Remediation potential of a synthesised polymer material for toxic metals and PFAS

By

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Abstract

Toxic metals and per- and polyfluoroalkyl substances (PFAS) are two key contaminants that can make water sources unsafe for use. Several remediation techniques have been studied and implemented to remove these contaminants from the environment, however, most typical treatment technologies are ineffective for PFAS removal. Adsorption is one method that has been shown to be effective for the removal of both toxic metals and PFAS, with several adsorbent materials being investigated. The development of materials that can effectively adsorb toxic metals and PFAS and be easily applied to contaminated sites is key for remediation. Further, materials that can adsorb multiple contaminants are particularly advantageous as environmental water is rarely polluted with one group of contaminants alone. A semi-open cell polymeric foam developed by Australian-owned company Sustainable Oil Recovery and Remediation for oil spill remediation was unexpectedly found to adsorb PFAS during implementation at Tuggerah Lake, resulting in an interest in determining whether it may be an effective adsorbent for toxic metals and PFAS as well as hydrocarbons. Here the material was tested using a spiking protocol, which involved soaking samples of the material in a solution spiked with toxic metals and/or PFAS for 24 hours, washing in ultrapure water, and finally extracting the samples, in acid for toxic metals and methanol for PFAS. A group of 26 metals were analysed using inductively coupled plasma-mass spectrometry and three PFAS via liquid chromatography-tandem mass spectrometry to determine adsorption capacity of the material. The effects of different solution matrices (artificial seawater and water containing oil) and modifications to the material (via heat treatment) on adsorption capacity were also determined and samples of the material that had been used at Tuggerah Lake were analysed. The majority of the toxic metals and all of the PFAS tested were shown to be adsorbed by the material, with copper, mercury, arsenic, perfluorooctane sulfonic acid, perfluorooctanoic acid and perfluorohexane sulfonic acid being the most successfully adsorbed. The solution matrix was shown to affect adsorption capacity, mostly in the case of the toxic metals, with the adsorption of some metals, such as tin, being highly dependent on the solution matrix. Heat treatment was also shown to affect adsorption, with some toxic metals being more effectively adsorbed by the heat treated material. However, the most effective form of the material was determine to be the low density untreated version. Overall, the testing and analysis completed has resulted in the identification of a material that shows potential for the remediation of toxic metals and PFAS.

Chapter 1: Introduction

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1.1 Introduction

Water pollution is a global issue that negatively impacts human and ecosystem health in both the short term and the long term.[1] It causes more than 50 diseases, including diarrhoea, gastrointestinal diseases, skin diseases, malnutrition and cancer, and can result in death.[2] According to the UNESCO 2021 World Water Development Report, about 829,000 people (including 300,000 children under the age of five) die each year from diarrhoea caused by unsafe drinking water, sanitation and hand hygiene.[3] Water pollution is mainly caused by industrial activities, such as mining, textile processing, and electronics manufacturing,[4] agricultural activities, natural factors and insufficient drinking water and wastewater treatment facilities.[2] This results in a variety of contaminants polluting water sources, including various toxic chemicals, organic and inorganic substances, toxic solvents and volatile organic chemicals.[2] Water pollution is also a problem that is not solved, but transformed, when the income levels of countries increase.[1] In low-income countries, the majority of pollutants primarily result from poor sanitation and litter caused by low levels of water treatment, whereas in high-income countries, the key pollutants present are caused by more intensive economic activities, and include pesticides, plastics, pharmaceuticals, industrial chemicals and detergents.[1, 4] Among the numerous pollutant types present in water environments, two key contaminant groups affecting water quality globally are toxic metals and per- and polyfluoroalkyl substances.

1.1.1 Toxic Metals

Toxic metals are metallic chemical elements and metalloids that are toxic to humans and the environment.[5] Some of these metals, including cobalt (Co), copper (Cu), chromium (Cr), iron (Fe) and nickel (Ni) are essential micro-nutrients required for biochemical and physiological functions.[6] Inadequate levels of these metals can result in deficiency diseases or syndromes, whilst excess can cause cellular and tissue damage, resulting in a variety of adverse effects.[6] Other toxic metals have no biological functions and are considered non-essential metals, including antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), gold (Au), lead (Pb), lithium (Li), mercury (Hg), silver (Ag) and tin (Sn).[6] Arsenic, cadmium, chromium, lead and mercury specifically are all systemic toxicants that are known to induce multiple organ damage, even at lower exposure levels.[6] Arsenic, cadmium, chromium (VI) and inorganic lead compounds also considered to be 'known' or 'probable' human carcinogens by the International Agency for Research on Cancer.[7]

1.1.1.1 *Applications and Contamination Pathways*

Toxic metals, such as those listed in section 1.1.1, are naturally occurring elements in the earth's crust, meaning environmental contamination can occur via natural causes including volcanic activity, soil erosion, metal corrosion, metal evaporation from soil and water and sediment re-suspension, and geological weathering.[5, 6, 8] However, toxic metal contamination primarily occurs due to anthropogenic activity, including industrial operations such as mining, smelting, the burning of coal in power plants and paper processing plants and agriculture due to their use in pesticides, insecticides and ffertilisers.[5, 6, 8] Contamination can also occur because of accidental releases such as oil spills, landfills, automobiles, roadwork and urban runoff.[5, 6, 8] From these sources, toxic metals can then enter the environment through the soil, sediment, surface water, groundwater, air and by bioaccumulating through the food chain,[5, 6] where humans are then exposed to the toxicants. The specific sources of contamination and the pathways by which humans are exposed vary based on the applications of each toxic metal (see Table 1 for a (non-exhaustive) list of individual toxic metals and their associated applications and human exposure pathways).

Table 1: Toxic metals applications and exposure pathways

Toxic Metal	Applications	Human Exposure Pathways	Ref.
Arsenic	Wood preservation, insecticides, semiconductor doping agent, bronze production, treatment of parasitic diseases in veterinary medicine	Ingestion – food (main exposure route for most people) and drinking water, inhalation of dust, dermal contact, parenteral route (to some extent)	5, 6
Cadmium	Phosphate fertiliser, pesticides, nickel-cadmium batteries, corrosion resistant plating, nuclear reactors, pigments	Inhalation – cigarette smoke and airborne particulates, ingestion – food	5, 6
Chromium	Alloys, metal ceramics, electroplating, leather tanning, industrial welding, dyes and pigments	Occupational exposure via inhalation, non-occupational exposure via ingestion – diet and water	5, 6

Lead	Lead-acid car batteries, ammunition and projectiles, lead crystal glass, corrosive liquid cannisters, roofing, stained glass windows, X-ray shielding devices, solder and pipes	Inhalation – dust particles and aerosols, ingestion – food, water and paints	5, 6
Mercury	Barometers, thermometers, chlorine manufacture, gold recovery, dental amalgams, compact fluorescent lightbulbs, caustic soda production, preservative for pharmaceutical products	Ingestion – fish consumption and dental amalgams, inhalation – vapours	5, 6
Tin	Tin-plated containers for food and equipment, solders and other alloys (bronze, brass, pewter and babbitt), dental amalgams (inorganic tin)	Ingestion – food and water, inhalation – dust and fumes	9

1.1.1.2 *Health and Environmental Impacts*

The health and environmental impacts of toxic metals, like their applications and human exposure pathways, also vary for each toxic metal. See Table 2 for a (non-exhaustive) list of individual toxic metals and their associated health and environmental impacts.

Table 2: Toxic Metal Health and Environmental Impacts

Toxic Metal	Health Impacts	Environmental Impacts	Ref.
Arsenic	Inorganic arsenic can cause gastrointestinal system irritation, lung irritation, decreased production of red and white blood cells, infertility and miscarriages and DNA damage Organic arsenic can cause stomach upsets and nerve damage	Inorganic forms such as arsenite and arsenate are lethal to the environment and living creatures	5, 8
Cadmium	Nephrotoxicity, infertility caused by a reproductive system failure, psychological disorders, central	Remains in the soils and sediments for several decades	5, 6, 8

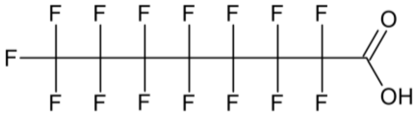
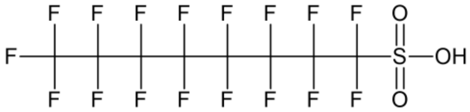
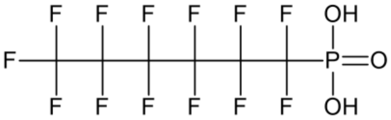
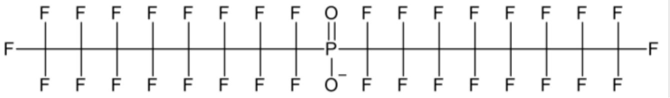
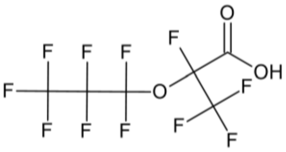
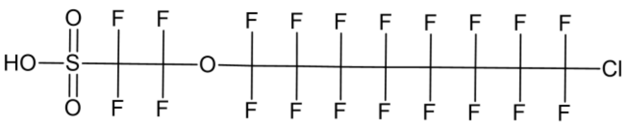
	nervous system complications, immune system deficiencies, cancer Chronic exposure can lead to changes in pulmonary function, decreases in bone mineral density and osteoporosis	High rates of soil-to-plant transfer result in cadmium accumulating in plants such as fruits and vegetables	
Chromium	Ingestion of Cr(VI) can cause acute poisoning, gastrointestinal ulceration, nausea and vomiting, fever, anaemia, toxic nephritis, male reproductive system damage and liver damage Inhalation or repeated dermal contact of Cr(VI) can cause chronic poisoning, allergic contact dermatitis and eczema, irritation of mucous membranes, bronchitis and pneumonia	Chromium phytotoxicity reduces root growth, causes leaf chlorosis, inhibits seed germination and depresses biomass. Affects the biological processes in plants such as maize, wheat, barley, cauliflower and vegetables Causes necrosis in plants	5, 6, 8
Lead	Hypertension, miscarriages, premature and low births, stillbirths, renal impairment, brain injury, peripheral nerve damage, sperm damage, cognitive impairment System toxicant that affects the kidneys, liver, central nervous system and reproductive system	Low concentrations cause instability in ion uptake in plants, leading to metabolic changes in in photosynthetic capacity and inhibition of growth High concentrations increases the production of reactive oxygen species, causing lipid membrane damage and damage to chlorophyll and photosynthetic processes, suppressing plant growth overall	5, 6, 8
Mercury	Inhalation causes lung irritation, eye irritation, rashes, vomiting and diarrhoea Genotoxic, causes DNA and chromosome damage, affects the reproductive system, leading to miscarriages, congenital disabilities and sperm damage in men	Adversely affects marine life by transforming into methyl mercury within organisms and undergoing biomagnification	5, 6, 8

	Gastrointestinal toxicity, neurotoxicity and nephrotoxicity		
Tin	Low intakes of inorganic tin compounds can cause fatigue, depression, shortness of breath, asthma, headaches and insomnia High intakes can cause skin rashes, nausea, diarrhoea, vomiting abdominal pain, headache and palpitations	Chronic tin poisoning in rats causes moderate testicular degeneration, severe pancreatic atrophy, neurological and renal damage	9

1.1.2 Per- and Polyfluoroalkyl Substances (PFAS)

Per- and polyfluoroalkyl substances (PFAS) are a class of over 14,000[10] anthropogenic aliphatic substances made up of an alkyl chain of varying carbon length, with the hydrogen atoms attached to the chain either totally (perfluoroalkyl) or partly (polyfluoroalkyl) replaced by fluorine atoms.[11-14] Specifically, at least one perfluoroalkyl ($–C_nF_{2n}–$) moiety must be present in the structure of a substance for it to be defined as a PFAS compound.[15-17] Their chemical structure (see Table 3) also includes a terminal functional group, such as a carboxylic, sulfonic, phosphonic, phosphinic, ether carboxylic or ether sulfonic acid group.[13, 18] PFAS have also been categorised into subgroups according to the length of their carbon chain, with the term "long-chain" referring to perfluoroalkyl carboxylic acids with eight or more carbons and perfluorosulfonic acids with six or more carbons. Consequently, "short-chain" refers to perfluoroalkyl carboxylic acids with seven or less carbons and perfluorosulfonic acids with five or less carbons.[12, 13, 19] The strong carbon-fluorine bonds present in PFAS compounds lead to their chemical and thermal stability and resistance to degradation. These compounds are also both hydrophilic and hydrophobic, due to the hydrophilic terminal functional group and the low polarisation of the fluorine atoms in the fluorinated alkyl tail, respectively.[12-14, 19] PFAS lipophilicity increases with increasing carbon chain length,[12] and at environmentally relevant pH values, PFAS are found in their anionic form, due to their low acid dissociation constants (pK_a).[12, 13]

