

## NET4MPLASTIC PROJECT

### Activity 3.1

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### LITERATURE REVIEW:

### LABORATORY ANALYSIS AND NEW TECHNOLOGIES FOR MARINE LITTER AND MICROPLASTICS IDENTIFICATION

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CONTRIBUTING PARTNERS	UNITS

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### 1 Introduction

In order to have a complete and exhaustive picture of mPs (micro plastics) nature, it is important to be able to identify their chemical nature, i.e. it is not enough to know only their size, shape and color. From the literature review, it came out that various technologies can be used.

Acronym	Description
AAS	Atomic Absorption Spectroscopy
ATR-FTIR	Attenuate Total Reflectance-Fourier Transform Infrared Spectroscopy
CARS	Coherent Anti-Stokes Raman Scattering
СТ	X-ray computed tomography
DLS	Dynamic Light Scattering
DSC	Differential scanning calorimetry
EDS /EDX	Energy Dispersive X-ray Specrometry / Analysis
EPS	Exopolysaccharides
FPA-FTIR	Focal Plane Array-Fourier Transform Infrared Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
GC-ITMS	Gas Chromatography-Ion Trap Mass Spectrometry
GC-MS	gas chromatography mass spectrometry
HSI	Hyperspectral Imaging Spectrometry
ICP-MS	Inductively Coupled Plasma mass spectrometry
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectrometry
μ-FTIR	micro-Fourier Transform Infrared Spectroscopy
MO	Optica Microscopy
μ-Raman	micro-Raman
MS	Mass spectrometry
NIR, vis-NIR	Near InfraRed spectroscopy, Visible-NearInfraRed Spectroscopy
NR	Nile Red
NTA	Nanoparticle tracking analysis
ОТ	Optical Tweezer
Py-GC-MS	Pyrolysis-Gas chromatography-mass spectrometry
Raman	Raman
SEC	Size exclusion chromatografy
SEM	Scanning Electron Microscopy
SIM	Selected-ion monitoring chromatographt
SL	Synchrotron light
SR-ATR	Single Reflection-Attenuate Total Reflectance

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Table 1: Techologies	for microplastic	monitoring (ac	ronyms and decsriptions	S)



SRS	Stimulated Raman Scattering
STEM / TEM	Scanning Trasmission Electron Microscopy / Trasmission Electron Microscopy
SWIR	Short wave infrared imagery.
TAC	Computed axial tomography
TED-GC-MS	Thermal Extraction Desorption gas chromatography mass spectrometry
TGA	Thermogravometric analysis
TOF-SIMS	Time-of-Flight - Secondary Ion Mass Spectrometry
XRD	X-ray diffraction
XRF	X-ray fluorescence spectroscopy

The most popular technique is FTIR, followed by the Raman. In table 1 there is a summary of the findings.

Technique	%
FTIR	43%
Raman	13%
SEM+EDS	9%
CG-MS	7%
HSI	5%
DSC+TGA	2%
NIR	3%
FPA-FTIR	3%
ICP-MS	2%
DLS	2%
SRS	1%
STEM/TEM	1%
other	1% each

Both FTIR and Raman are spectroscopic methods in which the matter is excited by a radiation and responds to this excitation, which leads to characteristic spectral fingerprints in the FTIR or Raman spectra.

Infrared spectroscopy (IR spectroscopy or vibrational spectroscopy) involves the interaction of infrared radiation (wavenumber range 400–4000 cm<sup>-1</sup> for Mid-IR) with matter. It covers a range of techniques, mostly based on absorption spectroscopy. Molecules absorb frequencies that are characteristic of their structure. These absorptions occur at resonant frequencies, i.e. the frequency of the absorbed radiation matches the vibrational frequency. The shape of the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling, affect the energies. The frequency of the vibrations is associated with a particular normal mode of motion and a particular bond type.



Fourier transform infrared (FTIR) spectroscopy is a measurement technique that allows to record infrared spectra. IR spectroscopy is often used to identify structures because functional groups give rise to characteristic bands in terms of both intensity and position (frequency).

A part of the IR radiation is absorbed depending on the molecular structure of the sample and finally measured in transmission or reflection mode (Käppler et al., 2016).

FTIR is applied mainly in two different modes of operation: attenuated total reflection FTIR (ATR-FTIR) which is used for handpicked mP (>500  $\mu$ m) and focal plane array (FPA) detector-based micro-FTIR (FPA-FTIR) which images mP particles on filters with a resolution of ca. 10-20  $\mu$ m. The size limit for FTIR single particle analysis is in the range of 10  $\mu$ m (Schwaferts et al., 2019).

In general, a FPA detector consists of a  $n \times n$  field of single detector elements. During data collection each element is read out individually resulting in  $n^2$  spectra within one measurement (Mintenig et al., 2017). With a focal-plane array detector, the total image acquisition time with FTIR can be reduced by two or

three orders (Zada et al., 2018).

Raman spectroscopy is a spectroscopic technique used to observe vibrational, rotational, and other lowfrequency modes in a system. Raman spectroscopy is commonly used in chemistry to provide a structural fingerprint by which molecules can be identified.

It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system.

Since the light source does not need to be infrared light, shorter wavelength lasers (e.g. 532 nm) can be utilized, which results in higher spatial resolution. Raman is, therefore, applied for the analysis of mP particles down to  $1 \mu m$  (Schwaferts et al., 2019).

Raman spectroscopy and FTIR are complementary. Raman spectroscopy can detect some molecular vibrations, which are IR inactive, and vice versa. Nevertheless, the technique of Raman spectroscopy would be interrupted by the presence of color, additives and attached contaminants microplastics (Qiu et al., 2016).



#### 2 Summary of Findings

In the review of Renner et al. (2018), the FTIR analysis percentage (comprehensive of micro-FTIR) was 46% and Raman analysis 11% (on 170 papers). It can therefore be argued that in the last two years the Raman analysis has grown in importance. This fact is probably due to the difference between the two techniques. As stated in the review of Araujo et al. (2018), compared with FTIR spectroscopy, Raman techniques show better spatial resolution (down to 1  $\mu$ m while that of FTIR is 10-20  $\mu$ m), has higher sensitivity to non polar groups, shows lower water interference and has narrower spectral bands.

On the other hand, Raman is prone to fluorescence interference, has an inherently low signal to noise ratio and might cause sample heating due to the use of a laser as light source, leading to background emission occasionally followed by polymer degradation.

Cabernard et al. (2018) presented an extensive experimental comparison on mPs samples analysed with both methods. After an optimization of the Raman parameters to overcome the fluorescence problems, the authors analysed different size classes of mPs using  $\mu$ -Raman and FTIR spectroscopy. The latter was mainly performed by attenuated total reflection (ATR)-FTIR and, in some cases, by FTIR imaging.

