanovic 2017; Wen *et al.* 2018).

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	Tubifex sp.	Chironomus sp.	Corbicula fluminea	Fish	Birds
Ecological niche	benthic	larvae benthic	benthic	pelagic or benthic	pelagic
Feeding strategy	suspension feeder	suspension feeder	filter feeder, deposit feeder	herbivorous, omnivorous or predatory	herbivorous, omnivorous or predatory
Key requirements of an indicator					
Sessile or weakly mobile	Y	Y	Y	Ν	Ν
Globally distributed (or similar species	Y	Y	Y	Y	Y
Ethically sound	Y	Y	Y	depends on species	Y (if faeces are sampled)
Already used as a bioindicator	Y	Y	Y	depends on species and age	Y
Abundant/ easy to sample	Y	Y	Y	Ν	Y (if faeces are sampled)
Low cost	Y	Y	Y	Ν	Y (if faeces are sampled)
Effects observed	N	Y	Y	Y and N	Y (with macroplastics)
Commercially important	(Y) (aquaculture)	Ν	Ν	Y	Ν
Ecologically important	N	Ν	Ν	Y	Y
Ease of analysis: microplastics	Y	Y	Y	Y	Y (if faeces are studied)
Ease of analysis: macroplastics	Ν	Ν	Ν	Y	Y
Example in studies	Hurley <i>et al.</i> 2017	Ziajahromi <i>et al.</i> 2018	Su <i>et al.</i> 2018	Pinheiro, Oliveira and Vieira 2017	Reynolds and Ryan 2018

Table 5.4. Potential indicator species for freshwater biota plastic contamination

Y = yes, N = no. "Effects detected" refers to laboratory studies (see text). Example studies refer to use as bioindicators.

5.6.2 Preparation of specimens before polymer analysis

If biota samples are digested whole, the organisms need to be rinsed to remove loosely attached particles. Organisms should be measured and weighed if possible. In any case, any microplastics detected following the digestion of whole animals cannot be allocated to a specific organ, tissue or uptake pathway. It needs to be decided, and reported, whether gut clearance before analysis will be allowed. If not, organisms must be preserved (by freezing or with chemicals such as ethanol) immediately after rinsing of the surface.

If gut clearance is attempted, the duration of the depuration period should be adapted to the typical gut passage time of the organism. Results should be evaluated as to number of particles or polymer mass per individual organism and, if possible, per gram of tissue as well. In larger organisms the intestinal tract will normally be removed from the body or even separated into functional units before microplastics analysis. Eventually, food chain transfer might be detected in predatory animals. Some small organisms may be gently macerated to

make them translucent (e.g. chironomid larvae; Erdbeer and Kiel 2019). Their bodies can then be inspected microscopically and potential microplastics detected using specific staining or spectroscopic methods (see also Chapter 6).

5.6.3 Plastic debris as a habitat in freshwater?

The surfaces provided by plastic debris may be used as a habitat by various freshwater organisms (Figure 5.9). If plastic debris is abundant at a site, it should be included in biological monitoring programmes. For example, increased oviposition of insects (e.g. the ocean insects *Halobates micans* and *Halobates sericeus*) has been observed in the presence of plastic (Goldstein, Rosenberg and Cheng 2012; Majer, Vedolin and Turra 2012). Insects' ecosystem functions are quantitatively even more important in freshwater compared to marine habitats. Such effects should be studied where possible. Both positive and negative impacts might be perceived, depending on the insect species (e.g. whether it is an important food source, a protected species or a pest).

Concerns have been raised that (micro)plastic debris in freshwater facilitates the enrichment and distribution of bacterial pathogens by providing preferable biofilm habitats (e.g. McCormick *et al.* 2014). A meta-analysis by Oberbeckmann and Labrenz (2020) clarified that although certain bacterial taxa are associated with microplastics, enrichment of potential pathogens cannot be substantiated. This is less clear in the case of fungi, whose communities on plastic differ from those on more natural surfaces (Kettner *et al.* 2017). In addition, the interaction of other potentially harmful microbes such as microalgae or protists with (micro)plastics needs further study.

Figure 5.9. Freshwater biofilms on plastic



Photographs: Tatjana Gaudl, UFZ

6. Sample preparation for different matrices (water, sediment, biota)

The processing of particle samples obtained from water column samples requires the removal of natural organic debris, which is typically achieved with acids, bases or oxidants (hydrogen peroxide or Fenton reagent) or enzymes. Some general advantages and disadvantages of these approaches are listed in Table 6.1.

Treatment	Advantages	Disadvantages	References
Acids	viscose/rayon fibres are destroyed, less false-positive results	nylon and other polymers can be damaged	Devriese <i>et al.</i> 2015; Van Cauwenberghe and Janssen 2014
Bases	many polymers resist 10% KOH; 1 M or 10 M NaOH can also be suitable	discolouration and physical weakening of polymers, nylon fibres can be destroyed	Cole <i>et al.</i> 2014; Foekema <i>et al.</i> 2013
Oxidants	high particle recovery in sediments (> 90% for PE, PP, PVC, PET, PS, PUR) with hydrogen peroxide (H_2O_2)	takes several days and does not remove organic matrix completely; discolouration; PE and PP particles may become significantly smaller	Nuelle <i>et al.</i> 2014
	Fenton's reagent: recovery of PP, PE, PVC, nylon, quick and cheap procedure	may not work as well with weathered particles; cooling recommended	Tagg <i>et al.</i> 2017
Enzymes	almost complete degradation of organic matter possible; chemically safe	may take many days, intact organisms must be small, several enzymes with different working conditions	Cole <i>et al.</i> 2014; Löder <i>et al.</i> 2017

Table 6.1. P	Pros and	cons of	chemical	treatments	for mic	roplastic	recovery	from	environmental	samples

6.1 Water samples

Water samples rarely contain large masses of inorganic particles, although flood samples may be an exception. Natural organic debris is common. While particles > 500 μ m may be sorted manually, finer fractions often show a close mixture of a few plastic particles and a large mass of natural organics. Care must be taken not to destroy polymer fibres or weathered plastic fragments with aggressive reagents. Therefore, although time-consuming (days to weeks), enzyme treatments provide the safest way to obtain representative microplastic samples (Löder *et al.* 2017).

Depending on sample composition with respect to proteins, carbohydrates, lipids and chitin, the enzymatic procedure can be adapted (Löder *et al.* 2017, supplementary information). Density separation is not always necessary for processing water column samples. If it is necessary, it should be performed after the enzymatic purification steps. The particles are much better separated then, and the density separation solution can be recycled more easily (Table 6.1). A general workflow for enzymatic treatment that can be adjusted to several sample types is shown in Figure 6.1.

Figure 6.1. Universal enzymatic purification protocol (Löder et al. 2017, modified)



The optimized protocol is suitable for purifying microplastics from a wide range of different environmental matrices, including plankton, extracted sediment and biota. Incubation times represent minimum values. Numbers in superscript represent the types of samples that are suggested to purify with the respective purification step: 1) plankton samples, 2) extracted sediment samples, 3) wastewater samples, 4) lipid-rich biota samples (e.g. mussels, fish gut content) and other lipid rich samples, 5) samples with a high polysaccharide content (e.g. food samples, samples with high loads of plant material or algae).

^{*1} Depending on the amount of matrix present, the samples can be divided before purification; depending on the amount of residue present, they can be reunified for analysis after purification.

*² The hydrogen peroxide steps can be replaced with wet peroxide oxidation, as described above.

6.2 Sediment samples

Sediments generally have a large ratio of natural and mostly inorganic particles to potential microplastic particles. Therefore, density separation is usually required. This is typically accomplished by using concentrated or saturated salt solutions. If mass-based analyses are planned, size fractionation of the sediments is necessary, which is best achieved by wet sieving before density separation. As mentioned earlier, a certain sequence of mesh sizes has been established: $500 \mu m$, $100 \mu m$, $50 \mu m$, $10 \mu m$ (Braun *et al.* 2018). Stainless steel sieves are preferable for preparing microplastics samples; if the samples are fractioned in the lab, sieves will ideally be combined in the form of an analytical wet sieving machine (Figure 6.2).



Figure 6.2. Wet sieving machine

Photograph: UFZ

The use of sodium chloride (NaCl) is currently recommended by both the Marine Strategy Framework Directive (MSFD) technical subgroup (Galgani *et al.* 2013) and the United States National Oceanographic and Atmospheric Administration (NOAA) (Masura *et al.* 2015). NaCl is widely available, cheap and non-toxic, but only light polymers can be reliably recovered. Other salt solutions require recycling because of cost and hazardous waste constraints. Recycling consists of filtration through pore sizes smaller than the microplastic particles to be detected and density adjustment (e.g. by evaporation). These guidelines follow the recommendation in the review by Prata *et al.* (2019) to choose sodium iodide (NaI) as a technically superior and safe alternative (Table 6.2.). It should also be kept in mind that the densest solution may not be the best choice for every sample. Fine sediments may have a density of around 1.6-1.8 g cm⁻³, so that they will not settle and will hinder the separation of microplastic particles (Coppock *et al.* 2017).



Salt	Maximum density of solution (g cm ⁻³)	Range of polymers*	Safety	Price	Comments
Sodium chloride (NaCl)	1.2	alkyd, polyester, PET and POM not separated; PVC and PVA only possibly separated	good	low	no recycling needed
Sodium iodide (Nal)	1.6	POM only possibly separated	good	medium	reacts with cellulose filters
Zinc chloride (ZnCl ₂)	1.6-1.7	no limitation	corrosive, toxic	medium	widely used
Zinc bromide (ZnBr ₂)	1.7	no limitation	corrosive	medium	
Sodium polytungstate (3 Na ₂ WO ₄ 9 WO ₃ H ₂ O)	3.1	no limitation	very corrosive	very high	

Table 6.2. Salts used for density separation of microplastics from sediments*

*List of polymers considered, taken from Prata et al. (2019): PP, PE, PA, PS acrylic, PMA, PUR, PVC, PVA, alkyd, polyester, PET, POM.

The experimental set-up for density separation varies considerably depending on sample size. Closed, non-plastic apparatus which avoid frequent sample transfer is preferable in order to avoid contamination and particle loss. A device specifically designed for this purpose is the Munich Plastic Sediment Separator (MPSS) developed by Imhof *et al.* (2012). It is made of stainless steel and holds up to 6 litres of sample. The top part is used as a vacuum filtration unit following the separation process, so that no sample transfer is necessary. It is commercially available from Hydro-Bios (https://www.hydrobios.de/product/microplastic-sediment-separatormpss/). However, its large size is impractical for small sediment samples and its dimensions result in a settling time of 12 hours per sample. In addition, cost would prevent its use by many groups.

Alternatives have been developed. One is suction enhanced density separation (Klein, Worch and Knepper 2015), whereby rising particles are sucked off and extraction liquid is continuously supplied. The disadvantage of this technique is that the total sample volume can become quite large. A new variant of this device was developed by Coppock *et al.* (2017). It is small-scale (380 mm high, 53 mm inner diameter) and works for coarse, medium and fine (clay/silt) sediments. Although the authors made it from plastic materials, a steel prototype has also been manufactured and tested successfully. This size extraction equipment is preferable when sediment layers in the cm range are being extracted, or when sample preparation is carried out on a research vessel or at a field station.

