Monitoring of microplastic pollution in the Arctic: recent developments in polymer identification, quality assurance and control, and data reporting

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Abstract

The pollution of the environment with plastics is of growing concern worldwide, including the Arctic region. While larger plastic pieces are a visible pollution issue, smaller microplastics are not visible with the naked eye. These particles are available for interaction by Arctic biota and have become a concern for animal and human health. The determination of microplastic properties includes several methodological steps, i.e., sampling, extraction, quantification, and chemical identification. This review discusses suitable analytical tools for the identification, quantification, and characterization of microplastics in the context of monitoring in the Arctic. It further addresses quality assurance and quality control (QA/QC), which is particularly important for the determination of microplastic in the Arctic, as both contamination and analyte losses can occur. It presents specific QA/QC measures for sampling procedures and for the handling of samples in the laboratory, either on land or on ship, and considering the small size of microplastics as well as the high risk of contamination. The review depicts which data should be mandatory to report, thereby supporting a framework for harmonized data reporting.

Key words: monitoring, microplastic, Arctic, QA/QC, reporting, FTIR, Raman, microscopy, py-GC/MS, TED-GC/MS

Résumé

La pollution de l'environnement par les plastiques est une préoccupation croissante dans le monde entier, y compris dans la région arctique. Alors que les plus gros morceaux de plastique constituent un problème de pollution visible, les microplastiques plus petits ne sont pas visibles à l'œil nu. Ces particules sont disponibles pour une interaction avec le biote arctique et sont devenues préoccupantes pour la santé animale et humaine. La détermination des propriétés des microplastiques comprend plusieurs étapes méthodologiques, à savoir l'échantillonnage, l'extraction, la quantification et l'identification chimique. Cette revue traite des outils analytiques appropriés pour l'identification, la quantification et la caractérisation des microplastiques dans le contexte de la surveillance dans l'Arctique. Elle aborde également l'assurance et le contrôle de la qualité (AQ/CQ), qui sont particulièrement importants pour la détermination des microplastiques dans l'Arctique, car des contaminations et des pertes d'analytes peuvent se produire. Elle présente des mesures spécifiques d'AQ/CQ pour les procédures d'échantillonnage et pour la manipulation des échantillons en laboratoire, que ce soit à terre ou sur un navire, et compte tenu de la petite taille des microplastiques ainsi que du risque élevé de contamination. L'étude décrit les données dont la déclaration devrait être obligatoire, soutenant ainsi un cadre pour la déclaration harmonisée des données. [Traduit par la Rédaction]

Introduction

Environmental pollution with plastics is a growing concern, for the public society and regulators, including governmental legislation. As a result, countries and regions increasingly require to establish monitoring programs. In recent years, several monitoring guidelines have been developed, mainly on macrolitter items and larger plastic particles, for example, by the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP 2019), the Oslo–Paris Convention for the Protection of the Marine Environment of the Northeast Atlantic (OSPAR 2019, 2020), the Baltic Marine Environment Protection Commission (HELCOM 2021), and the Arctic Monitoring and Assessment Programme (AMAP 2021), a working group under the Arctic Council targeting environmental pollution in the Arctic. These guidelines cover different types of environmental compartments and different size categories of plastics (e.g., specifically larger litter and (or) microplastic items).

Research in this field has led to rapid developments in the quantification and identification of plastic particles including microplastics. In addition to information on number or mass, chemical composition, and shape of plastic particles, there is an increasing interest and necessity within exposure, hazard, and risk assessment research to identify these particles not only as "plastics," but also according to all of the mentioned parameters (Kögel et al. 2020; Primpke et al. 2020a). Quality assurance and quality control (QA/QC) measures (Brander et al. 2020; Schymanski et al. 2021) need to be integrated in the analysis of microplastics in environmental samples to avoid bias. Sample integrity could be affected across the whole process of the survey and analytical process, for example, by contamination from fibres in air or clothing worn at the sampling stations (Prata et al. 2021) and emissions of particles from sampling vessels and sampling equipment (Suaria et al. 2020; Leistenschneider et al. 2021). In the laboratory, contamination can occur from laboratory equipment (Song et al. 2021) as well as protective clothing (Dris et al. 2017; Witzig et al. 2020). Moreover, the number of samples collected might be insufficient to represent the environmental niche or the population, and the extraction methods might not sufficiently remove interfering nonplastic matrix or not preserve the plastic analytes in a quantitative way. Furthermore, a loss of analyte might happen during processing, filtering, and transport of samples, analytes might not represent the hazard appropriately, and endpoint analysis might misidentify particle types, shapes, numbers, mass, and chemical identity (Kögel et al. 2022). All these issues may have an impact on the accuracy and comparability of the data and, if not recognized and controlled, could produce misleading results. Thus, QA/QC measures need to be included in all sampling and measurement campaigns, and their results reported and ideally quantified as measurement uncertainties. It is perhaps even more challenging to integrate QA/QC in research and monitoring in geographical areas such as the Arctic, where remote sampling locations

and potential technical limitations in processing facilities (e.g., lack of filters for water and air), combined with a need for warm, nowadays often synthetic outdoor clothing, make control measures harder to implement. In addition, samples from the Arctic can be unique and their collection expensive, which usually excludes potentially compromised samples that can be replaced or measurements repeated, making rigorous QA/QC even more important.

In general, data reporting is still challenged by a lack of harmonization and standardization in the field of microplastic analysis, including basic definitions of the central term "microplastics". For example, while standard bodies like the International Standardization Organization (ISO) define microplastics as materials based on plastic (ISO 2020), the California Water Boards (The California Water Boards 2022) and the European Chemicals Agency (ECHA 2019) define a minimum requirement of polymer content (e.g., in California 1 wt.%; The California Water Boards 2022). Besides the material, cut-off sizes for macroplastics, microplastics, and nanoplastics differ between different sources. For example, Hartmann et al. (2019) suggested 1–10 mm, 1 μm to 1 mm, and <1 μm for mesoplastics, microplastics, and nanoplastics, respectively. ISO (ISO 2020) defined large microplastic with 1–5 mm and microplastic with 1 μm to 1 mm, and Frias and Nash (2019) proposed 1 μm to 5 mm for the term microplastics. Furthermore, the introduction of the term "anthropogenic particles" was introduced when chemical identity cannot be confirmed (Athey et al. 2020; Adams et al. 2021; Athey and Erdle 2021). The European Union (EU) has, in the Marine Strategy Framework Directive, defined microlitter as small litter fragments below 5 mm covering both plastic and other man-made solids (European Commission 2017). The objective of this review was therefore to discuss the state of knowledge of litter and microplastic monitoring with regard to polymer identification, QA/QC, and data reporting accounting for Arctic conditions, to support a harmonized framework including specific recommendations.

Section 1. Recent developments in the analysis of microplastics

While each environmental compartment in the Arctic has its own regional-specific requirements, methods, and challenges with respect to microplastic sampling and sample extraction (Grøsvik et al. 2022; Kögel et al. 2022; Lusher et al. 2022; Martin 2022; Provencher et al. 2022), the final microplastic analysis procedures are typically conducted at laboratories and often follow similar pathways. The determination of the chemical identity of a particle serves the purpose of (i) confirmation of the particle as microplastics (in contrast to naturally occurring materials) and (ii) further information on specific polymer occurrences. Furthermore, to enable toxicological risk assessments, an accurate and robust characterization of the chemical composition of microplastic particles in food and environmental samples is crucial

because the chemical nature of the particles may influence the toxic effects on organisms (Avio et al. 2015; Booth et al. 2016; Rochman et al. 2017; Kögel et al. 2020).

A number of analytical techniques have been developed and reported, ranging from simple but less robust approaches, mainly based on visual inspection, to advanced instrumentation. As examples of advanced techniques, spectroscopy or thermal degradation coupled with gas chromatography–mass spectrometry (GC/MS) for the chemical identification of microplastic polymer types, and, to some degree, additives and sorbed toxicants, have been developed. In terms of research and development, microplastic analysis has reached a stage where well-established and widely used techniques exist for identification and semiquantification (i.e., robust conclusion of relative sample amounts in several samples; Hildebrandt et al. 2021). Nevertheless, the field continues to develop rapidly, including the introduction of entirely new approaches. In the following section, we review those analytical techniques that have already been applied in a large number of microplastic studies (Zarfl 2019; Primpke et al. 2020a; Ivleva 2021), and evaluate their possibilities and limitations for microplastic monitoring in the Arctic environment.

Microscopy enhanced visual identification

Owing to its simplicity and the wide availability of low-cost instrumentation, microscopy-enhanced visual identification continues to be one of the most commonly used identification and quantification methods for microplastics in environmental samples. It has been applied to a wide range of matrices, including natural waters, sediments, soils, air, wastewater treatment plant influents, effluents, process waters and sludge, aquatic and terrestrial organisms, as well as to products for human consumption (Primpke et al. 2020a). In general, guidelines for the identification of microplastic include visual parameters such as colour, colour distribution, shape, surface properties such as light reflection, as well as the width, length, and features of fibres, texture, and malleability (Martí et al. 2020; Lusher et al. 2020a; Primpke et al. 2020a). The majority of studies divide microplastics into six primary shape categories: fragments, beads, pellets, films, foams, and fibres (OSPAR 2015). However, other categories exist, complicating harmonized data assessment, and a broader range of categories may be required to account for this (Lusher et al. 2020a). Reporting on a minimum set of criteria in addition to individual focus-specific criteria will solve this problem to some extent.

