Hyperspectral imaging applied to microplastic monitoring in marine sediments from a highly contaminated coastal site (Taranto, southern Italy)

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Abstract In this work the presence of microplastics (MPs) within the marine sediments of the Mar Piccolo basin, located in Taranto (Apulia region, southern Italy) was evaluated for the first time using an innovative identification strategy based on hyperspectral imaging (HSI) operating in the short-wave infrared range (SWIR: 1000-2500 nm), combined with machine learning approaches. Sediment samples have been collected from 8 different sampling sites by means of a grab sampler in both bays of Mar Piccolo and then sieved. Hyperspectral images of known polymer particles and sediment samples of 5 size classes, from -4 mm to +710 μm, were acquired to build the calibration and validation dataset of the classification model. Several preprocessing algorithms were applied to improve the spectral differences between the selected classes of materials. After spectra preprocessing, principal component analysis (PCA) was applied to explore the spectral data variability. A hierarchical classification model based on partial least square-discriminant analysis (Hi-PLS-DA) was developed and applied to recognize MPs directly in marine sediment matrices. High-quality prediction results were obtained with values of recall and specificity close to 1. The classification model successfully identified MPs in marine sediments. The developed HSI-based identification strategy can represent a promising tool for rapid monitoring MPs with minimum preparation of samples, allowing to reduce analysis times.

Keywords: Hyperspectral imaging, microplastic pollution, marine environment, machine learning

Introduction

Plastic pollution represents one of the major environmental issues affecting coastal and marine ecosystems worldwide [1, 2]. In the last decade, the number of scientific publications dealing with macro- and micro-plastic pollution both in emerged and submerged environments has constantly increased [3-7]. Microplastics (MPs - i.e., particles with size smaller than 5 mm) are ubiquitous and comprehensive analyses [8-11] show that they are present in all the marine matrices (surface, water column, seafloor, biota), being marine sediment a sink for accumulation of MPs denser and lighter than seawater. In fact, positively buoyant plastics can increase their density and sink as a consequence of fouling by organisms and adherence of particles [12].

Based on their use and origin, MPs can be classified as “primary”, which include MPs indirectly used as row material for the production of polymer products and MPs for direct uses, such as in cleaning and beauty products, scrubs, and abrasives, and “secondary”, which include MPs that originate from the breakdown of larger plastic items into small fragments as a consequence of physical, mechanical, and chemical degradation or biological decomposition.

Due to its semi-enclosed characteristics and unique oceanographic setting, coupled with the high population density, the Mediterranean Sea is considered a hotspot for plastic pollution [13, 14]. The basin represents also one of the busiest shipping routes and receives inputs from highly densely populated river catchments (e.g., Nile, Ebro, and Po - UNEP, 2015 [15]). Based on the results of a large-scale study performed to analyze plastic debris in surface water in the Mediterranean Sea [16], different types of plastic items are predominant (pellets/granules, films, fishing threads, foam, fragments) and the majority is represented by fragments of larger objects (87.7%; e.g. bottles, caps) and thin films (5.9%; e.g. pieces of plastic bags or wrappings). On the other hand, according to the analysis performed by Papadimitriu and Allison [17] to assess current trends of MPs in the Mediterranean marine environment, the highest concentrations of MPs have been found in areas heavily polluted by agricultural, aquaculture, and industrial wastewater or characterized by and poor local waste management.

For what concerns the methodological aspects for sampling and analysis of MPs, the “Guidance on the monitoring of marine litter” published by the European Commission [18] represents the most recent reference document for guidelines and procedures. Although there is still a lack of standardized methods for the collection of MPs in sediments, grabs or cores are widely used to collect marine samples. Similarly, several methods are available for the MPs identification and classification.

Separation methods include density, electrostatic, magnetic, and oil and solvent extraction [19]. Among these, density separation is the most applied [20]. Nevertheless, it has the disadvantage of being time-consuming and

potentially hazardous for the discharging of polluting extraction solutions. The separation efficiency of such approaches is mainly related to the characteristics of MPs particles such as polymer type, size, and shape [21].
In this study, an innovative methodological approach based on hyperspectral imaging (HSI) is proposed to identify MPs in sediments collected in the Mar Piccolo basin (Gulf of Taranto, southern Italy) during a sampling campaign carried out in December 2022. The area of Taranto is characterized by the presence of high-density anthropogenic activities, including industrial districts, shipyards and arsenals, and intensive mussel aquaculture plants, which have led to relevant environmental modifications. The study area has been selected since, due to the high level of environmental risk, it is included in the Italian list of contaminated Sites of National Interest (SIN in Italian). Despite the numerous activities performed to assess the level and the extent of chemical contamination in the marine sediment [22-25], as well as the distribution of mega litter and anthropogenic traces on the seafloor [26, 27], no studies are available in the literature to define the MPs density and their most likely source. Recent investigations have focused on MPs occurrence in sediments sampled along the Ionian coast of the Basilicata Region [28]. Therefore, this research represents the first attempt to monitor the MPs distribution in the investigated sites.
In recent years, HSI has started to be applied for automated recognition of MPs from marine environments with reference to both sediments and seawater [29, 30]. In fact, the identification of polymers is particularly effective in the short-wave infrared (SWIR: 1000-2500 nm) range, based on their typical spectral signatures [31-33]. Therefore, HSI working in the SWIR range combined with machine learning approaches was applied to develop an efficient and rapid procedure for identifying MPs in marine sediments collected from Mar Piccolo basin.

Study area

The Mar Piccolo basin (Taranto, Apulia region, Southern Italy – Fig. 1a) is about 20 km^2 wide and it is divided in two bays, the First and the Second bay, with a maximum depth of 12 m and 8 m, respectively. It is a semi-enclosed sheltered sea with very low water circulation and characterized by the presence of several submarine springs that recharge the basins with freshwater. Such peculiar hydrogeological characteristics have determined typical transitional and lagoonal environmental features, which have favored the development of wide mussel farms. Despite its remarkable geo-environmental value, since the second half of the XIX century, the area has been strongly affected by the urbanization and industrialization processes such as the development of iron and steel industries, petrochemical and cement enterprises, and the construction of a military shipyard belonging to the largest Italian Navy naval base (Fig. 1b). The anthropogenic activities lead to the contamination of the different environmental matrices [34, 35, 36, 37, 25] such that the marine and coastal areas of Taranto have been considered one of the most polluted cities in Europe [38] and it has been included in the perimeter of the "SIN_07-Taranto" in 1998. The SIN covers a total area of 70 km^2 and includes the Mar Grande and Mar Piccolo coastal basins (Fig. 1c).

Fig. 1. Study area location. a) Geographical location of the Taranto area (Apulia Region). b) The green dashed circles identify the shipyards and docklands of the Italian Navy in the Mar Grande and Mar Piccolo (Bay I) and of the Italian Air Force in the Mar Piccolo (Bay II) whilst the blue circle identifies the ex-Tosi shipyard area. c) SIN_07 - Taranto perimeter. Blue lines identify the marine area included in the SIN perimeter whilst red lines identify the in-land areas. Background images in a) and b) were exported from Google Earth and modified by the authors whilst SIN perimeter in c) was provided by the Italian Ministry of the Environment.

The interest in the SIN of Taranto led various national, regional, and academic organizations to investigate the level of pollutants in the marine sediments. In 2010, the National Institute for Environmental Protection (ISPRA) determined the potential extent of the chemical pollution by analyzing sediment samples up to a depth of 3-5 m from the sediment-water interface [39]. The results of such activities were then updated with further

characterization by the Regional Agency for Environmental Protection (ARPA Puglia) [40, 41] and in 2015, the "Special Commissioner for urgent measures of reclamation, environmental improvements, and redevelopment of Taranto" (henceforth Special Commissioner) required multidisciplinary activities (geophysical, geotechnical, chemical, and sedimentological) to elaborate the site-specific geological model [42], the spatial distribution of organic and inorganic pollutants [43, 25], and the risk conceptual framework of the specific site [44]. Later on, different research was conducted to suggest specific protocols for efficient geo-morphodynamic and environmental characterization of the contaminated coastal areas [27]; mapping the traces of direct and indirect anthropogenic activities on the seafloor through the interpretation of morpho-acoustic data [36] and defining the distribution of trace metals by also evaluating the thickness of the sediments potentially affected by pollution [25].

Materials and methods

Marine sediments sampling and grain-size analysis

Marine sediments were collected using a grab sampler installed on board a ship. Sampling sites (MP_01 – MP_08) were defined in both sub-basins of the Mar Piccolo (the First Bay and the Second Bay – Fig. 2a) accounting for the distribution of the mussel farm facilities (Fig. 2b, c), that obstructed the passage of the ship, and the mouth of the main rivers that flow in the basins (Galeso and Cervaro). Once collected, samples were transferred to the laboratory of the Department of Earth and Geoenvironmental Sciences of University of Bari Aldo Moro (Italy) for granulometric analysis. To minimize background contamination, sediments were stored in glass containers covered with an aluminum foil, under light-absence conditions and kept at low temperatures.

