Plastics in the **Environment**

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Discussion Paper

within the scope of the research focus
Plastics in the Environment
Sources · Sinks · Solutions

Microplastics Analytics

Sampling, Preparation and Detection Methods

November 2018

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This discussion paper is based on the current state of knowledge and discussions in the research focus "Plastics in the Environment – Sources · Sinks · Solutions". This includes the organisation of two workshops on the cross-cutting issue "Methods for sampling, sample preparation and analysis (incl. reference materials)" on March 21-22, 2018 in Karlsruhe and July 5, 2018 in Augsburg with comprehensive discussion between all participants and additional specific technical contributions among others by:

- Dr. Claus G. Bannick, Federal Environment Agency Berlin
- Dr. Roland Becker, BAM Berlin
- Dr. Dieter Fischer, IPF Dresden
- Prof. Dr. Peter Grathwohl, Universität Tübingen
- Andrea Käppler, Leibniz Institute of Polymer Research Dresden
- Prof. Dr. Christian Laforsch, Universität Bayreuth
- Dr. Martin Löder, Universität Bayreuth
- Dr. Nicole Zumbülte, TZW Karlsruhe

The following joint research projects of the research focus participated in the workshops: EmiStop, ENSURE, MicBin, MicroCatch_Balt, MikroPlaTaS, PLASTRAT, RAU, REPLAWA, RUSEKU, SubµTrack, and TextileMission. In addition, some external projects have also contributed to the workshops (e.g. MiWa, MiPAq, MiKaMi, BASEMAN).

Content

1.Motivation/objective

This discussion paper aims to summarise the physicochemical analytical methods used in the research focus "Plastics in the Environment", in particular for the analysis of microplastics (MP)[1]. The objective is to present a pool of methods that is as standardised as possible and to make it available for use in science, businesses and administrations. Through peer discussion across projects, a compilation of comparable methods and results from various ongoing and completed projects was achieved.

Different methods are needed to answer specific questions. This applies not only to detection methods, but also to the sampling and processing/preparation methods associated with them, right up to the statistical evaluation of results. At the end of the document, an overview of the strengths and limitations of different methods with regard to a given problem can be found. An essential objective for the assessment of methods was the safe and comprehensible investigation of the transport paths and entry points into various environmental media such as water and soil using appropriate measurement and analytical methods.

A schematic representation of the interdependencies of MP analysis is shown in figure 1. As a rule, the objective of a measurement or a measurement program is based on a clear question/task or on an evaluation concept involving necessary assessment parameters, respectively (e.g. integration into an overall ecological context, thresholds for monitoring). A suitable detection method is then selected, which generates various result parameters (MP grade, mass content, number, shape, size, degradation status).

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[1] By definition, only thermoplastics and duroplastics are defined as plastics or microplastics. From a materials science point of view, plastics are a subgroup of polymers. Elastomers made from synthetic polymers (e.g. styrene butadiene rubber), chemically modified natural polymers (e.g. viscose, cellophane), and products based on synthetic polymers (e.g. fibers, coatings, tires) are equally considered in current research activities. They also produce microparticles that can be identified as synthetic polymers. To simplify matters, all these materials are colloquially referred to as "plastic / microplastics" in this document.
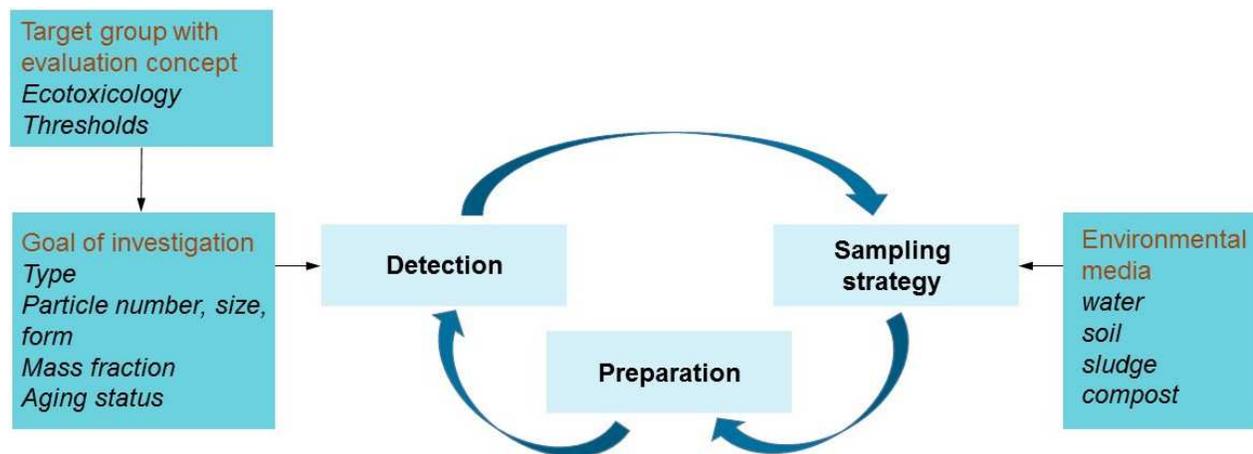
Figure 1: Schematic representation of interdependencies during MP detection

