Dissolved Pollutants in the Great Pacific Garbage Patch, December 2021

Dylan Hull

University of Washington

School of Oceanography, Box 357940

Seattle WA 98195-7940

dhull17@uw.edu

Abstract

The intent of this study was to identify and quantify dissolved chemical pollutants in the Northeastern Pacific Ocean. Samples were taken along a transect from Hawaii to San Diego that passed through the southern edge of the Great Pacific Garbage Patch. Determining pollutant loads can help with assessing the risk level of organisms in the open ocean to harmful chemical exposure. I utilized solid phase extraction to isolate dissolved pollutants in surface samples and identified the pollutants using gas chromatography – time of flight mass spectrometry. I expected to detect plasticizers and other persistent organic pollutants known to leach from plastics but also hypothesized that I might detect prescription drugs and non-steroidal anti-inflammatory drugs (NSAIDs). I found plasticizers in all samples, with diethyl phthalate being the most abundant, consistently ranking within the top 10 most abundant chemicals for every sample. These identified compounds landed in the range of .5 to 3 parts per million (PPM). No NSAIDS were found. Despite a negative slope of distance from shore to compounds identified, the transect had a lack of significant differences in chemical abundance and concentration between stations. This suggests a homogenous distribution of abundant anthropogenic compounds.

Plain Language Summary

I tried to detect man-made chemical pollutants dissolved in the waters of the Northeastern Pacific Ocean. Samples were taken between Hawaii and San Diego, with some of the stations landing in the Great Pacific Garbage Patch, a zone with a high abundance of land-based plastics and other garbage. Knowing which pollutants are in the water helps determine whether the organisms in this part of the ocean are susceptible to harmful effects from the chemicals. If the risk of harm can be determined, there will be motivation to make societal changes to prevent harmful chemicals from making their way into the open ocean. After filtering the water and extracting the dissolved chemicals, I identified them by separating them by their mass and chemical composition. I expected to see high levels of plastic-based chemicals and lower concentrations of chemicals used in drugs since there are a lot of plastics in the garbage patch and drugs would have to travel far from shore to be detected in the open ocean. While I did not find any drug-based chemicals, all samples contained chemicals commonly used in making plastics, including diethyl phthalate, which was the most abundant chemical in this study. Most identified compounds landed in the range of .5 to 3 parts per million. In general, there was no evidence for different levels of pollution between each station.

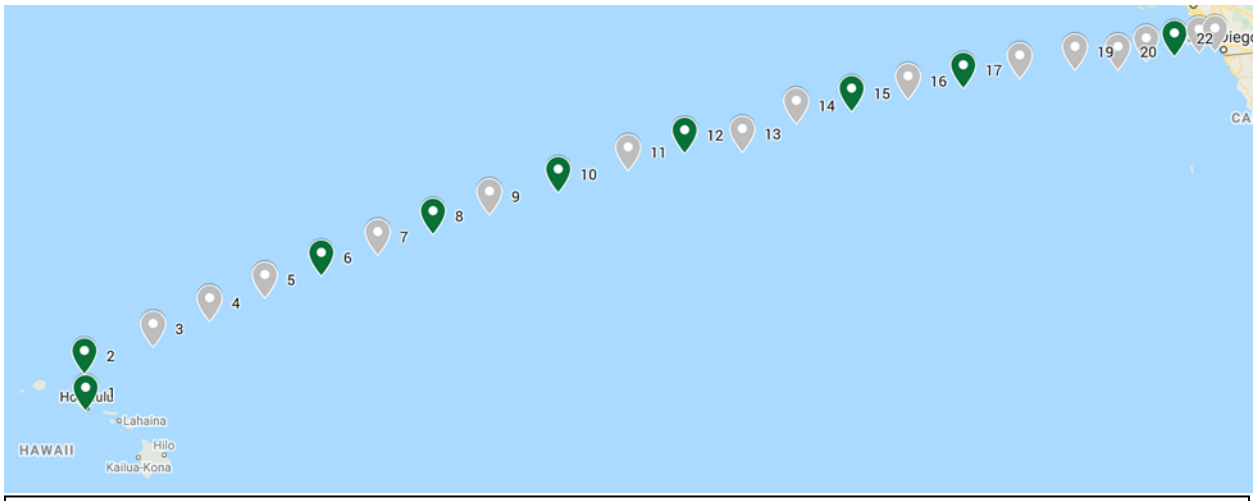

Figure 1: Stations along the path of the R/V Thomas G. Thompson's transit from Honolulu to San Diego. Green stations indicate where samples for this project were taken.