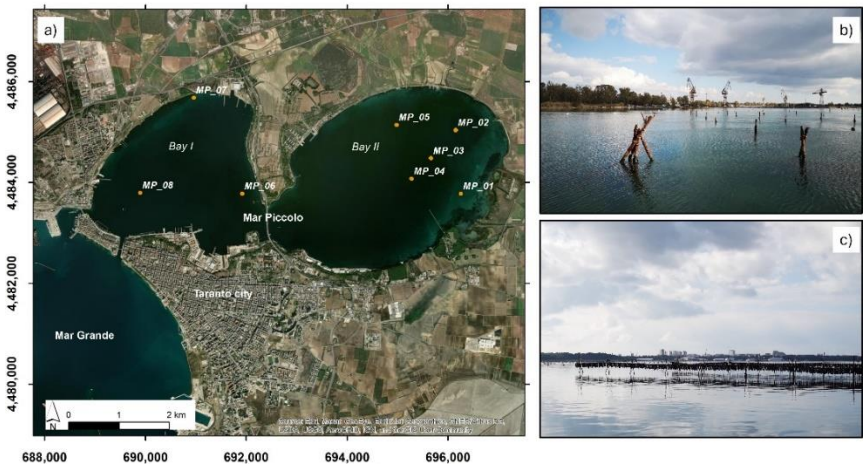


Fig. 2. a) Sampling sites in the Mar Piccolo Basin. b) Mussel farm facilities in the First Bay. c) Mussel farms in the Second Bay.

Grain-size analyses were carried out by following international standard procedures. For the sieving, a set of ASTM sieves with meshes of ½ phi from 4 mm to the minimum granulometric fraction was used. In the laboratory, samples were firstly weighed and then dried in the oven at a temperature between 30 and 50° C for at least three consecutive days. The temperature range was set to avoid modifications in the polymers' physical and structural properties. Then, each sample was quartered and set in a sieve column. The sand sediments from 2.0 mm to 0.063 mm were sieved with the vibrating screen for a duration of 20 min [45]. Subsequently, each retained fraction was weighed and the results were processed with a specific application for Microsoft Excel (Gradistat© v8), which yields distribution cumulative curves, and histograms, and statistically evaluates the main textural parameters. Grain-size analyses of the fraction < 63 μm were conducted by the use of Coulter counter that works on dispersing samples. The results of this analytical phase were then integrated into the analysis software.

Once sediment samples are categorized based on their textural parameters, effective methods for identifying MPs are needed.

Hyperspectral imaging

Hyperspectral image acquisitions were performed at the Raw Materials Laboratory (RawMaLab) of the Department of Chemical Engineering, Materials & Environment (DICMA) of Sapienza University of Rome (Italy) using the SISUChema XL™ Chemical Imaging Workstation (Specim Ltd., Oulu, Finland) equipped with the spectrograph ImSpector^{TM} N25E (Fig. 3). Hyperspectral images were acquired in push-broom mode, scanning the investigated samples line by line. The selected configuration uses a 31-mm lens with 50 mm field of view (FOV), a spatial resolution of 150 μm/pixel and a scanning speed of 17.35 mm/s. The device is equipped with a diffuse line illumination unit composed by halogen lamps, producing dual linear light covering a spectrum range from 920 to 2514 nm. Image data are automatically calibrated to reflectance by measuring an internal standard reference target before each sample scan.

Fig. 3. HSI acquisition platform used to acquire the examined marine sediment samples.

Marine sediment samples preparation for hyperspectral imaging analysis

Plastic waste flakes of 6 different polymers (Fig. 4a) and selected portions of marine sediment samples (Fig. 4b, 4c) collected from Mar Piccolo, subdivided in 5 size classes (-4/+2.8 mm, -2.8/+2 mm, -2/+1.4 mm, -1.4/+1 mm, and -1 mm/+710 µm), were used as calibration (CAL) and validation (VAL) datasets to build and apply the classification model.

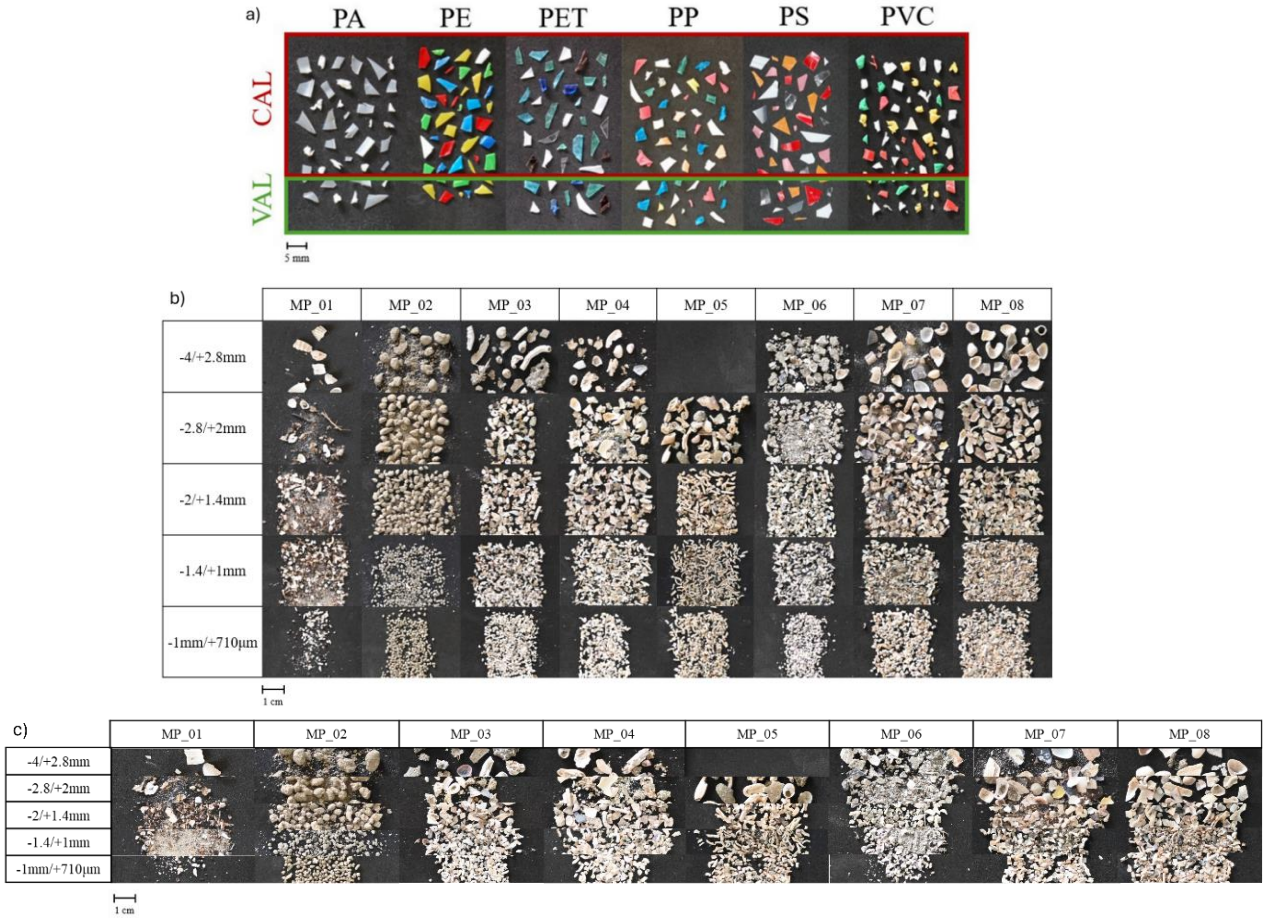
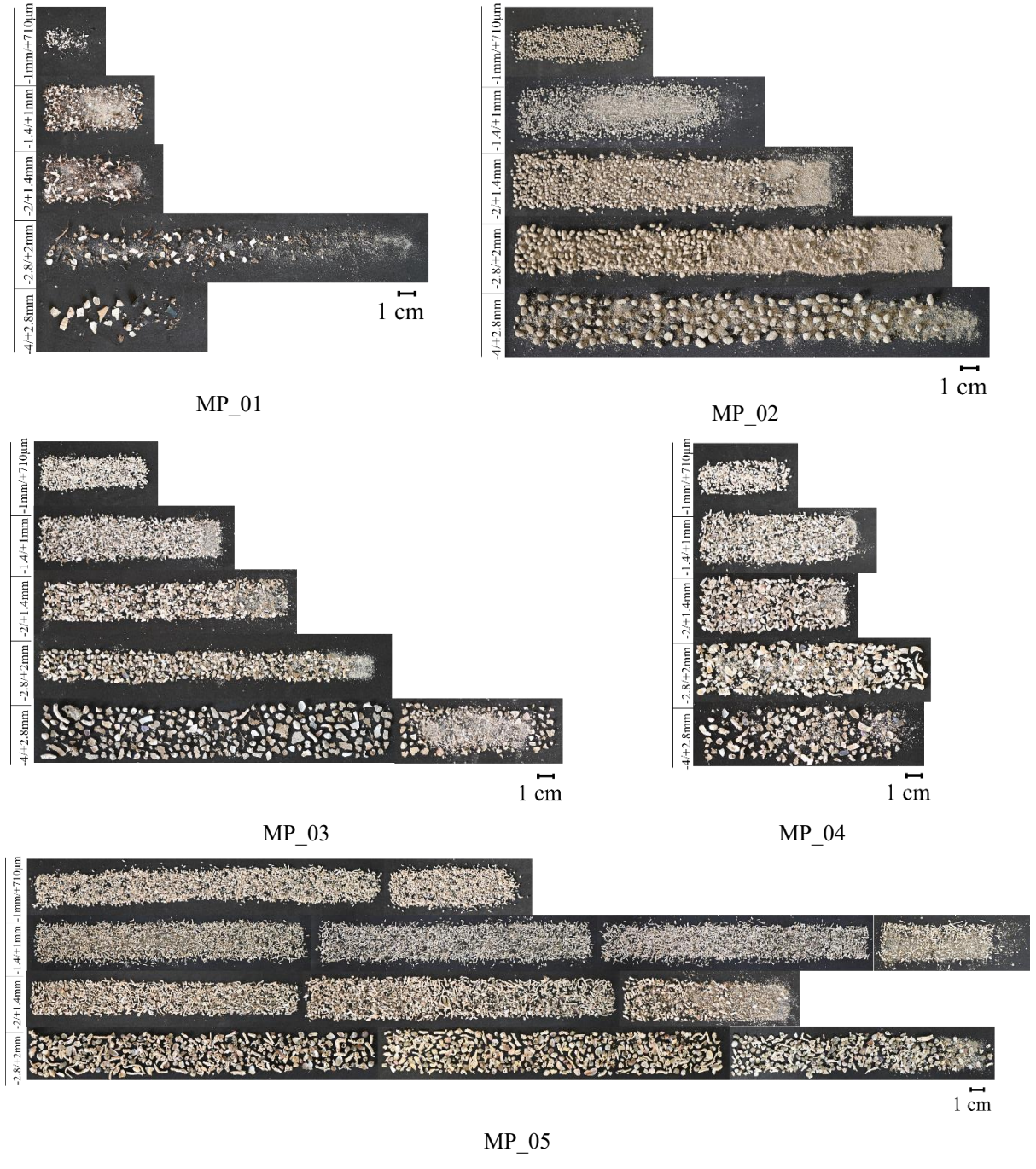


