Investigation of Microplastics and their Absorption of Polycyclic Aromatic Hydrocarbons and Compounds of Concern in Water Associated with their Removals by Engineering Systems

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March 2019 to March 2020

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March 24, 2020

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ACKNOWLEDGEMENTS

This project was supported by Hispanic-Serving Institution's Education Program Grant no. 2015-38422-24058 from the USDA National Institute of Food and Agriculture.

I cannot express enough gratitude to Dr. Pitiporn Asvapathanagul for the support and guidance during this phase of my academic career. Without Dr. Pitiporn I would not have had the opportunity to be part of the WRPI internship. She has supported me through my academic journey and has been a great mentor. I would also like to acknowledge the WRPI staff that worked very hard to make this experience smooth and efficient.

The completion of this study could not have been accomplished without the help of Dr. Varenka Lorenzi. Thank you for the countless hours teaching, supervising, and guiding me throughout the experimental process. The support from Tiffany Nguyen was also essential in the experimental process – thank you for your dedication of helping with the experiments. To Mariangel Fernandez who was supportive, encouraging, and has provided insight throughout my research, thank you. Lastly, I would like to acknowledge Dr. Roger Lo for providing material that was essential for conducting experiments.

Thank you to everyone that has supported me throughout my academic journey.

EXECUTIVE SUMMARY

In recent years concerns over the presence of microplastics (MPs) in the environment have gained attention. Microplastics are not only abundant in the environment but are also associated with adsorbing and transporting Compounds of Concern (CCs) that are toxic to terrestrial and aquatic organisms. Compounds of Concern include polycyclic aromatic compounds (PAHs) and compounds of emerging concern (CECs). Wastewater treatment plants (WWTPs) are a pathway for both MPs and CCs. Compounds adsorbed by MPs are released into bodies of water and onto agricultural lands as fertilizer after being subjected to treatment. Therefore, it is important to evaluate the effectiveness of engineering systems used in water treatment and water reclamation facilities. In this study, the adsorption of CCs by polymers and granular activated carbon (GAC) was reviewed. Specifically, the effectiveness of CC desorption by GAC from a polymer that is associated with causing adverse effects to smaller organisms – nylon, or polyamide (PA). The desorption of prevalent CCs found in local WWTPs was assessed to determine the effectiveness of a typical unit operation, GAC, employed to remove contaminants in wastewater effluent. Results suggested that GAC is not efficient in removing all CCs but was efficient in removing some – PAHs preferred adsorbing to nylon, while CECs were more likely to adsorb onto GAC.

PROJECT OBJECTIVES

Conducting research on an emerging environmental concern as a student is of importance when entering the field of Civil Engineering. Individuals designing future engineering systems that will make society more sustainable need to be aware of different environmental concerns. The research conducted for this project was based on an engineering system developed by Civil Engineers – water treatment plants. Treatment plants are essential in providing clean water for both human consumption and for discharging treated wastewater into bodies of water.

An emerging concern in the field of water treatment is the presence of plastic throughout the water cycle, including treatment plants. The presence of polymers in everyday activities and professions, such as the medical field or the construction field, make polymers an essential material that will continue to be used throughout the world. Plastics, or polymers, have been an essential man-made material in the development of society, but the advantageous corrosion-resistant properties of plastic have made the degradation of the material an environmental issue. Although plastics may be fragmented over time, the fragmented particles – microplastics – can remain in the environment for centuries. Microplastics are derived from direct manufacturing of small plastic particles, also known as primary MPs, or from fragmentation of larger particles, known as secondary MPs. The presence of MPs in the environment is significant. Studies have found plastic in remote mountain ranges, drinking water, and food consumed by humans. Although world agencies have not considered the presence of MPs a threat, the sorption properties of plastic is of concern – MPs have the potential to accumulate toxic compounds that will be consumed by organisms throughout the food chain. Society has minimal authority over

the adsorption of compounds by MPs in the environment, but the amount of compounds within engineering systems can be controlled.

The presence of MPs in treatment plants alongside CCs may contribute to the dispersal of concentrated contaminants, on the surface of plastics, to the environment. Modern engineering systems may subject MPs to GAC filtration, but there is little information on the efficiency of contaminant desorption from MP surfaces. The project focused on the sorption relation between nylon MPs, GAC, and ubiquitous hydrophobic organic contaminants found in potable water and wastewater treatment plants.

The intention of the study was to provide evidence for the effectiveness of contaminant desorption from MPs using a typical unit of operation, GAC. One concern with MPs being subjected to treatment is the possibility of GAC contributing to the adsorption of contaminants rather than desorbing contaminants from MPs. Releasing MPs with large concentrations of contaminants may cause adverse health effects to marine organisms, or smaller terrestrial organisms – studies have shown that worms in agricultural land exposed to MPs display decreased reproduction rates. With minimal data concerning MP contaminant adsorption in treatment plants, it is important to provide an insight on whether subjecting MPs to treatment is beneficial or unfavorable.

