NET4MPLASTIC PROJECT

Activity 3.1

D 3.1.1 c

LITERATURE REVIEW ON MONITORING: NANOPLASTIC

May, 30, 2019 - Version 1.0

.

CONTRIBUTING PARTNERS	UNITS

INDEX

1 Introduction

The definition of nanoplastic (nP) is not comprised in the recommendation of Arthur et al.(2009) nor in the Guidance on Monitoring of Marine Litter in European Seas of the EU Marine Strategy Framework Directive (MSFD, 2013). However, the microplastics (mPs) may be subject to degradation, leading to a size well below 5mm. Concern about how very small plastics can affect marine environments is growing. When can we talk about nP?

2 Summary of Findings

As reported in the review of Rios Mendoza et al.(2018), definition size of nP is varying during the time, ranging from <20μm (Wagner et al. 2014) to <1μm (da Costa, Santos, Duarte, & Rocha-Santos, 2016). Gigault et al.(2018) defined nanoplastics *as particles unintentionally produced (i.e. from the degradation and the manufacturing of the plastic objects) and presenting a colloidal behavior, within the size range from 1 to 1000 nm.*

Recently Hartmann et al. (2019) resumed the definition that nP can be all the plastic fragments with dimension from 1 to 1000nm (that is under 1μm), with an additional subdivision in nanoplastic from 1 to 100nm and submicron-plastic from 100 to 1000nm.

The "production" of nPs can have more than one source; they can derive from the degradation of mP due to environmental conditions (weathering) (water, pH, UV, rubbing, biota activity), but may also be present as, for example in personal care products (toothpaste and cosmetic product) (Strungaru et al., 2019; Hernandez et al., 2017), or as nanofiller in composites that, as macro and mP can be degraded with release of nP. Concern is pointed also on the nP deriving from waterwaste treatment (WWT) (Rios Mendoza et al., 2018).

As reported in various papers (Alimi et al., 2018; Gillibert et al., 2019; Rios Mendoza et al., 2018; Bergami et al., 2017; Mattsson, Hansson, & Cedervall, 2015; Bergmann, Gutow, & Klages, 2015) *the amount of nanoplastics spread in the oceans is currently unexplored, since conventional sampling methods (i.e. neuston nets having mesh size> 300 μm) as well as analytical techniques available for the identification of plastic polymers still prevent the isolation and quantification of the nano-fraction.*

Therefore, the main problems are related to the sampling methodology and pre-treatment methods both in water and in soil, although for soil it might be less concern. For example, the study of Hernandez (2017), focused on extraction of nanoparticle from a facial scrub, gives a hypothesis of solution using a sequential filtration as reported in fig.1 of Hernandez et al., (2017).

The literature concerning nP is focused on the extraction from biota samples (Galloway et al., 2017; Chae & An, 2017; Chen et al., 2017; van Weert et al., 2019; Okubo et al., 2018; Wu et al., 2019; Triebskorn et al., 2019), or on laboratory job (Lambert & Wagner, 2016; Chen et al., 2017; Okubo et al., 2018; Vered et al., 2019; Woods et al., 2018), using commercial nanoplastic/ fibres/ facewash or chemicals (like phthalates as plastic additives). Few studies on nP from natural environment (i.e. Ter Halle et al., 2016, Ter Halle et al., 2017).

In review of Schwaferts et al., (2019) there is an attempt to give a guide for sample preparation for nP detection and analysis. The first item is to avoid external contamination (no plastic objet use, no synthetic clothing wear, …); in many cases it will be necessary to remove the organic matrix (tissue, natural organic matter), taking into account that nP is considered as a colloid, this part can be very serious. It is very important to find a sufficiently mild protocol that does not alter the plastic particles and stabilizes them against aggregation (there are no suggestions for this item).

Regardless of the macro- and mP quantity in environment, that of nano dimension is probably very low, so a preconcentration must be done. Some suggestions are:

- Membrane filtration (filters of ceramics or polycarbonate)
- Ultrafiltration using nano-porous membrane
- Centrifugation and ultracentrifugation from suspensions
- Evaporation of solvent at reduced pressure (rotary evaporator)

The following item is the separation, also in this case some suggestions are reported:

- Field flow fractionation, with various separating fields: thermal, electric, gravity (or centrifugal), cross-flow
- Chromatography (HPLC, SEC and HDC)
- Electrophoresis on capillary

Schwaferts et al., (2019) reviewed which techniques from nanomaterial analysis may potentially be adapted to close the methodological gap for analysis of nP, as reported in fig.1. In fig. 2 of Schwaferts et al., (2019) there is a summary of the different techniques discussed in the review, with the particle size range for which they are adapted. In fig.3 a scheme of a protocol attempt is also reported.
More papers are found regarding the analytical techniques for characterization the nPs.
As stated by Renner et al., (2018), the smaller microplastics are, the more demanding analysis will be. This means that in case of nanoparticles (size<1μm), traditional spectroscopic measurements or comparable alternatives are unavoidable.
There exist some approaches for nanoparticles (metal or ceramic) that can be transferred; however, it is not enough to analyse the morphological properties of nanoparticles without their chemical characterization, i.e. without being able to differentiate them from natural non-plastic nanoparticles.

