



Nanoplastic Formation from Macro and Microplastics in Aqueous Solution

Joe Castleman, Scott Kaiser, Dr. Julie Peller, Valparaiso University



Abstract

Plastic pollution is a growing issue and has been found increasingly in our water systems. Given the massive, global extent of this pollution, it is important to understand the chemical reactivity of these plastics in water. Plastics fragment and weather over time, often turning into micro- and nanoplastics. Microplastics (MP) are plastic pieces smaller than 5 mm, and are a significant part of the plastic pollution in surface waters. The separate classification of nanoplastics (NP) was more recently adopted for plastic particles smaller than a micrometer. Nanoplastics display different properties and interactions. In our research, we discovered that microplastics, which do not mix with water, can be converted to nanoplastics upon the addition of certain chemical additives and vigorous mixing. These nanoparticles disperse evenly in water, similar to other colloidal solutions. The presence and size of the NP were studied using Raman spectroscopy, darkfield and lightfield microscopy and particle size analysis. We show that nanoplastics can be readily formed from a number of different plastics including common plastics, such as polyethylene (PE) milk jugs, polyethylene terephthalate (PET) water bottles, and polycarbonate (PC) safety glasses. This formation of nanoplastics is concerning, as it suggests they are more abundant and bio-available in natural environments than currently estimated. This could be a valuable step in chemically recycling plastic materials.



Figure 1. Microplastic pollution in water

Nanoplastic concentration analysis

- We found an average concentration of PE nanoplastics in water to be about 36.5 ppm.
- The data shown in Figure 2 suggests a lack of correlation between amount of solubilizer added and concentration of PE.
- Only one solubilizer was used in this experiment.