As an alternative to dense salt solutions, oils can be used to separate microplastics from the surrounding natural matrix. The lipophilicity of plastic particles is the key factor that makes them preferentially move into the oil phase. Oils are non-polar, hydrophobic and have a lower specific density than water. Different oils have been tested for the separation of microplastics: canola oil (Crichton *et al.* 2017), castor oil (Mani *et al.* 2019) or light paraffin oil. While canola oil is cheap, it has a higher specific density and polarity than light paraffin oil and produces an infrared spectrogram similar to that of the target plastic polymers, which can limit detection and identification of microplastics. Castor oil possesses one of the highest viscosities among plant oils and therefore forms a thick oil layer around the microplastics, which is beneficial for particle recovery (Mani *et al.* 2019). Natural organic matter from the samples will accumulate at the interface of oil and water. Samples with high organic matter content may therefore need repeated extraction or additional pre-cleaning steps.

Some available protocols suggest a combination of oil treatments with density separation (Imhof *et al.* 2012; Crichton *et al.* 2017). Based on limited studies thus far, this approach needs more testing with real samples, especially small particle fractions. However, several advantages justify such efforts:

- Iow cost;
- □ relatively small volume of reagents;
- □ avoidance of toxic or corrosive substances;
- □ avoidance of problematic lab waste;
- simple procedure (see Mani et al. 2019, supplementary information);
- □ short extraction time.

6.3 Biota samples

Biota contain relatively little inorganic material. However, not only does their natural organic content hinder microplastic detection, but lipids may interfere with spectroscopic detection and the identification of plastic polymers. It is therefore necessary to use thoroughly digested whole organisms, or the digestive tracts or other specific tissues, in most cases. Although published protocols using acids or bases may work well, the possibility to conserve fibres and small fragile particles is a clear advantage of enzymatic treatments (Table 6.3.).

Treatment	Organism	Comments	References
30% hydrogen peroxide (H_2O_2) at 65°C and 80 revolutions per minute (rpm) for no more than 72 hours	Asian clam <i>Corbicula fluminea</i> (frozen after sampling)	incubation time depending on degradation of soft tissue; fibres detected	Li <i>et al.</i> 2015; Su <i>et al.</i> 2018
Equal amounts of 10 M potassium hydroxide (KOH) and H_2O_2 (34.5-36.5%) for 96 hours at room temperature	freshwater gastropods Lanistes varicus, Melanoides tuberculata, Theodoxus fluviatilis	fibres detected; neutralization with formic acid after digestion period	Akindele, Ehlers and Koop 2019
15% H_2O_2 at 25°C for 48 h	freshwater macrozoobenthos fixed in 70% ethanol	samples homogenized and suspended in saline solution	Windsor <i>et al.</i> 2019
10% KOH at 60°C	Tubifex sp.	depuration period 24 hours; complete digestion at < 10 min	Hurley et al. 2017
13% KOH for 2-3 days at room temperature, then rinsing with ultrapure water and conservation in ethanol	Chironomid larvae	animals made translucent but not completely dissolved, staining of plastic particles within the body	Erdbeer and Kiel 2019
10 M NaOH at 60°C for 24 h 10% KOH at room temperature	fish intestines (frozen after sampling)	only particles > 250 µm considered long incubation up to weeks, no stirring	Biginagwa <i>et al.</i> 2016 Wesch <i>et al.</i> 2016; Foekema <i>et al.</i> 2013
Flushing with cold tap water on sieve	bird intestines (frozen after sampling)	500 µm sieve used, smaller particles detected due to adhesion to larger items	Holland, Mallory and Shutler 2016
Wet sieving with distilled water	bird faeces	stacked sieves 1 mm, 250 μm, 63 μm	Reynolds and Ryan 2018
Brushing and combining with the help of tap water, then wet sieving with distilled water	bird feather brushings	stacked sieves 1 mm, 250 μm, 63 μm	Reynolds and Ryan 2018

Table 6.3. Treatments for biota samples to detect microplastics

7. Sample analysis: sizes, shapes, polymer types, associated chemicals

The analysis of (presumptive) plastic samples consists of physical characterization, chemical characterization and, in some cases, biological characterization. Distinguishing between plastic and non-plastic particles is easy in the case of macroplastics and feasible in that of microplastics > 1 mm. There are indications that particles are made of plastic polymers: bright and "unnatural" colour, uniform thickness of fibres, or the absence of visible cellular structure. It has often been reported that a large fraction of particles are colourless and/or translucent, which might lead to false-negative observations – especially when particles are also weathered.

With smaller particles, visual/microscopic inspection has a high false-positive error rate (around 70 per cent; Hidalgo-Ruz *et al.* 2012) compared to spectroscopic identification. It is also time-consuming and subjective, so that results from different observers will vary. Auxiliary low-cost methods such as touching the particles with a hot needle or staining with dyes can be helpful. When a plastic particle is touched by a heated dissecting needle, the material will melt. This does not happen with natural fibres or mineral particles. Waxy substances which are not plastic according to common definitions may give false-positive results.

Among available staining dyes, Oil Red EGN, Eosin B, Hostasol Yellow 3G and Rose Bengal have been reported to be unsatisfactory because of their low specificity, but Nile Red staining in combination with fluorescence microscopy appears to be quite promising (Maes *et al.* 2017, Prata *et al.* 2019). Nile Red provides high recovery rates for plastics after 10-30 minutes of incubation, can be used with weathered plastics, and allows subsequent spectroscopy for confirmation (Maes *et al.* 2017). Some plastic types may give weak signals (PC, PUR, PET, PVC; Erni-Cassola *et al.* 2017), but this does not limit the use of Nile Red as a pre-selection method preceding chemical characterization.

Another option is to use the commercial iDye Poly colours for polyester and nylon (Figure 7.1; see Erdbeer and Kiel 2019). However, this does not target some of the most widely used polymers.



Figure 7.1. Plastic particles stained with iDye Poly within a macerated chironomid larva

Photograph: Laura Erdbeer

Although hot needles and staining methods are helpful for sorting and training, they do not allow identification of the polymer type. They can, however, be applied in the pre-selection of particles for later chemical characterization, which is often limited by high cost, availability of sophisticated equipment and skilled personnel, and complexity of data processing and evaluation.

If the polymer types in an environmental sample are to be determined, chemical characterization by particle-based or mass-based approaches can be used. The latter do not require complete separation of plastics from the surrounding matrix, but provide no information on particle morphology or surface characteristics and only limited clues to the dimensions of the microplastic particles, depending on how finely the sample has been size-fractioned. Moreover, these thermoanalytical methods are destructive, so that the plastic material cannot be recovered after the analysis. Sample masses have to be recorded at every preparatory step in order to report final results. Consequently, drinking water samples which contain very few small plastic particles (if any) and little solid matrix must be analysed using spectroscopic methods (see Chapter 5.4).

Mass-based analysis methods comprise pyrolysis-gas chromatography-mass spectrometry (Pyr-GC-MS) and thermoextraction (thermogravimetric analysis, TGA) and desorption coupled with mass spectrometry (TED-GC-MS). The advantage of TED-GC-MS is that relatively large sample masses can be processed, so that single samples are more likely to be representative (Dümichen *et al.* 2017). It has turned out to be favourable to include an internal standard in the analysis, especially with samples low in organic matrix. Any information about accessory components which might appear in the mass-based Pyr-GC-MS analysis cannot easily be connected to a specific plastic polymer in the sample without previous knowledge. Still, as acceptable thresholds for contaminants are more likely to be defined on a mass concentration basis than on the basis of particle counts in different size classes, these methods have great potential for future regular assessments or the monitoring of bulky matrices such as sediments and sewage sludge.

Regarding tyre and road wear particles, which are assumed to make up a large part of anthropogenic fine particulates in the environment, detection with ICP-MS is possible (Braun *et al.* 2018). The styrene-butadiene rubber component can also be detected by thermoanalytical methods (Eisentraut *et al.* 2018).

Particle-based methods consist of Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy. These are the most widely used approaches to identify plastic polymers in environmental samples. A recent review of 40 studies of microplastics in water and sediment reported that FTIR-based methods were used in 50 per cent of studies, while 32.5 per cent employed visual inspection, 10 per cent Raman spectroscopy, and the remainder electron microscopy, staining dyes and GC-MS methods (Prata *et al.* 2019). Both FTIR and Raman spectroscopy produce spectra based on the interaction of light with the presumptive polymer molecules and are therefore non-destructive.

Raman spectroscopy provides a molecular fingerprint spectrum based on the polarizability of chemical bonds. It is not sensitive to humidity, but to fluorescence signals in the sample. Detergents used in sample preparation or mineral precipitates may also cause problems. Raman microscopy theoretically allows detection of microplastic particles as small as 1 µm; however, the practical limit is around 10 µm. The disadvantages are

the need to use special low background filters for mapping and the long measurement time required (Anger *et al.* 2018). A specific variant of Raman, Coherent Anti-Stokes Raman Scattering (CARS), allows detection of micrometre-sized plastic particles within small translucent animals such as zooplankton (Cole *et al.* 2013; Huser and Chan 2015).

FTIR produces infrared spectra resulting from the change in dipole moment. While transmission FTIR is only suitable for even and translucent particles, Attenuated Total Reflection (ATR-) FTIR allows the identification of irregular, thick and opaque plastic samples. Micro-FTIR provides high resolution (down to 20 μm) maps of samples on filters without preselection of particles (Harrison, Ojeda and Romero-González 2012; Löder *et al.* 2015).

It is highly recommended to subject a substantial fraction of the presumptive plastic particles to spectroscopy. The MSFD subgroup (Galgani *et al.* 2013) recommended analysing all particles in the size range of 20-100 μ m and at least 10 per cent of particles in the range of 100-5,000 μ m. However, subsequent extrapolation to the total particle number will produce considerable uncertainty with heterogeneous samples.

In addition, near-infrared spectroscopy (NIRS) and mid-infrared spectroscopy (MIRS) can be applied for polymer analyses, although they are not as widely used and tested for microplastics. MIRS has the capability to identify black plastic particles, which is not possible with NIRS (Becker, Sachsenheimer and Klemenz 2017). Both NIRS and MIRS have been successfully used in plastic degradation studies (Mulbry, Reeves and Millner 2012).

The specific configurations of both spectroscopic and thermoanalytical methods have different prerequisites with respect to sample characteristics, detection limits, measuring times, and the potential for additional information (summarized in Table 7.1, which is based on Braun *et al.* 2018 and Prata *et al.* 2019).

Chemical characterization of plastic polymers in environmental samples requires comparison with the reference databases of known polymers. The information provided by instrument manufacturers is often insufficient, and considerable time and expert knowledge are needed to process the raw data. Recently, freeware for quick microplastic identification based on FTIR spectra (Raman spectra in development) has been provided by Aalborg University, Denmark, in collaboration with the Alfred Wegener Institute in Germany (siMPle: Systematic Identification of MicroPLastics in the Environment, 2020). siMPle combines the interface of MPHunter with AWI Automatic Pipeline for MP analysis. Users are required to register before downloading the software and reference or sample databases (Figure 7.2.). Contact information for the developers is provided.