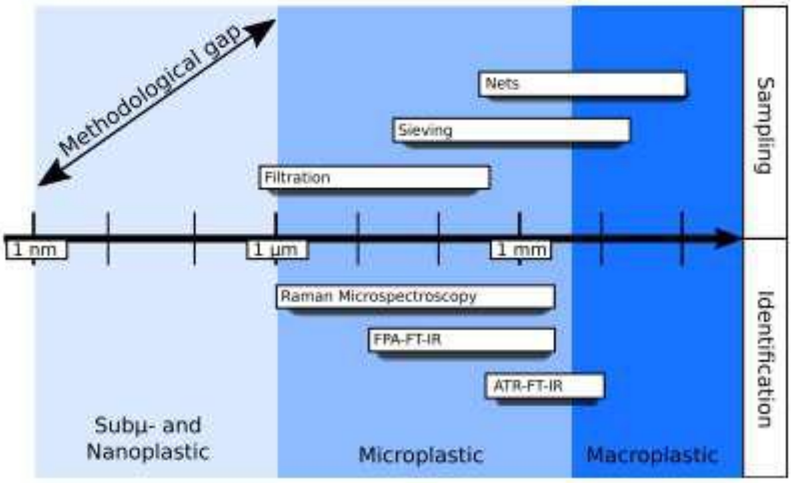

Fig. 1: The analysis of MP is established for particles down to 1 μm. (Schwaferts et al., 2019- fig.1)

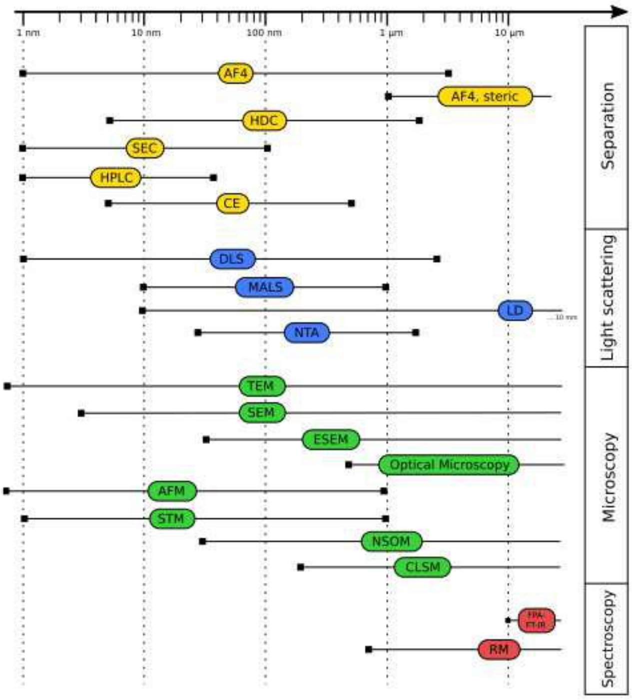

Fig. 2: Comparison of the particle size ranges for analysis with the different techniques (Schwaferts et al., 2019- fig.2)