Table 3: Chemical structures of some PFAS classifications[18]

PFAS classification	PFAS sub-category	Example Compound Structure
Perfluoroalkyl acids (PFAAs)	Perfluoroalkyl carboxylic acids (PFCAs) $C_nF_{2n+1}COOH$	 Perfluorooctanoic acid (PFOA)
	Perfluoroalkyl sulfonic acids (PFSAs) $C_nF_{2n+1}SO_3H$	 Perfluorooctane sulfonic acid (PFOS)
	Perfluoroalkyl phosphonic acids (PFPAs) $C_nF_{2n+1}PO_3H_2$	 Perfluorohexanephosphonic acid (PFHxPA)
	Perfluoroalkyl phosphinic acids (PFPiAs) $(C_nF_{2n+1})(C_mF_{2m+1})PO_2H$	 Bis(perfluorooctyl) phosphinic acid (C8/C8 PFPiA)
Per- and polyfluoroalkyl ether-based substances	Per- and polyfluoroether carboxylic acids (PFECAs)	 Hexafluoropropylene oxide dimer acid (GenX)
	Per- and polyfluoroether sulfonic acids (PFESAs)	 Perfluoro(2-((6-chlorohexyl)oxy)ethanesulfonic acid (F-53B)

Perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) were the most extensively produced PFAS and the most frequently detected in the environment,[11, 20] with PFOA being detected in water resources at higher levels than PFOS, due to its lower solid-liquid partition coefficient (K_d), which means it is less easily adsorbed onto particles.[20] However, their addition to the Stockholm Convention on Persistent Organic Pollutants in 2009 and 2019 respectively has limited their production and use.[13, 17, 21] This has resulted in the production of several alternatives, known as 'emerging' PFAS, to replace PFOS and PFOA, known as 'legacy' PFAS,[16, 17, 20] leading to the ubiquitousness of this class of chemicals. Another perfluoroalkyl sulfonic acid compound, perfluorohexane sulfonic acid (PFHxS), was also added to the Stockholm Convention on Persistent Organic Pollutants in 2022.[21] These 'emerging' PFAS compounds have minimal research data regarding aspects such as health impacts compared to the 'legacy' PFAS.[16]

1.1.2.1 *Applications and Contamination Pathways*

PFAS have been used for many decades in a variety of consumer and industrial products and processes[16, 20] as a result of their unique properties. Grease-resistant food packaging, coatings for non-stick cookware, waterproof clothing, textiles and carpets, and additives in cleaning products are some examples of consumer products that contain PFAS.[11, 12, 14, 18, 19] Industrial applications of PFAS include fire retardants, as surfactants in aqueous film forming foams (AFFFs) and hydraulic fluid for aircrafts, fluoropolymer manufacturing, pesticides, as well as in sealants, lubricants and emulsifiers used widely in the aerospace, military, automobile, construction and electronic industries.[11-14, 18, 20]

The variety of consumer and industrial applications of PFAS, as well as its resistance to degradation, has resulted in the presence of PFAS in the environment globally. Grunfeld et al. (2024) determined that PFAS is present in surface water and groundwater worldwide (see Figure 1).[17] Australia, China, Europe and North America appear to be hotspots for PFAS contamination relative to the rest of the world, however, these are also high-sampling zones, with monitoring efforts generally focused on places where contamination is likely. This indicates that there could be further PFAS contamination in other areas of the world at lower concentrations.[17]

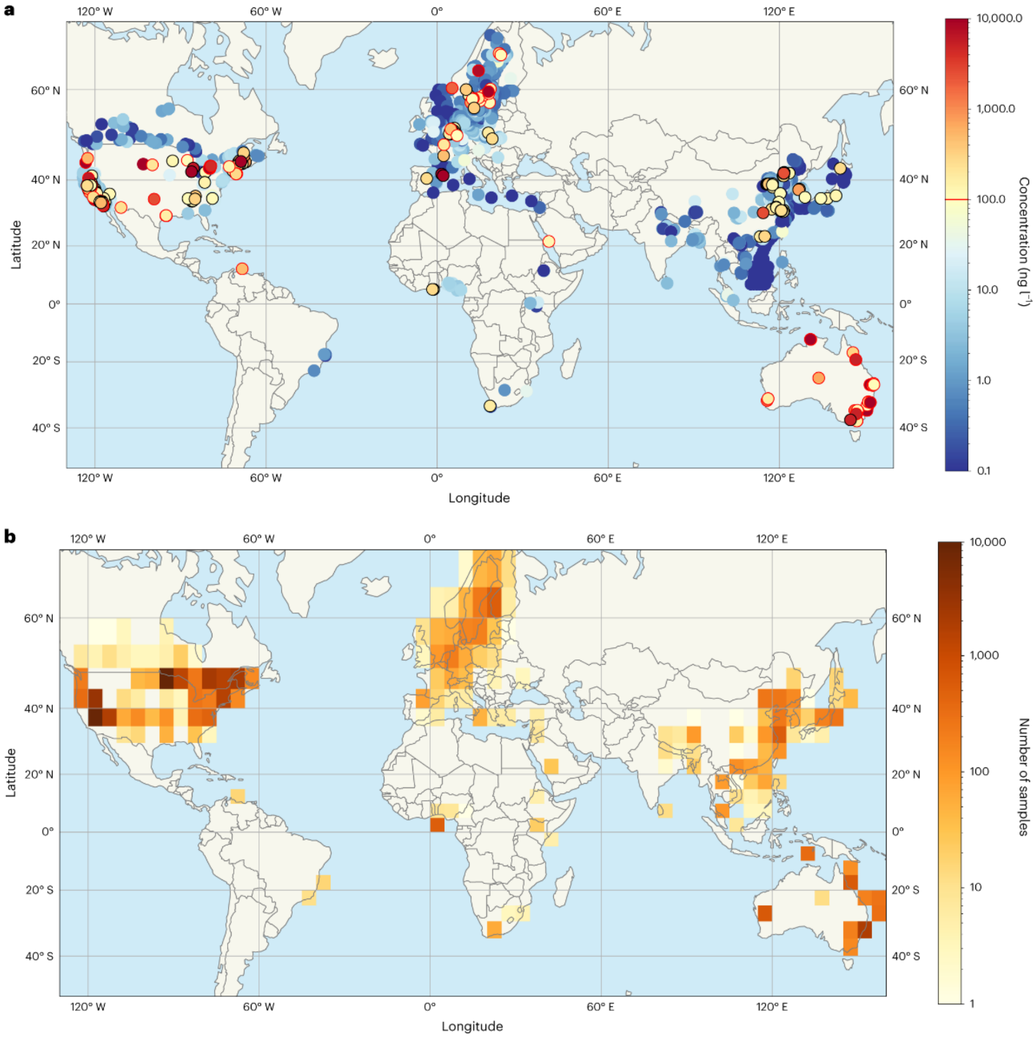


Figure 1: (a) Sum of concentration of 20 PFAS in surface water, groundwater and drinking water samples. (b) Number of PFAS samples available.[17]

Key sources of PFAS contamination are fluorochemical manufacturing facilities, wastewater treatment plants, landfills and firefighting training areas, such as military bases. Fluorochemical manufacturing facilities produce and utilise PFAS for goods manufacturing, and can release PFAS into the environment through emission, dispersion, spills, wastewater and solid waste disposal.[20] Wastewater treatment plants are another source of contamination as PFAS compounds are not effectively removed by conventional wastewater treatment technologies.[12, 18, 20] Aerobic and anerobic digestion are only able to break the carbon-carbon bonds along the PFAS alkyl chain, resulting in the formation of short-chain PFAS compounds.[12] Increased levels of PFAS in wastewater effluent and sludge compared to influent were even found, due to the biodegradation of PFAS precursor compounds, such as fluorotelomer sulfonates and fluorotelomer alcohols, into stable perfluoroalkyl acids during the wastewater treatment process.[18, 20] Disposal of PFAS-containing products into landfills at the end of their lifetime has resulted in landfills being another source of contamination, with PFAS being found in leachate from landfills in Australia[22] and the United States of America.[23] Finally, the historical release of PFAS from firefighting training activities without proper containment, treatment and disposal has resulted in their direct release into the environment at these sites. The use of AFFFs has been linked to PFAS contamination in surface water, groundwater, drinking water, air, sediment, soil and biota.[20] Other PFAS environmental contamination pathways include pipe leakage, atmospheric transport and deposition, precipitation and urban runoff.[20]

1.1.2.2 *Health and Environmental Impacts*

The health impacts of PFAS exposure are relatively unknown, due to the majority of toxicity data available being only for a small group of chemicals, mainly legacy PFAS such as PFOS and PFOA.[16] There are also many challenges associated with conducting epidemiological studies for PFAS, alongside the broad scope of contaminants.[20] These include difficulty in determining the effects of contaminant mixtures, the lack of an unexposed population to use as a control group, and various exposure factors such as source, geographical location, dosage, exposure duration and the complexity of the exposed body system.[20] Despite these uncertainties, current research has shown associations between PFAS exposure and a range of health effects (see Table 4).

Table 4: Human health effects associated with PFAS exposure

Health Effect Category	Effects of PFAS Exposure	Ref.
Immune function	Changes in inflammatory biomarkers and immune response Affects immune cell production, activity and signalling Causes immune cell death	20
Thyroid function	Alters thyroid hormones Potentially contributes to thyroid auto-immunity	16
Liver disease and cancer	Disrupts hepatic metabolism, leading to increased bile acid reuptake and lipid accumulation in the liver	16
Reproductive and developmental outcomes	Changes in embryo and foetus development and birth weight Increases risk of reproductive diseases	20
Respiratory system	Alters blood oxygen level	20

	Causes changes in cell structure and function of the lungs and airways	

PFAS is also known to bioaccumulate[11, 14] in freshwater and marine environments,[18] including in the protein-rich tissues of fish, due to their high protein-water partition coefficient (K_{pw}).[20] The bioaccumulation factor increases with increasing carbon chain length, and perfluorosulfonic acids are more bioaccumulative than perfluorocarboxylic acids with the same chain length.[12] PFOS and PFOA were also shown to decrease cell viability, increase cell apoptosis, increase the production of reactive oxygen species and increase oxidative stress in adult male mice when exposed to concentrations of 0.01, 0.1, 0.5 and 1 mM for 24h.[20]

1.2 Remediation of Toxic Metals and PFAS

The health and environmental impacts associated with toxic metal and PFAS exposure listed in sections 1.1.1.2 and 1.1.2.2 will continue to affect the populations and environments in which pollution has occurred as long as these contaminants remain in the environment. Environmental remediation describes the reduction or removal of contaminants from water and soil to protect living systems and the environment against further damage.[24] There are various remediation techniques that have been studied and implemented to reduce and remove toxic metals and PFAS in the environment.

1.2.1 Common Remediation Technologies

Various technologies exist for the removal of toxic metal ions, including chemical precipitation, ion exchange, membrane filtration and adsorption.[25, 26] However, most conventional treatment technologies are not effective at removing PFAS,[12, 14, 18] so other remediation techniques such as biological remediation, photocatalysis, anion exchange, adsorption and membrane filtration are being tested.[12, 13] See Table 5 for some examples of remediation technologies used for toxic metals and PFAS, as well as advantages and disadvantages associated with each technique. However, the most common remediation technique that can be used for both toxic metals and PFAS is adsorption.

Table 5: Advantages and disadvantages of remediation technologies for toxic metals and PFAS

Remediation Technology	Description of Technology	Contaminant/s Used For	Advantages	Disadvantages	Ref.
Chemical precipitation	The addition of chemicals, typically limestone, to precipitate metal ions out of water.	Toxic metals	Simple and easy to operate. Effective process.	Large amount of solids formed that need to be treated and/or disposed of. Highly sensitive to dosing of the precipitation agent.	27, 28
Phytoremediation	Removal, stabilisation and degradation of contaminants by green plants.	Toxic metals	Soil erosion control, biodiversity protection and adds aesthetic value.	Accumulation of contaminants in edible parts of crops and vegetables. Typically selective accumulation of one metallic element.	27, 29, 30
Nanofiltration	Membrane separation technology that uses size exclusion and an applied pressure to separate contaminants	PFAS (tested only) and toxic metals (implemented)	Provides consistent PFOS filtration at reasonable flux rates. Highly effective toxic metal removal.	Field-scale trials yet to be undertaken for PFAS removal. Treatment and/or disposal of spent membranes and highly concentrated	29, 31, 32

				retentate required.	