Introduction

Anthropogenic chemical pollutants pose a significant threat to life in the ocean (Crawford & Quinn, 2017). With these pollutants making their way into the ocean, organisms are at risk of ingesting them and incurring harmful effects. These harmful properties include penetration of cells and disruption of the endocrine system due to chemical interaction with biological molecules, which can be accentuated by bioaccumulation (Avio et al., 2015; Teuten et al., 2009). For example, BPA is known to have oestrogenic effects (Teuten et al., 2009). Determining anthropogenic chemical compositions in the open water is crucial for assessing the level of risk for the future. Location specific policies and cleanup plans can only be implemented if the pollutant distribution is well known. I sampled water along a transect from Honolulu to San Diego and identified which chemical pollutants are present and in what concentrations (Figure 1). This transect also passes through the southern edge of the Great Pacific Garbage Patch, which several samples were taken from. These samples were then analyzed using a gas

chromatography – time of flight mass spectrometer in a lab at the University of Washington – Seattle.

The Great Pacific Garbage Patch (GPGP) is an area in the North Pacific Gyre that is known to have especially high concentrations of plastic pollution. This high concentration is due to large scale ocean currents accumulating debris into this gyre (Egger et al., 2020). Pollutants adsorb and desorb from microplastics, which are prevalent in the garbage patch (Chen et al., 2017; Pan et al., 2019; Rios et al., 2010). However, previous literature on the topic has a distinct lack of information on dissolved chemical sampling in the garbage patch specifically. Several papers focus on the plastic pollution in the North Pacific Gyre, noting microplastic concentrations up to 42,000 particles per km^2 in the NW Pacific (Egger et al., 2020) and significant sinking of microplastics in the gyre with higher concentrations at lower depths (Pan et al., 2019). Many others discuss the adsorption of chemicals to microplastics, finding a lack of competitive effects of persistent organic pollutant (POP) adsorption to plastics (Bakir et al., 2012) and the ability of plastics to adsorb metals and act as a source of metals to the ecosystem (Munier & Bendell, 2018). I thus inferred that microplastics can act as a carrier to bringing land-based chemicals to the garbage patch. POPs and other pollutants were found to be adsorbed to plastics in the garbage patch at high enough concentrations to pose a risk to organisms (Chen et al., 2017; Rios et al., 2010), leaving the possibility open for other pollutants to do the same. Potentially, they may even be dissolved in the garbage patch if they are already known to be adsorbed to plastics there. Despite this possibility, only one paper I am aware of has focused on the dissolved chemicals within the eddies on the leeward side of the Hawaiian Islands, finding several dissolved pollutants both inside and outside of the eddies (Lipsy, 2011). This paper

found cumene, lilial, ethyl vanillin, dibutyl phthalate, bisphenol a, and dicyclohexyl phthalate in quantifiable amounts. I planned to replicate similar results in a different geographical area with larger water samples in order to find chemicals lower in concentration. While plastics are easily ingested and therefore a vessel for associated pollutants to enter an organism (Teuten et al 2009, A. Koelmans et al 2016), little is known about dissolved pollutants' main entryway to an organism. Before determining how they are being ingested, it is important to know which dissolved chemicals are present and exposed to organisms in the open ocean. Knowing this would give us more information on the harm these invisible pollutants could cause.

This study looks at pollutants dissolved in the water along the transect. I also collected plastics on filters with the potential for future analysis of chemicals adsorbed to those plastics. I expected that more pollutants would be found in higher concentrations within the garbage patch than in other open ocean areas due to the same factors that cause a plastic buildup in the area. The chemicals found in highest concentrations were expected to be plasticizers and other POPs, which are known to adsorb to plastics (Crawford & Quinn, 2017). I also expected to find measurable albeit lower concentrations of NSAIDs, prescription drugs, cumene, limonene, benzaldehyde, etc (Lipsy, 2011).

Methods

The research cruise traveled on the RV Thomas G. Thompson from Honolulu to San Diego on dates 17 December 2021 to 30 December 2021, passing through the southern edge of the Great Pacific Garbage Patch (Figure 1, Figure 2). I sampled water from the upper 3m of the ocean, chosen due to the high prevalence of microplastics in the waters of the Great Pacific

Garbage Patch relative to other depths (Egger et al., 2020). Using the Thompson's CTD, I collected 20L water samples along the ship's path, with an emphasis on samples near Hawaii and within the garbage patch. I collected samples in the open ocean outside of the garbage patch and close to the California coast for comparison purposes. The samples were then processed and analyzed on a mass spectrometer.

My methods involved sampling 20L of water at around 3m depth from the Thompson's CTD casts and processing the water to be run through a mass spectrometer (Figure 3) (Keil & Neibauer, 2009). The sample processing was split into two distinct sections: one section on board the R.V. Thompson (Figure 2) and one section on land in the lab (Figure 3).