Their conclusion are that for mPs > 500 $\mu$ m the two techniques produce comparable results with a slightly higher identification rate for  $\mu$ -Raman spectroscopy (+25%) as reported in table 3 (table S17 Cabernard et al., 2018).

It was further found in this study that manual analysis of mPs >500  $\mu$ m can be automated by using ASPEx- $\mu$ -Raman with no loss in the MP identification rate but a substantial decrease in the labor input and analysis time.

µ-Raman	ATR-FTIR	
+ higher identification rate (+25%)	- lower identification rate	
<ul> <li>identification of MP of all sizes and shapes including fibers and varnishes</li> </ul>	<ul> <li>restricted in the analysis of MP of 10– 500 µm*, fibers* and varnishes</li> </ul>	
<ul> <li>pigments obscure the polymer spectra due to fluorescence, absorbance or band overlay</li> </ul>	<ul> <li>more robust in the identification of the polymer type of pigmented particles</li> </ul>	
<ul> <li>possibility of automation by ASPEx-µ-Raman with no loss in identification rate</li> </ul>	- no possibility of automation	

Table 3: Comparison between  $\mu$ -Raman and (ATR)-FTIR (Cabernard et al., 2018).

\*this limitation may be overcome by coupling ATR-FTIR spectroscopy with a microscope (μ-ATR-FTIR spectroscopy).<sup>11</sup>

For mPs dimension from 10 to 500 µm the number of detected polymer types was nearly two times higher for ASPEx-µ-Raman than for FTIR imaging and the concentrations of mPs in this range was fount higher by ASPEx-µ-Raman compared with FTIR imaging, as reported in figure 1 (Cabernard et al., 2018).





Fig. 1: Size distribution of the mean MP concentration and fitted power law distribution for combined Raman (black) and FTIR analysis (red). The limits of the size classes shown in this figure are not equidistant due to the strong increase in MP concentration with decreasing particle size. (from Cabernard et al., 2018)

In the study of Lenz et al. (2015), the authors evaluated the applicability and limitations of Raman microspectroscopy relative to visual identification. They have shown, that pure visual identification using morphological criteria led to a misidentification of a substantial amount of particles (32%) and fibres (25%), which suggests that mPs studies using visual identification only involve a high level of uncertainty of the reported concentrations. The success rate of purely visually compared to Raman analysed particles decreased with size. For particles <100  $\mu$ m the success rate falls below 80%, which makes microscopic analysis an inappropriate method.

Käppler et al. (2018) in the Baseman project investigated mP particles from river sediments applying both micro-attenuated total reflection Fourier transform infrared spectroscopy (μ-ATR-FTIR) and pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) in combination with thermochemolysis.

Py-GC-MS is an analytical technique, which thermally degrades large molecules into smaller ones in an inert atmosphere (direct pyrolysis). Dependent on the pyrolysis temperature, this leads to a generation of characteristic, volatile degradation products, which resemble or can be traced back to their precursor polymers. By means of these pyrolysis products, separated on a GC column, the precursor polymers can be identified using a pyrolysis pattern (fingerprint) or single to few characteristic degradation products as diagnostic markers.

The subsequent mass spectrometric detection enables their selective and specific identification. Both methods,  $\mu$ -ATR-FTIR and Py-GC-MS, are well suited to characterize the chemical nature of environmental MPs and can complete each other.



A benefit of all spectroscopic techniques like  $\mu$ -ATR-FTIR is that they are non-destructive. One disadvantage of FTIR is that organic and inorganic impurities can overlap the polymer bands in the IR spectra and hinder the spectroscopic evaluation.

A considerable advantage of py-GCMS is the simultaneous identification and specification of the synthetic polymer and potentially associated additives inorganic contents and organic contaminations, to a certain extent, do not majorly disturb the measurement, because they are either not pyrolyzed (inorganic contaminants) or have discriminable different retention behavior and m/z values (organic contaminants). This means on the other hand that information about inorganic plastic fillers or pigments cannot be achieved using Py-GC-MS in principle.

The results of the investigation show that the evaluation effort for the most common plastics (e.g., PE, PP, PS, PET) was approximately the same for  $\mu$ -ATR-FTIR and Py-GC-MS. From data reported in table S2 it can be deduced that the minimum size was 230 $\mu$ m.

Harrison et al.(2012) developed an optimized method for the micro-FT-IR analysis of microplastics in vacuum-filtered sediment retentates. Reflectance micro-FT-IR analyses of polyethylene (PE) were compared with attenuated total reflectance FT-IR (ATR-FT-IR) measurements. Molecular mapping as a precursor to the imaging of microplastics was explored in the presence and absence of 150  $\mu$ m PE fragments, added to sediment at concentrations of 10, 100, 500 and 1000 ppm.

Tagg et al. (2015) present a method for the analysis of microplastics in wastewater samples using FPAbased reflectance micro-FT-IR imaging and  $H_2O_2$  pretreatment. All 50 microplastic particles investigated were successfully identified, with the wavenumber regions used for identification (Table S1, Supporting Information) providing reliable results for all polymer types

The study of Löder et al. (2015) tested the applicability of focal plane array detector-based micro-Fouriertransform infrared imaging (FPA-FTIR) for analysis of microplastics from environmental samples. The measurement with a high lateral resolution allowed for the detection of particles down to a size **of 20** μm in only a fractional part of time needed for chemical mapping.

Primpke et al. (2017) have studied in depth the FPA-FTIR method, presenting a largely automated analysis approach for FPA based  $\mu$ FTIR data, covering element by element spectral identification and validation realized by dedicated OPUS© (Bruker) macros. Data are then further analysed by Python and Simple ITK image processing modules, providing detailed information on the identity, quantity and size of MP particles in a given sample without human bias. OPUS© (Bruker) macros and Python script listings are provided in the supplementary informations.

An example of the obtained results is reported in Figure 2 (an extracted of their Figure 4).





Fig. 2: Zoom image derived after application of closing approach. (From figure 4 of Primpke et al., 2017).

The comparison between the manual and the automated analysis is shown in Figure 3 (Primpke et al., 2017).



Fig. 3: Comparison of 12 polymer classes found by automated analysis for all size classes (black), starting from particles larger than 625 μm2 (dark grey) and derived via manual analysis (light grey. (From figure 6 of Primpke et al., 2017).



The study of Frère et al., (2016) proposes a semi-automated Raman micro-spectroscopy method coupled to static image analysis that allows the screening of a large quantity of mPs in a time-effective way with minimal machine operator intervention. They used a Raman micro-spectrometer equipped with a Horiba Scientific ParticleFinder module for LabSpec6. This equipment provided easy and quick localization, counting and morphological characterization (size, area, perimeter, shape) of the 110 particles analysed.