Fig. 4. Source images of the samples used to build the calibration and validation datasets of the classification model. a) Polymer waste flakes selected for the calibration (red) and validation datasets (green). b) Marine sediments without MPs selected for the calibration dataset. c) Marine sediments without MPs selected for the validation dataset.

The selected polymers are among the most commonly used worldwide [46], i.e.: polyamide (PA), polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS) and polyvinyl chloride (PVC). These plastic samples were chosen to include a wide spectral variability based on shape, thickness and color. The sediment samples of the calibration and validation datasets were preliminary investigated under a Leica M2015C stereomicroscope to manually remove any MPs, in order to acquire the spectral signature of matrices.
Finally, the classification model was applied to the hyperspectral images of the real marine sediments from Mar Piccolo, subdivided in the 5 grain size classes and placed in monolayers of 5 cm strips (corresponding to the FOV of the used HSI configuration) to evaluate the presence of MPs in these environmental matrices (Fig. 5).
The acquired hypercubes were analyzed using PLS-toolbox (version 9.2, Eigenvector Research, Inc.) working into MATLAB environment (MATLAB R2022a, version 9.12, The Mathworks, Inc.).



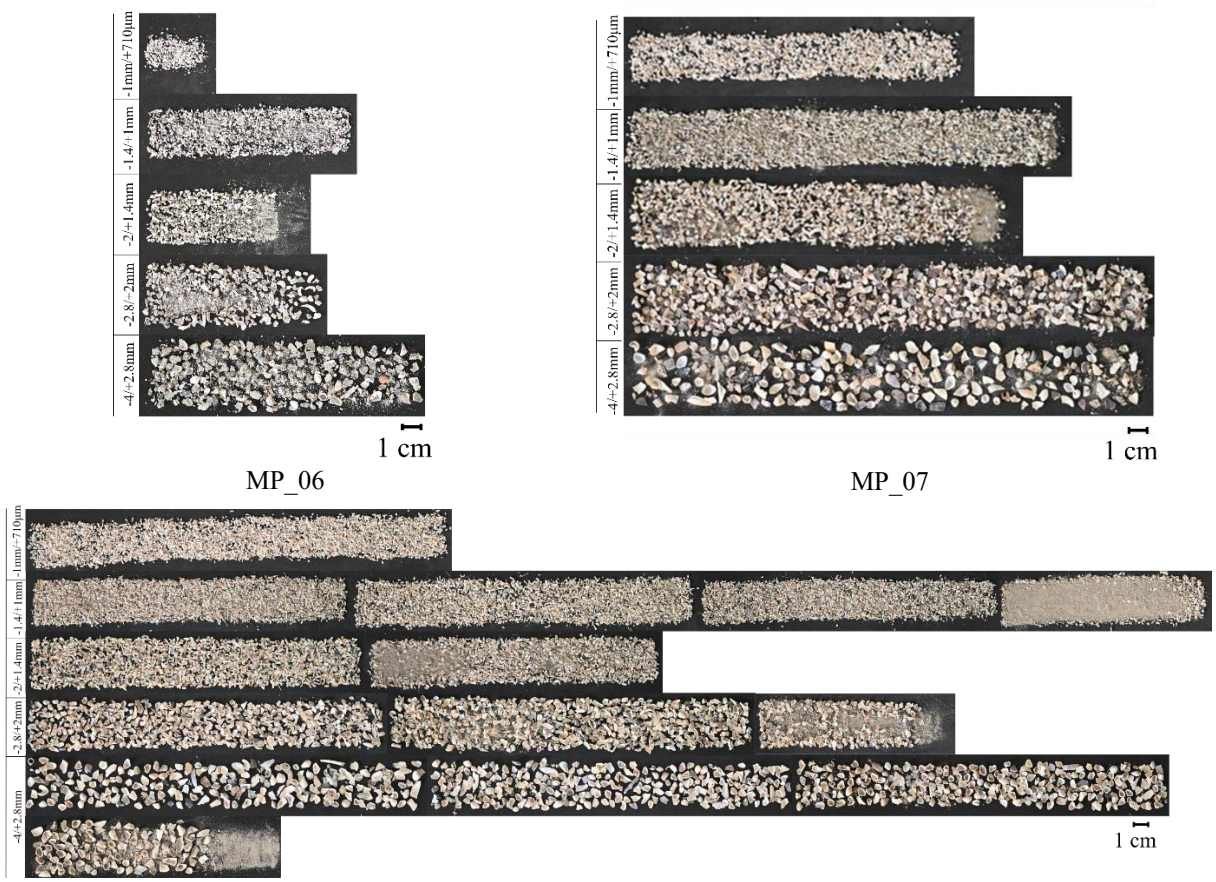


Fig. 5. Source images of the real marine sediments (from the Mar Piccolo) used to evaluate the presence of MPs by applying the classification model.

Data pre-processing and Principal Component Analysis (PCA)

Different pre-processing algorithms were applied to data, highlighting the spectral differences of the 7 selected classes of materials (i.e., PA, PE, PET, PP, PS, PVC and Sediment), eliminating undesirable phenomena and reducing noise, such as light scattering [47, 48]. The used pre-processing algorithms are: scattering correction methods (i.e., Multiplicative Scatter Correction – MSC; Detrend; Standard Normal Variate – SNV; Normalization), spectral derivatives (i.e., Savitzky-Golay polynomial derivative filters) and data centering (i.e., Mean Center - MC) [48, 49].

After pre-processing, PCA was applied to spectral data for exploratory purposes, providing an overview of the multivariate data [50].

Hi-PLS-DA classification model building and evaluation

Starting from the information obtained by PCA and given the complexity of the spectral data, a hierarchical classification approach (Hi-PLS-DA) was adopted, based on 6 PLS-DA classification models useful to identify the 7 selected classes of materials (i.e., PA, PE, PET, PP, PS, PVC and Sediment).

