Electronic Supplementary Material (ESI) for Environmental Science: Nano.


# Marine plastic litters: the unanalyzed nano-fraction

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## S.1. In-situ Dynamic Light Scattering

Thanks to an optical fiber remote head, the system used in this work is a dedicated DLS system for contact less in-situ measurement as illustrated on Figure S1. The main control unit contains usual blocks for DLS system: Laser, photon counting detector, hardware correlator while an optical fibers umbilical cable acts as an optical link between the main unit and the remote head (it transmits both incident laser towards the head and collected photons towards the detector). The effective probed sample volume could be monitored by switching temporarily a secondary laser trough the scattering optical path. Then the beams crossing point has to be placed within the vial. For the nano-plastics setup, DLS specifications were: laser of 658 nm with a 60mW power; the scattering angle is 170°, the working distance is fixed at 80 mm and the umbilical cable length is 2 m. Those parameters could be modified according to the user constraints.

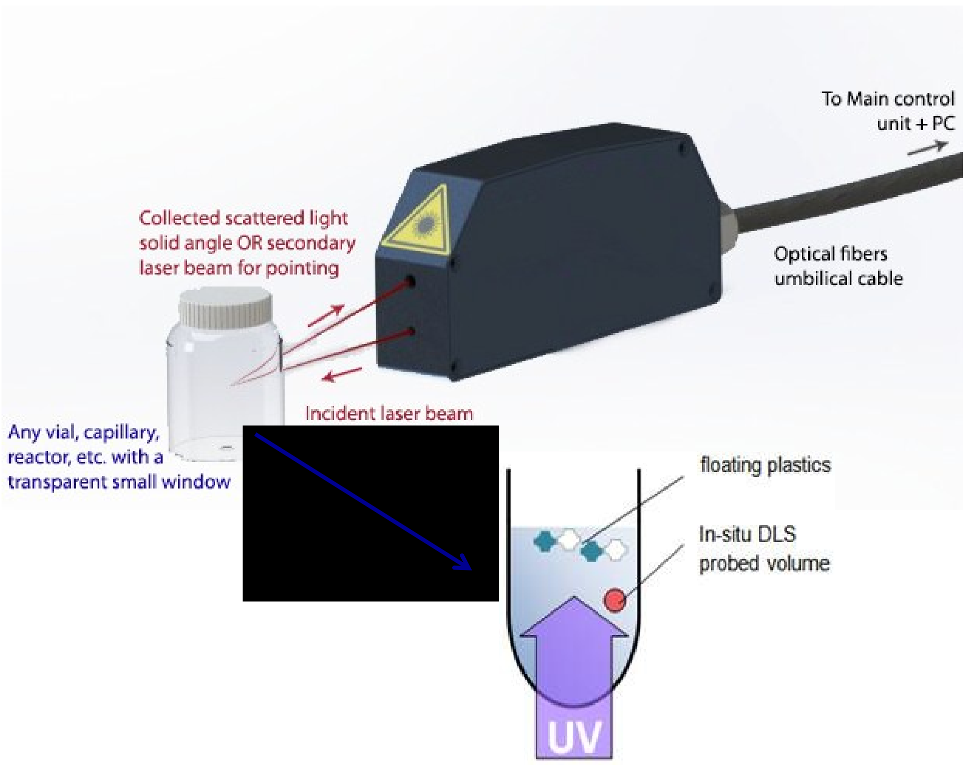


**Figure S1: Scheme of the in-situ DLS system coupled to the UV exposition for plastic litters**

## S.2. Size distribution of nano- and micro-plastics

The figure S2 represents the ACF obtained for highly diluted 200 nm polystyrene (PSL) standards (NIST-traceable Thermo Scientific) (see section S.2) with (red curve) and without (blue curve) additional trace of micro-polystyrene particles standards (few micrometers). The PSL were diluted until the light scattering baselines reached the one obtained for nano- and micro-plastics. The analyses were performed in the same conditions that the ones performed for nano-plastics and micro-plastics evidence.