Ghosal et al. (2018) have used Raman micro-spectroscopy to examine polymers and anthropogenically derived chemicals in laboratory based fish and select samples from the marine environment. They used an automated algorithm to remove the fluorescence background and reveal the underlying polymer spectrum. The source code for the algorithm, which includes a graphical user interface, is freely available at https://github.com/michaelstchen/modPolyFit.

Araujo et al. (2018) calculated, on the basis of the literature, the total analysis time per mm<sup>2</sup> for automate routines for mP identification using  $\mu$ -Raman and  $\mu$ -FTIR; the data are reported in their Table 2. Summarising, for  $\mu$ -Raman the times ranging from 20s/mm<sup>2</sup> (Frère et al., 2016) to 38h/mm<sup>2</sup> (Käppler et al., 2016), for  $\mu$ -FTIR from 19s/mm<sup>2</sup> (Tagg et al., 2015) to 111min/mm<sup>2</sup> (Elert et al. 2017)

Elert et al. (2017) make the consideration that not only the technical comparison between the established detection procedures is relevant but also, or even more importantly, a practical and user friendly classification of those methods in relation to what analytical information can be delivered by different techniques, is necessary.

Stimulated Raman scattering (SRS) microscopy, based on the coherent interaction of 2 different laser beams with vibrational levels in the molecules of the sample, would enable much faster detection and identification of microplastics (Zada et al., 2018).

Zada et al. (2018) developed an SRS-based method for faster detection of plastic microparticles with only a limited number of measurements at different wavenumbers. The authors selected the five most used polymers (PA6,6, PET, PS, PP and HDPE) for test the method.

There is no single vibrational frequency that is specific for all polymers and at the same time selective over other compounds, so SRS analysis at a single wavenumber setting would not be sufficient to detect all polymer materials. Firstly the authors calibrated the method determining six SRS wavenumber for discriminate the five reference materials. For microplastics detection with SRS, they acquired six images of a sample on the filter at the six chosen wavenumbers. At each location (pixel), the six intensities were joined into a vector and multiplied with the matrix B, resulting in a five-element vector. The vector set was then decomposed into five images, each representing a different polymer. The pixel intensities are scores for the identification of the polymers. An example of their results is reported in figure 4 (Zada et al., 2018).





Fig. 4: Stimulated Raman scattering imaging of the artificial test mixture. (e) to (i) are identification images of Nylon, PET, PS, polypropylene, and polyethylene, respectively, where perfect identification is expressed in white. In the stimulated Raman scattering overlay image (j), five binary versions of the five identification images were color coded and overlaid as follows: Nylon: red; PET: orange; PS: green; polypropylene: magenta, and polyethylene: yellow. Scale bar: 100 μm (same for graphs [e] to [i]). (From figure 3 of Zada et al., 2018)

Liao et al. (2017) build a handled SRS microscope that can analyse chemical contents of a sample in situ and in vivo (figure 5).



Fig. 5: Experimental design. (a) Excitation. (b) Handheld microscope. (c) Digital image of the handheld microscope. AOM: acousto-optical modulator; D: dichroic mirror; F: filter; G: galvo mirror; HWP: half waveplate; L: lens; OBJ: objective; PBS: polarizing beam splitter; PCF: photonics crystal fiber; PD: photodiode; QWP: quarter-wave plate; R: rod (SF-11); W: window. (Liao et al., 2017)



Very few paper were found on thermal analytical techniques (five); DSC was used for identify the polymer type from their crystallisation/melting point (Kühn et al., 2018, Shabaka et al., 2019); in two case (Kühn et al., 2018, Tunçer et al., 2018) as to confirm the FTIR results; in one case (Arhant et al., 2019) for characterize and understand changes in the mechanical behavior of Polyethylene Terephthalate (PET) induced by hydrolysis, especially for high degradation levels, through degree of crystallinity determination.

The only paper that deals with TGA is that of David et al. (2019). In this study, the authors evaluated the potential of a soil universal model method (SUMM) based on thermogravimetry (TGA) for the identification and quantification of microplastics in standard loamy sand. Blank and spiked soils (with amounts of one of four reference microplastic types: PET, PVC, LDPE and PS) were analyzed by TGA. For each sample, thermal mass losses (TML) in 10°C intervals were extracted and used for further analysis. In figure 6 there is an example of the average of all the results of thermal mass losses and first derivative (DTG) of mass loss of the investigated samples including the variance of mass losses.



**Concentration** [%wt] =  $\frac{0.5}{1} = \frac{2}{3} = \frac{5}{5}$  Blank Fig. 6: Plots of TML of blank soil enriched with PE, PET, PVC, and PS, respectively, at different concentrations. (David et al., 2019)

Also the gas chromatography was used, coupled with mass spectrometry in different configurations, that is pyrolysis (Py-) or thermal extraction and desorption (TED-). These are integrating method, which allows mass quantification.

Nuelle et al. (2014) used Py-GCMS for identification of mP extract from sediments. Fisher et al. (2017) demonstrate here Curie point (CP)-Py-GCMS combined with thermochemolysis (a pyrolytic methylation step) as an equally reliable and practical analytical method for eight relevant common consumer user plastics (PE, polypropylene (PP), PS, polyethylene terephthalate (PET), PVC, poly(methyl methacrylate) (PMMA), polycarbonate (PC), and polyamide 6 (PA6) detected simultaneously within a single GCMS run. In his work Dümichen et al. (2017) document the progress of TED-GC-MS as a fast tool for MP analysis in environmental samples. In a first step, unique polymer specific degradation products of major types of polymers have to be identified and selected for unambiguous identification in complex environmental samples. Subsequently real samples were screened for MP, taken from three different rivers, from a soil, a bio gas plant and a waste water treatment plant.



Other authors (de Lucia et al., 2018; Prunier et al., 2019; Karkanorachaki et al., 2018; León et al., 2019) used GC or GC-MS, or ICP-MS for the determinations of trace of element present in mP (metals, aromatic hydrocarbons (PAHs), pesticides, organochlorinated compounds, plastics additives in general).

#### A particular attention is giving on **Remote Sensing Imaging**.

Remote sensing images acquired by multispectral sensors, such as the widely used Landsat Thematic Mapper (TM) sensor, have shown their usefulness in numerous earth observation (EO) applications. A relatively small number of acquisition channels, BUT their discrimination capability is very limited when different types (or conditions) of the same species (e.g., different types of forest) are to be recognized. Hyperspectral sensors can be used to deal with this problem. The sensors are characterized by a very high spectral resolution that usually results in hundreds of observation channels (Melgani & Bruzzone, 2004).

Hyperspectral Imaging (HSI) provides very high dimensional data with hundreds of spectral channels ranging from the visible to the short wave-infrared region of the electromagnetic spectrum. Although HSI enables a detailed separation of similar surface materials, the spectral features are correlated especially in adjacent bands, thus providing redundant information. The redundant and correlated features also increase both the time and memory requirements making the classification computationally inefficient.