For the shipboard section, a water sample was first extracted from the surface ocean around 5m depth using the CTD and placed into 20L containers. The water sample was then filtered through a 47mm GF-75 glass fiber filter with a nominal pore size of 0.3 microns using vacuum filtration to remove large debris. This now-filtered water was dripped through Waters

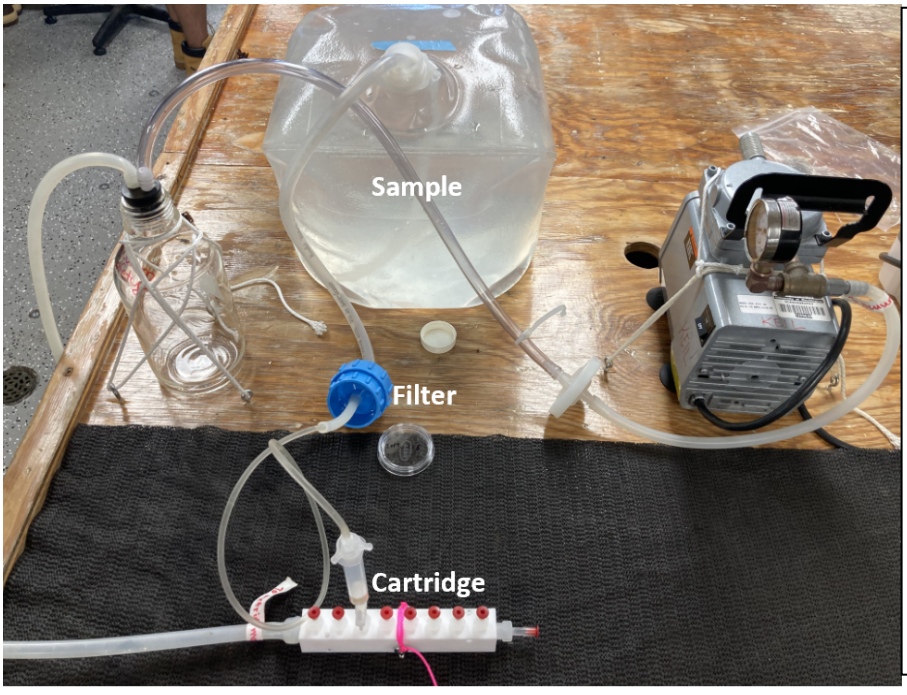

Figure 2: The filtration and cartridge setup on the RV Thompson. The filter is encased in a blue filter holder and the cartridges are held in an 8-cartridge manifold.

Oasis HLB 200mg sorbent solid phase extraction columns which had been prepped with 1ml each of ethyl acetate, methanol, and MilliQ. This allowed the pollutants to be extracted from the water. The extraction columns were then frozen and shipped back to Seattle.

In the lab, I removed the samples from the freezer and allowed them to warm to room temperature while rinsing out the ports of the extraction manifold with ethyl acetate. I then attached sodium sulfate cartridges to the bottom of the HLB cartridges and pipetted 5mL of ethyl acetate into the cartridges to elute the chemicals from the cartridge. This ethyl acetate was then dripped through the cartridges and collected in test tubes. Three more milliliters of ethyl acetate were used for a second rinse. The ethyl acetate was then evaporated using N_2 gas, rinsing the sides with extra ethyl acetate to recover any crystals on the sides of the tubes. Once the samples were crystallized, the crystals were dissolved in 1 mL ethyl acetate and the

