Xenobiotic contaminants in the equatorial Pacific near American Samoa

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Abstract

In this study, I examined the spatial distribution and concentration of various xenobiotic contaminants in the waters of the equatorial Pacific near American Samoa. Using state-of-the-art mass spectral techniques, I determined if pollutant loads increase near urban environments, as well as how individual manmade contaminants present spatially. I collected water samples in the region around American Samoa from December 28th, 2023, to January 11th, 2024, then extracted pollutant chemicals from the sample via solid phase extraction using hydrophilic-lipophilic balance (HLB) cartridges and performed analysis of chemical concentrations using gas chromatography-mass spectrometry (GC-MS). This was followed by a detailed spatial comparison of the chemical pollutants. Spatially, compound abundance was generally found to decrease moving away from urban environments. The highest concentration of a pollutant was 6.1 parts per billion of azelaic acid at Site 4. Industrial anthropogenic pollutants such as n-tridecane (0.065-0.12 ppb) and benzyl butyl phthalate (0.065-4.0 ppb) were confidently found near the airport and fuel depot in American Samoa, the latter of which has been provided evidence of being toxic to humans. Assessing the spatial distribution of xenobiotic pollutants in relation to urban environments can help improve current understanding of how much manmade pollution is entering and persisting in the ocean, which can endanger ecosystems and human health.

Plain Language Summary

I set out to detect manmade chemical pollutants surrounding America Samoa and the equatorial Pacific Ocean. I took water samples from December 28th, 2023, to January 11th, 2024 and tested them for pollutants. Understanding which pollutants are in the ocean can tell us how much we are contaminating the water and what dangers it might pose to the environment. I collected chemicals from the ocean samples on a cartridge, then I identified the compounds by their mass and chemical composition. Unique chemicals such as benzyl butyl phthalate – a compound that makes materials

more plastic and has shown evidence of being toxic to the human reproductive system - were found at near urban environments (CPSC, 2010). Compounds were generally found to decrease in abundance moving away from American Samoa and the urban environment.

Introduction

Xenobiotic pollutants are manmade chemicals that are foreign to an ecological system and are released into the environment by human activity. Chemicals used in flame retardants or sealants, such as polyfluoroalkyl substances (PFAS), or in medical settings, such as nonsteroidal anti-inflammatory drugs (NSAIDs), may leach into the ocean from stormwater runoff or wastewater discharge and have devastating impacts on ecosystems and human health (James et al., 2020).

Synthetic compounds can pose risks to marine ecosystems and people. Petroleum-based pollutants have been shown to decrease photosynthetic rates in phytoplankton and other photoautotrophs in the ocean, resulting in less oxygen production, highly impacting ecosystems (Landrigan et al., 2020). Beyond environmental impacts, benzyl butyl phthalate (BBP), a plasticizer (added to materials to increase their plasticity), has potential human health risks. BBP was found to have caused a reduction in human peripheral blood mononuclear cell viability by induction of cell necrosis (Sicińska, 2019). In previous studies it has been concluded that higher BBP concentrations may be associated with increased endometriosis in women (CPSC, 2010). Fentanyl, an opioid prescribed medically and frequently used illicitly, is lethal in small doses to humans, and is shown to cause hypoactive behavior in zebrafish larvae (Kirla et al., 2021). The presence of these types of pollutants could have extremely harmful impacts on not only ocean ecosystems, but also on human health.

This study focused on detecting the abundance of industrial, pharmaceutical, and commercial compounds, as well as various other xenobiotic contaminants to assess possible anthropogenic pollution in the marine environment of the equatorial Pacific. Similar research has focused on anthropogenic chemicals in the lee of Hawaii, or dissolved pollutants in the Great Pacific Garbage Patch, in which diethyl phthalate, dodecanoic acid, and nonanoic acid were found most commonly (Lipsy, 2011; Hull, 2021). In 2009 and 2010, a survey of contaminants of emerging concern found flame retardants, pharmaceuticals, PCBs, and polybrominated diphenyl ethers (PBDEs) at more than 50% of sites along the California coast (Alvarez, 2014). Although pain-relievers like salicylic acid are removed from sewage at high efficiencies of 99%, they are still detectable in treated wastewater that is then allowed to enter marine environments (Keil et al., 2011). Further research can inform us about how abundant “removed” chemicals such as these pain-relievers are in the equatorial Pacific region, as well as the efficacy of current pollution treatments.

A previous study found pollutant concentrations were 10-100 times higher in urbanized Puget Sound, WA, than in lowly populated Barkley Sound, BC (Keil et al., 2011). In this same study, dibutyl phthalate and benzaldehyde, a plasticizer and an industrial solvent, were not detected at all in Barkley Sound but were found to be in high abundance in Puget Sound. In my work I similarly looked at abundances of plasticizers and industrial solvents among other xenobiotic chemicals. I sampled in the open waters of the equatorial Pacific and near American Samoa, which have not been previously surveyed for pollutants. This presents unique anthropogenic pollution signatures and sources.

There is risk of bioaccumulation of certain toxic chemicals within marine food chains. PBDEs, used as flame retardants, are ubiquitous in marine environments and have the highest levels of contamination near urban shores (Yogui et al., 2009). PBDEs are toxic and tend to persist long after their release, accumulating in food chains and concentrating in high trophic levels (*Canadian Environmental Sustainability Indicators*, 2020). PBDEs are very similar to polychlorinated biphenyls (PCBs), which have been banned in the U.S. since 1979, but unlike PCBs, they have been found to be increasing rather than decreasing in concentration in biota and human tissues over the past thirty years, with the highest lipid concentrations being in salmon, fatty fish, tuna and sardines (Costa et al., n.d.). PBDEs are highly suggested to be endocrine disruptors and developmental neurotoxicants, but their effects in the ocean and on marine mammals are not well known. Alternative flame retardants to PBDEs include organophosphates like triphenyl phosphate, which pose their own environmental concerns. Triphenyl phosphate has been found to hinder DNA damage repair in liver cells and disturb the metabolism of zebrafish in low concentrations (Du et al., 2016).

In 2014, PBDEs and PFASs increased with urbanization along the California coast (James et al., 2020). Multiple studies show that proximity to industrial areas, industrialized agriculture, and places of high human population influence pollutant concentrations (Landrigan et al., 2020). I hypothesized I would find higher concentrations of contaminants near the urbanized coasts of American Samoa because of this, which generally was observed to be true. I also expected the Manu'a Islands, with a population of around only 800 people, near sampling Sites 7 and 8, to have a pollutant load more similar to open-ocean chemistry than coastal-ocean chemistry. This was also observed to be true. Detecting the presence and quantifying the concentration of these pollutants, as well as spatial patterns off the coast, can help us identify which contaminants are most abundant and have the potential to pose a danger to the ecosystem and to ourselves.