Alternative methods of polymer analyses listed by Prata *et al.* (2019) include characterizing the elemental composition of polymers by X-ray fluorescence spectrometry (Turner 2017). This approach may also detect some additives or adsorbed metals. Furthermore, scanning electron microscopy combined with an energy dispersive X-ray microanalyser has been used to collect information about the morphology and chemical composition of microplastics (Fries *et al.* 2013). Before this analysis, a pre-selection and mounting of particles is necessary.

-	•			•							
	Spectroscopic							Thermoanalytical			
	µRaman	CARS	μFTIR	FPA FTIR	µATR- FTIR	NIRS	MIRS	Pyr-GC-MS	Mod. Pyr- GC-MS	TED-GC-MS	DSC
Analyte mass	bn-bu	brl-bu	brl-bu	brl-bu	mg	mg		бл	mg	mg	mg
Maximum number of measurable particles per sample	10 ³ -10 ⁵		103-105	10 ³ -10 ⁵	F	undefined	undefined	-	undefined	undefined	undefined
Measuring time	p - q	٩	D	۲	min	min	min	Ч	٩	Ч	4
Detection level	1-10 µm	1-10 µm	20 µm	20 µm	25-50 µт	1%		< 1-0.5 µg	0.5-2.5 µg	0.5-2.5 µg	
Preparation for measurement	on special filter	on microscope slide	on special filter	on special filter	isolated particles	on filter		isolated particles	with or without filter	with or without filter	with or without filter
Destructive	Z	Z	z	z	z	z	Z	~	~	~	~
Additives detected	Pigments	z	z	z	z	z	z	~	Z	Z	Z
Particle size, shape, surface morphology detected	~	~	~	~	~		z	Z	z	Z	Z
Mass balances	Z	Z	z	z	z	z	Z	×	~	~	×
Specialties/ limitations		subcellular level					suitable for black particles				Only PE, PP

Table 7.1. Properties of analytical methods used to identify plastic polymers

Y = yes; N = no

Figure 7.2 Comparison of manual and automatic analysis of microplastics (from siMPle, https://simple-plastics.eu/).





FPA-μFT-IR-Imaging spectroscopy for MP analysis: First example of automatic pipeline (AWI)



8. Assessing sources, pathways and categories of plastics in freshwater bodies

This chapter provides examples of assessments of the movement of plastics through freshwater ecosystems. The categories of plastics typically found in freshwater systems are discussed, and several sampling methods presented in Chapter 5 are expanded upon by placing plastic transport in a catchment-scale context. There is also a discussion of factors determining sources, sinks and pathways of plastic contamination. Several examples are given of holistic approaches to the assessment of plastic transport on larger scales.

8.1 Categories of plastics in freshwater

8.1.1 Polymer types

Plastics come in many different polymer types, all of which have specific characteristics and applications. Table 8.1 summarizes the most common types and indicates their minimum and maximum density and main applications. The highest production plastics include PP (packaging), HDPE and LDPE (packaging), PS (packaging and other single-use items) and PVC (building and construction).

			· · · ·	
Polymer	Abbreviation	Density (g/cm ³)	Main application
		Min	Max	
Polyethylene	PE	0.91	0.97	packaging
Polypropylene	PP	0.9	0.91	many applications, but mainly packaging
Polyester	PES	1.24	2.3	textiles
Polyethylene terephthalate	PET	1.37	1.45	packaging
Polystyrene	PS	1.01	1.04	packaging
Expanded polystyrene	EPS	0.02	0.64	food packaging, construction material
Ethylene Vinyl Acetate	EVA	0.92	0.94	equipment for various sports
Alkyd	Al	1.67	2.1	paints, fibres
Polyvinyl chloride	PVC	1.16	1.58	building and construction
Polymethyl methacrylate	PMMA	1.17	1.2	electronics (e.g. touch screens)
Polyamide (nylon)	PA	1.02	1.05	automotive, textiles
Polyacrylonitrile	PAN	1.09	1.2	textiles
Polyvinyl alcohol	PVA, PVOH	1.19	1.31	textiles
Acrylonitrile butadiene styrene	ABS	1.06	1.08	electronics
Polyurethane	PUR	0.03	0.1	building and construction

Table 8.1. Common plastic polymer types and their density.

Plastics with densities higher than 1 g/cm³ are likely to sink in water. The percentages and most common products are calculated and assessed based on data from Schwarz et al. (2019), Borneman (2019) and PlasticsEurope (2019).

Identifying the composition of plastics in freshwater systems can provide valuable information about sources, travel paths, retention, potential sinks, consumer behaviour and waste management practices. From observations

in rivers to date, it can be seen that the composition of plastic contamination varies considerably among river systems. For example, in a study of the Saigon River, Viet Nam, the most abundant plastic polymer type was EPS (van Emmerik *et al.* 2018), which is mainly used for food boxes. In the Jakarta waterways, Indonesia, soft polyolefins (PS, LDPE and HDPE) were the types most often identified (van Emmerik *et al.* 2019a). Soft polyolefins are mainly used for plastic bags, foils and packaging. By comparing just these two river systems, some differences in sources and potential pathways can be identified. Low density EPS is mainly transported by means of natural drivers, such as wind and surface run-off. Soft polyolefins, on the other hand, are mainly transported after direct dumping, which may indicate less efficient waste management.

8.1.2 Size classes

Plastics are produced and found in many different size classes. They are generally identified as nanoplastics, microplastics, mesoplastics, macroplastics and megaplastics. Classifying plastics according to size yields valuable information on sources and sinks, as well as potential environmental impact. The exact definition of size categories varies in the literature. The definitions provided by GESAMP (2019) are used here (Table 8.2).

Size class	Common size
Nano	< 1 µm
Micro	1 μm-5 mm
Meso	5 mm-2.5 cm
Macro	2.5 cm-1 m
Mega	> 1 m

Table 8.2. Size categories of plastic litter

Note: Size refers to length along an item's longest axis.

The dimensions of plastic items and fragments can easily be determined using a gravelometer, which is designed to measure stone sizes (Figure 8.1).

Figure 8.1. Gravelometer



Photograph: Corinna Völkner, UFZ

8.1.3 Categorization protocols

Plastic litter is categorized in the field or in the lab. Field categorization is mainly carried out for mesoplastics or larger particles, as they can be identified by (a trained) eye. The benefit of categorization in the field is that no additional equipment is required, and data collection can be achieved more easily through citizen science initiatives. However, observer biases may exist, especially if participants are not well trained. Categorization of microplastics generally takes place in the lab, as additional equipment is required. Several examples of categorization protocols, for use in the field and the lab, are discussed below.

8.1.3.1 Field protocols

One of the most commonly used categorization protocols is the OSPAR beach litter classification guideline (OSPAR 2010). Beach stretches of either 100 m (all litter) or 1 km (only litter > 1.5 cm) are selected, and all litter (plastic and non-plastic) is categorized. There are 121 pre-defined item categories, including both plastic and non-plastic items. Recently this protocol was adapted for riverbank monitoring in Dutch rivers (van Emmerik *et al.* 2020). In that case only 100 m stretches are analysed, from the river edge to the upper side of the riverbank. All litter items are collected and classified in the field by citizen scientists.

Several other studies use similar, although less extensive, categorization protocols. This is mainly to make data collection easier for citizen scientists. For example, Kiessling *et al.* (2019) categorized plastic waste on the banks of nearly all major German rivers with the help of over 5,500 schoolchildren. Litter was categorized as plastic, metal, glass, food and other.

Rech *et al.* (2014) separated litter plastic based on buoyancy. Riverbank and floating items were classified as persistent buoyant (plastics, polystyrene and wood), short-time buoyant (cigarette butts, paper, carton, textile, rubber and other) and non-buoyant (concrete, pottery, glass and metal). A similar classification scheme can be adapted for plastics only.

For floating macroplastics, van Emmerik *et al.* (2018) and van Emmerik *et al.* (2019a) have proposed a categorization protocol with seven categories: PET (transparent plastic bottles), PS (products that contain consumables such as plates, cutlery and cups), EPS (foam objects such as lunch boxes and meat trays), PO_{hard} (bottle caps, containers and rigid plastics), PO_{soft} (bags, foils and wrappings), Multilayer (packaging with multiple layers) and Rest (all other objects that do not belong to one of the other categories). This protocol allows fast processing of samples and still quantifies the main plastic categories.

8.1.3.2 Lab protocols

Two of the most common techniques used to categorize plastic polymers in the lab are FTIR-ATR and Raman spectrometry (see also Chapter 7). FTIR-ATR (Fourier-transform infrared spectrometer with Attenuated Total Reflectance accessory) uses infrared reflectance spectrum to determine the molecular composition of the sampled material. Examples include the categorization of plastic polymer types in the Seine by Gasperi *et al.* (2014). Raman spectrometry is similar to FTIR-ATR. Rather than looking at the adsorption of infrared light, however, it measures the Raman scattering (inelastic scattering of monochromatic light). Examples include the categorization of microplastics in sediments in the Thames by Horton *et al.* (2017) and detection of microplastics in mineral water (Schymanski *et al.* 2018).

8.2 Linking plastic contamination to catchment attributes

The movement of plastic through the natural environment is driven by hydrometeorological, topographical and anthropogenic factors. Sources of plastic contamination are strongly associated with human activity. Plastic loads in rivers have been found to show high correlations with, for example, population density, urbanization, wastewater treatment and waste management practices (Best 2019). Common sources include wastewater treatment plants, landfills, densely populated urban areas, and recreational areas along lakes and rivers.

Several efforts have been made to construct a globally distributed estimate of plastic leakage into the natural environment. A recent study used available data on municipal solid waste generation and mismanaged waste fraction from the Waste Atlas (an interactive map with visualized waste management data) to provide a global mismanaged waste estimate with ~ 1 km² resolution (Lebreton and Andrady 2019). Several studies have also identified clear point sources of direct dumping of plastic waste in river systems in Chile (Rech *et al.* 2015), Romania (Mihai 2018) and Germany (Kiessling *et al.* 2019).

Once plastic is in the natural environment or has accumulated in landfills, it is transported over land into lakes and rivers owing to several natural factors. Wind speed/direction has been suggested as a main driver of plastic transport on land (e.g. Windsor *et al.* 2019), although fundamental studies or observational data confirming this is still lacking. Plastic transport has also been found to increase in response to rainfall events (e.g. Bruge *et al.* 2018; Castro-Jiménez *et al.* 2019; Tramoy *et al.* 2019). Additional plastics may enter a freshwater system through increased surface run-off, especially in urban areas, or combined sewer overflow as a result of heavy rainfall.