In his study, Taşkin et al. (2017) present a novel feature-selection technique based on High Dimensional Model Representation (HDMR). The proposed method begins with creating an auxiliary training set by randomly filling the feature space.

Bonifazi et al. (2017) in the DeFishGear project combined the classical digital imaging and the innovative hyperspectral imaging approaches in order to obtain a full classification of marine microplastic samples. An example of their results is reported in figure 7 (their figure 1.8).



Fig. 7: Digital image (a), hyperspectral image (b) and prediction map (c) obtained as result of the PLS-DA classification model. (Bonifazi et al.,2017 – Figure 1.8)

Serranti et al. (2018) applied HIS to samples collected by surface-trawling plankton nets from several parts of the world (i.e. Arctic, Mediterranean, South Atlantic and North Pacific). Reliable information on abundance, size, shape and polymer type for the whole ensemble of plastic particles in each sample was retrieved from single hyperspectral images.



Shan et al. (2018) obtained Hyperspectral images with wavelength range between 400 and 1000 nm from soil samples containing different materials including microplastics, fresh leaves, wilted leaves, rocks and dry branches. Supervised classification algorithms such as support vector machine (SVM), mahalanobis distance (MD) and maximum likelihood (ML) algorithms were used to identify microplastics from the other materials in hyperspectral images. To investigate the effect of particle size and color, white polyethylene (PE) and black PE particles extracted from soil with two different particle size ranges (1-5mm and 0.5-1 mm) were studied in this work.



#### 3 Annotated Bibliography

Araujo, C. F., Nolasco, M. M., Ribeiro, A. M. P., & Ribeiro-Claro, P. J. A. (2018). Identification of microplastics using Raman spectroscopy: Latest developments and future prospects. Water Research, 142, 426–440. https://doi.org/10.1016/j.watres.2018.05.060

#### <u>Synthesis</u>

This review discusses each drawback followed by a showcase of interesting and easily available solutions that contribute to faster and better identification of microplastics using Raman spectroscopy. Among discussed topics are: enhanced signal quality with better detectors and spectrum processing; automated particle selection for faster Raman mapping; comprehensive reference libraries for successful spectral matching. A last section introduces non-conventional Raman techniques (non-linear Raman, hyperspectral imaging, standoff Raman) which permit more advanced applications such as real-time Raman detection and imaging of microplastics.

# Arhant, M., Le Gall, M., Le Gac, P. Y., & Davies, P. (2019). Impact of hydrolytic degradation on mechanical properties of PET - Towards an understanding of microplastics formation. Polymer Degradation and Stability, 161, 175–182. https://doi.org/10.1016/j.polymdegradstab.2019.01.021 <u>Synthesis</u>

This study aims to characterize and understand changes in the mechanical behaviour of Polyethylene Terephthalate (PET) induced by hydrolysis, especially for high degradation levels. Thin films (200 mm) of PET were aged in water at temperatures from 110 C to 80 C for up to 150 days. Embrittlement occurs with chain scission during hydrolysis when molar mass of the polymer falls below 17 kg/mol. When the polymer is brittle, i.e. for high levels of degradation, the stress at break decreases linearly with the molar mass, and can be described by a simple mathematical expression.

# Bonifazi, G., Palmieri, R., Serranti, S., *Mazziotti C., Ferrari C.R.* (2017). Hyperspectral imaging based approach for monitoring of microplastics from marine environment, *in OCM 2017 - Optical Characterization of Materials - conference proceedings ed.by Beyerer Juergen, Puente León Fernando, Laengle Thomas - pag 193-205*

#### **Synthesis**

This study was addressed to detect and to recognize different types of microplastics coming from sampling in different sea areas adopting a new approach, based on HyperSpectral Imaging (HSI) sensors.

# Cabernard, L., Roscher, L., Lorenz, C., Gerdts, G., & Primpke, S. (2018). Comparison of Raman and FourierTransform Infrared Spectroscopy for the Quantification of Microplastics in the Aquatic Environment.EnvironmentalScienceScienceandTechnology,52(22),13279–13288.<a href="https://doi.org/10.1021/acs.est.8b03438">https://doi.org/10.1021/acs.est.8b03438</a>

#### **Synthesis**

The authors compared the two most promising techniques for MP analysis, namely, Raman and Fourier transform infrared (FTIR) spectroscopy, by analyzing MPs extracted from North Sea surface waters. Microplastics >500  $\mu$ m were visually sorted and manually analyzed by  $\mu$ -Raman and attenuated total reflection (ATR)-FTIR spectroscopy. Microplastics  $\leq$ 500  $\mu$ m were concentrated on goldcoated filters and analyzed by automated single-particle exploration coupled to  $\mu$ -Raman (ASPEx- $\mu$ -Raman) and FTIR imaging (reflection mode). The number of identified MPs >500 $\mu$ m was slightly higher for  $\mu$ -Raman (+23%)



than ATR-FTIR analysis. Concerning MPs  $\leq$ 500 µm, ASPEx-µ-Raman quantified two-times higher MP numbers but required a four-times higher analysis time compared to FTIR imaging.

David, J., Weissmannová, H. D., Steinmetz, Z., Kabelíková, L., Demyan, M. S., Šimečková, J., Tokarski, D., Siewert, C., Schaumann, G. E., & Kučerík, J. (2019). Introducing a soil universal model method (SUMM) and its application for qualitative and quantitative determination of poly(ethylene), poly(styrene), poly(vinyl chloride) and poly(ethylene terephthalate) microplastics in a model soil. Chemosphere, 225, 810–819. https://doi.org/10.1016/j.chemosphere.2019.03.078 <u>Synthesis</u>

## In this study is evaluated the potential of a soil universal model method (SUMM) based on thermogravimetry (TGA) for the identification and quantification of microplastics in standard loamy sand. Blank and spiked soils (with amounts of one of four microplastic types) were analyzed by TGA.

# de Lucia, G. A., Vianello, A., Camedda, A., Vani, D., Tomassetti, P., Coppa, S., Palazzo, L., Amici, M., Romanelli, G., Zampetti, G., Cicero, A. M., Carpentieri, S., Di Vito, S., & Matiddi, M. (2018). Sea water contamination in the Vicinity of the Italian minor islands caused by microplastic pollution. Water (Switzerland), 10(8). https://doi.org/10.3390/w10081108

#### **Synthesis**

The abundance and distribution of microplastics (MP) were evaluated in six "clean" sites (Italian minor islands) and in two "polluted" areas (near the mouth of two major Italian rivers). Samples of MP, plankton and persistent organic pollutants (POPs) were collected using a manta trawl (MA) and a plankton net (WP2), both lined with a 333 m mesh net. MP have been confirmed to be ubiquitous since they were found at each site, showing an average density of 0.3 0.04 items/m3 (values ranged from 0.641 to 0.119 ). When comparing the clean sites with the polluted ones, a significantly higher value of MP was found near the river mouths. The most common types of MP were synthetic filaments (50.24%), followed by fragments (30.39%), thin plastic films (16.98%) and spheres (2.39%). Infrared spectroscopy analysis highlighted that the most abundant polymers were polyethylene (PE-26%), polypropylene (PP-11%), polyethylene-terephthalate/polyester (PET/PEST-8%) and ethylene-vinyl-acetate (EVA-5%). Polychlorinated biphenyls and organochlorine pesticides were detected in all the samples with a high variability among sites and depths. This study adds to the existing information on the distribution of contaminants across the Mediterranean Sea, and is useful to policy makers who wish to implement effective measures to reduce MP pollution.

