Monitoring of microplastics in the marine environment

– Changing directions towards
quality controlled tailored solutions

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The ubiquitous occurrence of microplastics and other synthetic anthropogenic micro-sized particles in the marine environment has over the past decade gained substantial worldwide attention. This has resulted in the development of numerous methods to estimate the amount and type of microplastics present in different marine habitats (Hildago-Ruz *et al.* 2012; Prata *et al.* 2019; Renner *et al.* 2018). The need to design harmonized protocols to be used for monitoring concentrations and polymer composition of marine microplastics has been discussed for many years now, but it has proved to be difficult to agree on how to reach this goal.

In practise, there are three important aspects that need to be addressed when marine microplastics are monitored: how to carry out the field sampling, how to eliminate other particulate matter in the sample without harming the plastic itself, and how to accurately identify the particles. Throughout the whole monitoring procedure, it is of great importance to prevent and assess the contamination of the samples at each step of the process, from sampling to analyses.

In the HARMIC project, Nordic scientist with long term experience in microplastic research assessed different methods of sampling and sample preparation relevant for the establishment of common guidelines. It was also evaluated how these methods affected the analytical identification and quantification of microplastics and the requirements of appropriate quality assurance and quality control (QA/QC). The outcomes of the studies are discussed here from a monitoring perspective.

Marine microplastics

Microplastics are a diverse group of particles and may be generated from wear and tear of plastic-containing products, fragmenting from plastic litter or by intentional production.

Marine microplastics and other microlitter particles are included as descriptors in the Marine Strategy Framework Directive (MSFD) and must be considered when aiming to improve the environmental status of European marine waters.

The development of monitoring strategies has therefore been launched in several member states. Although there are guidance documents for marine microlitter monitoring produced by scientific expert groups (e.g. Galgani *et al.* 2013) and international research projects (Frias *et al.* 2018, Gago *et al.* 2018, GESAMP, 2019), the use of various approaches and development of better methods continues. In the Nordic region, a recent HELCOM coordinated, EU co-financed project (SPICE) collected information on published and on-going research and monitoring activities in the Baltic Sea (HELCOM, 2018). Experts from the contracting parties were asked specific questions regarding protocols used for sampling, sample treatments and analyses of microlitter/microplastics in different marine compartments (water surface, water column, sediment, beach sand, biota). Responses from the survey revealed that a wide range of methods were applied in this geographical region. It was also found that while some countries have had ongoing activities since 2007, others have initiated environmental sampling of microplastics rather recently.

Experiences from HARMIC studies

In the HARMIC project, four methodological studies were carried out with the purpose of optimizing the analysis of microplastics in seawater and marine sediments. Two of the studies focused on the collection of water samples and investigated how the measured microplastic concentrations were affected depending on how and where the sampling of seawater was carried out, while the other two studies compared methods for the preparation of water and sediment samples prior to the actual analyses of microplastic particles. The following basic quality criteria were set up for the different steps of microplastics sampling and analysis as directed towards microplastics monitoring:

Sampling

- The chosen sampling method depends on the aim of the study and must produce undisturbed samples which are representative of the microplastics concentration in the sampled matrix.
- At each site, the sample volume and the number of replicates must be sufficient to support subsequent statistical analysis.
- A description of the sampling location and weather conditions during sampling should be reported, in order to allow for an appropriate interpretation of the results.

Sample preparation

- Methods to remove excess materials and extract microplastics must not harm the plastic polymers, the environment or humans.
- Extraction efficiency for the chosen method should be considered, verified and reported.
- Methods should be designed so that the risk of contamination is minimized.

Sample analysis

- As many particle characteristics as possible (shape, colour, etc) should be reported.
- The methods should be designed to minimize the risk of contamination.

Water sampling

Many plastic polymers are lighter than water and are expected to float on the surface. This has resulted in most studies focusing on the microplastics on the water surface. An important part of HARMIC was therefore to compare the amount of microplastics at different depths of the water column. In summary the aim of this part of the study was to:

- Compare sampling at the sea surface vs. sampling in the water column.
- Compare two different protocols for degrading organic matter in the water samples before analyses.