During the early days of microplastic identification in environmental samples, visual identification was often the only technique applied. However, it has been recognized by many that the approach has a high misidentification rate if not combined with more diagnostic chemical analysis approaches (Hidalgo-Ruz et al. 2012; Lenz et al. 2015; Isobe et al. 2019). Visual identification is also affected by the visual acuity of the user and the equipment available (Lusher et al. 2020b). For this reason, GESAMP only recommends visual identification for particles >1 mm in the monitoring of marine ecosystems (GESAMP 2019). Similar recommendations have

recently emerged from working groups in Asia (Michida et al. 2020). However, this limit conflicts with the published research, where most studies utilizing visual identification report detection limits of between 100 μm and 1 mm (Primpke et al. 2020a). As a result, it has been recommended that optical microscopy be combined with spectroscopy analyses (table 10.10 in GESAMP 2019). A similar approach was also suggested by Löder et al. (2017), introducing a size fractionation pretreatment step, which allows division into larger (e.g., >500 μm) and smaller particles (e.g., <500 μm), prior to sample extraction (Löder et al. 2017). While the smaller particles require sample extraction, the larger particles can be picked manually, assisted by optical microscopy, and identified chemically afterwards.

In cases where a chemical analysis of suspected microplastic is unavailable, the particles can be subjected to additional tests that can increase confidence in their identification as microplastics and enhance the quality of the results compared to the use of unassisted microscopy. Key information about particle properties can be determined by testing the physical behaviour/properties via microforceps or a dissecting needle. For example, as plastics melt at elevated temperatures, the thermal behaviour of a particle can be investigated by a hot needle or a heating plate (Lusher et al. 2020a).

Visual identification is considered inexpensive due to low instrument costs compared to more advanced techniques (Primpke et al. 2020a), although the rather high amount of personnel working hours associated with the manual analysis by experts is sometimes overlooked. These costs can be reduced by combining the optical microscopy setups with digital cameras that allow computer-assisted image analysis (Cowger et al. 2020b), which reduces the personnel costs associated with manual particle counting. Moreover, the overall processing time of a filter investigated for microplastics depends on the applied identification protocol, the filter size used, the sample type (e.g., sediment and surface water), the targeted size classes, and the general distribution of particles (Thaysen et al. 2020; Primpke et al. 2020a; Cowger et al. 2020b).

When using visual identification, it is important to consider human limitations and individual variations in differentiating nonpolymeric particles and natural polymer-based particles (e.g., chitin or wool) from the microplastics of interest, which may introduce a bias (Hidalgo-Ruz et al. 2012; Isobe et al. 2019; Zarfl 2019; Primpke et al. 2020a). Such a bias is dependent on the experience level of the investigators and is significantly reduced for very experienced laboratories (Isobe et al. 2019). Therefore, an appropriate training period and reference sample sets or schemes are required to minimize the degree of bias as much as possible (Lusher et al. 2017). Furthermore, the level of experience needed for the analysis of microplastics increases with decreasing particle size and the correct identification becomes much more difficult for very small particle sizes (<100 μm). Some reported guidelines for microscopy-based visual identification in this size range exclude the selection of particles exhibiting properties that make identification challenging. For example, particles may be excluded that are black, brown, white, or clear in colour (Wiggin and Holland 2019). In such cases, the

generated data most likely represent an incomplete picture of the true levels of microplastic contamination and make comparability of data sets very challenging (Kögel et al. 2022). For the current stage of knowledge regarding the monitoring of microplastic particles, this is an acceptable and pragmatic solution to reduce bias, but it will need to be reconsidered and adjusted as research and method refinements continue. Nevertheless, it is important that any data sets using such methods highlight these issues so that other researchers and users of the data are aware of these limitations and can account for them when translating monitoring data into practical measures and mitigation actions.

Fluorescent staining of microplastics for microscopy and preselection of particles

The visual assessment of microplastics can be enhanced with the use of fluorescent dyes to stain particles; this is being increasingly applied to achieve a faster selection of microplastic particles and help reduce researcher bias (Maes et al. 2017; Zarfl 2019). Staining is typically conducted after sample fractionation or extraction steps to minimize staining of the nonplastic organic material. Possibly the most frequently applied dye for staining microplastics is Nile red (NR; Andrady 2011). NR is inexpensive, easy to handle, and effective for particle sizes from $\geq$300 μm down to 3–20 μm, thus expanding the range typically achievable for microplastic identification by optical microscopy (Primpke et al. 2020a). The application of NR has been demonstrated across various sample types, including microplastics in water samples, sands, sediments, biota samples, and atmospheric deposition samples (Primpke et al. 2020a), and it has also been shown to be effective for the most common polymer types, including polyethylene (PE), polypropylene (PP), polycarbonate (PC), high-density polyethylene (HDPE), low-density polyethylene (LDPE), polyurethane (PUR), expanded polystyrene, polyethylene-vinyl acetate, and polyamide (PA; Zarfl 2019; Primpke et al. 2020a). Whilst there is some indication that different polymer types stain sufficiently differently to allow a tentative identification (Maes et al. 2017; Crew et al. 2020), a robust characterization equivalent to direct chemical identification methods is currently not possible.

Method developments towards staining-based polymer distinction would likely include as much effort as direct chemical identification by spectroscopic methods. Furthermore, parameters such as particle size, shape, and solvents used may alter the staining behaviour. The difference in staining efficiency ranges from 0% to 100%, with variations in costraining of biological material depending on the polymer/solvent combination (Shim et al. 2016; Tamminga et al. 2017). Importantly, NR staining has limitations with regard to certain microplastic subclasses, including those which are black in colour, fibrous, and rubber-based (Erni-Cassola et al. 2017; Maes et al. 2017). Error rates for identification can be further reduced if stained particles undergo subsequent Fourier-transform infrared spectroscopy (FTIR) or Raman spectroscopy to confirm chemical identification (Sutton et al. 2016; Maes et al. 2017). When NR is introduced into

the analytical procedure in this way, i.e., after fractionation or extraction, the staining acts as a preselection step that helps the user narrow down the number of particles that should undergo chemical identification, potentially saving considerable time. This approach is a promising technique to highlight potential microplastics and guide researchers in eliminating nonplastic particles (Klein and Fischer 2019). This approach is beneficial because it reduces the time for subsequent analysis.

The main drawback of NR staining for microplastic identification is its lipophilic nature, potentially staining all lipid materials present in a sample (e.g., those derived from biota; Cooksey et al. 1987). It is therefore necessary that comprehensive sample extraction and clean up steps are applied to avoid the potential misidentification of natural materials, e.g., lipid droplets and microorganisms, as microplastics (Erni-Cassola et al. 2017; Wiggin and Holland 2019). The use of oxidizing agents and enzymes are examples of approaches for cleaning up samples (Primpke et al. 2020a; Lusher et al. 2020b). As a second pitfall, NR can precipitate as agglomerated particles if applied in certain concentrations and solvents. This limitation can lead to confusion with stained microplastics (A.M. Bienfait, personal communication, 2022). Furthermore, conclusive method harmonization is not currently available. This is exemplified by the large differences between recommended optimal staining concentrations, with literature values ranging from 0.1 to 2 μg mL^{-1} (Erni-Cassola et al. 2017) up to 1–1000 μg mL^{-1} (Maes et al. 2017).

Fourier-transform infrared spectroscopic approaches for microplastic analysis

FTIR could arguably be considered the most widely used of the comprehensive and robust microplastic analysis techniques. In reality, this is a "catch all" term for a range of different FTIR-based approaches. FTIR produces a spectral pattern by the transmission, absorbance, or reflectance of the polymer at all analysed wavelengths of infrared (IR) light, called an IR spectrum, resulting in a reproducible pattern, metaphorically called "fingerprint" of the polymer types. The obtained spectra are compared with reference spectra for each polymer type. The application of FTIR for analysis of microplastics in environmental samples was recently reviewed (Primpke et al. 2020a). The 161 reviewed publications used a range of different FTIR technologies, including single-particle analysis using handhelds, fibre optics, and microscope-supported systems (μFTIR). Attenuated total reflection (ATR) FTIR on single selected particles was applied in 58% of the reviewed studies. ATR-FTIR is often applied to identify the polymer type of plastic particles >300 μm, as it does not require any specific sample preparation and the analysis does not require advanced skills, or mathematical correction, by the operator (Primpke et al. 2020a). In contrast, when targeting plastic particles <300 μm, μFTIR combines visual microscopic imaging and particle-size determination with FTIR, allowing individual particles down to sizes of 10–20 μm to be detected restricted by the diffraction limit for IR spectroscopy (Käppler et al. 2016). Furthermore, such microscopes can also be coupled with an ATR unit, which allows the selective

analysis of either small particles or selected areas on larger particles (Käppler et al. 2018).

Given the range of FTIR techniques available, it can be important to carefully consider which is the most appropriate for a specific study or application (depending on availability). However, each comes with its own set of advantages and disadvantages. The following issues need to be considered when deciding which method to apply:

- ATR-FTIR microscopy can be very time consuming and incur high personnel costs especially for large numbers of samples, as in most cases the crystal needs to be placed onto the system manually or only small areas can be measured. Furthermore, there is also a high risk of sample contamination and loss during the movement of the crystal.
- µFTIR in transmission mode is often affected by total absorption of the IR beam especially for thick particles or strong absorbing materials, which makes it difficult or impossible to detect certain types of particles with a high light absorbance. Furthermore, very small particles can also result in a high signal-to-noise ratio.
- µFTIR in reflection mode needs a surface with good IR beam reflective properties to perform the measurement, which limits its applicability for very small particles, or with significant diffuse reflection.