Within river systems, plastic transport is mainly influenced by hydrological factors such as water level, flow velocity and river discharge. Positive relations between plastic transport and river discharge have been found in the Los Angeles River basin in the State of California (United States) (Moore, Lattin and Zellers 2011) and the Rhône River in France (Castro-Jiménez *et al.* 2019). Increased water levels may remobilize plastics that have accumulated on riverbanks and in riparian zones. Flow velocity determines transport rate and strongly influences horizontal distribution across a river's width (van Emmerik *et al.* 2018; van Emmerik *et al.* 2019a). Plastic transport is often obstructed by human activities such as shipping and by hydraulic infrastructure. For example, dams and urban trash receptacles act as accumulation zones for larger plastic items (Lebreton *et al.* 2017; Honingh *et al.* 2020).

Riverbanks, riparian vegetation, sediments and oceans are typical sinks of freshwater plastics. Due to water level variations, plastics (temporarily) accumulate on riverbanks. This may lead to daily and monthly depositions driven by the tide, with additional depositions due to extreme hydrological events. The latter also transport plastic items in riparian vegetation along a river. Plastic accumulates in sediments, which can be caused by its density or biofouling. The duration of plastic retention in sediments depends on shape size and density, as well as hydrological factors such as flow velocity. It has been demonstrated that the 2015 floods in the United Kingdom decreased sediment plastic concentration by 70 per cent (Hurley *et al.* 2018).

Large amounts of plastic are transported into the oceans. Many recent studies, using conceptual models, statistical models and/or measurements, have focused on estimating riverine plastic export. The best place to measure is in estuaries, where the river is connected to an ocean. However, most available quantification

methods are not well suited to quantify plastic transport in such areas. Only a few studies have focused on quantifying plastics in estuaries (e.g. Sadri and Thompson 2014). These studies have not estimated actual transport from the estuary to the ocean.

Box C. Examples of catchment-scale assessments

The Ebro River, Spain

The Mediterranean Sea is characterized by high accumulation of plastic. As it has been suggested that rivers are among the main sources of marine plastic contamination, the contribution of the Ebro River was assessed by Simon-Sánchez *et al.* (2019). To assess microplastic transport in the Ebro, three components of the ecosystem were sampled: beaches, benthic sediments, and surface waters in the river. By comparing microplastic concentrations and categories, it was found that the river acted as an efficient pathway for microplastics from land into the sea. Besides the sea, estuarine sediments were found to be important sinks of microplastics.

The Irwell and Mersey catchments, United Kingdom

Hurley *et al.* (2018) presented a catchment-scale assessment of microplastic transport. Forty locations on ten rivers in the upper Mersey and Irwell catchments in the Greater Manchester region were sampled before and after floods in 2015/16. At each location riverbed sediment was sampled and the total mass and amount of microplastics were determined. As a result of the floods, approximately 70 per cent of the microplastics stored in the riverbeds (0.85 metric tons, 14 billion particles) were flushed out of the catchment. This study emphasizes the importance of catchment-scale assessments, which increase understanding of how plastics travel from source to sink.

The Seine River, France

Plastic contamination in the Seine has been studied extensively (e.g. Gasperi *et al.* 2014; Dris *et al.* 2015; van Emmerik *et al.* 2019c). Tramoy *et al.* (2019) used a catchment-scale statistical approach to estimate total plastic emissions from the Seine into the Atlantic Ocean. First, a conceptual model was formulated for the pathway of plastic (waste production per capita – plastic rate of waste – leakage into the environment – fraction emitted). Second, data were obtained to estimate total annual plastic emissions. Data were collected from floating booms (Gasperi *et al.* 2014) and from published work (e.g. Jambeck *et al.* 2015). Total emissions of 1,100-5,900 metric tons per year were estimated, although it was emphasized that this estimate came with several uncertainties. Such a catchment-wide framework suggests specific directions for future research to quantify both land and riverine transport of plastic contamination.

The Adour River, France

Bruge et al. (2018) monitored litter in the Adour catchment for three years. Sampling was done at eight locations, from the river mouth to almost 300 km upstream. The samples were taken from riverbanks and riparian vegetation. It was found that 94 per cent of sampled litter items were plastic, with food and beverage packaging the most abundant categories. The system-scale approach demonstrated that litter composition at the beach varied considerably compared to inland sampling locations. It was also found that litter density increased from five items per 100 m² at the location furthest upstream (300 km) to 40-50 items per 100 m² at the one furthest downstream. Information about spatial variation in plastic density, transport and polymer type provide additional insights into the sources and sinks of plastic contamination.

9. Relationship between plastic contamination and other forms of dissolved and particulate contamination

9.1 Overview of contaminants

Contaminants, from either a natural source or anthropogenic activity, cause a range of problems in freshwater systems. The contaminants found there are typically categorized as 1) organic contaminants, 2) pathogens, 3) nutrients and agricultural run-off, 4) suspended solids and sediments (organic and inorganic), 5) Inorganic contaminants (salts and metals), 6) thermal contaminants of ar, although science-based initiatives in this regard are under way (e.g. Rochman 2013).

Most contaminants that interact with plastics are either organic or inorganic compounds. Increasing attention is being given to interactions with other emerging contaminants (i.e. nanomaterials and pharmaceutical waste).

9.1.1 Organic contaminants

Persistent organic pollutants (POPs) are carbon-based toxic compounds that do not break down easily in the environment. They remain intact, persisting long enough to bioaccumulate in the fat tissue of humans and animals. POPs enter freshwater systems through the discharge of municipal and industrial wastewater, through agricultural effluents, and from non-point source contamination.

9.1.2 Inorganic contaminants

Similarly, inorganic chemicals including heavy metals find their way into freshwater from municipal and industrial wastewater, mining operations and urban run-off. Inorganic contaminants (typically arsenic [As], calcium [Ca], cadmium [Cd], iron [Fe], mercury [Hg], sodium [Na], lead [Pb] and their compounds) in dangerous concentrations can harm or kill aquatic life and make water unfit for municipal or industrial applications.

9.1.3 Nanocontamination

Nanocontamination refers to particulate contaminants 1-100 nanometres (nm) in size with special properties such as a high surface area to volume ratio. Nanoparticles are a very large and growing class of contaminants originating from both natural (e.g. forest fires, volcanic eruptions) and artificial sources. They can be organic or inorganic (Naghdi *et al.* 2017). Like traditional contaminants, nanoparticles are unintentionally released into natural water during their production or through a waste stream. Some are considered toxic to freshwater ecosystems. For example, silver nanoparticles dissolved in water release silver ions which act as an antibiotic, destroying critical bacterial populations, while the photocatalyst nanomaterial titanium dioxide (TiO_2) can accelerate chemical reactions in water. Naghdi *et al.* (2017) present an overview of nanoparticles in the natural environment and associated measurement techniques.

9.1.4 Pharmaceutical contamination

Pharmaceutical contamination originates from prescription and over-the-counter medications including antibiotics, painkillers and antidepressants. A main pathway into freshwater systems is discharges from wastewater treatment plants, which are often inefficient at removing these products. Other pathways include direct releases from drug manufacturing, human and animal excretion, uncontrolled disposal of expired or unused medicines, animal husbandry and aquaculture (WHO 2012). While observed concentrations of pharmaceuticals in drinking water have been reported to be several orders of magnitude below the therapeutic dose (which means they likely present a negligible risk to human health), knowledge gaps exist. They include the assessment of risks to human health associated with long-term exposure to low concentrations of pharmaceuticals, as well as the possible combined effects of pharmaceutical mixtures (WHO 2012). However, many studies have looked at the effects of aquatic organisms' exposure to pharmaceutical contaminants. For example, Aliko *et al.* (2019) report changes in the nervous system of goldfish such as stressed behaviour and hyperactivity.

9.2 Plastics interaction with contaminants

Plastic contamination (macro- to nanoscale) may interact with other freshwater contaminants through varying mechanisms. Two general modes are recognized and discussed in this chapter: contaminants as 1) residual monomers or additives in plastic (during manufacturing), and as 2) sorbates on plastic waste (usually microplastics) (Figure 9.1).

9.2.1 Contaminants as non-polymerized free monomers

Non-polymerized free monomers are a type of organic contaminant that results from (or is a residue of) plastic production. Caused by residual monomers being "trapped" in the bulk material and remaining unpolymerized, they are considered possible organic contaminants because their low molecular weight allows them to easily mobilize away from the bulk polymer product and transfer to their surroundings. Most concerns about released toxic monomers have been related to human exposure via food packaging, particularly vinyl chloride as part of polyvinyl chloride (PVC) products and styrene as part of polystyrene products (Hahladakis *et al.* 2018).





9.2.2 Additives as plastic contaminants

One type of interaction occurs when the contaminant is already found in virgin plastic as a result of the manufacturing process. Although plastic is structurally based on polymer chains, almost all commercial plastics contain some amount of non-polymeric ingredients used to impart specific properties such as UV resistance, pliability, hardness and colour (Table 9.1). Some of these additives (e.g. polychlorinated biphenyls [PCBs] and mirex) are considered toxic and are on the Stockholm Convention's list of POPs. Note that the Stockholm Convention lists the 12 original POPs, POPs which have been added to the list, and POPs recommended for listing (Stockholm Convention 2019).

Plasticizers, often in the form of phthalates, are commonly incorporated in plastics since they increase flexibility to prevent shattering, although they are considered dangerous to human and animal development, with the most notable effects being those on reproductive health (Oehlmann *et al.* 2009; Talsness *et al.* 2009). A study ranking the hazard level of different polymers determined one type of PVC polymer to be the fifth most hazardous (out of 55) due to its plasticizer additive (Lithner, Larsson and Dave 2011). Similarly, flame retardants such as polybrominated diphenyl ethers (PBDEs) are a class of potentially toxic additives that have been shown to act as endocrine disrupters as well as being carcinogenic and neurotoxic (Darnerud 2003; Birnbaum and Staskal 2004). Other additives (heat stabilizers and slip agents) have been shown to contain trace metals, cadmium, zinc and lead (Munier and Bendell 2018).

The fact that potentially toxic compounds already exist within the chemical makeup of the plastic presents two pathways for exposure. This first is that as plastic breaks down into microplastics, it is more likely to be ingested by organisms and enter the food chain. For example, microplastics were observed in the gills, stomach and hepatopancreas of the fiddler crab following two-month exposure to fragments derived from polystyrene pellets (Brennecke *et al.* 2015). Browne *et al.* (2008) demonstrated experimentally that a species of mussel, *Mytilus edulis*, can ingest different sized plastic fragments that reside in their body (gut and circulatory system) for over 48 days. Overall, Gallo *et al.* (2018) reported that exposure to microplastics via different mechanisms has been demonstrated in more than 100 marine species ranging from zooplankton to whales. In the freshwater environment, although much less researched than marine species, biological impacts of microplastics have been observed in organisms such as zooplankton, crustaceans and mussels (Lambert and Wagner 2018). While freshwater invertebrates are considered more vulnerable to microplastics, vertebrate species (e.g. zebrafish and African catfish) have experienced considerable interaction risks such as ingestion, dermal uptake and chemical impacts (Scherer *et al.* 2018).