Sampling at the surface or in the water column

During a cruise in the northern Baltic Sea, microplastics samples were collected with a common manta trawl (Figure 1a), a trawl that is specially designed to collect particles in surface water, and with a MultiNet (Figure 1b), a multiple plankton sampler that is towed horizontally through the water column. The MultiNet used carried 5 individual nets which could be lowered to a specific water depth for sampling. The results showed that the total microplastics concentration in the water column may outnumber the concentrations found at the water surface. Although the depth distribution of particles in this study differed between sampling areas, the results clearly showed that data from surface water only does not provide a complete picture of the amount of microplastics in water. The vertical distribution of microplastics will depend on the abiotic and biotic variables of the sea area. For example, in the case of the Baltic Sea strong temperature and salinity stratification can prevent the mixing of the water column, which in turn may result in the accumulation of particles at specific pycnoclines.

Sampling with pump or surface trawl

The most commonly used sampling device for microplastics is still the manta trawl, or a similar type of neuston net, which

↑ Figure 1. Collection of surface microplastics with a manta trawl (a). Multinet (b) can be utilized both for sampling from the surface and different water layers below surface.

collects microplastics larger than 0.3mm from surface waters (Renner et al. 2017). However, different types of pumps equipped with a filter holder are also being applied. Field tests comparing sampling with an in-situ pump that collected water right below the surface and a surface trawl (Karlsson et al. 2018a), showed that the statistical uncertainty regarding the number of particles per sample was lower when the trawl was used because higher volumes were sampled. The trawl also sampled particles floating on the surface more efficiently. The pump had, however, other advantages: the precision of the filtered volume was higher, the contamination risk lower, and it provided the possibility of sequential filtration with filters of different mesh sizes.

Regardless of which method is applied, most important is to ensure that the samples contain a high enough number of particles and to take enough replicates to allow for statistical analyses of the data. This is vital in order to compensate for uncertainty related to counting statistics and patchiness of microplastic particles within the confined sampled space (Karlsson et al. 2018a).

Sediment sampling

Sediment for testing of the different microplastic extraction protocols were sampled with a Gemini corer. Sediment was collected from the top 2 cm of a sample with undisturbed surface (Figure 2). No comparison was however done between different methods for sediment sampling. The sampling was done outside the Swedish west coast in an area with several potential sources of microplastic pollution, from plastics industry (PE and PVC), a small city, commercial ships and leisure boat activities, aquaculture and traffic. The sample aliquots were pooled and divided into 15 replicates and frozen until analysis. Extraction experiments were carried out to evaluate the microplastic recovery rate after treating the sediment with the different pre-treatment methods.

→ Figure 2. Samples for collecting microplastics from the sediment were taken with a Gemini corer.

PHOTO: PKARIN MATTSON

Pre-treatment of water and sediment samples prior to analyses

The extraction of microplastics may include both a step where natural organic material is degraded and rinsed off the sample and a step where mineral particles are removed through density separation with a saturated saline solution. In general, water samples only require the first step, the removal of organic material, whereas sediment samples need to go through the density separation step.

Water samples

Sometimes water samples are clean enough to be analysed visually with stereomicroscopy even without any pre-treatment whereas at other times they may contain a substantial amount of zooplankton, remains of algal cells and other organic material which make direct analyses of microplastic particles impossible. Such samples must be treated in the laboratory aiming at removing organic material from the sample matrix. At present, there are several protocols available for digesting organic material, which rely on oxidative, acidic, alkaline and enzymatic methods (GESAMP 2019). In HARMIC studies, the samples that required pre-treatment were treated according to two different digestion protocols and the results were compared.

The particulate material in the water sample was collected on filters of the same mesh size that had been used for sampling the water in the field.

One set of the water samples were then treated according to the protocol by Löder *et al.* (2017). Organic material (e.g. detritus, phytoplankton, zooplankton) was removed using a stepwise treatment with the protease, cellulase and chitinase enzymes, and in addition to that hydrogen peroxide, an oxidizing agent. After this followed a density separation step where the sample material was mixed with a saturated ZnCl_2 solution to separate microplastic particles from heavier

material (see further *Sediment samples*). Depending on the sample characteristics the whole procedure may take up to 12 days for a sample to be ready for analyses, and each step in the procedure requires some handling.