Methods

Sampling took place from December 28, 2023, through January 11, 2024, in the equatorial Pacific Ocean off the coast of American Samoa aboard the *R/V Thomas G Thompson.* Surface ocean samples were taken by a 12 Niskin bottle CTD rosette and bucket tows. I collected the surface samples in 10-liter collapsible containers at each station as the ship steamed away from American Samoa. Sampling started at the harbor at Site 1 at 14.27°S and 170.70°W, then moved to sampling Sites 2-7 (Fig 1), retrieving water from the surface as the ship transited. Site 5 was offshore the urbanized environment of the city of Tafuna and the Pago Pago International Airport, and Site 2 was taken while refueling at the fuel depot.

Sampling continued toward the Manu'a Islands, where two samples were taken between islands (Fig. 1), then moved to the equator. To sample the open waters, I took three more samples approximately around these locations: 13.5°S and 169°W, 8°S and 169°W, and 3°S and 167°W. I anticipated there to be a decreasing change in chemical concentration moving away from the island and anthropogenic sources, therefore allowing for distance between samples to be greater.

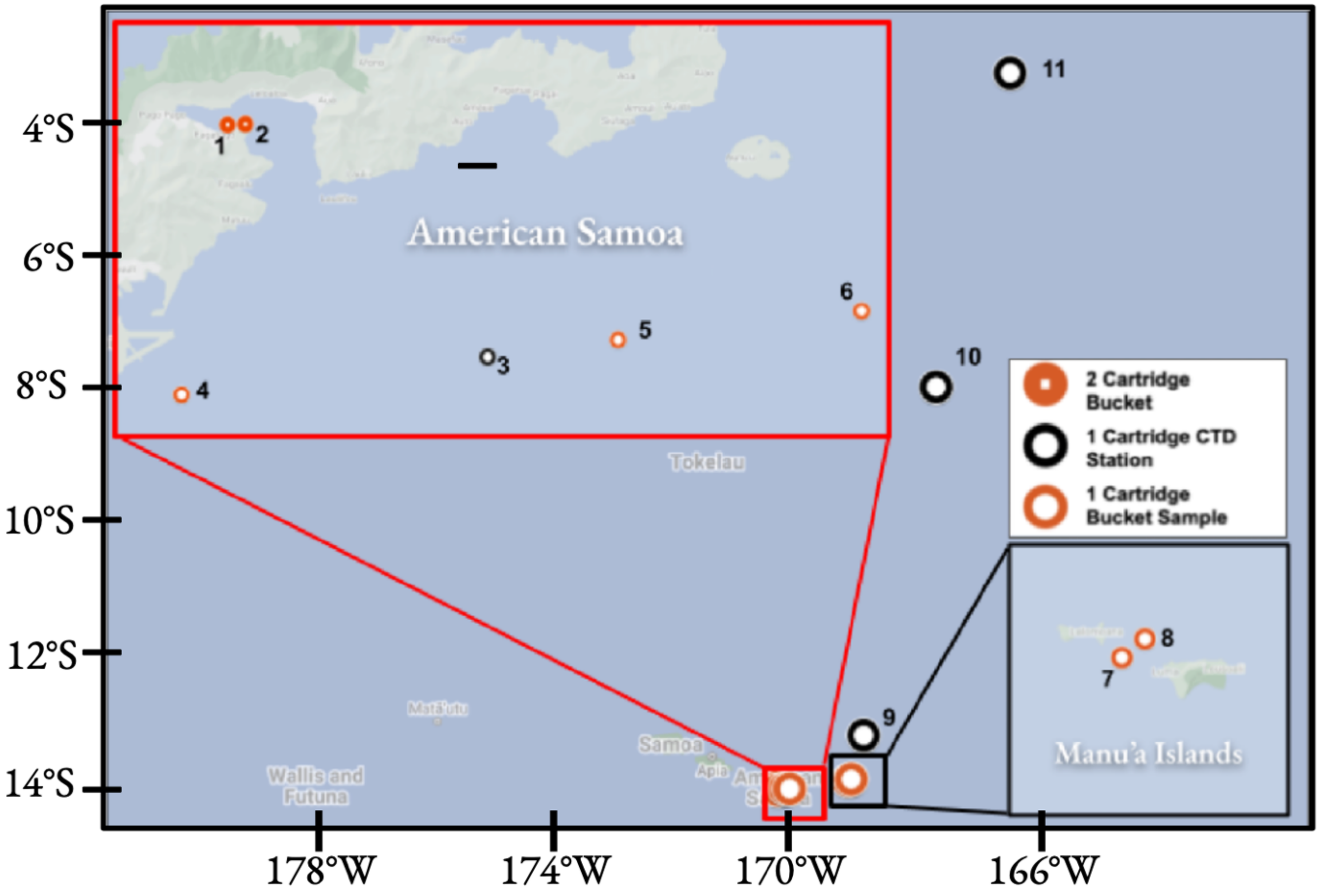

Figure 1: Sampling sites in the equatorial Pacific. Numbers beside each sampling site (indicated by circular markers) are site number. Small red box on the bottom indicates region where red-outlined inset of American Samoa lies on the larger map. Small black box indicates where black-outlined inset of the Manu'a Islands lies on the larger map. Legend shows how the sample was collected (by bucket (orange) or by CTD station Niskin bottle (black) and how many cartridges were used to filter a 10-liter sample (marker shape).

On board the ship I used HPLC-grade hydrochloric acid to acidify the samples to a pH of less than 3 in order to protonate the chemicals for extraction. I set up chemical extraction in accordance with the method of solid phase extraction found by Keil and Neibauer (2009), in which the ocean samples were gravity-dripped through HLB at a drip-rate of around 1-2 drops per second (Fig 2). I added 20 µL of 1 mM 3, 4 dihydroxybenzoic acid to the water sample as a recovery standard, then shook the sample to ensure it was well mixed. A 60 mL syringe was used to get the sample to flow through the cartridge. A 5-gallon jug collected waste that passed through the cartridge, which was neutralized before being disposed of.