1.2.1.1 *Multi-Toxicant Remediation*

It is important to note that the majority of investigation into remediation techniques for contaminant classes, such as toxic metals and PFAS, has resulted in the development of technologies designed to eliminate a certain contaminant using a single mechanism.[33] Since real-world effluent contains a mixture of contaminants, further investigation into the simultaneous removal of multiple contaminants is required.[34] One solution is to combine multiple highly selective single contaminant treatment processes, and clarify the optimal conditions required for the decontaminating agents, in order to determine their applicability and sustainability in a particular multiple contaminant system.[33] Alternatively, a particular material or process could be developed specifically for multi-toxicant remediation. Multiple studies are looking into adsorption and adsorbent materials for multi-toxicant remediation, using methods such as chemical and thermal of the surface of activated carbons, modified biochars and nanoadsorbents,[35] constructing graphene oxide-based materials and metal organic frameworks,[36] and undertaking investigations to explain the interactions between contaminants and the adsorbent surface.[34]

1.2.2 Adsorption

Adsorption is a process wherein a chemical in a solution is sorbed onto the surface of solid particles (adsorbent) (see Figure 2).[27, 33] Adsorption reactions are typically reversible, occur at relatively quick rates, and depend on various factors including pH, concentrations, and chemicals and adsorbents used.[27] It has been shown to be a simple technique with a relatively low cost and a high removal efficiency for both PFAS and toxic metals.[13, 19, 25, 26] There are various materials that have been researched and implemented for the adsorption of toxic metals and PFAS.

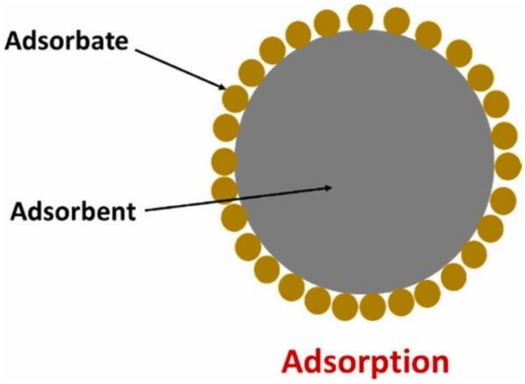


Figure 2: Mechanism of adsorption[37]

1.2.2.1 *Adsorption Materials*

The two main adsorbent materials used for the remediation of PFAS and toxic metals are activated carbon and ion exchange resins.[14, 19, 26] Biomaterials, polymers and minerals have also been tested for PFAS adsorption,[14, 19] however, the potential disadvantages associated with these materials, including complicated syntheses and expensive precursor materials, have slowed wider application of these materials.[14] Thus, the development of materials that effectively adsorb PFAS and toxic metals with scalable synthesis procedures is key for the remediation of PFAS and toxic metals in the environment. Different adsorbent materials also have varying degrees of adsorption (see Table 6 for examples of adsorbent materials and their degree of PFAS adsorption and Table 7 for examples of adsorbent materials and their degree of toxic metal adsorption).

Table 6: Adsorption capacity of various adsorbent types to PFAS

Adsorbent	PFAS being tested	Experimental Conditions	Adsorption Capacity (mg/g)	Ref.
Clay minerals	PFOS	Initial concentration = 0.2 mg/L	0.29-0.31	11
Kaolinite	PFOS	Initial concentration = 0.95 mg/L	0.08	11
Alumina	PFOA	Initial concentration = 0.1 mg/L	0.16×10^{-3}	11
Porous graphite	PFOS	Initial concentration = 100 mg/L	1240	11

Biochar from maize straw	PFOS	Initial concentration = 100 mg/L	91.6	11
Activated carbon from leaf biomass	PFOA PFOS	Influent concentrations tested = 0.5, 1.0, 1.5 and 2.0 mg/L	159.61 208.64 (maximum capacities)	11, 38
Modified silica	PFOS	Initial concentration = 2000 µg/L	55	11, 39

Table 7: Adsorption capacity of various adsorbent types to toxic metals

Adsorbent	Toxic metals being tested	Experimental Conditions	Adsorption Capacity	Ref.
Coconut-based activated carbon	Cadmium Nickel Zinc	Initial concentrations = 500 mg/dm^3	11.0000 mg/g 14.6375 mg/g 14.7175 mg/g	40
Modified peanut shells	Cadmium Copper Lead Nickel Zinc	Initial concentrations = 20 mM Solutions contained all five metal ions being tested Peanut shells preparation – unwashed and modified with phosphoric acid	0.37 mmol/g 0.82 mmol/g 1.09 mmol/g 0.30 mmol/g 0.32 mmol/g	41
Commercial resin – Duolite GT-73	Cadmium Copper Lead Nickel Zinc	Initial concentrations = 20 mM Solutions contained all five metal ions being tested	0.94 mmol/g 0.97 mmol/g 0.59 mmol/g 0.97 mmol/g 0.85 mmol/g	41
Commercial resin – Amberlite IRC-718	Cadmium Copper Lead Nickel	Initial concentrations = 20 mM Solutions contained all five metal ions being tested	2.26 mmol/g 2.04 mmol/g 1.45 mmol/g 2.20 mmol/g	41

	Zinc		2.36 mmol/g	
Commercial resin – Amberlite 200	Cadmium Copper Lead Nickel Zinc	Initial concentrations = 20 mM Solutions contained all five metal ions being tested	1.98 mmol/g 1.42 mmol/g 1.65 mmol/g 1.51 mmol/g 1.30 mmol/g	41

1.2.2.1.1 Activated Carbon

Activated carbon is a popular adsorbent due to its wide usability[42] and ability to be produced from a number of precursor materials, including coal, peat and coconut shell.[40] The large surface area and structure of the material,[43] which contains pores ranging from micro-pores to macro-pores,[40] means it is able to distribute contaminants on its large internal surface.[43] Since activated carbon surfaces are typically non-polar, it is suitable for adsorbing hydrophobic pollutants such as PFAS.[42] This adsorbent material has demonstrated to have a relatively high adsorption capacity for long chain PFAS compounds, such as PFOS, for which granular activated carbon had a removal efficiency of 80-100%.[18, 42] However, it was not as effective for the removal of short-chain PFAS, for example, only removing 64% of short-chain perfluorocarboxylic acid compounds during implementation at a drinking water treatment plant.[18] Activated carbon is also not easily regenerated after use as a PFAS adsorbent, even when using methanol or ethanol, meaning spent activated carbon likely cannot be reused and will need to be disposed of.[42] The adsorption of toxic metals using activated carbon has also been studied with some success.[40] Karnib et al. (2014) determined that the percentage of toxic metals removed by the activated carbon decreased with increasing metal concentration (30 ppm as opposed to 200 ppm), and that of the five metals tested (Ni, Cd, Pb, Zn and Cr), nickel had the highest removal percentage and chromium had the lowest.[43] Despite this, some level of removal was shown for all metals tested.

1.2.2.1.2 Polymers

Several synthetically modified polymers have been studied for the adsorption of PFAS. Cross-linked β-cyclodextrin-containing polymers with amino groups added to them showed a removal of greater than 96% for 7 perfluoroalkyl carboxylic acids and perfluoroalkyl sulfonic acids with carbon chain lengths ranging from 6 to 10, and 95% and 40% removal for short chain compounds perfluorobutansulfonic acid and perfluorobutanoic acid respectively.[18] Secondary amine hydrophobic polymers polyaniline, poly-o-toluidine and poly-o-anisidine also showed high removal efficacy, eliminating 98% of PFOA at a pH of 6.[18] Polyaniline has also been studied for the adsorption of heavy metals, due to it being a conducting polymer, an organic material with optical and electrical properties similar to metals and inorganic semiconductors.[37] It has been reported to be an effective adsorbent of toxic metals, adsorbing 95% of toxic metals onto the composite, and some composites also reduced the adsorbed metals to a less toxic state.[37]

1.3 Project Aims

1.3.1 Project Background

Australian-owned company Sustainable Oil Recovery & Remediation has developed a semi-open cell polymeric foam for the remediation of sites contaminated by oil spills, with a porous structure that can be modified during the manufacturing process. After the material unexpectedly adsorbed PFAS during implementation at Tuggerah Lake, there has been interest in determining whether the material can also adsorb PFAS and toxic metals. As the production of this material has already been scaled to a manufacturing level, if proven to be an effective adsorbent for PFAS and toxic metals, this material could be an effective and easily implemented solution for multi-toxicant remediation of contaminated sites, and used instead of applying several selective remediation technologies to remove each class of contaminants.

1.3.2 Project Aims and Objectives

The main aim of this project is to determine the capacity of this polymeric foam or sponge material to adsorb PFAS and toxic metals and the optimal form of the material to undertake this multi-toxicant adsorption. To fulfil this aim, I will achieve the following objectives:

- Test sponge samples in PFAS and toxic metal-spiked solutions to determine their capacity for adsorption.
- Determine the effects of different solution environments on adsorption.
- Modify the sponges and determine the effects on adsorption.
- Test environmental samples from Tuggerah Lake, where PFAS adsorption was observed.

Chapter 2: Materials and Methods

Chapter 2: Materials and Methods

2.1 Materials

Two sponge types were received from Sustainable Oil Recovery and Remediation, low density (LD) and high density sponges (HD), shredded into small pieces. Figure 3 shows images of the low density and high density sponges, which were taken using a Leica EZ4D optical microscope. Sponges that had been microwave treated for 1.5 minutes and 2 minutes, both in a 1200 W microwave, were also received for testing. Samples were delivered in vacuum sealed packs, which they were removed from upon arrival and stored in plastic containers for the duration of these experiments.

A batch of sponge pieces that had been used at Tuggerah Lake were also provided for testing, sealed in a vacuum sealed pack. These samples were stored in the -18°C freezer prior to sample preparation.

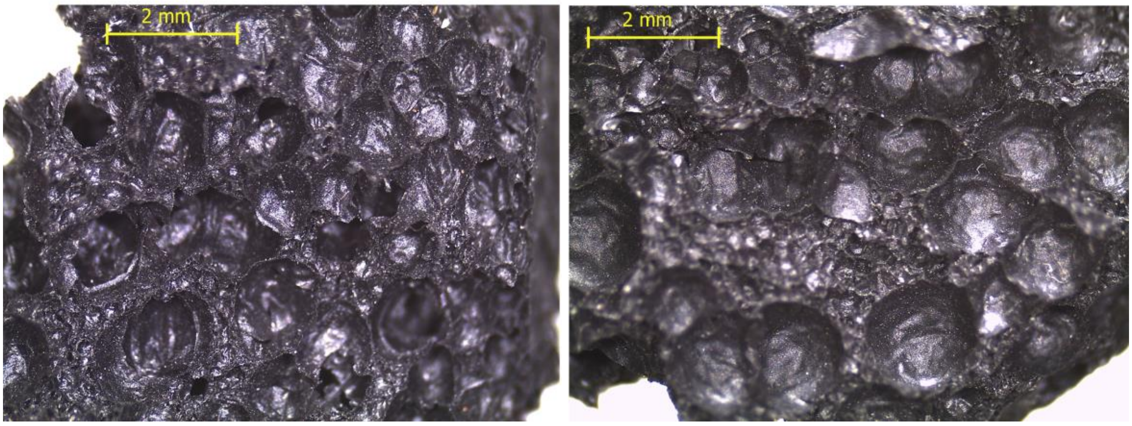


Figure 3: Optical microscope images of the untreated sponge types provided for testing, low density (left) and high density (right), at x12.5 magnification. Minimal difference in the porous structure can be seen between the two sponge densities.

2.1.1 Reagents

The metal mix A standard, containing 48 elements (ICP-MS-86A-A-500) and tin single element standard used in the spiking experiments (see section 2.4) were obtained from High-Purity Standards (Charleston, USA). The mercury single element standard was obtained from Agilent (Santa Clara, USA). PFHxS and PFOS salts were obtained from Ajax Chemicals (Sydney, Australia) and the PFOA salt was obtained from Sigma-Aldrich (Castle Hill, Australia). Metals standards were prepared using Seastar BASELINE trace metal grade 70% nitric acid and 32-35% hydrochloric acid (Choice Analytical; Thornleigh, Autralia), as well as ultrapure water obtain from an Arium® pro water generator from Sartorius (Dandenong, Australia). PFAS stock solutions and standards were prepared using LC-MS grade methanol (Supelco Hypergrade) obtained from Sigma Aldrich. The acetonitrile and isopropyl alcohol used in the LC-MS needle wash were of LC-MS grade and obtained from Honeywell via ChemSupply Australia (Port Adelaide, Australia). The ammonium acetate used in the LC-MS mobile phases were obtained from Sigma-Aldrich.

