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Correction

Correction: Ricciardi et al. Microplastics in the Aquatic Environment: Occurrence, Persistence, Analysis, and Human Exposure. *Water* 2021, *13*, 973

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The original publication [1] had an error regarding the affiliation for Maria Ricciardi. The order of affiliations 1 and 2 was changed to align with the current affiliation of this author.

There was an error in the original publication [1]. Section 3.2 contains paragraphs written in the original draft and not revised by the authors before the final submission.

A correction has been made to Section 3.2 Analytical Approaches for MP Separation, Identification, and Quantification. The corrected version is as follows:

"Several analytical methods have been developed to measure MP in water and the most important procedures include separation, identification, and quantification.

Separation of microplastics is usually achieved by sieves with mesh sizes from 0.038 to 4.75 mm, used singly or in a series. Moreover, filters with small mesh sizes (0.02–5 µm) are also used to separate small microplastics or nanoplastics [50,249]. For plastic particles <1 µm, chromatographic techniques, active, and passive separation, are typically used. Active separations, such as the field flow fractionation (FFF) technique [250], apply external fields into microfluidic environments for the separation of dispersed particles, while passive separations, such as hydrodynamic chromatography (HDC) [251], utilize hydrodynamic and surface forces to separate particles in liquid [252]. The extraction process is usually based on the different densities of the samples. When MPs are less dense than water, they can be directly separated using a net or filtered by filters or sieves [67]. Flotation is preferred with sediments. Low density plastics have a density range from 0.9 to 2.3 g/cm^3, while the density of sediments and soil particles is higher (2.6–2.7 g/cm^3). High density salt solutions such as $ZnCl_2$, $ZnBr_2$, NaCl, NaI, and $CaCl_2$ allow MPs to float and be separated from sediments that sink [253,254]. While this method is efficient for low-density microplastics, high-density microplastics such as polyvinyl chloride and polytetrafluoroethylene cannot be easily recovered. In order to separate plastics and organic matter from the minerals in the mixture solution after centrifugation, a rubber disc is inserted into the middle of a centrifuge tube. This expedient can prevent mineral particles from being resuspended, substantially reducing separation time [255]. Moreover, a high amount of organic matter could affect separation from MPs; for this reason, acid solvents, alkali solvents, or oxidation agents, including KClO (30%), NaOH (56% or 52.5 M), H_2SO_4 (96%), HNO_3 (65% or 22.5 M), and H_2O_2 (30% or 32.6 M), have been used to digest and remove organic matter from flotation [255]. However, a recent study demonstrated that many of these agents decompose, disintegrate, or modify the weight, number, and shapes of MP particles [256]. Polyamide (PA), polyester (PET), and polycarbonate (PC) have a low resistance to strong acids. PA, polyethylene (PE), and polypropylene (PP) are resistant to 10% KOH, but polycarbonate (PC) and PET are degraded. Treatment with NaOH 40% at T = 60 °C caused deformation of PA fibers, yellowing of PVC granules, and melding of polyethylene particles. Enzymatic digestion is a biological means to hydrolyze proteins and break tissues. Enzymes ensure no loss or degradation of plastics; however, enzymatic digestion can be long and expensive [257].

The quantification of MPs is still a major challenge, due to their special chemical and physical properties (very high molecular weights and poor solubility in most solvents). MPs cannot be analyzed by classical analytical methods such as Gas Chromatography-Mass Spectrometry (GC-MS) and Liquid Chromatography tandem-Mass Spectrometry (LC-MS/MS). Table 3 outlines the main analytical techniques employed for MP detection, advanced visualization, and counting, focusing on the operation principles, advantages, and disadvantages of each method.

Basically, two different analytical strategies have been discussed in recent publications [258–261]. The first one is based on the isolation of MP particles by density separation and spectroscopic identification [82,262,263] through Fourier-Transform Infrared Spectroscopy (FTIR, available in transmission, reflectance, and attenuated total reflectance, ATR) or Raman Spectroscopy. The reflectance and ATR modes do not require sample preparation steps for thick and opaque microplastics [264]. These methods deliver information about polymer species, particle numbers, and size distribution [265], important parameters used to estimate the microplastics' toxicological potential. Raman method spectroscopy (<125 mm and >5 mass%) [266], micro-Raman spectroscopy (>100 µm), micro-FTIR spectroscopy (>100 µm) [267], m-Raman spectroscopy (>1 mm), m-FTIR spectroscopy (>10 mm) [268], macroscopic dimensioned near-infrared (NIR) in combination with chemometrics (>10 mm and 1 mass%) [266], and hyperspectral imaging technology (0.5–5 mm) can be used to identify plastics type, but these techniques are time-consuming, and they can be expensive and result in an uncertain extrapolation of MP quantity [269]. For example, the ATR mode produces stable spectra even from irregular microplastic surfaces; however, a lot of microplastics are weathered or made of complex materials, thus an experienced operator is necessary for the acquisition and interpretation of the spectra. Moreover, the probe used in ATR is made of germanium and can be easily damaged by hard and sharp particles remaining on filter papers [264]. The Raman signal is suitable for particles below 20 µm, but the spectra are heavily influenced by dyes, additives, and organic and inorganic substances. In addition, some materials exhibit fluorescence, masking the vibrational information [270].