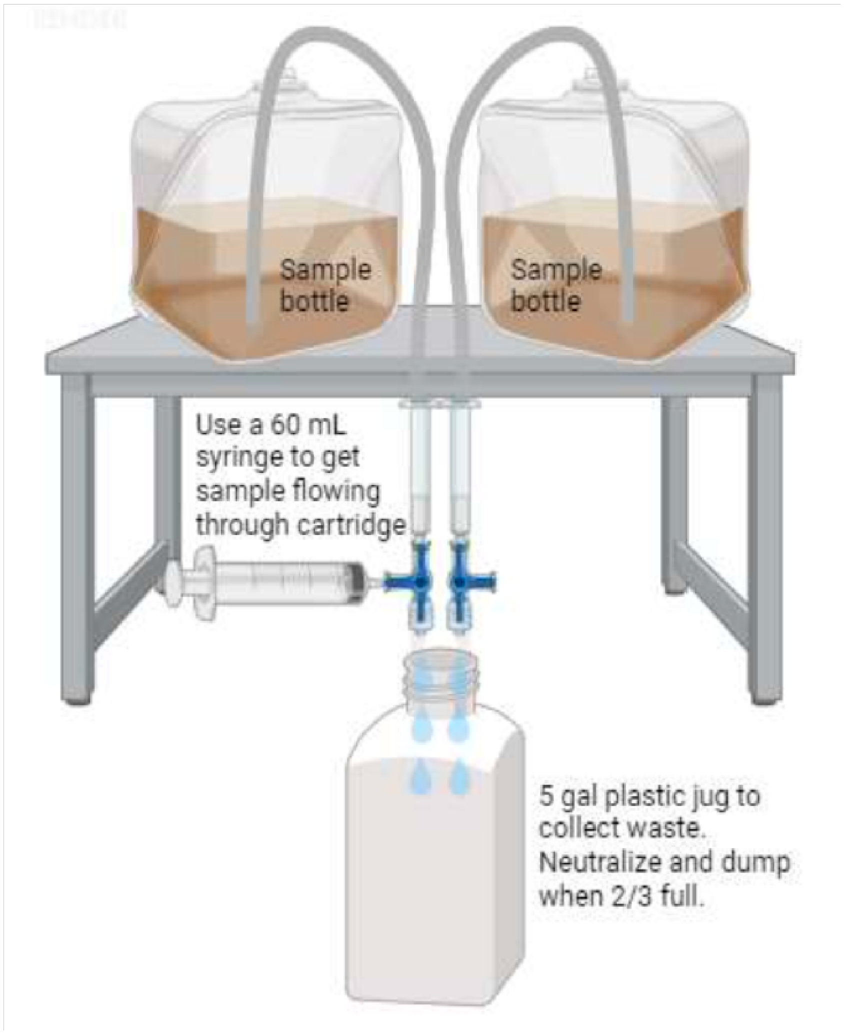

Figure 2: HLB cartridge extraction setup. 10 L collapsible container holding the seawater sample running into a HLB cartridge via tubing.

The solid-phase extraction of chemicals using HLB cartridges took place over the course of several hours or days depending on how much of a pollutant load was present to clog the cartridges (a 10-liter sample took approximately 24-48 hours to drip through the cartridge). Once the sample completely ran through, the cartridge cap was removed from the manifold, placed in a plastic bag and stored in a freezer. The cartridges were then shipped back to the University of

Washington for analysis. The GC blank was created by the exact same method but with deionized (DI) water.

Once I returned to the lab, I eluted the cartridges using ethyl acetate and performed GC-MS analysis with a Leco TruTOF Mass Spectrometer (Time of Flight Gas Chromatograph Mass Spectrometer). Flight time from the starting chamber to the detector directly relates to ion size, allowing for identification and quantification of pollutant chemicals of interest. Using NIST MS Search 2.0 and two chemical databases, I selected 33 compounds to focus on (Appendix A). One database was smaller and included primarily drug-related compounds, whereas the second was larger and all-inclusive with industrial and naturally occurring compounds. Compounds with similarities below 500 were excluded due to low confidence in correct compound identification. Other compounds were later removed due to being associated with cartridge bleed, process contamination, sedimentation, or natural sources. As seen with Figure 3, cyclopropanecarboxylic acid was detected but not included in my final analyses because it was present in the blank. Compound concentrations were calculated from a standard curve obtained from the standard drug mix, which was injected into the GC-MS system. The standard curve was based off known cotinine concentrations in the standard drug mix. I carried out an analysis of individual chemical abundance on Microsoft Excel.

