

1 **Monitoring of microplastic pollution in the Arctic: Recent developments in polymer identification,**
2 **quality assurance and control (QA/QC), and data reporting**

3
4 Authors: Sebastian Primpke^{1*}, Andy M. Booth², Gunnar Gerds¹, Alessio Gomiero³, Tanja Kögel⁴, Amy Lusher⁵, Jakob
5 Strand⁶, Barbara M. Scholz-Böttcher⁷, Francois Galgani⁸, Jennifer Provencher⁹, Stefano Aliani¹⁰, Shreyas Patankar¹¹
6 and Katrin Vorkamp¹²

7 *: Corresponding author: sebastian.primpke@awi.de

8 1: Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research, Biologische Anstalt Helgoland, Helgoland, Germany

9 2: Department of Climate and Environment, SINTEF Ocean, Trondheim, Norway

10 3: Norwegian Research Centre, Department of Climate and Environment, Stavanger, Norway (ORCID: 0000-0001-6496-6857).

11 4: Institute of Marine Research, P.O. Box 1870 Nordnes, N-5817 Bergen, Norway; Department of Biological Sciences, University of Bergen,
12 Bergen, Norway

13 5: Norwegian Institute for Water Research, Oslo, Norway; Department of Biological Sciences, University of Bergen, Bergen, Norway (ORCID:
14 0000-0003-0539-2974).

15 6: Aarhus University, Department of Ecoscience, Roskilde, Denmark

16 7: Institute for Chemistry and Biology of the Marine Environment (ICBM), University of Oldenburg, Germany

17 8: IFREMER, Chair of the EU Technical Group Marine Litter, France

18 9: Ecotoxicology and Wildlife Health Division, Environment and Climate Change Canada, Ottawa, ON, Canada (ORCID: 0000-0002-4972-2034)

19 10: Institute Marine Science - National Research Council of Italy, Pozzuolo di Lericci 19036, Italy 11: Ocean Wise Conservation Association, 101-
20 440 Cambie St., Vancouver, BC, Canada

21 12: Aarhus University, Department of Environmental Science, Roskilde, Denmark (ORCID: 0000-0002-1131-5687)

22

23

24

1

25 Abstract

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

38 Keywords

39 Monitoring, microplastic, Arctic, QA/QC, reporting, FT-IR, FTIR, Raman, microscopy, py-GC/MS, TED-
40 GC/MS

41

42

43

44

45

46

47 **Introduction**

48 Environmental pollution with plastics is a growing concern, for the public society and regulators, including
49 governmental legislation. As a result, countries and regions increasingly require to establish monitoring
50 programs. In recent years several monitoring guidelines have been developed, mainly on macrolitter items
51 and larger plastic particles, for example by the Joint Group of Experts on the Scientific Aspects of Marine
52 Environmental Protection (GESAMP, 2019), the Oslo-Paris Convention for the Protection of the Marine
53 Environment of the North-East Atlantic (OSPAR, 2019, OSPAR, 2020), the Baltic Marine Environment
54 Protection Commission (HELCOM, 2021), and the Arctic Monitoring and Assessment Programme (AMAP,
55 2021), a working group under the Arctic Council targeting environmental pollution in the Arctic. These
56 guidelines cover different types of environmental compartments and different size categories of plastics
57 (e.g. specifically larger litter and/or microplastic items).

58 Research in this field has led to rapid developments in the quantification and identification of plastic
59 particles including microplastics. In addition to information on number or mass, chemical composition,
60 and shape of plastic particles, there is an increasing interest and necessity within exposure, hazard and
61 risk assessment research to identify these particles not only as "plastics", but also according to all of the
62 mentioned parameters (Kögel et al., 2020, Primpke et al., 2020a). Quality assurance and quality control
63 (QA/QC) measures (Brander et al., 2020, Schymanski et al., 2021) need to be integrated in the analysis of
64 microplastics in environmental samples to avoid bias. Sample integrity could be affected across the whole
65 process of the survey and analytical process, for example by contamination from fibres in air or clothing
66 worn at the sampling stations (Prata et al., 2021), and emissions of particles from sampling vessels and
67 sampling equipment (Suaria et al., Leistenschneider et al., 2021). In the laboratory, contamination can
68 occur from laboratory equipment (Song et al., 2021) as well as protective clothing (Dris et al., 2017, Witzig
69 et al., 2020). Moreover, the number of samples collected might be insufficient to represent the
70 environmental niche or the population, the extraction methods might not sufficiently remove interfering

71 non-plastic matrix or not preserve the plastic analytes in a quantitative way. Furthermore, a loss of analyte
72 might happen during processing, filtering and transport of samples, analytes might not represent the
73 hazard appropriately, and endpoint analysis might misidentify particle types, shapes, numbers, mass and
74 chemical identity (Kögel et al., 2022). All these issues may have an impact on the accuracy and
75 comparability of the data and, if not recognized and controlled, could produce misleading results. Thus,
76 QA/QC measures need to be included in all sampling and measurement campaigns, and their results
77 reported and ideally quantified as measurement uncertainties. It is perhaps even more challenging to
78 integrate QA/QC in research and monitoring in geographical areas such as the Arctic, where remote
79 sampling locations, and potential technical limitations in processing facilities (e.g. lack of filters for water
80 and air), combined with a need for warm, nowadays often synthetic outdoor clothing, make control
81 measures harder to implement. In addition, samples from the Arctic can be unique and their collection
82 expensive, which usually excludes that potentially compromised samples can be replaced or
83 measurements repeated, making rigorous QA/QC even more important.

84 In general, data reporting is still challenged by a lack of harmonization and standardization in the field of
85 microplastic analysis, including basic definitions of the central term “microplastics”. For example, while
86 standards bodies like the International Standardization Organization (ISO) define microplastics as
87 materials based on plastic (ISO, 2020), the California Water Boards (The California Water Boards, 2022)
88 and the European Chemicals Agency (ECHA) (ECHA European Chemical Agency, 2019) define a minimum
89 requirement of polymer content (e.g. in California 1 w.t.%, The California Water Boards, 2022). Besides
90 the material, cut-off sizes for macro-, micro- and nanoplastics differ between different sources. For
91 example, Hartmann et al., 2019) suggested 1–10 mm, 1 μm –1 mm and <1 μm for meso-, micro- and
92 nanoplastics, respectively. ISO (ISO, 2020) defined large microplastic with 1–5 mm and microplastic with
93 1 μm –1 mm, and Frias and Nash, 2019) proposed 1 μm to 5 mm for the term microplastics. Further, the
94 introduction of the term “anthropogenic particles” was introduced when chemical identity cannot be

95 confirmed (Athey et al., 2020, Athey and Erdle, 2021, Adams et al., 2021). The European Union (EU) has,
96 in the Marine Strategy Framework Directive (MSFD), defined microlitter as small litter fragments below 5
97 mm covering both plastic and other man-made solids (EUROPEAN COMMISSION, 2017). The objective of
98 this review was therefore to discuss the state of knowledge of litter and microplastic monitoring with
99 regard to polymer identification, QA/QC and data reporting accounting for Arctic conditions, to support a
100 harmonized framework including specific recommendations.

101 **Section 1. Recent developments in the analysis of microplastics**

102 While each environmental compartment in the Arctic has its own regional-specific requirements, methods
103 and challenges with respect to microplastic sampling and sample extraction (PROVENCHER et al., 2022,
104 Strand and Murphy, 2022, Martin, 2022, Lusher et al., 2022, Kögel et al., 2022, Grøsvik et al., 2022), the
105 final microplastic analysis procedures are typically conducted at laboratories and often follow similar
106 pathways. The determination of the chemical identity of a particle serves the purpose of a) confirmation
107 of the particle as microplastics (in contrast to naturally occurring materials), and b) further information on
108 specific polymer occurrences. Furthermore, to enable toxicological risk assessments, an accurate and
109 robust characterisation of the chemical composition of microplastic particles in food and environmental
110 samples is crucial because the chemical nature of the particles may influence the toxic effects on organisms
111 (Avio et al., 2015, Booth et al., 2016, Rochman et al., 2017, Kögel et al., 2020).

112 A number of analytical techniques have been developed and reported, ranging from simple but less robust
113 approaches, mainly based on visual inspection, to advanced instrumentation. As examples of advanced
114 techniques, spectroscopy or thermal degradation coupled with gas chromatography-mass spectrometry
115 (GC/MS) for the chemical identification of microplastic polymer types, and, to some degree, additives and
116 sorbed toxicants, have been developed. In terms of research and development, microplastic analysis has
117 reached a stage where well-established and widely-used techniques exist for identification and semi-
118 quantification (i.e. robust conclusion of relative sample amounts in several samples, Hildebrandt et al.,

119 2021). Nevertheless, the field continues to develop rapidly, including the introduction of entirely new
120 approaches. In the following section, we review those analytical techniques which have already been
121 applied in a large number of microplastics studies (Zarfl, 2019, Primpke et al., 2020a, Ivleva, 2021), and
122 evaluate their possibilities and limitations for microplastic monitoring in the Arctic environment.

123 **Microscopy enhanced visual identification**

124 Owing to its simplicity and the wide availability of low cost instrumentation, microscopy-enhanced visual
125 identification continues to be one of the most commonly used identification and quantification methods
126 for microplastics in environmental samples. It has been applied to a wide range of matrices, including
127 natural waters, sediments, soils, air, wastewater treatment plant influents, effluents, process waters and
128 sludge, aquatic and terrestrial organisms, as well as to products for human consumption (Primpke et al.,
129 2020a). In general, guidelines for the identification of microplastic include visual parameters such as
130 colour, colour distribution, shape, surface properties such as light reflection, as well as the width, length
131 and features of fibres, texture and malleability (Martí et al., 2020, Lusher et al., 2020a, Primpke et al.,
132 2020a). The majority of studies divide microplastics into six primary shape categories: fragments, beads,
133 pellets, films, foams, and fibres (OSPAR, 2015). However, other categories exist, complicating harmonized
134 data assessment, and a broader range of categories may be required to account for this (Lusher et al.,
135 2020a). Reporting on a minimum set of criteria in addition to individual focus-specific criteria will solve
136 this problem to some extent.

137 During the early days of microplastic identification in environmental samples, visual identification was
138 often the only technique applied. However, it has been recognised by many that the approach has a high
139 misidentification rate if not combined with more diagnostic chemical analysis approaches (Hidalgo-Ruz et
140 al., 2012, Lenz et al., 2015, Isobe et al., 2019). Visual identification is also affected by the visual acuity of
141 the user and the equipment available (Lusher et al., 2020b). For this reason, GESAMP only recommends

142 visual identification for particles >1 mm in the monitoring of marine ecosystems (GESAMP, 2019). Similar
143 recommendations have recently emerged from working groups in Asia (Michida et al., 2020). However,
144 this limit conflicts with the published research, where most studies utilising visual identification report
145 detection limits of between 100 μm –1 mm (Primpke et al., 2020a). As a result, it has been recommended
146 that optical microscopy be combined with spectroscopy analyses (Table 10.10 in GESAMP, 2019). A similar
147 approach was also suggested by Löder et al. (2017), introducing a size fractionation pre-treatment step,
148 which allows division into larger (e.g., >500 μm) and smaller particles (e.g., <500 μm), prior to sample
149 extraction (Löder et al., 2017). While the smaller particles require sample extraction, the larger particles
150 can be picked manually, assisted by optical microscopy, and identified chemically afterwards.

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

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

166 When using visual identification, it is important to consider human limitations and individual variations in
167 differentiating non-polymeric particles and natural polymer-based particles (e.g., chitin or wool) from the
168 microplastics of interest, which may introduce a bias (Hidalgo-Ruz et al., 2012, Isobe et al., 2019, Zarfl,
169 2019, Primpke et al., 2020a). Such bias is dependent on the experience level of the investigators and is
170 significantly reduced for very experienced laboratories (Isobe et al., 2019). Therefore, an appropriate
171 training period and reference sample sets or schemes are required to minimise the degree of bias as much
172 as possible (Lusher et al., 2017). Furthermore, the level of experience needed for the analysis of
173 microplastics increases with decreasing particle size and the correct identification becomes much more
174 difficult for very small particle sizes (<100 µm). Some reported guidelines for microscopy-based visual
175 identification in this size range exclude the selection of particles exhibiting properties that make
176 identification challenging. For example, particles may be excluded that are black, brown, white, or clear in
177 colour (Wiggin and Holland, 2019). In such cases, the generated data most likely represent an incomplete
178 picture of the true levels of microplastic contamination and make comparability of datasets very
179 challenging (Kögel et al., 2022). For the current stage of knowledge regarding the monitoring of
180 microplastic particles, this is an acceptable and pragmatic solution to reduce bias, but it will need to be
181 reconsidered and adjusted as research and method refinements continue. Nevertheless, it is important
182 that any datasets using such methods highlight these issues so other researchers and users of the data are
183 aware of these limitations and can account for them when translating monitoring data into practical
184 measures and mitigation actions.

185 **Fluorescent staining of microplastics for microscopy and preselection of particles**

186 The visual assessment of microplastics can be enhanced with the use of fluorescent dyes to stain particles;
187 this is being increasingly applied to achieve a faster selection of microplastic particles and help reduce
188 researcher bias (Zarfl, 2019, Maes et al., 2017). Staining is typically conducted after sample fractionation
189 or extraction steps to minimize staining of the non-plastic organic material. Possibly the most frequently

190 applied dye for staining microplastics is Nile Red (NR; Andrady, 2011). NR is inexpensive, easy to handle
191 and effective for particle sizes from $\geq 300 \mu\text{m}$ down to $3\text{--}20 \mu\text{m}$, thus expanding the range typically
192 achievable for microplastic identification by optical microscopy (Primpke et al., 2020a). The application of
193 NR has been demonstrated across various sample types, including microplastics in water samples, sands,
194 sediments, biota samples, and atmospheric deposition samples (Primpke et al., 2020a), and it has also
195 been shown to be effective for the most common polymer types, including polyethylene (PE),
196 polypropylene (PP), polycarbonate (PC), high-density polyethylene (HDPE), low-density polyethylene
197 (LDPE), polyurethane (PUR), expanded polystyrene (EPS), polyethylene-vinyl acetate (PEVA) and
198 polyamide (PA; Zarfl, 2019, Primpke et al., 2020a). Whilst there is some indication that different polymer
199 types stain sufficiently differently to allow a tentative identification (Maes et al., 2017, Crew et al., 2020),
200 a robust characterization equivalent to direct chemical identification methods is currently not possible.