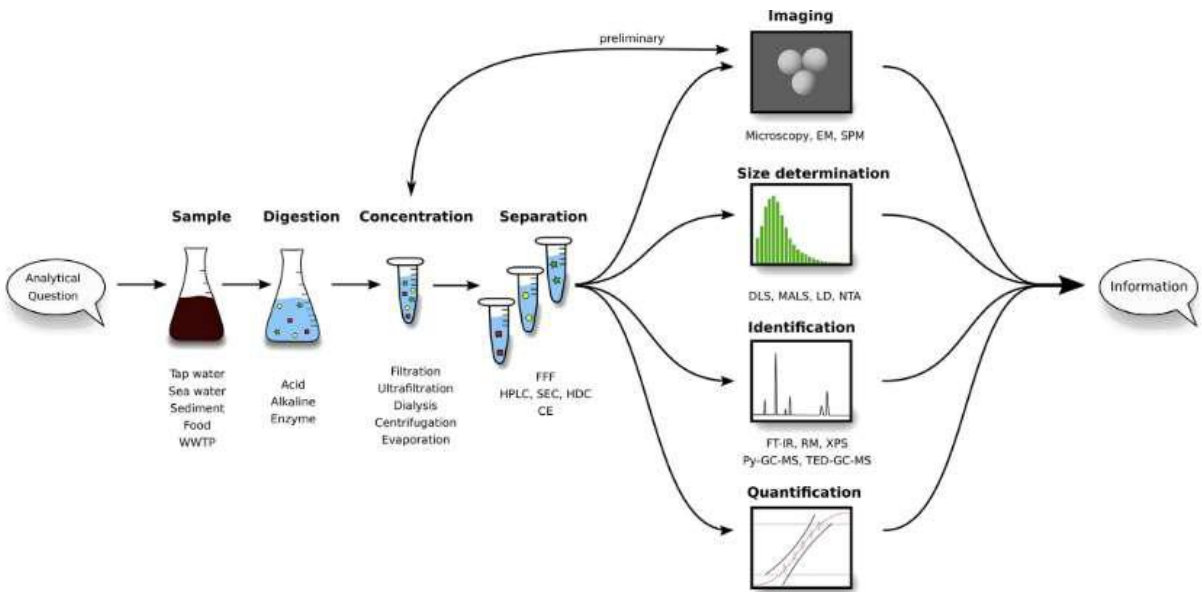

Fig. 3: Roadmap for the analytical process of subm- and nanoplastic particles. Starting from the sample in its matrix, we present and discuss the single steps that will lead to a full subm- and nanoplastic analysis (Schwaferts et al., 2019- fig.3).

In any case, going down 1μm all the analytical methods require specific expensive equipments.
The review of Shrivastava et al., (2019) is exhaustive about the techniques for the monitoring of nanoparticles in soil system. This kind of technologies can obviously be pertinent for nP too.
Gillibert et al., (2019) propose the use of optical tweezers in combination with Raman spectroscopy (RTs) that is capable to trap and manipulate micro and nanoparticles dispersed in liquid and their chemical analysis.
Galloway et al., (2017) used both Stimulated Raman Scattering (SRS) and Coherent anti-Stokes Raman Scattering (CARS) for studying the effects of nanoparticle-containing acrylic copolymer (ACP) dispersions (mean nanoparticle sizes: 80 nm and 110 nm) in aquatic invertebrates (Thamnocephalus platyurus; fairy shrimp) and Danio rerio zebrafish embryos after aquatic exposures.
Kim et al., (2019) evaluate nanoparticle tracking analysis (NTA) results with respect to the size estimation methods.
In the following paragraph a list of the main analysed papers are reported together with a brief synthesis.

3 Annotated Bibliography

Alimi, O. S., Farner Budarz, J., Hernandez, L. M., & Tufenkji, N. (2018). Microplastics and Nanoplastics in Aquatic Environments: Aggregation, Deposition, and Enhanced Contaminant Transport. Environmental Science and Technology, 52(4), 1704–1724. https://doi.org/10.1021/acs.est.7b05559

Synthesis

There is no clear consensus on the definition of MP and NP size in the literature; in this review, MPs and NPs are defined as plastic debris with diameters of 100 nm-5 mm and <100 nm, respectively.

At the nanoscale (particles smaller than 100 nm in size), plastics are difficult to be detect and can be transported in air, soil and water compartments. In this review, is first presented estimated loads of plastics in different environmental compartments. A critical review of the current knowledge vis-à-vis nanoplastic (NP) and microplastic (MP) aggregation, deposition, and contaminant co-transport in the environment is also given.

Important factors that affect aggregation and deposition in natural subsurface environments are identified and critically analyzed. Factors affecting contaminant sorption onto plastic debris are discussed. It is shown how polyethylene generally exhibits a greater sorption capacity than other plastic types. Finally, it is highlighted key knowledge gaps that need to be addressed to improve our ability to predict the risks associated with these ubiquitous contaminants in the environment by understanding their mobility, aggregation behaviour and their potential to enhance the transport of other pollutants.

Arthur, C., Baker, J., Bamford, H., & (eds). (2009). Proceedings of the international research workshop on the occurrence, effects and fate of microplastic marine debris, Sep 9-11, 2008. NOAA. Technical Memorandum NOS-OR&R-30. NOAA, Silver Spring 530pp. (January).

Synthesis

Workshop sessions were organized to focus on four main research topics: (1) the occurrence of small plastic debris in the marine environment, (2) the impacts of small plastic debris on the marine environment, (3) the impacts of small plastic debris exposure to persistent organic pollutants, and (4) the effect of oceanic microplastics on biogeochemical cycling of persistent organic pollutants.

One final session included three breakout groups: sources and sinks of plastics in the marine environment, effects of microplastic debris on marine organisms, and the role of microplastics in POP cycling and exposure.

Bergami, E., Pugnalini, S., Vannuccini, M. L., Manfra, L., Faleri, C., Savorelli, F., … Corsi, I. (2017). Long-term toxicity of surface-charged polystyrene nanoplastics to marine planktonic species Dunaliella tertiolecta and Artemia franciscana. Aquatic Toxicology, 189(June), 159–169. https://doi.org/10.1016/j.aquatox.2017.06.008

Synthesis

Plastic pollution has been globally recognized as a critical issue for marine ecosystems and nanoplastics constitute one of the last unexplored areas to understand the magnitude of this threat. However, current difficulties in sampling and identifying nano-sized debris make hard to assess their occurrence in marine environment. This study aims at evaluating the effects of 40 nm PS anionic carboxylated (PS-COOH) and 50 nm cationic amino-modified (PS-NH2) NPs in two planktonic species, the green microalga Dunaliella tertiolecta and the brine shrimp Artemia franciscana, respectively prey and predator.