The other exposure route is through leaching of the contaminant from the plastic into the surrounding aquatic environment. Although most marine-based studies suggest that the primary threat to human and animal health is through actual plastic ingestion, evidence suggests that chemical transfer can occur via dissolved constituents in seawater (Hermabessiere *et al.* 2017). Plastic additives have a low molecular weight (Lithner, Larsson, and Dave 2011) and are not chemically bonded to the polymer (Gewert, Plassmann and MacLeod 2015). These additives have already been detected in the marine environment as a result of degradation of plastic waste in the ocean (Hermabessiere *et al.* 2017). However, understanding and forecasting the potential hazard of released or leached additives is a challenge, as the mechanism is dependent on a number of factors including type of plastic and ambient conditions (e.g. temperature, sunlight, oxygen level) (Gewert, Plassmann and MacLeod 2015). In the freshwater environment capturing the effects of chemicals leaching from plastic is difficult (Lambert and Wagner 2018). Not only is it much less observed compared with the marine environment, but most reported studies are performed in the laboratory under exaggerated toxic conditions. For example Lithner, Nordensvan

and Dave (2012) looked at the effects of leachates from different polymer types on the freshwater species *Daphnia magna* and Bejgarn *et al.* (2015) examined the effects on the copepod *Nitocra spinipes*.

A number of studies illustrate the potential for toxic leachates to form from degrading plastic. For example, it was found that based on differing simulated weathering intensities/duration of assorted polymers, incidents of toxic leachates from a few different polymer types occured (Bejgarn *et al.* 2015). Another study looked at the effect of hydrophobicity (level of water solubility) on the formation of leachates as measured by larval survival and settlement of a barnacle species in seawater (Li *et al.* 2016). It has also been recognized that plastic waste in a landfill can produce dangerous leachates that eventually leak into local freshwater sources (Teuten *et al.* 2009). One study showed that the toxicity levels of two plastic sacks due to leaching differed based on the manufacturers' ingredients. This demonstrates that a wide diversity of chemicals are used by different plastic manufacturers even if the goal is to produce the same polymer (Hamlin, Marciano and Downs 2015).

Once contaminant compounds migrate and leach from the polymer source into the surrounding medium, they have the potential to be taken up by other organisms or adsorb onto other particles, including other available plastics.

9.2.3 Contaminants as adsorbates to plastic

Another mechanism is the adsorption (attachment) of contaminant compounds from the surrounding water to the plastic. Adsorption occurs because of the hydrophobicity of certain POPs and toxic metals (e.g. lead, cadmium, chromium and copper), which allows contaminants to more easily attract and adhere to other nonpolar materials such as plastics and fatty material. There are a number of published hydrophobic ratings for certain plastic additives and organic contaminants in the form of the octanol-water partitioning coefficient (log k_{ow}), which illustrates the likelihood of certain compounds to adsorb to plastic compared with others. In comparison with other surrounding media, hydrophobic compounds can accumulate on plastic debris at greater concentrations than in the surrounding water, sediment and suspended particles (Mato *et al.* 2001; Ogata *et al.* 2009, Teuten *et al.* 2009).

Plastics can adsorb contaminants primarily as a function of the concentration gradient, as it dictates the ease at which plastics can adsorb other compounds (Koelmans *et al.* 2013). Secondary drivers of the sorption of chemicals to plastics are not only factors relating to the surrounding aquatic environment such as temperature, pH, and salinity (Engler 2012), but also the physical state of the plastic. For example, when plastic undergoes weathering and/or degradation, the surface area to volume ratio of the plastic tends to increase, which supports an accumulation of dissolved contaminants (Rochman 2013).

As plastics have the potential to adsorb contaminants from their surrounding environment, the contaminant could be considered, for the time being, as removed from the system. For example, research by Rochman, Hentschel and Teh (2014) found long-term sorption of the metals zinc, cadmium and lead on different polymers such as PET, HDPE, PVC, LDPE and PP. Similarly, using a weak acid extraction method, Munier and Bendell (2018) found that copper and lead were detected as adsorbed metals on sampled plastic debris, primarily PVC plastic. Mato *et al.* (2001) found high concentrations of PCBs adsorbed to plastic pellets in seawater.

Plastics carrying adsorbed contaminants are known to play a role in transferring contaminants to organisms or other parts of the environment. For example, in an experiment with the peppery furrow shell clam not only did digested microplastics lead to mechanical injury of the gills, but when the microplastics had adsorbed contaminants (benzo(a)pyrene [BaP] and perfluorooctane), a negative influence over the assessed biomarkers was observed in their tissue (O'Donovan *et al.* 2018). Similar studies have documented toxicity levels and signs of bioaccumulation in marine mussels (Avio *et al.* 2015), Japanese medaka fish (Rochman 2013), and the lugworm *Arenicola marina* (L.) (Besseling *et al.* 2013), to name a few, when they were exposed to microplastics (such as polystyrene or polyethylene) that had some degree of adsorbed organic contaminants such as PCBs or polyaromatic hydrocarbons.

Microplastics have also been shown to interact with inorganic contaminants. For example, it was found that because different types of plastics are able to adsorb chromium over time, ingestion of these kinds of contaminated microplastics by marine organisms (in this study, the common goby) can induce toxic effects such as reduced predatory performance (Luís *et al.* 2015). Another recent study showed changed bioaccumulation rates in European seabass fish species due to exposure to mercury-adsorbed microplastic (Barboza *et al.* 2018).

It should be noted that the majority of observations documenting the role of microplastics as a contaminant carrier to aquatic organisms have been done in the marine ecosystem. Scherer *et al.* (2018) caution that the mechanism is likely to be different in freshwater, where the flux of chemicals (from wastewater streams) is relatively continuous, the abiotic conditions are different and the source of plastic contamination is "younger". Moreover, the generally higher concentrations of natural fine particles (turbidity) and of dissolved organic carbon in freshwater are likely to influence the interactions between microplastics and contaminants.

The presence of microplastics with other contaminants does not always indicate an increased risk of toxic exposure. Scherer *et al.* (2018) warn against assuming the "vector hypothesis" which characterizes microplastics as a simple transporter of waterborne contaminants to aquatic organisms. In reality, adsorption-desorption kinetics are much more complicated. Based on a number of factors such as microplastic concentration levels and aquatic species, negligible effects of bioaccumulation levels have been observed (Scherer *et al.* 2018). For example, it was found that there was no significant effect from bioaccumulation of bisphenol A (BPA) in freshwater zooplankton experimentally exposed to BPA-adsorbed polyamide microparticles (Rehse, Kloas and Zarfl 2018).

9.2.4 Contaminants mixed with plastic

In addition to observing toxicity levels for mixtures of microplastics with expected organic and metal contaminants, the influence of microplastics' interaction with emerging contaminants such as pharmaceuticals and nanocontaminants has been considered. Moreover, it is suspected that the interaction of plastics with other contaminants, referred to by Rochman (2013) as a "cocktail of contaminants", in the aquatic environment may lead to effects beyond what would occur as a result of a contaminant alone. In an experimental study by Ferreira *et al.* (2016) despite the common goby fish being exposed to a combination of gold nanoparticles, microplastics and temperature increase, observed metal toxicity did not change as a function of microplastics. In another study the effects of polyethylene microbeads mixed with triclosan (an antibacterial agent) on the marine copepod *Acartia tonsa* indicated that the microbeads increased the toxicity of triclosan (Syberg *et al.* 2017). Similarly, a study by Prata *et al.* (2018) found that when the pharmaceuticals procainamide and doxycycline were mixed with microplastics, the toxic effect on marine microalgae (as measured by chlorophyll concentrations and growth rate) was stronger than the effect of pharmaceuticals alone.
It should be noted that another possible mode of contaminant interaction occurs when plastic contamination, in the form of microplastics or nanoplastics, becomes integrated into the particulate or bed load of a freshwater system. Microplastics can then serve as carriers of adsorbed contaminants, metals, and pathogenic microorganisms and parasites. Microplastics have serious implications with respect to the role of wastewater treatment plants, which raises questions about their treatment processes and the quality of the effluent using current practices (Mason *et al.* 2016; Ziajahromi, Neale and Leusch 2016). For further information, see Chapter 5.5.

 Table 9.1. List of plastic additives by category (Hahladakis et al. 2018). Those of most concern are italicized

(Hermabessiere et al. 2017)

Category	Type of Additive
Functional	UV stabilizers antioxidant stabilizers (nonylphenol) heat stabilizers antistatic agents flame retardants (brominated flame retardants) plasticizers (phthalates) lubricants slip agents lubricants curing agents blowing agents blowing agents biocides
Colourant	pigments soluble azo dyes
Fillers	mica talc clay calcium carbonate barium sulphate
Reinforcement	glass fibres carbon fibres

10. Stakeholder feedback on existing monitoring and assessment activities in freshwater systems

These guidelines for harmonization of monitoring methodologies for plastics in rivers and lakes follow a *solution-oriented approach*, by providing guidelines for both the actual monitoring and its implementation. Implementation of water monitoring guidelines typically depend on countries' goals and capacities with respect to water quality monitoring (Kirschke *et al.* 2020). However, plastic monitoring is a rather new topic in the field of water quality monitoring and little information on the applicability of guidelines is available (Mathews and Stretz 2019). Against this background, an activity on the involvement of stakeholders in developing recommendations for plastic monitoring was organized (Figure 10.1). This included obtaining an initial understanding of the stakeholder landscape through a rough analysis, as well as better understanding of the goals and capacities of plastic monitoring through the design and circulation of a survey of stakeholders and a qualitative feedback process using virtual workshops. This chapter briefly presents details of each step, as well as findings from this process.

Figure 10.1. Three consecutive steps in stakeholder involvement



10.1 Stakeholder analysis

The goal of this first step was to obtain an overall understanding of relevant stakeholders in the field of plastic monitoring. First, general categories of potential stakeholder groups in the field of monitoring plastics were established based on conceptual knowledge of typical stakeholder categories in the field. Second, specific stakeholders in these categories were identified based on a snowballing technique. Respective sources included grey literature, scientific literature, and discussions with peers.

Special emphasis was given to four countries that represent different levels of human development according to the Human Development Index (HDI) (United Nations Development Programme 2020). The HDI was used as it was assumed that the level of human development affects capacities (e.g. human, financial and technical) for water quality monitoring. The countries chosen were Germany (0.936, very high HDI), Colombia (0.747, high HDI), Indonesia (0.694, medium HDI) and Nigeria (0.532, low HDI).

About 260 stakeholders with a direct relation to plastic monitoring in freshwater were identified. They were categorized as belonging to one of three main stakeholder groups or sectors: the public sector, the private sector and civil society. Within these categories different sub-groups of actors were identified, based on their scale of operation and functions in the monitoring process (Table 10.1). While these organizations are assumed to involve both genders, no gender-specific information was gathered throughout the stakeholder analysis, which focused on the institutional rather than the individual level.

In the public sector, international actors were identified (e.g. international organizations supporting knowledge exchange, river and dam commissions supporting in-depth monitoring, financial institutions providing financial support to monitoring activities), as well as local, regional and national authorities responsible for freshwater monitoring. The relevancy of waste management agencies and water providers was acknowledged with respect to the pathways of plastics into aquatic environments.