To analyze the sorption behavior of contaminants between MPs and GAC, both materials would be exposed to a solution with known amounts of contaminants – each material will be tested individually. After subjecting the media to the contaminants, the amount of contaminants adsorbed by the MP or the GAC would be determined. This would provide an overview of how both media adsorb individual compounds. The final step would include both MPs and GAC in the same solution and analyze how many contaminants are adsorbed by the two separate media.

Conducting this research would require the development of samples in a laboratory setting, preparing the samples for contaminant measurement, and required data analysis by comparing the amount of compounds adsorbed by MPs and by the GAC. Desorption rates would be portrayed as a higher concentration of compounds adsorbed by GAC and lower concentration of compounds on MPs.

PROJECT APPROACH

Analyzing the amounts of compounds being adsorbed by the MP and GAC media that was tested required a focus on specific compounds. In the CCs category, the two subgroups included five compounds from PAHs and three compounds from CECs – all eight of the compounds of focus were abundant in wastewater or potable water treatment plants. The five PAH compounds of focus were: fluoranthene, pyrene, chrysene, benzo[b]fluoranthene, and benzo[k]fluoranthene. Compounds of emerging concern included the following three compounds: caffeine, diethyltoluamide (DEET), and triclosan. All compounds listed under PAHs are known to be possibly toxic or carcinogenic to humans and organisms when exposed to high concentrations of the compounds. Compounds listed as CECs may not be confirmed as toxic or carcinogenic by government agencies, but they are present in treatment plants at a concerning rate.

Batch experiments were used to examine the concentration of CCs adsorbed by the two materials. During the process of conducting the study there were a period of method development that required testing of different equipment and approaches to the production of samples and extraction of compounds. Preparing samples required three different solutions, the

media that was being tested, and purified water. The CCs were contained in dichloromethane (DCM) solutions of known concentration. The three solutions contained: PAHs, CECs, and PAH Recovery Surrogates (PAH RS). The PAH RS was used as a benchmark for analyzing the extraction process efficiency.

To prepare the test samples, small glass vials were spiked with all three solutions and left to evaporate under a fume hood. Before introducing the nylon MPs or the GAC, 15 mL of purified water, provided by a Milli-Q instrument, was added to the evaporated vial. Duplicates of each sample were produced to decrease uncertainty of the final results. After applying the respective media into the newly produced solution, the samples were capped and shaken by hand in an invert-revert motion. The prepared samples were then stored in an orbital incubator for five days to control the ambient temperature and simulate movement – a five-day timeframe was determined to be the amount of time required for proper adsorption of compounds onto nylon and GAC.

To analyze the amount of compounds adsorbed by each media an extraction method was used. After multiple iterations of experiments, the filtration of the media was simplified to reduce the amount of compounds being lost throughout the process, but the final method of extraction was consistent. The material was removed from the solution using sanitized forceps and placed into their respective Bio-Science Extraction Thimbles. The media was then subjected to Soxhlet extraction to strip the compounds from the material onto DCM solution – a representation of the Soxhlet instrument is shown in Appendix A. To extract the compounds found in the original solution, DCM was introduced to strip away the compounds from the water.

The DCM and water solution was put through an ultrasonic cleaner, shown in Appendix C, for fifteen minutes to improve the process of removing compounds from the water. Since

DCM is the heavier solution, the two liquids separated and the DCM at the bottom of the vial was filtered through a sodium sulfate solution housed in a glass filter. A completed extraction would require three iterations of DCM extraction from the water to have the final product of compounds in DCM without water.

After having the separate DCM solutions, from the media(s) and from the original water solution, a concentrated form needed to be created. Using a Rotovapor set at 5 psi and 37°C, the DCM solutions were reduced to 1 ML after three iterations of rotovaping – the Rotovapor instrument is shown in Appendix B. Concentrated solution could then be analyzed by a Gas Chromatography/Mass Spectrometry (GCM) instrument. The instrument quantifies the amount of compounds in each solution by targeting specific analytes based on single ions to determine the correct compound and the amount associated with each compound.

This process produced the raw data for adsorption rates of compounds on both nylon and GAC. The data was analyzed to determine the efficiency of GAC adsorption with MPs present in the same solution. Although each compound interacted with each material differently, the overall sorption trend was determined.

PROJECT OUTCOMES

Throughout the experimental phase of the study different results were obtained based on the method of sample processing used. Although there were notable changes in the quantity of compounds adsorbed, the tendency of the adsorption of compounds was similar despite the changes in methodology. One factor contributing to the increased compounds adsorbed by both materials was the presence of a fiberglass filter – removing the filter from the filtration process

allowed more compounds to stay in the water solution. The final method used in the experiments resulted in a decrease of compounds on the MPs and the GAC but with a similar trend.

To magnify the amount of contaminant adsorbed by the two materials, nylon and GAC, three different concentrations were tested. Smaller concentrations did not portray accurate results because of the GCM instrument's measurement limitations. The final results, shown in Appendix D, indicated the ratio of known amounts of compounds, 50 ng and 500 ng, adsorbed by GAC and nylon at different concentrations.