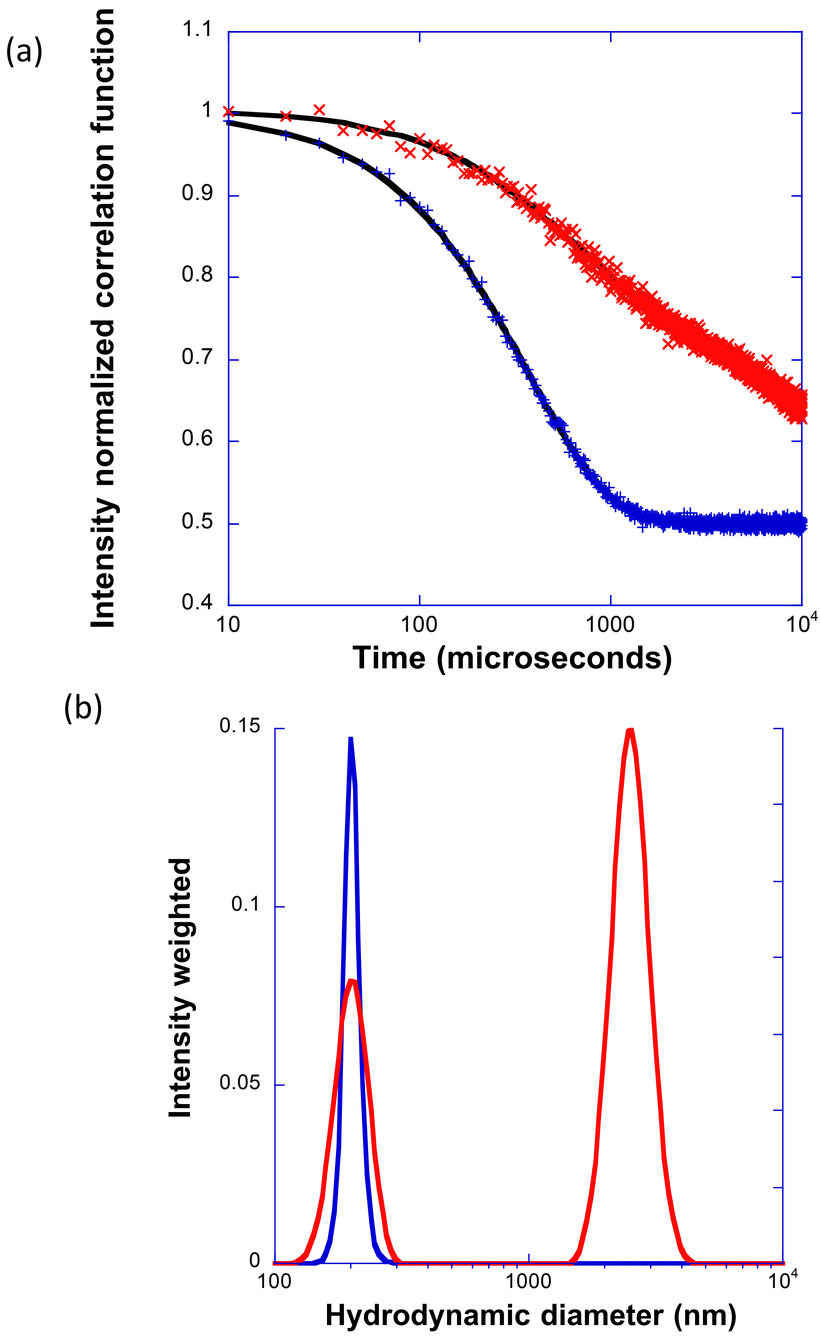


**Figure S2: (a) Auto-correlation functions obtained by the in-situ dynamic light scattering detector for highly diluted 200 nm PSL standards in blue and additional trace of micrometer PSL standards in red with the**

**corresponding fits in black line, with the (b) corresponding Intensity-weighted size distribution size distribution.**

## S.3. Typical infrared spectra of micro-plastics

Infrared spectra were recorded by attenuated total reflectance (ATR) using diamond ATR crystal on a ThermoNicolet Nexus apparatus. All images were taken with a nominal spectral resolution of 4 $cm^{-1}$; experiment used 16 scans. The recorded data were corrected in order to obtain transmission-like spectra using ATR Thermo correction (assuming the refractive index of the sample was 1.5).

Microplastics were in polyethylene. Typical methylene absorption band were in the region 1490-1420 $cm^{-1}$ (methylene scissoring peak) and 740-710 $cm^{-1}$ (methylene rocking peak). The oxidation (due to photochemical processes) lead to the formation of carbonyl moieties (carbonyl absorption bands in the region 1760-1690 $cm^{-1}$). The infrared spectra of the plastic debris were rather complicated compared to PE spectra. Most debris presented an adsorption band at 1540 and 1640 $cm^{-1}$; it is attributed to amide moieties and could be explained by the presence of the biofilm.

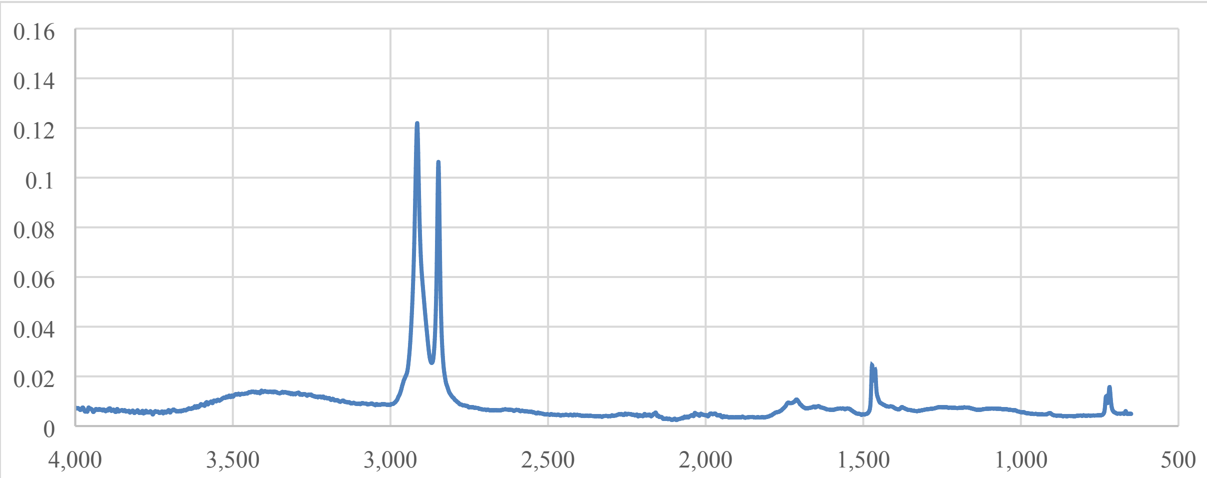


**Figure S3: ATR-FTIR spectrum of micro-plastics**