The environmental medium to be examined (e.g. water, soil, compost, sewage sludge) determines the sampling procedure. Sampling must result in a representative proportion of the tested medium with sufficient analyte content for the selected detection method to generate examination results that answer the given question.

Sample preparation depends on the environmental matrix to be examined (e.g. quality of the natural accompanying organics, proportions of inorganic substances), the sample quantity to be tested and the detection method selected. Here, differentiated representations are necessary depending on the environmental sample and detection method.

Therefore, the following **questions** need to be clarified at the beginning of every MP analysis:

- **Which goal can be achieved with the measurement?**
- **Which results are of interest/are required?**
- **For which environmental media and under which conditions /specialities should the measurements be made?**

The process recommendations listed above only apply to aqueous, near-water or solid samples (e.g. soil, sediment, compost). They correspond to the current state of knowledge.

There are so far no recommendations for MP analysis in air and biota. The same applies to the development and use of defined MP reference materials and comprehensive statistical considerations. This is an issue for future development of the discussion paper.

2.   Recommended approach

2.1 General recommendations for all analytical steps

During **all analytical steps (sampling, preparation, detection)**, "plastic-free" or **low-plastic working conditions** must be ensured. These include the avoidance of standard plastic products and the use of alternatives made of metal, glass or silicone. An exception is the use of plastics that are not to be detected or evaluated.

If possible, **samples should be handled in laminar flow boxes** in the laboratory, especially during the preparation process of wet samples and during the determination of particle numbers.

It must be determined beforehand, whether a **hygienisation of samples** is necessary. Sterilisation is a standard recommendation for the analysis of dry samples from wastewater, sewage sludge and organic wastes. Various methods with specific limitations can be applied:

i.   Steam sterilization: Melting of PE particles if necessary
ii.   Radiation sterilization (gamma, beta radiation, UV radiation): polymer degradation if necessary
iii. Chemical sterilisation (ozonisation): Chemical degradation of particles if necessary

The **measurement and control process** must be carried out and recorded **taking into account all analytical steps** and **comparable conditions for all samples** (same steps, same duration, same volume), even in a plastic-free or low-plastic working environment.

The **documentation and measurement of zero samples or blank value determination** for the applied detection methods is essential, since contamination during sampling, preparation and detection (contamination by air borne particles) can easily occur. According to current knowledge, a triple repetition is highly recommended for the blank value determination in the particle counting process (including sample preparation) of each campaign. For thermal analysis methods, blank value determination is also recommended for every measuring campaign, ideally the blank value is determined every day. For thermal analysis methods, a duplicate determination is suggested.

Determination and documentation of recovery rates using defined reference materials (number of particles and/or mass for MP of different polymer types/densities, particle sizes and shapes) must be presented for all analytical procedures and steps. This can be done by adding real samples with suitable reference materials or by determining recovery rates in suitable reference mixtures. Alternatively, reserved samples (homogeneity control) can be generated, which can later be made available for repetition and testing.

An investigation of the particle stability of various polymers under the conditions of the described sampling process (including ultrasound treatment), sample preparation (including chemical treatment) and detection methods should be documented. Depending on the type of polymer, particle sizes and state of aging, there may be degradation and/ or fragmentation of larger particles.

The **presentation of the results should be consistent/standardised**. In the future, the following information should always be provided, the presentation of results in other forms is possible, but only in addition:

    i.   MP number per volume for sampled water bodies (number / l) or per total dry matter for sampled solids (number / kg)

    ii.   MP mass per volume for sampled water bodies (µg / l) or per total dry matter for sampled solids (mg / kg)

It is always necessary to provide a precise description and comprehensible documentation of the amount of the sampled environmental aliquot, the prepared laboratory sample and the analysed sample.