## Dümichen, E., Eisentraut, P., Bannick, C. G., Barthel, A. K., Senz, R., & Braun, U. (2017). Fast identification of microplastics in complex environmental samples by a thermal degradation method. Chemosphere, 174, 572–584. https://doi.org/10.1016/j.chemosphere.2017.02.010

#### <u>Synthesis</u>

The authors developed a new thermoanalytical method as a first step for identifying microplastics in environmental samples. A sample amount of about 20 mg, which assures the homogeneity of the sample, is subjected to complete thermal decomposition. The specific degradation products of the respective polymer are adsorbed on a solid-phase adsorber and subsequently analyzed by thermal desorption gas chromatography mass spectrometry. For certain identification, the specific degradation products for the respective polymer were selected first. Afterwards real environmental samples from the aquatic (three different rivers) and the terrestrial (bio gas plant) systems were screened for microplastics. Mainly



polypropylene (PP), polyethylene (PE) and polystyrene (PS) were identified for the samples from the bio gas plant and PE and PS from the rivers. However, this was only the first step and quantification measurements will follow.

#### Elert A.M., Becker R., Duemichen E., Eisentraut P., Falkenhagen J., Sturm H., Braun U. (2017) Comparison of different methods for MP detection: What can we learn from them, and why asking the right question before measurements matters?, Environmental Pollution, 231, 1256-1264 Synthesis

This article presents a critical evaluation of two vibrational spectroscopies, Raman and Fourier transform infrared (FTIR) spectroscopy, and two extraction methods: thermal extraction desorption gas chromatography mass spectrometry (TED-GC-MS) and liquid extraction with subsequent size exclusion chromatography (SEC) using a soil with known contents of PE, PP, PS and PET as reference material.

#### Fischer, M., & Scholz-Böttcher, B. M. (2017). Simultaneous Trace Identification and Quantification of Common Types of Microplastics in Environmental Samples by Pyrolysis-Gas Chromatography-Mass Spectrometry. Environmental Science and Technology, 51(9), 5052–5060. https://doi.org/10.1021/acs.est.6b06362

<u>Synthesis</u>

In this study Curie-Point pyrolysis-gas chromatography–mass spectrometry combined with thermochemolysis is shown to be an excellent analytical tool to simultaneously identify and optionally quantify MP in environmental samples on a polymer specific mass related trace level. The method is independent of any mechanical preselection or particle appearance. For this purpose polymer characteristic pyrolysis products and their indicative fragment ions were used to analyze eight common types of plastics. Further aspects of calibration, recoveries, and potential matrix effects are discussed.

#### Frère, L., Paul-Pont, I., Moreau, J., Soudant, P., Lambert, C., Huvet, A., & Rinnert, E. (2016). A semiautomated Raman micro-spectroscopy method for morphological and chemical characterizations of microplastic litter. Marine Pollution Bulletin, 113(1–2), 461–468. https://doi.org/10.1016/j.marpolbul.2016.10.051

#### <u>Synthesis</u>

This study proposes a semi-automated Raman micro-spectroscopy method coupled to static image analysis that allows the screening of a large quantity of microplastic in a time-effective way with minimal machine operator intervention. The method was validated using 103 particles collected at the sea surface spiked with 7 standard plastics: morphological and chemical characterization of particles was performed in <3 h.

## Ghosal S., Chen M., Wagner J., Wang Z.M., Wall S. (2018) Molecular identification of polymers and anthropogenic particles extracted from oceanic water and fish stomach e A Raman microspectroscopy study, Environmental Pollution, 233, 1113-1124.

#### <u>Synthesis</u>

Pacific Ocean trawl samples, stomach contents of laboratory-raised fish as well as fish from the subtropical gyres were analyzed by Raman micro-spectroscopy (RMS) to identify polymer residues and any detectable persistent organic pollutants (POP). The goal was to access specific molecular information at the individual particle level in order to identify polymer debris in the natural environment. The identification process was aided by a laboratory generated automated fluorescence removal algorithm.



Harrison, J. P., Ojeda, J. J., & Romero-González, M. E. (2012). The applicability of reflectance micro-Fourier-transform infrared spectroscopy for the detection of synthetic microplastics in marine sediments. Science of the Total Environment, 416, 455–463. https://doi.org/10.1016/j.scitotenv.2011.11.078

#### <u>Synthesis</u>

Herein, an optimized method for the micro-FT-IR analysis of microplastics in vacuum-filtered sediment retentates was developed. Reflectance micro-FT-IR analyses of polyethylene (PE) were compared with attenuated total reflectance FT-IR (ATR-FT-IR) measurements.

### Käppler, A., Fischer, D., Oberbeckmann, S., Schernewski, G., Labrenz, M., Eichhorn, K. J., & Voit, B. (2016). Analysis of environmental microplastics by vibrational microspectroscopy: FTIR, Raman or both? Analytical and Bioanalytical Chemistry, 408(29), 8377–8391. https://doi.org/10.1007/s00216-016-9956-3

#### **Synthesis**

To solve the question of which is the best technique between FTIR and Raman for chemical identification of mP, the authors investigated environmental samples by both Raman and FTIR spectroscopy. Firstly, particles and fibres >500  $\mu$ m extracted from beach sediment samples were analysed by Raman and FTIR microspectroscopic single measurements. The results illustrate that both methods are in principle suitable to identify microplastics from the environment. However, in some cases, especially for coloured particles, a combination of both spectroscopic methods is necessary for a complete and reliable characterisation of the chemical composition.