With samples of decreasing particle size, the sample handling process becomes increasingly difficult and can easily lead to erroneous results due to unmeasurable losses and contamination. Particles of interest must be concentrated onto membrane filters, reflective slides or IR transparent slides, and windows to avoid sample loss. The filters applied in microplastic analysis vary and include metal-covered PC filters (Cabernard et al. 2018) and silicone membranes (Käppler et al. 2015, 2016), with aluminium oxide filters being the most widely applied (Löder et al. 2015; Primpke et al. 2020a). Combined with these particle concentration means, an approach to FTIR spectrometry for microplastic is to image an area, sometimes the entire filter, IR transparent slide, window area or a reproducible subset of particles. These particles can be identified by an automated procedure for the preselection of particles by visual identification (Cincinelli et al. 2017; Phuong et al. 2018), selection and counting by particle finders (Palatinus et al. 2019; Renner et al. 2019b; Brandt et al. 2020), or the complete spectroscopic imaging of the filter area (Löder et al. 2015; Tagg et al. 2015). Thus, a quantitative output depicting particle number, area, and chemical identity can be achieved. Examples of the various FTIR analysis modes applied to the same area of a filter containing microplastic are presented in Fig. 1.

Complications arise if particles overlap on filters/slides, which causes sequestration and misidentification of particle sizes and numbers. Practically, there must be a compromise between numbers of particles deposited on a filter and the accepted rate of overlap, as it cannot be completely avoided. Additionally, large numbers of particles increase measurement times. It is for these reasons that often a fraction of the total extracted particles is investigated within one measurement, especially when samples have high particle numbers

(Cabernard et al. 2018). Given these restrictions, prescreening methods that include staining are considered reasonable and do not appear to influence the IR-based analysis. To avoid staining or to achieve defined measurement times per sample in routines, chemical (hyperspectral) imaging (µFTIR) is the method of choice. With this approach, all particles can be analysed, even if they form particle clusters (see Figs. 1b–1f). Still, such cluster situations may lead to uncertainties in terms of particle numbers and sizes. Hyperspectral imaging via focal plane array (FPA) detectors (FPA-µFTIR) currently represents the state of the art in microplastic analysis because it allows fast and effective identification and quantification of microplastics in samples of a variety of different ecosystems and waste management systems (Primpke et al. 2020a). FPA-µFTIR analysis generates a large volume of spectra (e.g., 1.5–3 million), which can be analysed with the help of false colour images (Fig. 1c) or semi-automated data analysis (Primpke et al. 2020a). In principle, imaging can be performed by any FTIR microscope equipped with single-element mercury cadmium telluride detectors (Figs. 1b and 1c), but spatial resolution and measurement times increase significantly with imaged filter area (Harrison et al. 2012; Vianello et al. 2013) as visible in Fig. 1c compared to images derived using FPA systems (Figs. 1e and 1f).

Combining infrared microscopes with laser-based systems

In the last few years, the scope of IR microscopes has been extended from the application of FTIR to the use of quantum-cascade laser-based systems. Such systems use a tuneable laser, which allows rapid screening of a sample, which is different from FTIR. The advantage of these systems is the far higher brightness of the IR beam for measurement. In general, there are two pathways available, either using a particle counting approach also called laser-direct-IR (Hildebrandt et al. 2020) or FPA-based hyperspectral imaging (Primpke et al. 2020d). Commonalities between both methods include no requirement for liquid nitrogen to cool the detectors for measurement and that samples can be measured in a rapid fashion, marking these techniques as good candidates for monitoring of microplastics.

Raman spectroscopy for microplastic analysis

In recent years, Raman spectroscopy has seen a significant increase in application for the identification of microplastics in environmental samples. Measurements are performed on the particle surface and produce vibrational spectra complementary to FTIR and the chemical/polymer identification can be performed in a similar manner (see below). Most Raman spectrometers are connected to microscopes (µRAMAN), which increases the spatial resolution of the analysis and allows the determination of particle numbers, shape, and size, in addition to polymer type, within a single measurement (Cabernard et al. 2018). Raman spectroscopy allows particles down to 1 µm in size to be measured, which is a slight improvement over µFTIR. Typically considered nondestructive, µRaman spectroscopy uses a focused laser beam that may damage the analysed particles, which increases in

Fig. 1. Small filter area targeted by the different approaches to select particles for Fourier-transform infrared (FTIR) as well as Raman microscopy. (*a*) Visually selected particles for further analysis. (*b*) Manual chemical mapping using a predefined area of measurement fields (distance 20 μm). (*c*) False colour image (FTIR, integral of region 2980–2780 cm^{-1}) of the manually measured area. (*d*) Area selected for hyperspectral FTIR imaging. (*e*) Hyperspectral FTIR image collected with 3.5× FTIR lens (11.6 μm pixel size). (*f*) Hyperspectral FTIR image collected with 15× FTIR lens (2.7 μm pixel size).
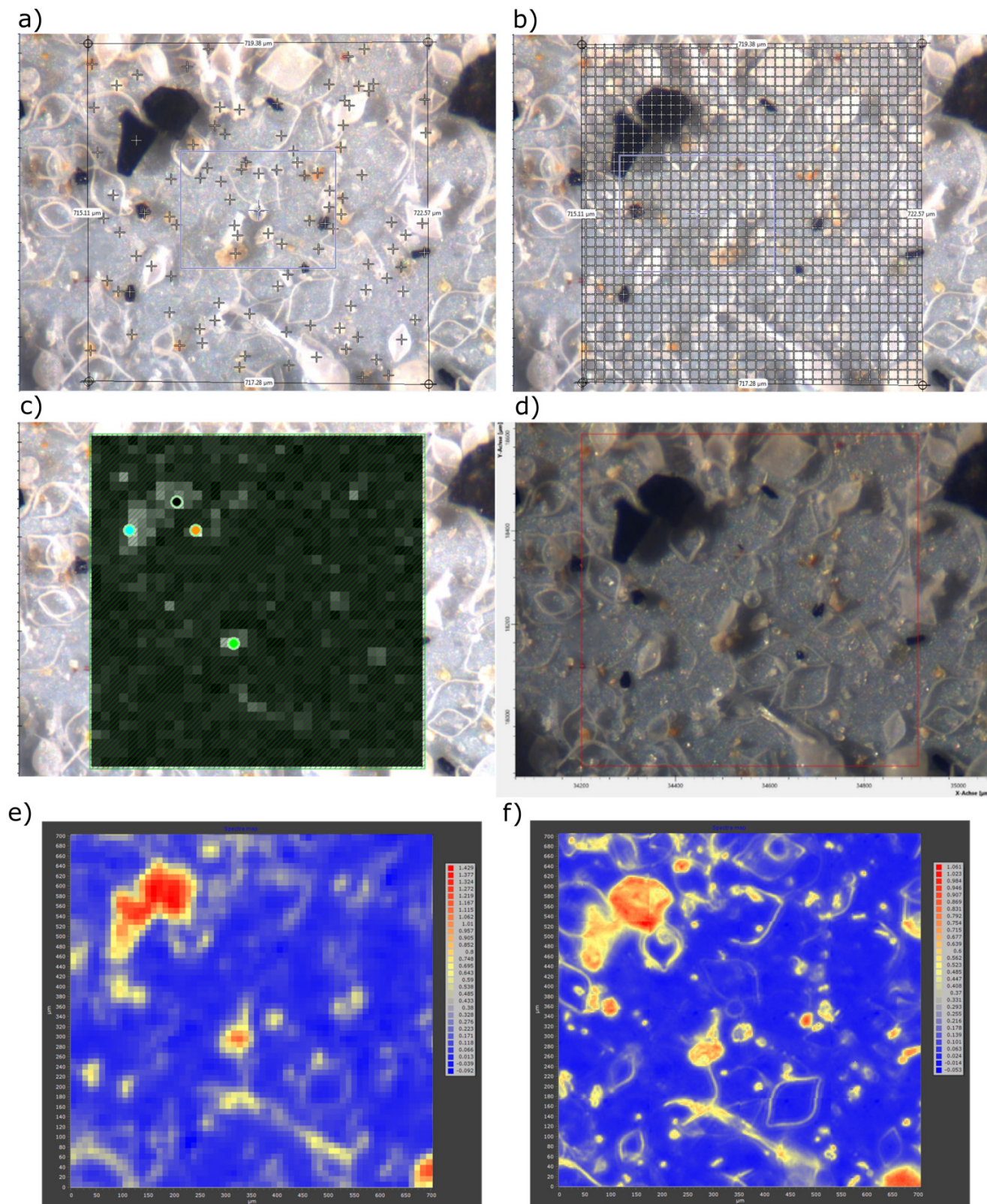
severity with the speed and spatial resolution of analysis because more energy is focused on the same small area.

As with FTIR analysis, larger particles (>300 μm) can be isolated and targeted as single particles for Raman analysis. The measurement of single particles is often performed on highly reflective surfaces to avoid background signals from the support materials such as metal-coated mirrors, aluminium sheets, or coated slides (Ossmann et al. 2017). For smaller particles (<300 μm), similar approaches can be used for automated particle identification on filter membranes (Frère et al. 2016). Common filters are metal-coated PC membranes or silicon membranes (Primpke et al. 2020a). The sample matrix influences the lower size of particles successfully characterized using Raman spectroscopy, for example, particles down to 1 μm were obtainable in simple matrices like drinking water, while in more complex sample matrices, identification of particles >5 μm has been demonstrated (Imhof et al. 2016; Käppler et al. 2016; Cabernard et al. 2018; Ossmann et al. 2018; Schymanski et al. 2018). Recently, it has been proposed that Raman spectroscopy might be able to measure particles at the upper edge of the nanoplastics size range (<1 μm; Schwaferts et al. 2019, 2020).