The experiment that magnified the adsorption rates of the compounds had 500 ng of each compound. Nylon is shown to adsorb larger amounts of the five PAHs - fluoranthene, pyrene, chrysene, benzo[b]fluoranthene, and benzo[k]fluoranthene – compared to GAC. Correspondingly, the three CECs – caffeine, diethyltoluamide (DEET), and triclosan – tended to significantly adsorb onto GAC and minimally adsorb onto Nylon. One CEC that did increase its adsorbency to nylon as concentration increased was triclosan.

A better depiction of the adsorbency trend with increased concentration of compounds is shown in Appendix E. The amount of CCs for every gram of material, GAC or nylon, increases with increased concentration of compound solutions. The graphs found in Appendix E enforce the idea that nylon tends to adsorb PAHs, while GAC is efficient at adsorbing DEET, caffeine, and the majority of triclosan.

CONCLUSION

The presence of microplastics (MPs) in engineering systems is concerning due to the adsorption characteristic of polymers. Treatment plants are known to release compounds of

concern (CCs) in treated effluent. With the presence of MPs and CCs in treatment plants, there is a possibility that subjecting plastics to treatment may increase the concentration of CCs on MP surfaces. This study analyzed the efficiency of GAC at desorbing CCs from MPs.

Results obtained from experimental data suggested that GAC was not efficient at filtering, or desorbing, specific compounds of concern. From the eight compounds of focus, three compounds from the compounds of emerging concern (CECs) subcategory – DEET, caffeine, and triclosan – were efficiently desorbed by activated carbon although triclosan also tended to attach to nylon. The remaining five compounds from the polycyclic aromatic compounds (PAHs) subcategory - fluoranthene, pyrene, chrysene, benzo[b]fluoranthene, and benzo[k]fluoranthene – were inclined to adsorb onto nylon.

Final analysis of the results suggest that GAC is not efficient at removing certain compounds from MPs and may contribute to the amount of compounds present on the MPs that are released into local bodies of water. This does not imply that treatment plants are inefficient as a whole – subjecting MPs through activated carbon is only one of the many treatments that treatment plants have to offer. The efficient desorption of CECs using activated carbon suggest that GAC can have an effect on the quality of effluent being released into bodies of water, but the lack of PAHs desorption suggest that effluent requires additional treatment by other means. Future studies should focus on the efficiency of CCs removal from MPs by other treatment processes, or analyze the efficiency of a treatment plant as a whole.

This experiential learning internship has allowed me to conduct research on an emerging topic that will likely affect my career. Having the opportunity to gain insight on the issue of microplastic will better prepare me for designing future engineering systems or facilities. It will also help me have a more sustainable mindset when entering an agency within the USDA.

REFERENCES

Corradini, F., Meza, P., Eguiluz, R., Casado, F., Huerta-Lwanga, E., and Geissen, V. (2019). "Evidence of microplastic accumulation in agricultural soils from sewage sludge disposal." *Science of The Total Environment*, 671, 411–420.

Dafouz, R., Cáceres, N., Rodríguez-Gil, J. L., Mastroianni, N., Alda, M. L. D., Barceló, D., Miguel, Á. G. D., and Valcárcel, Y. (2018). "Does the presence of caffeine in the marine environment represent an environmental risk? A regional and global study." *Science of The Total Environment*, 615, 632–642.

Erni-Cassola, G., Zadjelovic, V., Gibson, M. I., and Christie-Oleza, J. A. (2019). "Distribution of plastic polymer types in the marine environment; A meta-analysis." *Journal of Hazardous Materials*, 369, 691–698.

Lahive, E., Walton, A., Horton, A. A., Spurgeon, D. J., and Svendsen, C. (2019). "Microplastic particles reduce reproduction in the terrestrial worm Enchytraeus crypticus in a soil exposure." *Environmental Pollution*, 255, 113174.

"Microplastics in drinking-water." (2019). *Geneva: World Health Organization*. License: CC BY-NC-SA 3.0 IGO.

Parker, L. (2018). Plastic. *National Geographic*, (06.2018), pp.40-51.

Rakowska, M., Kupryianchyk, D., Grotenhuis, T., Rijnaarts, H., and Koelmans, A. (2012). "Extraction of sediment-associated polycyclic aromatic hydrocarbons with granular activated carbon." *Environmental Toxicology and Chemistry*, 32(2), 304–311.

Rogers, Emily. (2018). “Investigation of polycyclic aromatic hydrocarbons (PAH) absorption from seawater to model microplastic particles.” M.S. Thesis, Norwegian University of Science and Technology, Trondheim, Norway.

Sait, S. (2019). *Characterisation of microplastic fibres and their degradation under environmental conditions*. Norwegian University of Science and Technology.

UNEP (2016). *UNEP Frontiers 2016 Report: Emerging Issues of Environmental Concern*. United Nations Environment Programme, Nairobi, pp.32-43.