Contiguous Block method was applied as cross-validation for each rule, to evaluate the classification models and to select the number of Latent Variables (LVs) [31, 51].

The performances of the Hi-PLS-DA model applied to the validation dataset were measured in terms of statistical parameters (pixel-based) in prediction, i.e., recall (or sensitivity in binary classification), and specificity (Eq.1 and Eq.2), where values equal to 1 correspond to the perfect prediction value [52].

The particles classified by Hi-PLS-DA as MPs were subsequently validated using Fourier-Transform Infrared spectroscopy with Attenuated Total Reflection (FTIR-ATR).

$$Recall = \frac{TruePositive}{TruePositive + FalseNegative} \quad (1)$$

$$Specificity = \frac{TrueNegative}{TrueNegative + FalsePositive} \quad (2)$$

Results and discussion

Granulometric classes

According to the results of the grain-size analysis, the sediments of the Mar Piccolo show a large variety of granulometric classes, being mainly composed of silt (ranging from very coarse to medium silt) and sand (from very fine to coarse sand). In fact, sample sediments are characterized by a range of mean size limited between 0,898 phi (coarse sand) and 6,588 phi (medium silt). This information is also confirmed by the cumulative curves which also show the presence of poorly sorted sediments (Fig. 6).

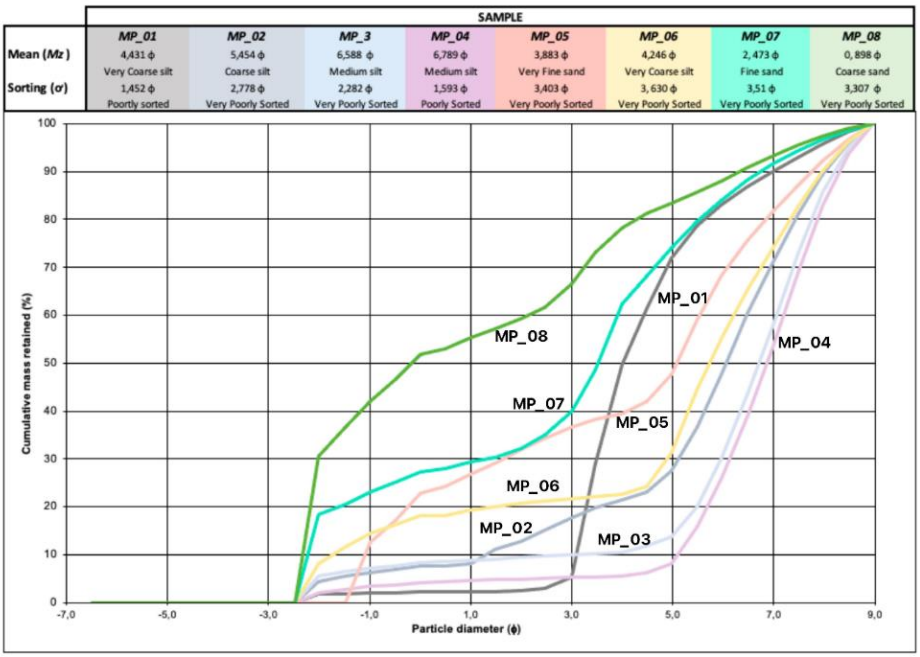


Fig. 6. Mar Piccolo sediments characterization. The values of the main granulometric parameters (mean size and sorting) are indicated in the upper part of the figure and showed using the cumulative curves. Each color in the table and graph correspond to a specific sediment sample.

Average raw reflectance spectra

The average raw reflectance spectra of the 7 selected classes of materials for the calibration dataset are reported in Fig. 7. Sediment and polymer classes show different spectral absorption bands in the SWIR range.

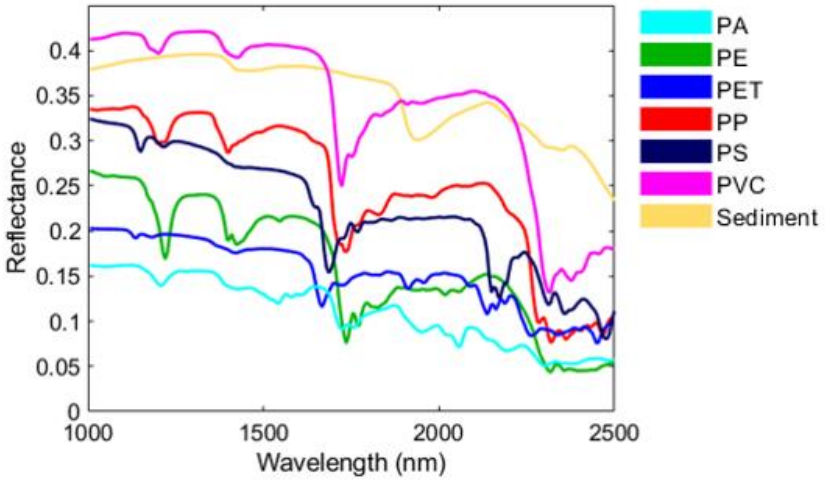


Fig. 7. Average raw reflectance spectra of the 7 selected classes of materials (i.e.: 6 polymers and sediment matrix) in the SWIR range.

Preprocessing strategies, PCA and characteristics of the Hi-PLS-DA model

The absorption bands in the SWIR range, corresponding to the harmonic and combination regions of the studied samples, were highlighted by the different preprocessing strategies selected for each rule and explored using PCA.

The results of PCA in terms of score plots, for each rule of the Hi-PLS-DA, are shown in Fig. 8. In PCA-RULE 1 (Fig. 8a), the score plot shows the clear separation between sediment scores and polymers scores (PA, PE, PET, PP, PS and PVC). In PCA-RULE 2 (Fig. 8b), the scores plot shows the division of PET+PS from PA+PE+PP+PVC score clouds. In PCA-RULE 3 (Fig. 8c), the score plot shows the separation between PET scores and PS scores. In PCA-RULE 4 (Fig. 8d), the scores plot highlights the division of two clouds related to PA+PE and PP+PVC score clouds. In PCA-RULE 5 (Fig. 8e), the score plot shows the division of PA and PE score clouds. In PCA-RULE 6 (Fig.8f), the score plot shows the division of PP and PVC score clouds.

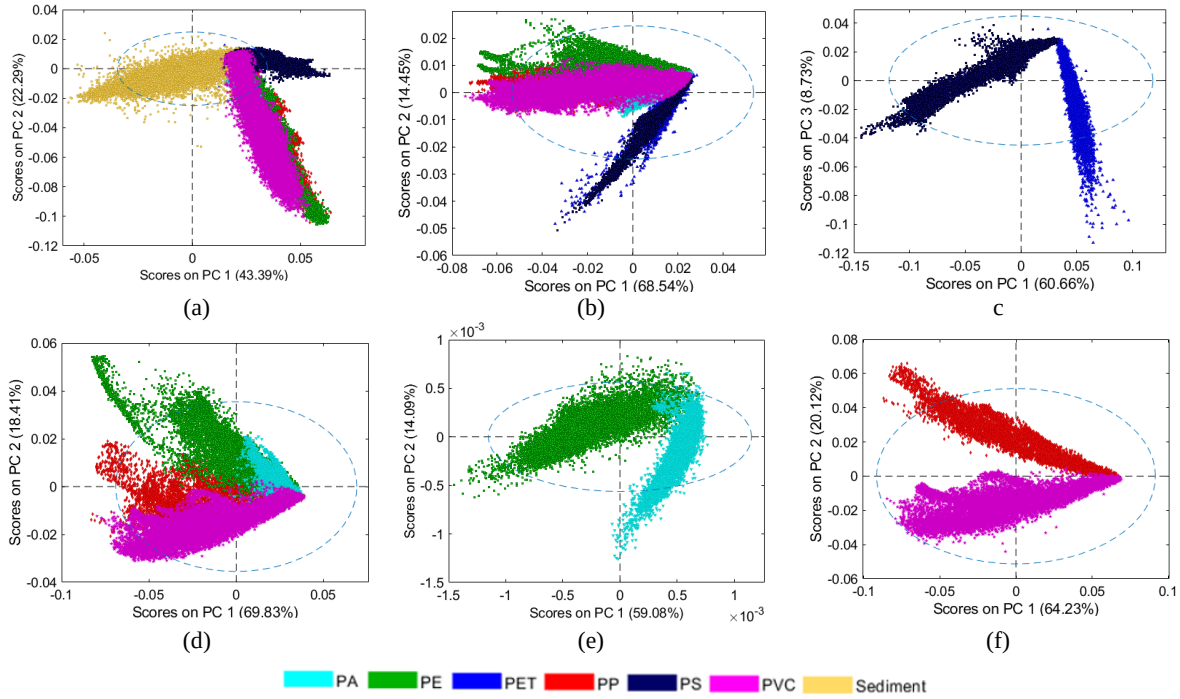


Fig. 8. PCA score plots related to the 6 different rules used to build the Hi-PLS-DA model.