201 Method developments towards staining-based polymer distinction would likely include as much effort as
202 direct chemical identification by spectroscopic methods. Furthermore, parameters such as particle size,
203 shape, and solvents used may alter the staining behaviour. The difference in staining efficiency ranges
204 from 0-100%, with variations in co-staining of biological material depending on the polymer/solvent
205 combination (Shim et al., 2016, Tamminga et al., 2017). Importantly, NR staining has limitations with
206 regards to certain microplastic subclasses, including those which are black in colour, fibrous, and rubber-
207 based (Maes et al., 2017, Erni-Cassola et al., 2017). Error rates for identification can be further reduced if
208 stained particles undergo subsequent FTIR or Raman spectroscopy to confirm chemical identification
209 (Sutton et al., 2016, Maes et al., 2017). When NR is introduced into the analytical procedure in this way,
210 i.e. after fractionation or extraction, the staining acts as a pre-selection step that helps the user narrow
211 down the number of particles that should undergo chemical identification, potentially saving considerable
212 time. This approach is a promising technique to highlight potential microplastics and guide researchers in

213 eliminating non-plastic particles (Klein and Fischer, 2019). This approach is beneficial because it reduces
214 the time for subsequent analysis.

215 The main drawback of NR staining for microplastic identification is its lipophilic nature, potentially staining
216 all lipid materials present in a sample (e.g., those derived from biota; Cooksey et al., 1987). It is therefore
217 necessary that comprehensive sample extraction and clean up steps are applied to avoid the potential
218 misidentification of natural materials, e.g., lipid droplets and microorganisms, as microplastics (Erni-
219 Cassola et al., 2017, Wiggin and Holland, 2019). The use of oxidising agents and enzymes are examples of
220 approaches for cleaning up samples (Lusher et al., 2020b, Primpke et al., 2020a). As a second pitfall, NR
221 can precipitate as agglomerated particles if applied in certain concentrations and solvents. This limitation
222 can lead to confusion with stained microplastics (Bienfait A.M., personal communication, 2022).

223 Furthermore, conclusive method harmonization is not currently available. This is exemplified by the large
224 differences between recommended optimal staining concentrations, with literature values ranging from
225 0.1–2 $\mu\text{g mL}^{-1}$ (Erni-Cassola et al., 2017) up to 1–1000 $\mu\text{g mL}^{-1}$ (Maes et al., 2017).

226 **Fourier-transform infrared spectroscopic approaches for microplastic analysis**

227 Fourier-transform infrared spectroscopy (FTIR) could arguably be considered the most widely used of the
228 comprehensive and robust microplastic analysis techniques. In reality, this a 'catch all' term for a range of
229 different FTIR-based approaches. FTIR produces a spectral pattern by the transmission, absorbance or
230 reflectance of the polymer at all analysed wavelengths of infrared light, called an IR-spectrum, resulting in
231 a reproducible pattern, metaphorically called "fingerprint" of the polymer types. The obtained spectra are
232 compared with reference spectra for each polymer type. The application of FTIR for analysis of
233 microplastics in environmental samples was recently reviewed (Primpke et al., 2020a). The 161 reviewed
234 publications used a range of different FTIR technologies, including single-particle analysis using handhelds,
235 fibre optics and microscope-supported systems (μFTIR). Attenuated total reflection (ATR)-FTIR on single

236 selected particles was applied in 58% of the reviewed studies. ATR-FTIR is often applied to identify the
237 polymer type of plastic particles >300 μm as it does not require any specific sample preparation and the
238 analysis does not require advanced skills, or mathematical correction, by the operator (Primpke et al.,
239 2020a). In contrast, when targeting plastic particles <300 μm , μFTIR combines visual microscopic imaging
240 and particle-size determination with FTIR, allowing individual particles down to sizes of 10–20 μm to be
241 detected restricted by the diffraction limit for IR spectroscopy (Käppler et al., 2016). Furthermore, such
242 microscopes can also be coupled with an ATR unit, which allows the selective analysis of either small
243 particles or selected areas on larger particles (Käppler et al., 2018).

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

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

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

272 Complications arise if particles overlap on filters/slides which causes sequestration and misidentification
273 of particle sizes and numbers. Practically, there must be a compromise between numbers of particles
274 deposited on a filter and the accepted rate of overlap, as it cannot be completely avoided. Additionally,
275 large numbers of particles increase measurement times. It is for these reasons that often a fraction of the
276 total extracted particles is investigated within one measurement, especially when samples have high
277 particle numbers (Cabernard et al., 2018). Given these restrictions, pre-screening methods which include
278 staining are considered reasonable and do not appear to influence the IR-based analysis. To avoid staining
279 or to achieve defined measurement times per sample in routines, chemical (hyperspectral) imaging (μ FTIR)
280 is the method of choice. With this approach, all particles can be analysed, even if they form particle clusters
281 (see Figure 1B to 1F). Still, such cluster situations may lead to uncertainties in terms of particle numbers

282 and sizes. Hyperspectral imaging via focal plane array (FPA) detectors (FPA- μ FTIR), currently represents
283 the state of the art in microplastic analysis because it allows fast, effective identification and quantification
284 of microplastics in samples of a variety of different ecosystems and waste management systems (Primpke
285 et al., 2020a). FPA- μ FTIR analysis generates a large volume of spectra (e.g., 1.5–3 million), which can be
286 analysed with the help of false colour images (Figure 1C) or semi-automated data analysis (Primpke et al.,
287 2020a). In principle, imaging can be performed by any FTIR microscope equipped with single element
288 mercury cadmium telluride (MCT) detectors (Figure 1B and 1C), but spatial resolution and measurement
289 times increase significantly with imaged filter area (Harrison et al., 2012, Vianello et al., 2013) as visible in
290 Figure 1C compared to images derived using FPA systems (Figure 1E and 1F).

291 **Combining infra-red microscopes with laser-based systems**

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

300 **Raman spectroscopy for microplastic analysis**

301 In recent years, Raman spectroscopy has seen a significant increase in application for the identification of
302 microplastics in environmental samples. Measurements are performed on the particle surface and
303 produce vibrational spectra complementary to FTIR and the chemical/polymer identification can be
304 performed in a similar manner (see below). Most Raman spectrometers are connected to microscopes

305 (μ RAMAN), which increases the spatial resolution of the analysis and allows the determination of particle
306 numbers, shape and size, in addition to polymer type, within a single measurement (Cabernard et al.,
307 2018). Raman spectroscopy allows particles down to 1 μ m in size to be measured, a slight improvement
308 over μ FTIR. Typically considered non-destructive, μ Raman spectroscopy uses a focused laser beam that
309 may damage the analysed particles, which increases in severity with the speed and spatial resolution of
310 analysis because more energy is focused on the same small area.

311 As with FTIR analysis, larger particles (>300 μ m) can be isolated and targeted as single particles for Raman
312 analysis. The measurement of single particles is often performed on highly reflective surfaces to avoid
313 background signals from the support materials such as metal-coated mirrors, aluminium sheets, or coated
314 slides (Ossmann et al., 2017). For smaller particles (<300 μ m), similar approaches can be used for
315 automated particle identification on filter membranes (Frère et al., 2016). Common filters are metal-
316 coated PC membranes or silicon membranes (Primpke et al., 2020a). The sample matrix influences the
317 lower size of particles successfully characterized using Raman spectroscopy, for example, particles down
318 to 1 μ m were obtainable in simple matrices like drinking water while in more complex sample matrices
319 identification of particles >5 μ m has been demonstrated (Imhof et al., 2016, K appler et al., 2016,
320 Cabernard et al., 2018, Ossmann et al., 2018, Schymanski et al., 2018). Recently, it has been proposed that
321 Raman spectroscopy might be able to measure particles at the upper edge of the nanoplastics size range
322 (<1 μ m; Schwaferts et al., 2019, Schwaferts et al., 2020).

323 Raman spectroscopy is advantageous in that each particle can be documented by shape and size, allowing
324 for immediate calculation of particle numbers, size, and shape distributions. These processes can be
325 automatized using a particle-finder mechanism to determine particle shape, size, and polymer type, which
326 can reduce both researcher bias and measurement time although individual measurements can take long
327 (Frère et al., 2016, Cabernard et al., 2018, von der Esch et al., 2020a). As with FPA- μ FTIR, some Raman
328 instruments can measure the entire filter area with the imaging system. However, Raman imaging systems

329 have long measurement times. Measurement times also differ between studies, for example, single
330 particle analysis can take from just a few seconds to almost an hour (Primpke et al., 2020a). Consequently,
331 sample analysis times can range from several days to weeks, especially for samples containing small
332 particles ($<10\ \mu\text{m}$) in high numbers (>1000 particles per filter; Primpke et al., 2020a). To circumvent such
333 long measurement times, often partial analysis of the filter membranes (0.1–30% of the area) is performed
334 (Schymanski et al., 2018, Cabernard et al., 2018, Ossmann et al., 2018). However, a controlled method for
335 ensuring representative analysis when using subsamples is currently being debated (Schwaferts et al.,
336 2021, Brandt et al., 2021), and going forward approaches should be established to ensure that analysis is
337 (i) viable from a cost and time perspective, and (ii) produces representative and comparable data.

338 Imaging the whole filter area allows the identification and characterization of more particles in the same
339 sample (Käppler et al., 2016, Araujo et al., 2018). Subsampling is challenging due to inhomogeneous
340 distribution on the analysis filter or window (Thaysen et al., 2020, Brandt et al., 2021), but good results
341 have been obtained by bootstrap estimations (Schwaferts et al., 2021). However, the measurement times
342 required for Raman imaging are considerably longer than those required by FTIR imaging. For example, an
343 area of $1\ \text{mm}^2$ had a scanning time of 38 h for a measurement at $10\ \mu\text{m}$ resolution (Käppler et al., 2016).
344 A promising approach is stimulated Raman scattering (Zada et al., 2018), which decreases the
345 measurement time significantly, but is limited to particles of $12\ \mu\text{m}$ in size and a few polymer types.
346 Compared to FTIR, Raman spectroscopy has plenty of parameters which can be adjusted to improve the
347 signal to noise ratio, including spectral range, excitation wavelength, the applied objective, resolution, and
348 the number of accumulations. In summary, Raman is much slower than FTIR microscopy for routine bulk
349 sample analysis. However, Raman has the capability to identify niche polymers and smaller size classes if
350 time is not a limitation.

351 **Reference library searches**

352 Chemometric methods applied for spectral identification in FTIR and Raman spectroscopy/microscopy are
353 similar. The identification of a microplastic particle typically comprises imaging of the individual particle,
354 measurement of a raw spectrum and determination of key particle details (dimensions, area and shape)
355 by image analysis. Following processing, the spectrum is then matched to the most similar reference
356 spectrum available in the spectral library and the polymer type determined (Figure 2). Respective
357 reference spectra are collected in spectral libraries, which are available commercially, publicly free of
358 charge or are compiled by the different laboratories for their own specific purposes. It is important to use
359 a library containing the analytes, but also to avoid the use of too extensive libraries with non-relevant
360 analytes, as this increases the risk of misidentification, especially for small particles, where the signal-to-
361 noise ratios are smaller. Some spectra of natural polymers can be similar to those of artificial polymers. To
362 overcome limitations by manufacturers as well as the use of different spectral databases for library
363 searches, open source software tools have recently been made available, which have the additional
364 advantage of offering harmonizing potential in microplastic analysis (Primpke et al., 2020b, Cowger et al.,
365 2021).

366 Nevertheless, matching the spectrum of a particle to a known polymer spectrum in a reference library
367 often remains a challenge, due to a combination of factors that include spectral changes caused by
368 weathering and degradation processes, contamination, optical distortions, and the presence of
369 copolymers. Advances in chemometric techniques point to potential approaches that may be adopted to
370 balance the competing priorities of efficient measurements and accurate identification (da Silva et al.,
371 2020, Chabuka and Kalivas, 2020, Wander et al., 2020, Faltynkova et al., 2021). These methods include
372 the application of machine learning to identify useful portions of hyperspectral images and hence lower
373 the computational capacity needed to completely process the aforementioned large numbers of spectra
374 involved. Still, there is a strong debate ongoing which approach yields the best balance. Currently, studies

375 comparing several of these find that for example Pearson correlation, which is often applied for library
376 searches, is still one of the optimal operating approaches (Levermore et al., 2020, Morgado et al., 2021).

377 **Thermoanalytical methods combined with gas chromatography and mass spectrometry**

378 The characterisation of organic polymers by thermal degradation methods has a long and multifaceted
379 tradition. Accordingly, polymer producing and processing industry, forensic science, and polymer analysis
380 in general use these techniques in a broad field of applications (Wampler, 2006, Tsuge et al., 2011, Kusch,
381 2012, Kusch et al., 2013, Kusch, 2014). A comprehensive collection of pyrolytic data for polymers and co-
382 polymers is provided by Tsuge et al. (2011). Additionally, commercial databases of polymer pyrograms and
383 related data are available (e.g. F-Search by Frontier Lab; >1000 polymers, 500 additives). The destructive
384 nature of thermal methods makes them the ideal concluding step in a complementary and comprehensive
385 succession starting with optical chemical identification methods such as FTIR or Raman spectroscopy.

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

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

- 398 • Filament pyrolyser: Samples are typically introduced in open or semi-closed quartz tubes and placed
399 in a heated platinum coil. These are heated isothermally or with a temperature program (Fries et al.,
400 2013, Dekiff et al., 2014, Nuelle et al., 2014).
- 401 • (Micro)furnace pyrolyser: Samples are transferred into stainless steel cups that are heated in a ceramic
402 oven. Here, they are pyrolysed at a given temperature or heated with a temperature program (ter
403 Halle et al., 2016, Hermabessiere et al., 2018, K ppler et al., 2018, Fischer and Scholz-B ttcher, 2019,
404 Gomiero et al., 2019a).
- 405 • Curie point (CP) pyrolyser: Samples are introduced on wires or in semi-closed ferromagnetic targets.
406 Their alloy defines a discrete, exact pyrolytic temperature that is almost instantaneously reached when
407 placed in a high-frequency coil chamber. Accordingly, pyrolysis is performed exclusively isothermally.
408 Alloys are available for a broad temperature range (Fischer and Scholz-B ttcher, 2017).