For a parallel set of water samples, the protocol by von Friesen *et al.* (2019) was applied. This method was originally designed for the analyses of microplastics in biota. The filters were incubated with a pancreatic enzyme preparation originally meant for humans with pancreatic insufficiency (CREON®). This protocol involved only one treatment step and samples were ready for analysis after 24 hours.

The samples incubated with the stepwise method of Löder *et al.* (2017) were almost completely free from all excess material but microplastics and cotton fibres. This made them very easy to analyse both with stereomicroscopy, which is good enough for separating microplastics from non-plastic particles, and with automated analyses with Fourier Transform Infrared (FTIR) or Raman spectroscopy, where the specific polymer of the plastic particles is revealed. Water samples treated with pancreatic enzymes (von Friesen *et al.* 2019) were free from most organic material but contained a substantial quantity of chitinous zooplankton carapaces. When the samples were wet the chitin making up the carapaces was almost transparent so the visual analyses with stereomicroscopy was only moderately obstructed. However, for further analyses with e.g. FTIR or Raman spectroscopy the carapaces might have to be individually picked from the filters.

It should be emphasized that both the visual analyses with stereomicroscopy and the interpretation of spectra from FTIR and Raman spectroscopy require a well-trained staff if the results are to be reliable. The need for training is often brought

up as a reason to not use stereomicroscopic analysis for microplastics.

A quality check of the two methods used to remove organic matter (Löder *et al.* 2017 and von Friesen *et al.* 2019) was carried out by adding reference particles of different plastic polymers to the samples before the treatment and analysing both the recovery rate and any adverse effects on the particles. Stereomicroscopic inspection was used to reveal larger structural differences and to verify the percentage of recovered particles. Changes in the molecular structure associated with polymer degradation may be observed using vibrational spectroscopy like Raman spectroscopy or FTIR. In the present study, analysis with Raman was applied. Information on the formation of microcracks and smaller structural changes may be obtained with scanning electron microscopy, however this was not done in the present study.

Both digestion protocols used for treatment of water samples were checked for their impact on microplastics of different polymer types. Inspection of the particles before and after treatment revealed that incubation with pancreatic enzymes (von Friesen *et al.* 2019) had no observed effect, neither visual nor on FTIR spectra, on any of the following polymers: polyester, polyethylene terephthalate (PET), polypropylene (PP), low-density polyethylene (LDPE), expanded polystyrene (EPS), polylactic acid (PLA), Nomex, (an aramid polymer) and modacrylic (von Friesen *et al.* 2019).

The effects of the stepwise enzymatic protocol (Löder *et al.* 2017) has been tested on the following plastic polymers: polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), polyurethane (PUR), polyamide (PA), polyethylene terephthalate (PET), polystyrene (PS), polycarbonate (PC) and

poly (methyl methacrylate (PMMA). There were no detectable changes in Raman spectra for any of the polymers. Visual change was considered to be negligible.

Both protocols used for pre-treatment of water samples prior to microplastic analyses had their pros and cons:

Stepwise enzymatic incubation (Löder *et al.* 2016):

- + Very clean samples with no remains of zooplankton carapaces. This enables both visual analysis with stereomicroscopy and automated spectroscopic analyses with FTIR and Raman.
- + No alterations of Raman spectra for microplastics.
- Many work steps involved which may increase risk of contamination.
- Relatively expensive, both because of the extensive work effort and the many chemicals used.
- Discolouration of PET.

Incubation with only pancreatic enzymes (von Friesen *et al.* 2019):

- + The method involves few work steps, which lowers the risk for contamination.
- + Rapid and relatively cheap both by the amount of work effort and price of chemicals.
- + No alterations in FTIR spectra or discolouration of particles.
- Carapaces of zooplankton remain (but samples may still be clean enough for visual analyses with stereomicroscopy).

← Figure 3. The scaled down version of the Plastic sediment Separator used in HARMIC studies.

Sediment samples

To extract microplastics from sediment samples the efficiency of two different methods for the degradation of organic matter and two different saline solutions for density separation were tested. This resulted altogether in four combinations of digestion and density separation methods.