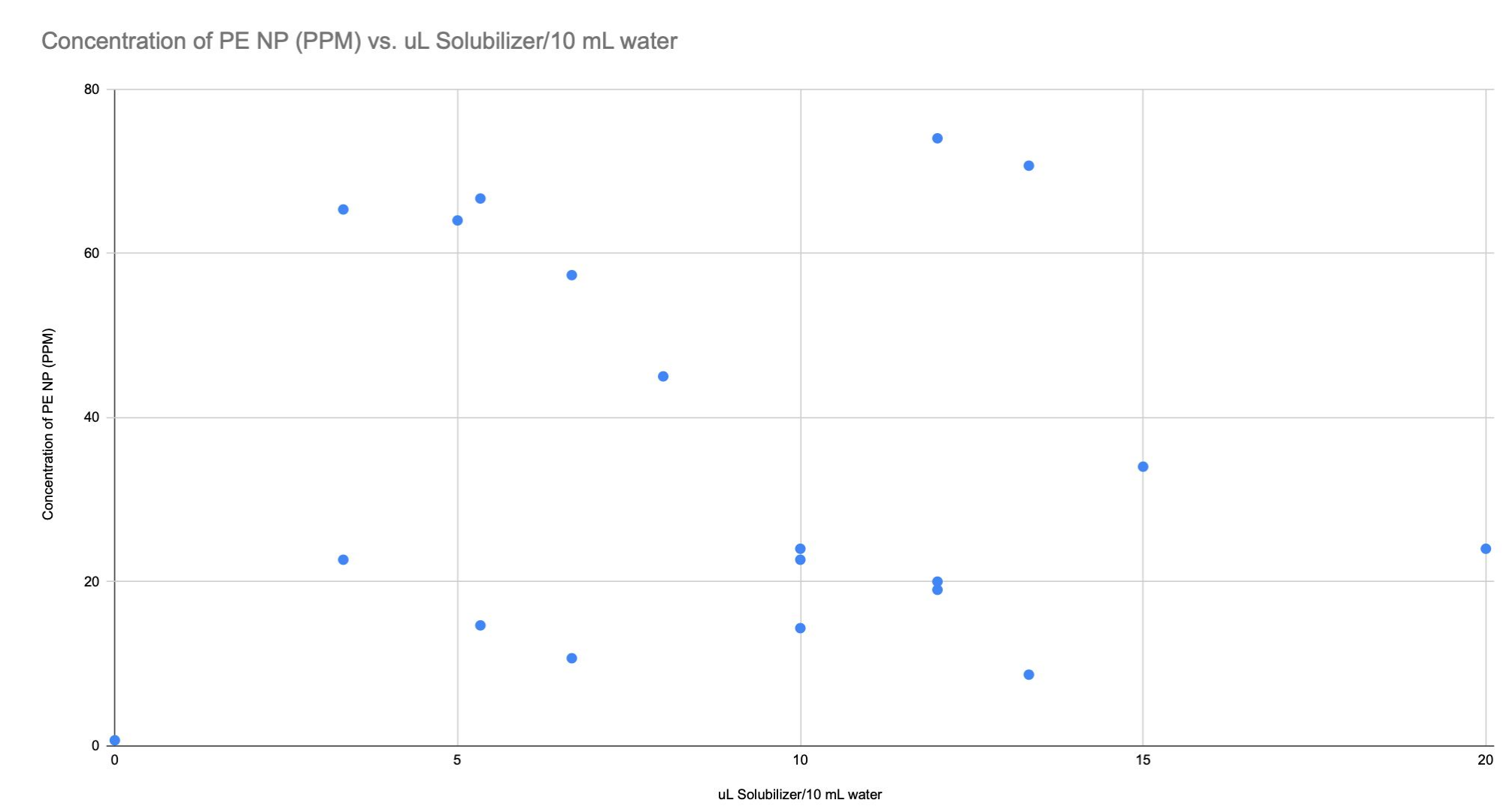


Figure 2. Concentration of NP (ppm) measured in samples versus amount of solubilizer (uL/10 mL water).