409 The overall capacity of the individual techniques ranges from 1.5 mg (CP) to 50 mg (micro furnace). Since
410 sample amounts might influence the heat transfer, and accordingly the pyrolytic performance, sample
411 volumes of around 1 mg or less are preferred and guarantee optimal operating conditions. Before pyrolysis
412 is performed under polymer decomposition conditions, a potential stepwise heating and analysis of
413 sample is beneficial (e.g. temperature programmed heating or a so called "double shot" option). It enables
414 further valuable and additional information to be gained about the low molecular, volatile sample content,
415 e.g. low molecular organic additives, monomers, and accumulated smaller organic contaminants can be
416 desorbed from the sample in a first moderate heating program. In this context, the use of a cryo-focussing
417 unit enhances chromatographic performance.

418 TGA subjects the polymer to a temperature controlled decomposition process, where the weight of the
419 polymer changes in a characteristic way that can be recorded as a function of temperature. Polymer
420 identification can be performed by the analysis of the generated decomposition gases (Tsuge et al., 2011,
421 Seefeldt et al., 2013). Recently, a TGA variant named thermo extraction desorption (TED)-GC/MS has been
18

422 introduced (Duemichen et al., 2015, Duemichen et al., 2017, Duemichen et al., 2019). Here, the volatile
423 decomposition gases are trapped and concentrated on a solid phase absorber bar, subsequently
424 thermodesorbed and transferred into a GC/MS. The sample capacity of TED-GC/MS is stated as 100 mg.

425 **Thermal multi-polymer identification combined with GC/MS coupling**

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

435 In particular, the generation of highly specific pyrolysis products, combined with the resolving power of
436 gas chromatography as a function of time, allows the simultaneous detection and identification of multiple
437 polymers in a mixture within a single GC run. Retention time data of characteristic polymer degradation
438 products and characteristic indicator ion(s) from their respective mass spectra are the key properties
439 employed. From the MS data extracted in an ion chromatogram, representatives for each polymer are
440 generated. They usually reflect a highly improved signal to noise ratio and enable polymer detection even
441 at trace levels. To date, more than 10 different basic polymer types have been included in successful py-
442 GC/MS applications for simultaneous microplastic detection in various complex matrices (Fischer and
443 Scholz-Böttcher, 2017, Fischer and Scholz-Böttcher, 2019, Dierkes et al., 2019, Gomiero et al., 2019a,
444 Dehaut et al., 2020, Primpke et al., 2020c). Similarly, TED-GC/MS has been successfully applied to identify

445 different synthetic polymers in complex environmental samples (Dümichen et al., 2015, Dumichen et al.,
446 2017, Eisentraut et al., 2018).

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

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

462 **Thermal multi-polymer quantification combined with GC/MS coupling**

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

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

474 In TED-GC/MS, only the trapped gaseous products of the pyrolysed sample (via TGA) are analysed via
475 GC/MS after subsequent thermal desorption. Thermogravimetric analyser sampling cups enable a direct
476 sample measurement for microplastics if their content exceeds 0.4% w/w (Dümichen et al., 2015,
477 Dumichen et al., 2017, Eisentraut et al., 2018). A high organic content in the sample matrix can perturb
478 the analytical performance. This influence can be reduced by sequential heating, removing compounds
479 that are more thermolabile than the targeted polymers.

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

489 **Synergies between thermoanalytical and spectroscopic methods**

490 Spectroscopic and thermoanalytical methods generate highly complementary data (Hendrickson et al.,
491 2018, K  ppler et al., 2018, Primpke et al., 2020c, Kirstein et al., 2021). Thermal degradation methods
492 provide the mass of a specific polymer that is defined by the detected polymer backbone (Primpke et al.,
493 2020c, Dibke et al., 2021, Roscher et al., 2021b). Spectroscopic methods such as FTIR and Raman methods
494 provide particle size and number information, but the conversion to mass-related data has clear limits as
495 it assumes ideal ellipsoid shape of a particle (Simon et al., 2018, Mintenig et al., 2020, Primpke et al.,
496 2020c). Few large particles have a higher impact on mass data compared to the contribution of a high
497 number of very small particles, highlighting the complementary nature of number counts (per size fraction)
498 and mass information.

499 **Quality control/Quality assurance (QA/QC)**

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

507 Starting with sampling, there are various factors to be considered. Samples may be contaminated by the
508 atmosphere, the vessel/instruments used for sampling and other factors at the sampling location.
509 Awareness of this issue has increased with the number of published studies leading to various mitigation
510 and methodological recommendations. To account to atmospheric deposition and contamination from
511 personnel conducting the sampling, the exposure of filters in petri dishes or filtered water in sampling to

512 ambient air is recommended as a minimum at the sampling stations (Brander et al., 2020). Such blanks
513 can be accompanied by field blanks that mimic the sampling process, for example by using pre-filtered
514 water and exposing it as if it was a sample. In contrast to atmospheric blanks, which require minimal
515 storage and application space, field blanks of large scale sampling equipment may be associated with
516 larger logistical constraints e.g. on research vessels as they need to be moved, processed and analysed in
517 the same way as the environmental samples at the sampling station.

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

530 In contrast to the sampling step, the determination of recovery rates during sample extraction and particle
531 separation has already been regularly applied and compared for larger microplastics items. For smaller
532 particles, especially those <100 µm, such experiments are not typically performed on a regular basis. This
533 is largely due to the lack of suitable reference materials in this size range and the fact that the commercially
534 available reference materials are primarily spherical particles, which limits their applicability.
535 Nevertheless, the inclusion of procedural controls is important for investigating the influence of the

536 selected methodology on the separation quality. As this influence can vary from person to person, for
537 different matrices and with each adjustment of the method, it is recommended that procedural controls
538 accompany all individual analysis campaigns and are implemented regularly.

539 In the laboratory, procedural blanks allow the level and potential sources of particle contamination to be
540 determined. Similarly, how any identified sources of contamination are addressed adds another layer of
541 complexity to data reporting and QA/QC. Known contamination or background levels observed in blanks
542 are often subtracted from the particle count or checked in relation to the derived particles numbers. These
543 procedures are of high value for source tracking of contamination. For example, it has been demonstrated
544 by the application of procedural blank samples that a high number of PP particles were emitted from a
545 sampling device (Mintenig et al., 2019), PA particles were introduced to fish samples by a meat mincer
546 packing (Gomiero et al., 2020) and that stearates used on nitrile gloves can act as a potential false positive
547 for all types of analytical procedures (Witzig et al., 2020). Within the scope of research into microplastics
548 shapes, colours and sizes, a blank correction might be linked to these parameters, e.g. by separation of
549 colours and the use of unique coloured clothing and materials in contact with the sample. Similar
550 approaches are available if polymer identification techniques are applied, which may result in even more
551 complex situations due to a large variety of polymer types and sizes. However, the question remains how
552 many blanks are needed for a representative description of laboratory background levels, to be applied in
553 blank correction. An example using an automated analysis approach can be found in the supplementary
554 information of (Roscher et al., 2021a). Still, other approaches might be used and need to be evaluated in
555 the future.

556 Procedural blanks are also very important for the determination of LODs and LOQs. In analogy to the
557 common practice in analytical chemistry that refers to the signal to noise ratio, LOD and LOQ can be
558 transferred to particles as three (LOD) and ten times the standard deviation (LOQ), respectively, of the
559 average number of particles in the procedural blanks (Hildebrandt et al., 2021). These values allow a direct

560 comparison of data quality and provide meta-data for data studies and modelling, as well as assessments
561 of achievable sensitivity and its variation among laboratories.

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

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

580 To quantify the recovery efficiency during the analysis procedure of real samples, the utilization of ISTDs
581 is a widespread practice in analytical chemistry. Its successful application requires that the ISTD and
582 analyte(s) exhibit an almost identical behaviour. Any loss of analyte should be mirrored by the ISTD, while
583 their relative ratio remains constant and enables quantification. While this is convertible for soluble
25

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

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

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

607 **Data processing and reporting in the field of microplastic research**

608 Due to the fact, that various spectroscopy and thermoanalytical methods currently exist for a range of
609 instrument types produced by different manufacturers using a series of software and databases, the
610 quality and comparability of the derived microplastic data are influenced by these factors. While the
611 comparison of analytical methods is still hampered by the small number of designated polymer standards
612 available (von der Esch et al., 2020b, Seghers et al., 2021), the first application of ring trials (Isobe et al.,
613 2019, Müller et al., 2020, van Mourik et al., 2021) are beginning to present their results on the
614 comparability of laboratories and matrices.

615 Given the challenges to produce comparable data, both within and between laboratories, researchers
616 have focused on analyses in a harmonized manner, both at the instrument level (Renner et al., 2019b,
617 Brandt et al., 2020, von der Esch et al., 2020a) as well as the data processing level. Various commercial
618 and researcher-derived databases for the identification of microplastics by FTIR and Raman spectroscopy
619 are currently available (Cabernard et al., 2018, Primpke et al., 2018, Primpke et al., 2020b, Munno et al.,
620 2020, De Frond et al., 2021). De Frond et al. (2021) have shown that the combined use of such published
621 databases yields higher scores than the application of only commercial ones. As these databases were
622 specifically designed for microplastic analysis, they contain data related to both natural materials and
623 weathered plastics, which increases the data quality. The presence of protein-based natural polyamides
624 in the database is especially important to avoid confusion with synthetic polyamide (Primpke et al., 2020d).
625 These databases can be easily applied via open access software such as 'siMPle' or 'Open Specy' (Primpke
626 et al., 2020b, Cowger et al., 2021). In a recent example, data was harmonized within a Citizen Science
627 project following this approach (Kiessling et al., 2021). This development of open access software is
628 accompanied by the improvement of the chemical identification approaches by other chemometric
629 methods (Mecozzi et al., 2016, Renner et al., 2017, Renner et al., 2019a, Hufnagl et al., 2019, Kedzierski et
630 al., 2019, da Silva et al., 2020), some of which are already commercially available (e.g. Purency).

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

636 While these issues raised above primarily focus on the generation of data, the actual reporting of data
637 often lacks the use of a common database and reporting format. In the scope of the AMAP microplastic
638 monitoring guidelines, several options have been discussed. For example, data for air levels or atmospheric
639 deposition samples could be reported to the EBAS Database, operated by the Norwegian Institute for Air
640 Research (NILU; AMAP, 2021). Data for the marine environment could potentially be reported to the
641 Environmental Database operated by the International Council for the Exploration of the Sea (ICES; AMAP,
642 2021).

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

644 The AMAP guidelines for monitoring of litter and microplastic in the Arctic suggest as first priority
645 compartments to establish the monitoring of microplastic in water and sediment (AMAP, 2021). In
646 addition, monitoring of plastic particles is recommended in seabirds (for particles of > 1mm, generally
647 speaking) and on beaches, the latter in terms of beach litter (AMAP, 2021). In addition to the general
648 challenges associated with the monitoring of microplastics, the Arctic region presents a number of
649 logistical, cost and technical difficulties (PROVENCHER et al., 2022, Strand and Murphy, 2022, Martin,
650 2022, Lusher et al., 2022, Kögel et al., 2022, Grøsvik et al., 2022 this issue). In this section we summarize
651 the general challenges associated with establishing and conducting robust microplastic monitoring and
652 outline the additional factors that must be addressed when monitoring microplastic in the Arctic.

653 **Research and monitoring strategies**

654 One of the major issues in microplastics monitoring concerns the effort (cost, time, equipment) that is
655 needed to sample and extract microplastics from different environmental matrices. For example,
656 sediment, which is often considered the most relevant matrix for MP, is also one of the most difficult
657 matrices to sample, especially as the water column depth increases. This becomes even more difficult in
658 the Arctic where sampling sites are often long distances from the mainland and where the water column
659 can be very deep. Sampling equipment also needs to be able to withstand the extremes of the Arctic
660 environment. The diversity of plastic material present in the marine environment has created
661 methodological challenges, especially for the targeted, quantitative analyses of microplastics (GESAMP,
662 2016).

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

678 predominantly made of synthetic textiles, which increases the risk of contamination. There is therefore a
679 need to harmonize procedures to mitigate airborne contamination, to ensure that this is adequately
680 considered and addressed in all monitoring studies.

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

689 As highlighted by GESAMP (2019), many of the methods used and reported for microplastic sampling and
690 sample processing have key limitations. One example is the use of manta trawl nets for collecting
691 microplastic present in surface waters. These nets typically have a pore size of 330 μm to prevent collection
692 of too much microbiota, but this means that microplastics below 330 μm are not effectively collected.
693 Given that particle numbers have been demonstrated to increase almost exponentially with decreasing
694 particle size (Cabernard et al., 2018, Kooi et al., 2021, Primpke et al., 2020d,) manta nets have the potential
695 to miss the vast majority (by number) of microplastics present in the surface water. As a result, it is widely
696 acknowledged that further research into improving sampling and sample processing methods is needed,
697 as well as more harmonization of sampling design in terms of the number and the size of replicates, the
698 spatial area and the frequency of sampling. This is particularly important in the Arctic, where the high costs
699 associated with microplastic monitoring need to generate robust and valuable data (Mallory et al., 2018).
700 In addition, time series are planned for litter and microplastic in the Arctic, which should be inherently
701 consistent. Finally, working at the Arctic scale could also support the future development of automated
30

702 sensors and real time measurements in extreme environments. This will open up for new possibilities of
703 *in situ* analysis in the environmental compartments of the Arctic.

704 **Balancing cost and time**

705 In the scope of a recent review (Primpke et al., 2020a) and the AMAP guidelines (AMAP, 2021), different
706 methods for the analysis of microplastics were assessed with regard to the associated costs for
707 microplastic identification and quantification. In most cases, the methods offering the best degree of
708 accuracy and the largest particle size range were expensive due to a combination of high instrument costs
709 (purchase and operation), or personnel requirements (time and competence level). In contrast, the
710 cheaper approaches typically have a much higher degree of uncertainty and/or a much more limited
711 particle size range, although they can also be more resource demanding in terms of personnel costs
712 relative to some of the more advanced techniques. All methods were found to have both positive and
713 negative aspects. For example, optical microscopy is inexpensive from an instrumental point of view and
714 can be easier to use in the field or on a research vessel. However, the personnel demand is often rather
715 high because of the number of potential samples to be analysed manually. In addition, the success of
716 optical microscopy and the quality and value of the data produced are strongly linked to the experience
717 of the investigator, which may induce a human bias and are dependent on the application of strict and
718 harmonized identification guidelines. In contrast, chemical identification by microscopy-spectroscopy
719 requires rather expensive instrumentation but the high level of automation significantly reduces the
720 personnel costs. As a result, the personnel costs for microscopy-spectroscopy analysis are typically 1-2
721 hours per sample, while this increases to 4-7 hours when using optical microscopy methods (even those
722 supported by dye staining). In the case of monitoring in the Arctic, a good compromise between chemical
723 accuracy, field work applicability, and costs needs to be defined. As an example, the individual needs
724 presented in Table 1 were derived from the AMAP Monitoring Guidelines (AMAP, 2021).