The two digestion protocols used for the sediments were:

- 1) incubation with pancreatic enzymes (the same treatment as for the water samples, von Friesen *et al.* 2019), and
- 2) incubation with (0.022 mol/L) sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$), (0.45 mol/L) KOH, and (0.67 mol/L) NaClO . The latter is a modification of Strand *et al.* (2016), where one-hour incubation with chemicals was combined with repeated (3 times) centrifuge and wash cycles. After centrifugation, the sediments were moved back into the glass jars.

The two density separation protocols were 1) a saturated ZnCl_2 solution with a density of $1.77 \text{ g}\cdot\text{cm}^{-3}$, and 2) a saturated NaCl solution with a density of $1.2 \text{ g}\cdot\text{cm}^{-3}$. Density separation was carried out using a modified (scaled down; Figure 3) Munich Plastic Sediment Separator (MPSS, Imhoff *et al.*, 2012). Note: pre filtering of sample extract with pH adjustment may be needed if the ZnCl_2 solution is combined with an alkaline sediment extract containing KOH because of precipitation of ZnOH_2 .

After digestion of the organic material the sediment samples were mixed with the saline solution for three hours. The sediment/saline solution mix was then left to separate according to particle density so that particles with higher density than the solution had sunk to the bottom (mainly mineral particles) and particles of a density similar or lighter than the saline solution remained floating. The saline solution fraction was filtered in sequence over filters with a 300, 100 and 50 μm mesh size, and the collected material was analysed with stereomicroscopy and Raman spectroscopy.

The sample analyses showed that both digestion methods were equally efficient at eliminating the organic material in the sediment samples. A method quality check revealed that neither of them resulted in any detectable, harmful effects on plastic polymers, which could be observed visually, or in the Raman spectra.

Figure 4 highlights the need for sample treatment, an untreated sediment sample and microplastics extracted from a sediment with the aid of the sample treatment protocol. An example of microplastics from one of the sediment samples is shown in Figure 5.

The recovery of microplastic particles in the sediment samples was considerably higher using ZnCl_2 than NaCl for the density separation step. This was expected since several plastic polymers have a density that is higher than the density of a saturated NaCl solution but lower than saturated ZnCl_2 (e.g. PVC and PET). However, using ZnCl_2 also resulted in a larger number of non-plastic particles floating up to the surface, making the analyses of the samples more difficult. It should

The pros and cons of using ZnCl_2 and NaCl for density separation of microplastics from sediments are summarized here.

ZnCl_2 :

- + Collects most plastic polymer types.
- May also collect other non-plastic particulate matter which makes the analyses more difficult.
- Relatively expensive, but it can be reused.
- Hazardous to humans and the environment which affects both work in the laboratory and the disposal of used solution.

NaCl :

- + Non-toxic and easy to handle.
- + Available to everyone, affordable.
- ± Collects polymers with a density $<1.2 \text{ g}\cdot\text{cm}^{-3}$, which includes many of the most common polymer types, e.g. PE and PP.
- Does not collect polymers with a density $>1.2 \text{ g}\cdot\text{cm}^{-3}$, which includes e.g. PVC and PET.

also be noted that NaCl is nontoxic and can be disposed of without any special precautions, whereas ZnCl_2 is classified as toxic to humans and hazardous to the aquatic environment, and all liquids and sediment need to be treated as chemical waste.

↓ Figure 4. A sediment sample prior to any pre-treatment.

↑ Figure 5. Litter particles, including microplastics, from sediment.

Monitoring microplastics

– the aim determines the means

Environmental agencies and researchers have expressed the need for standardized methods to monitor microplastics. Due to the multifaceted nature of microplastic pollution in terms of polymer types, sizes and shapes it is, however, reasonable to discuss how strict such a protocol should be. There are also geographical and regional differences in the characteristics of the matrices where the samples are collected. For example, the grain-size of the sediment affects how much fine material will float when the density separation is being carried out, and thus possibly also affects what chemicals should be used for pre-treatment. Likewise, the depth where water samples are being collected, or the sampling season can make a crucial difference in the amounts and types of organic material present in the samples—again affecting the selection of the most suitable methods. We would argue that there is room for flexibility in the design of the monitoring protocols, so that they are adapted to the specific study questions as long as the methods live up to a set standard of quality criteria.