PFAS are used as polymerisation aids in fluoropolymer manufacturing, which results in contamination being a common issue during PFAS analysis. To minimise PFAS contamination of samples, the use of fluoropolymers should be avoided as much as possible.[44] In these experiments, PFAS-free polypropylene and polyethylene containers, lids and vials were used for all reagents, standards and samples.

2.1.2 Artificial Seawater

An artificial seawater solution was prepared from the chemical composition listed in Takaloo et al. (2011),[45] which was based on the ASTM D1141-98 Standard Practice for Preparation of Substitute Ocean Water. Table 8 shows the chemical composition of the solution and where each chemical used was provided from. The mixture was inverted several times and sonicated for 20 minutes to ensure all salts had properly dissolved and mixed.

Table 8: Chemical composition of artificial seawater prepared (based on ASTM D1141-98).[45]

Chemical	Quantity (g/L)	Source of Chemical
Sodium Hydrogen Carbonate ($NaHCO_3$)	0.201	ChemSupply Australia
Calcium Chloride ($CaCL_2$)	1.158	Ajax Chemicals
Magnesium Chloride Hexahydrate ($MgCl_2.H_2O$)	11.112	Sigma-Aldrich
Strontium Chloride Hexahydrate ($SrCl_2.H_2O$)	0.042	Merck (Darmstadt, Germany)
Sodium Chloride (NaCl)	25.534	Sigma-Aldrich
Sodium Sulfate (Na_2SO_4)	4.094	ChemSupply Australia
Potassium Chloride (KCl)	0.695	ChemSupply Australia

Potassium Bromide (KBr)	0.201	Ajax Chemicals
Boric Acid (H_3BO_3)	0.201	Ajax Chemicals
Sodium Fluoride (NaF)	0.201	Merck

2.1.3 Water and Oil Solutions

Ultrapure water and oil and salt water and oil (using the artificial seawater preparation procedure outlined in section 2.1.2 above) solutions were also prepared by adding 125 µL of a metal-free oil standard into each of the 1 L Schott bottles containing the ultrapure water and salt water in order to make up a 100 ppm oil solution. A concentration of 100 ppm was chosen as the Australian Maritime Safety Authority states that oily mixtures only become visible to people and remote sensing equipment from concentrations of 60 ppm and must be reported to the relevant authority at these concentrations.[46] CONOSTAN® PremiSolv ICP Solvent (now part of Analytichem, Baie D'Urfe, Canada) was the standard used.

2.2 Sponge Sample Preparation Procedure

Individual sponge pieces were selected for sampling and cut to an approximate size of 1 cm x 0.5 cm x 0.5 cm for all tests. Sponge samples were also weighed using an analytical balance to ensure a maximum difference of 15 mg between all sponge samples to be tested as part of a particular batch. These preparation steps were undertaken in order to limit variations in the sponge occurring due to its variable pore structure and differences in surface area.

Figure 4 shows all testing undertaken on these sponge samples. Initial sponge testing involved the leaching tests outlined in section 2.3 and extractions of unspiked sponge samples using the procedures in sections 2.4.1 and 2.4.2. The spiked tests following this tested the sponge material in spiked solutions containing metals only, PFAS only and a mix of both contaminant groups, as well as with four different solutions matrices, ultrapure water, salt water, ultrapure water and oil and salt water and oil. All of these tests were undertaken with the low density and high density untreated sponges only. Additional spiked testing of both the untreated and treated sponge samples was then undertaken, with the toxic metals/PFAS mix spiked solution in the ultrapure water and salt water matrices. Finally, the extraction of sponge samples that had been used at Tuggerah Lake was undertaken using the extraction protocols in sections 2.4.1 and 2.4.2. Analysis of these samples was undertaken using inductively coupled plasma-mass spectrometry

(ICP-MS) and liquid chromatography-tandem mass spectrometry (LC-MS/MS) (protocols outlined in sections 2.6.1 and 2.6.2).

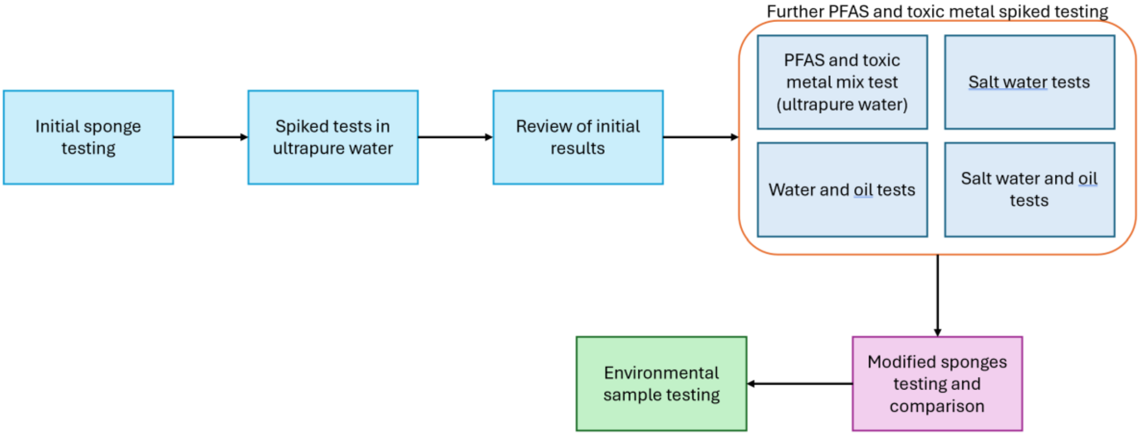


Figure 4: Experimental plan for testing of sponge remediation potential

2.3 Leaching Tests

Sponge samples were individually placed in 15 mL Falcon tubes containing 10 mL of each of the four solution matrices to be tested throughout these experiments and soaked for 48 hours, with intermittent inverting. Tests were performed in triplicate for each of the two untreated sponge types provided (LD and HD), resulting in a total of 24 samples across the four solution matrices.

2.4 Spiked Tests

The spiked testing process involved three parts: the soak cycle, the wash cycle and the extraction. During the soak cycle, 10 mL of 50 ppb solutions of toxic metals, PFAS or a toxic metals/PFAS mix were prepared in one of the four solutions listed previously in 15 mL Falcon tubes. Individual sponge samples were placed into the tubes and soaked for 24 hours, inverting intermittently.

Following this, any excess solution absorbed by the sponge samples was squeezed out back into the soak solution and sponge samples were placed in a wash solution of 10 mL of ultrapure water in a 15 mL Falcon tube. Initially, three wash durations were tested: 1 hour, 4 hours and 24 hours, with the sample tubes being inverted every 30 minutes for the 1-hour and 4-hour wash durations, and intermittently for the 24 hour wash duration. The 1-hour wash duration was used for all sponge samples during the untreated and treated sponge testing and comparison experiments.

After the wash, any excess solution absorbed by the sponge samples was once again squeezed out, and the sponges were dried. The sponges were weighed to determine their level of dryness and considered dry once the recorded weights were the same as or lower than the initial weights recorded before the start of the spiking tests. These samples were then extracted using the procedures outlined in sections 2.4.1 and 2.4.2 below.

All solutions from the soak, wash and extraction cycles were analysed using ICP-MS for the toxic metals samples and LC-MS/MS for the PFAS samples. Controls were also analysed for each version of the spiked solutions to measure the change in contaminant concentration in the soak cycle solution the sponge was placed in. Any concentrations detected in the wash cycles were then subtracted from these amounts, and the concentration per mass of the sponge sample was calculated to determine the expected adsorption. Experimental adsorption for each sponge was also determined by calculating the concentration per mass of the sponge sample using the extracted solutions.

2.4.1 Toxic Metals Extraction Procedure

The sponge samples analysed for toxic metals adsorption were extracted using 1 mL of a 1:1 mixture of 70% nitric acid and 32-35% hydrochloric acid in 15 mL Falcon tubes. Samples were extracted in the acid mixture for 1 hour, with the sample tubes swirled every 6-8 minutes. After extraction, the acid solutions were diluted to 15 mL, excess solution absorbed by the sponge was squeezed back into the extracted solution and the sponge samples were removed.

2.4.2 PFAS Extraction Procedure

The sponge samples analysed for PFAS adsorption were extracted using 2 mL of LC-MS grade methanol in 15 mL Falcon tubes. A glass rod was used to fully immerse each sponge sample in the methanol. Samples were then sonicated for 5 minutes and extracted in the solution for 50 minutes, with the sample tubes swirled every 6-8 minutes. Following this, the glass rod was used once again to ensure all sponge samples were fully immersed in the methanol before the samples were again sonicated for 5 minutes. Excess solution absorbed by the sponge was then squeezed back into the extracted solution and the sponge samples were removed.

2.5 Calibration Standards

A 7-point calibration curve was developed for both toxic metals analysis using ICP-MS and PFAS analysis using LC-MS/MS. For toxic metals analysis, mixed metals standards were prepared at nominal concentrations of 10 ppb, 20 ppb, 30 ppb, 40 ppb, 50 ppb, 60 ppb and 70 ppb. For PFAS analysis, PFAS standards were prepared at nominal concentrations of 10 ppb, 25 ppb, 50 ppb, 75 ppb, 100 ppb, 125 ppb and 150 ppb.

2.6 Instrumentation

2.6.1 Inductively Coupled Plasma-Mass Spectrometry

Analysis of the 26 toxic metals tested as part of these experiments was performed on an Agilent 7700 ICP-MS. Samples were introduced via 1.02 mm internal diameter Tygon tubing connected to a three-channel peristatic pump. All samples were made up in a solution of 2% nitric acid and 1% hydrochloric acid, and the internal standard was a 100 ng mL^{-1} solution of Rhodium in 1% HNO_3. The samples and the internal standard were combined in a post pump T connector and the combined solution was delivered to the ICP-MS using a MicroMist nebuliser and Scott type double pass spray chamber, cooled to 2°C. Samples were continuously delivered to the ICP-MS at a flow rate of 0.1 mL min^{-1} for 1 minute to allow for signal stabilisation, followed by a 30 second wash of 2% HNO_3. The ICP-MS parameters are detailed in Table 9. Agilent Technologies ICP-MS Chemstation software was used for all instrument control and data analysis.

The 26 metals analysed were aluminium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, germanium, arsenic, selenium, rubidium, strontium, cadmium, tin, barium, mercury, lead, lanthanum, praseodynium, neodymium, samarium, europium, gadolinium and dysprosium.

Table 9: ICP-MS Parameters

Parameter	Value	Unit
RF Power	1550	W
Carrier gas flow rate	0.70	L min^{-1}
Makeup gas flow rate	0.50	L min^{-1}
Sample depth	8.0	Mm
Extract 1, 2	0.0, -140	V

Omega bias, lens	-80, 5.0	V
Cell entrance, exit	-30, -50	V
Octopole bias, RF	200, -10	V
Deflect	-3.8	V
He flow	4.5	$mLmin^{-1}$

2.6.2 Liquid Chromatography-Tandem Mass Spectrometry

The method used for PFAS analysis using the LC-MS/MS was adapted from the method developed by Lockwood et al (2019).[44]

2.6.2.1 *Ultra-High-Performance Liquid Chromatography (UHPLC)*

Separation of the of the three PFAS compounds tested as part of these experiments (PFHxS, PFOA and PFOS) was performed on a Shimadzu (Rydalmere, Australia) Nexera MP UHPLC using a Phenomonex Luna Omega 2.1 x 50 mm, 1.6 µm C18 column. Internal standards were not used for PFAS analysis as most of the samples analysed were from the spiked experiments, wherein a known amount was spiked into samples. The mobile phases used were ultrapure water (A) and methanol (B), each containing 2 mM of ammonium acetate. Initial conditions were 20% B, which were held for 0.2 minutes, before being raised to 70% at 2.4 minutes then 95% at 5 minutes. The gradient was held at 95% for 2 minutes before returning to the initial conditions and equilibrated for 4 minutes. A flow rate of 0.6 mL min^{-1} and column temperature of 50°C were used. An injection volume of 1 µL was used for all samples. An exterior needle wash was performed before and after each injection with 500 µL of a wash consisting of a 1:1:1:1 ratio of water, acetonitrile, methanol and isopropyl alcohol to prevent carry over of strongly adsorbing compounds.