Raman spectroscopy is advantageous in that each particle can be documented by shape and size, allowing for immediate calculation of particle numbers, size, and shape distributions. These processes can be automatized using a particle-finder mechanism to determine particle shape, size, and polymer type, which can reduce both researcher bias and measurement time although individual measurements can take long (Frère et al. 2016; Cabernard et al. 2018; von der Esch et al. 2020a). As with FPA-μFTIR, some Raman instruments can measure the entire filter area with the imaging system. However, Raman imaging systems have long measurement times. Measurement times also differ between studies, for example, single particle analysis can take from just a few seconds to almost an hour (Primpke et al. 2020a). Consequently, sample analysis times can range from several days to weeks, especially for samples containing small particles (<10 μm) in high numbers (>1000 particles per filter; Primpke et al. 2020a). To circumvent such long measurement times, often partial analysis of the filter membranes (0.1%–30% of the area) is performed (Cabernard et al. 2018; Ossmann et al. 2018; Schymanski et al. 2018). However, a controlled method for ensuring representative analysis when using subsamples is currently being debated (Brandt et al. 2021; Schwaferts et al. 2021), and going forward approaches should be established to ensure that analysis is (i) viable from a cost and time perspective and (ii) produces representative and comparable data.

Imaging the whole filter area allows the identification and characterization of more particles in the same sample (Käppler et al. 2016; Araujo et al. 2018). Subsampling is challenging due to inhomogeneous distribution on the analysis filter or window (Thaysen et al. 2020; Brandt et al. 2021), but good results have been obtained by bootstrap estimations (Schwaferts et al. 2021). However, the measurement times required for Raman imaging are considerably longer than those required by FTIR imaging. For example, an area of 1 mm^2 had

a scanning time of 38 h for a measurement at 10 μm resolution (Käppler et al. 2016). A promising approach is stimulated Raman scattering (Zada et al. 2018), which decreases the measurement time significantly but is limited to particles of 12 μm in size and a few polymer types. Compared to FTIR, Raman spectroscopy has plenty of parameters that can be adjusted to improve the signal-to-noise ratio, including spectral range, excitation wavelength, the applied objective, resolution, and the number of accumulations. In summary, Raman is much slower than FTIR microscopy for routine bulk sample analysis. However, Raman has the capability to identify niche polymers and smaller size classes if time is not a limitation.

Reference library searches

Chemometric methods applied for spectral identification in FTIR and Raman spectroscopy/microscopy are similar. The identification of a microplastic particle typically comprises imaging of the individual particle, measurement of a raw spectrum, and determination of key particle details (dimensions, area, and shape) by image analysis. Following processing, the spectrum is then matched to the most similar reference spectrum available in the spectral library and the polymer type determined (Fig. 2). Respective reference spectra are collected in spectral libraries, which are available commercially, publicly free of charge, or are compiled by the different laboratories for their own specific purposes. It is important not only to use a library containing the analytes, but also to avoid the use of too extensive libraries with non-relevant analytes, as this increases the risk of misidentification, especially for small particles, where the signal-to-noise ratios are smaller. Some spectra of natural polymers can be similar to those of artificial polymers. To overcome limitations by manufacturers as well as the use of different spectral databases for library searches, open source software tools have recently been made available, which have the additional advantage of offering harmonizing potential in microplastic analysis (Primpke et al. 2020b; Cowger et al. 2021).

Nevertheless, matching the spectrum of a particle to a known polymer spectrum in a reference library often remains a challenge, due to a combination of factors that include spectral changes caused by weathering and degradation processes, contamination, optical distortions, and the presence of copolymers. Advances in chemometric techniques point to potential approaches that may be adopted to balance the competing priorities of efficient measurements and accurate identification (Chabuka and Kalivas 2020; da Silva et al. 2020; Wander et al. 2020; Faltynkova et al. 2021). These methods include the application of machine learning to identify useful portions of hyperspectral images and, hence, lower the computational capacity needed to completely process the aforementioned large numbers of spectra involved. Still, there is a strong debate ongoing as to which approach yields the best balance. Currently, studies comparing several of these find that, for example, Pearson correlation, which is often applied for library searches, is still one of the optimal operating approaches (Levermore et al. 2020; Morgado et al. 2021).

Fig. 2. Example of a microplastic particle identified by Raman spectroscopy using a combination of several spectral databases (Cabernard et al. 2018; Munno et al. 2020; von der Esch et al. 2020a). Left side: Particle image, raw Raman spectra, and particle details derived by image analysis. Right side: Processed spectra (red) and assigned library spectrum (blue) for the selected particle and reference spectra (highlighted in violet) combined with material name and further information.

Thermoanalytical methods combined with gas chromatography and mass spectrometry

The characterization of organic polymers by thermal degradation methods has a long and multifaceted tradition. Accordingly, polymer producing and processing industry, forensic science, and polymer analysis in general use these techniques in a broad field of applications (Wampler 2006; Tsuge et al. 2011; Kusch 2012; Kusch et al. 2013; Kusch 2014). A comprehensive collection of pyrolytic data for polymers and copolymers is provided by Tsuge et al. (2011). Additionally, commercial databases of polymer pyrograms and related data are available (e.g., F-Search by Frontier Lab; >1000 polymers, 500 additives). The destructive nature of thermal methods makes them the ideal concluding step in a complementary and comprehensive succession starting with optical chemical identification methods such as FTIR or Raman spectroscopy.

For microplastic identification with thermal methods, polymers are first degraded into polymer-specific products. This is performed at elevated temperatures (e.g., at 600 °C) in an oxygen-free environment to avoid combustion to elements, which would provide less analytical information. Coupled with GC, the generated volatile products are separated as a function of time producing a pyrogram. The pyrogram is the equivalent of a polymer fingerprint and allows a first qualitative analysis. If a mass spectrometer (MS) is used for detection, further specific identification of all generated compounds and even polymer-specific quantification is possible.

The most common and established instruments are online pyrolyzers coupled with GC and MS (py-GC/MS) and thermogravimetric analysers (TGA) combined with evolved gas analysis (EGA) for the systematic decomposition of polymers. Pyrolyzers differ in terms of temperature generation and mode of operation, heat transfer, and sample targets sizes crucial for sample capacity (Wampler 2007). The following ones are the most common types:

- Filament pyrolyzer: Samples are typically introduced in open or semiclosed quartz tubes and placed in a heated platinum coil. These are heated isothermally or with a temperature program (Fries et al. 2013; Dekiff et al. 2014; Nuelle et al. 2014).
- (Micro)furnace pyrolyzer: Samples are transferred into stainless steel cups that are heated in a ceramic oven. Here, they are pyrolyzed at a given temperature or heated with a temperature program (ter Halle et al. 2016; Hermabessiere et al. 2018; Käppler et al. 2018; Fischer and Scholz-Böttcher 2019; Gomiero et al. 2019a).
- Curie point (CP) pyrolyzer: Samples are introduced on wires or in semiclosed ferromagnetic targets. Their alloy defines a discrete, exact pyrolytic temperature that is almost instantaneously reached when placed in a high-frequency coil chamber. Accordingly, pyrolysis is performed exclusively isothermally. Alloys are available for a broad temperature range (Fischer and Scholz-Böttcher 2017).

The overall capacity of the individual techniques ranges from 1.5 mg (CP) to 50 mg (microfurnace). Since sample amounts might influence the heat transfer, and accordingly

the pyrolytic performance, sample volumes of around 1 mg or less are preferred and guarantee optimal operating conditions. Before pyrolysis is performed under polymer decomposition conditions, a potential stepwise heating and analysis of sample is beneficial (e.g., temperature programmed heating or a so-called "double shot" option). It enables further valuable and additional information to be gained about the low molecular, volatile sample content, e.g., low molecular organic additives, monomers, and accumulated smaller organic contaminants can be desorbed from the sample in a first moderate heating program. In this context, the use of a cryo-focussing unit enhances chromatographic performance.

TGA subjects the polymer to a temperature-controlled decomposition process, where the weight of the polymer changes in a characteristic way that can be recorded as a function of temperature. Polymer identification can be performed by the analysis of the generated decomposition gases (Tsuge et al. 2011; Seefeldt et al. 2013). Recently, a TGA variant named thermo extraction desorption (TED) GC/MS has been introduced (Dümichen et al. 2015, 2017, 2019). Here, the volatile decomposition gases are trapped and concentrated on a solid phase absorber bar, subsequently thermodesorbed and transferred into a GC/MS. The sample capacity of TED-GC/MS is stated as 100 mg.

Thermal multipolymer identification combined with GC/MS coupling

The high diversity of pyrolytic polymer decomposition patterns combined with the high compound resolution power of GC/MS coupling outperforms pure EGA techniques. In principle, all thermal methods connected to a GC/MS detection rely on the same principle of polymer identification, irrespective of the pyrolytic system. The degradation products released from polymers heated at defined temperatures and under the exclusion of oxygen are characteristic for the respective polymer types. Some have a rather unique GC resolving power prior to detection by MS, resulting in a characteristic pyrogram acting as a fingerprint for polymer-type identification. Ideally, 1–10 μg of polymer are necessary to generate a diagnostic pyrogram. However, individual particles with a mass as low as 0.3 μg isolated from a sediment sample have been shown to be sufficient for a successful polymer identification (Käppler et al. 2018).

