Nanoplastics Are Common in Water: Types of Formation and Molecular Interactions

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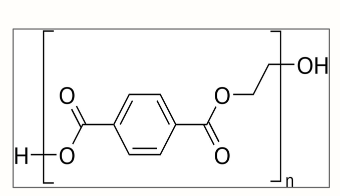
Abstract

Plastics are synthetic polymers currently present in nearly every aspect of life. From bottles, foam packaging, and food containers to clothes, electronics, medical equipment, and more, plastic usage has become commonplace. Plastics are widespread, lasting pollutants in all ecosystems. Nanoplastics, defined as plastic pieces less than a micrometer in diameter, are readily formed from the fragmentation of larger plastic pieces. Nanoplastics formed or present in water were studied to determine sources, sizes and quantities as well as interactions with other substances. Polyethylene (PE) and polyethylene terephthalate (PET) microplastics were mixed with pure water and a liquid organic compound to create nanoplastics. Mixtures were shaken, subjected to further ultrasound mixing, and the suspensions were extracted with diisopropyl ether to remove the liquid organic. Quantification of extraction efficiency was attempted with GC-MS, massing after evaporation, and fluorescent dye and fluorescent detection. In addition, nanoplastics mixtures were analyzed using Raman spectroscopy and microscopy before and after extractions. We determined that pure laboratory water contains nanoplastic particles, that mixing of PE microplastics in water creates nanoplastics, and that a variety of liquid organic compounds function as solubilizers, significantly accelerating nanoplastics formation. We also found that nanoplastic particles exhibit different Raman spectra under certain conditions, suggesting interactions between nanoplastics and solubilizer molecules.

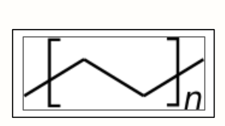
Background

Plastics are synthetic carbon polymers, often containing other chemical additives.

Examples of plastic polymers



Polyethylene terephthalate (PET)

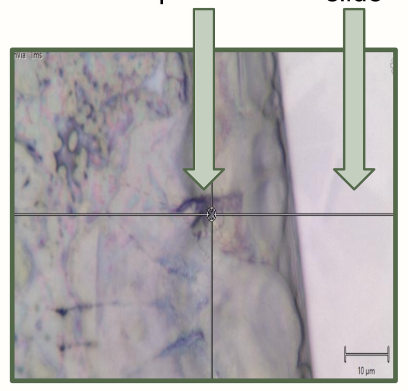


Polyethylene (PE)

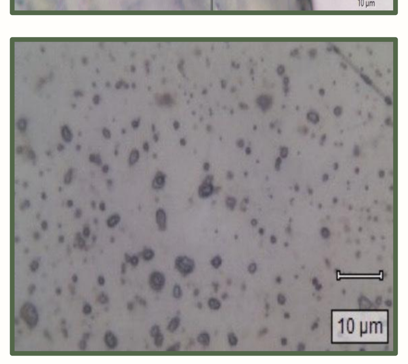
Microplastics are plastic pieces between 1 μm and 5 mm

Nanoplastics are plastic pieces smaller than 1 μm

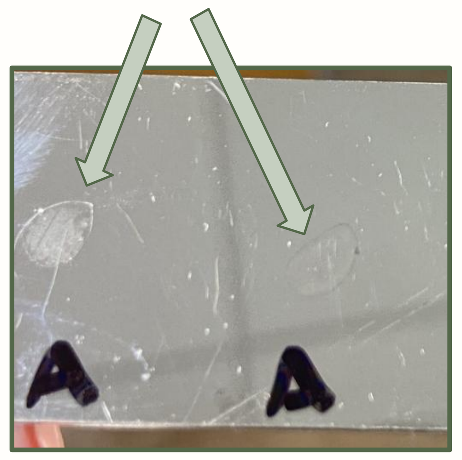
Upon contact with water, plastics fragment into micro and nano particles. Nanoplastics have been found in natural bodies of water and drinking water.



Dried edge of sample droplet from drinking water. Raman Microscope, 20x view. Spectrum under 532 nm laser matched polypropylene standard.