For environmental sponge samples, an additional internal needle wash was performed, consisting of a 500 µL wash of the 1:1:1:1 wash of water, acetonitrile, methanol and isopropyl alcohol followed by a 500 µL wash of 20% methanol during each run. An ACQUITY® PFC isolator column (Waters; Rydalmere, Australia) was also installed between the solvent mixer and autosampler to minimise PFAS contamination from the polytetrafluoroethylene HPLC solvent lines during analysis of the environmental samples. This column retains these contaminants, allowing any PFAS contamination from the system to elute after the analytes, preventing interference during the analysis.

2.6.2.2 *Mass Spectrometry*

Detection was performed using a Shimadzu LCMS-8060 triple quadrupole mass spectrometer operated in negative ionisation and multiple reaction monitoring (MRM) mode. The interface voltage and temperature used were -0.5 kV and 300°C. Nebulising, heating and drying gas flows were set at 3, 10 and 10 L min^{-1} respectively, and collision gas was operated at a pressure of 270 kPa. MRM parameters (see Table 10) were used at -0.5 kV for transitions from the [M-H]$^-$ ion using the LabSolutions software. Both quantification and qualification ions were used for each compound.

Table 10: Multiple reaction monitoring parameters used during LC-MS/MS analysis.

PFAS Compound	Transition (m/z)	Q1 PreBias (V)	Collision Energy (eV)	Q3 PreBias (V)
PFHxS*	399.00 → 80.00	11	40	9
PFHxS	399.00 → 99.05	13	34	5
PFOA*	412.95 → 369.00	15	10	11
PFOA	412.95 → 169.05	15	17	9
PFOS*	499.00 → 80.00	9	58	9
PFOS	499.00 → 99.05	9	40	5

* Quantification ion.

2.7 Environmental Testing

Sponge samples that had been used at Tuggerah Lake were thawed completely and 1 cm x 0.5 cm x 0.5 cm samples were cut from several of the sponge pieces for testing. These samples were then extracted using the metals and PFAS extraction protocols outlined in section 2.4.1 and 2.4.2.

Chapter 3: Results and Discussion

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3.1 Determination of Existing Contaminants in Sponge Material

The native sponge material was first examined to determine whether any of the target toxic metals or PFAS were already present and would need to be accounted for during spiked testing, as well as during environmental application of the material. This included the leaching tests outlined in Section 2.3, as well as acid and methanol extractions of un-spiked sponge samples (methods outlined Section 2.4.1 and 2.4.2).

3.1.1 Metals

Two of the 26 metals tested, aluminium and zinc, were detected in the sponge material itself. These metals were present in all four solutions' matrices and the extracted solutions for both the low- and high-density variations of the sponge, with zinc present in higher concentrations than aluminium in all tests (see Table 11). The concentrations of zinc and aluminium in the samples were highly variable, as shown by the large standard deviations, but were much higher than the concentrations of other adsorbed metals found in the results of the spiked testing (see sections 3.2.1, 3.3.1 and 3.4.1). This means that any aluminium and zinc that may have been adsorbed onto the sponge and consequently extracted during the spiked testing process was not able to be identified in these experiments.

Table 11: Concentrations of aluminium and zinc leached out and extracted from the native sponge material. Higher concentrations of zinc were detected than aluminium.

	Aluminium Concentration (mg/kg)	Zinc Concentration (mg/kg)
Leaching in Ultrapure Water	LD: 0.65 ± 0.42 HD: 0.087 ± 0.15	LD: 840 ± 240 HD: 220 ± 120
Leaching in Saltwater	LD: 28 ± 11 HD: 18 ± 6.9	LD: 760 ± 350 HD: 460 ± 110
Leaching in Ultrapure Water containing Oil	LD: 2.8 ± 0.62 HD: 0.70 ± 0.34	LD: 1500 ± 200 HD: 480 ± 120
Leaching in Saltwater containing Oil	LD: 52 ± 14 HD: 36 ± 16	LD: 800 ± 110 HD: 440 ± 39

Acid Extraction of Sponge Samples	LD: 660 ± 450 HD: 160 ± 200	LD: 5800 ± 1600 HD: 1800 ± 250

It is known that the material contained aluminium and zinc, so their appearance in the extracted solutions is not completely unexpected. However, the leaching of these metals into all of the solution matrices tested indicates a potential additional impact for the environmental application of the adsorbent, increased local concentrations of aluminium and zinc in the body of water being remediated. Although the Australian Drinking Water Guidelines (ADWGs) does not contain guideline values based on health considerations for aluminium and zinc, it does include aesthetic values. The guideline value for aluminium is 0.2 mg/L, based on post-flocculation problems, with < 0.1 mg/L being considered a desirable level, and the value for zinc is 3 mg/L, with taste problems occurring at levels higher than this.[47] Since all of the leached zinc concentrations and all except one of the leached aluminium concentrations are above these levels, this may cause the body of water to be an undesirable water source even after remediation if local water treatment infrastructure does not account for the removal of aluminium and zinc.

The leached concentrations of aluminium and zinc also exceed the default guideline values (DGVs) according to the Australian & New Zealand guidelines for fresh and marine water quality (see Table 12). These guidelines are used for the monitoring and management of water quality for natural and semi-natural water resources in order to preserve ecosystem conditions. The default values are recommended for generic applications in the absence of more relevant guidelines, such as jurisdictional or site-specific guidelines.[48] As with the ADWGs, all of the leached zinc concentrations and all except one of the leached aluminium concentrations are above the DGVs for all levels of species protection, which may result in negative impacts to aquatic ecosystems.[8, 49] However, the conditions of implementation for environmental application of the sponge material will be different to those seen during laboratory testing. There is a much larger difference between the sponge mass and the volume of water in the lake or other water body the sponge is being used in compared to the ratio of the sponge mass and volume of water during these experiments. This would result in a larger dilution area for the leached aluminium and zinc. Additionally, current environmental testing of the sponge has mainly involved applications to stormwater outlets. Provided future environmental applications continue to be similar in nature, water would often be flowing through the sponge as it exits the outlet, decreasing the likelihood for the leached metals to build up. These differences in conditions may limit the impact of leaching during environmental applications. To confirm the level of impact, water quality monitoring undertaken during the implementation of this material in contaminated environments should include aluminium and zinc in the list of analytes monitored.

Table 12: Australian & New Zealand Guidelines for Fresh and Marine Water Quality DGVs for aluminium and zinc.[48]

Level of species protection (%)	Default guideline value (µg/L)		Comments
	Aluminium (pH >6.5)[1]	Zinc	
99	27	3.3	Recommended for application for high ecological/conservation value systems.
95	55	8.0	Recommended for application for slightly to moderately disturbed systems.
90	80	12	Recommended for application to highly disturbed systems.
80	150	21	Recommended for application to highly disturbed systems.

3.1.2 PFAS

Minimal concentrations of PFHxS, PFOA and PFOS were present in the leaching and sponge only methanol extraction results, with 20 of the 30 sponge samples analysed not obtaining a concentration above the limit of quantification (LOQ) for at least one of the three PFAS compounds tested, typically PFHxS. After performing a blank subtraction on the data, 11 of the 30 samples showed PFHxS concentrations above the LOQ, one sample showed a PFOA concentration above the LOQ and 18 samples showed PFOS concentrations above the LOQ and only one of these concentrations was larger than 100 ppt. This indicates that these PFAS are likely not present in the sponge material. The low concentrations are instead likely due to the presence of these PFAS in the water and methanol solutions these tests were undertaken in, or in the solvents used during LC-MS analysis.

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[1] There is also a default guideline value provided for aluminium at pH <6.5: 0.8 µg/L for an unknown level of species protection.

3.2 Adsorption vs. Association

The wash cycle was used during spiked testing throughout this study to remove any excess spiked solution that had been absorbed by the sponge and would consequently decrease the accuracy of adsorption capacities determined through this testing. The wash cycles were also key to determining whether the sponge material was successfully adsorbing the tested toxic metals and PFAS onto its porous structure or if the contaminants were just loosely associated to the sponge samples. Three wash durations were tested as part of the initial batches of spiked testing to achieve this – if the contaminants were being adsorbed, they would remain on the surface of the sponge sample until extraction, and if they were only loosely associated, they would be washed off during the wash cycle. This was tested with all four solution matrices and with spiked solutions containing one and both contaminant groups with similar results, however, the metals only and PFAS only ultrapure water results have been used in sections 3.2.1 and 3.2.2 to represent the overall outcomes of this part of the experimental process. This testing was also undertaken to determine the optimal wash duration to be used in later spiked testing experiments to compare the untreated and treated sponge samples provided for this research.

3.2.1 Metals

The toxic metals tested were shown to adsorb onto the porous structure of the sponge, as metal concentrations were detected in the extracted solutions. While concentrations were also found in the wash solutions, indicating some excess spiked solution or loosely associated metal ions being washed off, many metals showed larger concentrations in the extracted solutions than in the wash solutions, indicating the majority of the metal ions present in the spiked solution were adsorbed onto the porous structure of the sponge rather than being loosely associated. This occurred in metals that were strongly adsorbed onto the adsorbent, such as arsenic (see Figure 5) and less effectively adsorbed metals, such as cadmium (see Figure 6).

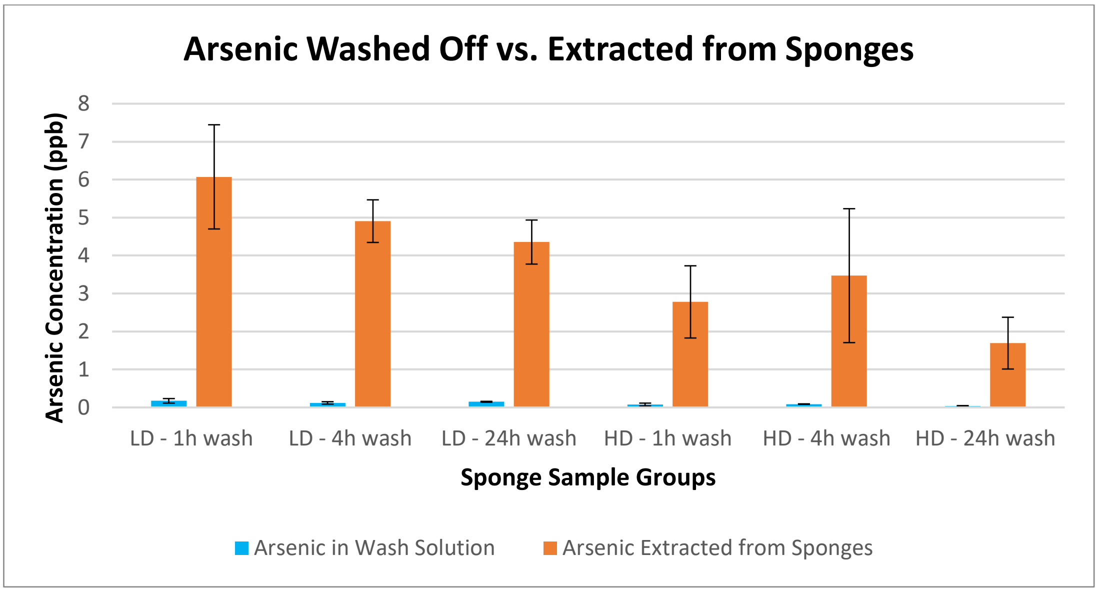

Figure 5: Arsenic concentration in wash vs. extracted solutions (metals only ultrapure water test), LD=low density sponge, HD=high density sponge. Arsenic was shown to adsorb effectively to the sponge, with notably higher concentrations in the extracted solution than the wash solution.

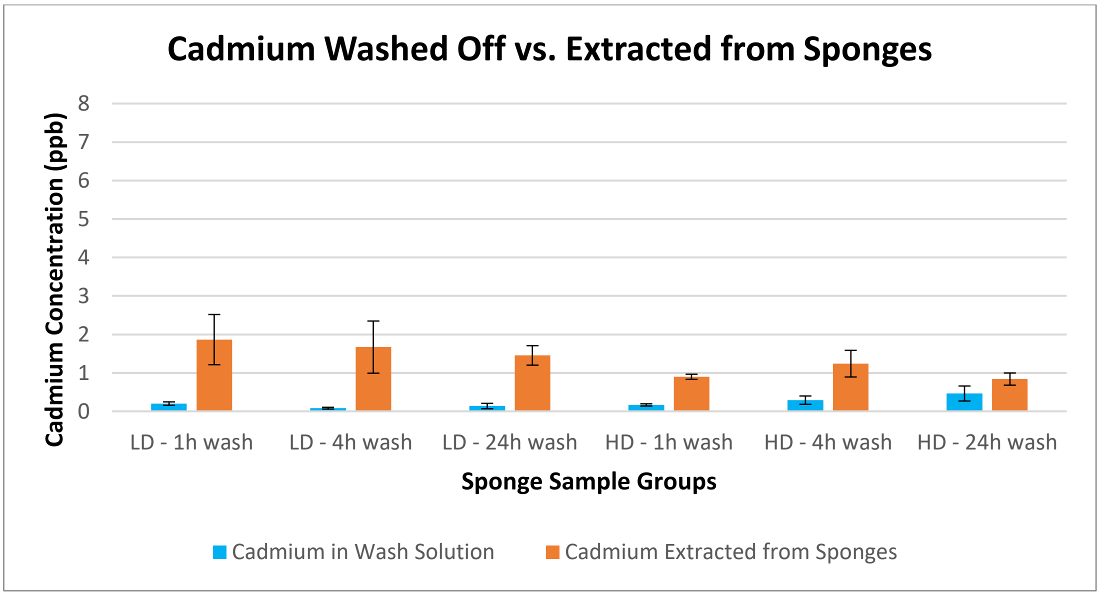

Figure 6: Cadmium concentration in wash vs. extracted solutions (metals only ultrapure water test). LD=low density sponge, HD=high density sponge. Cadmium adsorbed less effectively to the sponge, but still showed higher concentrations in the extracted solution than the wash solution.