The structure of the hierarchical model is shown in Fig. 9, displaying the relationships between the different rules. The preprocessing strategies selected for each rule and evaluated using the information obtained by PCA are reported in Table 1.

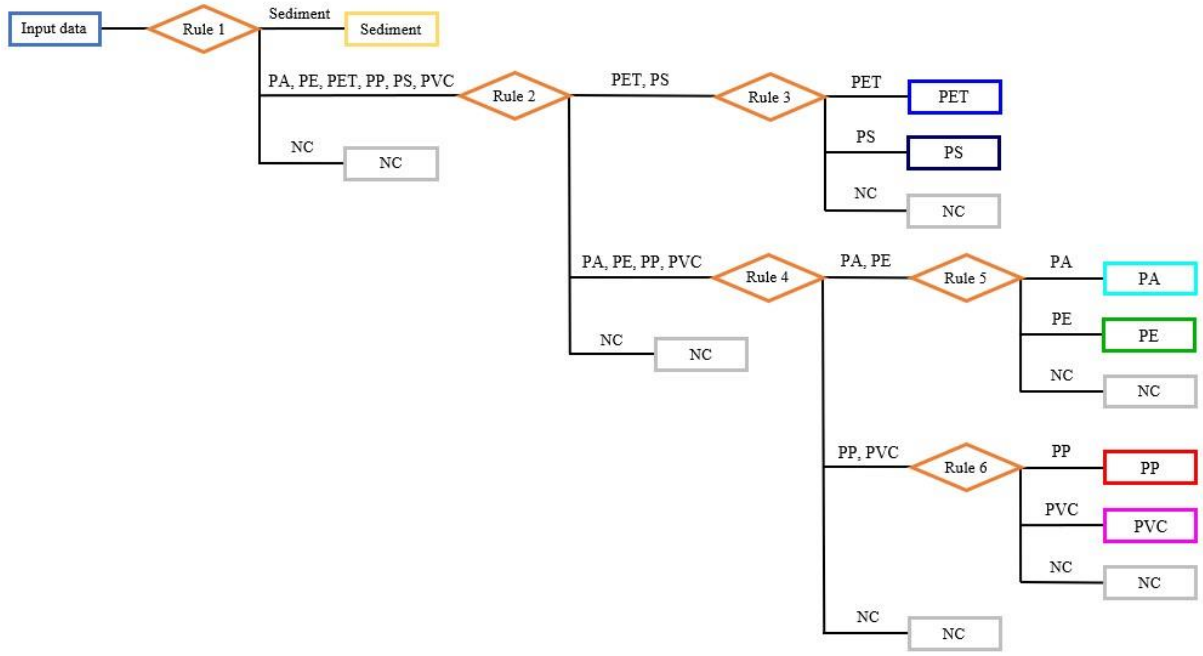


Fig. 9. Structure of the Hi-PLS-DA model.

Table 1. Pre-processing strategies used for the 6 rules of the Hi-PLS-DA model and corresponding output.

Rules	Applied preprocessing	Output
Rule 1	Detrend, 1st Derivative, MC	2 outputs: Sediment/PA+PE+PET+PP+PS+PVC
Rule 2	Gap segment 1st Derivative, Multiway center	2 outputs: PET+PS/PA+PE+PP+PVC
Rule 3	1st Derivative, MC	2 outputs: PET/PS
Rule 4	Detrend, 1st Derivative, MC	2 outputs: PA+PE/PP+PVC
Rule 5	Normalize, 1st Derivative, MC	2 outputs: PA/PE
Rule 6	Baseline, 1st Derivative, MC	2 outputs: PP/PVC

Classification performance

The classification results of the validation dataset in terms of false color predicted images are shown in Fig. 10. A satisfactory classification was achieved for each class by Hi-PLS-DA, considering the complex spectral scenario, except for some pixels attributed to the PA class at the edges of some sediment particles, in particular in grain-size classes -2/+1.4 mm of MP_01 and MP_03 and -1.4/+1 mm of MP_01 and MP_04.

The classification results of validation dataset in terms of statistical parameters in prediction phase are shown in Table 2. In particular, the classification model shows high-quality prediction performance, with recall and specificity values from 0.99 to 1.00.

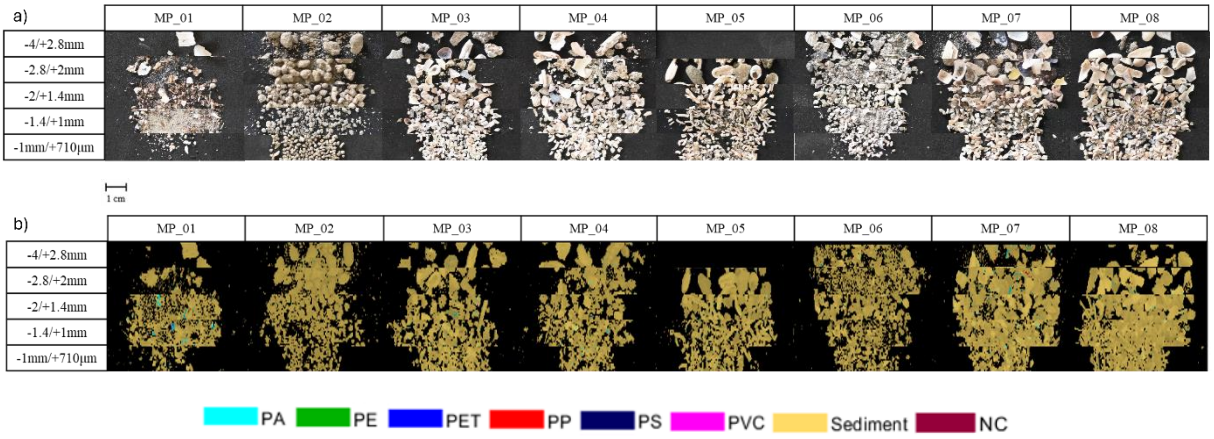


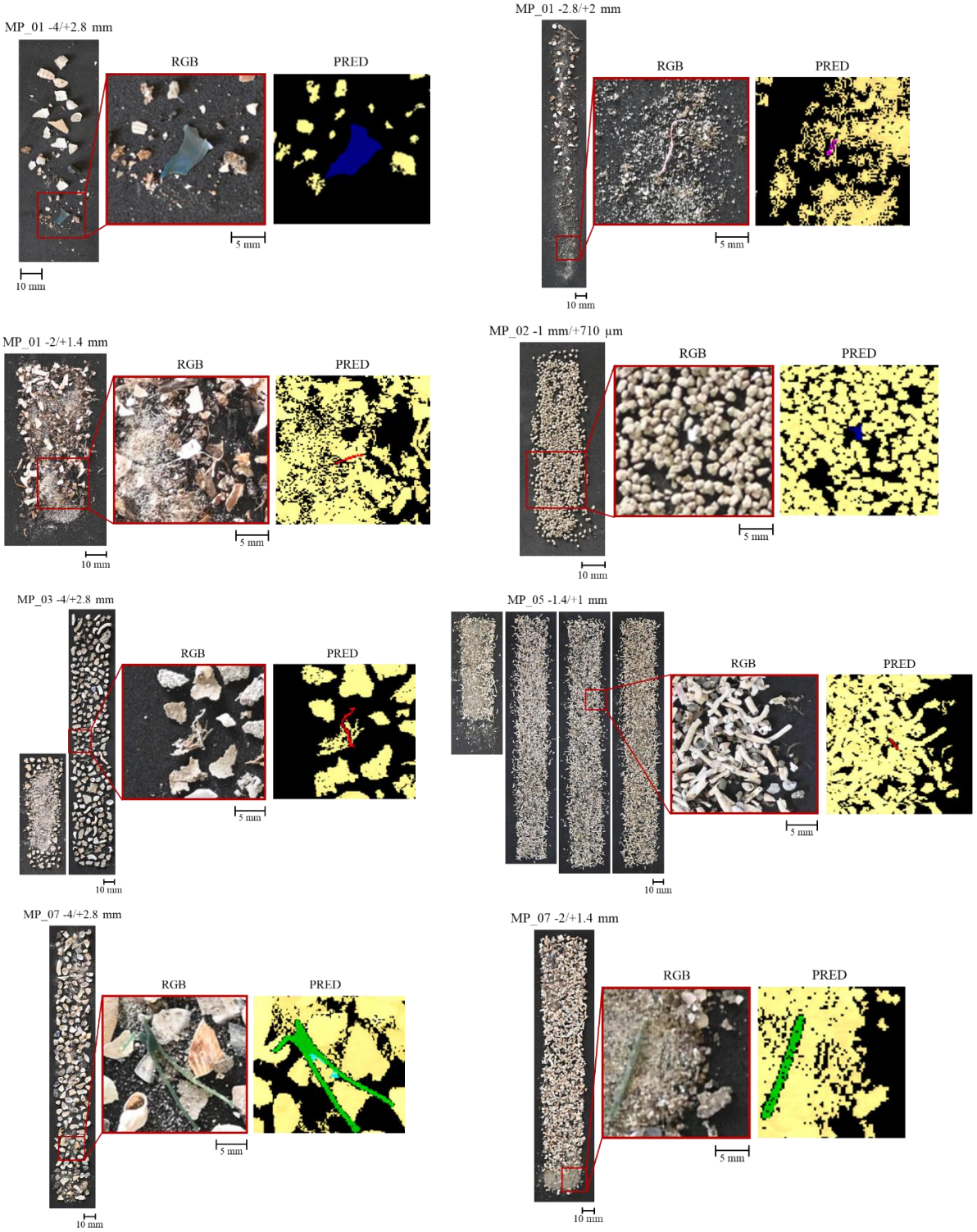
Fig. 10. a) Source images of validation dataset. b) Hyperspectral images of the validation dataset showing the classes predicted by Hi-PLS-DA.

