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Low molecular weight polymers in aquatic environments as pollutants of emerging concerns: recovery, quantification and microstructure

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Abstract Microplastics and, more in general, synthetic polymer debrides of anthropic origin are accumulating in the environment, in particular in marine water and sediments, with risks associated for aquatic organisms and humans not well wholly understood. In this contribution it is reported a new method for the isolation of microplastics from surface seawater and the quantification by solution ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR) with respect to a known concentration of an internal standard (mesitylene) dissolving the microplastics in 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2). TCE-d_2 is a high boiling solvent that allowed the analysis and quantification of poly(ethylene) (PE) and poly(dimethyl siloxane) (PDMS) MPs at 80 °C.

Keywords: microplastics; nanoplastics; recovery; seawater; marine; quantification, microfiltration, NMR spectroscopy, standard method

1. Introduction

Microplastics (MPs) and, more in general, synthetic polymer debrides (SPDs) of anthropic origin are currently accumulating in the environment[1] where the risks associated with aquatic organism life and human health are currently not well understood and result in emerging concern in the public opinion. Micro-fragments of low molecular weight SPDs often escape from the conventional filtering systems of municipal water, and their fate is the sea[2] and the marine sediments where they accumulate. Accurate protocols for the isolation, qualitative and quantitative identification, and characterization of these polymer samples in aquatic environment are not still well defined and accepted in the scientific community. In this contribution a new method for the quantification and characterization of MPs by solution ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (^{1}H - ^{13}C-NMR) is proposed with the aim to assess their origin. This method has been applied in a real case study: 120 samples of surface seawater, coming from two campaigns of sampling in the Mediterranean Sea, namely in the Gulf of Salerno and of Policastro in South Italy, have been collected and the corresponding data analyzed with unprecedented detail and precision.

2. Results

2.1. Recovery of microplastics from surface seawater

Four coastal surface seawater sampling campaigns (each including 30 samples taken within a distance of 20 km from the coast) were carried out along the coast, comprising the Amalfi Coast and the Gulf of Salerno, in Italy, in the period of time 14/06/2021 - 23/06/2021, repeated in the period 19/07/2021-28/07/2021, and along the Cilento Coast and the Gulf of Policastro, in Italy, in the period 27/10/2021-09 /11/2021, repeated in the period 22/11/2021 - 13/12/2021. Two liters of surface seawater were collected in glass bottles and microfiltered with a stainless steel Buchner-type apparatus, using cellulose nitrate filters with a pore size of 0.45 µm; these filters ensure filterability of seawater and the quantitative recovery of the particulate with a size bigger than 0.45 µm. Actually filters with porosity lower than 0.22 µm failed because of heavy clogging, with a consequent worsening of the analytical protocol for the quantitative weight estimation of the MPs. The filter is finally dissolved in acetone and the particulate completely recovered by centrifugation, then washed with fresh water, and dried by conventional methods. The MPs samples were analyzed by ^{1}H NMR spectroscopy using mesitylene as internal standard for the quantitative and qualitative assessment of the polymer samples. Low molecular weight polyethylene (PE) and polydimethylsiloxane (PDMS) were identified in high concentration in the proximity of the estuary of the local rivers; isolated islands of SPDs[3] were found in the Gulf of Salerno likely because of sea currents. A full assessment of the MPs concentration in the region of interest was created using the SURFER software. Furthermore, ^{13}C NMR and DOSY experiments of the PE

samples allowed assessing their very low molecular weight (≈1 kDa) and the presence of highly oxidized polymer chains. These results well compare with those from wastewater treatment plants of the same region (Tavernola (SA) and Punta Gradelle (NA) plants). Low molecular weight PDMS samples are also found in the same specimen with a lower concentration. Polypropylene (PP) concentration is always significantly lower than that of PE; noteworthy the PE/PP weight ratio in marine water is typically found 4:1 when these polymers result from degradation of SPDs in the environment. In our opinion these findings suggest that the molecular weight PE found in the Gulf of Salerno could belong from the PE waxes largely used for coating applications, food industry, cosmetics and detergents instead of coming prevalently from SPDs degradation. The concentration of PDMS comparable to that of PE seems to support the same conclusion. Actually silicone-based antifoamers are largely used in different fields for end use applications.

2.1. Ponderal quantification of surface seawater microplastics

The weight analysis of the microplastic content was carried out by introducing a known quantity of mesitylene into the samples as an internal standard, through which the microplastic. From the integrals of the signals of the PE methylene groups (1.12 ppm) and the mesitylene methyl groups (2.10 ppm, 1.12 ppm) have been thus determined the PE concentrations, in term of mg of the polymer per m^3 of seawater. Analogously the concentrations of PDMS have been determined from the corresponding methyl signals (-0.07 ppm).

PE concentration was in the range 0.7-70 mg_{PE}/m^3 while that of PDMS was below 3.2 mg_{PDMS}/m^3. As expected from the large use of PE with respect to PDMS, the concentration of the polyolefin largely exceeded that of the polysiloxane.

Coastal areas with higher population density, comprising wastewater treatment plants, port areas and rivers, are clearly the hot-spots for the emission of PE and PDMS microplastics. The areas with the highest concentration of this SPDs are near the Amalfi Coast and the port of Salerno with PE concentration peaks of 70 and 50 mg_{PE}/m^3, respectively. The maximum values reached in the Cilento coastal area and near Sapri in the Gulf of Policastro were about 18 and 15 mg_{PE}/m^3, respectively. The mentioned areas coincide with those with a greater population density and with the presence of wastewater treatment plants whose treated effluents are discharged into rivers or sea.

The PDMS concentration found in the two sampling campaigns is very low and narrow in the range 0-3.2 mg_{PDMS}/m^3. The Amalfi Coast and the port area of Salerno are again the areas with the highest concentration of these synthetic polymers.

The developed method of recovery, concentration and weight determination of the microplastic occurrence is unprecedented, especially for the level of sensitivity achieved. The detection limit in the order of 1 $mg_{SPDs}/m^3_{seawater}$ is far below the previous methods and yet still optimizable.

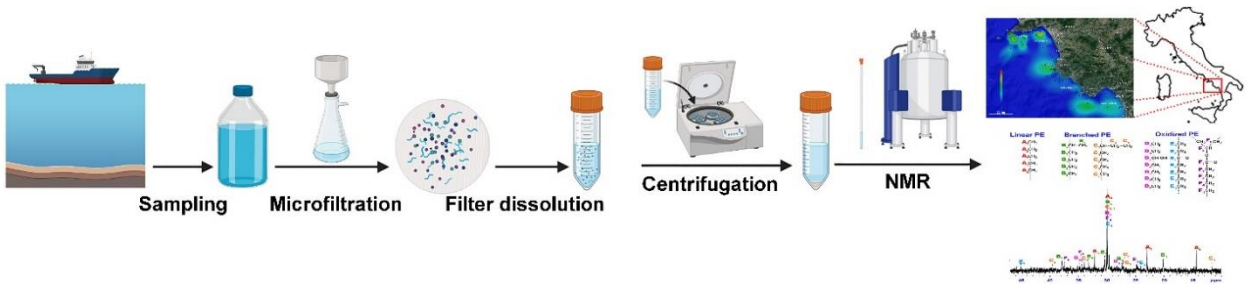

Figure 1. Schematic procedure for the recovery, NMR identification, quantification and microstructural assessment of MPs of synthetic organic polymers in a geographical region of interest

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