In particular, the generation of highly specific pyrolysis products, combined with the resolving power of GC as a function of time, allows the simultaneous detection and identification of multiple polymers in a mixture within a single GC run. Retention time data of characteristic polymer degradation products and characteristic indicator ion(s) from their respective mass spectra are the key properties employed. From the MS data extracted in an ion chromatogram, representatives for each polymer are generated. They usually reflect a highly improved signal-to-noise ratio and enable polymer detection even at trace levels. To date, more than 10 different basic polymer types have been included in successful py-GC/MS applications for simultaneous microplastic detection in various complex matrices (Fischer and Scholz-Böttcher 2017, 2019; Dierkes et al. 2019; Gomiero et al. 2019a;

Dehaut et al. 2020; Primpke et al. 2020c). Similarly, TED-GC/MS has been successfully applied to identify different synthetic polymers in complex environmental samples (Dümichen et al. 2015, 2017; Eisentraut et al. 2018).

The thermal degradation behaviour and resulting intensities of selected polymer-indicator products determine the instrumental limits of detection (LOD) for the respective polymers. Generally, the limit of quantification (LOQ) is at the nanogram level for the individual polymer, but it can be affected by residual sample matrix (Fischer and Scholz-Böttcher 2019). To avoid interferences resulting from high background signals, an adequate pretreatment to remove and reduce inorganic and organic matrices is highly recommended prior to py-GC/MS analysis of environmental samples (Fischer and Scholz-Böttcher 2017, 2019; Gomiero et al. 2020). Typically, microplastic extracts from environmental samples are concentrated on pyrolytic inert filters (glass fibre or ceramic, e.g., anodisc; Fischer and Scholz-Böttcher 2017, 2019; Gomiero et al. 2019a; Primpke et al. 2020c). Optional online derivatization, e.g., with tetramethylammonium hydroxide can be applied to increase the py-GC/MS detection sensitivity for more challenging polymers such as polyester or polyether (Challinor 2001; Fischer and Scholz-Böttcher 2017).

An overview of common polymer-based materials, examples of their application in consumer products, their respective polymer backbones, and MS identifier ions yielding the various polymer clusters used for polymer quantification are present in Fig. 3.

Thermal multipolymer quantification combined with GC/MS coupling

Quantification is performed by either external calibration or related to an internal standard (ISTD$_{py}$) that is added directly before pyrolysis. The ISTD$_{py}$ is able to reduce negative, sample-dependent, and complex interactions that can occur within the pyrolytic process (Fischer and Scholz-Böttcher 2019). Calibration curves can be established between the mass of a polymer standard and its instrument signal.

This mass reflects the "bulk" concentration of the respective polymer in the sample because py-GC/MS does not distinguish, e.g., between pure polymer, copolymer, or other admixtures (Fischer and Scholz-Böttcher 2017, 2019). The resulting mass-related data are independent of particle properties such as shape, size, density, texture, surface aberrations, colour, brightness, opacity, or weathering. Microplastic quantification requires an adequate digestion cleanup step to ensure subsequent chromatographic performance and data quality, especially with an increasing content of nonplastic organic material in a sample (Fischer and Scholz-Böttcher 2019).

In TED-GC/MS, only the trapped gaseous products of the pyrolyzed sample (via TGA) are analysed via GC/MS after subsequent thermal desorption. Thermogravimetric analyser sampling cups enable a direct sample measurement for microplastics if their content exceeds 0.4% w/w (Dümichen et al. 2015, 2017; Eisentraut et al. 2018). A high organic content in the sample matrix can perturb the analytical performance. This influence can be reduced by sequential heating,

Fig. 3. Overview of the materials for various fields of applications, their respective polymer backbones, and identifier ions yielding the various polymer clusters used for polymer quantification (for further details, see Primpke et al. (2020*c*) and Dibke et al. (2021)).
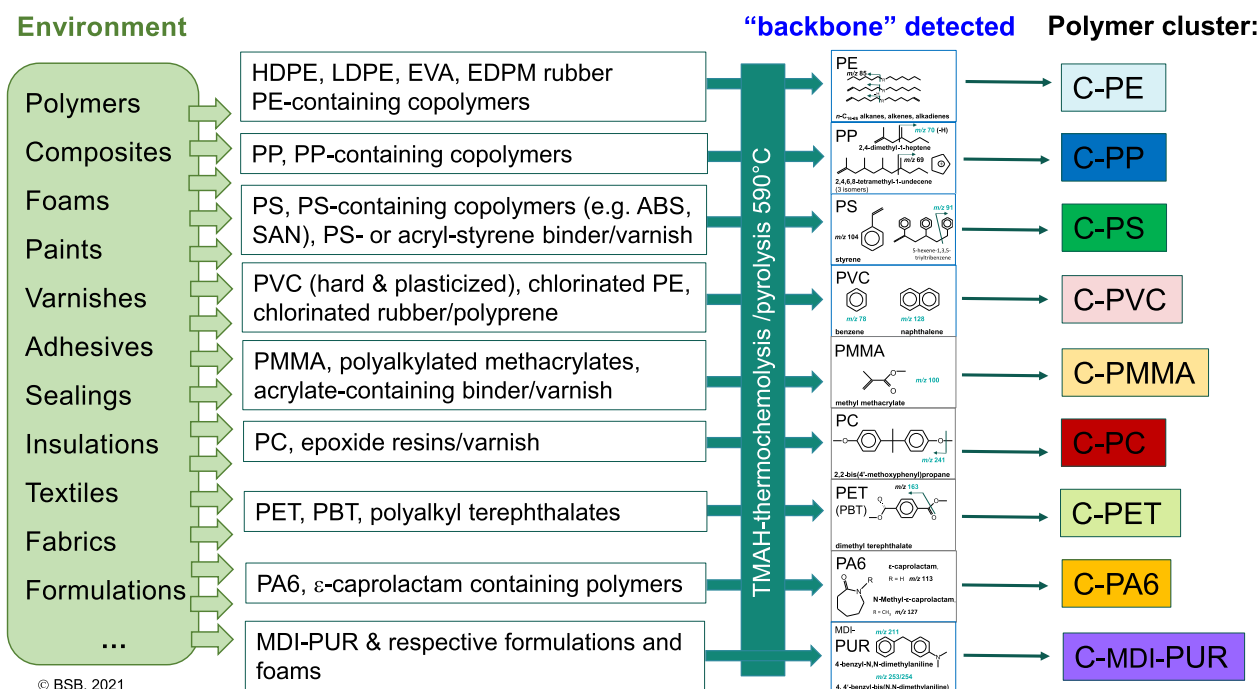
removing compounds that are more thermolabile than the targeted polymers.

LOQs are mainly determined by the GC/MS-system detector rather than by the pyrolysis method employed, and typically below 1 μg for almost all polymers, even when single-stage quadrupole MS with nominal resolution is applied (Fischer and Scholz-Böttcher 2019). LOQs in the lower nanogram or picogram range are possible with respect to instrumentation and processing modes, e.g., using triple quadrupole GC/MS or high-resolution MS, such as Orbitrap. If the data acquisition is performed in full scan mode, a retrospective data analysis of originally nontargeted polymer types is possible from stored data files if indicator ions and, if possible, retention times are available. The application of an internal standard additionally allows the generation of at least semiquantitative masses of these polymers. This compensates for the general destructive nature of thermal methods.

Synergies between thermoanalytical and spectroscopic methods

Spectroscopic and thermoanalytical methods generate highly complementary data (Hendrickson et al. 2018; Käppler et al. 2018; Primpke et al. 2020*c*; Kirstein et al. 2021). Thermal degradation methods provide the mass of a specific polymer that is defined by the detected polymer backbone (Primpke et al. 2020*c*; Dibke et al. 2021; Roscher et al. 2022). Spectroscopic methods such as FTIR and Raman methods provide particle size and number information, but the conversion to mass-related data has clear limits as it assumes ideal ellipsoid shape of a particle (Simon et al. 2018; Mintenig et al. 2020; Primpke et al. 2020*c*). Few large particles have a higher

impact on mass data compared to the contribution of a high number of very small particles, highlighting the complementary nature of number counts (per size fraction) and mass information.

Quality control/quality assurance

QA/QC measures are essential for microplastic investigations. Many QA/QC issues have been identified (Brander et al. 2020) and appropriate QA/QC measures are currently being developed for research and monitoring of microplastics. Such measures cover all parts of the analytical procedure, i.e., sampling, sample extraction/matrix reduction, and analysis. Each of these steps has its own challenges for QA/QC, but given the omnipresence of microplastics in all environments, contamination is a particularly critical issue in microplastic analysis. Blank samples have a central role in microplastic sampling, sample processing, and instrumental analysis.

Starting with sampling, there are various factors to be considered. Samples may be contaminated by the atmosphere, the vessel/instruments used for sampling, and other factors at the sampling location. Awareness of this issue has increased with the number of published studies leading to various mitigation and methodological recommendations. To account for atmospheric deposition and contamination from personnel conducting the sampling, the exposure of filters in Petri dishes or filtered water in sampling to ambient air is recommended as a minimum at the sampling stations (Brander et al. 2020). Such blanks can be accompanied by field blanks that mimic the sampling process, for example, by using prefiltered water and exposing it as if it were a sample. In contrast to atmospheric blanks, which require minimal

storage and application space, field blanks of large-scale sampling equipment may be associated with larger logistical constraints, e.g., on research vessels as they need to be moved, processed, and analysed in the same way as the environmental samples at the sampling station.