Microplastic to Nanoplastic Formation and Isolation



Figure 3. PE microplastics (floating on top) and water

Chemical additive, vigorous mixing

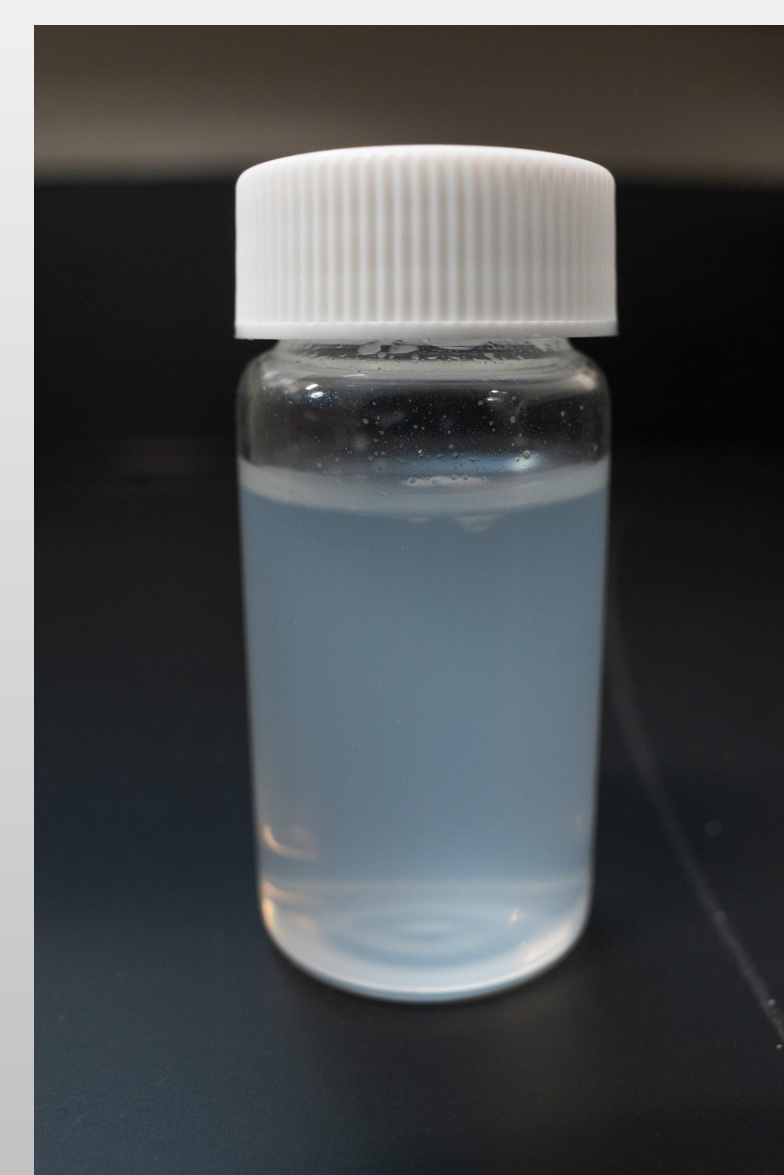


Figure 4. PE NP aqueous suspension

Liquid evaporation

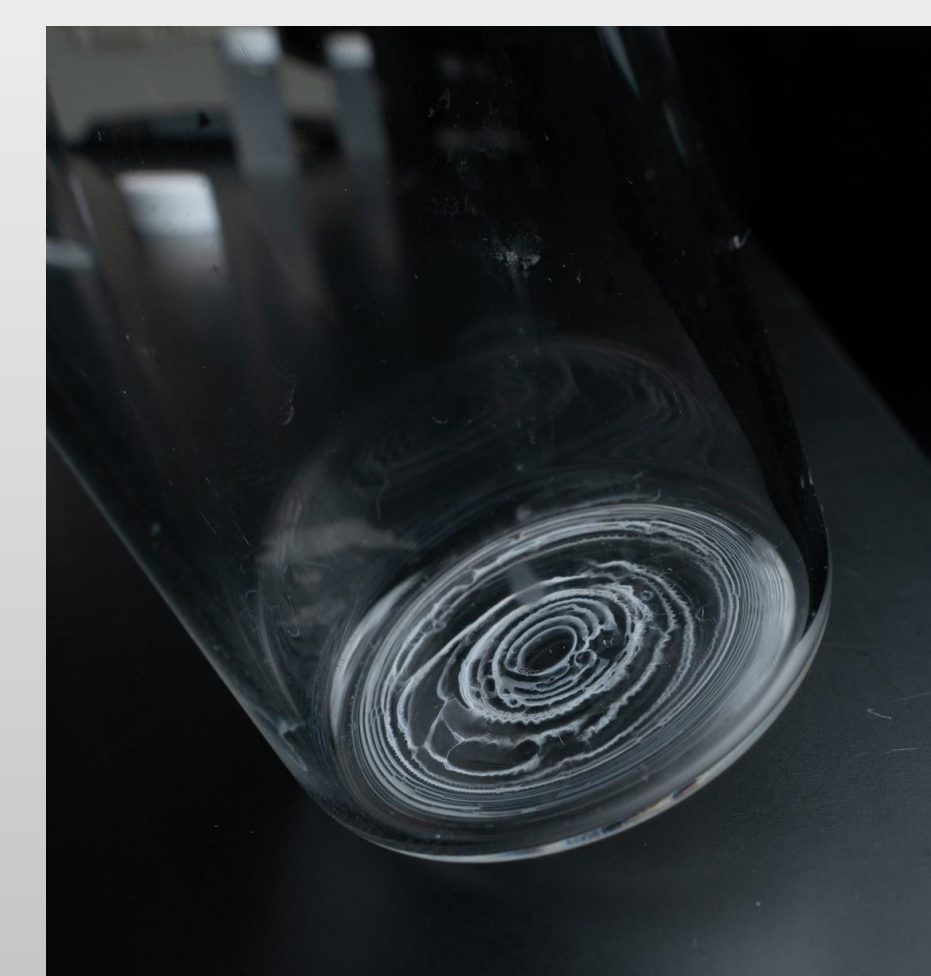


Figure 5. PE residue on bottom of vial after evaporation of liquid

Creating Real World Nanoplastics

Are there limitations to creating NP in water? We have tested different types and sizes of plastics and successfully created NP in all cases. To the best of our knowledge, NP have not been made in water using real world plastic materials. Figures 6-9 are the suspensions of nanoplastics that formed from the various plastic materials shown in the pictures.



Figure 6. Disposable mask (PP, mixed plastic) and different layers of mask turned into nanoplastics