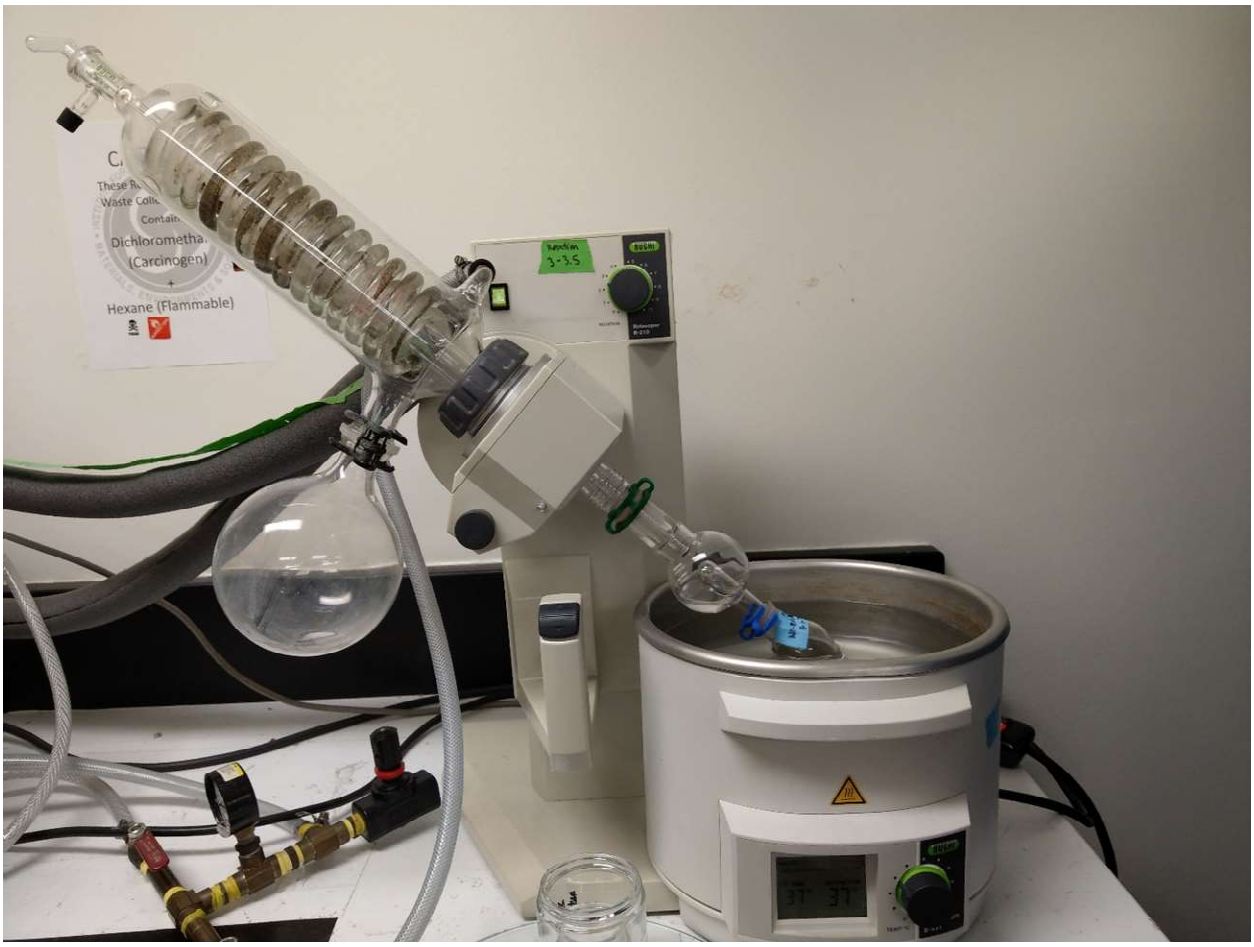
Weeks, J., Guiney, P., and Nikiforov, A. (2011). “Assessment of the environmental fate and ecotoxicity of N,N-diethyl-m-toluamide (DEET).” *Integrated Environmental Assessment and Management*, 8(1), 120–134.

Ziajahromi, S., Neale, P. A., Rintoul, L., and Leusch, F. D. (2017). “Wastewater treatment plants as a pathway for microplastics: Development of a new approach to sample wastewater-based microplastics.” *Water Research*, 112, 93–99.