725 To reduce the demand and costs for the chemical identification of microplastics, the approach of
726 subsampling is commonly applied in microplastic research (Mintenig et al., 2020, Brandt et al., 2021,
727 Thaysen et al., 2020, Schwaferts et al., 2021). Depending on the type of spectroscopy applied, this can be
728 performed via a minimum number of randomly selected particles or small fields of views which follow a
729 random or specialized pattern by the instrumentation. These approaches can be performed among all size
730 classes and minimum values range from 50 particles per sample (Mintenig et al., 2020) for particles
731 >300 μm to several thousand particles (Schymanski et al., 2021) for particles <300 μm . For imaging
732 approaches and automated particle counting approaches the data is more complex to address. Currently
733 researchers have not agreed on an optimal strategy. While Mintenig et al. (2020) found that 66% of the
734 filter should be analysed using imaging techniques, other studies suggested to use different shapes or a
735 defined number of a small fields (Brandt et al., 2021, Schwaferts et al., 2021). In the context of monitoring,
736 either of these approaches is considered sufficient for determining the total number of plastic particles in
737 a sample. Splitting the sample prior to chemical analysis is another way to reduce analytical costs, although
738 this can only be performed during sample handling in the laboratory and may induce risks such as missing
739 polymer types or over/underestimating the total load of microplastics (Abel et al., 2021).

740 **Implications for reporting on microplastics**

741 Researchers have developed, implemented and reported a diverse range of methods and non-
742 standardized approaches for microplastic sample collection, extraction, and analysis. These are often
743 insufficiently described or exhibit critical differences that result in many studies being neither comparable
744 nor reproducible. Each method typically has its strengths and weaknesses, and there are continued efforts
745 to further optimize existing methods, as well as develop new ones that represent improvements in
746 throughput, LODs/LOQs and reproducibility. Attempts to develop optimized approaches have contributed
747 to the rapid evolution and diversity of the methods applied in the last few years and made comparison of
748 datasets increasingly difficult, especially when reports on method validation are incomplete. In addition

749 to this diversity of methodologies, the situation is compounded by the research community using a broad
750 range of data reporting formats. This includes differences in the classification of microplastic properties
751 (e.g. size, shape, colour), as well as in the units in which microplastic data are reported, including particle
752 number or mass concentrations.

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

763 A further complicating issue can be that microplastic data are not always reported or archived in open
764 access formats. A recent publication has provided a comprehensive set of recommendations and
765 guidelines for the reporting of microplastic data that aims to increase the reproducibility and comparability
766 between studies (Cowger et al., 2020a). The authors provided a Mind Map in which general method groups
767 flow from the primary term "Microplastics Reporting Guidelines." The interactive Mind Map is available
768 as an Open Science Framework project (OSF) in which users can access more details. We suggest that the
769 same methodological quality criteria and data reporting criteria are clearly recommended by all
770 monitoring programs developed around the world, where modifications are introduced to support specific
771 variations in program requirements. Here, the Arctic represents a good example and the recently
772 published AMAP Guidelines were developed specifically to be as relevant as possible for the Arctic

773 ecosystems, communities and research scientists (AMAP, 2021). Any key differences from other
774 monitoring programs should be clearly highlighted and justified in individual monitoring programs to help
775 achieve harmonization across microplastic studies conducted by different research groups around the
776 world.

777 **Recommendations for the characterisation and quantification of microplastics in an Arctic monitoring**
778 **program**

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

782 For the reporting of the data across compartments suggested for monitoring of microplastics in the Arctic,
783 a harmonized scheme for size classes, colours, shapes and polymer types should be used. To achieve this,
784 microplastic shape should be determined by optical microscopy, where visual identification should follow
785 the categorisation scheme published by Lusher et al. (2020) to achieve harmonized data (Lusher et al.,
786 2020a). To allow cross-analysis among databases, as the recommended ICES database also acts as a
787 contributor, the following eight colours (Table 2) should be reported along with these shapes in
788 accordance with the colour characterisation applied in the EMODnet database ([https://www.emodnet-](https://www.emodnet-bathymetry.eu/)
789 [bathymetry.eu/](https://www.emodnet-bathymetry.eu/)):

790 It is crucial that the size classes are reported in a manner that allows harmonized data reporting across
791 various monitoring guidelines and databases, as well as different environmental matrices and geographical
792 regions. Therefore, we currently recommend that identified microplastics are reported in the following
793 size classes: >1 mm, 1 mm – 300 µm, <300 µm – LOD_{size} (limit of detectable size for a specific analytical
794 approach). The lower detection limit in size (LOD_{size}) of the data should be reported separately to allow
795 better contextualization for future use. This should be performed for each polymer type selected for

796 inclusion in the Arctic monitoring program (see Table 3), where the analysis was determined as mandatory
797 in the respective guideline (see Table 4 for the Arctic).

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

807 Where thermoanalytical methods are applied, it is recommended to pyrolyse the entire processed sample,
808 rather than using aliquots, to achieve high sensitivity and to be able to work in a “comfortable” calibration
809 range. With respect to the expected polymer concentration, sample volume should be thoughtfully
810 adjusted before any preconcentration procedure. The expected polymer mass should be located in the
811 middle of quantification range of the polymer. This range varies across different instrumentations, but
812 typically covers 0.5 – 100 μg polymer. As mass-related data for polymers or, more precisely, polymer
813 clusters (Figure 3) are still rare, relevant publications and experts should be consulted. From data already
814 available, the expected mass ranges of total microplastic are in the ppt to ppb level for ocean water
815 (Fischer and Scholz-Böttcher, 2019, Primpke et al., 2020c, Dibke et al., 2021), in the ppb level for sediments
816 (Fischer and Scholz-Böttcher, 2019, Gomiero et al., 2019a, Primpke et al., 2020c), and in the ppb to ppm
817 level for biota (Fischer and Scholz-Böttcher, 2017, Gomiero et al., 2020).

818 For data produced by thermoanalytical methods, polymers should be obligatory and addressed as polymer
819 clusters of the respective polymer type (Figure 3). Any quantification should be performed using defined,

820 backbone-pure polymer types for calibration. The resulting data should then be expressed as respective
821 polymer clusters to gain the highest degree of comparability and harmonization in between datasets. LODs
822 and LOQs should be always related to an actual measured concentration and should never be
823 extrapolated. The reporting of additional information concerning microplastic/polymer concentrations
824 that are calculated via signal to noise ratios or those that result from a calculation based on a very low
825 concentration calibration curve is recommended.

826 **4. Acknowledgements**

827 The authors thank Chelsea Rochman for her advice and comments to improve the manuscript. This work
828 contributes to projects that have received funding from European Union's Horizon 2020 Coordination and
829 Support Action programme under Grant Agreement 101003805 (EUROqCHARM), from the High North
830 Research Centre for Climate and the Environment (The Fram Centre; Grant nr. pa092018) and the
831 Norwegian Research Council (Grant nr. 287939, 301157 and 312262), and the SUMAG3-project supported
832 by DANCEA (Danish Cooperation for Environment in the Arctic) through the Danish Environmental
833 Protection Agency. T.K. was funded through the Institute of Marine Research, Bergen, Norway by the
834 Ministry of Trade, Industry and Fisheries, Norway. K.V. was funded through the program "Miljøstøtte til
835 Arktis" of the Danish Environmental Protection Agency.

836 **We value the comments of 2 anonymous reviewers, who improved an earlier version of this**
837 **manuscript**

838 **Competing interests statement**

839 Competing interests: The authors declare there are no competing interests.

840 **CRedit authorship contribution statement**

841 SPr: Conceptualization, Writing – Original draft, Writing – Review and editing. SPa: Data curation, Writing
 842 – Review and editing. AL: Conceptualization, Writing – Original draft, Writing – Review and editing. AB:
 843 Conceptualization, Writing – Original draft, Writing – Review and editing. GG: Writing – Original draft,
 844 Writing – Review and editing. JS: Writing – Original draft, Writing – Review and editing. BSB:
 845 Conceptualization, Writing – Original draft, Writing – Review and editing. JP: Project
 846 administration, Writing – Review and editing. SA: Writing – Original draft, Writing – Review and editing.
 847 AG: Writing – Original draft, Writing – Review and editing. KV: Data curation, Writing – Review and editing.
 848 TK: Conceptualization, Writing – Original draft, Writing – Review and editing. FG: Writing – Original draft,
 849 Writing – Review and editing.

850 References

- 851
- 852 ABEL, S. M., PRIMPKE, S., INT-VEEN, I., BRANDT, A. & GERDTS, G. 2021. Systematic identification of
 853 microplastics in abyssal and hadal sediments of the Kuril Kamchatka trench. *Environmental*
 854 *Pollution*, 269, 116095.
- 855 ADAMS, J. K., DEAN, B. Y., ATHEY, S. N., JANTUNEN, L. M., BERNSTEIN, S., STERN, G., DIAMOND, M. L. &
 856 FINKELSTEIN, S. A. 2021. Anthropogenic particles (including microfibers and microplastics) in
 857 marine sediments of the Canadian Arctic. *Science of The Total Environment*, 784, 147155.
- 858 AMAP 2021. AMAP Litter and Microplastics Monitoring Guidelines. Version 1.0. Arctic Monitoring and
 859 Assessment Programme. Arctic Monitoring and Assessment Programme (AMAP).
- 860 ANDRADY, A. L. 2011. Microplastics in the marine environment. *Marine Pollution Bulletin*, 62, 1596-1605.
- 861 ARAUJO, C. F., NOLASCO, M. M., RIBEIRO, A. M. P. & RIBEIRO-CLARO, P. J. A. 2018. Identification of
 862 microplastics using Raman spectroscopy: Latest developments and future prospects. *Water*
 863 *Research*, 142, 426-440.

- 864 ATHEY, S. N., ADAMS, J. K., ERDLE, L. M., JANTUNEN, L. M., HELM, P. A., FINKELSTEIN, S. A. & DIAMOND,
865 M. L. 2020. The Widespread Environmental Footprint of Indigo Denim Microfibers from Blue
866 Jeans. *Environmental Science & Technology Letters*, 7, 840-847.
- 867 ATHEY, S. N. & ERDLE, L. M. 2021. Are We Underestimating Anthropogenic Microfiber Pollution? A
868 Critical Review of Occurrence, Methods, and Reporting. *Environmental Toxicology and*
869 *Chemistry*, n/a.
- 870 AVIO, C. G., GORBI, S., MILAN, M., BENEDETTI, M., FATTORINI, D., D'ERRICO, G., PAULETTO, M.,
871 BARGELLONI, L. & REGOLI, F. 2015. Pollutants bioavailability and toxicological risk from
872 microplastics to marine mussels. *Environmental Pollution*, 198, 211-222.
- 873 BOOTH, A. M., HANSEN, B. H., FRENZEL, M., JOHNSEN, H. & ALTIN, D. 2016. Uptake and toxicity of
874 methylmethacrylate-based nanoplastic particles in aquatic organisms. *Environmental Toxicology*
875 *and Chemistry*, 35, 1641-1649.
- 876 BRANDER, S., RENICK, V., FOLEY, M., LUSHER, A., STEELE, C., WOO, M., CARR, S., HELM, P., BOX, C.,
877 ANDREWS, B. & ROCHMAN, C. 2020. Sampling and QA/QC, or how many blanks do I need?: A
878 guide for scientists investigating the occurrence of microplastics across different matrices.
879 *Applied Spectroscopy*, paper submitted.
- 880 BRANDT, J., BITTRICH, L., FISCHER, F., KANAKI, E., TAGG, A., LENZ, R., LABRENZ, M., BRANDES, E.,
881 FISCHER, D. & EICHHORN, K.-J. 2020. High-Throughput Analyses of Microplastic Samples Using
882 Fourier Transform Infrared and Raman Spectrometry. *Applied Spectroscopy*, 0003702820932926.
- 883 BRANDT, J., FISCHER, F., KANAKI, E., ENDERS, K., LABRENZ, M. & FISCHER, D. 2021. Assessment of
884 Subsampling Strategies in Microspectroscopy of Environmental Microplastic Samples. *Frontiers*
885 *in Environmental Science*, 8.
- 886 CABERNARD, L., ROSCHER, L., LORENZ, C., GERDTS, G. & PRIMPKE, S. 2018. Comparison of Raman and
887 Fourier Transform Infrared Spectroscopy for the Quantification of Microplastics in the Aquatic
888 Environment. *Environmental Science & Technology*, 52, 13279-13288.

- 889 CHABUKA, B. K. & KALIVAS, J. H. 2020. Application of a Hybrid Fusion Classification Process for
890 Identification of Microplastics Based on Fourier Transform Infrared Spectroscopy. *Applied*
891 *Spectroscopy*, 74, 1167-1183.
- 892 CHALLINOR, J. M. 2001. Review: the development and applications of thermally assisted hydrolysis and
893 methylation reactions. *Journal of Analytical and Applied Pyrolysis*, 61, 3-34.
- 894 CINCINELLI, A., SCOPETANI, C., CHELAZZI, D., LOMBARDINI, E., MARTELLINI, T., KATSOYIANNIS, A., FOSSI,
895 M. C. & CORSOLINI, S. 2017. Microplastic in the surface waters of the Ross Sea (Antarctica):
896 Occurrence, distribution and characterization by FTIR. *Chemosphere*, 175, 391-400.
- 897 COOKSEY, K. E., GUCKERT, J. B., WILLIAMS, S. A. & CALLIS, P. R. 1987. Fluorometric determination of the
898 neutral lipid content of microalgal cells using Nile Red. *Journal of Microbiological Methods*, 6,
899 333-345.
- 900 COWGER, W., BOOTH, A. M., HAMILTON, B. M., THAYSEN, C., PRIMPKE, S., MUNNO, K., LUSHER, A. L.,
901 DEHAUT, A., VAZ, V. P., LIBOIRON, M., DEVRIESE, L. I., HERMABESSIERE, L., ROCHMAN, C., ATHEY,
902 S. N., LYNCH, J. M., DE FROND, H., GRAY, A., JONES, O. A. H., BRANDER, S., STEELE, C., MOORE, S.,
903 SANCHEZ, A. & NEL, H. 2020a. Reporting Guidelines to Increase the Reproducibility and
904 Comparability of Research on Microplastics. *Applied Spectroscopy*, 74, 1066-1077.
- 905 COWGER, W., GRAY, A., CHRISTIANSEN, S. H., DEFROND, H., DESHPANDE, A. D., HEMABESSIERE, L., LEE,
906 E., MILL, L., MUNNO, K., OSSMANN, B. E., PITTROFF, M., ROCHMAN, C., SARAU, G., TARBY, S. &
907 PRIMPKE, S. 2020b. Critical Review of Processing and Classification Techniques for Images and
908 Spectra in Microplastic Research. *Appl Spectrosc*, 74, 989-1010.
- 909 COWGER, W., STEINMETZ, Z., GRAY, A., MUNNO, K., LYNCH, J., HAPICH, H., PRIMPKE, S., DE FROND, H.,
910 ROCHMAN, C. & HERODOTOU, O. 2021. Microplastic Spectral Classification Needs an Open
911 Source Community: Open Specy to the Rescue! *Analytical Chemistry*, 93, 7543-7548.
- 912 CREW, A., GREGORY-EAVES, I. & RICCIARDI, A. 2020. Distribution, abundance, and diversity of
913 microplastics in the upper St. Lawrence River. *Environmental Pollution*, 260, 113994.