Potential contamination is not the only issue to consider when sampling for microplastics. The applied sampling device (e.g., sediment sample corer type, water filtration net, or filtration system) and the mesh sizes employed can strongly affect the outcome of any microplastic study. With a variety of methods utilized by researchers around the world, combined with the limited number of standard procedures available noncommercially for microplastic investigation, the tools and methods used need to be reported in detail (Cowger et al. 2020*a*) to ensure the correct data interpretation and use. With respect to microplastic extraction and clean-up, only very limited information is available on how such methods and devices perform in terms of the reported recovery rates and in comparison to one another. For that reason, replicate samples are advisable, if possible. Data on reproducibility and recovery rates of sampling would be of interest to the scientific community. In addition, the variability of microplastic occurrence in different environmental compartments should also be considered in the sampling process and reflected in an appropriate number of replicates.

In contrast to the sampling step, the determination of recovery rates during sample extraction and particle separation has already been regularly applied and compared for larger microplastics items. For smaller particles, especially those <100 μm, such experiments are not typically performed on a regular basis. This is largely due to the lack of suitable reference materials in this size range and the fact that the commercially available reference materials are primarily spherical particles, which limits their applicability. Nevertheless, the inclusion of procedural controls is important for investigating the influence of the selected methodology on the separation quality. As this influence can vary from person to person, for different matrices, and with each adjustment of the method, it is recommended that procedural controls accompany all individual analysis campaigns and are implemented regularly.

In the laboratory, procedural blanks allow the level and potential sources of particle contamination to be determined. Similarly, how any identified sources of contamination are addressed adds another layer of complexity to data reporting and QA/QC. Known contamination or background levels observed in blanks are often subtracted from the particle count or checked in relation to the derived particle numbers. These procedures are of high value for source tracking of contamination. For example, it has been demonstrated by the application of procedural blank samples that a high number of PP particles were emitted from a sampling device (Mintenig et al. 2019), PA particles were introduced to fish samples by a meat mincer packing (Gomiero et al. 2020), and that stearates used on nitrile gloves can act as a potential false positive for all types of analytical procedures (Witzig et al. 2020). Within the scope of research into microplastics shapes, colours, and sizes, a blank correction might be linked to these parameters, e.g., by separation of colours and the use of unique coloured

clothing and materials in contact with the sample. Similar approaches are available if polymer identification techniques are applied, which may result in even more complex situations due to a large variety of polymer types and sizes. However, the question remains as to how many blanks are needed for a representative description of laboratory background levels, to be applied in blank correction. An example using an automated analysis approach can be found in the supplementary information of Roscher et al. (2021). Still, other approaches might be used and need to be evaluated in the future.

Procedural blanks are also very important for the determination of LODs and LOQs. In analogy to the common practice in analytical chemistry that refers to the signal-to-noise ratio, LOD and LOQ can be transferred to particles as three (LOD) and ten times the standard deviation (LOQ), respectively, of the average number of particles in the procedural blanks (Hildebrandt et al. 2021). These values allow a direct comparison of data quality and provide metadata for data studies and modelling, as well as assessments of achievable sensitivity and its variation among laboratories.

Beyond these measures, laboratory air should also be monitored with regard to contamination from fibres and particles. Ideally, sample handling would take place in clean rooms, although not all laboratories may have such facilities. By using laminar-flow cabinets for sample handling, a similar air quality can be achieved while keeping the cost within a medium price range (Wesch et al. 2017; Schymanski et al. 2021). Particle filter units, like the often used "Dustbox" that contains HEPA14 filters, can be used to remove particles from ambient air and are more commonly available now due to the COVID-19 pandemic. These specially designed filtration units remove dust particles and fibres with a high efficiency and can be applied to clean the laboratory air in general.

While the challenges discussed above encompass potential overestimation bias due to contamination, to avoid or correct for underestimation bias, method validation needs to be implemented to determine microplastics recovery efficiency. This can be achieved by spiking samples early in the process with known amounts of marked or unmarked reference microplastics, followed by conducting the sampling, extraction filtration, and endpoint analysis procedures on those samples and quantifying the recovery. To be considered reliable, such reference microplastics need to closely represent the particles expected in the sample with respect to size, shape, and polymer type. In addition, the exact original polymer content of the (ideally natural) reference sample has to be known in advance. Both requirements can only be fulfilled to a limited extent. Most importantly, the results of recovery experiments allow the quality of the applied, specific analytical protocol to be assessed.

To quantify the recovery efficiency during the analysis procedure of real samples, the utilization of ISTDs is a widespread practice in analytical chemistry. Its successful application requires that the ISTD and analyte(s) exhibit an almost identical behaviour. Any loss of analyte should be mirrored by the ISTD, while their relative ratio remains constant and enables quantification. While this is convertible for soluble compounds and sample analysis in solution, this is not

the case for particulate analytes, such as microplastics, especially if they exhibit a high degree of diversity in terms of size and shape. The loss of ISTD particles during sample preparation does not mean that an equivalent number of analyte particles have been lost as well. Although labelled polymers appear to fulfil the principal requirements for an ISTD, they are only suitable for general recovery experiments but not for (particle) quantification based on internal standardization. Nevertheless, labelled or metal-doped polymers (Mitrano et al. 2019) are highly relevant, e.g., to study transport processes related to MP with respect to environmental pathways or cellular interactions and residence times.

The use of ISTD for MP quantification is applicable if an identical analytical behaviour of the analyte and the ISTD can be assured. So far, successful applications are restricted to MP (mass) quantification by thermal methods. Examples include (i) solvent extraction of selected (solvable) polymers using a solvable ISTD (e.g., deuterated PS; Dierkes et al. 2019), (ii) thermal extraction of polymers from the sample without further preconcentration steps (Eisentraut et al. 2018), and (iii) the addition of ISTDs prior to the thermal decomposition process to compensate a variety of interactions during the pyrolytic process as the final determination step (Fischer and Scholz-Böttcher 2019; Dibke et al. 2021; Goßmann et al. 2021).

Improving the quality of microplastic analysis is an ongoing research field in itself. The scientific development would benefit from detailed reporting of QA/QC measures and issues, for a better understanding of pitfalls and limitations and a better description of what is achievable. External QC measures, as widely applied in other fields of analytical chemistry, are still under development for microplastic research and monitoring. First interlaboratory studies still report challenges in the accuracy and precision of microplastic determinations in environmental samples (van Mourik et al. 2021). Attempts are ongoing to produce reference materials, which can support the laboratory's internal QA/QC (von der Esch et al. 2020b; Seghers et al. 2021).

Data processing and reporting in the field of microplastic research

Due to the fact that various spectroscopy and thermoanalytical methods currently exist for a range of instrument types produced by different manufacturers using a series of software and databases, the quality and comparability of the derived microplastic data are influenced by these factors. While the comparison of analytical methods is still hampered by the small number of designated polymer standards available (von der Esch et al. 2020b; Seghers et al. 2021), the first application of ring trials (Isobe et al. 2019; Müller et al. 2020; van Mourik et al. 2021) is beginning to present their results on the comparability of laboratories and matrices.

Given the challenges to produce comparable data, both within and between laboratories, researchers have focused on analyses in a harmonized manner, both at the instrument level (Renner et al. 2019b; Brandt et al. 2020; von der Esch et al. 2020a) and the data processing level. Various commercial and researcher-derived databases for the identification of microplastics by FTIR and Raman spectroscopy are currently

available (Cabernard et al. 2018; Primpke et al. 2018; Munno et al. 2020; Primpke et al. 2020b; De Frond et al. 2021). De Frond et al. (2021) have shown that the combined use of such published databases yields higher scores than the application of only commercial ones. As these databases were specifically designed for microplastic analysis, they contain data related to both natural materials and weathered plastics, which increases the data quality. The presence of protein-based natural PAs in the database is especially important to avoid confusion with synthetic PA (Primpke et al. 2020d). These databases can be easily applied via open access software such as "siMPle" or "Open Specy" (Primpke et al. 2020b; Cowger et al. 2021). In a recent example, data were harmonized within a Citizen Science project following this approach (Kiessling et al. 2021). This development of open access software is accompanied by the improvement of the chemical identification approaches by other chemometric methods (Mecozzi et al. 2016; Renner et al. 2017; Hufnagl et al. 2019; Kedzierski et al. 2019; Renner et al. 2019a; da Silva et al. 2020), some of which are already commercially available (e.g., Purency).

Independent of their source, novel and existing methods need to be targeted by QA/QC using procedural controls, negative controls, and, for the harmonization of analysis, a performance comparison with existing reference data sets if available. To avoid any confusion with occurring natural materials, identification techniques should be regularly investigated for unknown sources and potential interferences (Witzig et al. 2020).

While the issues raised above primarily focus on the generation of data, the actual reporting of data often lacks the use of a common database and reporting format. In the scope of the AMAP microplastic monitoring guidelines, several options have been discussed. For example, data for air levels or atmospheric deposition samples could be reported to the EBAS Database, operated by the Norwegian Institute for Air Research (AMAP 2021). Data for the marine environment could potentially be reported to the Environmental Database operated by the International Council for the Exploration of the Sea (ICES; AMAP 2021).

Section 2. Implications for the identification of microplastics in the Arctic

The AMAP guidelines for monitoring of litter and microplastic in the Arctic suggest as first priority compartments to establish the monitoring of microplastic in water and sediment (AMAP 2021). In addition, monitoring of plastic particles is recommended in seabirds (for particles of >1 mm, generally speaking) and on beaches, the latter in terms of beach litter (AMAP 2021). In addition to the general challenges associated with the monitoring of microplastics, the Arctic region presents a number of logistical, cost, and technical difficulties (Grøsvik et al. 2022; Kögel et al. 2022; Lusher et al. 2022; Martin 2022; Provencher et al. 2022, this issue). In this section, we summarize the general challenges associated with establishing and conducting robust microplastic

monitoring and outline the additional factors that must be addressed when monitoring microplastic in the Arctic.