In the private sector, waste management companies and water providers were identified as stakeholder groups in regard to the pathways of plastics into aquatic environments. Agricultural companies and fisheries were also identified as stakeholders in view of the impact plastics may have on food production. In addition, environmental monitoring companies can provide technical know-how for plastics monitoring.

In civil society, scientific societies and institutes account for research projects conducted on plastic monitoring in freshwater. Moreover, civil society in general (including, for example, non-governmental organizations and citizen science activities) was identified as a stakeholder sub-type to account for the public voice in water quality monitoring. Concerning citizen science activities, local fishers or residents of polluted areas may be particularly important in that they are directly affected by plastic contamination and may be interested in sharing their perceptions of plastics in the basin.

Main types	Sub-types	Function in the monitoring process
Public sector	international actors such as organizations, commissions and financial institutions	supporting knowledge exchange and in-depth monitoring, giving financial support
	local, regional and national authorities	performing freshwater monitoring
	waste management agencies and water providers	performing plastic monitoring to ensure the quality of their service
Private sector	waste management companies and water providers	performing plastic monitoring to ensure the quality of their service
	agricultural companies and fisheries	performing plastic monitoring to ensure the quality of their product
	environmental monitoring companies	providing technical know-how on plastics monitoring
Civil society	scientific societies and institutes	research on plastic monitoring in freshwater
	NGOs and citizen science projects	raising awareness, gathering data on plastics in freshwater and addressing contamination through various activities, raise awareness of gender-related effects

Table 10.1. Stakeholders in freshwater monitoring and their functions

10.2 Survey of stakeholders

The survey "Monitoring Plastics in Freshwater Systems" assessed plastic monitoring practices in freshwater systems globally. The survey consisted of 13 questions about 1) the identity of stakeholders, 2) the relevant monitoring case, 3) current and future monitoring practices, and 4) limitations. The survey was circulated in July and September 2019 to 260 stakeholders identified in the stakeholder analysis and an indefinite number of other stakeholders who were reached by means of snowballing. Out of 129 stakeholders who viewed the survey, 53 started to answer it and 24 completed it.

The 24 respondents mainly came from the public sector (75 per cent). Only a limited number belonged to the private sector (17 per cent) or civil society (8 per cent). Levels of experience ranged from no experience in plastic monitoring (29 per cent), less than three years (42 per cent), four to six years (25 per cent), and up to more than seven years of experience (4 per cent). Roles in plastic monitoring differed, with most respondents responsible for designing monitoring programmes (14 respondents), data collection (nine respondents), and education (eight respondents). A smaller number of participants indicated they had roles in coordination (two respondents), financing, citizen observation and advocacy, and spatial modelling. Of these respondents, 6 (26 per cent) were female and 18 (74 per cent) were male.

In terms of the scale of the monitoring case, respondents mostly referred to a (sub-) national level (19 respondents). A smaller number also indicated the international level (involving at least two countries) to be relevant (five respondents). With respect to the countries, most answers referred to countries with a very high HDI level (54 per cent; Austria, France, Hungary, Lithuania, Norway, Poland, the United Kingdom and the United States). A smaller number referred to countries with a high HDI (8 per cent; Colombia), a medium HDI (21 per cent; Indonesia, Bangladesh, and Cambodia) and a low HDI (17 per cent, Nigeria). All respondents mentioned rivers (24 respondents), but lakes (10 respondents), estuaries (seven respondents), and reservoirs (four respondents) were also cited as water bodies of interest in plastic monitoring. Whereas very high and high HDI countries indicated that all types of water bodies (rivers, lakes, estuaries, and reservoirs) were of interest, medium and low HDI countries mainly focused on river water bodies and mentioned only a limited number of lakes and estuaries.

Respondents were asked about driving factors for water quality monitoring, based on five types of beneficial uses as described in the United States Clean Water Act (United States Environmental Protection Agency 2020): recreation in and on the water (referring to tourism), public water supply (referring to drinking water provision), agricultural use (referring to cultivation of crops for food and energy supply), propagation of fish, shellfish and wildlife (referring to fishing and biodiversity), and industrial use (referring to production of various goods). In addition, there was an open answer category. An attempt was made to determine the relevance of driving factors based on a 1-4 scale, with 1 indicating low relevance and 4 indicating high relevance. The results show that all driving factors were considered to be of relevance, but in different degrees, with rather high relevance for the propagation of fish, shellfish and wildlife (average = 2.78) and slightly lower relevance for public water supplies (average = 2.49), recreation in and on the water (average = 2.48), industrial uses (average = 2.27), agricultural uses (average = 2.11) and other factors (average = 2.19) across all respondents. Moreover, there were some differences between very high and high HDI countries and medium and lower HDI countries. While the propagation of fish, shellfish and wildlife was perceived as a relevant driver in all countries, lower HDI countries put more emphasis on different driving factors, especially agriculture (Figure 10.2).

Figure 10.2. Reasons for plastic monitoring in freshwaters



The survey also asked which legal frameworks in the field of waste and wastewater management were relevant in specific cases. About one-third of respondents mentioned a specific framework (eight respondents; e.g. the European Water Framework Directive [2000/60/EC], Indonesia's Presidential Decree No 83/2018, and the Safe Drinking Water Act and the Clean Water Act in the United States). Around one-third mentioned that other frameworks were of relevance, without any further specification (seven respondents), while one-third indicated there was no framework of relevance (seven respondents).

In terms of current and future monitoring practices, the survey asked about the compartment where plastic was monitored or was planned to be monitored, with options provided for the water surface (floating plastics), the water column (suspended plastics), the shoreline (washed up plastics), biota (ingested plastics) and sediments (precipitated plastics), along with an open answer category. The survey also asked about the means of monitoring (visual assessment, sampling, and laboratory analysis) and regularity (one time only, or regularly) in terms of all compartments.

The results show that all compartments are relevant in current and future monitoring, although there are differences in the methodologies used and the regularity of monitoring. Concerning the methodologies used, the results show a slight change in the roles of visual assessment, sampling and laboratory analysis over time, with an expected slight decrease in importance for visual assessment and an expected slight increase for sampling and laboratory analysis (Figure 10.3). In regard to regularity of sampling, the differences between current and future monitoring are particularly striking. While there are a limited number of one-time-only and regular samplings in all compartments, respondents are planning more regular sampling in all compartments in the future (Figure 10.4).





Figure 10.4. Current and future regularity of plastics monitoring in freshwater



The survey also asked about potential limiting factors, namely the existence of relevant legal frameworks for monitoring plastics (as part of waste or wastewater management), relevant monitoring guidelines, clear responsibilities, financial resources (e.g. for instruments, human resources), human resources (e.g. recruiting of people educated in monitoring techniques) and technical equipment (e.g. buckets, chemical reagents), together with other limitations. The degree of limitations could be presented on a 1-4 scale, with 1 indicating no limitations and 4 strong limitations. The results demonstrate that all factors are perceived to limit the monitoring of plastics in freshwater. However, the degree of limitation varies between very high and high HDI countries and medium and lower HDI countries. While legal frameworks, monitoring guidelines, clear responsibilities and financial resources are similarly relevant in both higher and lower HDI countries, lower HDI countries in particular emphasize the lack of technical equipment and human resources (Figure 10.5). These results provide a broad picture of limitations, but additional challenges seem relevant, such as gender-specific restrictions to monitoring, among others.





In an open answer category, respondents emphasized that mismanaged solid waste is a main cause of plastic contamination in freshwater. In addition, monitoring plastics in freshwater would be needed to complement plastic monitoring in marine environments. To address this problem, legal frameworks and, in particular, common methodological standards would be required.

Summing up, all 24 respondents reported that they were involved in projects that addressed plastic monitoring in freshwaters. They also expressed a clear willingness to perform more regular measurements of plastics in freshwater in the future. However, there were some differences between higher and lower HDI countries with respect to the drivers and limitations of plastic monitoring. Whereas both higher and lower HDI countries understand the propagation of fish, shellfish and wildlife to be a main driving factor for monitoring, medium and lower HDI countries also emphasize agricultural uses and water provision. In regard to limitations, both higher and lower HDI countries mentioned the importance of clear responsibilities. However, low and medium HDI countries underline lack of technical equipment while higher HDI countries emphasize lack of financial resources.

10.3 Qualitative feedback at workshops

In addition to the survey feedback process, there was an effort to obtain more in-depth feedback on plastic monitoring practices: What are the main challenges in plastic monitoring and how can they be overcome? To receive such in-depth feedback, two virtual workshops with participants from Colombia, Hungary, Indonesia, Nigeria and the United States took place on 27 and 28 August 2019, consisting of 6 (46 per cent) women and 7 (54 per cent) men, including the project team. The discussions touched on challenges in the countries' implementation of guidelines on harmonizing methodologies for monitoring plastic in freshwater environments. The following reflects some major implementation-related points made during the discussions.

10.3.1 Source of contamination

Participants emphasized that plastic contamination in freshwater environments mostly has land-based sources. One of these is *mismanaged solid waste*. Efforts to prevent further plastic contamination in freshwater must therefore include the improvement of waste management systems (e.g. by closing open/illegal dumpsites or introducing recycling systems). Another reason for the occurrence of plastic debris in freshwater is *relocation of solid waste after climatic events* such as heavy rainfall, floods and storms. Areas with poor solid waste management appear to be especially vulnerable in this regard. There is a clear need for guidance on how to prevent or remediate the flux of plastics into freshwater caused by climatic events.

10.3.2 International cause vs. local implementation

Pointing out the sources of plastic contamination in aquatic systems led to a discussion on the scope of the problem and its solution. Plastic problems and solutions are often found at a local level. However, the international level was highlighted in particular. Examples of problems at this level are the export of solid waste from developed to developing countries (which often have less sophisticated waste management systems) and the transboundary transport of plastic debris that enters freshwater in one country and ends up in that of another. International initiatives to monitor plastics in freshwater can be part of the solution to these problems. An international network to exchange collected data and share experience in monitoring plastic in freshwaters was considered to be of value not only as a way to iteratively optimize method standardization and create thresholds for plastic contamination in the future, but also as an incentive for national and local governments to take action in this field.

10.3.3 General relevance vs. prioritizing monitoring methods

Generally, the guidelines are perceived as being very timely and important in helping to approach the topic of monitoring plastics in freshwaters. However, participants also highlighted that there is no perfect method. The role of methods depends on the context (e.g. the goals of the monitoring process, human and financial resources, technical equipment). In addition, there are always trade-offs between different methodologies. Methodologies for monitoring should be based on goals and resources in countries.

10.3.4 A vicious cycle: from data to legal frameworks, or from legal frameworks to data?

In accordance with the results of the stakeholder survey, the workshop participants agreed that specific legal frameworks on plastics (particularly microplastic contamination) are needed to encourage implementation of

monitoring systems to measure plastics in freshwater. Since there are as yet no clear data on the negative impacts of plastics in aquatic ecosystems, the political will of governments to act in terms of legal frameworks or funding remains relatively low. Dissemination of information and communications among different types of actors may help to break through this vicious cycle.