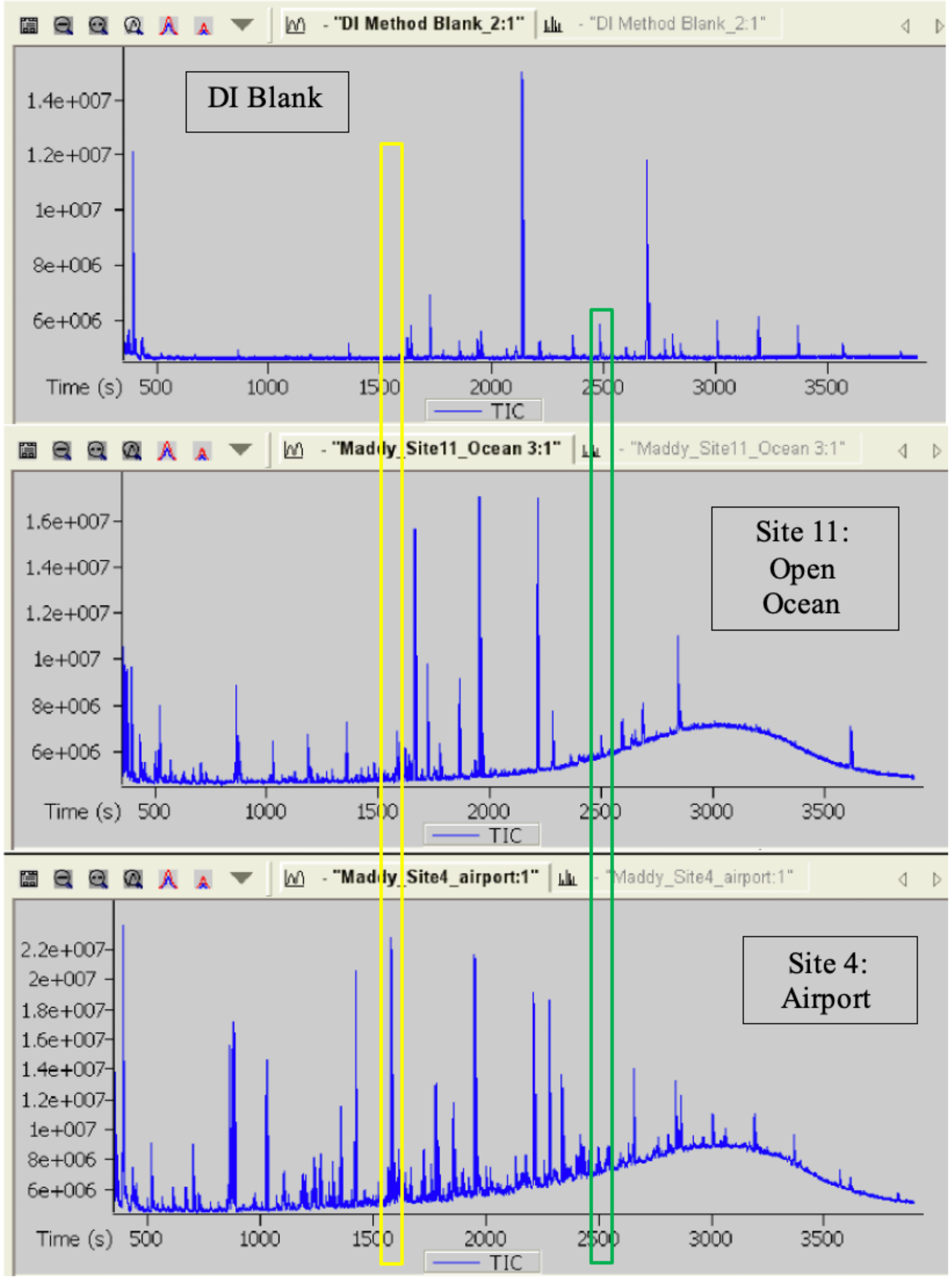

Figure 3. Three different chromatograms are pictured (from top to bottom: deionized water HLB blank, sample 11 from the open ocean, and sample 4 near the Pago Pago Airport). X-axis is retention time, y-axis is relative abundance of the compound. The yellow, longer rectangle highlights the compound azelaic acid (represented by blue peak), which was present only at Site 4 but not in the blank or Site 11. The green, shorter rectangle highlights the compound cyclopropanecarboxylic acid, which appears in the blank, Site 4, and Site 11.

Results

Out of thirty-three chemicals of interest, Site 2 near the fuel depot of American Samoa had the highest number of compounds detected with a count of 23 (Table 1; Fig 4). Site 1 at the harbor detected 20 compounds, and Site 4 near the airport detected 17. All other sites detected less than twelve chemical compounds. Despite Site 4 only having detected 17 unique compounds, it had the largest total concentration at around 22.3 ppb (Fig 4).

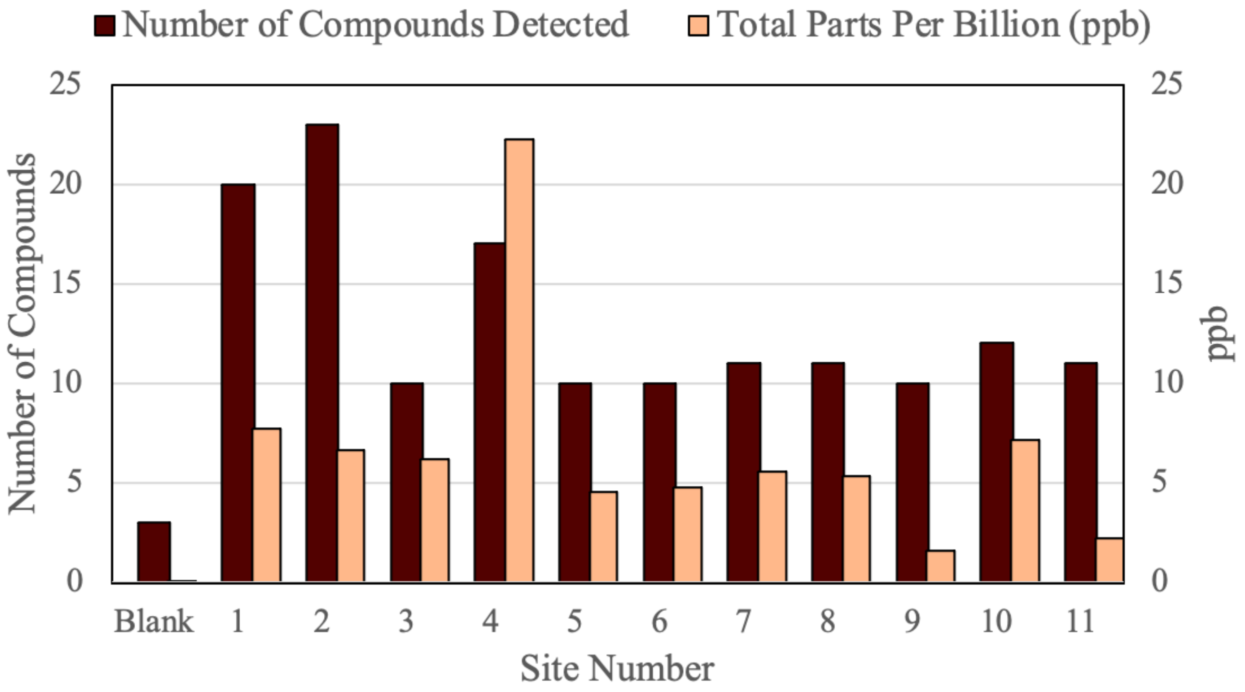

Figure 4. Sites plotted with total parts per billion of all compounds (right-hand y-axis) and number of detected compounds (left-hand y-axis).

While sites 1 and 2 had the largest number of compounds detected, they only had slightly larger total concentrations (ppb) than the remaining sites (Fig 4). There were five compounds which appeared exclusively at Site 1, three which appeared exclusively at Site 2, and three which appeared exclusively at Site 4 (Table 1). All other sites had no compounds completely unique to their location.

Sample	Latitude, Longitude	Distance from Port (km)	Number of Compounds Detected	Number of Compounds Unique to Site	Unique Compounds (Numerical ID)
DI Blank	NA	NA	3	0	NA
Site 1: Harbor	-14.2757, -170.6867	1.00	20	5	11, 12, 26, 27, 33
Site 2: Fuel Depot	-14.2756, -170.6826	1.44	23	4	25, 31, 32
Site 3: Offshore	-14.3319, -170.6216	9.40	10	0	NA
Site 4: Airport	-14.3411, -170.6982	7.38	17	3	17, 18, 19
Site 5: Offshore	-14.3278, -170.5890	12.02	10	0	NA
Site 6: Offshore	-14.3207, -170.5280	17.82	10	0	NA
Site 7: Olosega	-14.2104, -169.5818	119.31	11	0	NA
Site 8: Olosega	-14.1813, -169.5470	123.29	11	0	NA
Site 9: 13.5°S	-13.4995, -169.3342	169.60	10	0	NA
Site 10: 8°S	-8.0126, -168.1875	747.84	12	0	NA
Site 11: 3°S	-2.9994, -167.0005	1317.46	11	0	NA

Table 1. Sample location indicated by site number as well as short description of prominent feature or latitude (sites 9-11). "Offshore" labels indicate that sites are located offshore American Samoa. Distance from port is not equivalent to distance from shore. Compounds are counted from Appendix A's list of thirty-three chemical compounds of interest. Unique Compounds' names can be found in Appendix A under their numerical ID.