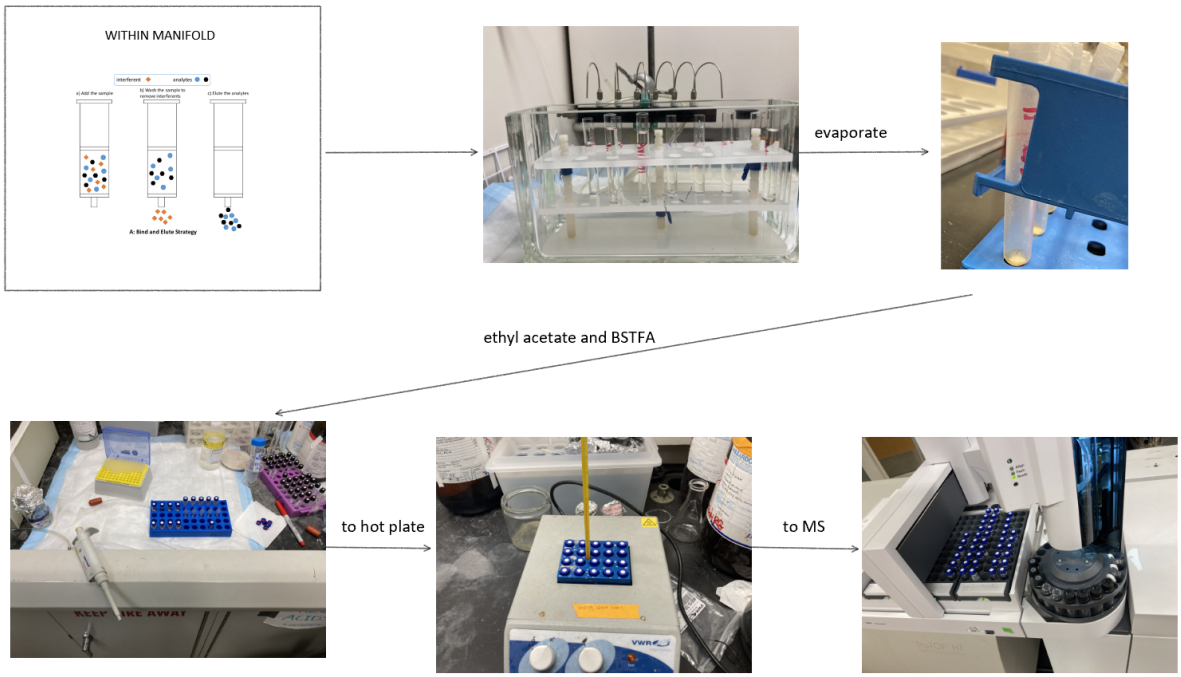

Figure 3: The method for concentrating chemicals from the extraction columns to be run through the mass spectrometer. Elution followed by dissolution and heating before being placed into the GC mass spectrometer.

resulting solution was pipetted into GC vials. Once those vials were allowed to sit for any excess sodium sulfate crystals to settle to the bottom, 50 microliters of the samples and 50 microliters of BSTFA were pipetted into different GC vials with vial inserts. The new vials were then heated for 10 minutes at 60 degrees C. At this point, they were ready to be run on the mass spectrometer. A blank was also run using DI water to determine chemicals that were present in the sample due to the method. Abundance lists and concentrations were computed after subtracting the signal to noise ratio (S/N) found in the blank from the measured S/N per sample. The results were analyzed primarily using R within RStudio as well as Microsoft Excel.

Results

There was a total of 166 known compounds present in the samples, as well as 28 unknown compounds. Of those compounds, there were several present at all or almost all

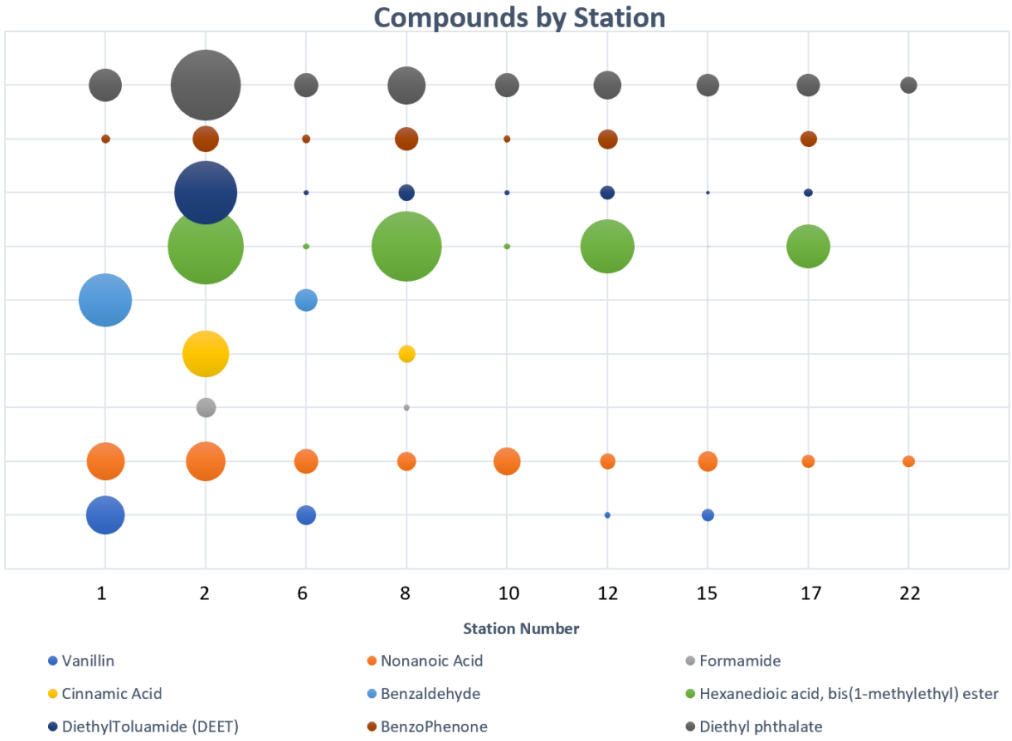

Figure 4: A selection of chemicals organized by stations at which they were found. Bubble size represents the concentration of each compound.