- 914 DA SILVA, V. H., MURPHY, F., AMIGO, J. M., STEDMON, C. & STRAND, J. 2020. Classification and
915 Quantification of Microplastics (<100 μm) Using a Focal Plane Array–Fourier Transform Infrared
916 Imaging System and Machine Learning. *Analytical Chemistry*, 92, 13724-13733.
- 917 DE FROND, H., RUBINOVITZ, R. & ROCHMAN, C. M. 2021. $\mu\text{ATR-FTIR}$ Spectral Libraries of Plastic Particles
918 (FLOPP and FLOPP-e) for the Analysis of Microplastics. *Analytical Chemistry*, 93, 15878-15885.
- 919 DEHAUT, A., HERMABESSIERE, L. & DUFLOS, G. 2020. Microplastics Detection Using Pyrolysis-GC/MS-
920 Based Methods. In: ROCHA-SANTOS, T., COSTA, M. & MOUNEYRAC, C. (eds.) *Handbook of*
921 *Microplastics in the Environment*. Cham: Springer International Publishing.
- 922 DEKIFF, J. H., REMY, D., KLASMEIER, J. & FRIES, E. 2014. Occurrence and spatial distribution of
923 microplastics in sediments from Norderney. *Environmental Pollution*, 186, 248-256.
- 924 DIBKE, C., FISCHER, M. & SCHOLZ-BÖTTCHER, B. M. 2021. Microplastic Mass Concentrations and
925 Distribution in German Bight Waters by Pyrolysis–Gas Chromatography–Mass
926 Spectrometry/Thermochemolysis Reveal Potential Impact of Marine Coatings: Do Ships Leave
927 Skid Marks? *Environmental Science & Technology*, 55, 2285-2295.
- 928 DIERKES, G., LAUSCHKE, T., BECHER, S., SCHUMACHER, H., FÖLDI, C. & TERNES, T. 2019. Quantification of
929 microplastics in environmental samples via pressurized liquid extraction and pyrolysis-gas
930 chromatography. *Analytical and Bioanalytical Chemistry*, 411, 6959-6968.
- 931 DRIS, R., GASPERI, J., MIRANDE, C., MANDIN, C., GUERROUACHE, M., LANGLOIS, V. & TASSIN, B. 2017. A
932 first overview of textile fibers, including microplastics, in indoor and outdoor environments.
933 *Environmental Pollution*, 221, 453-458.
- 934 DUEMICHEN, E., BARTHEL, A.-K., BRAUN, U., BANNICK, C. G., BRAND, K., JEKEL, M. & SENZ, R. 2015.
935 Analysis of polyethylene microplastics in environmental samples, using a thermal decomposition
936 method. *Water Research*, 85, 451-457.

- 937 DUEMICHEN, E., EISENTRAUT, P., BANNICK, C. G., BARTHEL, A. K., SENZ, R. & BRAUN, U. 2017. Fast
938 identification of microplastics in complex environmental samples by a thermal degradation
939 method. *Chemosphere*, 174, 572-584.
- 940 DUEMICHEN, E., EISENTRAUT, P., CELINA, M. & BRAUN, U. 2019. Automated thermal extraction-
941 desorption gas chromatography mass spectrometry: A multifunctional tool for comprehensive
942 characterization of polymers and their degradation products. *Journal of Chromatography A*,
943 1592, 133-142.
- 944 DÜMICHEN, E., BARTHEL, A.-K., BRAUN, U., BANNICK, C. G., BRAND, K., JEKEL, M. & SENZ, R. 2015.
945 Analysis of polyethylene microplastics in environmental samples, using a thermal decomposition
946 method. *Water Research*, 85, 451-457.
- 947 DUMICHEN, E., EISENTRAUT, P., BANNICK, C. G., BARTHEL, A. K., SENZ, R. & BRAUN, U. 2017. Fast
948 identification of microplastics in complex environmental samples by a thermal degradation
949 method. *Chemosphere*, 174, 572-584.
- 950 ECHA EUROPEAN CHEMICAL AGENCY 2019. ECHA REACH Annex XV Restriction Report Proposal for a
951 Restriction: "Substances Names: Intentionally added Microplastics".
952 https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&cad=rja&uact=8&ved=2ahUKEwids8LfvZ_1AhUJRPEDHT0HCmkQFnoECAYQAQ&url=https%3A%2F%2Fecha.europa.eu%2Fdocuments%2F10162%2F05bd96e3-b969-0a7c-c6d0-441182893720&usg=AOvVaw2XIMP7M_S88jTVSJipcJT_s
953
954
955
- 956 EISENTRAUT, P., DUMICHEN, E., RUHL, A. S., JEKEL, M., ALBRECHT, M., GEHDE, M. & BRAUN, U. 2018.
957 Two Birds with One Stone-Fast and Simultaneous Analysis of Microplastics: Microparticles
958 Derived from Thermoplastics and Tire Wear. *Environmental Science & Technology Letters*, 5, 608-
959 613.

- 960 ERNI-CASSOLA, G., GIBSON, M. I., THOMPSON, R. C. & CHRISTIE-OLEZA, J. A. 2017. Lost, but Found with
961 Nile Red: A Novel Method for Detecting and Quantifying Small Microplastics (1 mm to 20 μ m) in
962 Environmental Samples. *Environmental Science & Technology*, 51, 13641-13648.
- 963 EUROPEAN COMMISSION 2017. Commission Decision (EU) 2017/848 of 17 May 2017 laying down criteria
964 and methodological standards on good environmental status of marine waters and specifications
965 and standardised methods for monitoring and assessment, and repealing Decision 2010/477/EU
966 (Text with EEA relevance.). In: COMMISSON, E. (ed.) L 125/43. Official Journal of the European
967 Union.
- 968
- 969 FALTYNKOVA, A., JOHNSEN, G. & WAGNER, M. 2021. Hyperspectral imaging as an emerging tool to
970 analyze microplastics: A systematic review and recommendations for future development.
971 *Microplastics and Nanoplastics*, 1, 13.
- 972 FISCHER, M. & SCHOLZ-BÖTTCHER, B. M. 2017. Simultaneous Trace Identification and Quantification of
973 Common Types of Microplastics in Environmental Samples by Pyrolysis-Gas Chromatography-
974 Mass Spectrometry. *Environ. Sci. Technol.*, 51, 5052-5060.
- 975 FISCHER, M. & SCHOLZ-BÖTTCHER, B. M. 2019. Microplastics analysis in environmental samples – recent
976 pyrolysis-gas chromatography-mass spectrometry method improvements to increase the
977 reliability of mass-related data. *Analytical Methods*, 11, 2489-2497.
- 978 FRÈRE, L., PAUL-PONT, I., MOREAU, J., SOUDANT, P., LAMBERT, C., HUVET, A. & RINNERT, E. 2016. A
979 semi-automated Raman micro-spectroscopy method for morphological and chemical
980 characterizations of microplastic litter. *Marine Pollution Bulletin*, 113, 461-468.
- 981 FRIAS, J. P. G. L. & NASH, R. 2019. Microplastics: Finding a consensus on the definition. *Marine Pollution*
982 *Bulletin*, 138, 145-147.

- 983 FRIES, E., DEKIFF, J. H., WILLMEYER, J., NUELLE, M.-T., EBERT, M. & REMY, D. 2013. Identification of
984 polymer types and additives in marine microplastic particles using pyrolysis-GC/MS and scanning
985 electron microscopy. *Environmental Science-Processes & Impacts*, 15, 1949-1956.
- 986 GESAMP 2016. Sources, Fate and Effects of Microplastics in the Marine Environment (Part 2). *Journal*
987 *Series GESAMP Reports and Studies*, #93, 221.
- 988 GESAMP 2019. Guidelines for the Monitoring and Assessment of Plastic Litter in the Ocean. *Journal*
989 *Series GESAMP Reports and Studies*.
- 990 GOMIERO, A., HAAVE, M., BJORØY, Ø., HERZKE, D., KÖGEL, T., NIKIFOROV, V. & ØYSÆD, K. B. 2020.
991 Quantification of microplastic in fillet and organs of farmed and wild salmonids-a comparison of
992 methods for detection and quantification (SALMODETECT). *NORCE report*.
993 [https://scholar.google.com/citations?view_op=view_citation&hl=en&user=q35OKk0AAAAJ&cita](https://scholar.google.com/citations?view_op=view_citation&hl=en&user=q35OKk0AAAAJ&citation_for_view=q35OKk0AAAAJ:QIV2ME_5wuYC)
994 [tion_for_view=q35OKk0AAAAJ:QIV2ME_5wuYC](https://scholar.google.com/citations?view_op=view_citation&hl=en&user=q35OKk0AAAAJ&citation_for_view=q35OKk0AAAAJ:QIV2ME_5wuYC).
- 995 GOMIERO, A., OYSAED, K. B., AGUSTSSON, T., VAN HOYTEMA, N., VAN THIEL, T. & GRATI, F. 2019a. First
996 record of characterization, concentration and distribution of microplastics in coastal sediments
997 of an urban fjord in south west Norway using a thermal degradation method. *Chemosphere*, 227,
998 705-714.
- 999 GOMIERO, A., STRAFELLA, P., ØYSÆD, K. B. & FABI, G. 2019b. First occurrence and composition
1000 assessment of microplastics in native mussels collected from coastal and offshore areas of the
1001 northern and central Adriatic Sea. *Environmental Science and Pollution Research*, 26, 24407-
1002 24416.
- 1003 GOßMANN, I., HALBACH, M. & SCHOLZ-BÖTTCHER, B. M. 2021. Car and truck tire wear particles in
1004 complex environmental samples – A quantitative comparison with “traditional” microplastic
1005 polymer mass loads. *Science of The Total Environment*, 773, 145667.

- 1006 GRØSVIK, B. E., GRANBERG, M., KÖGEL, T., LUSHER, A., GOMIERO, A., HALLDORSSON, H. P., MADSEN, A.
1007 K., BAAK, J. E., GULS, H. D. & MAGNUSSON, K. 2022. Microplastics in Arctic invertebrates – status
1008 on occurrence and recommendations for future monitoring. *Arctic Science*, This Issue, submitted.
- 1009 HARRISON, J. P., OJEDA, J. J. & ROMERO-GONZALEZ, M. E. 2012. The applicability of reflectance micro-
1010 Fourier-transform infrared spectroscopy for the detection of synthetic microplastics in marine
1011 sediments. *Science of the Total Environment*, 416, 455-463.
- 1012 HARTMANN, N. B., HUFFER, T., THOMPSON, R. C., HASSELLOV, M., VERSCHOOR, A., DAUGAARD, A. E.,
1013 RIST, S., KARLSSON, T., BRENNHOLT, N., COLE, M., HERRLING, M. P., HESS, M. C., IVLEVA, N. P.,
1014 LUSHER, A. L. & WAGNER, M. 2019. Are We Speaking the Same Language? Recommendations for
1015 a Definition and Categorization Framework for Plastic Debris. *Environ Sci Technol*, 53, 1039-1047.
- 1016 HELCOM 2021. HELCOM Guidelines for monitoring beach litter. 4.
- 1017 HENDRICKSON, E., MINOR, E. C. & SCHREINER, K. 2018. Microplastic Abundance and Composition in
1018 Western Lake Superior As Determined via Microscopy, Pyr-GC/MS, and FTIR. *Environmental
1019 Science & Technology*, 52, 1787-1796.
- 1020 HERMABESSIERE, L., HIMBER, C., BORICAUD, B., KAZOUR, M., AMARA, R., CASSONE, A. L., LAURENTIE,
1021 M., PAUL-PONT, I., SOUDANT, P., DEHAUT, A. & DUFLOS, G. 2018. Optimization, performance,
1022 and application of a pyrolysis-GC/MS method for the identification of microplastics. *Analytical
1023 and Bioanalytical Chemistry*, 410, 6663-6676.
- 1024 HIDALGO-RUZ, V., GUTOW, L., THOMPSON, R. C. & THIEL, M. 2012. Microplastics in the Marine
1025 Environment: A Review of the Methods Used for Identification and Quantification.
1026 *Environmental Science & Technology*, 46, 3060-3075.
- 1027 HILDEBRANDT, L., EL GAREB, F., ZIMMERMANN, T., KLEIN, O., EMEIS, K., PROEFROCK, D. & KERSTAN, A.
1028 2020. Fast, Automated Microplastics Analysis Using Laser Direct Chemical Imaging:
1029 Characterizing and quantifying microplastics in water samples from marine environments.