One exception to this general result of higher concentrations in the extracted solution as opposed to the wash solution was mercury, which had larger concentrations wash off of the sponge than the other metals (see Figure 7). Concentrations of Hg in the wash and extracted solutions were similar, differing from the other metals, which generally had notably higher metals concentrations in the extracted solutions than the wash solutions. There was an exception in the result shown in the 24-hour wash cycle for the high density sponge samples, wherein the average concentration of mercury in the wash was notably higher than the average concentration extracted from the sponge. However, the mercury concentrations shown to be extracted from the sponge samples, which were not minimal amounts like the concentrations seen in the wash solutions for arsenic and cadmium in Figure 5 and Figure 6, mean that some of the metal is still adsorbing onto the sponge.

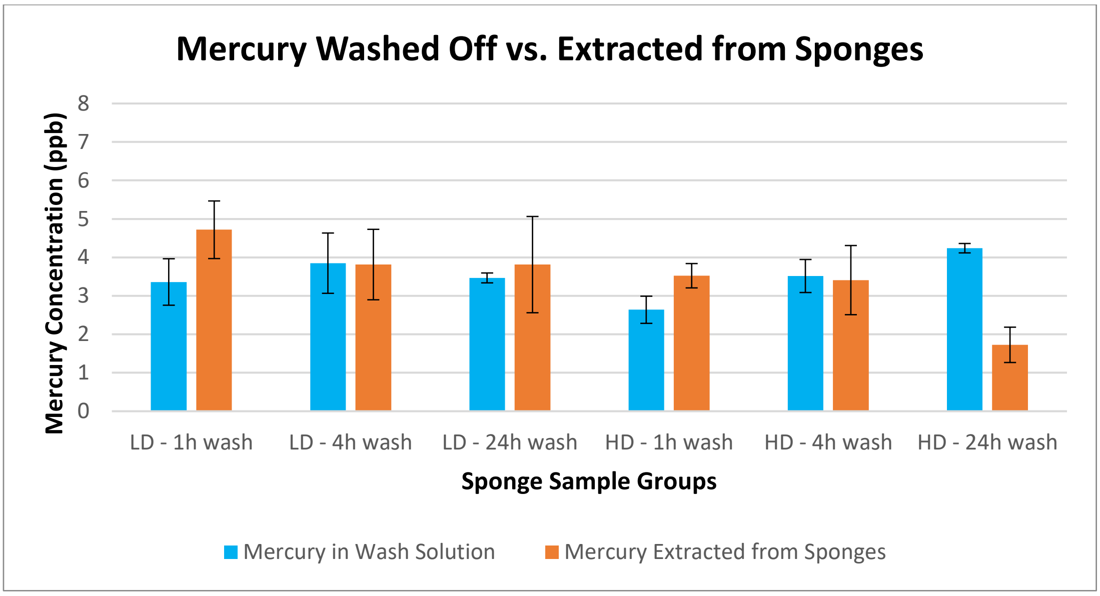

Figure 7: Mercury concentration in wash vs. extracted solutions (metals only ultrapure water test). LD=low density sponge, HD=high density sponge. Mercury was shown to adsorb effectively to the sponge, but a lot was also shown to be washed off.

While the concentration of metals in the wash solution generally increased as the wash duration increased, this was not to a notable level, and thus these metals results indicated that a 1-hour wash duration would be sufficient for later spiked tests.

3.2.2 PFAS

The three PFAS tested were also shown to adsorb onto the porous structure of the sponge, as PFAS concentrations were detected in the extracted solutions. This aligns with the initial hypothesis made after PFAS concentrations were detected in the adsorbent material during application at Tuggerah Lake, that the material does successfully take up PFAS. The PFAS compounds showed similar results to many of the metals, with much larger concentrations being detected in all of the extracted PFAS solutions than the wash solutions. Similarly to most of the metals, both the more effectively adsorbed PFHxS and PFOS, as well as the less effectively adsorbed PFOA, all showed a distinct difference between the wash and extracted solutions (see Figure 8, Figure 9 and Figure 10).

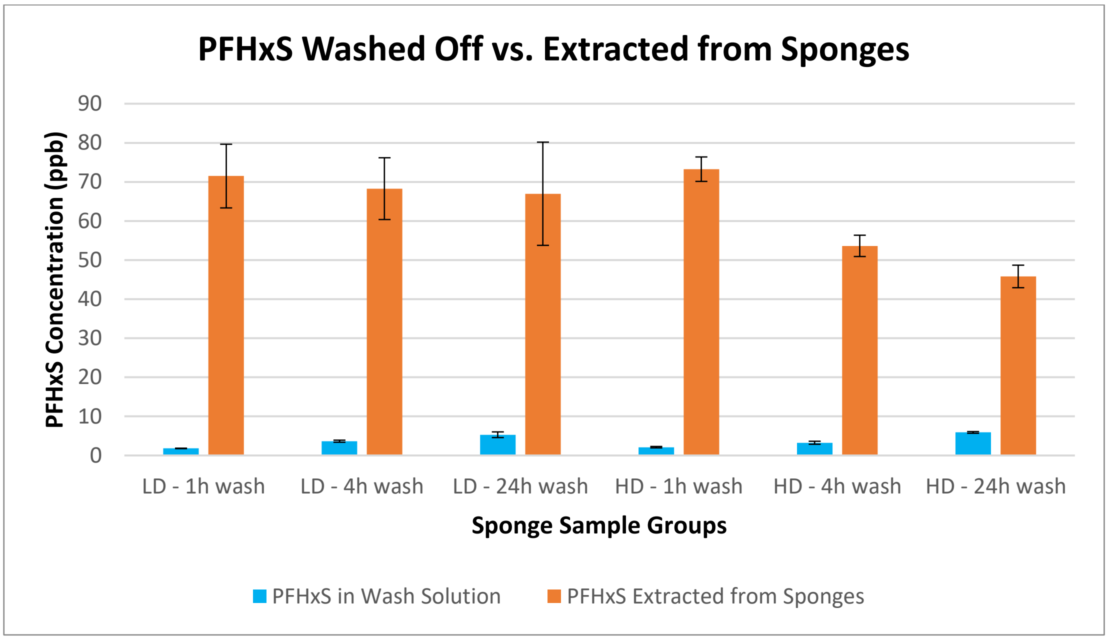

Figure 8: PFHxS concentration in wash vs. extracted solutions (PFAS only ultrapure water test). LD=low density sponge, HD=high density sponge. PFHxS adsorbed effectively to the sponge, with notably higher concentrations in the extracted solution than the wash solution.

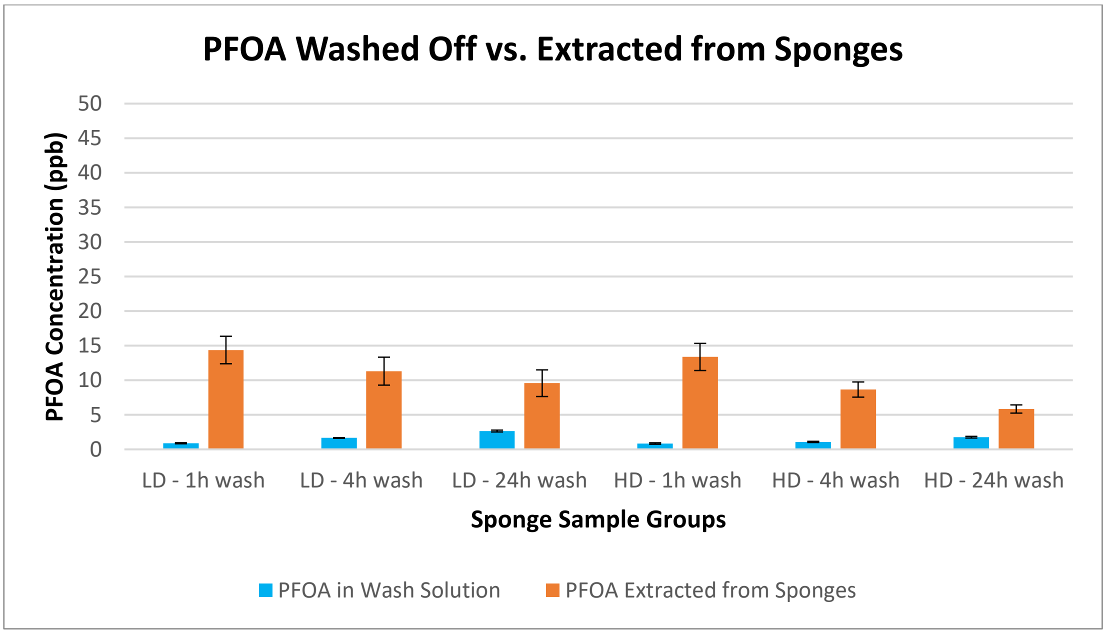

Figure 9: PFOA concentration in wash vs. extracted solutions (PFAS only ultrapure water test). LD=low density sponge, HD=high density sponge. PFOA adsorbed effectively to the sponge, with notably higher concentrations in the extracted solution than the wash solution.

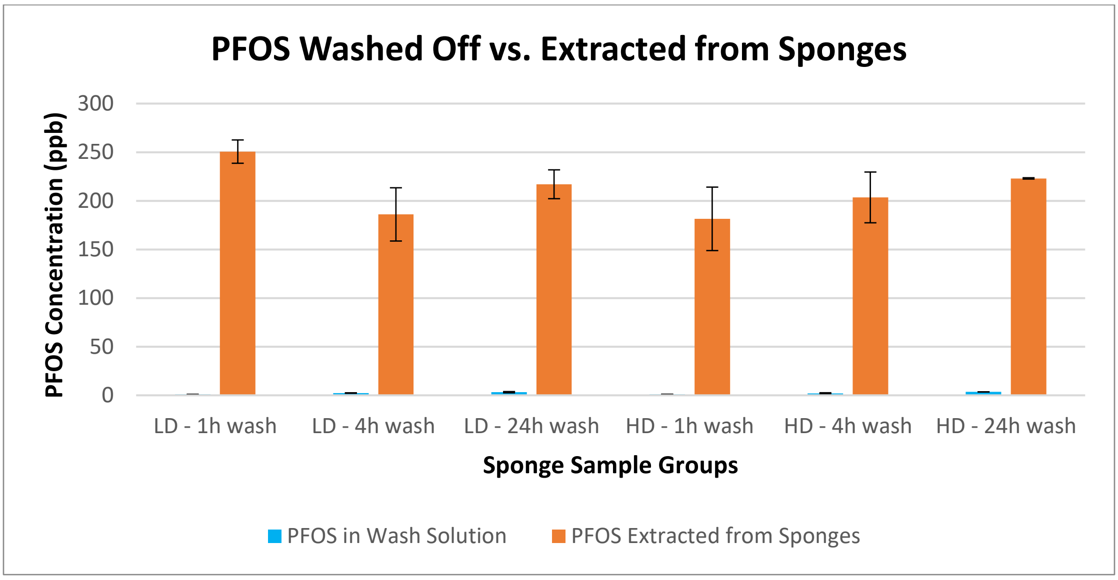

Figure 10: PFOS concentration in wash vs. extracted solutions (PFAS only ultrapure water test). LD=low density sponge, HD=high density sponge. PFOS adsorbed effectively to the sponge, with notably higher concentrations in the extracted solution than the wash solution.