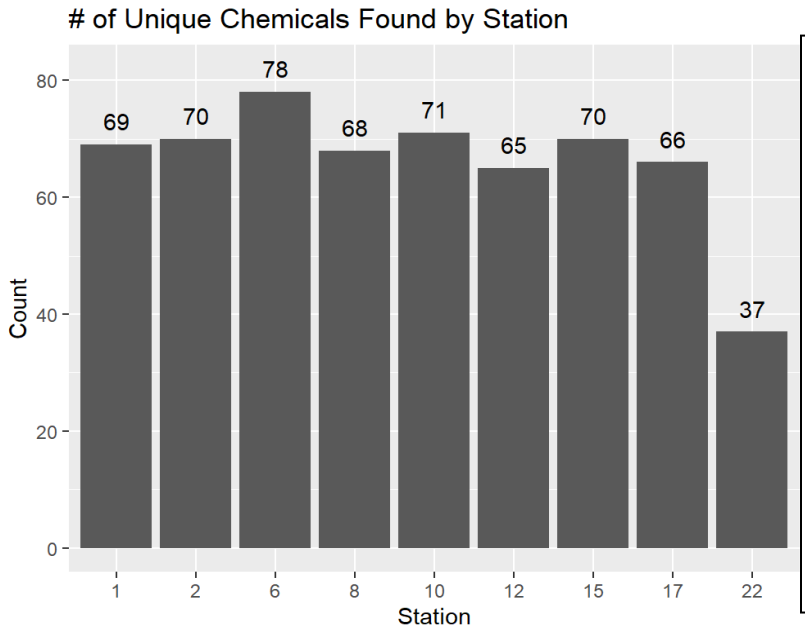

Figure 5: The number of chemicals found at each station. Each station was given a list of compounds found by the mass spectrometer with station 6 receiving the highest number and station 22 receiving the lowest. It is important to note that only 10L of water were processed at station 22.

stations, while some were much less common. For example, nonanoic acid, a known plasticizer, was found at all nine stations; in contrast, benzaldehyde, a compound used in cherry or almond flavoring, was only found at stations 1 and 6 (Figure 4).

The number of chemicals found at each station was also determined and compared to the distance from shore of each station. The highest number of chemicals for a specific station was at Station 6 and the lowest was at Station 22 (Figure 5). Using linear regression, there was a slight negative trend when relating number of compounds found to the distance each station was from shore, although this slope lacks significance (Figure 6). There was a similar lack of significance when considering only anthropogenic compounds (Figure 6); compounds were considered abundant anthropogenic compounds if they appeared on multiple abundance lists and were determined to be anthropogenic (Table 1). Station 22 was removed from the dataset for linear regression as an outlier as only 10L of water were processed. In comparing GPGP location and station location, it was determined that Stations 10 and 12 would be considered as

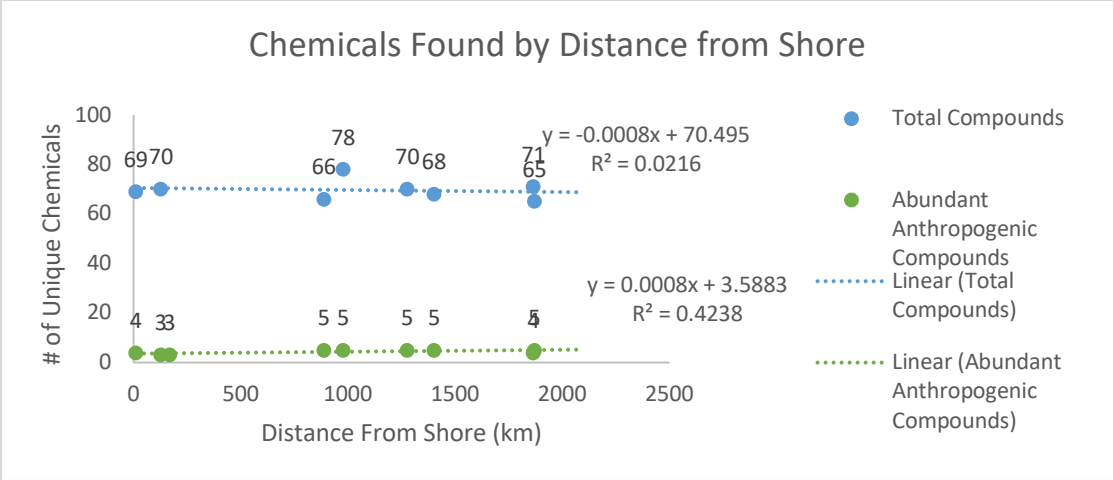

Figure 6: This figure presents the number of compounds as a function of distance from the closest shore. The linear regression performed here shows slopes that lack significance for both total compounds and abundant anthropogenic compounds.

garbage patch stations with Stations 8 and 15 considered on the fringe but classified as garbage patch and open ocean, respectively. Stations 6 and 17 would be open ocean stations which leaves stations 1, 2, and 22 as near coast stations for comparison purposes.