APPENDIX A: Soxhlet Extraction

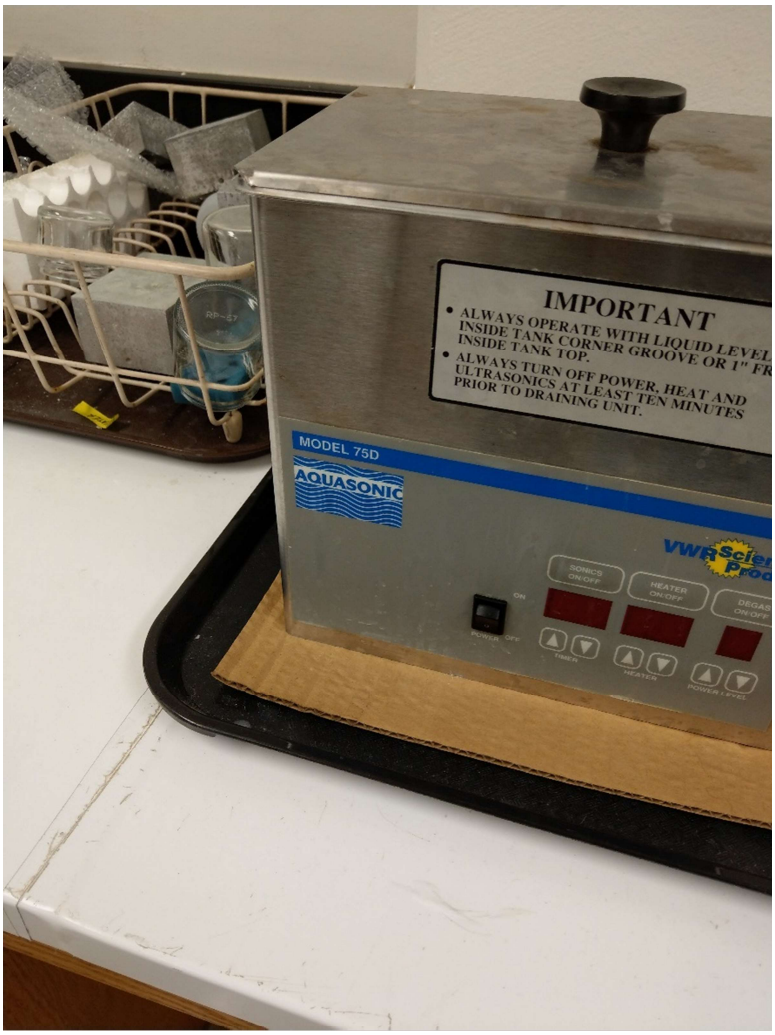
Soxhlet process set-up for extraction of compounds from microplastics or granular activated carbon.

APPENDIX B: RotoVapor



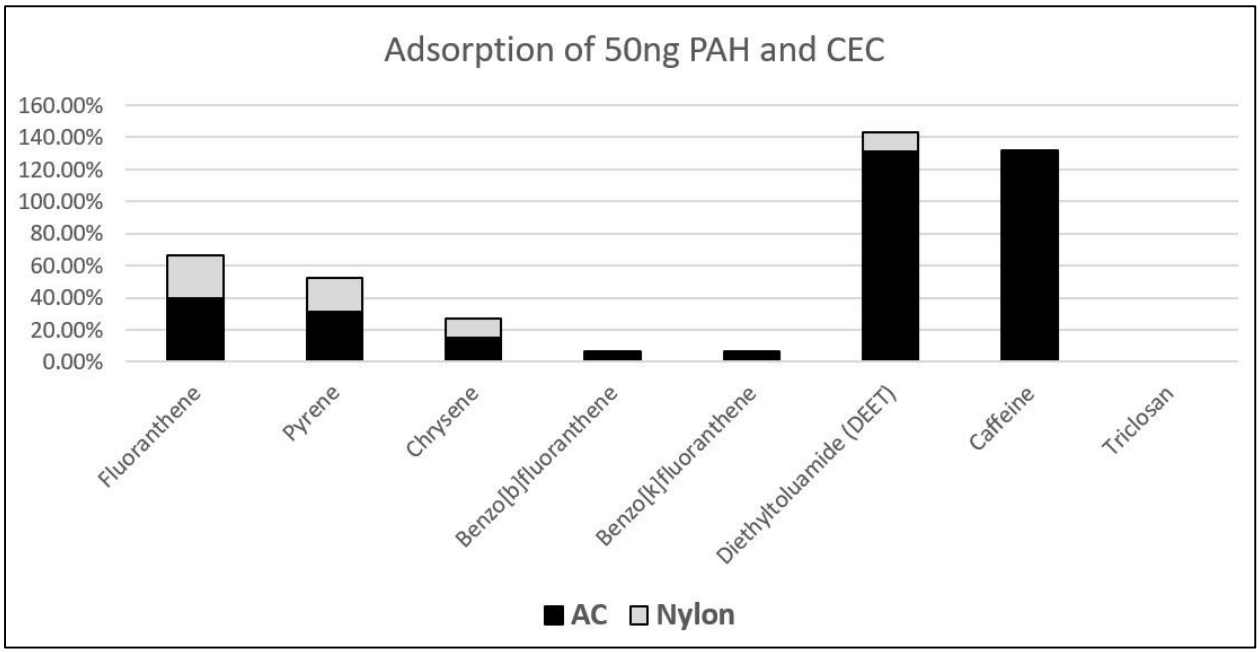
RotoVapor set-up for concentrating the final solutions for Gas Chromatography/Mass Spectrometry (GCM) analysis.