Bergmann, M., Gutow, L., & Klages, M. (Eds.). (2015). Marine Anthropogenic Litter. Springer Open - ISBN 978-3-319-16509-7 ISBN 978-3-319-16510-3 (eBook). https://doi.org/10.1007/978-3-319-16510-3

Synthesis

This book consists of five major sections. In the first section, Peter Ryan gives a historical synopsis of marine litter research. The second section of the book addresses abiotic aspects of marine litter pollution and the third one covers the biological and ecological implications of marine litter.

The fourth section of this book is dedicated entirely to the young but rapidly expanding field of microplastic research. Because of the small size and the diversity of plastic polymers, the detection, proper identification and quantification of microplastics are challenging, which hampers the comparability of results from different studies. Therefore, Martin G.J. Löder and Gunnar Gerdts composed a critical appraisal of methods and procedures applied in this field including a case study that demonstrates how improper methodology easily leads to a misevaluation of the contamination of habitats and organisms. Nanoparticles, even smaller particle size (<1 µm), are of particular concern as they are more likely to pass biological membranes and affect the functioning of cells including blood cells and photosynthesis. Albert A. Koelmans, Ellen Besseling and Won J. Shim summarize what little is known about this litter fraction, whose significance in the marine environment is just coming to light.

The final section of this book moves away from natural science towards the socio-economic implications of marine anthropogenic litter.

Chae, Y., & An, Y. J. (2017). Effects of micro- and nanoplastics on aquatic ecosystems: Current research trends and perspectives. Marine Pollution Bulletin, 124(2), 624–632. https://doi.org/10.1016/j.marpolbul.2017.01.070

Synthesis

This review covers 83 studies that investigated the distribution of microplastics and the ecotoxicity of micro- and nanoplastics in marine and freshwater ecosystems. The studies indicated that micro-sized plastics and plastic debris were distributed at various concentrations in aquatic ecosystems around the world. They had various effects on the growth, development, behavior, reproduction, and mortality of aquatic animals.

Chen, Q., Gundlach, M., Yang, S., Jiang, J., Velki, M., Yin, D., & Hollert, H. (2017). Quantitative investigation of the mechanisms of microplastics and nanoplastics toward zebrafish larvae locomotor

activity. Science of the Total Environment, 584–585, 1022–1031. https://doi.org/10.1016/j.scitotenv.2017.01.156

Synthesis

This study investigated the direct and indirect toxic effects of microplastics and nanoplastics toward zebrafish (Danio rerio) larvae locomotor activity.

da Costa, J. P., Santos, P. S. M., Duarte, A. C., & Rocha-Santos, T. (2016). (Nano)plastics in the environment - Sources, fates and effects. Science of the Total Environment, 566–567, 15–26. https://doi.org/10.1016/j.scitotenv.2016.05.041

Synthesis

In this review, the Authors describe the most relevant sources of nanoplastics and offer some insights into their fate once released into the environment. Furthermore, they overview the most prominent effects of these small particulates, while identifying the key challenges scientists currently face in the research of nanoplastics in the environment. Lastly, it is given a brief summary of the economic impacts of the pollution caused by plastic litter – a potential key source of nanoplastics – in the oceans, the most common destination of these contaminants.

Galloway, T. S., Dogra, Y., Garrett, N., Rowe, D., Tyler, C. R., Moger, J., … Wiench, K. (2017). Ecotoxicological assessment of nanoparticle-containing acrylic copolymer dispersions in fairy shrimp and zebrafish embryos. Environmental Science: Nano, 4(10), 1981–1997. https://doi.org/10.1039/c7en00385d

Synthesis

Nanoparticle-containing polymer dispersions are widely used, but little is known of their environmental effects. This paper studied the bioavailability, uptake, tissue localization and effects of nanoparticle-containing acrylic copolymer (ACP) dispersions (mean nanoparticle sizes: 80 nm and 110 nm) in aquatic invertebrates after aquatic exposures. Aqueous and dietary exposures resulted in no ecotoxicological effects in fairy shrimp or zebrafish.

Gigault, J., Halle, A. ter, Baudrimont, M., Pascal, P. Y., Gauffre, F., Phi, T. L., … Reynaud, S. (2018). Current opinion: What is a nanoplastic? Environmental Pollution, 235, 1030–1034. https://doi.org/10.1016/j.envpol.2018.01.024

Synthesis

The term “nanoplastics” is still under debate, and different studies have set the upper size limit at either 1000 nm or 100 nm. The aim of the present work is to propose a definition of nanoplastics, based on recently published and unpublished research definition of nanoplastics. The authors define nanoplastics as particles unintentionally produced (i.e. from the degradation and the manufacturing of the plastic objects) and presenting a colloidal behavior, within the size range from 1 to 1000 nm.