Table 2. Recall and specificity values in prediction of validation dataset obtained by Hi-PLS-DA model.

Class	Recall (Pred)	Specificity (Pred)
PA	0.99	0.99
PE	0.99	0.99
PET	1.00	0.99
PP	1.00	0.99
PS	1.00	0.99
PVC	0.99	0.99
Sediment	0.99	0.99

The classification results in terms of predicted images of the real marine sediments and the corresponding source images are shown Figure 11. MPs in the sediment samples were properly identified by the Hi-PLS-DA model. In total, the classification model correctly recognized 11 MPs. The composition of such particles was verified by FTIR-ATR, confirming the correct recognition obtained by the developed HSI-based strategy. The results show a wide variability in MPs distribution with respect to grain size classes. Therefore, no correlations are highlighted between the presence of MPs and grain size classes. Concerning the MPs distribution with respect to sampling points in the Mar Piccolo basin, the results show a higher number of MPs particles in the MP_07 sample (4

particles), followed by MP_01 (3 particles). In the other sampling sites, i.e. MP_02, MP_03, MP_05 and MP_08, only 1 MP particle is recognized for each point. On the contrary, in the MP_04 and MP_06 sampling points no MPs particles are found.



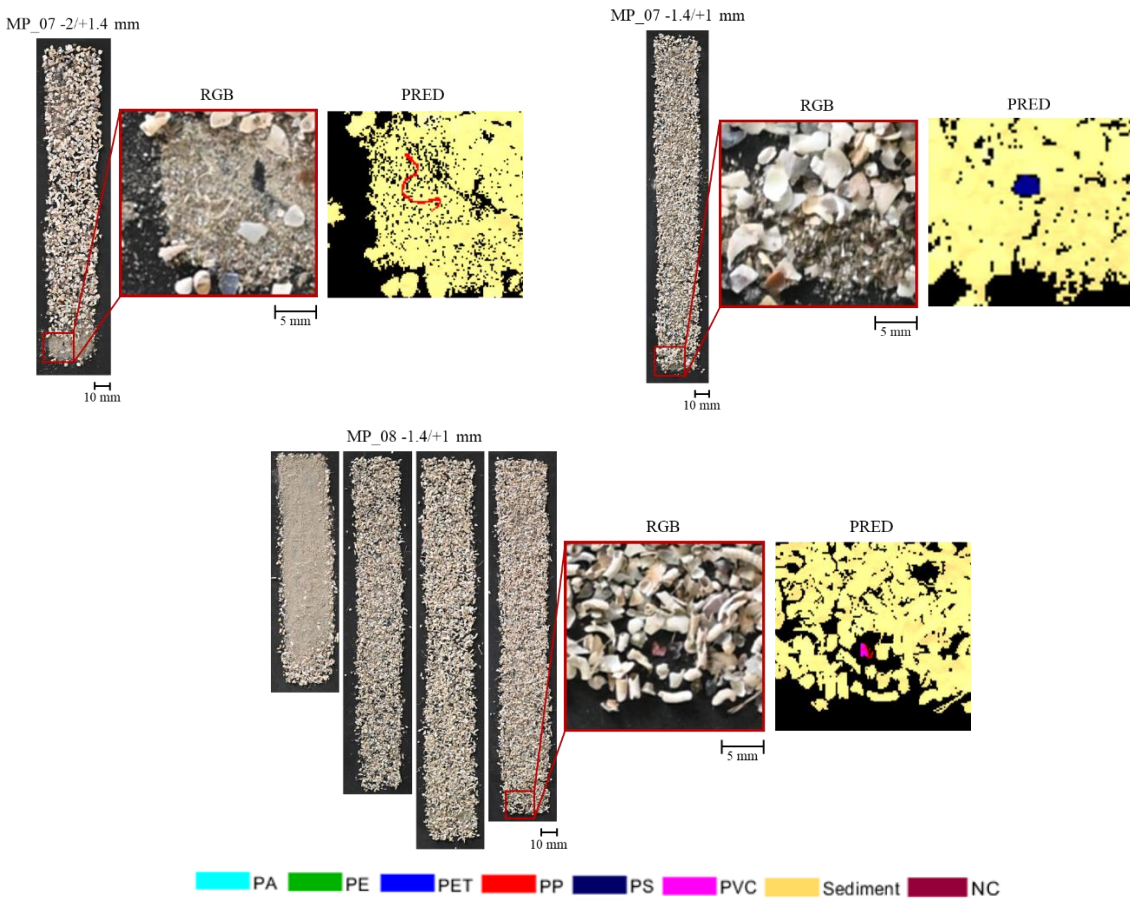


Fig. 11. Real marine sediment samples investigated by the Hi-PLS-DA model. Details of both source images and predicted hyperspectral images in which the presence of MPs is highlighted.

The abundances of polymers (number of particles and number %) constituting the MPs identified in the real marine sediment samples by Hi-PLS-DA model are shown in Fig. 12. In particular, the most abundant polymer is PP, followed by PS, PE and PVC, whereas PA and PET are not detected. Furthermore, the type of polymers found in the real marine sediments is in agreement with the results of other studies carried out on marine environments [53, 54], reflecting their common use in plastic products with a short-life cycle [55].

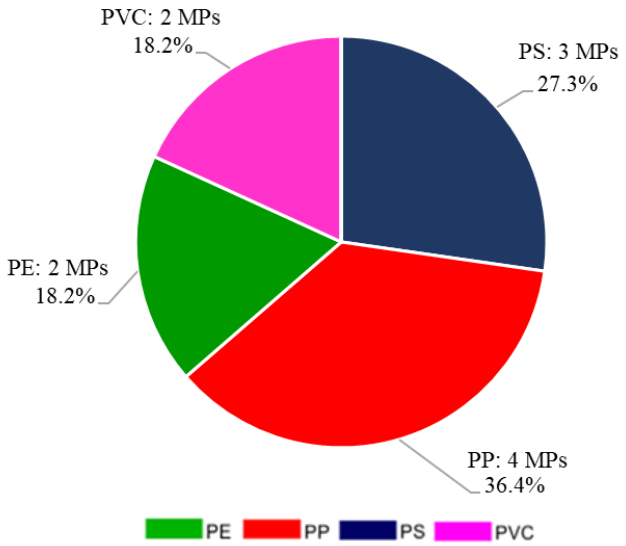


Fig. 12. Abundance (number of particles and number %) of polymers identified by the Hi-PLS-DA model in the real marine sediment samples.

Conclusions

In recent years, MPs have emerged as a significant focus in environmental studies. However, there are still numerous technical limitations and concerns that need to be addressed to enhance environmental monitoring efforts. This study aimed to assess the feasibility of utilizing HSI for the rapid and non-destructive identification of MPs in marine sediments from Mar Piccolo basin (Apulia region, Italy). Marine sediments were collected using a grab sampler on a ship from 8 different collection points and grain-size analysis was carried out. The Mar Piccolo sediments exhibit a diverse range of granulometric classes, mainly composed of silt and sand. Five grain-size classes were investigated (-4/+2.8 mm, -2.8/+2 mm, -2/+1.4 mm, -1.4/+1 mm, and -1 mm/+710 µm) using HSI in the SWIR range, combined with machine learning approaches. In particular, a subset of these marine sediments, cleaned from MPs, along with known polymer particles from waste, was utilized to build a calibration and validation dataset of a hierarchical classification model based on PLS-DA (Hi-PLS-DA). Furthermore, the known plastic particles were selected to include a wide spectral variability by polymer type (among the most widespread: PA, PE, PET, PP, PS and PVC), shape, thickness and color, with average sizes ranging from 900 µm to 4 mm. The Hi-PLS-DA model exhibited high-quality prediction performance applied to the validation dataset, with recall and specificity values ranging from 0.99 to 1.00. Subsequently, the model was applied to verify the presence of MPs in the real set of marine sediments from the Mar Piccolo basin. Overall, the classification model successfully identified a total of 11 real MPs, with PP being the most abundant polymer (36.4%), followed by PS (27.3%), PE (18.2%), PVC (18.2%). The identification results showed that the higher number of MPs particles was found in the MP_07 sampling site, followed by MP_01. In MP_02, MP_03, MP_05 and MP_08 sampling sites, only 1 MP sample is recognized for each. No MPs particles are found in the MP_04 and MP_06 sampling sites. Moreover, no correlations are shown between the presence of MPs and grain size classes.