APPENDIX C: Sonicator

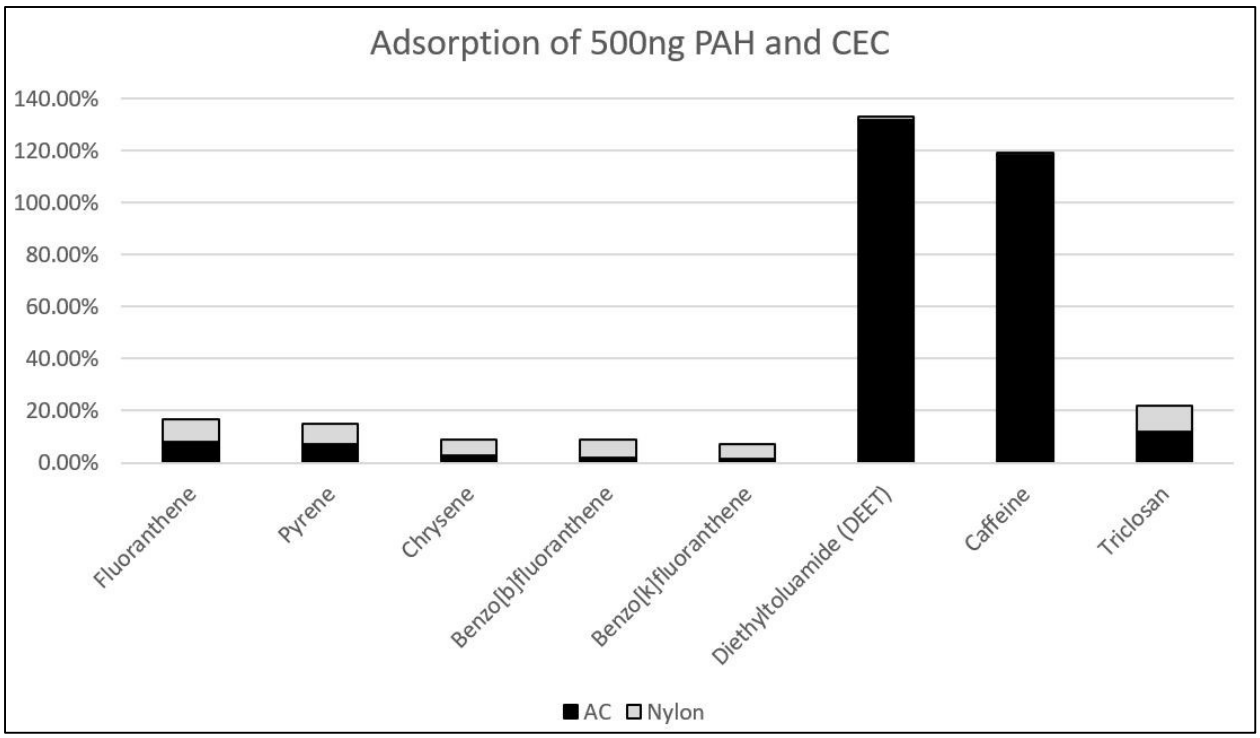


Sonicator instrument used for agitating dichloromethane and water interaction to remove compounds of concern from water.