10.3.5 Governance strategies

Governance strategies to address plastic contamination in freshwater were discussed. The focus was mainly on three strategies to address plastic waste: economic incentives (e.g. deposit systems for plastic bottles); information campaigns (e.g. on the quality of potable water, in order to reduce the amount of plastic water bottles); and rules and regulations (e.g. banning certain types of plastics). Specific combinations of such governance strategies may be considered when specific problems are addressed.

10.3.6 Summary of workshop feedback

The discussions during the virtual workshops showed that developing and developed countries face similar difficulties with the implementation of monitoring programmes for plastics in freshwater environments. However, the type and intensity of hurdles to overcome in addressing plastic contamination in freshwater and setting up monitoring programmes may differ in different settings, such as between countries at high and low levels of human development.

11. Summary of recommendations for monitoring plastics in freshwater

11.1 Designing a monitoring programme

Generally, the effort required to monitor plastics, in terms of technical equipment and the training level of staff, increases with decreasing particle size. While floating macroplastics can simply be observed from a bridge and manually counted, sampling and analysing microplastics requires specialized equipment, access to lab facilities and costly instruments such as microscopes and, for example, FTIR spectrometers. Thus, it is recommended to design a hierarchal monitoring programme which monitors macroplastics using basic methods. (Figure 4.3).

Plastic concentrations in freshwater systems such as rivers and lakes/reservoirs can be considered highly variable, both in space and time. Hydrologic events may mobilize material from a catchment, resulting in a considerable change in the plastic concentration. Temporal variations could be systematic (e.g. increasing concentrations with increasing discharge). This systematic behaviour might be used to extrapolate from the observed data to periods where only metadata such as river discharge are available. Therefore, fewer monitoring locations with frequent measuring intervals can create valuable insights into the behaviour of the observed system.

Key recommendations for designing a plastic monitoring programme are:

- Build around existing sampling and analysis protocols, as well as classification schemes, to ensure consistent data.
- □ Integrate plastic monitoring into existing programmes for other substances and make use of available metadata such as river discharge.
- □ Carry out frequent, long-term observations rather than high spatial variation.
- Carry out sampling and analysis that can use simpler methods, rather than fewer samples needing advanced analysis.

Ideally, monitoring of freshwater plastics should encompass the entire size range from macroplastics to micro- and even nanoplastic particles. Although microplastics have attracted far greater societal attention than macroplastics, larger items make up a significant portion of plastic contamination in freshwater and the oceans. Macroplastics can be easily monitored, e.g. by counting from a bridge (van Emmerik *et al.* 2019a ; see also Chapter 5). They do not require access to laboratories and highly specialized analytical equipment, as is the case for microplastics.

It is recommended that monitoring programmes initially start with macroplastics if the analytical infrastructure for microplastics is not available or not yet operational. Macroplastic monitoring can be supported by citizen science. Similar to litter from beach clean-ups, plastic debris collected from riverbanks and lake shores can be weighed, counted and classified using established protocols (see annexes 1, 2 and 3).

If microplastics are to be assessed or monitored, it is highly recommended to choose the lower size limit (according to widely published protocols) to facilitate comparability of data. More mass-based microplastic data are needed in order to establish mass balances for aquatic systems. To understand exposure, microplastics monitoring in biota should be accompanied by sampling of the surrounding environmental media.

11.2 Sampling

Overall, sampling procedures involve collecting plastic to analyse composition, polymer type, item type, size and mass distribution. In addition, sampling can reveal the plastic concentration at a given point in space and time. However, as shown in Chapter 5, techniques to recover plastic debris in freshwater vary based on the type of water body type and the matrix of interest (i.e. sediment, biota). Chapter 6 details the sample preparation for each of these types. Overall, the most common sampling technique uses nets, where mesh size depends on the plastic size of interest. It is cheaper and easier to sample macroplastics than microplastics, which require more sophisticated sampling equipment. Specific recommendations for different water bodies and matrices are summarized in Table 4.1.

Microplastics in drinking water have a much smaller size distribution, from < 10 μ m to > 100 μ m. Sampling and detection methods are therefore somewhat specialized. To confirm not only the presence of microplastics in drinking water supply, but also the source(s) of contamination, samples should be taken at different stages along the supply chain. Because in drinking water there are both low concentrations of microplastics and smaller particle sizes, a relatively high volume of water should be sampled. Most commonly, FTIR microscopy is used to determine microplastic contamination of drinking water. To detect even smaller sizes, micro-Raman spectroscopy has been used. When working with samples such as drinking water that are expected to have low concentrations of microplastics, it is especially important to avoid contaminating them.

11.3 Analysis

Sample analysis (described in Chapter 7) includes physical characterization, chemical characterization and, in some cases, biological characterization. Distinguishing between plastic and non-plastic particles is easy in the case of macroplastics and feasible in that of microplastics > 1 mm. For sorting and identifying small plastic particles, the use of hot needles and staining methods is recommended. To identify the polymer type, particle-based or mass-based approaches to chemical characterization can be used. Characterization of plastic polymers in environmental samples requires comparison with reference databases of known polymers, which are available as a freeware product ("(siMPle"). In addition, some alternative analysis techniques include X-ray fluorescence spectrometry and scanning electron microscopy, combined with an energy-dispersive X-ray microanalyser.

11.4 Additional considerations

11.4.1 Explore possible advances in monitoring methods

Recent studies have demonstrated the potential use of new technologies for advanced macroplastic monitoring. Unmanned Aerial Vehicles (UAVs) have been used to measure floating macroplastics in rivers and accumulated plastics on beaches. Camera-based systems are also increasingly used for plastic monitoring in rivers. Both technologies have significant potential for integration with artificial intelligence (AI) analysis tools, which could potentially automate plastic monitoring of riverine systems even further (Kylili *et al.* 2019). The use of spaceborne remote sensing for plastic detection in coastal zones has been explored. Although the temporal and spatial frequency of satellite data may still be inefficient, future initiatives could be suitable for plastic monitoring in dynamic riverine systems.

11.4.2 Sampling after storm or flood events

For the transport of many materials, it has been found that most of the annual load is caused by single events. In the case of plastic such data are still scarce, but available research suggests that extreme events may also govern total annual riverine plastic transport. In rivers such as the Rhône the Saigon, the Seine and the Tiber it has been observed that monthly plastic transport differed by an order of magnitude. In Romania it that plastic transport into rivers and lakes was driven mainly by floods. The importance of floods in microplastics transport was demonstrated by Hurley *et al.* (2018), which found a 70 per cent post-flood decrease in microplastic concentration in river sediments across several catchments in the United Kingdom. In addition to floods, other natural hazards may result in additional plastic mobilization. Several studies have suggested that the 2011 Great East Japan Earthquake caused considerable increases in plastic emissions from land into the ocean. Plastics found in the Great Pacific Garbage Patch and in North America were related to this single event (Lebreton *et al.* 2018). The guidelines therefore recommend a wider geographic distribution of plastic sampling following extreme events.

11.4.3 Dams and reservoirs in plastic contamination and assessment

Many rivers worldwide are dammed. Dams and reservoirs are likely to be at least temporary sinks for plastic of various sizes. Evidence suggests that microplastic concentrations in the water column in a reservoir decrease while respective concentrations in the sediment increase. However, data to support this relationship are sparse to date. It is recommended to include (rather than purposely avoiding) dams when planning river or catchment monitoring programmes. If reservoirs have pre-dams, plastic sampling should be focused there. If pre-dams are dredged, an analysis of plastic content is recommended along with other sediment analyses.

Some freshwater reservoirs are used for drinking water abstraction. According to the current state of knowledge, drinking water from various sources contains very few small plastic particles and there is no scientific evidence that drinking water safety is threatened by plastics. If particle loads in drinking water are assessed, extreme care has to be taken to avoid contamination, thus creating a "false alarm", as very large volumes of water are processed and the relevant particles are so small that they can easily be transported through the air.

11.4.4 Plastics in the context of other forms of contamination

Some contaminants are associated with the production and use of plastics. Some may be found in plastic-rich aquatic systems because they have a common source: waste, wastewater, or other results of human activities. The contaminants will be distributed according to the susceptibility/partitioning behaviour and availability of the plastic and of other environmental media. In monitoring, priority should be given to the media to which humans and freshwater biota are exposed, namely water and sediments. However, from a scientific perspective studies are needed to elucidate the possible gender-differentiated effects or non-effects of plastic-associated contamination in natural populations.

Regarding risk assessment, the effects of mixtures need to be considered, as well as particle-based versus mass-based perspectives. Current knowledge, largely based on estimates, suggests that the ecotoxicological risk of microplastics is low and not widespread, but is not zero (Adam, Yang and Nowack 2019; Backhaus and Wagner 2019), which may change with increasing plastic contamination in many parts of the world.

11.5 Data management and availability

11.5.1 Data availability

Ongoing efforts to harmonize sampling and analytical protocols will improve the comparability of collected monitoring data. To minimize barriers to data exchange, the format of data and metadata should be compatible with national or international database structures. In particular, the global water quality database GEMStat (https://gemstat.org) can serve as an example. It should be noted that plastic is currently not in the GEMStat parameter list, although its inclusion is under consideration.

11.5.2 Metadata

Especially in rivers and lakes, many environmental factors influence plastic concentrations at the time of sampling. For data interpretation it is essential to provide not only the locations and timing of sampling, but also data on ambient environmental conditions which might influence the observed concentrations such as:

- Let time and duration of the sampling (e.g. visual counting);
- geographic location of the sampling site;
- D precipitation during and prior to the sampling;
- wind direction during and before the sampling exercise;
- General discharge during and prior to sampling (rivers).

11.5.3 Units

Often concentrations of plastic are reported as items per volume. If possible, it is recommended to report both item counts and mass. In the case of rivers (e.g. when items are visually counted from bridges) it may not be possible to report concentrations. The use of the International System of Units (SI) is highly recommended.

12. Policy recommendations for intervention and prevention

To go from data to action, there is a need to formulate, implement and evaluate relevant intervention and prevention policies. Intervention policies refers here to policies meant to reduce existing plastic concentrations in freshwater, whereas prevention policies are intended to prevent the input of plastics to the environment. While both intervention and prevention policies are of interest in countries, their priority and design will differ immensely depending on local conditions such as existing plastic contamination, current waste management systems, and local stakeholders' interest in addressing plastic contamination of freshwater (Figure 12.1).

Figure 12.1. Conceptual flow of plastic from production to consumption, waste management and leakage into the natural environment (land, rivers and ocean) with possible points of action for policies



In all cases policymaking, implementation and evaluation for reducing plastics in freshwater are challenging and call for specific policy approaches. The challenges are generally associated with conflicts, system complexity and uncertainty (Kirschke *et al.* 2017).

Conflicts: Conflicts typically exist between different stakeholder groups (e.g. environmental interest groups, industries and consumers). Such conflicts reflect different priorities, such as the use of plastics in production vs. the reduction of plastic consumption. Even if the goal of plastic reduction is shared by different types of stakeholders, there are still different ideas about the best ways to reduce plastics in the environment. For example, while some argue for better management of plastic waste, others prefer to prohibit the use of plastics in industrial production processes.