The optimization of a monitoring protocol starts already in the selection of which matrix (water, sediment or biota) to analyse. Since it is not feasible to monitor all matrices everywhere, prioritization is needed. Here the purpose of the monitoring programme must be clearly stated, and the aims set. If the purpose of the monitoring is to detect long-term trends of microplastics in the marine environment, sediments might be the most suitable matrix since it is the sink where most particles will be sequestered. Although plastics can be transported far by surface water currents, most plastic will eventually accumulate in the sediment (Koelmans *et al.* 2017). Sinking of initially buoyant plastics has also been confirmed by field observations (Holmström, 1975) and field tests (Karlsson *et al.* 2018b). Since both particles of high and low density tend to end up in sediments, sediment sampling can also be used for studying the general composition of marine microplastics.

If the purpose of monitoring instead is to detect time trends of microplastic emissions from a point source, such as a wastewater treatment plant or an industry, sampling of the water surface or water column would ideally provide information on the single process or pathway. The water concentrations outside a discharge tube are a direct reflection of the microplastic concentration in the effluent water, whereas it may be very difficult to predict where on the sea floor the discharged plastic particles are likely to be deposited. It may, however, also be difficult to capture the actual release from a point source due to the hydrodynamics of the recipient, (Granberg *et al.* 2019, Magnusson *et al.* 2016, Railo *et al.* 2018).

To allow for spatial and temporal comparisons the sampling method within a monitoring program needs to be consistent since the comparability between sampling methods is limited. It is for example a great risk that the microplastics concentration in a water sample differs depending on whether it has been collected with a pump or a trawl, or if it was collected at the surface or deeper down in the water column. Similarly, microplastics concentrations in sediment samples collected from a defined part of the sediment, e.g. the upper centimetres, will differ from concentrations in samples that also include sediment from a greater depth. However, this does not mean that one specific sampling method is best suited for all monitoring programmes. Different management or research questions could benefit from different types of sampling methods. When analysing for example microplastics in water samples the high sampling volume accuracy of a pump might be preferable in one context whereas in another it might be more important to take advantage of the high-volume throughput of the trawl.

Concerning the extraction of microplastics from the collected samples it is less obvious that identical protocols must be

↑ Figure 6. Basic principle of the identification steps for the sediment samples. Handpicked anthropogenic particles, imaged in detail and identified with Raman spectroscopy.

followed. This applies as long as it can be verified that the selected method complies with a set standard of quality criteria. It might for example not be necessary to expose the samples to expensive and time-consuming procedures like incubation with chitinase if the samples do not contain any carapaces from zooplankton or other matter rich in chitin.

The requirements for sample quality and purity are higher when aiming to analyse smaller particles and are also determined by the analytical methods used for particle identification. If the analyses are done by combining visual identification by stereomicroscopy with spectroscopy (e.g. FTIR) from manually selected particles, a higher amount of natural particulate matter in the samples might be acceptable, whereas cleaner samples are an advantage when performing automated analyses with Raman or FTIR spectroscopy.

Since each method has its pros and cons, all particles in a sample should ideally be analysed both visually with stereomicroscopy and with e.g. FTIR or Raman spectroscopy (Figure 6). With FTIR/Raman spectroscopy the polymer composition of the particles can be identified, whereas visual inspection can discriminate plastics and other synthetic particles from other materials and, in combination with physical manipulation of the particles, will reveal the particle shape, colour and texture, something that is of great value

when trying to identify the particle source. However, although automated full sample identification with FTIR and Raman spectroscopy are techniques that are rapidly being developed, and techniques that most likely will be used for monitoring in the future, they are still not fully optimized and validated. At present they are also only available at a limited number of research laboratories.

The choice of analytical methods is also governed by the size of particles to be analysed. Visual identification with stereomicroscopy is possible for particles down to ~100 μm Lenz et al. (2015) but for smaller particles there is an increased risk of getting both false positive and false negative identifications. A definite size range for this cannot be set, as often is the case with microplastics, since the results depend on the quality of samples, equipment, reference libraries (in the case of spectroscopy) and personal commitment and experience. However, this is something that currently applies to all techniques used for microplastic analyses.