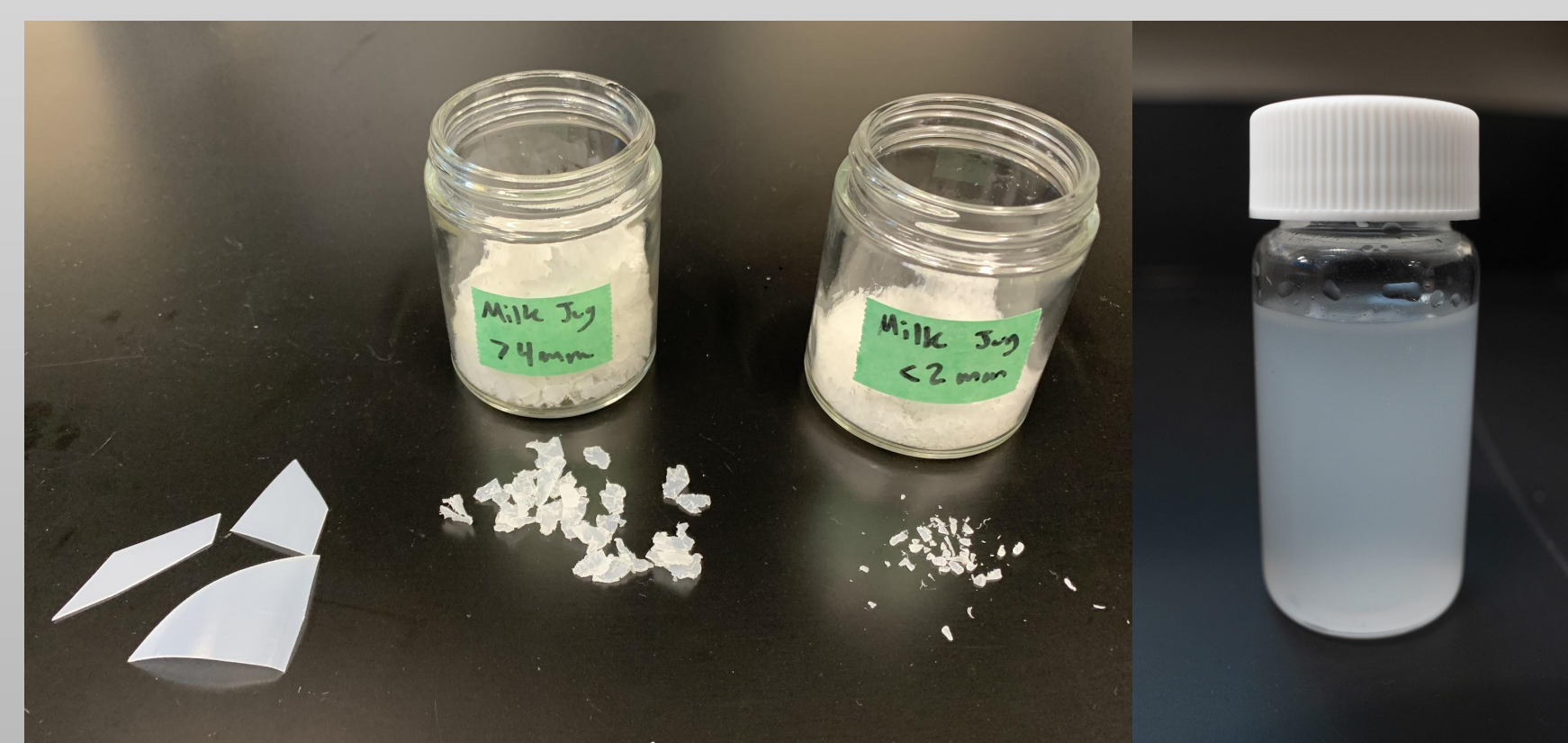


Figure 8. Different sizes of milk jug PE and the milk jug turned into nanoplastics