- 1030 HILDEBRANDT, L., ZIMMERMANN, T., PRIMPKE, S., FISCHER, D., GERDTS, G. & PRÖFROCK, D. 2021.
1031 Comparison and uncertainty evaluation of two centrifugal separators for microplastic sampling.
1032 *Journal of Hazardous Materials*, 414, 125482.
- 1033 HUFNAGL, B., STEINER, D., RENNER, E., LÖDER, M. G. J., LAFORSCH, C. & LOHNINGER, H. 2019. A
1034 methodology for the fast identification and monitoring of microplastics in environmental
1035 samples using random decision forest classifiers. *Analytical Methods*, 11, 2277-2285.
- 1036 IMHOF, H. K., LAFORSCH, C., WIESHEU, A. C., SCHMID, J., ANGER, P. M., NIESSNER, R. & IVLEVA, N. P.
1037 2016. Pigments and plastic in limnetic ecosystems: A qualitative and quantitative study on
1038 microparticles of different size classes. *Water Res*, 98, 64-74.
- 1039 ISO 2020. ISO/TR 21960:2020 Plastics — Environmental aspects — State of knowledge and
1040 methodologies.
- 1041 ISOBE, A., BUENAVENTURA, N. T., CHASTAIN, S., CHAVANICH, S., CÓZAR, A., DELORENZO, M., HAGMANN,
1042 P., HINATA, H., KOZLOVSKII, N., LUSHER, A. L., MARTÍ, E., MICHIDA, Y., MU, J., OHNO, M.,
1043 POTTER, G., ROSS, P. S., SAGAWA, N., SHIM, W. J., SONG, Y. K., TAKADA, H., TOKAI, T., TORII, T.,
1044 UCHIDA, K., VASSILLENKO, K., VIYAKARN, V. & ZHANG, W. 2019. An interlaboratory comparison
1045 exercise for the determination of microplastics in standard sample bottles. *Marine Pollution*
1046 *Bulletin*, 146, 831-837.
- 1047 IVLEVA, N. P. 2021. Chemical Analysis of Microplastics and Nanoplastics: Challenges, Advanced Methods,
1048 and Perspectives. *Chemical Reviews*, 121, 11886-11936.
- 1049 KÄPPLER, A., FISCHER, D., OBERBECKMANN, S., SCHERNEWSKI, G., LABRENZ, M., EICHHORN, K. J. & VOIT,
1050 B. 2016. Analysis of environmental microplastics by vibrational microspectroscopy: FTIR, Raman
1051 or both? *Analytical and Bioanalytical Chemistry*, 408, 8377-8391.
- 1052 KÄPPLER, A., FISCHER, M., SCHOLZ-BÖTTCHER, B. M., OBERBECKMANN, S., LABRENZ, M., FISCHER, D.,
1053 EICHHORN, K.-J. & VOIT, B. 2018. Comparison of μ -ATR-FTIR spectroscopy and py-GCMS as

- 1054 identification tools for microplastic particles and fibers isolated from river sediments. *Analytical*
1055 *and Bioanalytical Chemistry*, 410, 5313-5327.
- 1056 KÄPPLER, A., WINDRICH, F., LÖDER, M. G. J., MALANIN, M., FISCHER, D., LABRENZ, M., EICHHORN, K. J. &
1057 VOIT, B. 2015. Identification of microplastics by FTIR and Raman microscopy: a novel silicon filter
1058 substrate opens the important spectral range below 1300 cm⁻¹ for FTIR transmission
1059 measurements. *Analytical and Bioanalytical Chemistry*, 407, 6791-6801.
- 1060 KEDZIERSKI, M., FALCOU-PRÉFOL, M., KERROS, M. E., HENRY, M., PEDROTTI, M. L. & BRUZAUD, S. 2019. A
1061 machine learning algorithm for high throughput identification of FTIR spectra: Application on
1062 microplastics collected in the Mediterranean Sea. *Chemosphere*, 234, 242-251.
- 1063 KIESSLING, T., KNICKMEIER, K., KRUSE, K., GATTA-ROSEMARY, M., NAUENDORF, A., BRENNECKE, D.,
1064 THIEL, L., WICHELS, A., PARCHMANN, I., KÖRTZINGER, A. & THIEL, M. 2021. Schoolchildren
1065 discover hotspots of floating plastic litter in rivers using a large-scale collaborative approach.
1066 *Science of The Total Environment*, 789, 147849.
- 1067 KIRSTEIN, I. V., HENSEL, F., GOMIERO, A., IORDACHESCU, L., VIANELLO, A., WITTGREN, H. B. &
1068 VOLLERTSEN, J. 2021. Drinking plastics? – Quantification and qualification of microplastics in
1069 drinking water distribution systems by μ FTIR and Py-GCMS. *Water Research*, 188, 116519.
- 1070 KLEIN, M. & FISCHER, E. K. 2019. Microplastic abundance in atmospheric deposition within the
1071 Metropolitan area of Hamburg, Germany. *Science of the total environment*, 685, 96-103.
- 1072 KÖGEL, T., BJØRØY, Ø., TOTO, B., BIENFAIT, A. M. & SANDEN, M. 2020. Micro- and nanoplastic toxicity on
1073 aquatic life: Determining factors. *Science of The Total Environment*, 709, 136050.
- 1074 KÖGEL, T., HAMILTON, B. M., GRANBERG, M. E., PROVENCHER, J., HAMMER, S., GOMIERO, A.,
1075 MAGNUSSON, K. & LUSHER, A. L. 2022. Current efforts on microplastic monitoring in Arctic fish
1076 and how to proceed. *Arctic Science*, submitted.

- 1077 KOOI, M., PRIMPKE, S., MINTENIG, S. M., LORENZ, C., GERDTS, G. & KOELMANS, A. A. 2021.
1078 Characterizing the multidimensionality of microplastics across environmental compartments.
1079 *Water Research*, 202, 117429.
- 1080 KUSCH, P. 2012. Pyrolysis-Gas Chromatography/Mass Spectrometry of Polymeric Materials. In: MOHD,
1081 M. A. (ed.) *Advanced Gas Chromatography - Progress in Agricultural, Biomedical and Industrial*
1082 *Applications*. London, UK: IntechOpen.
- 1083 KUSCH, P. 2014. Identification of Synthetic Polymers and Copolymers by Analytical Pyrolysis-Gas
1084 Chromatography/Mass Spectrometry. *Journal of Chemical Education*, 91, 1725-1728.
- 1085 KUSCH, P., OBST, V., SCHROEDER-OBST, D., FINK, W., KNUPP, G. & STEINHAUS, J. 2013. Application of
1086 pyrolysis-gas chromatography/mass spectrometry for the identification of polymeric materials in
1087 failure analysis in the automotive industry. *Engineering Failure Analysis*, 35, 114-124.
- 1088 LEISTENSCHNEIDER, C., BURKHARDT-HOLM, P., MANI, T., PRIMPKE, S., TAUBNER, H. & GERDTS, G. 2021.
1089 Microplastics in the Weddell Sea (Antarctica): A Forensic Approach for Discrimination between
1090 Environmental and Vessel-Induced Microplastics. *Environmental Science & Technology*, 55,
1091 15900-15911.
- 1092 LENZ, R., ENDERS, K., STEDMON, C. A., MACKENZIE, D. M. A. & NIELSEN, T. G. 2015. A critical assessment
1093 of visual identification of marine microplastic using Raman spectroscopy for analysis
1094 improvement. *Marine Pollution Bulletin*, 100, 82-91.
- 1095 LEVERMORE, J. M., SMITH, T. E. L., KELLY, F. J. & WRIGHT, S. L. 2020. Detection of Microplastics in
1096 Ambient Particulate Matter Using Raman Spectral Imaging and Chemometric Analysis. *Analytical*
1097 *Chemistry*, 92, 8732-8740.
- 1098 LÖDER, M. G. J., IMHOF, H. K., LADEHOFF, M., LOSCHEL, L. A., LORENZ, C., MINTENIG, S., PIEHL, S.,
1099 PRIMPKE, S., SCHRANK, I., LAFORSCH, C. & GERDTS, G. 2017. Enzymatic Purification of
1100 Microplastics in Environmental Samples. *Environmental Science & Technology*, 51, 14283-14292.

- 1101 LÖDER, M. G. J., KUCZERA, M., MINTENIG, S., LORENZ, C. & GERDTS, G. 2015. Focal plane array detector-
1102 based micro-Fourier-transform infrared imaging for the analysis of microplastics in
1103 environmental samples. *Environmental Chemistry*, 12, 563-581.
- 1104 LUSHER, A., PROVENCHER, J. F., BAAK, J. E., HAMILTON, B. M., VORKAMP, K., HALLANGER, I. G., PIJOGGE,
1105 L., LIBOIRON, M., BOURDAGES, M. P. T., HAMMER, S., GAVRILO, M., VERMAIRE, J. C.,
1106 LINNEBJERG, F. J., MALLORY, M. L. & GABRIELSEN, G. W. 2022. Monitoring litter and
1107 microplastics i Arctic birds and mammals. *Arctic Science*, accepted.
- 1108 .
- 1109 LUSHER, A. L., BRATE, I. L. N., MUNNO, K., HURLEY, R. R. & WELDEN, N. A. 2020a. Is It or Isn't It: The
1110 Importance of Visual Classification in Microplastic Characterization. *Applied Spectroscopy*, 74,
1111 1139-1153.
- 1112 LUSHER, A. L., MUNNO, K., HERMABESSIERE, L. & CARR, S. 2020b. Isolation and Extraction of
1113 Microplastics from Environmental Samples: An Evaluation of Practical Approaches and
1114 Recommendations for Further Harmonization. *Applied Spectroscopy*, 74, 1049-1065.
- 1115 LUSHER, A. L., TIRELLI, V., O'CONNOR, I. & OFFICER, R. 2015. Microplastics in Arctic polar waters: the first
1116 reported values of particles in surface and sub-surface samples. *Scientific Reports*, 5, 14947.
- 1117 LUSHER, A. L., WELDEN, N. A., SOBRAL, P. & COLE, M. 2017. Sampling, isolating and identifying
1118 microplastics ingested by fish and invertebrates. *Analytical Methods*, 9, 1346-1360.
- 1119 MAES, T., JESSOP, R., WELLNER, N., HAUPT, K. & MAYES, A. G. 2017. A rapid-screening approach to
1120 detect and quantify microplastics based on fluorescent tagging with Nile Red. *Scientific Reports*,
1121 7.
- 1122 MALLORY, M. L., GRANT GILCHRIST, H., JANSSEN, M., L.MAJOR, H., MERKEL, F., F.PROVENCHER, J. &
1123 STRØM, H. 2018. Financial costs of conducting science in the Arctic: examples from seabird
1124 research. *Arctic Science*, 4, 624-633.

- 1125 MARTÍ, E., MARTIN, C., GALLI, M., ECHEVARRÍA, F., DUARTE, C. M. & CÓZAR, A. 2020. The Colors of the
1126 Ocean Plastics. *Environmental Science & Technology*, 54, 6594-6601.
- 1127 MARTIN 2022. this issue. *Arctic Science*, submitted.
- 1128 MECOZZI, M., PIETROLETTI, M. & MONAKHOVA, Y. B. 2016. FTIR spectroscopy supported by statistical
1129 techniques for the structural characterization of plastic debris in the marine environment:
1130 Application to monitoring studies. *Marine Pollution Bulletin*, 106, 155-161.
- 1131 MICHIDA, Y., CHAVANICH, S., CHIBA, S., CORDOVA, M. R., CÓZAR CABAÑAS, A., GALGANI, F., HAGMANN,
1132 P., HINATA, H., ISOBE, A., KERSHAW, P., KOZLOVSKII, N., LI, D., LUSHER, A. L., MARTÍ, E., MASON,
1133 S. A., MU, J., SAITO, H., SHIM, W. J., SYAKTI, A. D., TAKADA, H., THOMPSON, R., TOKAI, T.,
1134 UCHIDA, K., VASILENKO, K. & WANG, J. 2020. Guidelines for Harmonizing Ocean Surface
1135 Microplastic Monitoring Methods.
- 1136 MINTENIG, S. M., KOOI, M., ERICH, M. W., PRIMPKE, S., REDONDO- HASSELERHARM, P. E., DEKKER, S. C.,
1137 KOELMANS, A. A. & VAN WEZEL, A. P. 2020. A systems approach to understand microplastic
1138 occurrence and variability in Dutch riverine surface waters. *Water Research*, 115723.
- 1139 MINTENIG, S. M., LÖDER, M. G. J., PRIMPKE, S. & GERDTS, G. 2019. Low numbers of microplastics
1140 detected in drinking water from ground water sources. *Science of the Total Environment*, 648,
1141 631-635.
- 1142 MITRANO, D. M., BELTZUNG, A., FREHLAND, S., SCHMIEDGRUBER, M., CINGOLANI, A. & SCHMIDT, F.
1143 2019. Synthesis of metal-doped nanoplastics and their utility to investigate fate and behaviour in
1144 complex environmental systems. *Nat Nanotechnol*, 14, 362-368.
- 1145 MORGADO, V., PALMA, C. & BETTENCOURT DA SILVA, R. J. N. 2021. Microplastics identification by
1146 infrared spectroscopy – Evaluation of identification criteria and uncertainty by the Bootstrap
1147 method. *Talanta*, 224, 121814.
- 1148 MÜLLER, Y. K., WERNICKE, T., PITTROFF, M., WITZIG, C. S., STORCK, F. R., KLINGER, J. & ZUMBÜLTE, N.
1149 2020. Microplastic analysis—are we measuring the same? Results on the first global comparative

- 1150 study for microplastic analysis in a water sample. *Analytical and Bioanalytical Chemistry*, 412,
1151 555-560.
- 1152 MUNNO, K., DE FROND, H., O'DONNELL, B. & ROCHMAN, C. M. 2020. Increasing the Accessibility for
1153 Characterizing Microplastics: Introducing New Application-Based and Spectral Libraries of Plastic
1154 Particles (SLOPP and SLOPP-E). *Analytical Chemistry*, 92, 2443-2451.
- 1155 NUELLE, M.-T., DEKIFF, J. H., REMY, D. & FRIES, E. 2014. A new analytical approach for monitoring
1156 microplastics in marine sediments. *Environmental Pollution*, 184, 161-169.
- 1157 OSPAR 2015. Guidelines for Monitoring of plastic particles in stomachs of fulmars in the North Sea area.
1158 *OSPAR Commission Agreement 2015-03*, pp 26.
- 1159 OSPAR 2019. Coordinated Environmental Monitoring Programme (CEMP) Guidelines for Monitoring and
1160 Assessment of plastic particles in stomachs of fulmars in the North Sea area. *OSPAR Commission*
1161 *Agreement 2015-03, As amended by EIHA 2016. Updated in 2019 (Annex 1 to replace previous*
1162 *Annex 1, 2, 3), , pp 28.*
- 1163 OSPAR 2020. CEMP Guidelines for marine monitoring and assessment of beach litter. *OSPAR Agreement*
1164 *2020-02.*
- 1165 OSSMANN, B. E., SARAU, G., HOLTMANNSPOTTER, H., PISCHETSRIEDER, M., CHRISTIANSEN, S. H. &
1166 DICKE, W. 2018. Small-sized microplastics and pigmented particles in bottled mineral water.
1167 *Water Research*, 141, 307-316.
- 1168 OSSMANN, B. E., SARAU, G., SCHMITT, S., HOLTMANNSPOTTER, H., CHRISTIANSEN, S. & DICKE, W. 2017.
1169 Development of an optimal filter substrate for the identification of small microplastic particles in
1170 food by micro-Raman spectroscopy. *Analytical and Bioanalytical Chemistry*, 409, 4099-4109.
- 1171 PALATINUS, A., VIRSEK, M. K., ROBIC, U., GREGO, M., BAJT, O., SILJIC, J., SUARIA, G., LIUBARTSEVA, S.,
1172 COPPINI, G. & PETERLIN, M. 2019. Marine litter in the Croatian part of the middle Adriatic Sea:
1173 Simultaneous assessment of floating and seabed macro and micro litter abundance and
1174 composition. *Marine Pollution Bulletin*, 139, 427-439.