The abundance of microplastics, as for most other particles, increases exponentially with smaller sizes, and therefore all recent environmental risk assessment reports emphasize the role of detection of smaller microplastic sizes (SAPEA 2019). In order to do that more elaborate sampling schemes and methods for analysis are required, which for monitoring purposes may not yet be feasible or even necessary. Nevertheless, it should be recommended that, if possible, not only the abundance of microplastics, but also their size distributions, are reported. Preferably, particle concentrations should also be expressed as both number abundances and as mass concentrations.

The volume or mass of a water or sediment sample that is analysed will affect how representative it is for the sampling

area. The number of detected microplastic particles must be well above blank samples. On the other hand, if a sample contains too many particles it may also the analyses may also complicate the analysis.

Regardless of which matrices and methods are being used, it is crucial to minimize and estimate contamination by procedural blank controls covering the whole procedure, from sampling to analysis. It is also advised that each person doing the sample preparation does their own quality controls with recovery testing. It is important that the methods are described sufficiently detailed. For spectroscopic identifications this would for example include both the acquisition method and the methods that are used for spectral comparison. Furthermore, detailed sampling locations and prevailing environmental conditions, such as heavy rain fall, wind force, and direction of current should be reported since it may affect the environmental particle concentration.

Conclusion

Surveys on marine microplastics may be carried out for different reasons (e.g. observing time trends outside vs. away from point sources), on different matrices (e.g. sediment, seawater or marine biota) and with the aim to detect different types of particles (e.g. heavy vs. light density plastic polymers). The combination of different requirements for different habitats is complex, and it may therefore be better to create a flexible setup, with tailored solutions suitable for specific matrices and aims. Certain aspects related to reporting and quality assessments and reporting do, however, need to be standardized in order to ensure a basic level of comparability.

Quality assurance procedures should be incorporated as established monitoring protocols for sampling and analytical parameters and the reporting of assessment criteria. These

should include both internal procedures for blanks (incl. field blanks), recoveries of reference particles in different size fractions and external QA procedures like laboratory intercalibration frameworks and analyses of certified reference materials. We recommend that standardized international QA/QC guidelines with a comprehensive reporting format are created. Coordinated arrangements for data submission and management, preferably in international databases that can host and secure the data on applied methods and measured variables must also take place. However, the external procedures are not yet fully developed for microplastic analyses.

Useful remarks when selecting a protocol for microplastic monitoring

- Based on the present guidance on monitoring European marine waters to assess the state of the sea, microplastics monitoring should be carried out in different matrices and preferably in a way that enables the detection of sources. According to the MSFD criteria environmental sampling must include both water and sediment, and it is also advisable to include coastline sampling.
- Monitoring should also enable the identification of artificial polymer particles from other litter materials. However, some sample treatment methods may harm certain materials.
- The analytical method defines the quality requirements (in terms of purity) of the sample.
- For closer examination of microplastics and for the characterization of sample material composition advanced spectroscopy should be applied (FTIR, Raman). This is increasingly critical for sizes below 100-300µm.
- Sometimes it can be acceptable to use a less expensive, quicker but maybe not as efficient method. However, the

chosen method must fulfil the proposed set of quality criteria.

- Point sources discharging to water bodies should be monitored directly at the discharge point and/or at a location in the recipient where particles are likely to aggregate or settle. This can be estimated, e.g. by hydrodynamic modelling.
- When aiming to detect long-term trends and compositions of a wide variety of microplastics in the marine environment, analyses of sediments is likely to give more relevant information than that of water. It is, however, important that the sediment samples are collected where microparticles are likely to accumulate.

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Monitoring of microplastics in the marine environment

– Changing directions towards quality controlled tailored solutions

The need for harmonized monitoring protocols for marine microplastic has been discussed for many years, but how to reach this goal has not been agreed upon. Important questions addressed when microplastics are monitored are: how to carry out field sampling, how to eliminate other particulate matter from a sample without harming the microplastics, and how to accurately identify the particles, while also preventing and assessing potential sample contamination at each step from sampling to analyses. In the project HARMIC, Nordic scientist with long term experience in microplastic research, applied and evaluated different methods for sampling and sample preparation relevant for the establishment of common guidelines. The outcomes of the studies are discussed from a monitoring perspective, including aspects of quality assurance and quality control.