Figure 7. Water bottle (PET) and water bottle turned into nanoplastics



Figure 9. Safety glasses (PC) and the safety glasses turned into nanoplastics

Results from Raman analysis

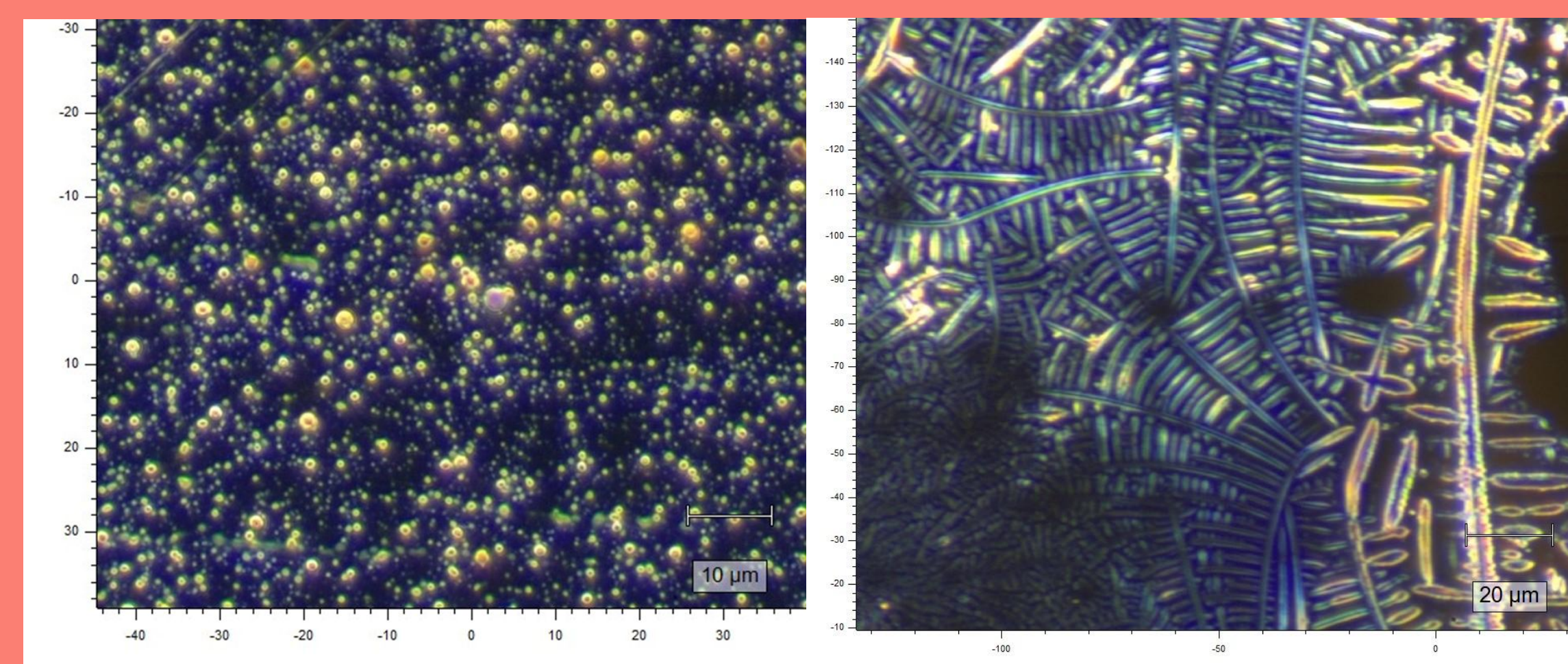


Figure 10. Dark field microscopy images of (left) deposited NP from an aqueous solution of suspended commercial PE NP and (right) PET from a plastic water bottle.

Table 1. Particle size analysis of commercial PE NP.

Equivalent circle diameter (µm)	Total number	0 - 0.4	0.4 - 0.8	0.8 - 1.2	1.2 - 1.6	1.6 - 2	2 - 2.4	2.4 - 2.8	2.8 - 3.2	3.2 - 3.6	3.6 - 4
Number of Particles	1777	712	554	270	125	69	33	9	4	0	1
Equivalent Circle diameter (µm)	0.633										

Discussion

We have been able to create NP from any size of PE and from other plastics we have tested so far (PS, PET, PC, various types of PE) using several common chemical solubilizers. The ease of NP formation suggests that NP have been contaminating biological systems since the conception of plastics. This is particularly concerning because of how widespread and ubiquitous MP pollution has become. Therefore, the magnitude of NP in the environment is unknown and likely underestimated due to mostly unexpected phenomenon. This formation of NP suspensions also has the potential to be useful in the chemical recycling of plastic, which relies on the conversion of polymers back to smaller units. These NP suspensions in water may offer an additional, greener, nonhazardous pathway for chemical recycling.

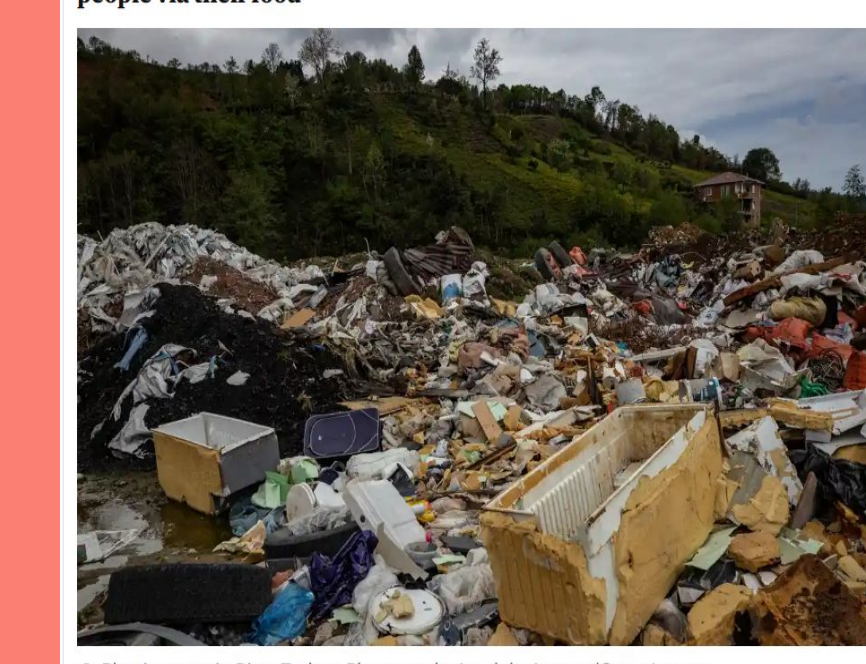
Are MP/NP affecting our health?