- 1175 PHUONG, N. N., POIRIER, L., LAGARDE, F., KAMARI, A. & ZALOUK-VERGNOUX, A. 2018. Microplastic
1176 abundance and characteristics in French Atlantic coastal sediments using a new extraction
1177 method. *Environmental Pollution*, 243, 228-237.
- 1178 PRATA, J. C., REIS, V., DA COSTA, J. P., MOUNEYRAC, C., DUARTE, A. C. & ROCHA-SANTOS, T. 2021.
1179 Contamination issues as a challenge in quality control and quality assurance in microplastics
1180 analytics. *Journal of Hazardous Materials*, 403, 123660.
- 1181 PRIMPKE, S., CHRISTIANSEN, S. H., COWGER, W., DE FROND, H., DESHPANDE, A., FISCHER, M., HOLLAND,
1182 E. B., MEYNS, M., O'DONNELL, B. A., OSSMANN, B. E., PITTROFF, M., SARAU, G., SCHOLZ-
1183 BOTTCHER, B. M. & WIGGIN, K. J. 2020a. Critical Assessment of Analytical Methods for the
1184 Harmonized and Cost-Efficient Analysis of Microplastics. *Applied Spectroscopy*, 74, 1012-1047.
- 1185 PRIMPKE, S., CROSS, R. K., MINTENIG, S. M., SIMON, M., VIANELLO, A., GERDTS, G. & VOLLERTSEN, J.
1186 2020b. Toward the Systematic Identification of Microplastics in the Environment: Evaluation of a
1187 New Independent Software Tool (siMPle) for Spectroscopic Analysis. *Applied Spectroscopy*, 74,
1188 1127-1138.
- 1189 PRIMPKE, S., FISCHER, M., LORENZ, C., GERDTS, G. & SCHOLZ-BOTTCHER, B. M. 2020c. Comparison of
1190 pyrolysis gas chromatography/mass spectrometry and hyperspectral FTIR imaging spectroscopy
1191 for the analysis of microplastics. *Analytical and Bioanalytical Chemistry*, 412, 8283-8298.
- 1192 PRIMPKE, S., GODEJOHANN, M. & GERDTS, G. 2020d. Rapid Identification and Quantification of
1193 Microplastics in the Environment by Quantum Cascade Laser-Based Hyperspectral Infrared
1194 Chemical Imaging. *Environ Sci Technol*, 54, 15893-15903.
- 1195 PRIMPKE, S., WIRTH, M., LORENZ, C. & GERDTS, G. 2018. Reference database design for the automated
1196 analysis of microplastic samples based on Fourier transform infrared (FTIR) spectroscopy.
1197 *Analytical and Bioanalytical Chemistry*, 410, 5131-5141.
- 1198 PROVENCHER, J., ALIANI, S., BERGMANN, M., BOURDAGES, M., BUHL-MORTENSEN, L., GALGANI, F.,
1199 GOMIERO, A., GRANBERG, M., GRØSVIK, B. E., HAMILTON, B. M., T., K., LARSEN, J. R., LUSHER, A.

- 1200 L., MALLORY, M. L., MURPHY, P., PEEKEN, I., PRIMPKE, S., STRAND, J. & VORKAMP, K. 2022.
1201 Future monitoring of litter and microplastics in the Arctic – challenges, opportunities and
1202 strategies. *Arctic Science (this issue)*, under review.
- 1203 RENNER, G., SAUERBIER, P., SCHMIDT, T. & SCHRAM, J. 2019a. Robust Automatic Identification of
1204 Microplastics in Environmental Samples Using FTIR Microscopy. *Analytical Chemistry*, 91.
- 1205 RENNER, G., SCHMIDT, T. & SCHRAM, J. 2019b. Automated rapid & intelligent microplastics mapping by
1206 FTIR microscopy: A Python-based workflow. *MethodsX*, 7.
- 1207 RENNER, G., SCHMIDT, T. C. & SCHRAM, J. 2017. A New Chemometric Approach for Automatic
1208 Identification of Microplastics from Environmental Compartments Based on FT-IR Spectroscopy.
1209 *Analytical Chemistry*, 89, 12045-12053.
- 1210 ROCHMAN, C. M., REGAN, F. & THOMPSON, R. C. 2017. On the harmonization of methods for measuring
1211 the occurrence, fate and effects of microplastics. *Analytical Methods*, 9, 1324-1325.
- 1212 ROSCHER, L., FEHRES, A., REISEL, L., HALBACH, M., SCHOLZ-BÖTTCHER, B., GERRIETS, M., BADEWIEN, T.
1213 H., SHIRAVANI, G., WURPTS, A., PRIMPKE, S. & GERDTS, G. 2021a. Microplastic pollution in the
1214 Weser estuary and the German North Sea. *Environmental Pollution*, 288, 117681.
- 1215 ROSCHER, L., HALBACH, M., NGUYEN, M. T., HEBELER, M., LUSCHTINETZ, F., SCHOLZ-BÖTTCHER, B. M.,
1216 PRIMPKE, S. & GERDTS, G. 2021b. Microplastics in two German wastewater treatment plants:
1217 Year-long effluent analysis with FTIR and Py-GC/MS. *Science of The Total Environment*, 152619.
- 1218 SCHWAFERTS, C., NIESSNER, R., ELSNER, M. & IVLEVA, N. P. 2019. Methods for the analysis of
1219 submicrometer- and nanoplastic particles in the environment. *Trac-Trends in Analytical*
1220 *Chemistry*, 112, 52-65.
- 1221 SCHWAFERTS, C., SCHWAFERTS, P., VON DER ESCH, E., ELSNER, M. & IVLEVA, N. P. 2021. Which particles
1222 to select, and if yes, how many? *Analytical and Bioanalytical Chemistry*, 413, 3625-3641.

- 1223 SCHWAFERTS, C., SOGNE, V., WELZ, R., MEIER, F., KLEIN, T., NIESSNER, R., ELSNER, M. & IVLEVA, N. P.
1224 2020. Nanoplastic Analysis by Online Coupling of Raman Microscopy and Field-Flow
1225 Fractionation Enabled by Optical Tweezers. *Analytical Chemistry*, 92, 5813-5820.
- 1226 SCHYMANSKI, D., GOLDBECK, C., HUMPF, H. U. & FURST, P. 2018. Analysis of microplastics in water by
1227 micro-Raman spectroscopy: Release of plastic particles from different packaging into mineral
1228 water. *Water Research*, 129, 154-162.
- 1229 SCHYMANSKI, D., OßMANN, B. E., BENISMAIL, N., BOUKERMA, K., DALLMANN, G., VON DER ESCH, E.,
1230 FISCHER, D., FISCHER, F., GILLILAND, D., GLAS, K., HOFMANN, T., KÄPPLER, A., LACORTE, S.,
1231 MARCO, J., RAKWE, M. E. L., WEISSER, J., WITZIG, C., ZUMBÜLTE, N. & IVLEVA, N. P. 2021.
1232 Analysis of microplastics in drinking water and other clean water samples with micro-Raman and
1233 micro-infrared spectroscopy: minimum requirements and best practice guidelines. *Analytical and*
1234 *Bioanalytical Chemistry*, 413, 5969-5994.
- 1235 SEEFELDT, H., DUEMICHEN, E. & BRAUN, U. 2013. Flame retardancy of glass fiber reinforced high
1236 temperature polyamide by use of aluminum diethylphosphinate: thermal and thermo-oxidative
1237 effects. *Polymer International*, 62, 1608-1616.
- 1238 SEGHERS, J., STEFANIAK, E. A., LA SPINA, R., CELLA, C., MEHN, D., GILLILAND, D., HELD, A., JACOBSSON, U.
1239 & EMTEBORG, H. 2021. Preparation of a reference material for microplastics in water—
1240 evaluation of homogeneity. *Analytical and Bioanalytical Chemistry*.
- 1241 SHIM, W. J., SONG, Y. K., HONG, S. H. & JANG, M. 2016. Identification and quantification of microplastics
1242 using Nile Red staining. *Marine Pollution Bulletin*, 113, 469-476.
- 1243 SIMON, M., VAN ALST, N. & VOLLERTSEN, J. 2018. Quantification of microplastic mass and removal rates
1244 at wastewater treatment plants applying Focal Plane Array (FPA)-based Fourier Transform
1245 Infrared (FT-IR) imaging. *Water Research*, 142, 1-9.
- 1246 SONG, Z., LIU, K., WANG, X., WEI, N., ZONG, C., LI, C., JIANG, C., HE, Y. & LI, D. 2021. To what extent are
1247 we really free from airborne microplastics? *Science of The Total Environment*, 754, 142118.

- 1248 STRAND, J. & MURPHY, P. 2022. This issue. *Arctic Science*, Submitted.
- 1249 SUARIA, G., ACHTYPI, A., PEROLD, V., LEE JASMINE, R., PIERUCCI, A., BORNMAN THOMAS, G., ALIANI, S. &
1250 RYAN PETER, G. 2020. Microfibers in oceanic surface waters: A global characterization. *Science*
1251 *Advances*, 6, eaay8493.
- 1252 SUTTON, R., MASON, S. A., STANEK, S. K., WILLIS-NORTON, E., WREN, I. F. & BOX, C. 2016. Microplastic
1253 contamination in the San Francisco Bay, California, USA. *Marine Pollution Bulletin*, 109, 230-235.
- 1254 TAGG, A. S., SAPP, M., HARRISON, J. P. & OJEDA, J. J. 2015. Identification and Quantification of
1255 Microplastics in Wastewater Using Focal Plane Array-Based Reflectance Micro-FT-IR Imaging.
1256 *Analytical Chemistry*, 87, 6032-6040.
- 1257 TAMMINGA, M., HENGSTMANN, E. & FISCHER, E. K. 2017. Nile Red Staining as a Subsidiary Method for
1258 Microplastic Quantification: A Comparison of Three Solvents and Factors Influencing Application
1259 Reliability. *Journal of Earth Sciences & Environmental Studies* 2.
- 1260 TER HALLE, A., LADIRAT, L., GENDRE, X., GOUDOUNECHE, D., PUSINERI, C., ROUTABOUL, C., TENAILLEAU,
1261 C., DUPLOYER, B. & PEREZ, E. 2016. Understanding the Fragmentation Pattern of Marine Plastic
1262 Debris. *Environmental Science & Technology*, 50, 5668-5675.
- 1263 THAYSEN, C., MUNNO, K., HERMABESSIERE, L. & ROCHMAN, C. M. 2020. Towards Raman Automation for
1264 Microplastics: Developing Strategies for Particle Adhesion and Filter Subsampling. *Appl*
1265 *Spectrosc*, 74, 976-988.
- 1266 THE CALIFORNIA WATER BOARDS. 2022. Available:
1267 https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/microplastics.html
1268 [Accessed 07th January 2022].
- 1269 TSUGE, S., OHTANI, H. & WATANABE, C. 2011. *Pyrolysis-GC/MS Data Book of Synthetic Polymers*, Elsevier
1270 B.V.
- 1271 VAN MOURIK, L. M., CRUM, S., MARTINEZ-FRANCES, E., VAN BAVEL, B., LESLIE, H. A., DE BOER, J. &
1272 COFINO, W. P. 2021. Results of WEPAL-QUASIMEME/NORMANS first global interlaboratory study

- 1273 on microplastics reveal urgent need for harmonization. *Science of The Total Environment*, 772,
1274 145071.
- 1275 VIANELLO, A., BOLDRIN, A., GUERRIERO, P., MOSCHINO, V., RELLA, R., STURARO, A. & DA ROS, L. 2013.
1276 Microplastic particles in sediments of Lagoon of Venice, Italy: First observations on occurrence,
1277 spatial patterns and identification. *Estuarine Coastal and Shelf Science*, 130, 54-61.
- 1278 VON DER ESCH, E., KOHLES, A. J., ANGER, P. M., HOPPE, R., NIESSNER, R., ELSNER, M. & IVLEVA, N. P.
1279 2020a. TUM-ParticleTyper: A detection and quantification tool for automated analysis of
1280 (Microplastic) particles and fibers. *PLOS ONE*, 15, e0234766.
- 1281 VON DER ESCH, E., LANZINGER, M., KOHLES, A. J., SCHWAFERTS, C., WEISSER, J., HOFMANN, T., GLAS, K.,
1282 ELSNER, M. & IVLEVA, N. P. 2020b. Simple Generation of Suspensible Secondary Microplastic
1283 Reference Particles via Ultrasound Treatment. *Frontiers in Chemistry*, 8.
- 1284 WAMPLER, T. P. 2006. Pyrolysis Techniques in the Analysis of Polymers and Rubbers. *Encyclopedia of*
1285 *Analytical Chemistry*.
- 1286 WAMPLER, T. P. 2007. *Applied Pyrolysis Handbook*, Boca Raton, Florida, USA., CRC-Press.
- 1287 WANDER, L., VIANELLO, A., VOLLERTSEN, J., WESTAD, F., BRAUN, U. & PAUL, A. 2020. Exploratory
1288 analysis of hyperspectral FTIR data obtained from environmental microplastics samples.
1289 *Analytical Methods*, 12, 781-791.
- 1290 WARD, J. E., ZHAO, S., HOLOHAN, B. A., MLADINICH, K. M., GRIFFIN, T. W., WOZNIAK, J. & SHUMWAY, S.
1291 E. 2019. Selective Ingestion and Egestion of Plastic Particles by the Blue Mussel (*Mytilus edulis*)
1292 and Eastern Oyster (*Crassostrea virginica*): Implications for Using Bivalves as Bioindicators of
1293 Microplastic Pollution. *Environmental Science & Technology*, 53, 8776-8784.
- 1294 WESCH, C., ELERT, A. M., WÖRNER, M., BRAUN, U., KLEIN, R. & PAULUS, M. 2017. Assuring quality in
1295 microplastic monitoring: About the value of clean-air devices as essentials for verified data.
1296 *Scientific Reports*, 7, 5424.

