Detecting Microplastics in the Environment with Fluorescence Spectroscopy

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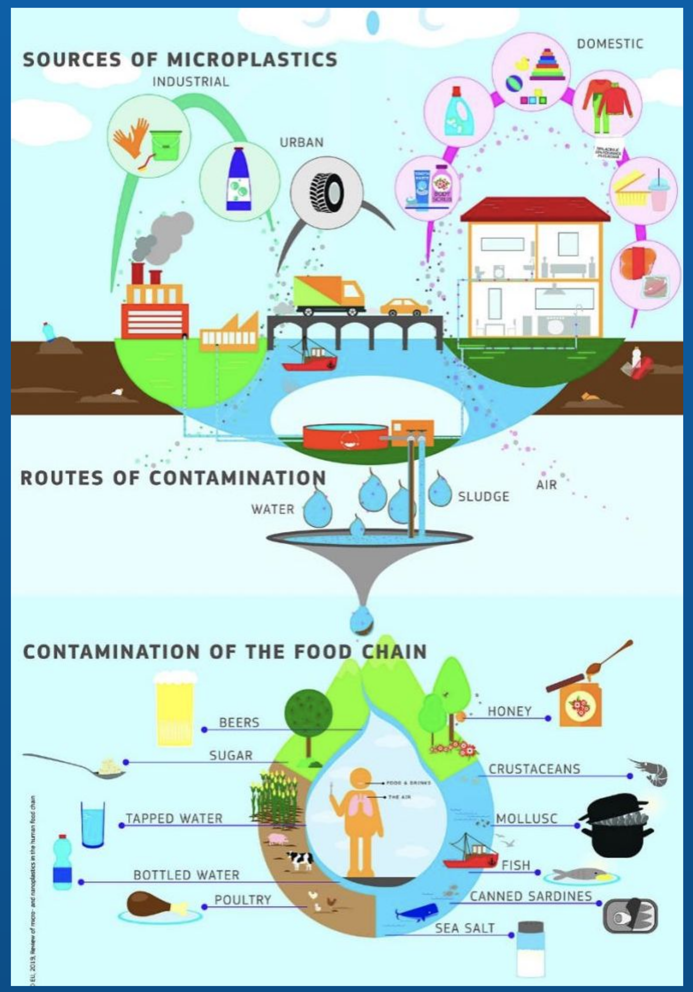
Abstract

Our grand challenge is to solve the problem of microplastic pollution in the ocean. We sought to find an efficient method to identify microplastics in natural seawater samples as current sampling methods are costly and time-consuming. Fluorescence spectroscopy was explored and showed promising results as a quick way to differentiate between and identify specific plastic varieties.

Introduction

- Marine plastic pollution is an enormous global concern, with an estimated minimum 5.25 trillion particles in circulation (Eriksen et al., 2014).
- Microplastics are able to successfully move up marine food chains, starting with zooplankton and ending inside human bodies (Toussaint et al., 2019).
- Microplastics have been confirmed to be detrimental to human physiology (Zettler et al., 2013). Chemicals such as DDT and BPA have been found to adhere to microplastics, which when ingested lead to physiological harm. (Smith, 2018).
- The microplastic dilemma moves beyond the physical mass of the polymer and its disruptive ability to clog the earth's waterways and pollute ecosystems; but is causing toxic, irreversible damage to earth's inhabitants at an alarming speed.

Figure 1: Sources and Routes of Microplastic Contamination



Methods

- Microplastic solutions were created for the initial testing by grinding down plastic bags, PVC, and styrofoam using a saw and sandpaper. A mass of 2 g was added to 200 mL of deionized water and the solution was left outside exposed to sunlight for a week.
- Each solution was filtered with a funnel fitted with filter paper to remove large plastic particles.
- A HORIBA Aqualog Fluorescence Spectrometer was used to obtain Excitation-Emission Matrices (EEM) for each solution.