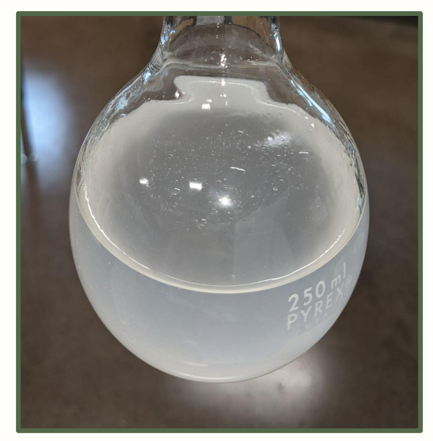
Pure lab water sample. Raman Microscope, 100x view. Spectrum under 532 nm laser matched polypropylene standard.



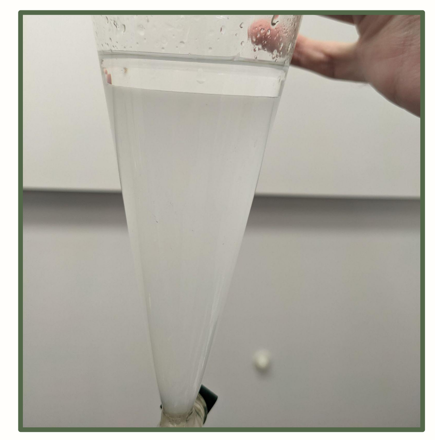
Dried water droplets from pure lab water on a stainless steel slide. The presence of film indicates plastic, verified using Raman spectroscopy.

Solubilization, Extraction, and Analysis of Nanoplastics

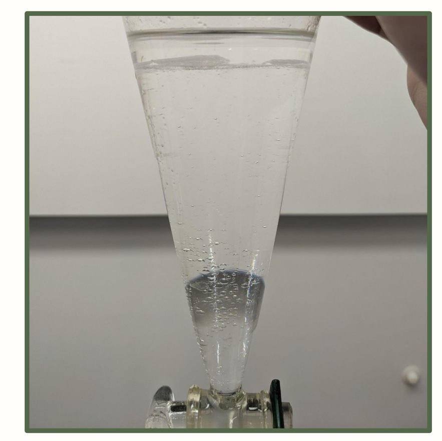
Nanoplastic suspensions were made dissolving 3–4 mg microplastics and 500 μL solubilizer (liquid organic) in 200 mL pure H_2O. This mixture was shaken for at least 1 minute, then subjected to ultrasound mixing for 2 hours.



PE suspension using octanoic acid

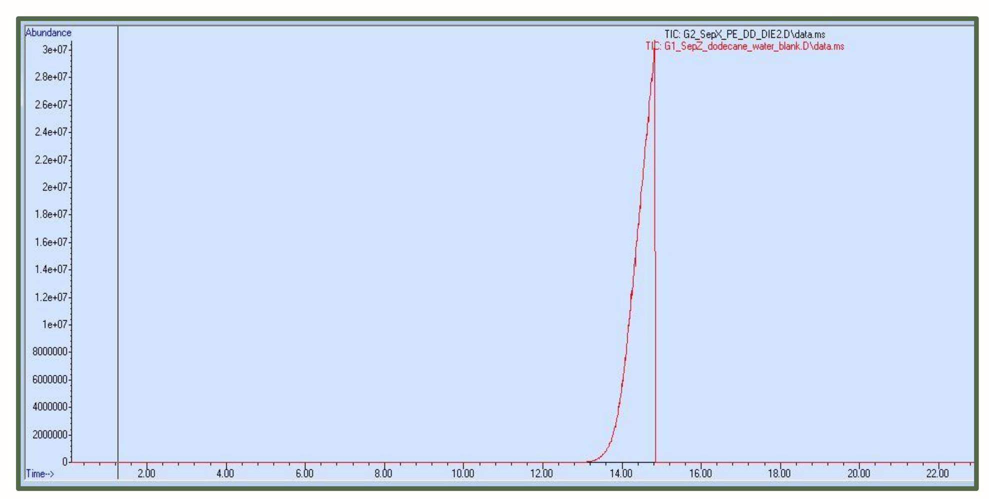


PE suspension using dodecane, pre-mixing (top layer is DIE)