APPENDIX D: Adsorption of 50ng and 500ng

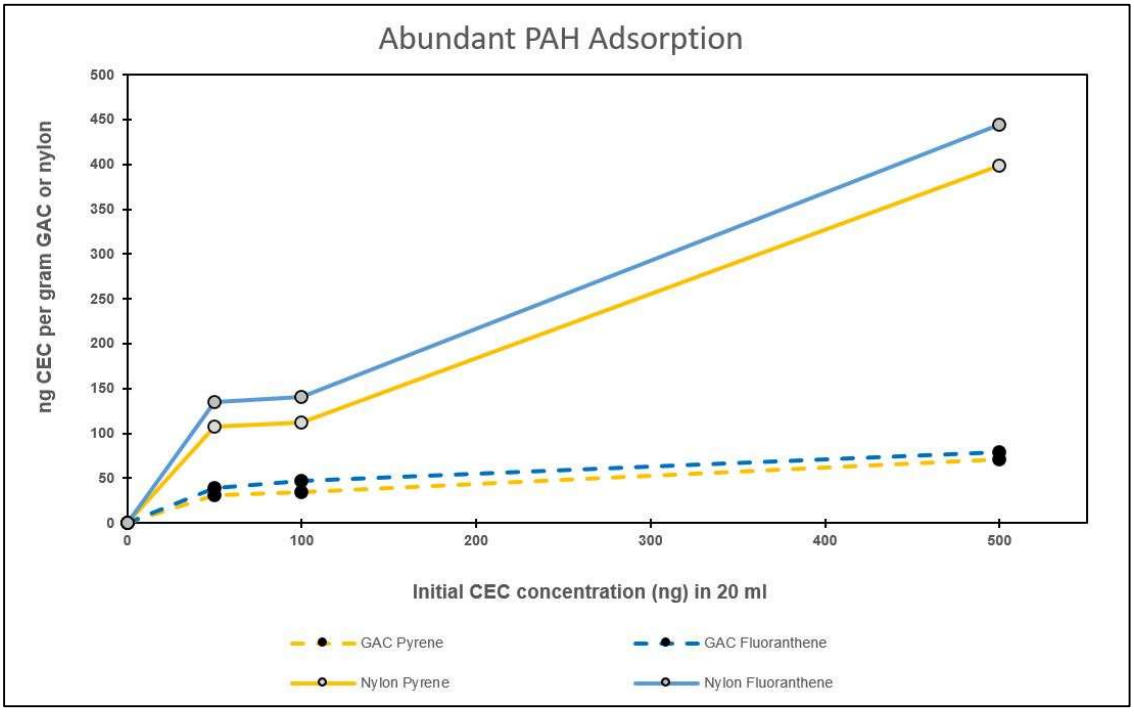


Ratio of GAC and Nylon adsorption of 50ng of compounds

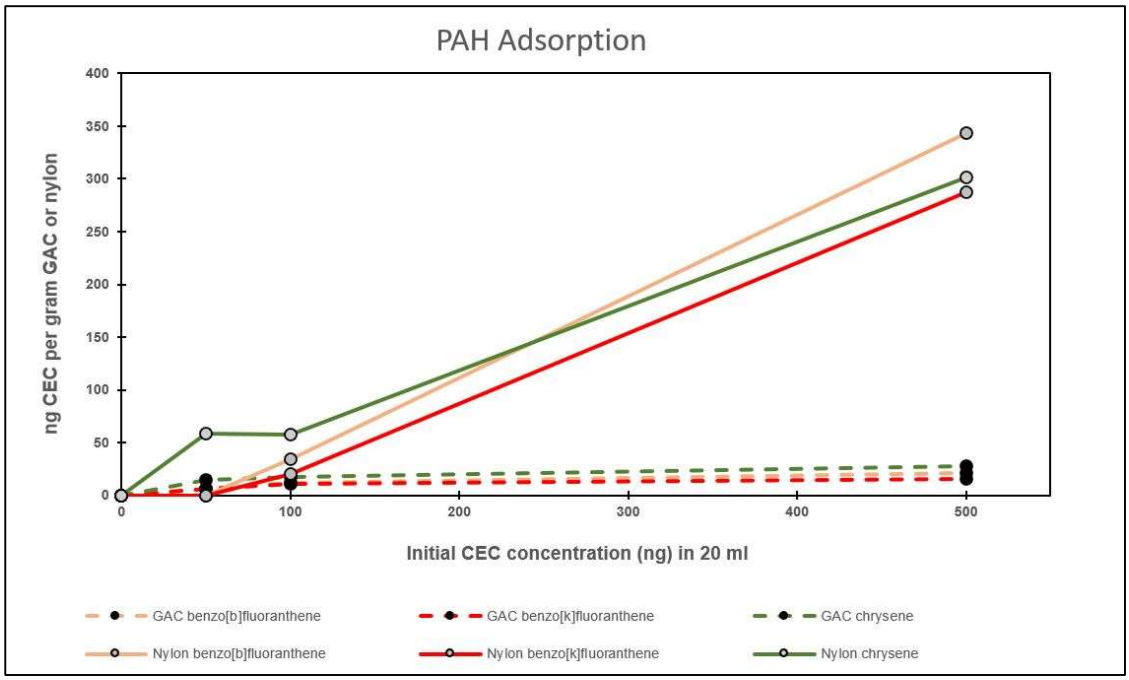


Ratio of GAC and Nylon adsorption of 500ng of compounds

APPENDIX E: Adsorbency Trend PAHs

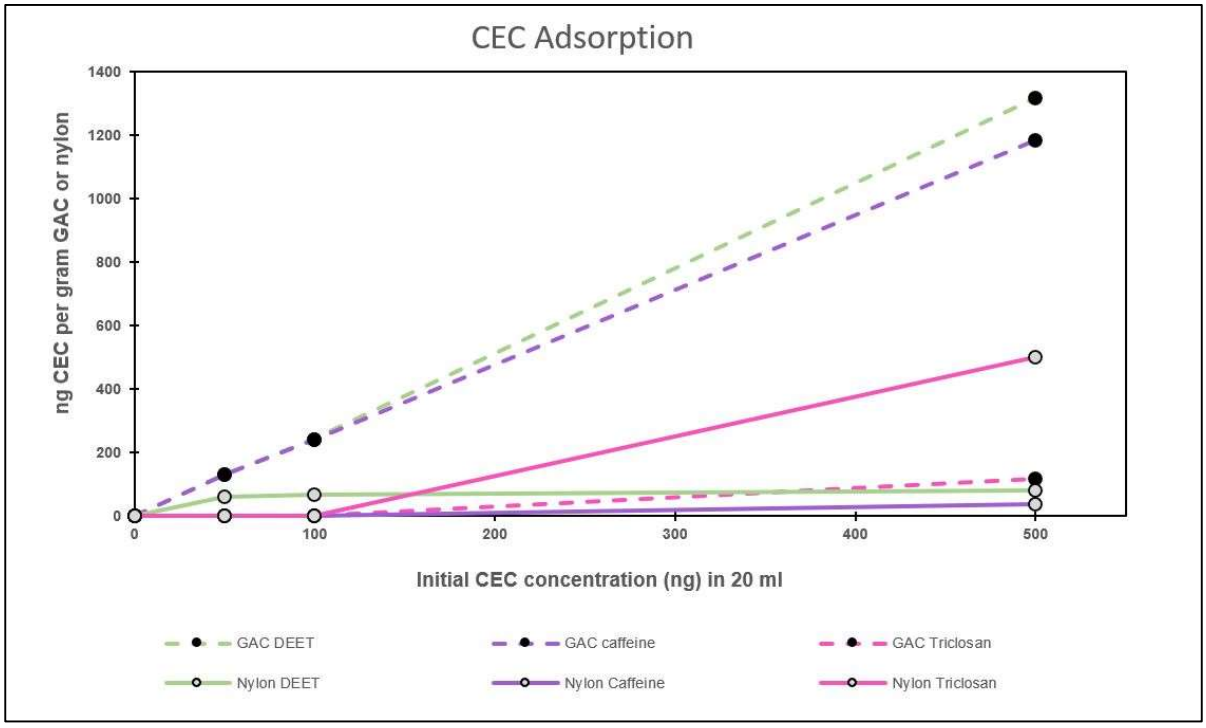


Adsorption trend for the most abundant PAHs present in treatment plants



Adsorption trend for carcinogenic PAHs present in treatment plants

APPENDIX F: Adsorbency Trend CECs



Adsorption trend for CECs present in treatment plants

APPENDIX G: Data: Compound Recovery

	Granular Activated Carbon ng recoved per gram GAC					Nylon Microplastics ng recoved per gram nylon MPs			
	0	**50**	**100**	**500**		**0**	**50**	**100**	**500**
Naphthalene	0	10.24	9.66	15.05	Naphthalene	0	21.2	0	0
2-Methylnaphthalene	0	7.1	6.95	18.42	2-Methylnaphthalene	0	0	0	13.2
1-Methylnaphthalene	0	3.66	5.06	17.56	1-Methylnaphthalene	0	0	0	10.1
Biphenyl	0	1	4.83	29.52	Biphenyl	0	0	0	22.1
2,6-Dimethylnaphthalene	0	0	7.48	46.27	2,6-Dimethylnaphthalene	0	0	0	36.7
Acenaphthylene	0	0	2.48	22.09	Acenaphthylene	0	0	0	30.45
Acenaphthene	0	0	5.93	61.56	Acenaphthene	0	0	0	44.15
2,3,5-Trimethylnaphthalene	0	0	9.36	155.87	2,3,5-Trimethylnaphthalene	0	0	0	108.95
Fluorene	0	2.36	4.89	23.63	Fluorene	0	18.15	0	140.65
Dibenzothiophene	0	6.69	12.91	108.08	Dibenzothiophene	0	21.45	23.5	263.9