Site 1, 2, and 4 had the smallest distances from port. However, this measure is only a rough proxy for urbanization. Site 4 was much closer to the coast than Site 3 and therefore was treated as a nearshore location despite its distance from port measurement. Site 3 on the other hand, despite having a similar distance from port as Site 4, was considered an offshore location (Figure 1).

The highest number of industrial class compounds were found at Site 2 and 4 (Fig 5A). Sub-classifications of industrial class included classes E, F, and G. The highest number of drug class compounds were found at Site 2. The sub-classification of plasticizers under industrial class compounds found the highest detection at Site 1 and 2. Fuel components were only detected at Sites 1, 2, and 4. The largest total ppb was found at Site 4 in Class A (all compounds) as well as for Mixed Source, Industrial, Plasticizer, and Preservative & Pesticide classes (Fig 5B). Largest total ppb of drug class compounds was found at Site 3. Average ppb was 10-100 degrees of magnitude larger at Site 4 than the average areas for other sites in Class A as well as Mixed Source, Industrial, and Preservative & Pesticide classes.

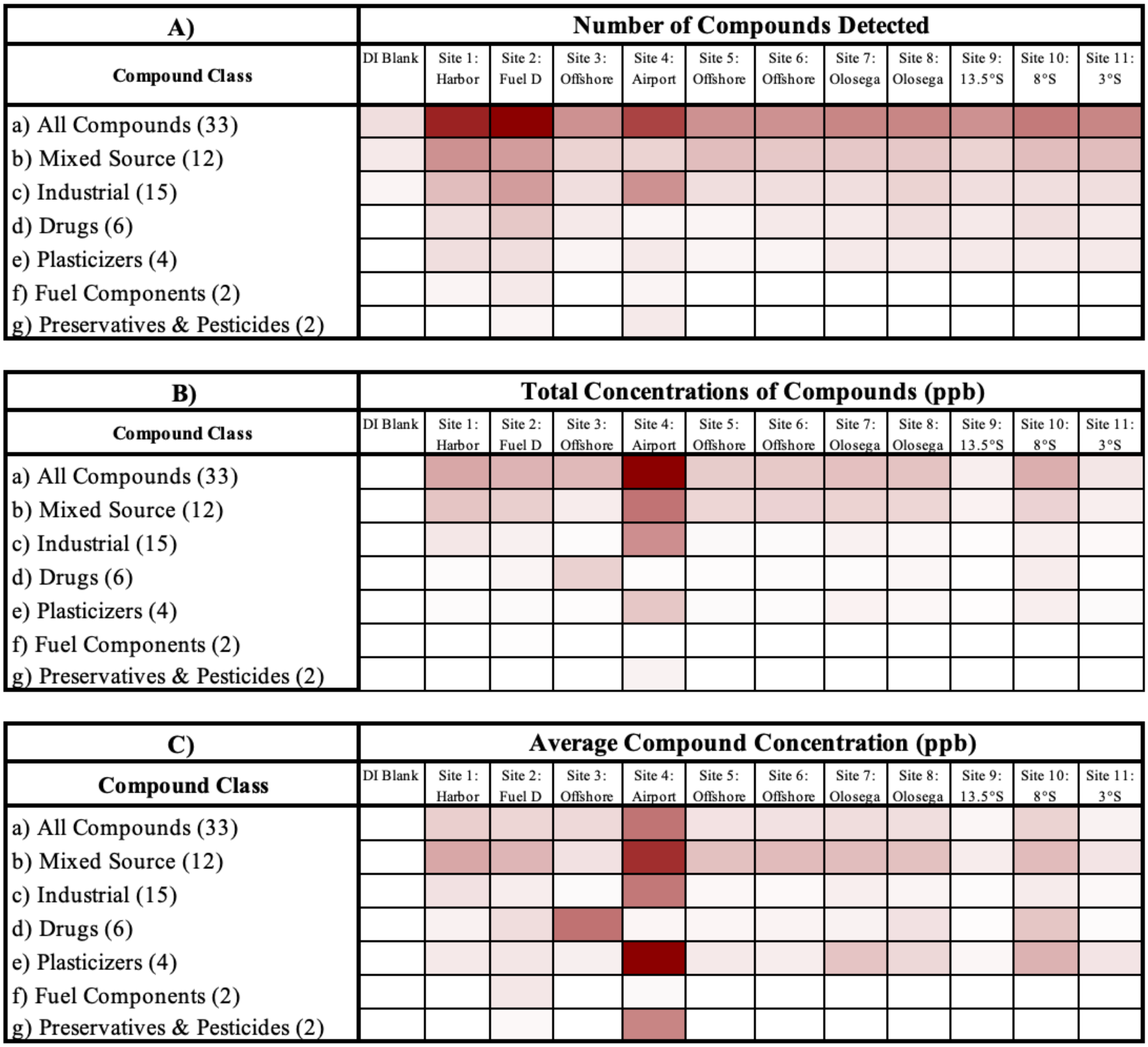

Figure 5. Type of heat map is indicated by x-axis label at the top of each panel. Sites are along the x-axis with descriptions. DI blank was collected at the UW Seattle campus. Compound classes labeled a-g are on the y-axis, with the number of compounds per class listed in parentheses next to each. Industrial class c) includes compounds from class e, f, and g. Site 2 "Fuel D" refers to it being located at the fuel depot. The "offshore" label under Sites 3, 5 and 6 refers to them being offshore of American Samoa.

In all major classifications, there were compounds found nearly everywhere (Fig 6). Nearly ubiquitous compounds included compounds 1-5 in the Mixed Source Class, compounds 13 and 14 in the Industrial Class, and compounds 28 and 29 in the Drug Class. Among some ubiquitous compounds, such as nonanoic acid, there was a relatively small range of concentrations despite vast spatial variation.

Diethyl phthalate and diisobutyl phthalate were detected at various sampling sites (Fig 6). Diethyl phthalate was found nearly ubiquitously, whereas diisobutyl phthalate was found only at inland Sites 1 and 2, as well as Site 4 near the airport (Fig 6; Appendix A).