PE suspension using dodecane after mixing with DIE

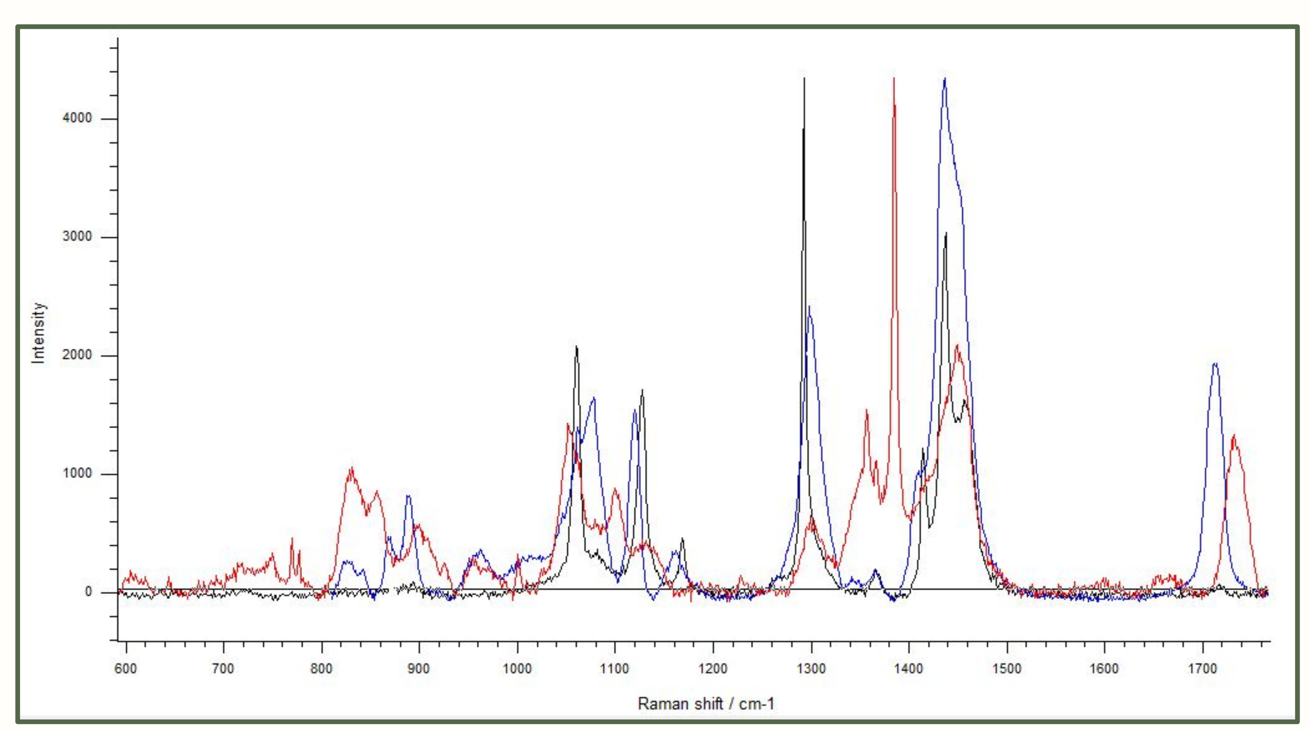
Diisopropyl ether (DIE) removes the solubilizer compound leaving just the nanoplastics in water, a clear solution.



GC-MS chromatogram showing the dodecane in the aqueous layer before (red) and after extraction (black)