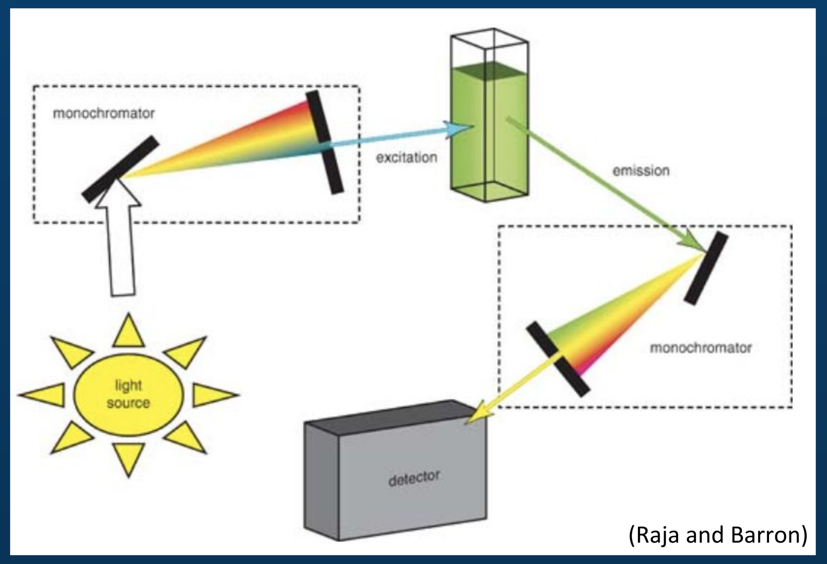


Figure 2: Overview of Fluorescence Spectroscopy Technique

Fluorescence spectroscopy works by exciting the compounds within a sample at a variety of wavelengths, leading to the emission of different wavelengths of light. The EEM graphically visualizes the variables of excitation, emission, and intensity.

Preliminary Results

EEM Spectra from the breakdown of different plastic polymers (polyethylene, polystyrene, and PVC) in aqueous solution.