# Käppler, A., Fischer, M., Scholz-Böttcher, B. M., Oberbeckmann, S., Labrenz, M., Fischer, D., Eichhorn, K. J., & Voit, B. (2018). Comparison of μ-ATR-FTIR spectroscopy and py-GCMS as identification tools for microplastic particles and fibers isolated from river sediments. Analytical and Bioanalytical Chemistry, 410(21), 5313–5327. https://doi.org/10.1007/s00216-018-1185-5

#### **Synthesis**

In this blind study, the authors investigated 27 single MP particles and fibers of unknown material isolated from river sediments. Successively micro-attenuated total reflection Fourier transform infrared spectroscopy ( $\mu$ -ATR-FTIR) and pyrolysis gas chromatography-mass spectrometry (py-GCMS) in combination with thermochemolysis were applied. Both methods differentiated between plastic vs. non-plastic in the same way in 26 cases, with 19 particles and fibers (22 after re-evaluation) identified as the same polymer type. To illustrate the different approaches and emphasize the complementarity of their information content, the authors exemplarily provide a detailed comparison of four particles and three fibers and a critical discussion of advantages and disadvantages of both methods.

## Karkanorachaki, K., Kiparissis, S., Kalogerakis, G.C., Yiantzi, E., Psillakis, E., Kalogerakis, N. (2018). Plastic pellets, meso- and microplastics on the coastline of Northern Crete: Distribution and organic pollution. Marine Pollution Bulletin 133, 578–589

#### **Synthesis**

This study investigates the temporal and spatial distribution of plastic pellets and fragments in sandy beaches along the coastline of Northern Crete, during 2013.



#### Kühn, S., van Oyen, A., Booth, A. M., Meijboom, A., & van Franeker, J. A. (2018). Marine microplastic: Preparation of relevant test materials for laboratory assessment of ecosystem impacts. Chemosphere, 213, 103–113. https://doi.org/10.1016/j.chemosphere.2018.09.032

#### **Synthesis**

For this study, macroplastic litter was collected on a Dutch beach and cryo-milled to create a microplastic mixture for environmental impact assessments. The sample composition followed proportions of marine plastic litter types observed in an earlier large beach cleanup. Polymer composition of the sample was assessed by infrared spectroscopy (ATR-FTIR) and differential scanning calorimetry analysis (DSC). The particle size distribution of the cryo-milled microplastics showed that particles 0.5e2.0mm represented 68% of mass, but smaller sizes (<2 mm) strongly dominated numerically. Inductively coupled plasma spectroscopy (ICP-MS and ICP-OES) analysis of the microplastic mixture revealed a broad range of metals and other elements (e.g. Al, Cd, Cr, Fe, Mg, Pb, S and Zn), representing common inorganic additives used as colorants, fillers and stabilisers. GC-MS analysis identified a broad range of organic plasticisers, stabilisers, antioxidants and flame retardants.

# Lenz, R., Enders, K., Stedmon, C. A., MacKenzie, D. M. A., & Nielsen, T. G. (2015). A critical assessment of visual identification of marine microplastic using Raman spectroscopy for analysis improvement. Marine Pollution Bulletin, 100(1), 82–91. https://doi.org/10.1016/j.marpolbul.2015.09.026 <u>Synthesis</u>

MP  $\geq$ 10 µm diameter filtered from below the sea surface in the European and subtropical North Atlantic were simultaneously identified by visual microscopy and Raman micro-spectroscopy. Visually identified particles below 100 µm had a significantly lower percentage confirmed by Raman than larger ones indicating that visual identification alone is inappropriate for studies on small microplastics.

#### León, V. M., García-Agüera, I., Moltó, V., Fernández-González, V., Llorca-Pérez, L., Andrade, J. M., Muniategui-Lorenzo, S., & Campillo, J. A. (2019). PAHs, pesticides, personal care products and plastic additives in plastic debris from Spanish Mediterranean beaches. Science of the Total Environment, 670, 672–684. https://doi.org/10.1016/j.scitotenv.2019.03.216

#### <u>Synthesis</u>

In this study the role of plastic debris as a pollution vector has been evaluated by determining the concentrations of hydrophobic organic contaminants in polymers from three Western Mediterranean coastal areas as well as their potential transfer to seawater. Plastic debris was sampled at three Iberian Peninsula Southeastern beaches, each affected by different predominant anthropogenic activities (tourism, agriculture, urban activities, transport and industry). Plastic debris was characterized by attenuated total reflection Fourier-transform infrared spectrometry. The organic contaminants were extracted from plastics by ultrasonic extraction with methanol and quantified by stir bar sorptive extraction coupled to gas chromatography–mass spectrometry (GC–MS).

#### Liao, C.-S., Wang, P., Huang, C. Y., Lin, P., Eakins, G., Bentley, R. T., Liang, R., & Cheng, J.-X. (2017). In Vivo and in Situ Spectroscopic Imaging by a Handheld Stimulated Raman Scattering Microscope . ACS Photonics, 5(3), 947–954. https://doi.org/10.1021/acsphotonics.7b01214 Synthesis

This article report the first background-free fiber-delivered handheld SRS microscope for in situ chemical imaging. By temporally separating the two ultrafast pulses propagating in the fiber and then overlapping them on a sample through a highly dispersive material, the authors detected a stimulated Raman signal



that is 200 times weaker than the background induced by the fiber. Broad applications of the handheld SRS microscope were demonstrated through in situ ambient-light chemical mapping of pesticide on a spinach leaf, cancerous tissue versus healthy brain tissue in a canine model, and cosmetic distribution on live human skin. A lab-built objective lens further reduced the size of the pen-shaped microscope to about one centimeter in diameter.

#### Löder, M. G. J., Kuczera, M., Mintenig, S., Lorenz, C., & Gerdts, G. (2015). Focal plane array detectorbased micro-Fourier-transform infrared imaging for the analysis of microplastics in environmental samples. Environmental Chemistry, 12(5), 563-581. https://doi.org/10.1071/en14205 Synthesis

# This study is the first to fill this gap by using focal plane array detector-based micro-Fourier-transform infrared imaging for analysis of microplastics from environmental samples. As a result of our iteratively optimised analytical approach (concerning filter material, measuring mode, measurement parameters and identification protocol), we were able to successfully measure the whole surface (>10-mm diameter) of filters with microplastics from marine plankton and sediment samples. The measurement with a high lateral resolution allowed for the detection of particles down to a size of 20 $\mu$ m in only a fractional part of time needed for chemical mapping.

### Melgani, F., & Bruzzone, L. (2004). Classification of Hyperspectral Remote Sensing. IEEE Trans. Geosci. Remote Sens., 42(8), 1778–1790.

#### **Synthesis**

This paper addresses the problem of the classification of hyperspectral remote sensing images by support vector machines (SVMs).

## Mintenig, S. M., Int-Veen, I., Löder, M. G. J., Primpke, S., & Gerdts, G. (2017). Identification of microplastic in effluents of waste water treatment plants using focal plane array-based micro-Fourier-transform infrared imaging. Water Research, 108(November), 365–372. https://doi.org/10.1016/j.watres.2016.11.015 Synthesis

# This study investigated MP in the effluents of 12 WWTPs in Lower Saxony, Germany. Samples were purified by a plastic-preserving enzymatic-oxidative procedure and subsequent density separation using a zinc chloride solution. For analysis, attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FT-IR) and focal plane array (FPA)-based transmission micro-FT-IR imaging were applied. This allowed the identification of polymers of all MP down to a size of 20 mm.