The classification of MP analyses into **size classes** according to Table 1 is recommended. This classification is based on a numerical model and the "historic definition" of MP. Small particles that occur in higher quantities are grouped into narrower classification clusters than the larger particles, which are more relevant in terms of mass and classified into wider clusters. This also enables a higher methodological feasibility of processes (including feasibility of filtration, detection limits in analytics) and a better integration of particle quantities/masses in impact analyses (i.e. for environmental assessments). The following size **classes** are proposed: **5,000 – 1,000 µm, <1,000 – 500 µm, <500 – 100 µm, <100 – 50 µm, <50 – 10 µm, <10 – 5 µm, <5 – 1 µm**. The application of individual fraction stages should be oriented towards the extraction of solid samples. The maximum dimension of a particle or film fragment or the length of a fibre defines the size class.

Table 1: Particle size classification

Classification		Large microplastics	Microplastics						
Particle size classes	µm	5,000 – 1,000	1,000 – 500	500 – 100	100 – 50	50 – 10	10 – 5	5 – 1
Average particle size	µm	3,000	750	300	75	30	7.5	3
Mass of an individual particle*	mg	14.13	0.221	0.014	2.2E-04	1.4E-05	2.2E-07	1.4E-08
Number of particles in 14.13 mg	Number	1	64	1,000	6.4E+04	1.0E+06	6.4E+07	1.0E+09

* Assuming a density of 1 g/ml.

2.2 Identification of the goal and task of MP analysis

The determination of one or more quantitative or qualitative detection methods depends specifically on the objectives and tasks of a project or an existing requirement. Currently, two methods are being used in the detection of microplastics. The first determines the total content of the different plastics; the second one analyses particle numbers and sizes for specific plastics.

The detection of very small MP particles (less than 10 µm) is comparatively complex and based in particular on ecological, human and ecotoxicological considerations. Smaller particles can have more significant effects (e.g. penetration of cells) than larger particles. Furthermore, the properties of individual particles (surface morphology and chemical structure) can also be decisive for the analysis of effect and origin. The ability to detect small to very small particles is therefore an important basis for the detection and evaluation of all size ranges of microparticles in the environment.

In a general classification, the following **objectives** can be distinguished:

Objective: Identification and determination of mass of MPs
From a regulatory point of view, mass contents are an important parameter for estimating the occurrence of MP. They are suitable when it comes to the regular, repeated determination of MP in the context of monitoring and the control of the effectiveness of measures against plastic inputs.

The nominal range of particle size for which these provisions are to be made must be defined in advance. This grouping into size classes (Table 1) makes it possible to assign the total contents to a specific particle size range. The contents of the different plastics can be measured in a consistent way, regardless of particle shape, number and size. In principle, it has to be taken into account that a few large particles are more significant in terms of mass balance than many small particles.

Objective: Identification of particle number, size and shape of MPs
Determining the exact number, size and shape of particles provides a very comprehensive, detailed picture of the occurrence of MP in environmental samples.
The nominal particle size range for which these provisions are to be made must be defined in advance, too. The particles of the different plastics can thereby be measured in a

consistent way according to particle shape, number and size. Classification into size classes (Table 1) allows for comparing the total contents for a specific particle size range. In principle, there are significantly more small than large particles. The analysis of very small particles is complex and partly limited for real samples (< 5 µm). The evaluation methods must guarantee homogeneity of the analysed environmental sample aliquots, as often only a fraction of the sample can be analysed.

Objective: Characterisation of specific properties of individual MP particles

The individual characterisation of specific properties of isolated particles, e.g. the state of degradation, the surface structure or condition, and the analysis of additives can be relevant for evaluating the interaction with the environment, but also for assessing their sources, entry paths, and fate. Such analyses may require prior, and in some cases very complex, isolation of individual particles.

2.3 Selection of the detection method related to the problem

Basically, there are three different detection approaches. **Spectroscopic methods can** capture and assign the characteristics of specific chemical structure of polymers using reference spectra. In **thermoanalytical methods**, the sample is pyrolysed under inert conditions and specific decomposition products of the individual polymers are detected. Finally, **chemical methods** are used to decompose the samples and detect specific fragments of polymers or elements.