Compounds such as 1, 13, 14, and 29 did appear to generally decrease in concentration moving away from sites near urbanization (Fig 6). However, other compounds such as 9 and 16 had unexpected spatial patterns, with 9 appearing only near the harbor and the most open-ocean sites, and 16 becoming detected more frequently as we transited away from American Samoa. Other compounds such as 11, 12, 17, 18, 19, 25, 26, 27, 31, 32, and 33 were detected at one site only, with uses as industrial solvents, fuels, plasticizers, and insecticides (Fig 6). Singular spatial occurrences were isolated to Sites 1, 2, and 4: the most urban locations.

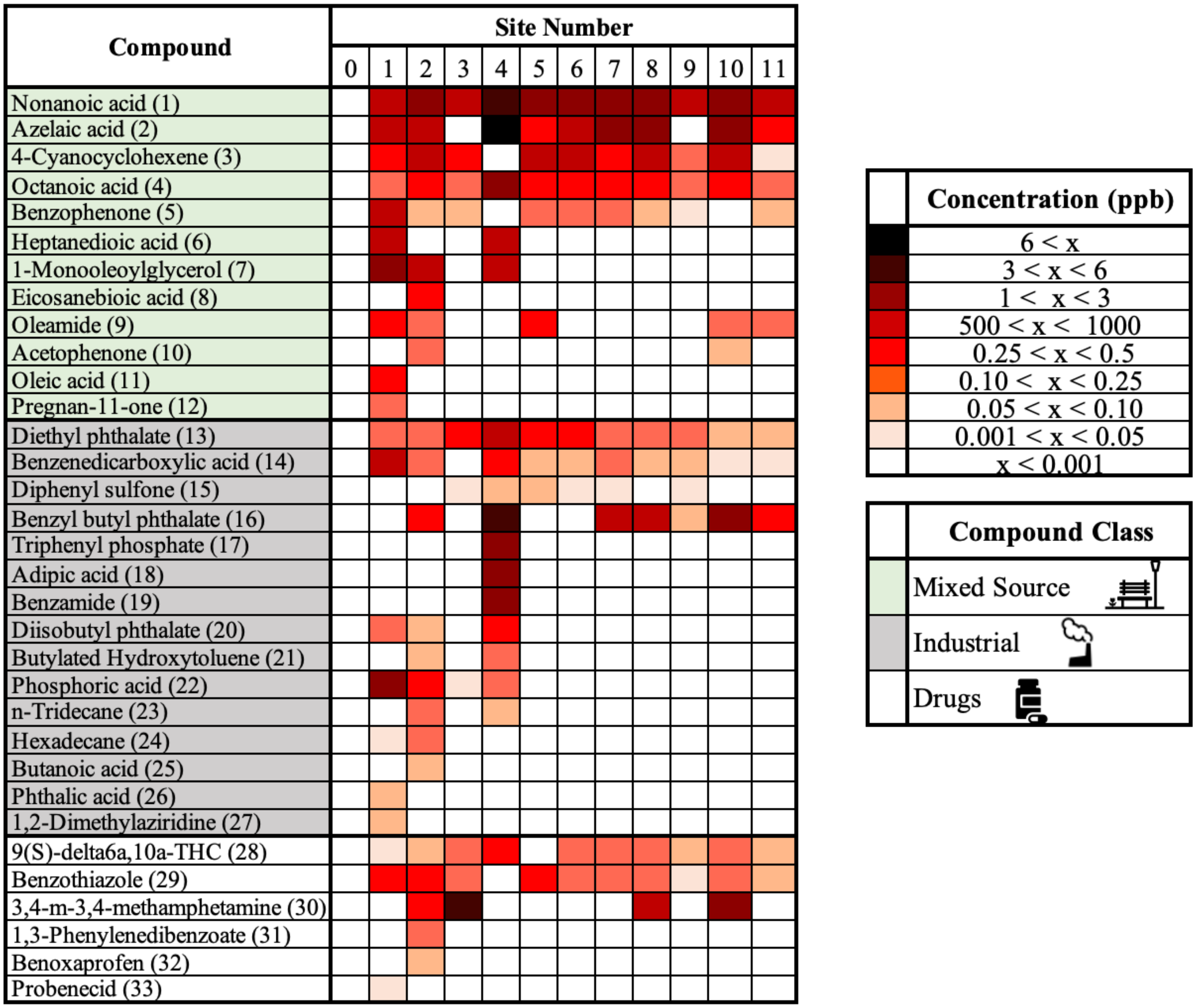

Figure 6. Site number is indicated along the x-axis at the top, with zero representing the DI HLB blank. Compound name is on the y-axis, the number in parentheses indicates Appendix A numerical ID. Full compound names can be found in Appendix A. Top legend shows colors associated with ranges of concentration values in parts per billion (represented as "x"). Bottom legend shows what the color associated with each compound name indicates in terms of classifications.

Discussion

Spatial Variation of Compounds

Compound abundance was found to generally decrease with increasing distance from American Samoa (Fig 4; Fig 6). Moving from Site 1 to Site 11 toward the open ocean, there was an observable decrease in compound abundance. Among nearly ubiquitous compounds, azelaic acid was detected at nine out of eleven sites, but was almost four times more abundant at urban Sites 1 and 4 (Fig 5). At Site 4, nonanoic acid had nearly double the abundance of the other sites, and 1,2-Benzenedicarboxylic acid had a relatively high abundance at Site 4 as well. There is a general trend of increased compound abundance at urban coastal sites 1, 2, and 4, and decreased compound abundance at offshore sites 3, 5, 6, 7, 8, 9, 10 and 11 (Table 1). There was a significant difference in number of compounds detected between the coastal sites and the offshore grouping, with an average of 20 compounds detected per coastal site, and 10.6 compounds per offshore site (unpaired t-test; $p < 0.05$).