### Nuelle, M. T., Dekiff, J. H., Remy, D., & Fries, E. (2014). A new analytical approach for monitoring microplastics in marine sediments. Environmental Pollution, 184, 161–169. https://doi.org/10.1016/j.envpol.2013.07.027

#### <u>Synthesis</u>

A two-step method was developed to extract microplastics from sediments. First, 1 kg sediments was preextracted using the air-induced overflow (AIO) method, based on fluidisation in a sodium chloride (NaCl) solution. The original sediment mass was reduced by up to 80%. As a consequence, it was possible to reduce the volume of sodium iodide (NaI) solution used for the subsequent flotation step. Recoveries of the whole procedure for polyethylene, polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polystyrene and polyurethane with sizes of approximately 1 mm were between 91



and 99%. After being stored for one week in a 35% H2O2 solution, 92% of selected biogenic material had dissolved completely or had lost its colour, whereas the tested polymers were resistant. Microplastics were extracted from three sediment samples collected from the North Sea island Norderney. Using pyrolysis gas chromatography/mass spectrometry, these microplastics were identified as PP, PVC and PET.

## Primpke, S., Lorenz, C., Rascher-Friesenhausen, R., & Gerdts, G. (2017). An automated approach for microplastics analysis using focal plane array (FPA) FTIR microscopy and image analysis. Analytical Methods, 9(9), 1499–1511. https://doi.org/10.1039/c6ay02476a

#### **Synthesis**

In this study is present an automated approach to reduce the time demand currently needed for data analyses. We developed a novel analysis pipeline, based on the OPUS© Software by Bruker, followed by image analysis with Python and Simple ITK image processing modules.

#### Prunier, J., Maurice, L., Perez, E., Gigault, J., Pierson Wickmann, A-C., Davranche, M., Ter Halle, A. (2019). Trace metals in polyethylene debris from the North Atlantic subtropical gyre. Environmental Pollution 245, 371-379

#### **Synthesis**

In this study, plastic debris collected from the North Atlantic subtropical gyre was analyzed for trace metals; as a comparison, new packaging materials were also analyzed. Both the new items and plastic debris showed very scattered concentrations. The new items contained significant amounts of trace metals introduced as additives, but globally, metal concentrations were higher in the plastic debris. The results provide evidence that enhanced metal concentrations increase with the plastic state of oxidation for some elements, such as As, Ti, Ni, and Cd. Transmission electron microscopy showed the presence of mineral particles on the surface of the plastic debris.

## Qiu, Q., Tan, Z., Wang, J., Peng, J., Li, M., & Zhan, Z. (2016). Extraction, enumeration and identification methods for monitoring microplastics in the environment. Estuarine, Coastal and Shelf Science, 176, 102–109. https://doi.org/10.1016/j.ecss.2016.04.012

#### <u>Synthesis</u>

This review summarizes the methods and techniques in the extraction from sediment, seawater and organisms, and assesses their advantages and limitations according to different experimental conditions, such as salt solution and reagents added to remove organic matter. Similarly, this overview includes the enumeration methods of microplastics by many kinds of microscopes (e.g. stereomicroscope, fluorescent microscope, scanning electron microscope). Advantages and challenges of using micro-FTIR, ART-FTIR, FPA-FTIR, Pry-GC/MS, and Raman spectroscopy in the identification methods are also discussed.

## 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

#### **Synthesis**

In this review the authors examine the literature regarding microplastics. There is still a lack of standardisation, and therefore, used methodologies varied widely. Most researchers performed controversially discussed visual examination, but it became more and more a supporting tool to reduce measuring effort. To that account, especially infrared or Raman microscopy were used for chemical characterisation. This indicates that dimensions of analysed microplastics changed to micrometre scaling.



However, those microscopy technologies were used for particle by particle characterisation, and therefore, it is still challenging to handle the mass of data. Alternatively, thermal extraction and desorption gas chromatography is a useful integrating analysis approach, which allows a multicomponent characterisation of environmental samples without any complex sample preparation.

## Safavi S.M., Masoumi H., Mirian S.S., Tabrizchi M. (2010). Sorting of polypropylene resins by color in MSW using visible reflectance spectroscopy -Waste Management, 30, 2216–2222. <u>Synthesis</u>

In this paper, an automated sorter is proposed for distinguishing polypropylene (PP) plastics based on their color. This sorting system uses visible (VIS) reflectance spectroscopy to separate PP resins according to their colors. A "Three-Filter" identification algorithm was developed to recognize the PP color (blue, red, green, white or yellow), and accordingly, give the command for throwing or not throwing PP to a series of electro pneumatic valves. The proposed sorting system was demonstrated to be fast and accurate, despite the presence of different labels and surface contamination on the PP resins.

## 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>

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.

## Serranti, S., Palmieri, R., Bonifazi, G., & Cózar, A. (2018). Characterization of microplastic litter from oceans by an innovative approach based on hyperspectral imaging. Waste Management, 76(2018), 117–125. https://doi.org/10.1016/j.wasman.2018.03.003

#### <u>Synthesis</u>

An innovative approach, based on HyperSpectral Imaging (HSI), was developed in order to set up an efficient method to analyze marine microplastic litter. HSI was applied to samples collected by surface trawling plankton nets from several parts of the world (i.e. Arctic, Mediterranean, South Atlantic and North Pacific). Reliable information on abundance, size, shape and polymer type for the whole ensemble of plastic particles in each sample was retrieved from single hyperspectral images.

# Shabaka, S. H., Ghobashy, M., & Marey, R. S. (2019). Identification of marine microplastics in Eastern Harbor, Mediterranean Coast of Egypt, using differential scanning calorimetry. Marine Pollution Bulletin, 142(January), 494–503. https://doi.org/10.1016/j.marpolbul.2019.03.062 Synthesis

No attempts have been made to identify or assess marine plastic litter in Egypt. The authors provide, for the first time, a precise, simple, and cost-effective method to identify microplastics in Eastern Harbor by using differential scanning calorimetry (DSC). This screening revealed the presence of ten polymers in seawater and shoreline sediments. Most of the extracted microplastics are secondary microplastics, as they appear to be remnants of larger plastic fragments.