A comparison of the methods is shown in Table 2; the values/data determined are based on practical tests. The available detection methods differ – independent of the parameters for sampling and preparation – in their methodological performance and feasibility per measurement. This includes the analysable sample mass or number of particles in a measurement, the detection limits with regard to particle size and mass, the necessary preparation of the sample in the measuring instrument, and the time for execution and evaluation of the measurement.

The detection methods also differ – independent of the parameters for sampling and preparation – in their generation of the result per measurement. These include the identification of polymer type and possible additives, the analysis of the degradation state, the determination of particle number, size, shape and surface quality as well as of particle masses. The comparison of results is presented in Table 3. The information shown is based solely on direct information generated from the measurement.

The conversion of results of MP particle analyses into mass contents is only possible with considerable errors, since the particles are often not uniformly spheric and the material density cannot be specified accurately enough due to undefined structures. In addition, the spherical diameter cannot be determined exactly, but it enters the volume formula of a sphere with the third power (high fault levels possible).

In the presentation and documentation of results, the quantity of environmental aliquots analysed and the process duration/hours of work per sample must also be taken into account.

There is a high risk of misinterpretation when measuring real samples using solely imaging methods (e.g. light and electron microscope) and particle counting methods (e.g. light scattering, laser scattering). Therefore, they must be carried out with comparative and blank samples and only in combination with other chemical or chemical-physical analysis techniques.

Further detection methods are also possible but are not addressed here. These include various chemical methods (e.g. molecular weight determination, chemical degradation and subsequent LC), staining with Nil Red and subsequent fluorescence detection, the application of TGA-FTIR/MS or TGA-GC-MS and hyperspectral imaging methods. No recommendations have been made to date.

Table 2: Prerequisite detection method (for abbreviations of methods, see appendix)

Characteristics	Spectroscopic						Thermoanalytical				Chemical
	μ Raman	μ FTIR (trans)	FPA FTIR (trans)	μ ATR-FTIR	ATR-FTIR / Raman	NIR	Py-GC-MS	Mod. Py-GC-MS*	TED-GC-MS	DSC	ICP-MS
Dimension of the specimen mass	ng - μg	ng - μg	ng - μg	mg	mg	mg	μg	mg	mg	mg	mg
Maximum number of measurable particles per sample	$10^3 - 10^5$	$10^3 - 10^5$	$10^3 - 10^5$	1	1	Undefined	1	Undefined	Undefined	Undefined	Undefined
Dimension measuring time (including preparation for measurement)	h - d	d	h	min	min	min	h	h	h	h	min
Detection level (in sample tests)	1 – 10 μm	20 μm	20 μm	25 – 50 μm	500 μm	1 %	<< 1 - 0.5 μg	0.5 – 2.5 μg	0.5 – 2.5 μg		ppm
Preparation for measurement	On filter	On special filter	On special filter	Isolated particles	Isolated particles	On filter	Isolated particles	Filtrate or with filter	Filtrate or with filter	Filtrate	Filtrate

* Depending on the individual design of the pyrolysis unit, larger sample quantities can also be pyrolysed (Curie point filament, Micro furnace). They are shown here separately as Large Volume (LV) Py-GC-MS.

Table 3: Generation of results for different detection methods (for abbreviations of methods, see appendix)

Characteristics	Spectroscopic						Thermoanalytical				Chemical
	μ Raman	μ FTIR (trans)	FPA FTIR (trans)	μ ATR-FTIR	ATR-FTIR	NIR / Hyper-spectral Imaging	Py-GC-MS	Mod. Py-GC-MS	TED-GC-MS	DSC	ICP-MS
Type of polymer	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Only PE, PP	Only tyre abrasion
Detectable additives	Pigments	No	No	No	No	No	Yes	No	No	No	No
Particle surface (chemical)	Yes	No	No	No	Yes	Yes	No	No	No	No	No
State of degradation*	Surface Oxidation	No	No	Surface Oxi-dation	Surface Oxi-dation	No	Oxi-dation	No	No	Mol. weight	No
Particle number, particle size, particle shape, particle surface morphology	Yes	Yes	Yes	Yes	Yes	No	No	No	No	No	No
Mass balances	No	No	No	No	No	No	No	Yes	Yes	Yes	Yes

2.4 Identification of sampling procedure with respect to the environmental medium

Water sampling

The sample volume depends on the number and size of the MP and on the expected particle quantity.