Research and monitoring strategies

One of the major issues in microplastics monitoring concerns the effort (cost, time, and equipment) that is needed to sample and extract microplastics from different environmental matrices. For example, sediment, which is often considered the most relevant matrix for MP, is also one of the most difficult matrices to sample, especially as the water column depth increases. This becomes even more difficult in the Arctic where sampling sites are often long distances from the mainland and where the water column can be very deep. Sampling equipment also needs to be able to withstand the extremes of the Arctic environment. The diversity of plastic material present in the marine environment has created methodological challenges, especially for the targeted, quantitative analyses of microplastics (GESAMP 2016).

The technical constraints associated with some of the different methods limit their use for purposes other than monitoring, at least in the short term. For example, the difficulties with adequately extracting and measuring the smallest microplastics from environmental samples, especially those smaller than 10 μm, means that a full picture of microplastic pollution is almost impossible to achieve at present. These limitations also prohibit the monitoring of microplastic ingested by small organisms, whose food size ranges are restricted (i.e., 10–80 μm for mussels; Ward et al. 2019; Gomiero et al. 2019b). It is also important to highlight that smaller microplastics are more difficult and take more time and resources to identify and quantify. At present, there is still a lack of analytical methods capable of characterizing and quantifying very small-sized microplastics and nanoplastics in environmental samples. In general, we do not see that such technical challenges cause any additional difficulties within the context of microplastic monitoring in the Arctic, as the sample preparation and analysis steps typically take place in the laboratory. It is also important to highlight the risks of sample contamination, which primarily occurs during sampling and sample processing, as discussed above, and which increases for smaller microplastics. Here, the Arctic presents a specific challenge, as personnel conducting the sampling need to wear a significant amount of outdoor clothing for protection against the weather and low temperatures. Nowadays, such clothing is predominantly made of synthetic textiles, which increases the risk of contamination. There is therefore a need to harmonize procedures to mitigate airborne contamination, to ensure that this is adequately considered and addressed in all monitoring studies.

Traditionally, data sets have been difficult to compare due to the wide variety of methodological approaches that are applied by different researchers to extract, identify, quantify, and characterize MPs. The majority of these method inconsistencies can be related to: (i) differences in the lower and upper size limit examined; (ii) the sensitivity of the applied extraction technique; and (iii) differences in sampling technique, all leading to a wide variety of efficiencies and reporting units (Lusher et al. 2015). These challenges are sought to overcome with a set of harmonized guidelines for monitoring in the Arctic, including specific recommendations for microplastic monitoring in several compartments, while leaving room for updates as research progresses and new knowledge becomes available (AMAP 2021).

As highlighted by GESAMP (2019), many of the methods used and reported for microplastic sampling and sample processing have key limitations. One example is the use of manta trawl nets for collecting microplastic present in surface waters. These nets typically have a pore size of 330 μm to prevent collection of too much microbiota, but this means that microplastics below 330 μm are not effectively collected. Given that particle numbers have been demonstrated to increase almost exponentially with decreasing particle size (Cabernard et al. 2018; Primpke et al. 2020d; Kooi et al. 2021) manta nets have the potential to miss the vast majority (by number) of microplastics present in the surface water. As a result, it is widely acknowledged that further research into improving sampling and sample processing methods is needed, as well as more harmonization of sampling design in terms of the number and the size of replicates, the spatial area, and the frequency of sampling. This is particularly important in the Arctic, where the high costs associated with microplastic monitoring need to generate robust and valuable data (Mallory et al. 2018). In addition, time series are planned for litter and microplastic in the Arctic, which should be inherently consistent. Finally, working at the Arctic scale could also support the future development of automated sensors and real-time measurements in extreme environments. This will open up for new possibilities of in situ analysis in the environmental compartments of the Arctic.

Balancing cost and time

In the scope of a recent review (Primpke et al. 2020a) and the AMAP guidelines (AMAP 2021), different methods for the analysis of microplastics were assessed with regard to the associated costs for microplastic identification and quantification. In most cases, the methods offering the best degree of accuracy and the largest particle size range were expensive due to a combination of high instrument costs (purchase and operation) or personnel requirements (time and competence level). In contrast, the cheaper approaches typically have a much higher degree of uncertainty and (or) a much more limited particle size range, although they can also be more resource demanding in terms of personnel costs relative to some of the more advanced techniques. All methods were found to have both positive and negative aspects. For example, optical microscopy is inexpensive from an instrumental point of view and can be easier to use in the field or on a research vessel. However, the personnel demand is often rather high because of the number of potential samples to be analysed manually. In addition, the success of optical microscopy and the quality and value of the data produced are strongly linked to the experience of the investigator, which may induce a human bias and are dependent on the application of strict and harmonized identification guidelines. In contrast, chemical identification by microscopy–spectroscopy requires rather expensive instrumentation, but the high level of

automation significantly reduces the personnel costs. As a result, the personnel costs for microscopy–spectroscopy analysis are typically 1–2 h per sample, while this increases to 4–7 h when using optical microscopy methods (even those supported by dye staining). In the case of monitoring in the Arctic, a good compromise between chemical accuracy, field work applicability, and costs needs to be defined. As an example, the individual needs presented in Table 1 were derived from the AMAP Monitoring Guidelines (AMAP 2021).

To reduce the demand and costs for the chemical identification of microplastics, the approach of subsampling is commonly applied in microplastic research (Mintenig et al. 2020; Thaysen et al. 2020; Brandt et al. 2021; Schwaferts et al. 2021). Depending on the type of spectroscopy applied, this can be performed via a minimum number of randomly selected particles or small fields of views that follow a random or specialized pattern by the instrumentation. These approaches can be performed among all size classes and minimum values range from 50 particles per sample (Mintenig et al. 2020) for particles >300 μm to several thousand particles (Schymanski et al. 2021) for particles <300 μm. For imaging approaches and automated particle counting approaches, the data are more complex to address. Currently, researchers have not agreed on an optimal strategy. While Mintenig et al. (2020) found that 66% of the filter should be analysed using imaging techniques, other studies suggested to use different shapes or a defined number of a small field (Brandt et al. 2021; Schwaferts et al. 2021). In the context of monitoring, either of these approaches is considered sufficient for determining the total number of plastic particles in a sample. Splitting the sample prior to chemical analysis is another way to reduce analytical costs, although this can only be performed during sample handling in the laboratory and may induce risks such as missing polymer types or over/underestimating the total load of microplastics (Abel et al. 2021).

Implications for reporting on microplastics

Researchers have developed, implemented, and reported a diverse range of methods and nonstandardized approaches for microplastic sample collection, extraction, and analysis. These are often insufficiently described or exhibit critical differences that result in many studies being neither comparable nor reproducible. Each method typically has its strengths and weaknesses, and there are continued efforts to further optimize existing methods, as well as develop new ones that represent improvements in throughput, LODs/LOQs, and reproducibility. Attempts to develop optimized approaches have contributed to the rapid evolution and diversity of the methods applied in the last few years and made comparison of data sets increasingly difficult, especially when reports on method validation are incomplete. In addition to this diversity of methodologies, the situation is compounded by the research community using a broad range of data reporting formats. This includes differences in the classification of microplastic properties (e.g., size, shape, and colour), as well as in the units in which microplastic data are reported, including particle number or mass concentrations.

We feel that it is important to highlight that utilization of different methods to generate microplastic data are not necessarily an issue in itself. The challenge is that the methods must be fit for purpose and able to deliver data of a comparable quality. Unfortunately, the different methods reported in the microplastic literature have resulted in significant variation in the quality and value of microplastic data that are available to users (e.g., risk assessors and regulators). There is, therefore, a need for tools that can help users of microplastic data to assess the quality and value of reported studies and data sets. This issue has been identified within the scientific community and the first generation of data quality assessment tools are already starting to become available (e.g., https://fare.grida.no/). In addition, interlaboratory comparisons have been conducted by organizations with long-term experience in the field of QA/QC in analytical chemistry (van Mourik et al. 2021).

A further complicating issue can be that microplastic data are not always reported or archived in open access formats. A recent publication has provided a comprehensive set of recommendations and guidelines for the reporting of microplastic data that aims to increase the reproducibility and comparability between studies (Cowger et al. 2020a). The authors provided a Mind Map in which general method groups flow from the primary term "Microplastics Reporting Guidelines". The interactive Mind Map is available as an Open Science Framework project in which users can access more details. We suggest that the same methodological quality criteria and data reporting criteria are clearly recommended by all monitoring programs developed around the world, where modifications are introduced to support specific variations in program requirements. Here, the Arctic represents a good example and the recently published AMAP Guidelines were developed specifically to be as relevant as possible for the Arctic ecosystems, communities, and research scientists (AMAP 2021). Any key differences from other monitoring programs should be clearly highlighted and justified in individual monitoring programs to help achieve harmonization across microplastic studies conducted by different research groups around the world.

Recommendations for the characterization and quantification of microplastics in an Arctic monitoring program

Our first recommendation is that microplastic monitoring in the Arctic follows general developments in microplastic monitoring and seeks to follow and implement these to ensure comparability at the global scale.

For the reporting of the data across compartments suggested for monitoring of microplastics in the Arctic, a harmonized scheme for size classes, colours, shapes, and polymer types should be used. To achieve this, microplastic shape should be determined by optical microscopy, where visual identification should follow the categorization scheme published by Lusher et al. (2020a) to achieve harmonized data (Lusher et al. 2020a). To allow cross-analysis among databases,

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Table 1. Cost estimation for the presented analytical techniques ranging from optical methods towards chemical analysis based on data from Primpke et al. (2020a).