Gillibert, R., Balakrishnan, G., Deshoules, Q., Tardivel, M., Magazzù, A., Donato, M. G., … Gucciardi, P. G. (2019). Raman Tweezers as a Tool for Small Microplastics and Nanoplastics Identification in Sea Water. Preprints, (January), 1–49. https://doi.org/10.20944/preprints201901.0227.v1

Synthesis

In this paper, the authors propose the use of optical tweezers, as an analytical tool for the study of micro- and nano- plastics in sea water. In particular, they exploit the combination of optical tweezers with Raman spectroscopy (Raman Tweezers, RTs) to optically trap plastic particles with sizes from tens of µm down to 90nm and unambiguously reveal their chemical composition.

Results are shown on commercial and artificially fragmented/aged micro- and nanoplastics (90nm – 10 µm diameter) made of PP, PS, PE, Nylon, PVC. Optical tweezers (OT) are a tool capable to trap and manipulate micro and nanoparticles dispersed in liquid, by exploiting the tiny forces that light exerts on matter. The so-called Raman Tweezers (RT) have found applications in several fields including cells sorting, virology, nanomaterials analysis.

Hartmann, N. B., Hüffer, T., Thompson, R. C., Hassellöv, M., Verschoor, A., Daugaard, A. E., … Wagner, M. (2019). Are We Speaking the Same Language? Recommendations for a Definition and Categorization Framework for Plastic Debris. Environmental Science and Technology, 53(3), 1039–1047. https://doi.org/10.1021/acs.est.8b05297

Synthesis

This review critically discus the advantages and disadvantages of a unified terminology for “plastic debris”, propose a definition and categorization framework, and highlight areas of uncertainty. Going beyond size classes, the reported framework includes physicochemical properties (polymer composition, solid state, solubility) as defining criteria and size, shape, color, and origin as classifiers for categorization.

Hernandez, L. M., Yousefi, N., & Tufenkji, N. (2017). Are there nanoplastics in your personal care products? Environmental Science and Technology Letters, 4(7), 280–285. https://doi.org/10.1021/acs.estlett.7b00187

Synthesis

Several studies have reported on the occurrence and toxicity of microplastics in soils and waters; however, because of methodological challenges, the presence and impact of nanoplastics (<100 nm) in natural systems have been largely ignored. Microbeads used in consumer products such as scrubs and shampoos are processed by mechanical means that may lead to their fragmentation into potentially more hazardous nanoplastics. In this study, three commercial facial scrubs containing polyethylene microbeads (∼0.2 mm diameter) were examined to verify whether they contained nanoplastics. Particulates in the scrubs were fractionated using sequential filtration to isolate <100 nm particles. Scanning electron microscopy was used to confirm the presence of nanoparticles ranging in size from 24 ± 6 to 52 ± 14 nm. X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy were used to confirm that the identified nanoparticles consisted of polyethylene. This study confirms the presence of nanoplastics in personal care products containing polyethylene microbeads and highlights the need for further studies to characterize the release and distribution of nanoplastic litter in natural aquatic and soil environments.

Kim, A., Beng Ng, W., Bernt, W., Cho, N. Validation of Size Estimation of Nanoparticle Tracking Analysis on Polydisperse Macromolecule Assembly. Nature, Scientific Reports 9, Article number: 2639 (2019)
Synthesis
This study aimed to evaluate nanoparticle tracking analysis (NTA) results with respect to the size estimation methods for NTA. First, monodisperse reference standards of known size values were measured using NTA and compared with dynamic light scattering (DLS). The size analysis of acquired particle tracks of NTA was processed by direct conversion of the tracks and with the two maximum likelihood estimation (MLE)-based methods, namely finite track length adjustment (FTLA) and the iterative method. The comparison confirmed that both of the two MLE-based methods can recover a narrow size distribution of the monodisperse reference standards. The estimation methods were also applied to estimate the size distribution of polydisperse vesicle samples prepared in various polydispersity conditions to verify if FTLA and the iterative method are applicable for polydisperse samples of unknown size distribution. While the iterative method achieved results comparable with DLS, the results from FTLA deviated from those of DLS as it assumes an arbitrary size distribution that may not be appropriate for polydisperse samples. In addition, the size distribution of NTA acquired with the estimation methods was converted into an intensity-weighted size distribution from its number-weighted distribution to investigate if the conversion gives a better comparison with the DLS results.

Lambert, S., & Wagner, M. (2016). Formation of microscopic particles during the degradation of different polymers. Chemosphere, 161, 510–517. https://doi.org/10.1016/j.chemosphere.2016.07.042
Synthesis
This study investigated the formation and size distribution of microscopic plastic particles during the degradation of different plastic materials. Particle number concentrations in the size range 30nm-60nm were measured by nanoparticle tracking analysis (NTA) and Coulter Counter techniques. Each of the plastics used exhibited a measureable increase in the release of particles into the surrounding solution, with polystyrene (PS) and polylactic acid (PLA) generating the highest particle concentrations.
Particle size distribution models were used to examine more closely the size distribution data generated by NTA. Overall, the results indicate that at the beginning of plastic weathering processes chain scission at the polymer surface causes many very small particles to be released into the surrounding solution and those concentrations may vary between plastic types.