The chemicals with the highest concentrations at each station were also quantified and totaled to determine the most abundant compounds found in the open ocean. In this case,

Table 1: Compounds and number of occurrences for which they are within the 10 most concentrated compounds at each station. Source was determined based on primary uses/occurrences in nature or industry.

Compound	Source	# Occurences
Diethyl Phthalate	Anthropogenic	9
Dodecanoic acid, trimethylsilyl ester	Natural	8
Dibutyl phthalate	Anthropogenic	7
Nonanoic acid, trimethylsilyl ester	Both	6
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	Anthropogenic	6
Benzenesulfonamide, N-butyl-	Natural	5
Hexadecanoic acid, trimethylsilyl ester	Natural	5
5-(4-Chlorophenyl)thiophene-2-carboxylic acid	Natural	4
Hexanedioic acid, bis(1-methylethyl) ester	Anthropogenic	4
Propanoic acid	Both	4
Bisphenol A	Anthropogenic	3
Decanoic acid, trimethylsilyl ester	Both	3
Trimethylsilyl vanillin	Anthropogenic	3
Benzaldehyde, 3,5-dimethoxy-4-[(trimethylsilyl)oxy]-	Anthropogenic	2
Benzophenone	Anthropogenic	2
Butane, 2-phenyl-3-(trimethylsilyloxy)-	Anthropogenic	2
Octanoic acid, trimethylsilyl ester	Anthropogenic	2
Silane, trimethyl(phenylmethoxy)-	Natural	2

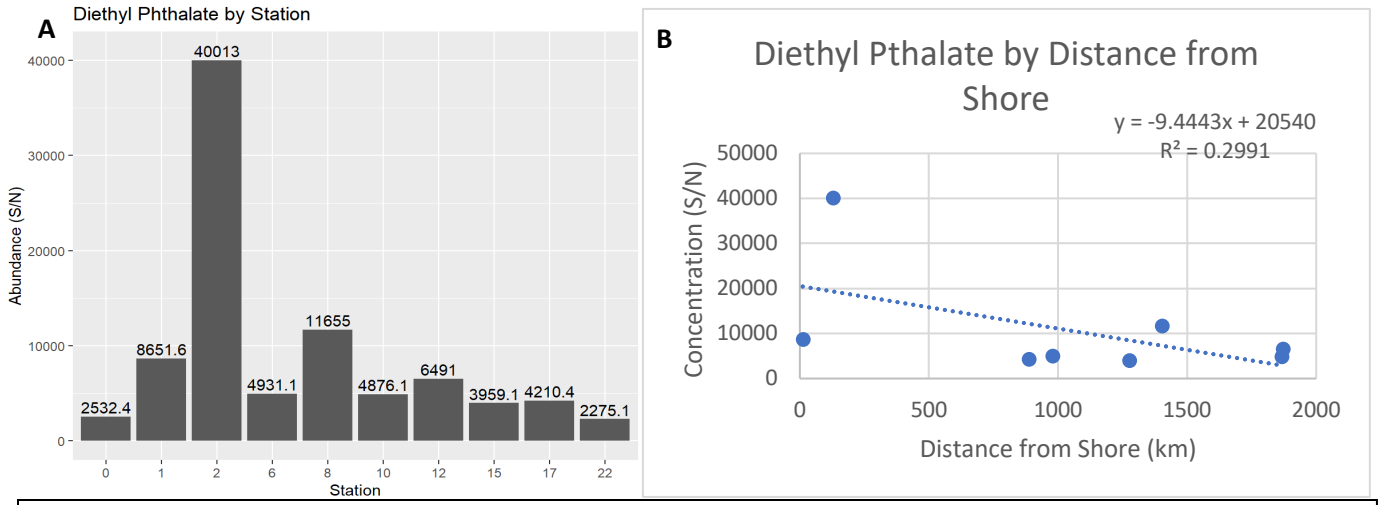

Figure 7: A) The signal to noise ratio (S/N) for diethyl phthalate at each station. **B)** The S/N of diethyl phthalate as a function or the station's distance from shore. Diethyl phthalate was determined to be the most common compound across the sample stations. It is a known plasticizer and is therefore anthropogenically sourced. Station 0 is a method blank.

abundant compounds are both common across stations and highly concentrated at each station it appears. Since it is highly concentrated, between .5 and 3.5 PPM, it will appear in the abundance list for a given station, which is a list of the 10 most concentrated compounds at each station. These abundance lists were found and the number of times each compound appeared in these lists was recorded (Table 1). Diethyl phthalate would be considered the most abundant due to its appearance in every list. The diethyl phthalate distribution shows a major peak at station 2 (3 PPM) with smaller increases at station 8 and station 1 (Figure 7A). The trend suggests that diethyl phthalate decreases with distance from shore, with a low R^2 value of .2991 (Figure 7B).