Working mode	Unit	Visual identification		Fluorescent staining	Fourier-transform infrared spectroscopy (FTIR)			Raman spectroscopy		Pyrolysis-(Py)-GC/MS		Thermal extraction desorption (TED)-GC/MS
		None	Microscope	Nile red	Qualitative	Particle-based microscopy	Imaging microscopy	Qualitative	Particle-based microscopy	Qualitative	Quantitative	
LOD		1 mm	100 µm	3–20 µm	>300 µm	25 µm	10 µm	>300 µm	1 µm	~1 µg IP, PD	«1 µg PD, Mix	<1 µg PD, Mix
Field applicability		Good	Good	No	Handheld	No	No	Handheld	No	No	No	No
Automated data evaluation		No	No	No*	No	Yes	Yes	Yes**	Yes	No	No***	No***
Measurement time[a]	min	1	60	35	1	360	240	2	2580 ≥ 10 000	35–120	120	120
Data analysis time[a]	min	NA			1	60	360	1	1	5–10	60****	60****
Personnel working time[a]	min	1	60	35	2	120	60	3	60–580	5	30 (qual.) 72 (quant.)****	30 (qual.) 72 (quant.)****
Typical fractions per sample		50 P	7 fm	7 fm	50 P	1 fm	1 fm	50 P	1 fm	50 P	1–5 CQ	1–5 CQ
Average working time per sample	min	PND	420	245	PND	120	60	PND	60	PND	72–216	72–216
Monitoring		+	+	+	+	+	+	+	+	+	+	+
Modelling		+	+	+	+	+	+	+	+	+	+	+
Routine		–	+	+	+	+	+	+	+	–	+	+
Research		–	–	–	+	+	+	+	+	+	+	+
Risk assessment		–	–	–	+	+	+	+	+	–	–	–
Polymer identification		–	–	–	+	+	+	+	+	+	+	+
Particle number determination		+	+	+	+	+	+	+	+	–	–	–
Mass determination		+	–	–	+	–	–	+	–	+	+	+
Particle sizes determination		+	+	+	+	+	+	+	+	–	–	–

Note: CQ, pyrolysis cubs or quartz tubes; F, filters; IP, isolated particle; GC/MS, gas chromatography-mass spectrometry; LOD, limits of detection; min, minute; Mix, mixture of polymers; P, particle; PD, polymer dependent; PND, particle number dependent. * mage analysis possible, ** for Raman microscopes, *** autosamplers are available, and **** calculated based on a micro-furnace system with an average sequence size (6 standards, 10 samples).
[a]Calculated for one filter/particle per analysis.

Table 2. Eight-colour classes for data reporting based on the EMODnet database (https://www.emodnet-bathymetry.eu/)

Black/grey	Blue/green	Brown/tan	White/cream	Yellow	Orange/pink/red	Transparent	Multicolor

Table 3. Polymer types recommended for reporting of microplastics in the Arctic.

Polymer type name	Examples of materials included (detailed level)
Polyethylene based	HDPE, LDPE, and copolymers with a major PE fraction
Polypropylene based	PP copolymers with a major PP fraction
Polystyrene based	PS copolymers with a major PS fraction
Polyamide based	All types of PA like the various nylons
Polyurethane based	All types of PUR
Polymeth (ester)acrylate based	All types of PM(ester)A
Polyester	PET, all other types of polyesters
ABS	ABS
Polycarbonate	PC
Rubbers, sealing	Other rubbers, like EPDM
Rubbers, automotive	TWP
Paint/varnish particles	If separate from PM(R)A
Ethylene-vinyl acetate	
Cellulose acetate and similar	
Nitrile rubbers	
Natural rubber derivatives	
Polyacrylonitrile	
Polyfluorinated polymers	e.g., PTFE
Polychlorinated polymers	e.g., PVC, chlorinated PE, and various chlorinated polymers
Silicone rubbers and coatings	
Other plastics	e.g., PEEK
Other rubbers	
Other microlitter materials	

Note: Reproduced from the AMAP Guidelines (AMAP 2021).

as the recommended ICES database also acts as a contributor, the following eight colours (Table 2) should be reported along with these shapes in accordance with the colour characterization applied in the EMODnet database (https://www.emodnet-bathymetry.eu/).

It is crucial that the size classes are reported in a manner that allows harmonized data reporting across various monitoring guidelines and databases, as well as different environmental matrices and geographical regions. Therefore, we currently recommend that identified microplastics are reported in the following size classes: >1 mm, 1 mm to 300 μm, and <300 μm to LOD_{size} (limit of detectable size for a specific analytical approach). The lower detection limit in size (LOD_{size}) of the data should be reported separately to allow better contextualization for future use. This should be performed for each polymer type selected for inclusion in the Arctic monitoring program (see Table 3), where the analysis was determined as mandatory in the respective guideline (see Table 4 for the Arctic).

Where a specific polymer type was actively not included as part of the identification and analysis method, a value of "not applicable" (N/A) should be reported. Where a specific polymer type was included but not observed within an individual sample or data set, a value of 0 should be reported. This critical distinction ensures that "absence" and "unmeasured" polymer types can be separated in the data. The reported data for polymer type analysis by spectroscopy should include information on the subsampling approach applied. In the case of microplastic sizes between 1 mm and 300 μm, this analysis is considered mandatory for most compartments selected for microplastics monitoring in the Arctic (Table 4; AMAP 2021). Due to the large number of commercial databases and available software, details about those utilized in a specific study should be reported as metadata.

Where thermoanalytical methods are applied, it is recommended to pyrolyse the entire processed sample, rather than using aliquots, to achieve high sensitivity and to be able to work in a "comfortable" calibration range. With respect to the expected polymer concentration, sample volume should be thoughtfully adjusted before any preconcentration procedure. The expected polymer mass should be located in the middle of quantification range of the polymer. This range varies across different instrumentations, but typically covers 0.5–100 μg polymer. As mass-related data for polymers or, more precisely, polymer clusters (Fig. 3) are still rare, relevant publications and experts should be consulted. From data already available, the expected mass ranges of total microplastic are in the ppt to ppb level for ocean water (Fischer and Scholz-Böttcher 2019; Primpke et al. 2020c; Dibke et al. 2021),

Table 4. The demanded data accuracy for monitoring in the Arctic for the individual compartments covering different size classes.

Matrix	Number	Mass	Size	Subsampling recommended	Size and shape	Colour	Chem-ID
Air	Mandatory	–	<300 μm	No*	Mandatory	–	Yes
Water	Mandatory	–	5000–300 μm	For Chem-ID	Beneficial	Beneficial	Yes (1 mm to 300 μm)**
Water	Mandatory	–	<300 μm down to LOD	Nice to have	Beneficial	Beneficial	Nice to have
Sediments	Mandatory	Beneficial	5000–300	For Chem-ID	Mandatory	Mandatory	Yes (1 mm to 300 μm)**
Sediments	Beneficial	Beneficial	300 down to LOD	For Chem-ID	Mandatory	Mandatory	Beneficial
Ice	Not defined	Beneficial	5000–300	–	Mandatory	Mandatory	Yes (1 mm to 300 μm)**
Ice	Beneficial	Beneficial	300 down to LOD	–	Beneficial	Beneficial	Beneficial
Shorelines***	Mandatory		>25 mm	Not defined	Not defined	Not defined	Not defined
Soils	Mandatory	–	5000–300 μm	Yes	Yes	Yes	Beneficial
Biota	Mandatory	–	>100 μm	For Chem-ID	Mandatory	Beneficial	Yes
Fish	Mandatory	Mandatory	>300 μm	For Chem-ID	Size mandatory; shape beneficial	Beneficial	Yes (1 mm to 300 μm)**
Fish	Beneficial	Beneficial	<300 μm	For Chem-ID	Size beneficial; shape beneficial	Beneficial	Yes (1 mm to 300 μm)**
Bird	Mandatory	Mandatory	5000 to >300 μm	For Chem-ID	Beneficial	Beneficial	Yes (1 mm to 300 μm)**
Mammal	Mandatory	Mandatory	>2.5 cm to 300 μm	For Chem-ID	Size mandatory; shape beneficial	Beneficial	Yes (1 mm to 300 μm)**
Mammal	Beneficial	Beneficial	<300 μm to LOD	For Chem-ID	Beneficial	Beneficial	Beneficial

Note: Chem-ID, Chemical identification. *Subsampling should be avoided, ** analysis of at least a subsample, and *** no microplastics defined. Adapted from (AMAP 2021).

in the ppb level for sediments (Fischer and Scholz-Böttcher 2019; Gomiero et al. 2019*a*; Primpke et al. 2020*c*), and in the ppb to ppm level for biota (Fischer and Scholz-Böttcher 2017; Gomiero et al. 2020).

For data produced by thermoanalytical methods, polymers should be obligatory and addressed as polymer clusters of the respective polymer type (Fig. 3). Any quantification should be performed using defined, backbone-pure polymer types for calibration. The resulting data should then be expressed as respective polymer clusters to gain the highest degree of comparability and harmonization in between data sets. LODs and LOQs should be always related to an actual measured concentration and should never be extrapolated. The reporting of additional information concerning microplastic/polymer concentrations that are calculated via signal-to-noise ratios or those that result from a calculation based on a very low concentration calibration curve is recommended.

Acknowledgements

Article information

Notes

This paper is part of a Collection entitled "Litter and Microplastics in the Arctic".

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Jennifer Provencher served as an Associate Editor at the time of manuscript review and acceptance; peer review and editorial decisions regarding this manuscript were handled by Eivind Farmen and Lisa Loseto.

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Competing interests

The authors declare there are no competing interests.

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