According to previous experience and based on the "normal distribution" shown in Table 1, significantly more MP particles are present in the smaller size ranges.

The sample volume in the lower µm range can be smaller (in the milliliter or liter range) because the statistical probability of obtaining a representative cross-section of small particles expected is greater with a high number of particles. If the entire size range down to the upper µm range is to be covered during sampling, significantly larger volumes of water must be filtered (50 l to over several cubic meters). Very large representative sample volumes are necessary to be taken in the almost solids-free water body.

An overview of literature references and recommendations for sampling volumes is shown in Table 4.

Table 4: Overview of recommended volumes of water to be sampled based on literature references

	Very high solids content	**Rich in solids**	**Low in solids**	**Nearly solids-free**
Filterable substances / plankton	More than 500 mg/L	100 – 500 mg/L	1 -100 mg/L	Less than 1 mg/L
Examples	Sewage plant intake	Street drainage	Sewage plant effluent, surface waters	Groundwater, mineral water, drinking water
Recommended sample volume for particle analysis of ~ 1000 – 50 µm	50 l	5 m³	15 m³	5000 m³
Recommended sample volume for particle analysis of ~ 50 – 1 µm	5 ml	500 ml	1 l	500 l

The use of the particle size classes shown in Table 1 is recommended for all water filtration processes, so that results can be evaluated according to the size classes and for

comparison of different investigations. Furthermore, they contribute to reducing filter cake formation.

In the case of filter cartridges or sieve cascades, a verification of the defined pore size or the nominal mesh size must be documented. Filterability must be ensured over the entire sampling period as well as the complete removal of filter residues from previous measurements with repeated use of the materials. Control tests are therefore recommended using standardised procedures (ISO 2942 Hydraulic fluid power – Filter elements – Verification of fabrication integrity and determination of the first bubble point). For sampling particles smaller than 10 µm, pressure filtration is necessary (~ 2-6 bar) due to the low water permeability of the filters.

The immersion depth and the orientation of the sampling tube with respect to the direction of flow (angle to the incident flow) during the sampling process is to be documented. Ideally, the hydrodynamic conditions should be documented as well (possibility of isokinetic sampling). The buoyancy behaviour (density of different plastics) of particles smaller than 50 µm is not relevant.

When using neuston or plankton nets or cascades (especially for marine water), the particle classification described above must also be used. A transfer of the present recommendations to marine waters has not yet been specified.

Further sampling methods, such as sediment traps, membrane filter systems and flow centrifuges are known, but have not yet been sufficiently characterised for MP measurements. Therefore, no recommendations are made to date. Furthermore, there are no recommendations either for preferred sampling by means of random samples or aggregate samples. When using collection containers for continuous sampling, care must be taken to homogenize the sample during further processing (biological growth, sedimentation or flotation effects).

In the documentation and representation of sampling methods, the sampled water volume and the effectively filtered water volume must always be represented.
A basic statistical analysis for the sampling of MP in waters is still pending.

Solids sampling
In this section, first hints for the sampling of soils, sediments and secondary fertilizers, e.g. sewage sludge and composts are given. The sampling of these materials is already legally regulated in various directives with regard to the analysis of nutrients or pollutants, such as metal ions or persistent organic substances, and is substantiated by standards

for sampling, processing/preparation and corresponding detection methods; a selection is shown in Table 5.

Table 5: Overview of legal regulations with information on sampling of soils and materials as well as further standards for sampling of solids

Environmental medium	Regulations	Standards
Soil, sediment, soil with sewage sludge	Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV-1999) - Annex 1 Sewage Sludge Ordiance (AbfKlärV-2017) Annex 1, Section 1.1	ISO 10381 Part 1-5: Soil quality - Sampling DIN EN 932-1: Tests for general properties of aggregates. Methods for sampling. DIN 19671-1: Soil drilling apparatus for drawing soil samples in agricultural engineering; groove borers, tube borers DIN 4021: Ground exploration by excavation, boring and sampling DIN 38414-11: German standard methods for the examination of water, waste water and sludge; sludge and sediments (group S); sampling of sediments (S 11)
Sewage sludge	Sewage Sludge Ordiance (AbfKlärV-2017) Annex 1, Section 2.1 Fertilizer Ordinance (DüMV)	DIN EN ISO 5667-13: Water quality - Sampling: Guidance on sampling of sludge DIN 19698-1: Characterization of solids - Sampling of solid and semi-solid materials: Guidance for the segmental sampling of stockpiles of unknown composite DIN 38414: German standard methods for the examination of water, waste water and sludge; sludge and sediments (group S); determination of leachability by water (S 4)
Compost	Biowaste Ordiance (BioAbfV-) Annex 3, Nr. 1.1 2013-04 Fertilizer Ordinance (DüMV)	DIN EN 12579: Soil improvers and growing media - Sampling DIN 51750: Sampling of liquid petroleum products DIN EN ISO 5667-13 Water quality -- Sampling: Guidance on sampling of sludge