Discussion

Determining the chemical composition and concentration within each sample provided a map of which chemical pollutants were present in which areas along the transect. With stations 10 and 12 being considered GPGP stations, it was expected that they would have the highest number of chemical pollutants identified. However, the highest number of identified compounds was found at station 6, an open ocean station (Figure 5). This correlates with manta net tows deployed on the same cruise, where the highest plastic weight was found at station 6 (Miller, 2022). This is promising in suggesting that plastic abundance is related to the number of compounds present at a given station.

Station 2, which is at Station ALOHA (a famous time series waypoint), had the highest concentrations per chemical across measured chemicals (Figure 4). Station 2 is considered a coastal station that is bordering on open ocean. The stations closest to shore were expected to have the highest concentrations of both anthropogenic and natural compounds, so it is surprising that station 2 has the highest concentrations when stations 1 and 22 were closer to shore. This expectation was due to proximity to human settlements and the high biological activity in the coastal environment. Using linear regression to determine compound occurrence, I could not establish a relationship between distance from shore and the number of compounds present in the samples. The R^2 value and exceptionally low slope obtained through regression does not show promise in establishing a relationship between distance from shore and the number of compounds appearing in each sample (Figure 6). For abundant anthropogenic compounds, the slope was also too low to make any significant conclusions (Figure 6). Thus, we cannot claim there is any statistically significant relationship between the number of chemical compounds present in a sample and the distance each station was from shore.

When comparing data to another, more coastal dataset, it seems that certain compounds are less common farther from shore. No traces of salicylic acid, cumene, or limonene were found despite being found in a prior study done closer to the Hawaiian Islands (Lipsy 2011). Despite this, there were traces of benzaldehyde, vanillin, and dibutyl phthalate found at several stations (Figure 4).

Three compounds that appeared in most abundance lists were diethyl phthalate, dodecanoic acid, and nonanoic acid; these compounds' relative sources are anthropogenic, natural, and a mixture of both (Table 1). Those that are anthropogenic would be sourced from land while natural sources would be produced by physical or biological processes in the ocean. The most abundant compound, diethyl phthalate, is a plasticizer that is commonly used in soft plastics. Dodecanoic acid is a biological compound, while nonanoic acid is biological but also commonly used as a plasticizer as well. Diethyl phthalate was found at every station in concentrations higher than the blank. This suggests that it was present along the entire transect, even in the open ocean. There was a decrease in concentration as the stations moved further from shore that suggests it was more common in the coastal regions (Figure 7B). The slope of the regression line is not significant, however, and the peak at station 2 is likely causing the trend as a significant influential outlier (per Cook's Distance outlier method). Diethyl phthalate is just one example of an exceptionally widespread chemical. Other abundant anthropogenic compounds included the plasticizers dibutyl phthalate and hexanedioic (adipic) acid, as well as octanoic acid and benzophenone, which are used in the manufacturing of perfumes and dyes (Table 1). Using a chi-squared goodness of fit test, I also determined there

was not enough evidence to suggest a difference in the number of abundant anthropogenic compounds based on station classification (garbage patch, open ocean, or coastal).

Conclusion

Plasticizers are heavily used in plastic products and are known to leach from these plastics that make their way into the ocean (Crawford and Quinn, 2017). With data supporting a constant leaching of plasticizers into the oceanic environment, plasticizer pollution should be viewed as a contributor to overall plastic pollution along with the solid plastic pieces they come from. Using diethyl phthalate as an indicator of overall anthropogenic chemical pollution, I can suggest that coastal regions could be more susceptible to plasticizer pollution. However, the open ocean should not be forgotten when discussing the possibility of dissolved anthropogenic chemicals making their way into pelagic waters. With 10 anthropogenically-sourced compounds found to be abundant, we should continue to monitor the dissolved pollutants that reach the open ocean. These compounds are appearing far offshore, not just coastal regions where they originate. Due to their abundance and potential uptake by biological organisms, the biological effects of these compounds should be investigated in future studies of both pelagic and coastal regions.

Acknowledgements

I would like to thank Dr. Jaqui Neibauer and Dr. Rick Keil for help throughout the project and in particular for their expertise in running the experiments. Dr. Kathy Newell and the rest of the OCEAN 445 professors were exceptional in their help with the creation of this thesis paper. I would also like to thank the crew of the Thompson for providing me the opportunity to sail on their ship and their help with collecting samples. Finally, I would like to thank the UW School of Oceanography for funding this cruise and allowing undergraduates like myself a wonderful opportunity to perform research.