Recent studies establish that microplastics are present in human blood. MP and NP have also been found digestive tracts and other organs. MP have also been found in the placenta. People are exposed to plastics in numerous ways. Transmission of MP is predominantly through the air, food, and water. Currently, the effects of MP on humans are relatively unknown, although negative effects have been found in smaller organisms.

Carrington, Damian. "Microplastics Found in Human Blood for First Time." *The Guardian*, Guardian News and Media, 24 Mar. 2022. <https://www.theguardian.com/environment/2022/mar/24/microplastics-found-in-human-blood-for-first-time>.
 Carrington, Damian. "Microplastics Cause Damage to Human Cells, Study Shows." *The Guardian*, Guardian News and Media, 8 Dec. 2021. <https://www.theguardian.com/environment/2021/dec/08/microplastics-damage-human-cells-study-plastic?text=Microplastics%20cause%20damage%20to%20human%20cells%20in%20the%20laboratory%20at%20levels%20relevant%20to%20human%20exposure>.

Microplastics cause damage to human cells, study shows

Harm included cell death and occurred at levels of plastic eaten by people via their food



Microplastics found in human blood for first time

Exclusive: The discovery shows the particles can travel around the body and may lodge in organs

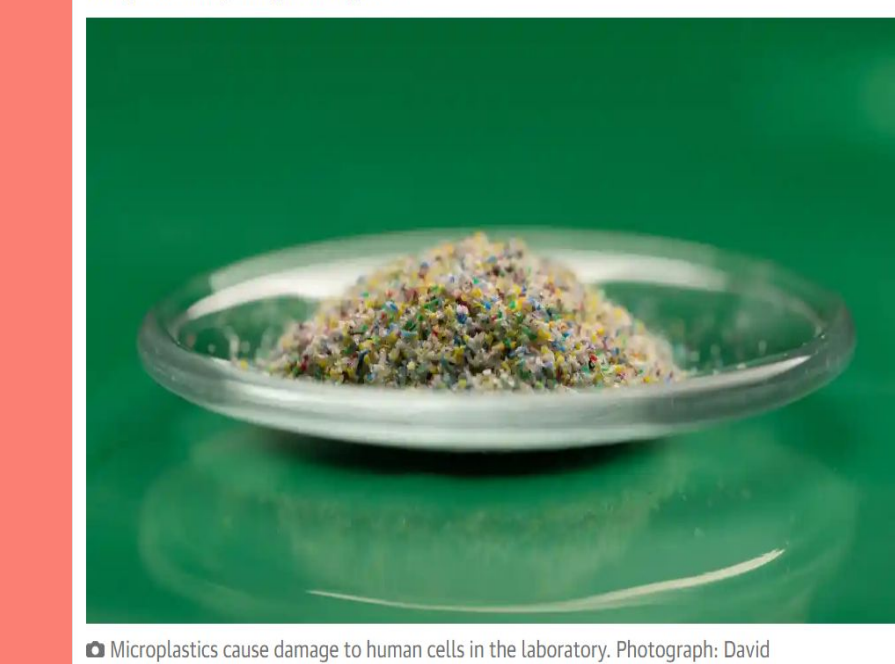


Figure 11. News articles showing the likely dangers of microplastics to humans. Nanoplastics are much more difficult to study.

Looking Forward

- Figuring out how to best quantify the nanoplastics
- Analyzing different solubilizers efficacy
- Testing different kinds of plastic
- Improving isolation methods

Acknowledgments

NSF EAGER Grant award number 2035499: Laboratory Radiation Chemistry Methods to Induce Rapid Aging of Microplastics in Water to Assess Fundamental Chemical Reactivity Changes

Dr. Sarah Shidler, Renishaw, Inc.

Dr. Gregory Horne, Idaho National Laboratory

Dr. Stephen Mezyk, California State University, Long Beach

Valparaiso University