With the exception of the Biowaste Ordinance and the Fertilizer Ordinance, MP is not taken into account in the existing legislation in Germany, nor in standardisation. Nevertheless, the sampling strategies and methods listed there, in particular for soils, sewage sludge and compost, should be used as a guide.

A final evaluation of the methods with regard to their applicability for plastic analyses is still pending, as is a basic statistical consideration for the sampling of MP in solids.
When developing sampling strategies for soils, the use of the soil and the associated characteristics of the specific soil horizons have to be considered. The relevant sampling depths can then be derived from this (Table 6).

Table 6: Use dependent sampling depths of soils (see Federal Soil Protection and Contaminated Sites Ordinance)

Effect pathway	Use	Sampling depth
Soil-Human	Children's playground, residential areas	0-10 cm [1]
		10-35 cm [2]
	Park and leisure facilities	0-10 cm [1]
	Industrial and commercial properties	0-10 cm [1]
Soil-cultivated crop	agriculture, kitchen garden	0-30 cm [3]
		30-60 cm
	grassland	0-10 cm [4]
		10-30 cm

1) Contact area for oral and dermal uptake of pollutants, additional 0-2 cm for relevance of inhalative uptake path; 2) 0-35 cm, average thickness of deposited soil layers: at the same time max. depth reached by children; 3) working horizon; 4) main root area

The number of sampling points depends on the area to be examined:

> 10,000 m²: min. 10 partial areas, 1 mixed sample per partial area, 15-25 incremental samples

10,000 – 1,000 m²: min. 3 partial areas, 1 mixed sample per partial area, 15-25 incremental samples

< 1,000 m²: No subsamples

Soil sampling strategies (including sludge or compost) depend on the type of solid to be investigated and its properties (soil type, granularity, pH, organic matter, dry residue), as well as on the pattern of expected local distribution.

A determination of the spatial distribution of individual samples on a subarea can be carried out in different ways and has to be defined depending on the spatial conditions (e.g. point-shaped, strip-shaped, locally limited distributions). If prior information is available, sampling should be based on the expected contamination history and presented in an appropriate description of the sampling plan (e.g. cross-shaped sampling, transects, statistical distribution). These methods should be applied to the sampling of sediments (subhydric soils) and semi-terrestrial soils (water level, surf zone, splash zone).

The choice of sampling methods for soil surfaces is based on the economic proportionality of the methods; manual methods such as Pürckhauer, manual rotary drills, ground-breaking or grooving cylinders can be used here.

The required sample quantity depends on the maximum grain size and must be sufficient to ensure laboratory tests and retention samples after proper preparation. Coarse materials (> 5 mm) and external substances must be extracted from the total sample quantity and separately added to the laboratory analysis. Their mass fraction of the sampled aggregate material shall be determined and documented.

There are separate regulations / standards for the sampling of a sewage sludge mixture, sewage sludge compost and bio-waste. In particular, these take into account the number of partial samples and volumes. Furthermore, the provide explanations on how to fulfil the usual safety rules in microbiological laboratories, in particular with regards to the Ordinance on Safety and Health Protection for Activities with Biological Agents, when working with such fresh and freeze-dried samples (e.g. by heating the sample for 20 minutes at 121 degrees Celsius in an autoclave).

The field sample should be prepared to serve as a laboratory sample by means of coarse screening/coarse crushing and subsequent homogenization (fractionated dividing). Dry sieving with 5 mm is recommended, the upper limit of "large microplastics" (Table 1). According to the guideline value for a laboratory sample (< 2mm grain size ~ approx. 1 l or 500 g fine soil), this corresponds to 2.5 l or 1250 g for a grain size < 5 mm, or 0.5 l or 250 g fine soil for a grain size < 1 mm.