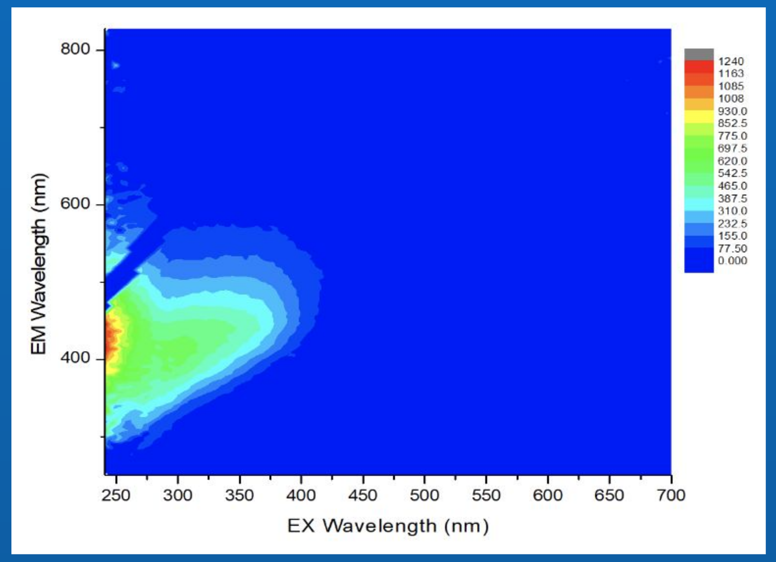


Figure 3: Polyethylene EEM

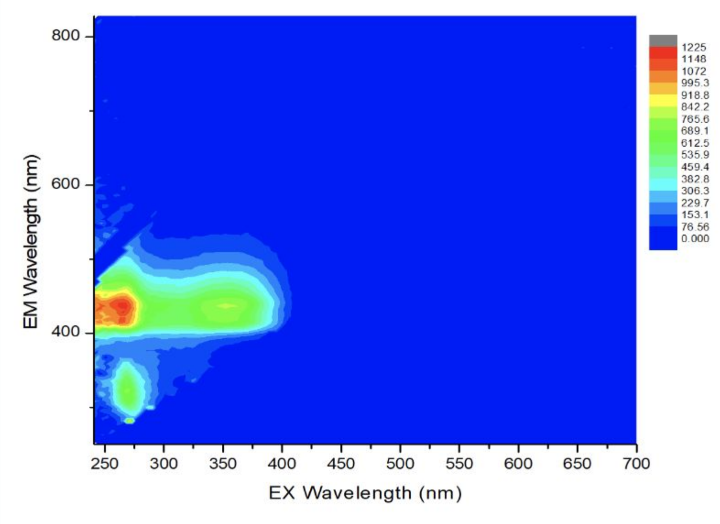


Figure 4: Polystyrene EEM

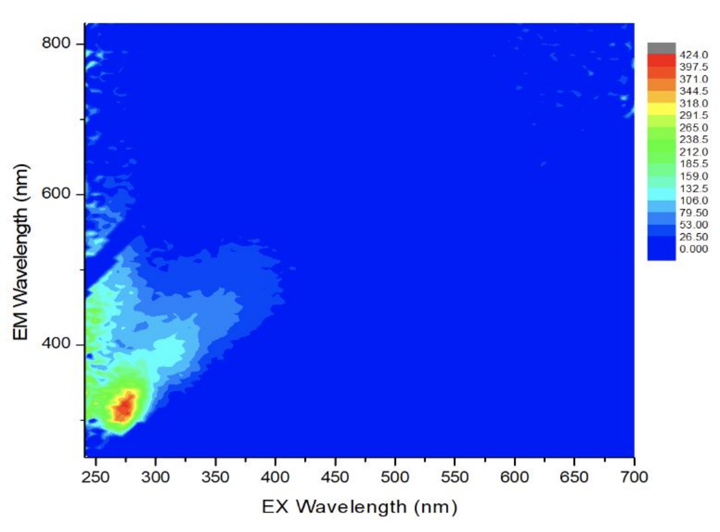
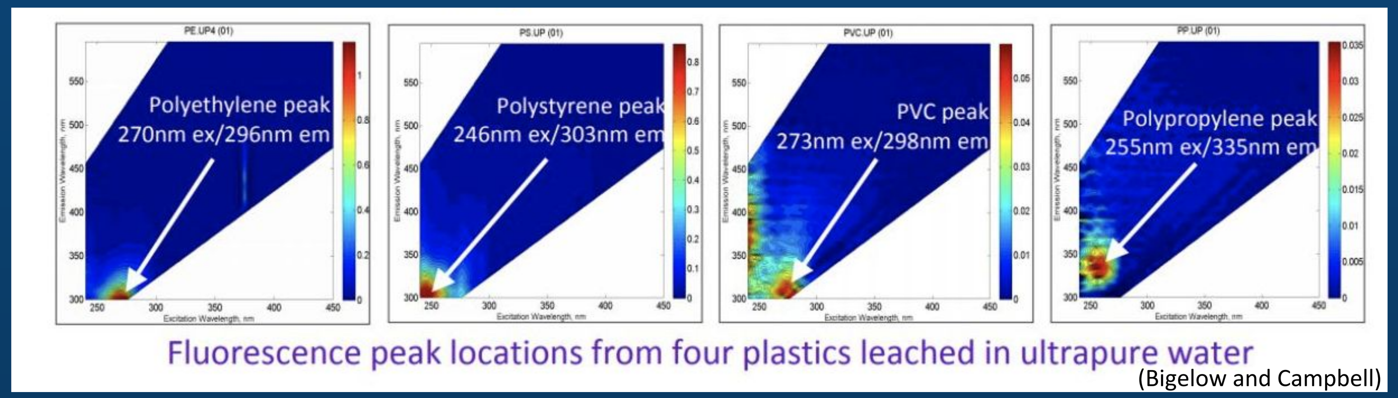


Figure 5: PVC EEM

Discussion

As evident in Figures 3-5, there are distinct peaks for each plastic variety, indicating that fluorescence spectroscopy might be a useful method in differentiating between various plastic types. The most obvious peaks in the plastics included (in nm): polyethylene at 240 ex/425 em, polystyrene at 275 ex/420 em and 270 ex/325 em, and PVC at 275 ex/315 em. All of these excitation/emission results were unique leading to the conclusion that fluorescence spectroscopy can likely be used to determine what types of plastic are present in a natural solution. Although natural samples will have have more components causing the EEM's to be more difficult to analyze, the preliminary work suggests the method will be potentially useful as it is quicker and easier to analyze than current methods like GC/MS.

Figure 6: Comparison to Previous Results by Researchers at San Diego State



There are notable differences between the EEM's we took and those found from previous work, especially for polyethylene and polystyrene. These inconsistencies are likely a result of contamination from the plastics used in our study, as they were not pure polymers. The plastic bags and styrofoam used could potentially have had other plastic constituents or microscopic contaminants. Despite this, the results for PVC are quite similar with our work reflecting a peak at 275 ex/315 em and that of the previous study being at 273 ex/298 em, allowing for the conclusion that there is potential in this method.