The PFAS results showed an average increase in concentration of 1.2 ppb in the wash solution with increasing wash durations, but this increase is not to a notable level. Thus, these results agreed with the toxic metals results and confirmed that a wash duration of 1-hour would be sufficient to remove any spiked solution that had been absorbed into the sponge or any contaminants that were loosely associated to the sample. Thus, a 1-hour wash duration was adopted for the spiked testing to compare the non-treated and treated sponge types.

3.3 Effect of Solution Matrices

The four solution matrices tested: ultrapure water, salt water, ultrapure water with oil and salt water with oil were prepared and tested to simulate environmental conditions and determine their effect on the sponge material's adsorption capacity. The salt water solutions were used to simulate marine environments and the oil used to simulate an oil spill, the original use case of this material. These solutions were shown to impact the adsorption capacity of the sponge material. The presence of both target contaminant groups (toxic metals and PFAS), as opposed to just one, also had an impact that differed depending on the specific metal or PFAS. These results can give an indication as to which contaminants the adsorbent is most effective at removing, and in which environments, an important consideration when determining the appropriateness of applying the adsorbent to a specific contaminated site.

3.3.1 Metals

Different adsorption behaviours were observed across the 26 metals. Arsenic, copper, manganese, mercury and lead typically showed the highest levels of adsorption. Chromium, nickel, tin, barium and cadmium showed medium adsorption levels. Finally, the lanthanides (lanthanum, praseodynium, neodymium, samarium, europium, gadolinium and dysprosium), cobalt, vanadium, germanium, selenium and rubidium typically showed the lowest level of adsorption onto the sponge. Figure 11 and Figure 12 show a selection of environmentally relevant toxic metals to represent the results from these experiments. Cadmium, tin and lead typically showed the highest level of adsorption to the sponge in the metals only ultrapure water solutions. Specifically, adsorption was an average of 3.2x, 8.8x and 1.8x higher respectively across both sponge densities, in this matrix, indicating that the material may be most suitable for removing these contaminants from fresh water environments with minimal or no PFAS pollution, particularly in the case of tin. Arsenic and copper did not show notable differences in adsorption levels across the solutions tested, indicating that they may be effectively removed from all of the tested environments.

The lanthanides, cobalt, vanadium, germanium, selenium and rubidium also showed minimal differences in adsorption capacities across the solutions tested, however, these metals also showed consistently low uptake by the sponge, indicating that only low concentrations of these metals would be adsorbed during environmental application. The highest adsorption capacity for chromium and nickel were seen in the metals/PFAS mix ultrapure water solutions. Adsorption of chromium and nickel by the low density sponges was 3.3x and 3.4x higher in this matrix than in the metals only ultrapure water solution and was 10x and 11x higher by the high density sponges. This indicates the sponge may be most appropriate for removing these metals in fresh water environments that also contain PFAS pollution. Barium, manganese and mercury showed the highest adsorption levels in the metals/PFAS mix salt water and oil solutions, with manganese and mercury also showing high levels of uptake in the metals only water and oil and metals only salt water and oil solutions. This indicates that the material may adsorb these metals most effectively in marine and fresh-water environments where an oil spill has occurred, the original application of the sponge material. Generally, the most effective and ineffective matrices for adsorption of a particular metal was generally the same for both the low and high density sponges.

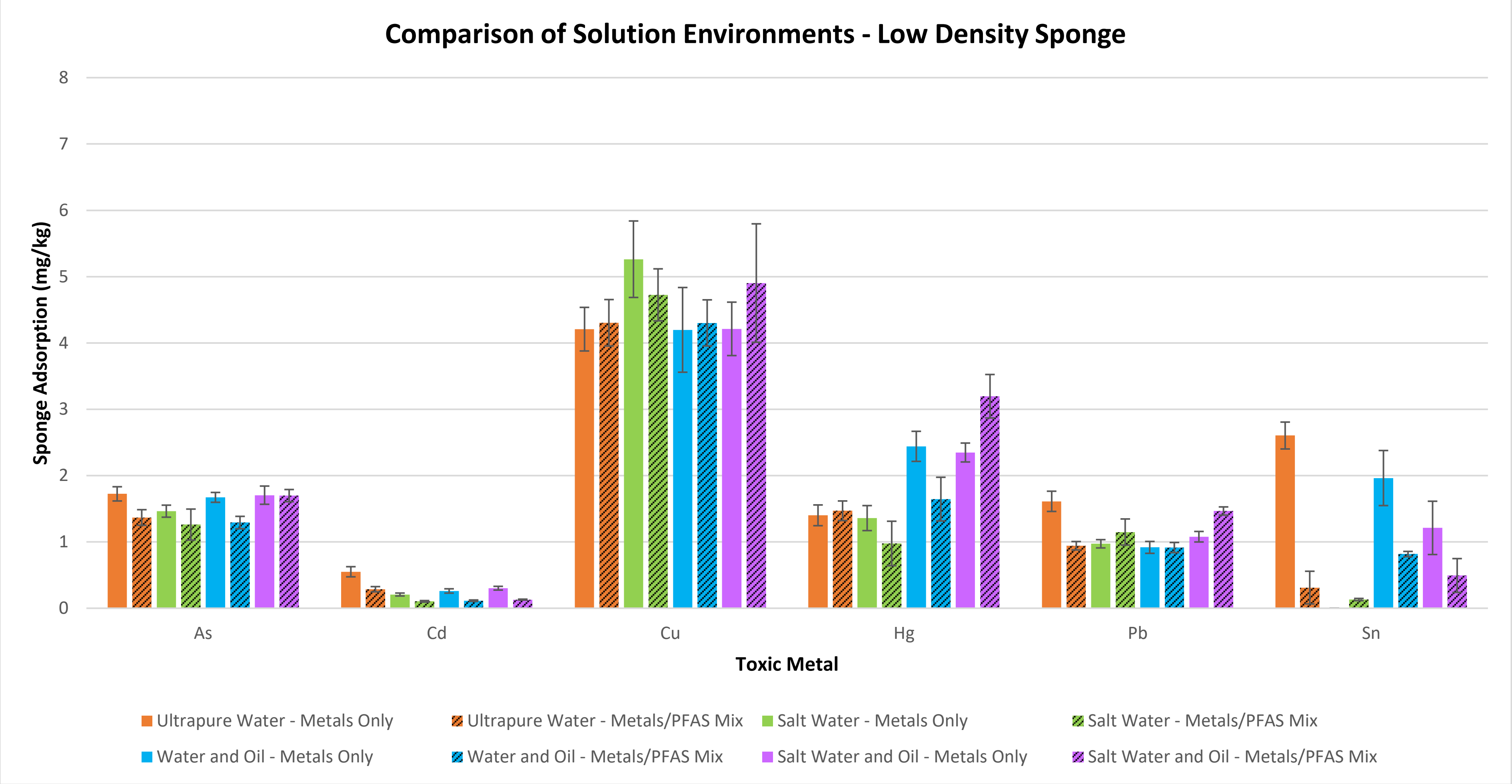

Figure 11: Adsorption of selected metals onto low density sponge material, normalised to the sponge mass. Adsorption of As, Cd, Cu and Pb was consistent across matrices while Sn was highly matrix dependant.

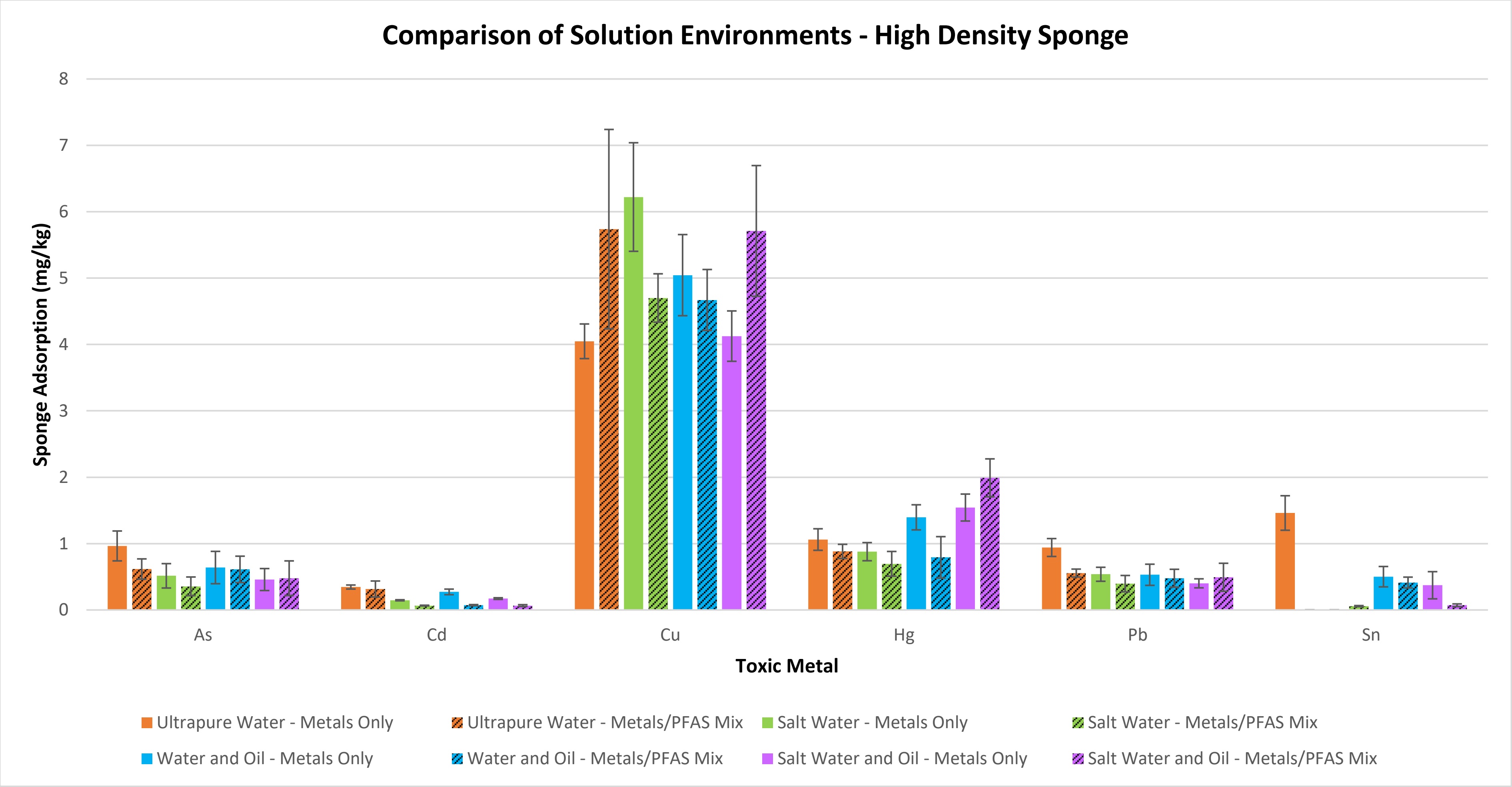

Figure 12: Adsorption of selected metals onto high density sponge material, normalised to the sponge mass. Adsorption of As, Cd, Cu and Pb was consistent across matrices while Sn was highly matrix dependant.

3.3.2 PFAS

All three PFAS compounds were shown to be effectively adsorbed by the sponge material across all tested matrices. PFHxS and PFOA were seen to have the highest adsorption levels in the PFAS only ultrapure water solutions and PFOS had the highest adsorption in the PFAS only ultrapure water and oil and metals/PFAS mix salt water and oil solutions. However, these adsorption levels were on average 1.8x (PFHxS) 2.0x (PFOA) or 1.6x (PFOS) higher than the concentrations obtained for the other matrices across both the low and high density sponges. Further, there were generally minimal differences between the impact of the solution matrices on the low density vs. the high density sponges, as was also seen with the toxic metals. As a result, both the low and high density sponge material would be an effective PFAS adsorbent in fresh water environments, marine environments and environments where an oil spill has occurred, both with and without additional toxic metals contamination.

It is important to note that Figure 13 and Figure 14, which depict these results were developed using expected adsorption rather than the extraction solutions, determined by measuring changes in PFAS levels in the spiked solutions and normalising the change in concentration by mass of the sponge sample. This is due to vast differences seen in extracted concentrations between different sample batches, hypothesised to be due to the incomplete extraction of some samples. One key difference between these two sets of results is that the extracted concentrations show PFOS to generally adsorb to the sponge at higher concentrations than PFHxS and PFOA, whereas the calculated adsorption levels have shown the opposite. This could be due to loss to the polypropylene and polyethylene containers the samples were stored in prior to analysis. While sample loss would occur in this manner for all three compounds, PFOS would see the largest losses, as adsorption has been shown to increase with chain length and compounds with sulfonic acid functional groups have been shown to adsorb more than compounds with carboxylic acid functional groups.[50] Appendices B and C contain tables showing the expected and actual adsorptions.