- 1297 WIGGIN, K. J. & HOLLAND, E. B. 2019. Validation and application of cost and time effective methods for
1298 the detection of 3–500 µm sized microplastics in the urban marine and estuarine environments
1299 surrounding Long Beach, California. *Marine Pollution Bulletin*, 143, 152-162.
- 1300 WITZIG, C. S., FÖLDI, C., WÖRLE, K., HABERMEHL, P., PITTRÖFF, M., MÜLLER, Y. K., LAUSCHKE, T., FIENER,
1301 P., DIERKES, G., FREIER, K. P. & ZUMBÜLTE, N. 2020. When Good Intentions Go Bad—False
1302 Positive Microplastic Detection Caused by Disposable Gloves. *Environmental Science &*
1303 *Technology*, 54, 12164-12172.
- 1304 ZADA, L., LESLIE, H. A., VETHAAK, A. D., TINNEVELT, G. H., JANSEN, J. J., DE BOER, J. F. & ARIESE, F. 2018.
1305 Fast microplastics identification with stimulated Raman scattering microscopy. *Journal of Raman*
1306 *Spectroscopy*, 49, 1136-1144.
- 1307 ZARFL, C. 2019. Promising techniques and open challenges for microplastic identification and
1308 quantification in environmental matrices. *Analytical and Bioanalytical Chemistry*, 411, 3743-3756.

1309

1310

1311

1312

1313

1314

1315

1316

1317

1318 **Figure Captions:**

1319 Figure 1: Small filter area targeted by the different approaches to select particles for Fourier-Transform
1320 Infrared (FTIR) as well as Raman microscopy. a) Visually selected particles for further analysis; b) Manual
1321 chemical mapping using a pre-defined area of measurement fields (distance 20 μm); c) False colour image
1322 (FTIR, integral of region 2980-2780 cm^{-1}) of the manually measured area; d) Area selected for
1323 hyperspectral FTIR imaging; e) Hyperspectral FTIR image collected with 3.5x FTIR lens (11.6 μm pixel size),
1324 f) Hyperspectral FTIR image collected with 15x FTIR lens (2.7 μm pixel size).

1325 Figure 2: Example of a microplastic particle identified by Raman spectroscopy using a combination of
1326 several spectral databases (Cabernard et al., 2018, Munno et al., 2020, von der Esch et al., 2020a). Left
1327 side: Particle image, raw Raman spectra and particle details derived by image analysis. Right side:
1328 Processed spectra (red) and assigned library spectrum (blue) for the selected particle and reference
1329 spectra (highlighted in violet) combined with material name and further information.

1330 Figure 3: Overview of the materials for various fields of applications, their respective polymer backbones
1331 and identifier ions yielding the various polymer clusters used for polymer quantification (for further details
1332 see Primpke et al. (2020c) and Dibke et al. (2021).

1333

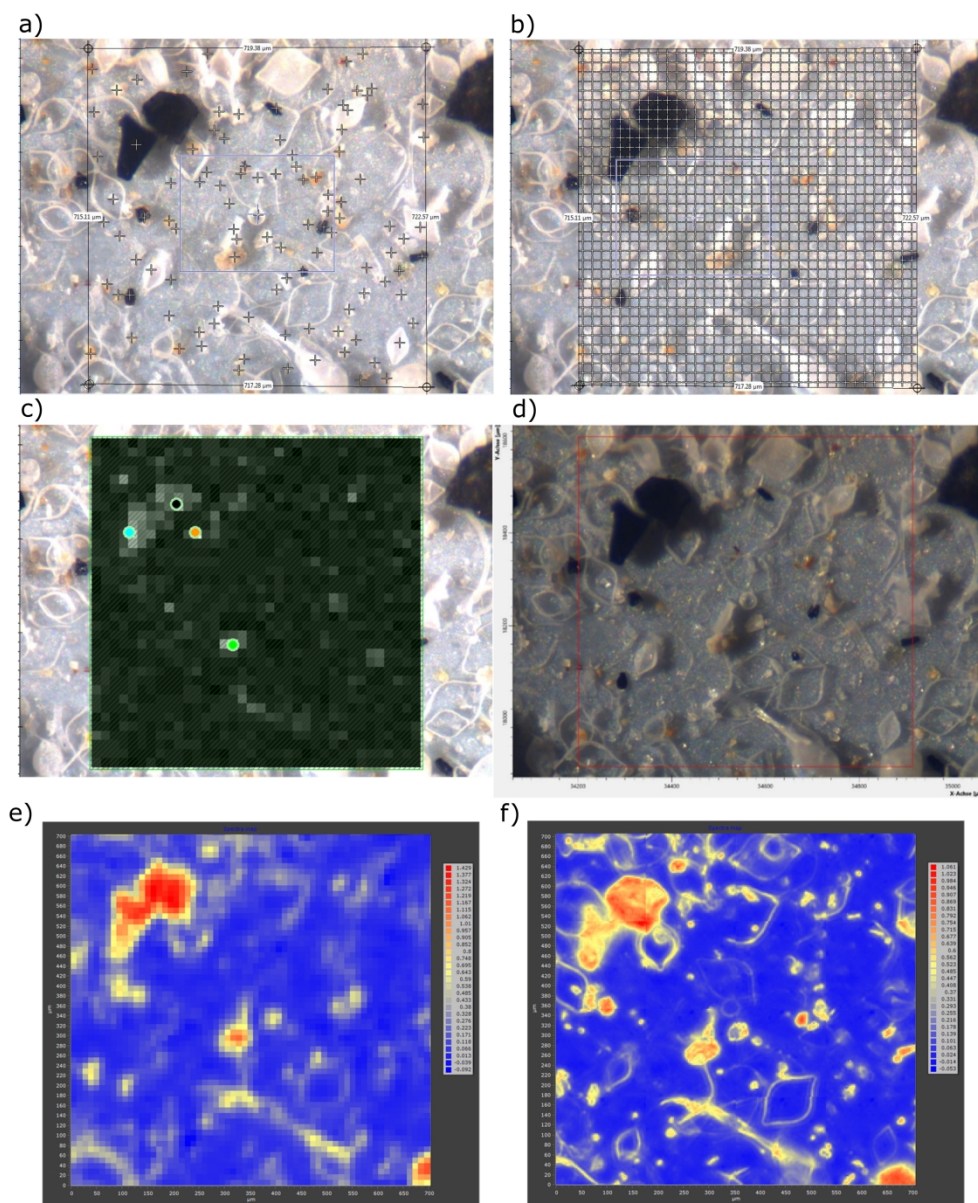


Figure 1: Small filter area targeted by the different approaches to select particles for Fourier-Transform Infrared (FTIR) as well as Raman microscopy. a) Visually selected particles for further analysis; b) Manual chemical mapping using a pre-defined area of measurement fields (distance 20 μm); c) False 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 3.5x FTIR lens (11.6 μm pixel size), f) Hyperspectral FTIR image collected with 15x FTIR lens (2.7 μm pixel size).

423x508mm (300 x 300 DPI)

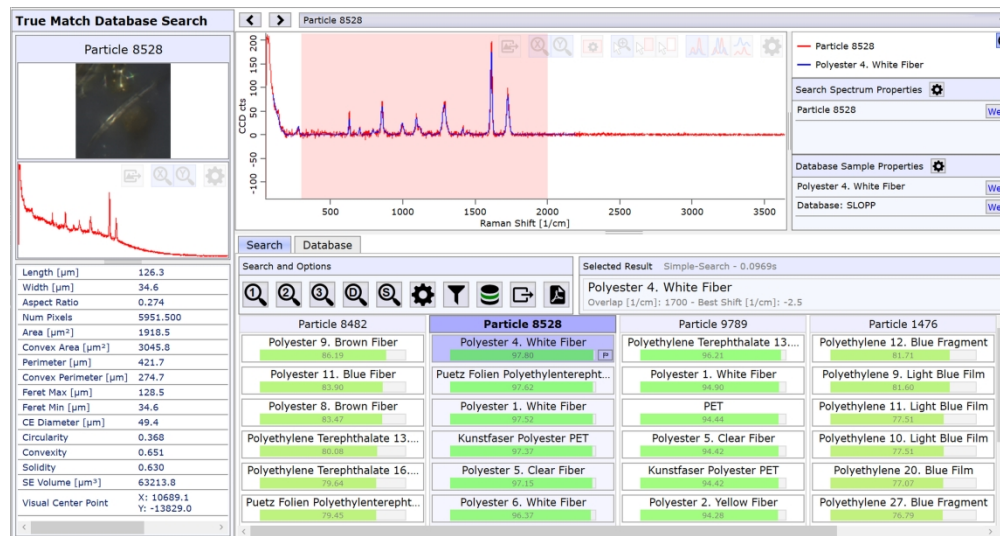


Figure 2: Example of a microplastic particle identified by Raman spectroscopy using a combination of several spectral databases (Cabernard et al., 2018, Munno et al., 2020, von der Esch et al., 2020a). Left side: Particle image, raw Raman spectra and particle details derived by image analysis. Right 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.

706x374mm (144 x 144 DPI)

Arctic Science Downloaded from cdnsciencepub.com by FISKERIDIREKTORATET on 09/27/22
 Only. This Just-IN manuscript is the accepted manuscript prior to copy editing and page composition. It may differ from the final official

Environment

- Polymers
- Composites
- Foams
- Paints
- Varnishes
- Adhesives
- Sealings
- Insulations
- Textiles
- Fabrics
- Formulations
- ...

□ BSB, 2021

- HDPE, LDPE, EVA, EDPM rubber
PE-containing copolymers
- PP, PP-containing copolymers
- PS, PS-containing copolymers (e.g. ABS, SAN), PS-or acryl-styrene binder/varnish
- PVC (hard & plasticized), chlorinated PE, chlorinated rubber/polyprene
- PMMA, polyalkylated methacrylates, acrylate-containing binder/varnish
- PC, epoxide resins /varnish
- PET, PBT, polyalkyl terephthalates
- PA6, ε-caprolactam containing polymers
- MDI-PUR & respective formulations and foams

“backbone” detected

Polymer cluster:

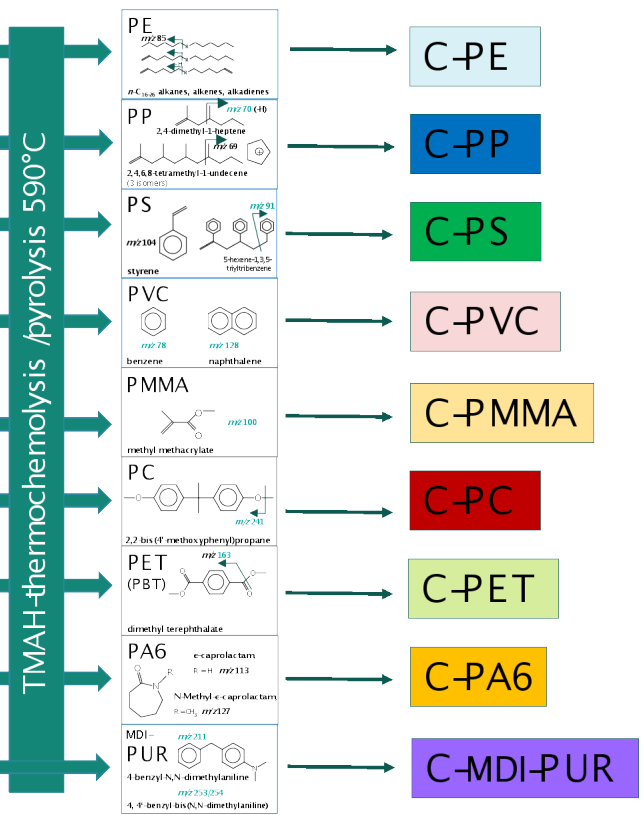


Table 1: Cost estimation for the presented analytical techniques ranging from optical methods toward chemical analysis based on data from Primpke et al. (2020a).

Working mode	Unit	Visual identification		Fluorescent staining	Fourier-transform infrared (FTIR) spectroscopy			Raman spectroscopy		Pyrolysis-(Py)-GC/MS		Thermal extraction desorption (TED)-GC/MS
		None	Microscope	Nile red	qualitative	pParticle 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 - > 10000	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 F	7 F	50 P	1 F	1 F	50 P	1 F	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		+	+	+	+	+	+	+	+	-	-	-

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

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

BLACK/ GRAY	BLUE/ GREEN	BROWN/ TAN	WHITE/ CREAM	YELLOW	ORANGE/ PINK/RED	TRANSPARENT	MULTICOLOR
----------------	----------------	---------------	-----------------	--------	---------------------	-------------	------------

Table 3: Polymer types recommended for reporting of microplastics in the Arctic. Reproduced from the AMAP Guidelines (AMAP, 2021).

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, various chlorinated polymers
Silicone rubbers and coatings	
Other plastics	e.g., PEEK
Other rubbers	
Other microlitter materials	

Table 4: The demanded data accuracy for monitoring in the Arctic for the individual compartments covering different size classes. Chem-ID: Chemical identification *Subsampling should be avoided, ** Analysis of at least a subsample, *** No microplastics defined. Adapted from (AMAP, 2021).

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 (1mm - 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 (1mm - 300 µm) **
Sediments	Beneficial	Beneficial	300 - down to LOD	For Chem-ID	Mandatory	Mandatory	Beneficial
Ice	x	Beneficial	5000 - 300	-	Mandatory	Mandatory	Yes (1mm - 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 (1mm - 300 µm) **
Fish	Beneficial	Beneficial	< 300 µm	For Chem-ID	Size beneficial shape beneficial	Beneficial	Yes (1mm - 300 µm) **
Bird	Mandatory	Mandatory	5000 - >300 µm	For Chem-ID	Beneficial	Beneficial	Yes (1mm - 300 µm) **
Mammal	Mandatory	Mandatory	> 2.5 cm - 300 µm	For Chem-ID	Size mandatory, shape Beneficial	Beneficial	Yes (1mm - 300 µm) **
Mammal	Beneficial	Beneficial	< 300 µm to LOD	For Chem-ID	Beneficial	Beneficial	Beneficial