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Complexity: System complexity pertains to a large number of dynamic and interconnected factors that influence the successful design and implementation of intervention and prevention measures. These factors are often ascribed to different facets of the social-ecological system, including different stakeholder interests, governance conditions, industrial production schemes, natural conditions and technological developments. Their management is often challenging, given the abundance of sub-factors, unclear developments, and strong positive and negative interactions.

Uncertainty: Uncertainty challenges policy formulation, implementation and evaluation. While these guidelines are a starting point for gathering and analysing data in different contexts, data uncertainty will remain in view of public authorities' generally limited resources for water quality monitoring. Human dimensions provide additional uncertainty, for example about the effects of prevention and intervention measures on human behaviour.

To address these challenges, governance research recommends that policymakers consider a wide range of activities (e.g. Kirschke and Newig 2017; Mathews and Stretz 2019). They include the following:

Capacities of public authorities: It is highly recommended to provide responsible public authorities with appropriate resources for planning and implementation. Planning under complex conditions can only be successful with the necessary human and financial resources. Such resources are needed in order to organize stakeholder dialogues, model system complexities, and gather data and knowledge. Policy implementation also requires funding (e.g. to control compliance or for economic instruments).

Diversity of stakeholders: Public authorities should involve a broad range of stakeholders in addressing the problem. In terms of monitoring, citizen science is an acknowledged way to increase both scientific data and knowledge and awareness on the side of citizens (San Llorente Capdevila *et al.* 2020). Additionally, it is recommended that specific measures are put in place to ensure the equal participation of women and their organizations, as well as gender experts in stakeholder engagements. This is in line with UNEP's Resolution 4/17 which calls for "Promoting gender equality and the human rights and empowerment of women and girls in environmental governance".

Integrated nexus thinking: In planning prevention and intervention policies, responsible public authorities should be guided by integrated nexus thinking. Nexus thinking typically calls for involving different sectors in the planning process. In the case of plastic contamination, involving the water and waste management sectors is particularly important. However, other sectors (e.g. agricultural and industrial) are also relevant. Different sectors are typically represented by different public authorities, non-governmental organizations (NGOs) and private companies. Their involvement is crucial to mediate conflicts between stakeholders, understand system complexity and reduce uncertainty.

Diversity of governance instruments: The use of diverse governance instruments to address complex problems is emphasized. Such instruments are typically structured as rules and regulations ("sticks"), information and cooperation ("sermon"), and economic incentives ("carrots"). Whereas all these policy implementation instruments have their place, they are not necessarily used in all countries. In particular, economic incentives are typically neglected compared with regulations and information campaigns. Countries may consider discussing more openly and creatively which combinations of instruments have the greatest relevance in a given context.

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Annex 1: OSPAR sorting protocol

OSPAR ID	UNEP ID	ITEMS	TOTAL
1		4/6 pack yokes	
2		Bags (e.g. shopping)	
3		Small plastic bags, e.g., freezer bags	
112		Plastic bag ends	
4		Drinks (bottles, containers and drums)	
5		Cleaner (bottles, containers and drums)	
6		Food containers including fast food containers	
7		Cosmetics (bottles & containers, e.g. sun lotion, shampoo, shower gel, deodorants)	
8		Engine oil containers and drums ≤ 50 cm	
9		Engine oil containers and drums > 50 cm	

Table A1. Example of categories used in the OSPAR sorting protocol (Wenneker and Oosterbaan 2010)

Annex 2: Sorting protocol for net sampling

Table A2. Example of sorting protocol used by van Emmerik et al. (2019)

Name	Properties	Common use
PET (polyethylene teerphthalate)	always clear softens at 80°C	soft drink bottles salad containers
PO soft (soft polyolefins) Includes: High/low density polyethylene (HDPE, LDPE) foils Polypropylene (PP) foils	coloured waxy surface softens at 70°C	shopping bags
PO hard (hard polyolefins) Includes: High/low density polyethylene (HDPE, LDPE) rigids Polypropylene (PP) rigids	waxy surface softens at 70°C	milk bottles shampoo and chemical bottles ice cream tubs lunch boxes
Multilayer Includes: Polyethylene (PE) foils Multilayered foils	flexible, glossy surface, printed foils	food packaging
PS (Polystyrene)	clear rigid glassy softens at 195°C	brittle toys straws plastic cutlery CD cases
EPS (Expanded polystyrene)	foams	polystyrene cups foamed meat trays
Other		

Annex 3: Schone Rivieren (Clean Rivers) protocol

Figure A1. Example of sorting categories (Stichting De Noordzee 2021; https://www.noordzee.nl).



River name	
Province	
Country	
Areacode/ coordinates survey area	
Date of survey: (d/m/y)	
Start time	_:_
End time	_:_
Name surveyor 1	
E-mail surveyor 1	
Name surveyor 2	
E-mail surveyor 2	

Was the survey conducted?	Yes/No
If no, please specify:	

Did you divert from the predetermined 100 metres?	Yes/No
If yes, please specify why and the length of the survey area	
Please specify the width of the survey area	

Were there any circumstances that influenced the	
survey? Please specify (e.g. high water levels).	
Note the recognisable items that are not on the survey list here with OSPAR-ID (others).	

Ospar ID	Plastic en styofoam	Total number items found
15	Caps/lids	
4.2	Plastic bottles >< 1/2 liter	
4.1	Plastic bottles > 1/2 liter	
40	Industrial packaging, plastic sheeting	
3	Small plastic bags	
117.1	Plastic/polystyrene pieces 0 - 2,5 cm (hard pieces of plastic)	
46.1	Plastic/polystyrene pieces 2,5 - 50 cm (hard pieces of plastic)	
47.2	Plastic/polystyrene pieces > 50 cm (hard pieces of plastic)	
1172	Styrofoam 0 - 2,5cm (pieces)	
462	Styrofoam 2,5cm - 50 cm (pieces)	
472	Styrofoam > 50 cm (pieces)	
6.1	Styrofoam foodpackaging (e.g. take-away hamburger packaging)	
212	Styrofoam cups	



- IVO natuur educatie Soup



21	Plastic cups	
117.2	Plastic pieces of foils 0 - 2,5 cm (soft plastic)	
46.2	Plastic pieces of foils 2,5 - 50cm (soft plastic)	
47.1	Plastic pieces of foils > 50cm (soft plastic)	
22.1	Straws	
22.2	Stirring rods	
19	Candy wrappers/ crisps and snack packaging	
6	Food containers (e.g. butter containers)	
4.3	Labels of beverage bottles	
64	Cigarette buds	
63	Cigarette packaging (also record paper packaging here)	
5	Cleaner packaging (bottles, containers and drums)	
1	4/6-pack yokes	
16	Lighters	
14	Car parts	
22	Cutlery	
22.1	Plates	
481	Waterfilters	
36	Light/glow sticks (tubes with fluid)	
38	Buckets	
38.1	Flowerpots/ trays	
43	Shotgun cartridges	
25	Gloves (household, typical washing up gloves – soft plastic)	
113	Gloves (industrial/professional gloves - thicker plastic)	
42	Hard hats	
10	Jerry cans	
11	Injection gun containers	
13	Crates	
39	Strapping bands and tie-wraps	
39.1	(Duct) tape	
19.1.	Lolly sticks (with hole on top)	
8	Engine oil containers and drums <50 cm	
9	Engine oil containers and drums > 50 cm	
24	Mesh vegetable bags	
2.1.	Garbage bags	
17	Pens and pencils	
20	Toys & party poppers	
35	(sport) Fishing gear (floats, bait bowls, packaging of sport fishing products, fishing line)	
2	Shopping bags	
31	Rope diameter > 1 cm	
32	String and cord < 1 cm	
35.1	Dolly rope (nylon threads and filaments – orange/ blue/ black coloured)	
43.1	Fireworks (only plastic or combined with paper)	

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48 Other plastic/polystyrene items (record recognisable items in the remarks field with OSPAR ID)

Ospar ID	Rubber	Total
49	Balloons, including plastic valves, ribbons, strings etc.	
49.1	Balloons sticks	
52	Tyres and belts	
53	Other rubber pieces (record recognisable items in the remarks field with OSPAR ID)	

Ospar ID	Textile	Total
54	Clothing	
57/44	Footwear (Shoes, boots and slippers)	
55	Carpet	
59	Other textiles (record recognisable items in the remarks field with OSPAR ID)	

Ospar ID	Paper	Total
62.1	Drink cartons	
67.1.	Pieces of paper 0 > 50cm	
61	Cardboard boxes and packaging	
65	Cardboard cups	
66	Papers and magazines	
60	Bags	
67	Other paper items (record recognisable items in the remarks field with OSPAR ID)	

Ospar ID	Wood (processed)	Total
72	Popsicle sticks	
72.1	Cutlery	
68	Corks	
73	Paint brushes	
69	Pallets	
74	Other wood < 50 cm (record recognisable items in the remarks field with OSPAR ID)	
75	Other wood > 50 cm (record recognisable items in the remarks field with OSPAR ID)	

Ospar ID	Metal	Total
81	Foil wrappers and aluminium foil	
81.1.	Capsules (e.g. coffee and chocolate milk)	
81.2	Beverage sachets	
78	Beverage cans	
79	Electric appliances	
83	Industrial scrap iron (including cables, pipe, etc.)	
77	Bottle caps	

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84	Oil drums	
88	Wire, wire mesh, barbed wire	
76	Aerosol/Spray cans	
86	Paint tins	
80	Fishing weights	
82	Food cans	
120	Disposable BBQ's	
89	Other metal pieces < 50 cm (record recognisable items in the remarks field with OSPAR ID)	
90	Other metal pieces > 50 cm (record recognisable items in the remarks field with OSPAR ID)	

Ospar ID	Glass	Total
91	Bottles and pots	
92	Light bulbs/ tubes	
93	Other glass items (record recognisable items in the remarks field with OSPAR ID)	

Ospar ID	Sanitary	Total
7	Cosmetic packaging (bottles & containers e.g. sun lotion)	
98	Plastic cotton bud sticks (ridges on both sides)	
982	Cardboard bud sticks	
102.2	Wet wipes	
97	Condoms and packaging	
99	Sanitary towel/panty liners/backing strips and packaging	
18	Combs/hair brushes	
100	Tampons, tampon applicators and packaging	
102.3	Toilet paper	
101	Toilet fresheners	
102	Other sanitary items (record recognisable items in the remarks field with OSPAR ID)	

Ospar ID	Medical	Total
103	Medical containers/ packaging (pills, contact lenses, contact fluid)	
104	Syringes	
105	Other medical items (record recognisable items in the remarks field with OSPAR ID). Please also record face masks here.	

Ospar ID	Micro litter - Nurdles	Total number of nurdles found
	Representative area of 50×50 cm within the high water line (parallel to the	
	waterline) of the survey area. Collect the upper 3 cm of soil and count	
	number of nurdles.	

References

van Emmerik, T., Loozen, M., Oeveren, K. van, Buschman, F. and Prinsen, G. (2019). Riverine plastic emission from Jakarta into the ocean. *Environmental Research Letters 14*(8), 084033. https://doi.org/10.1088/1748-9326/ ab30e8. Accessed 30 August 2020.

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