References

Avio, C. G., Gorbi, S., Milan, M., Benedetti, M., Fattorini, D., D'Errico, G., Pauletto, M., Bargelloni, L., & Regoli, F. (2015). Pollutants bioavailability and toxicological risk from

microplastics to marine mussels. *Environmental Pollution*, *198*. https://doi.org/10.1016/j.envpol.2014.12.021

Bakir, A., Rowland, S. J., & Thompson, R. C. (2012). Competitive sorption of persistent organic pollutants onto microplastics in the marine environment. *Marine Pollution Bulletin*, *64*(12), 2782–2789. https://doi.org/10.1016/J.MARPOLBUL.2012.09.010

Bakir, A., Rowland, S. J., & Thompson, R. C. (2014). Enhanced desorption of persistent organic pollutants from microplastics under simulated physiological conditions. *Environmental Pollution*, *185*, 16–23. https://doi.org/10.1016/J.ENVPOL.2013.10.007

Chen, Q., Reisser, J., Cunsolo, S., Kwadijk, C., Kotterman, M., Proietti, M., Slat, B., F. Ferrari, F., Schwarz, A., Levivier, A., Yin, D., Hollert, H., & A. Koelmans, A. (2017). Pollutants in Plastics within the North Pacific Subtropical Gyre. *Environmental Science & Technology*, *52*(2), 446–456. https://doi.org/10.1021/acs.est.7b04682

Crawford, C. B., & Quinn, B. (2017). The interactions of microplastics and chemical pollutants. *Microplastic Pollutants*, 131–157. https://doi.org/10.1016/B978-0-12-809406-8.00006-2

Egger, M., Sulu-Gambari, F., & Lebreton, L. (2020). First evidence of plastic fallout from the North Pacific Garbage Patch. *Scientific Reports 2020 10:1*, *10*(1), 1–10. https://doi.org/10.1038/s41598-020-64465-8

Keil, R. G., & Neibauer, J. A. (2009). Analysis of cooking spices in natural waters. *Limnology and Oceanography: Methods*, *7*(DEC), 848–855. https://doi.org/10.4319/LOM.2009.7.848

Koelmans, A., A. Bakir, G. Allen Burton, & C. Janssen, (2016). Microplastic as a Vector for Chemicals in the Aquatic Environment: Critical Review and Model-Supported Reinterpretation of Empirical Studies. *Environmental Science & Technology*, *50*(7), 3315–3326. https://doi.org/10.1021/acs.est.5b06069

Lara-Martín, P., A. Chiaia-Hernández, M. Biel-Maeso, R. Baena-Nogueras, & J. Hollender, (2020). Tracing Urban Wastewater Contaminants into the Atlantic Ocean by Nontarget Screening. *Environmental Science & Technology*, *54*(7), 3996–4005. https://doi.org/10.1021/acs.est.9b06114

Lipsy, R. F. (2011). Eddy impact on anthropogenic chemicals in the lee of Hawai'i.

Miller, A. (2022). Marine bacteria colonization rate.

Munier, B., & L. I. Bendell, (2018). Macro and micro plastics sorb and desorb metals and act as a point source of trace metals to coastal ecosystems. *PLOS ONE*, *13*(2), e0191759. https://doi.org/10.1371/JOURNAL.PONE.0191759

Pan, Z., Sun, X., Guo, H., Cai, S., Chen, H., Wang, S., Zhang, Y., Lin, H., & Huang, J. (2019). Prevalence of microplastic pollution in the Northwestern Pacific Ocean. *Chemosphere*, *225*, 735–744. https://doi.org/10.1016/J.CHEMOSPHERE.2019.03.076

Rios, L. M., Jones, P. R., Moore, C., & Narayan, U. v. (2010). Quantitation of persistent organic pollutants adsorbed on plastic debris from the Northern Pacific Gyre's "eastern garbage patch." *Journal of Environmental Monitoring : JEM*, *12*(12), 2226–2236. https://doi.org/10.1039/C0EM00239A

Teuten, E. L., Saquing, J. M., Knappe, D. R. U., Barlaz, M. A., Jonsson, S., Björn, A., Rowland, S. J., Thompson, R. C., Galloway, T. S., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Viet, P. H., Tana, T. S., Prudente, M., Boonyatumanond, R., Zakaria, M. P., Akkhavong, K., … Takada, H. (2009). Transport and release of chemicals from plastics to the environment and to wildlife. *Philosophical Transactions of the Royal Society B: Biological Sciences*, *364*(1526), 2027–2045. https://doi.org/10.1098/RSTB.2008.0284