Future Research

- The goal of future work will be to both standardize a process for microplastic detection and then apply it to natural samples. This will be begun by purchasing laboratory grade polymers in order to eliminate the possibility of contamination from impure plastic products.
- Figure 7 below shows that submerging polystyrene in DI water and subjecting it to UV light caused microplastics in the water to increase exponentially. Using this method we can accurately create microplastic solutions and control their concentrations (Lambert et al., 2016).
- Ocean samples will be obtained by utilizing a method called surface microlayer sampling. Since microplastics are often buoyant in water, a sieve and glass drum are used to collect only the top 1 mm of surface water (Li et al., 2017).
- Lifetime fluorescence spectroscopy will also be tested as another potential aid in plastic identification by determining the fluorescence lifetimes of the plastics.

Figure 7: Microplastic Concentrations after UV Light Exposure

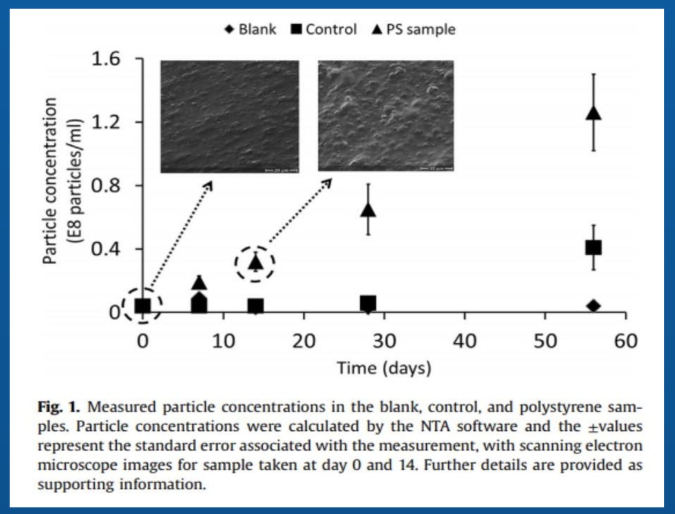


Figure 8: Rotating Drum Microlayer Sampler

Conclusion

- Fluorescence spectroscopy shows promise in being able to accurately detect and measure microplastics in artificial water samples.
- The results can likely be applied towards natural aquatic samples in order to determine whether microplastics are present in the solution, and if so, what types of plastic the particles are made up of.
- Developing a more efficient method for identifying microplastics will be central to furthering research in solving the grand challenge of marine microplastic pollution.

References

Bigelow, A.; Campbell, C. Detecting Microplastics in Water Streams Using Fluorescence Spectroscopy. https://ca-nv-awwa.org//CANV/downloads/2015/afc15presentations/DetectingMicroplasticsinWaterStreams.pdf (accessed May 8, 2020).

Eriksen, M. C. M.; Plastic Pollution in the Worlds Oceans: More than 5 Trillion Plastic Pieces Weighing over 250,000 Tons Afloat at Sea. *PLOS ONE* 2014, *9* (12).

Lambert, S., & Wagner, M. (2016). Characterisation of nanoplastics during the degradation of polystyrene. *Chemosphere*, 145, 265-268.

Li, Jingyi, Liu, Huihui, & Che, J. Paul (2017). Microplastics in freshwater systems: A review on occurrence, environmental effects, and methods for microplastics detection. *Science Direct,* 137, 362-374.

Raja, P. M. V.; Barron, A. R. 1.11: Fluorescence Spectroscopy. https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Book:_Physical_Methods_in_Chemistry_and_Nano_Science_(Barron)/01:_Elemental_Analysis/1.11:_Fluorescence_Spectroscopy (accessed Apr 27, 2020).

Sea Surface Microlayer Sampling. http://archive.sccwrp.org/Homepage/PhotoGallery.aspx?category=Sea Surface Microlayer Sampling (accessed May 8, 2020).

Smith, M.; Love, D. C.; Rochman, C. M.; Neff, R. A. Microplastics in Seafood and the Implications for Human Health. 2018. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6132564/ (accessed Apr 28, 2020).

Toussaint, B.; Raffael, B.; Angers-Loustau, A.; Gilliland, D.; Kestens, V.; Petrillo, M.; Rio-Echevarria, I. M.; Eede, G. V. D. Review of Micro- and Nanoplastic Contamination in the Food Chain. *Food Additives & Contaminants: Part A* **2019**, *36* (5), 639–673.

Zettler, E. R.; Mincer, T. J.; Amaral-Zettler, L. A. Life in the "Plastisphere": Microbial Communities on Plastic Marine Debris. *Environmental Science & Technology* 2013, *47* (13), 7137–7146.