Mattsson, K., Hansson, L. A., & Cedervall, T. (2015). Nano-plastics in the aquatic environment. Environmental Sciences: Processes and Impacts, 17(10), 1712–1721. https://doi.org/10.1039/c5em00227c
Synthesis

This Review describes the possible sources of nano-sized plastic, its distribution and behavior in nature, the impact of nano-sized plastic on the well- being of aquatic organisms, and the difference of impact between nano- and micro-sized particles. Micro-sized plastics degrade subsequently into nano-sizes whereas nano-sized particles may be released directly into nature. Such particles have a different impact on aquatic organisms than larger pieces of plastic due to their small size, high surface curvature, and large surface area. The amount of nano-sized plastic particles in the aquatic environment is not known since most analytical techniques exclude these small particles.

MSFD Technical Subgroup on Marine Litter (2013). Guidance on Monitoring of Marine Litter in European Seas, European Commission Joint Research Centre Institute for Environment and Sustainability.

<u>Synthesis</u>

This document is the Final Report "Guidance on Monitoring of Marine Litter in European Seas", the output of the work of the TSG-ML between 2012 and 2013. The objective of such Guidance is to provide MS with recommendations and information needed to commence the monitoring of the MSFD Descriptor 10. It describes specific protocols and considerations to collect, report and assess data on marine litter, in particular beach litter, floating litter, seafloor litter, litter in biota and microlitter.

Okubo, N., Takahashi, S., & Nakano, Y. (2018). Microplastics disturb the anthozoan-algae symbiotic relationship. Marine Pollution Bulletin, 135(May), 83–89. https://doi.org/10.1016/j.marpolbul.2018.07.016

<u>Synthesis</u>

In the present study, the authors examined the effects of microspheres and microplastics in commercial facewash, on the initiation of the symbiotic relationship in anthozoan-algae symbiosis. The results demonstrated that these microparticles significantly suppress it, suggesting that increase in microplastics in coral reefs threatens the cornerstone of coral reef ecosystems through disturbing the coral-Symbiodinium symbiosis.

Renner, G., Schmidt, T. C., & Schram, J. (2018). Analytical methodologies for monitoring micro(nano)plastics: Which are fit for purpose? Current Opinion in Environmental Science & Health, 1, 55–61. https://doi.org/10.1016/j.coesh.2017.11.001

<u>Synthesis</u>

In this review the authors have worked through more than 170 peer reviewed research papers that were published between 2015 and 2017 and deal with microplastics analysis to figure out, how identification of microplastics is currently performed. That is: Which method can be used to analyse a certain type of microplastics and what kind of information can be obtained by its using?

All researchers can agree with: a practical identification method for microplastics is always connected to their dimensions, the smaller microplastics are, the more demanding analysis will be. This means that in case of real microparticles, spectroscopic measurements or comparable alternatives are unavoidable.

Rios Mendoza, L. M., Karapanagioti, H., & Álvarez, N. R. (2018). Micro(nanoplastics) in the marine environment: Current knowledge and gaps. Current Opinion in Environmental Science & Health, 1, 47–51. https://doi.org/10.1016/j.coesh.2017.11.004.

<u>Synthesis</u>

There are several sources of Micro (nanoplastics) such as micro and nanoparticle production or fragmentation off bigger plastics. Nanoplastics can have a bigger capacity to concentrate toxic compounds either associated with its production or sorbed from the environment has not been extensively evaluated. Indications suggest that nanoplastics carry more toxics than microplatics (more than million times than seawater). These nanoplastics can also carry microorganisms. There is no harmonization of methodologies for sampling and analysis of micro(nanoplastics) and there are limits in the accuracy of sizes of these particles that can be detected. Calculation of their possible concentrations in the environment is biased by the analytical instrumentation.

This paper summarizes the knowledge gaps in the analysis and repercussions of micro(nanoplastics) in the analysis and repercussions of micro(nanoplastics) in the environment and organisms.

Schwaferts, C., Niessner, R., Elsner, M., & Ivleva, N. P. (2019). Methods for the analysis of submicrometer- and nanoplastic particles in the environment. TrAC - Trends in Analytical Chemistry, 112, 52–65. https://doi.org/10.1016/j.trac.2018.12.014