Shan, J., Zhao, J., Liu, L., Zhang, Y., Wang, X., & Wu, F. (2018). A novel way to rapidly monitor microplastics in soil by hyperspectral imaging technology and chemometrics. Environmental Pollution, 238, 121–129. https://doi.org/10.1016/j.envpol.2018.03.026



#### Synthesis

Hyperspectral imaging technology has been investigated as a possible way to detect microplastics contamination in soil directly and efficiently in this study. Hyperspectral images with wavelength range between 400 and 1000 nm were obtained from soil samples containing different materials including microplastics, fresh leaves, wilted leaves, rocks and dry branches. Supervised classification algorithms such as support vector machine (SVM), mahalanobis distance (MD) and maximum likelihood (ML) algorithms were used to identify microplastics from the other materials in hyperspectral images. To investigate the effect of particle size and color, white polyethylene (PE) and black PE particles extracted from soil with two different particle size ranges (1-5mm and 0.5-1 mm) were studied in this work...

#### Tagg, A. S., Sapp, M., Harrison, J. P., & Ojeda, J. J. (2015). Identification and Quantification of Microplastics in Wastewater Using Focal Plane Array-Based Reflectance Micro-FT-IR Imaging. Analytical Chemistry, 87(12), 6032–6040. https://doi.org/10.1021/acs.analchem.5b00495 Synthesis

A new method for the analysis of microplastics in wastewater was developed. A pretreatment step using 30% hydrogen peroxide (H2O2) was employed to remove biogenic material, and focal plane array (FPA)based reflectance micro-Fourier-transform (FT-IR) imaging was shown to successfully image and identify different microplastic types (polyethylene, polypropylene, nylon-6, polyvinyl chloride, polystyrene). Microplastic-spiked wastewater samples were used to validate the methodology, resulting in a robust protocol which was nonselective and reproducible (the overall success identification rate was 98.33%). The use of FPA-based micro-FT-IR spectroscopy also provides a considerable reduction in analysis time compared with previous methods, since samples that could take several days to be mapped using a singleelement detector can now be imaged in less than 9 h (circular filter with a diameter of 47 mm)..

#### Taskin, G., Kaya, H., & Bruzzone, L. (2017). Feature selection based on high dimensional model representation for hyperspectral images. IEEE Transactions on Image Processing, 26(6), 2918–2928. https://doi.org/10.1109/TIP.2017.2687128

#### Synthesis

In hyperspectral image analysis, the classification task has generally been addressed jointly with dimensionality reduction due to both the high correlation between the spectral features and the noise present in spectral bands, which might significantly degrade classification performance. In supervised classification, limited training instances in proportion with the number of spectral features have negative impacts on the classification accuracy, which is known as Hughes effects or curse of dimensionality in the literature. In this paper, the authors focus on dimensionality reduction problem, and propose a novel feature selection algorithm, which is based on the method called high dimensional model representation.

#### Tuncer, S., Artüz, O. B., Demirkol, M., & Artüz, M. L. (2018). First report of occurrence, distribution, and composition of microplastics in surface waters of the Sea of Marmara, Turkey. Marine Pollution Bulletin, 135(May), 283–289. https://doi.org/10.1016/j.marpolbul.2018.06.054 <u>Synthesis</u>

This work, carried out in the fourteen sites in the area, is the first reference to the detection of MP distribution at surface waters in the Sea of Marmara, Turkey. As a result of this study, the average level of MP in the surface was determined to be 1.263 item/m2. The results were higher compared of the most other adjacent regions and show that the Sea of Marmara started to face that problem.



Zada, L., Leslie, H. A., Vethaak, A. D., Tinnevelt, G. H., Jansen, J. J., de Boer, J. F., & Ariese, F. (2018). Fast microplastics identification with stimulated Raman scattering microscopy. Journal of Raman Spectroscopy, 49(7), 1136–1144. https://doi.org/10.1002/jrs.5367

#### <u>Synthesis</u>

The authors identified polyethylene terephthalate particles extracted from a commercial personal care product, demonstrating also the thousand-fold higher speed of mapping with SRS compared with conventional Raman



#### 3.1 Additional References

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Li, R., Zhang, L., Xue, B., & Wang, Y. (2019). Abundance and characteristics of microplastics in the mangrove sediment of the semi-enclosed Maowei Sea of the south China sea: New implications for location, rhizosphere, and sediment compositions. Environmental Pollution, 244, 685–692. https://doi.org/10.1016/j.envpol.2018.10.089

Pan, Z., Guo, H., Chen, H., Wang, S., Sun, X., Zou, Q., Zhang, Y., Lin, H., Cai, S., & Huang, J. (2019). Microplastics in the Northwestern Pacific: Abundance, distribution, and characteristics. Science of the Total Environment, 650, 1913–1922. https://doi.org/10.1016/j.scitotenv.2018.09.244

Pan, Z., Sun, X., Guo, H., Cai, S., Chen, H., Wang, S., Zhang, Y., Lin, H., & Huang, J. (2019). Prevalence of microplastic pollution in the Northwestern Pacific Ocean. Chemosphere, 225, 735–744. https://doi.org/10.1016/j.chemosphere.2019.03.076

Savoca, S., Capillo, G., Mancuso, M., Bottari, T., Crupi, R., Branca, C., Romano, V., Faggio, C., D'Angelo, G., & Spanò, N. (2019). Microplastics occurrence in the Tyrrhenian waters and in the gastrointestinal tract of two congener species of seabreams. Environmental Toxicology and Pharmacology, 67(January), 35–41. https://doi.org/10.1016/j.etap.2019.01.011

Suaria, G., Avio, C. G., Mineo, A., Lattin, G. L., Magaldi, M. G., Belmonte, G., Moore, C. J., Regoli, F., & Aliani, S. (2016). The Mediterranean Plastic Soup: synthetic polymers in Mediterranean surface waters. Scientific Reports, 6(1), 37551. https://doi.org/10.1038/srep37551

Wolff, S., Kerpen, J., Prediger, J., Barkmann, L., & Müller, L. (2019). Determination of the microplastics emission in the effluent of a municipal waste water treatment plant using Raman microspectroscopy. Water Research X, 2, 100014. https://doi.org/10.1016/j.wroa.2018.100014

Xiong, X., Wu, C., Elser, J. J., Mei, Z., & Hao, Y. (2019). Occurrence and fate of microplastic debris in middle and lower reaches of the Yangtze River – From inland to the sea. Science of the Total Environment, 659, 66–73. https://doi.org/10.1016/j.scitotenv.2018.12.313

Yan, M., Nie, H., Xu, K., He, Y., Hu, Y., Huang, Y., & Wang, J. (2019). Microplastic abundance, distribution and composition in the Pearl River along Guangzhou city and Pearl River estuary, China. Chemosphere, 217, 879–886. https://doi.org/10.1016/j.chemosphere.2018.11.093

Zobkov, M. B., Esiukova, E. E., Zyubin, A. Y., & Samusev, I. G. (2019). Microplastic content variation in water column: The observations employing a novel sampling tool in stratified Baltic Sea. Marine Pollution Bulletin, 138(May 2018), 193–205. https://doi.org/10.1016/j.marpolbul.2018.11.047