Pollutant loads were found to be higher near urban and industrial areas, or at coastal sites near the harbor, the fuel depot, and the airport (sites 1, 2, and 4 respectively) (Fig 4). The largest number of industrial class compounds were detected at Site 2 and Site 4 (Fig 5). The sub-classification of plasticizers under industrial class compounds found the highest detection at Site 1 and 2, and the sub-classification of fuel component compounds were only detected at Sites 1, 2, and 4 (Fig 5). This is in accordance with a previous survey done in 2014, in which PBDEs and PFASs increased with urbanization along the California coast (James et al., 2020). The largest total concentration (ppb) was found at Site 4 for all compounds as well as for Mixed Source, Industrial, Plasticizer, and Preservative & Pesticide classes (Fig 5). In addition, average individual chemical compound area was 10-100 times larger at Site 4 than for other sites in all classes besides Class F (Fig 5). This follows the trend seen in North American waters, where pollutant concentrations were found to be 10-100 times higher in urbanized Puget Sound, WA, than in lowly populated Barkley Sound, BC (Keil et al., 2011). Unlike the 2011 study by Keil et al., this study took place near American Samoa, which is nearly eighty times less populated than Puget Sound with a population of almost fifty thousand compared to Puget Sound's four million. However, the phthalate detected in 2011 in Puget Sound (dibutyl phthalate) had an average concentration of ~700 ng/L compared to ~395 ng/L detected near American Samoa's coast at Site 4 (Keil et al., 2011). Puget Sound's abundantly larger population seems to have little effect on plasticizer abundance, and suggests that population plays less of a role on pollutant load than the presence of industrial or urban areas.

I hypothesized that sampling sites 7 and 8 between the Manu'a Islands would have pollutant loads similar to open-ocean sites. This open-ocean pollutant chemistry was observed in my results. With a population of less than a thousand people, the Manu'a Islands were found to have similar pollutant loads to the open-ocean chemistry than the coastal-ocean chemistry (Sites 1, 2, and 4). Sites 7 and 8 at the Manu'a Islands both detected only eleven unique compounds, which fits in the range of the offshore ocean chemistry grouping (Table 1). Total pollutant area was also less than that for coastal sites 1, 2, and 4, and in correspondence with the lower pollutant area of all other offshore sites (Fig 4). While sparsely populated, the islands were expected to show some similarities to coastal pollutant signatures. However, other factors such as wind and current direction, solubility, and population size were likely more important in determining pollutant chemistry rather than the binary presence of human population.

Classifications and Compounds of Special Interest

Mixed-source compounds had natural, commercial, industrial, or numerous other origins and uses, of which one could not be conclusively decided as the main source. Compounds nonanoic acid and azelaic acid are produced industrially together through ozonolysis of oleic acid, however, both have natural sources as well. Oleic acid's singular detection at Site 1 near the harbor suggests that could be primarily anthropogenically sourced. Nonanoic acid and azelaic acid were both found nearly ubiquitously, with highest concentrations at Site 4 near the airport. Azelaic acid is used industrially in a variety of ways, including preparation of plasticizers and as a thickening agent in lithium greases. It is also used commercially as an acne-medication, and naturally occurs in grains. However, azelaic acid had an abnormally high concentration of 6.1 ppb at Site 4, nearly twice as large as any other compound concentration (Fig 6). Proximity to the highly industrialized area near the airport at Site 4 indicates this abnormally high concentration has a high industrial source component. Nonanoic acid was also found to be ubiquitous in 2021 in the Great Pacific Garbage Patch (Hull, 2021). Again, it is possible that these compounds had both anthropogenic and natural sources but were highest at Site 1 and Site 4 due to increased anthropogenic input. In future studies, chlorophyll data corresponding to sampling sites could be used as a proxy for primary productivity and help understand the main cause of mixed-source compound spatial variation.

Industrial compounds were found in highest abundance at Site 4 (Fig 5). Triphenyl phosphate, a flame-retardant and plasticizer, was detected in high abundance only at Site 4 (Fig 6). Diphenyl sulfone, metabolite of triphenyl phosphate and a high-temperature industrial solvent, was found in highest abundance at Site 4 and 5. A survey of contaminants of emerging concern in 2009 and 2010 found flame retardants and pharmaceuticals at more than half of the sampling sites along the California coast (Alvarez, 2014). There were not enough coastal sampling sites to state whether flame-retardants specifically have a consistent presence in the waters of American Samoa.

Drug-classified chemicals were detected in highest abundance at Site 3, just offshore American Samoa (Fig 5). Compound 3,4-methylenedioxymethamphetamine (MDMA), is a recreational drug that was detected at coastal, offshore, and open-ocean sites (Fig 6). Due to samples from Site 10 and 11 being held in containers previously used in sites 1-8, it is possible that the containers were not cleaned thoroughly enough to remove traces of chemicals from previous sites and these residual chemicals leached into the samples. MDMA was not detected in the blank and held a similarity over 500 for all sites of detection, so it is unlikely the compound was misidentified, but certainly possible.

Three different phthalates were detected in this study: diethyl phthalate, diisobutyl phthalate, and benzyl butyl phthalate (Fig 6). Diethyl phthalate was found ubiquitously; however, the highest abundance was localized to Sites 3, 4, 5, and 6. Benzyl butyl phthalate had a spatial distribution which saw an increase in detection moving away from American Samoa, which was opposite to the trend seen with most other chemicals (Fig 6). Diisobutyl phthalate was found only at coastal Sites, 1, 2, and 4. Phthalic acid, a conjugate acid of phthalates, was detected only at Site 1. Spatial distribution within the plasticizer class followed no distinct pattern. However, diisobutyl phthalate and phthalic acid were contained to coastal sites. In studies done in the Puget Sound and lee of Hawaii in 2011 and the Great Pacific Garbage Patch in 2021, dibutyl phthalate was found to be one of the major pollutants (Keil et al., 2011; Lipsy, 2011; Hull, 2021). This plasticizer was detected in my samples, however, the GC-MS system indicated various types of dibutyl phthalate being detected and showed repeated peaks in the blank, which removed its viability as a unique compound. However, presence of plasticizers in general coincides with the detection of plasticizers in these previous studies.

Fuel components appeared in low abundance in comparison to other compound classes (Fig 5). The detection of n-tridecane and hexadecane exclusively near the coastal sites (the fuel depot and the airport), while low, does indicate that there is anthropogenic influence on ocean chemistry. It is possible that long hydrocarbons in fuels are lower in concentration due to low solubility or polarity interferences with the GC-MS system. In future studies, running standards of each compound could allow us to understand how individual chemicals respond to the GC-MS system and affect concentration readings. The Fuel Component Class along with the Preservative & Pesticide Class contained only two compounds. This is due to the fact that various compounds which included these uses also had commercial or industrial purposes, limiting them to the mixed source class.