<u>Synthesis</u>

The analytical methods for microplastic have a particle size limit of a few micrometers so that new methods have to be developed to cover the nanometer range. This contribution reviews the progress in environmental nanoplastic analysis and critically evaluates which techniques from nanomaterial analysis may potentially be adapted to close the methodological gap. Following the sampling and sample treatment, there is the determination of the mP particle size and number e alternatively, the mass content e and the identification of the polymer. To that end, there are (i) techniques that combine microscopic and spectroscopic analysis and (ii) thermoanalytical methods. In spectroscopy, mP can be measured on a particle by particle basis with attenuated total reflection Fourier transform-infrared spectroscopy (ATR-FT-IR), where mP particles (usually larger than 500 μm) are handpicked. Smaller particles are collected on filters and identified with focal plane array micro-FT-IR (FPA-FT-IR) or Raman microspectroscopy (RM) with particle sizes down to 10 μm and 1 μm, respectively. Thermoanalytical MP detection, on the other hand, provides polymer and additive characterization and quantifies by mass content of MP in a sample. Its limits of detection (LODs) depend on the polymer type and are in the range of nanograms to micrograms

Shrivastava, M., Srivastav, A., Gandhi, S., Rao, S., Roychoudhury, A., Kumar, A., … Singh, S. D. (2019). Monitoring of engineered nanoparticles in soil-plant system: A review. Environmental Nanotechnology,

Monitoring and Management, 11(November 2018), 100218. https://doi.org/10.1016/j.enmm.2019.100218

Synthesis

Soil and water are the ultimate natural sink for the engineered nanoparticles (ENPs). The size and shape of the ENPs ultimately determine the degree of toxicology. Therefore, monitoring of nanoparticles in soil plant system is not merely essential, but more information is needed on their size allocation and physical properties. Various techniques have been found to be pertinent for ENPs characterization in toxicological and ecotoxicological studies.

In this review, the authors have highlighted existing as well as promising developments in the area of ENPs detection and quantifications in soil-plant system.

Strungaru, S. A., Jijie, R., Nicoara, M., Plavan, G., & Faggio, C. (2019). Micro- (nano) plastics in freshwater ecosystems: Abundance, toxicological impact and quantification methodology. TrAC - Trends in Analytical Chemistry, 110, 116–128. https://doi.org/10.1016/j.trac.2018.10.025

Synthesis

This review outlines the recent advances made on examination of the potential toxicological effects of MP and NP on freshwater biota, as well as the available analytical methods employed to identify and quantify them in environmental samples. The authors pointed out that the majority of the studies conducted on model organisms in laboratory conditions used PE and PS micro- (nano) spheres previously characterized at high concentrations after short-exposure, purchased from different companies.

Ter Halle, A., Jeanneau, L., Martignac, M., Jardé, E., Pedrono, B., Brach, L., & Gigault, J. (2017). Nanoplastic in the North Atlantic Subtropical Gyre. Environmental Science and Technology, 51(23), 13689–13697. https://doi.org/10.1021/acs.est.7b03667

Synthesis

The presence of small plastic particles at the micro- and nanoscales is of growing concern, but nanoplastic has not yet been observed in natural samples. In this study, there are examined four size fractions (meso-, large micro-, small micro-, and nanoplastics) of debris collected in the North Atlantic subtropical gyre. To obtain the nanoplastic portion, the colloidal fraction of seawater was isolated. After ultrafiltration, the occurrence of nanoscale particles was demonstrated using dynamic light scattering experiments. The chemical fingerprint of the colloids was obtained by pyrolysis coupled with gas chromatography−mass spectrometry. The authors demonstrated that the signal was anthropogenic and attributed to a combination of plastics. The polymer composition varied among the size classes. At the micro- and nanoscales, polyvinyl chloride, polyethylene terephthalate, polystyrene and polyethylene were observed. There was also observed changes in the pyrolytic signals of polyethylene with decreasing debris size, which could be related to the structural modification of this plastic as a consequence of weathering.

Ter Halle, A., Ladirat, L., Gendre, X., Goudouneche, D., Pusineri, C., Routaboul, C., … Perez, E. (2016). Understanding the Fragmentation Pattern of Marine Plastic Debris. Environmental Science and Technology, 50(11), 5668–5675. https://doi.org/10.1021/acs.est.6b00594

Synthesis

The global estimation of microplastic afloat in the ocean is only approximately 1% of annual global plastic inputs. This reflects fundamental knowledge gaps in the transformation, fragmentation, and fates of microplastics in the ocean. In order to better understand microplastic fragmentation this paper proceeded to a thorough physicochemical characterization of samples collected from the North Atlantic subtropical gyre during the sea campaign Expedition seventh Continent in May 2014. (See article n.4)

The results were confronted with a mathematical approach. The introduction of mass distribution in opposition to the size distribution commonly proposed in this area clarify the fragmentation pattern. The mathematical analysis of the mass distribution points out a lack of debris with mass lighter than 1 mg. Characterization by means of microscopy, microtomography, and infrared microscopy gives a better understanding of the behavior of microplastic at sea. Flat pieces of debris (2 to 5 mm in length) typically have one face that is more photodegraded (due to exposure to the sun) and the other with more biofilm, suggesting that they float in a preferred orientation. Smaller debris, with a cubic shape (below 2 mm), seems to roll at sea. All faces are evenly photodegraded and they are less colonized. The breakpoint in the mathematical model and the experimental observation around 2 mm leads to the conclusion that there is a discontinuity in the rate of fragmentation: it is hypothesized that the smaller microplastics, the cubic ones mostly, are fragmented much faster than the parallelepipeds.