Phenanthrene	0	48.53	55.93	119.9	Phenanthrene	0	195.5	196.1	429.65
Anthracene	0	8.15	12.53	46.09	Anthracene	0	31.5	28.75	243
1-Methylphenanthrene	**0**	**27.07**	**38.99**	**91.31**	**1-Methylphenanthrene**	**0**	**91.55**	**95.6**	**391.3**
Fluoranthene	0	39.47	46.44	79.03	Fluoranthene	0	134.35	140.2	443.65
Pyrene	0	31.22	34.4	70.45	Pyrene	0	107.35	112.4	398.8
Benz[a]anthracene	0	11	16.17	26.5	Benz[a]anthracene	0	39.8	45.7	368.15
Chrysene	0	15.02	17.13	28.06	Chrysene	0	58.6	57.35	301.8
Benzo[b]fluoranthene	0	6.44	12.17	21.12	Benzo[b]fluoranthene	0	0	34.15	343.4
Benzo[k]fluoranthene	0	6.6	10.57	15.38	Benzo[k]fluoranthene	0	0	20.3	287.05
Benzo[e]pyrene	0	8.79	12.04	19.59	Benzo[e]pyrene	0	0	32.2	268.3
Benzo[a]pyrene	0	5.68	6.11	13.49	Benzo[a]pyrene	0	0	22.35	246.45
Perylene	0	3.83	5.98	11.63	Perylene	0	0	11.9	138.35
Indeno[1,2,3-c,d]pyrene	0	0	4.43	9.29	Indeno[1,2,3-c,d]pyrene	0	0	30.55	195.25
Dibenz[a,h]anthracene	0	0	3.17	7.34	Dibenz[a,h]anthracene	0	0	13.25	115.5
Benzo[g,h,i]perylene	0	0	6.63	10.26	Benzo[g,h,i]perylene	0	0	25	148.1
Diethyltoluamide (DEET)	0	130.98	242.92	1315.62	Diethyltoluamide (DEET)	0	60.35	68.85	80.85
Caffeine	0	132.1	242.47	1184.11	Caffeine	0	0	0	38.05
Triclosan	0	0	0	118.82	Triclosan	0	0	0	501.85

Compound recovery (ng) of all CCs present in PAH, CEC, and PAH RS solutions