In conclusion, the results demonstrated the efficacy of the proposed procedure, combining HSI with machine learning, for the rapid and automated detection of MPs > 710 µm in marine sediments. This study presents an efficient approach that reduces analysis time and facilitates environmental monitoring efforts. Future research will explore marine sediments of smaller sizes, particularly those with a diameter <710 µm, requiring a different HSI architecture set up, for acquisitions with a smaller spatial resolution, and the building of a new classification model.

Acknowledgements

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References

1. Thushari, G.G.N., Senevirathna, J.D.M. Plastic pollution in the marine environment. Heliyon 6, e04709. (2020). https://doi.org/10.1016/j.heliyon.2020.e04709
2. UNEP, 2021 – United Nations Environment Programme. From Pollution to Solution: A Global Assessment of Marine Litter and Plastic Pollution. https://wedocs.unep.org/20.500.11822/36963 (2021).
3. Ansari, M., Farzadkia, M. Beach debris quantity and composition around the world: A bibliometric and systematic review. Marine Pollution Bulletin 178, 113637. (2022). https://doi.org/10.1016/j.marpolbul.2022.113637
4. Cesarano, C., Aulicino, G., Cerrano, C., Ponti, M., Puce, S. Scientific knowledge on marine beach litter: A bibliometric analysis. Marine Pollution Bulletin 173, 113102. (2021). https://doi.org/10.1016/j.marpolbul.2021.113102
5. Pauna, V.H., Buonocore, E., Renzi, M., Russo, G.F., Franzese, P.P. The issue of microplastics in marine ecosystems: A bibliometric network analysis. Marine Pollution Bulletin 149, 110612. (2019). https://doi.org/10.1016/j.marpolbul.2019.110612
6. Zhang, Y., Pu, S., Lv, X., Gao, Y., Ge, L. Global trends and prospects in microplastics research: A bibliometric analysis. Journal of Hazardous Materials 400, 123110. (2020). https://doi.org/10.1016/j.jhazmat.2020.123110
7. Zhou, Y., Wang, J., Zou, M., Yin, Q., Qiu, Y., Li, C., Ye, B., Guo, T., Jia, Z., Li, Y., Wang, C., Zhou, S. Microplastics in urban soils of Nanjing in eastern China: occurrence, relationships, and sources. Chemosphere 303, 134999. (2022).
8. Okoffo, E.D., Tan, E., Grinham, A., Gaddam, S.M.R., Yip, J.Y.H., Twomey, A.J., Thomas, K.V., Bostock, H. Plastic pollution in Moreton Bay sediments, Southeast Queensland, Australia. Science of the Total Environment 920. (2024). https://doi.org/10.1016/j.scitotenv.2024.170987
9. Bakaraki Turan, N., Sari Erkan, H., Onkal Engin, G. Current status of studies on microplastics in the world’s marine environments. Journal of Cleaner Production 327. (2021). https://doi.org/10.1016/j.jclepro.2021.129394

10. Costa, M.F., Barletta, M. Microplastics in coastal and marine environments of the western tropical and sub-tropical Atlantic Ocean. Environmental Sciences: Processes and Impacts 17, 1868–1879. (2015). https://doi.org/10.1039/c5em00158g
11. Cole, M., Lindeque, P., Halsband, C., Galloway, T.S. Microplastics as contaminants in the marine environment: A review. Marine Pollution Bulletin 62, 2588–2597. (2011). https://doi.org/10.1016/j.marpolbul.2011.09.025
12. Lobelle, D., Cunliffe, M. Early microbial biofilm formation on marine plastic debris. Marine Pollution Bulletin 62, 197–200. (2011). https://doi.org/10.1016/j.marpolbul.2010.10.013
13. Ziveri, P., Grelaud, M., Pato, J. Actions of cities and regions in the Mediterranean Sea area to fight sea pollution. European Parliament, Policy Department for Structural and Cohesion Policies, Brussels. (2023).
14. Sharma, S., Sharma, V., Chatterjee, S. Microplastics in the Mediterranean Sea: Sources, Pollution Intensity, Sea Health, and Regulatory Policies. Front. Mar. Sci. 8. (2021). https://doi.org/10.3389/fmars.2021.634934
15. UNEP, 2015 – Marine Litter Assessment in the Mediterranean ISBN No: 978-92-807. (2015).
16. Cózar, A., Sanz-Martín, M., Martí, E., González-Gordillo, J.I., Ubeda, B., Gálvez, J.Á., Irigoien, X., Duarte, C.M. Plastic Accumulation in the Mediterranean Sea. PLOS ONE 10, e0121762. (2015). https://doi.org/10.1371/journal.pone.0121762
17. Papadimitriu, M., Allinson, G. Microplastics in the Mediterranean marine environment: a combined bibliometric and systematic analysis to identify current trends and challenges. Micropl. & Nanopl. 2, 8. (2022). https://doi.org/10.1186/s43591-022-00026-2
18. Galgani, F., Ruiz-Orejón, L.F., Ronchi, F., Tallec, K., Fischer, E.K., Matiddi, M., Anastasopoulou, A., Andresmaa, E., Angiolillo, M., Bakker Paiva, M., Booth, A.M., Buhhalko, N., Cadiou, B., Clarò, F., Consoli, P., Darmon, G., Deudero, S., Fleet, D., Fortibuoni, T., Fossi, M.C., Gago, J., Gérigny, O., Giorgetti, A., González-Fernández, D., Guse, N., Haseler, M., Ioakeimidis, C., Kammann, U., Kühn, S., Lacroix, C., Lips, I., Loza, A.L., Molina Jack, M.E., Norén, K., Papadoyannakis, M., Pragnel-Raasch, H., Rindor, A., Ruiz, M., Setälä, O., Schulz, M., Schultze, M., Silvestri, C., Soederberg, L., Stoica, E., Storr-Paulsen, M., Strand, J., Valente, T., van Franeker, J., van Loon, W.M.G.M., Vighi, M., Vinci, M., Vlachogianni, T., Volckaert, A., Weiel, S., Wenneker, B., Werner, S., Zeri, C., Zorzo, P., Hanke, G. Guidance on the Monitoring of Marine Litter in European Seas - An update to improve the harmonised monitoring of marine litter under the Marine Strategy Framework Directive. (Report). Publications Office of the European Union. (2023). https://doi.org/10.2760/59137
19. He, D., Zhang, X., & Hu, J. Methods for separating microplastics from complex solid matrices: Comparative analysis. Journal of Hazardous Materials, 409, 124640. (2021).
20. Van Cauwenberghe, L., Devriese, L., Galgani, F., Robbens, J., & Janssen, C. R. Microplastics in sediments: a review of techniques, occurrence and effects. Marine environmental research, 111, 5-17 (2015).
21. Ahmed, M. B., Rahman, M. S., Alom, J., Hasan, M. S., Johir, M. A. H., Mondal, M. I. H., ... & Yoon, M. H. Microplastic particles in the aquatic environment: A systematic review. Science of The Total Environment, 775, 145793. (2021).
22. Cardellicchio, N., Buccolieri, A., Di Leo, A., & Spada, L. Heavy metals in marine sediments from the Mar Piccolo of Taranto (Ionian Sea, southern Italy). Annali di Chimica: Journal of Analytical, Environmental and Cultural Heritage Chemistry, 96(11-12), 727-741(2006).
23. Cardellicchio, N., Buccolieri, A., Giandomenico, S., Lopez, L., Pizzulli, F., & Spada, L. Organic pollutants (PAHs, PCBs) in sediments from the mar piccolo in taranto (ionian sea, southern Italy). Marine pollution bulletin, 55(10-12), 451-458. (2007).
24. Di Leo, A., Annicchiarico, C., Cardellicchio, N., Cibic, T., Comici, C., Giandomenico, S., & Spada, L. Mobilization of trace metals and PCBs from contaminated marine sediments of the Mar Piccolo in Taranto during simulated resuspension experiment. Environmental Science and Pollution Research, 23, 12777-12790. (2016).
25. Marsico, A., Rizzo, A., Capolongo, D., De Giosa, F., Di Leo, A., Lisco, S., ... & Scicchitano, G. Spatial Distribution of Trace Elements in Sub-Surficial Marine Sediments: New Insights from Bay I of the Mar Piccolo of Taranto (Southern Italy). *Water*, *15*(20), 3642 (2023).
26. Bracchi, V.A., Marchese, F., Savini, A., Chimienti, G., Mastrototaro, F., Tessarolo, C., Cardone, F., Tursi, A., Corselli, C. Seafloor integrity of the Mar Piccolo Basin (Southern Italy): quantifying anthropogenic impact. Journal of Maps 12, 1–11. (2016). https://doi.org/10.1080/17445647.2016.1152920
27. Rizzo, A., De Giosa, F., Di Leo, A., Lisco, S., Moretti, M., Scardino, G., ... & Mastronuzzi, G. Geo-Environmental Characterisation of High Contaminated Coastal Sites: The Analysis of Past Experiences in Taranto (Southern Italy) as a Key for Defining Operational Guidelines. *Land*, *11*(6), 878. (2022).
28. Cofano V, Mele D, Lacalamita M, Di Leo P, Scardino G, Bravo B, Cammarota F, Capolongo D. Microplastics in inland and offshore sediments in the Apulo-Lucanian region (Southern Italy). Mar Pollut Bull. doi: 10.1016/j.marpolbul.2023.115775. (2023).