The transfer of the laboratory sample into a test sample may include hygienization and adequate sample homogenization (rotation sample divider/cross- riffling process); freeze-drying is recommended during drying to avoid strong agglomeration of the soil. For fractional sieving, wet sieving is recommended for grading curves < 100 µm.

2.5 Identification of sample preparation with respect to detection and environmental medium

The selection and sequence of the treatment process depends on the investigated environmental matrix and the chosen detection method (see Figure 1). In principle, processes for removing inorganic (e.g. silicates, carbonates, minerals) and organic matrix (e.g. humic substances, bacteria, cellulose) can be distinguished. Since different proportions and compositions of the matrix exist depending on the environmental compartment, no generally applicable recommendations can be given so far.

In order to detect possible degradation phenomena during the processing of different MP varieties, sizes, geometries and degradation states, recovery experiments with suitable reference materials and reference mixtures must be carried out and documented.

It is reasonable to prepare samples after fractionation (wet sieving). Working in laminar flow boxes (problem of blank values) can take several days because of the exposure time. The duration of the process / working hours in relation to the investigated environmental aliquot should be recorded. Moreover, there should be a realistic assessment of the used chemicals in terms of costs (especially for large amount of samples) and their toxicity.

Removal of the inorganic matrix
The preparation of water samples (filtrates) to remove the inorganic matrix is proposed for all spectroscopic detection methods. For solid samples (e.g. soil, sediment) a separation of the inorganic matrix is always described.

Methods for **density separation** using saturated salt solutions (e.g. NaCl, $ZnCl_2$, wolframates, NaI, $CaCl_2$, KBr) are generally proposed. These salt solutions represent different density separation limits and can separate polymers smaller than this density limit. The viscosity of the solution and the static charge of particles can be critical. The pH value of the solutions must be checked (carbonate formation or decomposition).

Using a centrifuge to support the separation effect is possible. The parameters relevant to the method (separation limit, sample mass, volume, activation and settling periods) must be documented and presented comprehensively with regard to sampling and subsequent detection. The systematic investigation of the effectiveness for MP varieties, sizes, geometries and degradation conditions is pending. For this reason, no generally applicable recommendations have been made so far.

For a (supporting) separation by means of hydrophobic interactions (e.g. silicone oils, paraffin oils), no generally valid recommendations can be given.
So far, there is no comprehensive competence available for density separation by means of static charging.

Removal of the organic matrix
For samples from water (filtrates) and for samples from solids (e.g. soil, sediment) treatment processes for removing the organic matrix are proposed for all spectroscopic detection methods. The separation of the organic matrix is not described in thermoanalytical methods.

The parameters relevant to the processes (type of chemicals or enzymes, concentration, enzyme activity, exposure time, temperature, pH value) must be comprehensively represented, also with regard to sampling and subsequent detection. The systematic

investigation of the effectiveness for MP varieties, sizes, geometries and degradation conditions is pending.

The preparation of the samples with oxidizing hydrogen peroxide solutions (Fenton reagent) is proposed most frequently. An alternative is treatment with ozone-water. Handling of samples with diluted or concentrated acids or bases is also common. An alternative is enzymatic processing. It is considered very harmless for MP, but the long exposure time of two weeks and more is a disadvantage.

3. Appendix

1) List of abbreviations of methods

Abbreviation	Full name
µ ATR-FTIR	Micro attenuated total reflection Fourier transformation infrared spectroscopy
µ FTIR (trans)	Fourier transformation infrared spectroscopy microscopy in transmission mode
µ Raman	Raman microscopy
ATR-FTIR	Attenuated total reflection Fourier transformation infrared spectroscopy
DSC	Differential scanning calorimetry
FPA FTIR (trans)	Fourier transform infrared spectroscopy microscopy in transmission mode with focal plane array detector
LC	Liquid chromatography
Mod. Py-GC-MS	Pyrolysis gas chromatography mass spectrometry with upstream thermal conditioning of the samples
MPSS	Munich Plastic Sediment Separator
NIR	Near infrared spectroscopy
ICP-MS	Inductively coupled plasma mass spectrometry
Py-GC-MS	Pyrolysis gas chromatography mass spectrometry
TED-GC-MS	Thermal extraction desorption gas chromatography mass spectrometry

2) Other abbreviations

Abbreviation	Full name
MP	Microplastic
PE	Polyethylene
PP	Polypropylene
UV radiation	Ultraviolet radiation