Environmental and Human Health Risks

Plasticizer BBP was detected at six out of the eleven sampling sites that were taken in this study (Fig 6). Spatial variation of BBP was counter to what was observed with most compounds in that there were high concentrations of the compound at open-ocean sites, yet it was missing altogether at coastal Site 1 and less offshore Sites 5 and 6 (Fig 6). This compound had a similarity of 942 out of 1000 at Site 4, meaning it is unlikely to have been misidentified. It is possible that traces of BBP remained in reused sample containers or tubing for open-ocean sites, providing a false detection. BBP's highest concentration was nearly 4.0 ppb at Site 4, the second highest concentration detected in this entire study (Fig 6). This compound's relatively high abundance poses a possible risk to human health. Studies have shown that BBP can alter gene expression and may increase carcinogenesis susceptibility as a result, and there is evidence that BBP is toxic to the human reproductive system under the Federal Hazardous Substances Act (FHSA) (CPSC, 2010). In addition, BBP was found to have caused a reduction in human peripheral blood mononuclear cell viability by induction of cell necrosis (Sicińska, 2019). Its ability to be absorbed dermally and orally raises questions of safety in relation to marine waters containing BBP.

MDMA, also known as "ecstasy," was identified at relatively high concentrations at Sites 2, 3, 8 and 10 (Fig 6). MDMA has typical psychotropic and neurotoxic effects, but also "has been described to induce severe cognitive impairment in humans" (Saez-Briones & Hernandez, 2013). It is toxic in large enough doses. Whether dermal absorption in concentrations of 0.5-1.0 ppb would have noticeable effects is unknown, as well as its impact on marine organisms. Another recreational drug, cannabinoid compound 9(S)-delta6a,10a-THC, was found at all sites except 5 (Fig 6). There are natural sources of cannabinoids, however, whether this compound has an origin in marine systems is unknown, as is its impact on said marine environments.

Organophosphate flame retardants, known as alternatives to PBDEs, were detected in this study. The phosphates in these flame retardants are derivatives of phosphoric acid, which was found in highest concentration at Site 1 at ~1.0 ppb, though it was also detected in lower concentration at Site 4 (Fig 6). Triphenyl phosphate was unique to Site 4 at 2.1 ppb. When studying the compound’s multiplex toxicity in zebrafish, triphenyl phosphate was able to hinder DNA damage repair in liver cells and significantly disturb the metabolic pathways for lipid biosynthesis in concentrations of 50-300 ppb (Du et al., 2016). Triphenyl phosphate would have to be several times higher in concentration near American Samoa to have marine organisms possibly exhibit these behaviors. Effects of repeated exposure on aquatic species at known concentrations are not yet known.

Food preservative butylated hydroxytoluene (BHT), found at Sites 2 and 4, while recognized as generally safe by the U.S. Food and Drug Administration in small concentrations, has been shown to induce genotoxicity and carcinogenicity in non-human models (Wang & Kannan, 2019). There are no known effects from BHT on marine mammals. Further studies would have to be conducted to understand environmental and human impacts at concentrations that were detected in this study.

Conclusion

Xenobiotic contaminants were detected in higher abundances near coastal sites for most compounds (Fig 5; Fig 6). There was a significant difference in the number of compounds detected at coastal sites in comparison to offshore sites. Fifteen industrial chemicals, including plasticizers and fuel components, were in the largest abundance in the coastal site grouping at the fuel depot and near the airport (Fig 5). Drug-class compounds were highest at Site 3 offshore American Samoa. Factors such as current and wind directions could have impacted compound detection. For future studies, collecting chlorophyll data could help deduce whether mixed-source compounds were sourced anthropogenically or naturally. Several compounds in this study, such as BBP and MDMA, have been provided evidence for being harmful to human or animal health in certain concentrations. Studies on aquatic organism response to these contaminants, as well as solubility properties and dermal absorption at observed concentrations, could allow for a better understanding of environmental and human health concerns.

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Appendix A: Compound Names

Compounds names associated with numerical ID.

1. Nonanoic acid
2. Azelaic acid
3. 4-Cyanocyclohexene
4. Octanoic acid
5. Benzophenone
6. Heptanedioic acid
7. 1-Monooleoylglycerol
8. Eicosanebioic acid
9. Oleamide
10. Acetophenone
11. Oleic acid
12. Pregnan-11-one, 17-hydroxy-3,20-bis[(trimethylsilyl)oxy]-, (3à,5á,20S)-
13. Diethyl phthalate
14. 1,2-Benzenedicarboxylic acid
15. Diphenyl sulfone
16. Benzyl butyl phthalate
17. Triphenyl phosphate
18. Adipic acid
19. Benzamide
20. Diisobutyl phthalate
21. Butylated hydroxytoluene
22. Phosphoric acid
23. n-Tridecane
24. Hexadecane
25. Butanoic acid
26. Phthalic acid, ethyl pentadecyl ester
27. 1,2-Dimethylaziridine
28. 9(S)-delta6a,10a-THC
29. Benzothiazole
30. 3,4-Methylenedioxybenzoyl-3,4-methylenedioxymethamphetamine
31. 1,3-Phenylenedibenzoate
32. Benoxaprofen
33. Probenecid

Appendix B: Compound Classes with Full Compound Names

Compound Class	*Chemicals Included*
a) All Compounds	Appendix A. Compounds
b) Mixed-Source (12)	[Octanoic acid], [Nonanoic acid], [Heptanedioic acid], [Azelaic acid], [Acetophenone], [Benzophenone], [Oleamide], [Oleic acid], [4-Cyanocyclohexene], [Eicosanebioic acid, dimethyl ester], [1Monooleoylglycerol], [Pregnan-11-one, 17-hydroxy-3,20bis[(trimethylsilyl)oxy]-, (3à,5á,20S)-]
c) Industrial (15)	[1,2-Dimethylaziridine], [(1,2-Benzenedicarboxylic acid], [Diphenyl sulfone], [Phosphoric acid, 2,3bis[(trimethylsilyl)oxy]propyl ester], [Triphenyl phosphate], [Adipic acid], [Butanoic acid], [Diethyl phthalate], [Diisobutyl phthalate], [Benzyl butyl phthalate], [Phthalic acid, ethyl pentadecyl ester], [n-Tridecane], [Hexadecane], [Benzamide], [Butylated Hydroxytoluene]
d) Drugs (6)	[Probenecid], [Benoxaprofen], [Benzothiazole], [1,3Phenylenedibenzoate], [9(S)-delta6a,10a-THC], [3,4-Methylenedioxybenzoyl-3,4-methylenedioxymethamphetamine]
e) Plasticizers (4)	[Diethyl phthalate], [Diisobutyl phthalate], [Benzyl butyl phthalate], [Phthalic acid, ethyl pentadecyl ester]
f) Fuel Components (2)	[n-Tridecane], [Hexadecane]
g) Preservatives & Pesticides (2)	[Benzamide], [Butylated Hydroxytoluene]

Compounds with similarities below 500 or those associated with cartridge bleed, process contamination and sedimentation have been removed.