29. Serranti, S., Palmieri, R., Bonifazi, G., & Cózar, A. Characterization of microplastic litter from oceans by an innovative approach based on hyperspectral imaging. *Waste Management*, 76, 117-125. (2018).
30. Serranti, S., Fiore, L., Bonifazi, G., Takeshima, A., Takeuchi, H., Kashiwada, S. Microplastics characterization by hyperspectral imaging in the SWIR range. *Proceedings of SPIE Future Sensing Technologies 2019*, Vol. 11197, Article Number 1119710. (2019).
31. Bonifazi, G., Capobianco, G., Cucuzza, P., Serranti, S., & Uzzo, A. Recycling-oriented characterization of the PET waste stream by SWIR hyperspectral imaging and variable selection methods. *Detritus*, 18, 42-49. (2022).
32. Bonifazi, G., Capobianco, G., & Serranti, S. Fast and effective classification of plastic waste by pushbroom hyperspectral sensor coupled with hierarchical modelling and variable selection. *Resources, Conservation and Recycling*, 197, 107068. (2023).
33. Bonifazi, G., Capobianco, G., Cucuzza, P., & Serranti, S. Hyperspectral imaging coupled with data fusion for plastic packaging waste recycling. *Proceedings of SPIE Future Sensing Technologies 2023*, Vol. 12327, Article number 123270K). (2023).
34. Cardellicchio, N., Buccolieri, A., Leo, A. D., Librando, V., Minniti, Z., & Spada, L. Methodological approach for metal pollution evaluation in sediments collected from the Taranto Gulf. *Toxicological & Environmental Chemistry*, *91*(7), 1273-1290. (2009).
35. Cardellicchio, N., Annicchiarico, C., Di Leo, A., Giandomenico, S., & Spada, L. The Mar Piccolo of Taranto: an interesting marine ecosystem for the environmental problems studies. *Environmental Science and Pollution Research*, *23*(13), 12495-12501. (2016).
36. Rizzo, A., De Giosa, F., Donadio, C., Scardino, G., Scicchitano, G., Terracciano, S., Mastronuzzi, G. Morpho-bathymetric acoustic surveys as a tool for mapping traces of anthropogenic activities on the seafloor: The case study of the Taranto area, southern Italy. Marine Pollution Bulletin 185, 114314. https://doi.org/10.1016/j.marpolbul.2022.114314 (2022).
37. Rizzo, A., Scicchitano, G., & Mastronuzzi, G. A set of guidelines as support for the integrated geo-environmental characterization of highly contaminated coastal sites. Scientific Reports, 14(1), 8198. (2024).
38. Spada, L., Annicchiarico, C., Cardellicchio, N., Giandomenico, S., Di Leo, A. Mercury and methylmercury concentrations in Mediterranean seafood and surface sediments, intake evaluation and risk for consumers. Int. J. Hyg. Environ. Health 215 (3), 418–426. (2012).
39. Ausili, A., Bergamin, L., & Romano, E. Environmental status of Italian coastal marine areas affected by long history of contamination. Frontiers in Environmental Science, 8, 34. (2020).
40. Vitone, C., Federico, A., Puzrin, A.M., Ploetze, M., Carrassi, E., Todaro, F. On the geotechnical characterisation of the polluted submarine sediments from taranto. Environ. Sci. Pollut. Res. 23 (13), 12535–12553 (2016).
41. Todaro, F., De Gisi, S., Labianca, C., Notarnicola, M. Combined assessment of chemical and ecotoxicological data for the management of contaminated marine sediments. Environmental Engineering & Management Journal (EEMJ) 18 (10). (2019).
42. Valenzano, E., Scardino, G., Cipriano, G., Fago, P., Capolongo, D., De Giosa, F., Mastronuzzi, G. Holocene morpho-sedimentary evolution of mar piccolo basin (taranto, Italy). Geografia Fisica e Dinamica Quaternaria 41, 119–135. (2018).
43. Massari, F., Cotugno, P., Tursi, A., Milella, P., Lisco, S., Scardino, G., Corbelli, V. Mapping of Organotin compounds in sediments of Mar Piccolo (Taranto, Italy) using Gas Chromatography-Mass Spectrometry analysis and geochemical data. In: 2021 International Workshop on Metrology for the Sea; Learning to Measure Sea Health Parameters (MetroSea), 21-26IEEE. (2021).
44. Cotecchia, F., Vitone, C., Sollecito, F., Mali, M., Miccoli, D., Petti, R., Corbelli, V. A geo-chemo-mechanical study of a highly polluted marine system (Taranto, Italy) for the enhancement of the conceptual site model. Sci. Rep. 11 (1), 1–26. (2021).
45. Lapietra, I., Lisco, S., Capozzoli, L., De Giosa, F., Mastronuzzi, G., Mele, D., Milli, S., Romano, G., Sabatier, F., Scardino, G. & Moretti, M. A potential beach monitoring based on integrated methods. Journal of Marine Science and Engineering, 10(12), 1949. (2022).
46. PlasticsEurope. The Circular Economy for Plastics: A European Analysis (2024).
47. Vidal, M., Amigo, J.M. Preprocessing of hyperspectral images. Essential steps before image analysis, Chemom. Intel. Lab. Syst. 117 138–148, https://doi.org/10.1016/j.chemolab.2012.05.009. (2012)
48. Rinnan, Å., Van den Berg, F., Engelsen, S.B., Review of the most common preprocessing techniques for near-infrared spectra, TrAC - Trends Anal, Chem 28 1201–1222, (2009)https://doi.org/10.1016/j.trac.2009.07.007.
49. Eigenvector, Model Building: Preprocessing Methods. https://wiki.eigenvector.com/index.php?title=Model_Building:_Preprocessing_Methods (accessed 26 April 2024).
50. Bonifazi, G., Fiore, L., Pelosi, C., Serranti, S., Evaluation of plastic packaging waste degradation in seawater and simulated solar radiation by spectroscopic techniques. Polymer Degradation and Stability. Volume 207. (2023). https://doi.org/10.1016/j.polymdegradstab.2022.110215.

51. Ballabio, D., Consonni, V. Classification tools in chemistry. Part 1: Linear models. PLSDA. Anal. Methods, 5, 3790–3798 (2013)
52. Cucuzza, P., Serranti, S., Capobianco, G., Bonifazi, G. Multi-level color classification of post-consumer plastic packaging flakes by hyperspectral imaging for optimizing the recycling process, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 302, (2023) https://doi.org/10.1016/j.saa.2023.123157.
53. Perumal K. and Muthuramalingam S. Global sources, abundance, size, and distribution of microplastics in marine sediments - A critical review. Estuarine, Coastal and Shelf Science. Volume 264. ISSN 0272-7714. (2022). https://doi.org/10.1016/j.ecss.2021.107702.
54. Marques Mendes A., Golden, N., Bermejo, R., Morrison L. Distribution and abundance of microplastics in coastal sediments depends on grain size and distance from sources. Marine Pollution Bulletin. Volume 172. ISSN 0025-326X (2021). https://doi.org/10.1016/j.marpolbul.2021.112802.
55. Erni-Cassola, G., Zadjelovic, V., Gibson, M. I., Christie-Oleza, J.A. Distribution of plastic polymer types in the marine environment; A meta-analysis. Journal of Hazardous Materials. Volume 369. Pages 691-698. ISSN 0304-3894 (2019). https://doi.org/10.1016/j.jhazmat.2019.02.067.