Residue of PE left after water was evaporated

Molecular Interactions Between the Organic Solubilizer and Nanoplastics



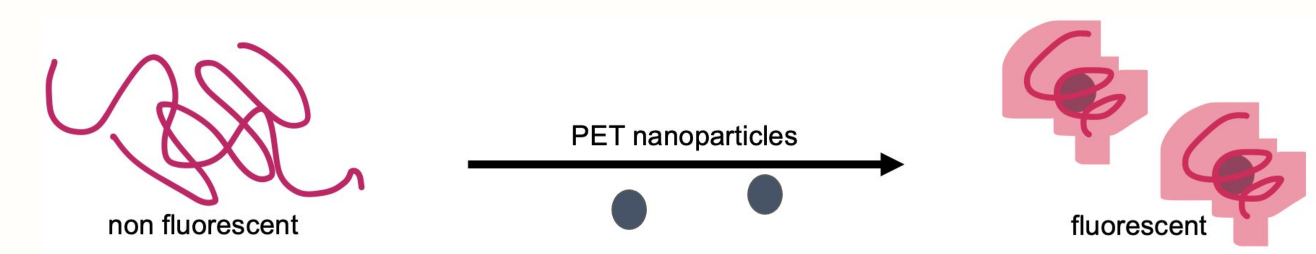
Raman spectra of PE microplastic (black), neat 2-dodecanone (blue), and PE nanoplastics made using 2-dodecanone (red). The PE nanoplastic particles contain 2-dodecanone and the spectrum has different and shifted peaks. Notably, the 2-dodecanone carbonyl peak (~1700 cm^{-1}) is shifted when the solubilizer is associated with PE nanoplastics.

Nanoplastics Solubilization Data

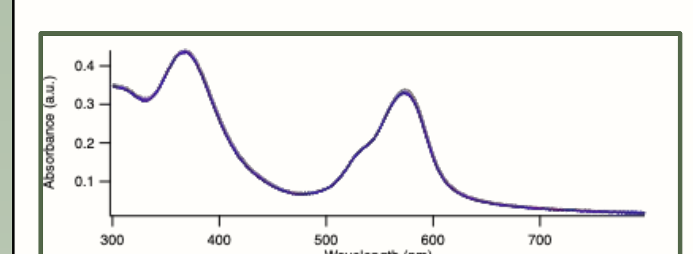
Compound	PE	PET
Heptane	✗	✓
Dodecane	✓	✓
Isooctane	✗	✗
2-Heptanone	✗	✗
2-Dodecanone	✓	✓
Methyl Octanoate	✓	✓
Methyl Decanoate	✓	✓
Octanoic Acid	✓	✓
Decanal	✓	✓
Octanol	✓	✓
Toluene	✓	✓
Benzaldehyde	✗	✗

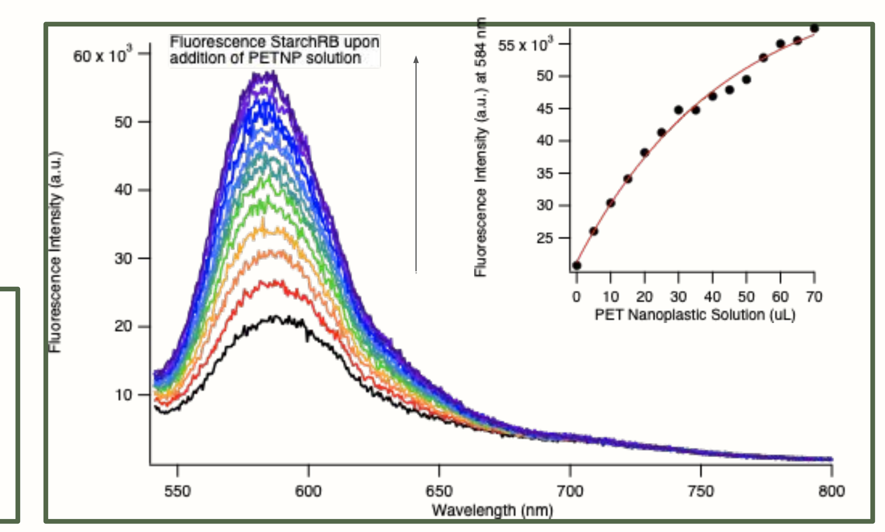
Outcomes of attempted PE and PET solubilization with a variety of liquid organics. Check marks indicate successful solubilization of approximately 3 mg of plastic in 200 mL water.

Fluorescence Data



An aqueous solution of starch polymer modified with rhodamine B has "turn-on" quantitative fluorescence upon addition of aqueous PET or PE nanoparticles.





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- Compostable Pak (https://www.compostablepak.com/)

References

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