The second strategy is based on thermal decomposition coupled to mass spectrometry, which is more suitable for MP quantification. Unice et al. [253] developed a method for polymers of tires (sample amount of 0.5 mg) using pyrolysis-gas chromatography mass spectrometry (pyr-GC-MS). Quantification was based on specific pyrolysis products and deuterated internal standards. The method needed only minor sample preparations and yielded a limit of detection of 14 µg/g of tire tread in soil and sediments. For the quantification of thermoplastics, Duemichen et al. [254] described a combination of thermal extraction with thermogravimetric analysis and subsequent analysis with thermal desorption gas chromatography mass spectrometry (TDS-GC-MS) that required a sample quantity of more than 20 mg. After pyrolysis at 600 °C and enrichment of the degradation products on solid-phase absorbers, plastic species were quantified by GC-MS analysis detecting polymer-specific decomposition products [271]. The deficiencies of these methods are the expense of the equipment and the complicated operation process.

Identification of microplastics passes through visualization analysis to characterize the color, shape, and light transmission, using naked eyes or analytical methodologies like optical microscopy [34,272,273]. Different microscopy techniques can be used according to the dimension and the physical properties of the MP samples. A stereomicroscope, thanks to two separated optical paths, allows for obtaining three-dimensional images of a specimen.

Polarized light microscopy permits the acquisition of images at different heights [274]. Electron microscopy is useful for ambiguous particles [275,276]. In particular, electron microscopy coupled with X-ray (SEM-EDS) is a useful analytical technique to obtain high-resolution and chemical information and can identify plastic particles in complex matrices. Despite the efficiency of this technique for the chemical and morphological characterization of particles, there are some disadvantages associated with SEM-EDS analysis, such as a long time for the sample preparation and analysis, instability of some polymers, complex protocols for the analysis, and high costs of instrumentation [252].

Recently, new advanced techniques have been proposed for the characterization of microplastics, and sometimes, microplastics were produced in the laboratory to obtain standard reference materials. Monteleone et al. [277] used fluorescence lifetime imaging microscopy (FLIM) to characterize microplastics. Several kinds of microplastics produced with a cryogenic swilling mill, with and without heat treatment, were subjected to FLIM with excitation wavelengths of 470 nm and 440 nm. The fluorescence lifetimes of each microplastic were evaluated and compared and no significant differences emerged in the fluorescence lifetimes of PET samples coming from different countries; therefore, the lifetimes measured did not depend on the origin of the microplastics.

Berto et al. [278] reported a preliminary characterization of carbon stable isotopes ($^{13}\delta$) of different plastic polymers. Stable isotope analysis is a technique that measures the relative abundance of stable isotopes giving an isotopic ratio that can be used as a research tool. It is widely used in food analysis [279,280], in forensic cases [281], and in medical diagnostics [282] for the monitoring of indoor and outdoor air quality [283,284] and the characterization of commercial cleaning products [285]. This technique has been applied only rarely to assess the presence of microplastics. A proof-of-concept study was performed with fully labeled ^{13}C polyethylene to follow its fate across the aquatic microbial–animal interface. It emerged that the biodegradation of PE-MPs (<100 µm) occurred in natural waters, becoming part of nutritionally valuable biomolecules for aquatic organisms [286].

In [278,287], standard petroleum and plant-derived polymers were analyzed to estimate the carbon isotope ratio. The $^{13}\delta$ values of several polymers spanned over a wide range: PTFE, silicon, and ABS showed $^{13}\delta$ values between −41% and −35%, petroleum polymers had 13 values between −34% and −24%, and PLA (a biodegradable polyester derived from the fermentation of starch and condensation of lactic acid) had a value of −14%. Thus, this technique showed an interesting perspective for the discrimination between petroleum and plant-derived polymers in aquatic environments. Furthermore, unlike vibrational spectroscopy techniques such as Raman, it is not sensitive to variables such as colors.

Another analytical method includes high temperature gel-permeation chromatography (HT-GPC) coupled with an IR detector. HT-GPC-IR can assess polyolefin microbeads in aqueous environments and more complex matrices such as personal care products [288] and also gives the distribution of molecular masses.

In conclusion, FTIR and Raman spectroscopy are commonly used for identifying the polymeric composition of microplastics, whereas mass spectrometry-based methodologies, even though they require a lower amount of sample, are more expensive and trickier to operate. The same can be said by comparing optical microscopy, the most used technique for microplastic visualization, with the most advanced techniques such as SEM-EDS.

Consequently, interlaboratory analyses should be performed to provide comparability of data regarding the chemical characterization and quantification of microplastics. In fact, the use of one technique can only lead to the overestimation or underestimation of microplastics. Fragmented microplastics were underestimated and fibers were overestimated using stereomicroscopy compared to FTIR in samples coming from sea surface microlayers and beach sand. The total abundance by FT-IR was higher than by microscopy both in the sea surface microlayers and beach sand samples. Stereomicroscopy mainly allowed for the identification of 50–100 µm fragmented microplastics, while FTIR also identified smaller sizes [289].

Therefore, in Scheme 1, we reported a possible simple protocol for the identification of microplastics in aqueous samples that can include a first preparation step of the sample (identification of organic matter presence with the preliminary treatment of degradation), separation with sieves with different mesh sizes, a visualization step with a microscope to count and estimate the sizes of the MPs, and in the end, a screening with FT-IR or Raman to identify the chemical composition of the MPs.

Although new accurate and sophisticated analytical methods have been reported for microplastic detection and characterization, FT-IR and Raman spectroscopy remain those commonly used for identifying the polymeric composition of microplastics due to their inexpensiveness and user-friendliness."

The authors state that the scientific conclusions are unaffected. This correction was approved by the Academic Editor. The original publication has also been updated.

Reference

1. Ricciardi, M.; Pironti, C.; Motta, O.; Miele, Y.; Proto, A.; Montano, L. Microplastics in the Aquatic Environment: Occurrence, Persistence, Analysis, and Human Exposure. *Water* **2021**, *13*, 973. [CrossRef]