Triebskorn, R., Braunbeck, T., Grummt, T., Hanslik, L., Huppertsberg, S., Jekel, M., … Köhler, H. R. (2019). Relevance of nano- and microplastics for freshwater ecosystems: A critical review. TrAC - Trends in Analytical Chemistry, 110, 375–392. https://doi.org/10.1016/j.trac.2018.11.023

Synthesis

The paper critically reviews the state-of-the-science on (1) microplastics (MP) types and particle concentrations in freshwater ecosystems, (2) MP and nanoplastics (NP) uptake and tissue translocation, (3) MP/NP-induced effects in freshwater organisms, and (4) capabilities of MP/NP to modulate the toxicity of environmental chemicals. Although there is a considerable number of toxicity studies, a conclusive assessment of the risk posed by NP and MP for aquatic organisms is hardly possible up to now. This is due to the fact that, for larger particles, most MP concentrations tested were orders of magnitude higher than environmental concentrations, thus only allowing conclusions on potential hazard. In addition, for smaller MP and NP, environmental exposure data are still scarce due to still existing restrictions of analytical methods.

van Weert, S., Redondo-Hasselerharm, P. E., Diepens, N. J., & Koelmans, A. A. (2019). Effects of nanoplastics and microplastics on the growth of sediment-rooted macrophytes. Science of the Total Environment, 654, 1040–1047. https://doi.org/10.1016/j.scitotenv.2018.11.183

Synthesis

The authors provide an experimental study exploring nano- and microplastic effects on the growth of sediment-rooted macrophytes. Myriophyllum spicatum and Elodea sp. were exposed to sediments amended with six doses of polystyrene (PS) nanoplastic (50–190 nm, up to 3% sediment dry weight) and PS microplastic (20–500 µm, up to 10% dry weight) under laboratory conditions.
The study did not aim for the elucidation of the exact mechanistic processes that cause the effects, however, particle size seems to play an important factor.

Vered, G., Kaplan, A., Avisar, D., & Shenkar, N. (2019). Using solitary ascidians to assess microplastic and phthalate plasticizers pollution among marine biota: A case study of the Eastern Mediterranean and Red Sea. Marine Pollution Bulletin, 138(October 2018), 618–625. https://doi.org/10.1016/j.marpolbul.2018.12.013

Synthesis

For understanding the significant effect that MP and its additives may have on marine environments, the authors examined the levels of phthalate acid esters (PAEs) and MP in Herdmania momus and Microcosmus exasperatus sampled along the Mediterranean and Red Sea coasts of Israel. High levels of dibutyl phthalate (DBP) and bis (2-ethylhexyl) phthalate (DEHP) were found in ascidians at the majority of sampling sites, and MP particles were found in ascidians at all sites. As efficient filter-feeders and being widely-distributed, invasive ascidians present fundamental opportunities for the environmental monitoring of microplastic and its additives worldwide. The high levels of pollutants revealed emphasize the need for further research into the magnitude and effects of MP and PAEs in these regions.

Woods, M. N., Stack, M. E., Fields, D. M., Shaw, S. D., & Matrai, P. A. (2018). Microplastic fiber uptake, ingestion, and egestion rates in the blue mussel (Mytilus edulis). Marine Pollution Bulletin, 137(November), 638–645. https://doi.org/10.1016/j.marpolbul.2018.10.061

Synthesis

In this study, the authors investigate the ingestion rate and fate of MPF taken up by the blue mussel (Mytilus edulis) from Gulf of Maine coastal waters. They used microplastic fibers (MPF) concentrations ranging from 3 to 30 particles mL−1 to mimic natural concentrations and allow quantitative MPF detection. In addition, we present a new method to measure low concentrations of MPF in the water column, by using a FlowCam fluid imaging flow cytometer (FIT Maine, USA).
MPF were obtained by carefully shaving fibers from a newly purchased neon pink polyethylene terephthalate (PET) fleece with sharp stainless steel scissors.

Wu, J., Jiang, R., Lin, W., & Ouyang, G. (2019). Effect of salinity and humic acid on the aggregation and toxicity of polystyrene nanoplastics with different functional groups and charges. Environmental Pollution, 245, 836–843. https://doi.org/10.1016/j.envpol.2018.11.055

Synthesis

This work investigates the impact of different functional groups on the aggregation behaviour and toxicity influenced by high salinity and humic acid (HA). Four nanoplastics with different functional groups, the polystyrene nanoplastics (PS), carboxyl-modified (PS-COOH) and oppositely charged amino-modified nanoplastics (n-PS-NH2 and p-PS-NH2) were selected and studied. The aggregation mechanism was interpreted using the Derjaguin - Landau - Verwey- Overbeek (DLVO) theory.

Furthermore, the relationship between aggregation and toxicity of NPs with and without HA was investigated using Daphnia magna which is a sensitive and important aquatic species in freshwater food chains.