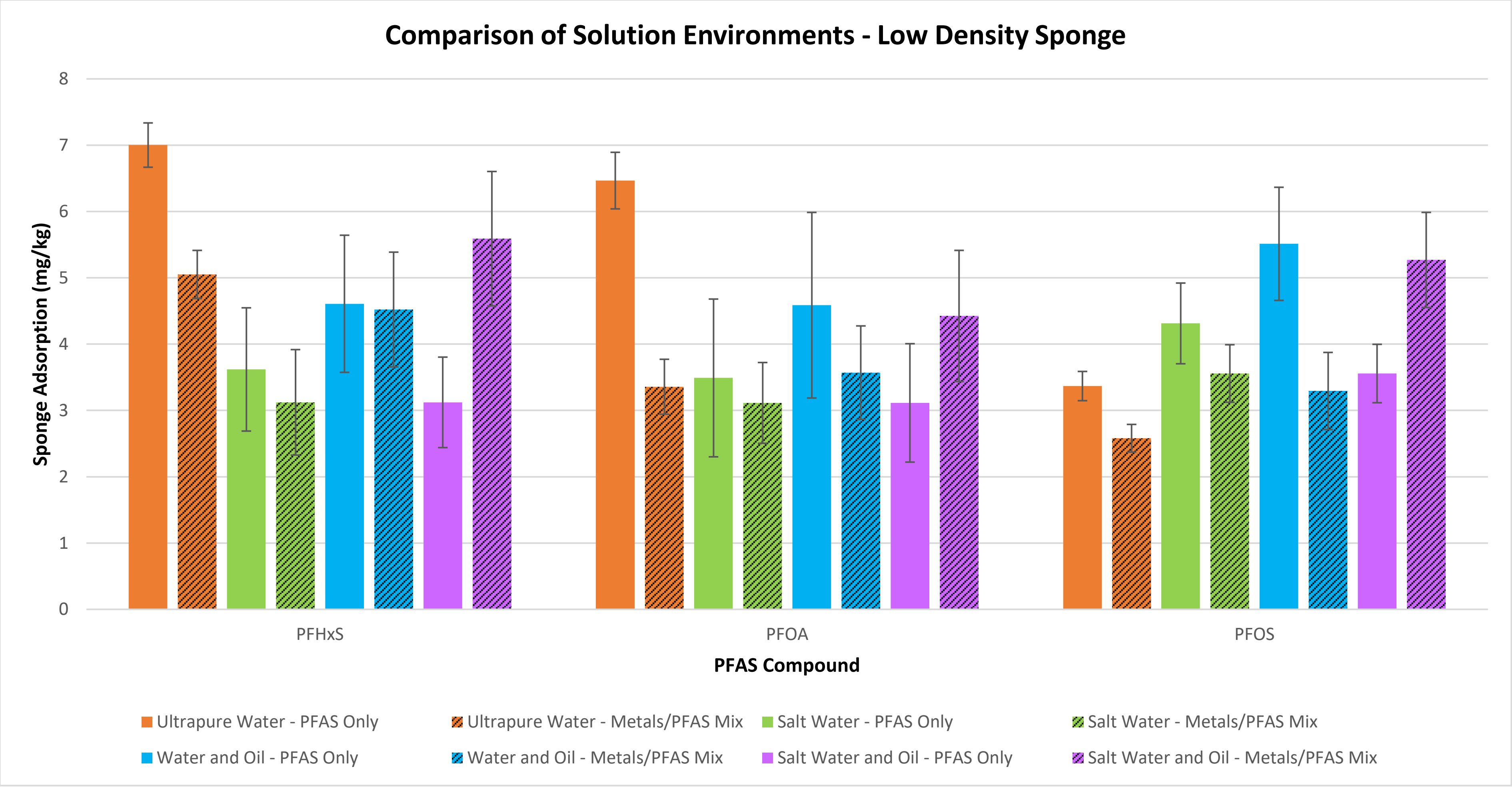

Figure 13: Adsorption of PFAS onto low density sponge material, normalised to the sponge mass. Adsorption was generally consistent across matrices, with some variation shown.

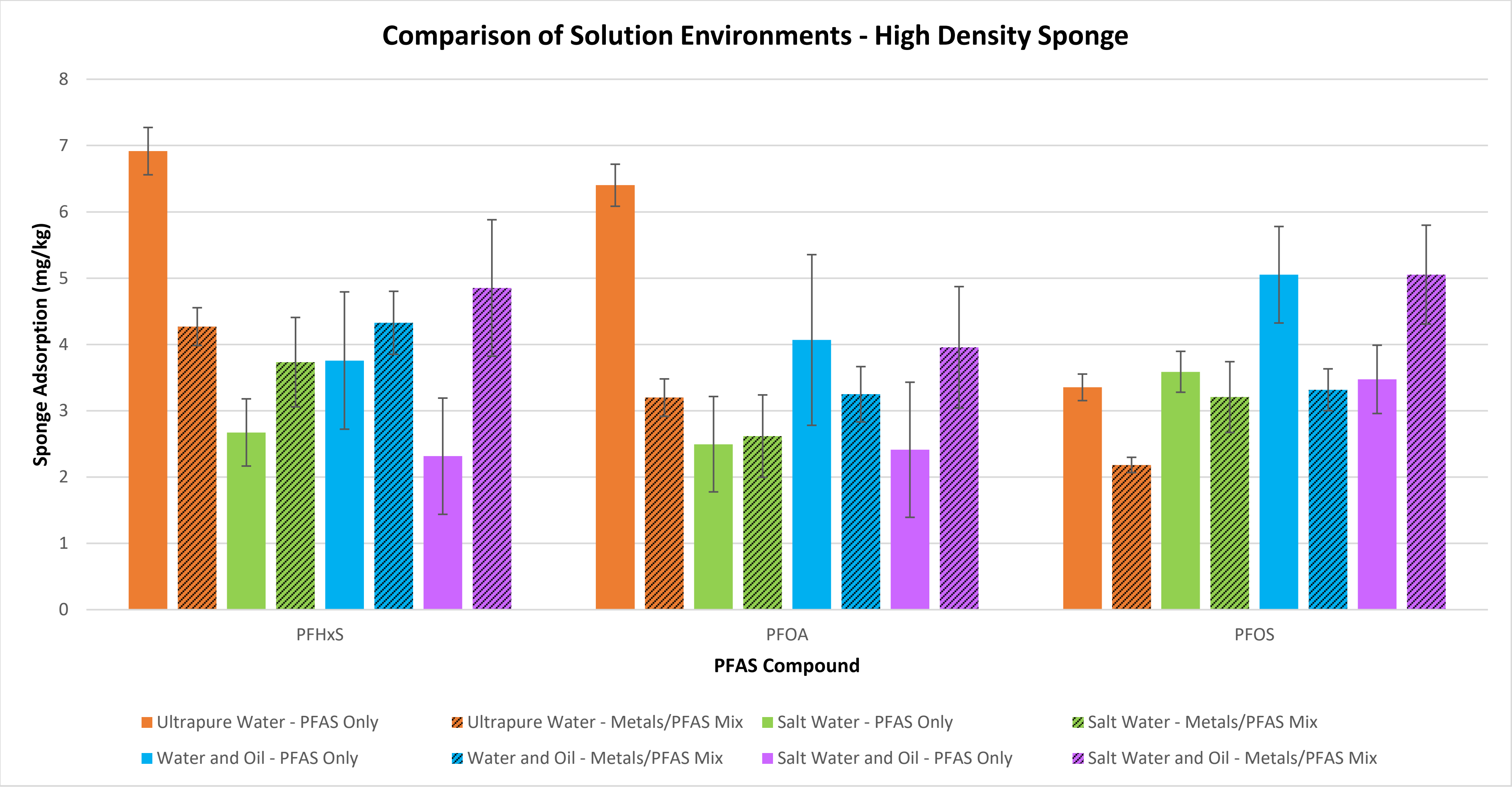

Figure 14: Adsorption of PFAS onto high density sponge material, normalised to the sponge mass. Adsorption was generally consistent across matrices, with some variation shown.

3.4 Comparison of Untreated and Treated Sponges

The process used to manufacture the sponge material has the potential to be modified to change the properties of the sponge material. To determine whether further modification of the manufacturing process would result in a version of the material more effective for toxic metal and PFAS remediation, the adsorption capacity of two batches of microwave-treated sponge samples (microwave treatment for 1.5 minutes and 2 minutes) was tested and compared to the untreated low and high density sponges. The treated and untreated sponge samples were tested in ultrapure water and salt water matrices in order to determine the optimal form of the sponge.

During testing, the microwave-treated sponges were generally found to be more brittle and prone to flaking during the spiking tests than the untreated sponges, particularly in the case of the 2-minute treated samples, some of which would break when squeezed or compressed during the experiments to remove excess water. The microwave modification also resulted in more variation within the batch, particularly for the 1.5-minute treated samples, which had some individual sponge pieces that were brittle throughout, some that were quite hard in the centre but still spongey in texture, and some with a texture quite similar to the untreated sponges. This inconsistency and tendency of the microwave-treated sponges to flake off would need to be considered prior to environmental application and confirmation that the casing used to contain the shredded sponge pieces can effectively prevent any sponge residue from passing through and into the environment.

3.4.1 Metals

The version of the sponge material with the highest adsorption capacity for toxic metals varied with the particular metal. The low density sponge was shown to have the highest adsorption capacity for the selected metals shown in Figure 15 and Figure 16. The adsorbed concentrations for the low density sponge samples were also shown to be significantly different from both treated samples for all of the selected metals in ultrapure water and all except for tin in salt water (p-values for all Student’s t-tests completed to determine this significant difference are in Table 13). The one instance where low density sponges do not have the highest adsorbed concentration for these metals is copper in salt water, wherein the high density sponges have the highest value, but there is no significant difference between these extracted concentrations.

On the other hand, manganese and some of the less adsorbed metals (chromium, germanium, lanthanum, praseodynium and neodymium) adsorbed most effectively to the 2-minute treated samples. However, this was only seen in ultrapure water, because in salt water all of the metals, except chromium, recorded higher adsorption levels to the 1.5-minute treated material. In the case of selenium specifically, the highest adsorbed concentrations were seen in the high density untreated material.

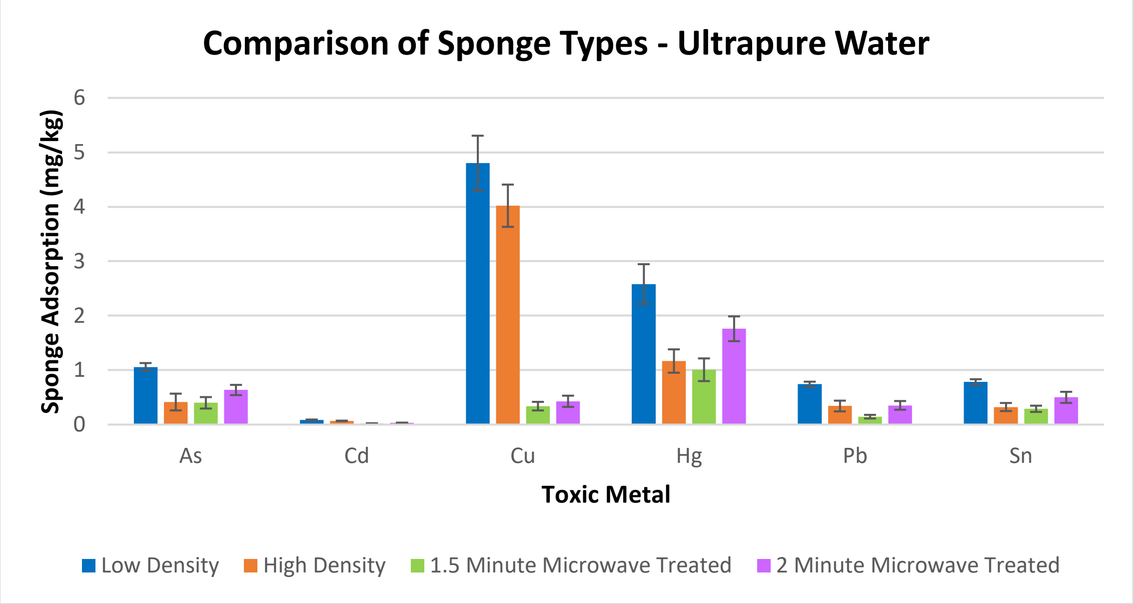

Figure 15: Comparison of non-treated and treated sponge types for selected toxic metals - ultrapure water. The low density sponge adsorbed the selected metals most effectively.

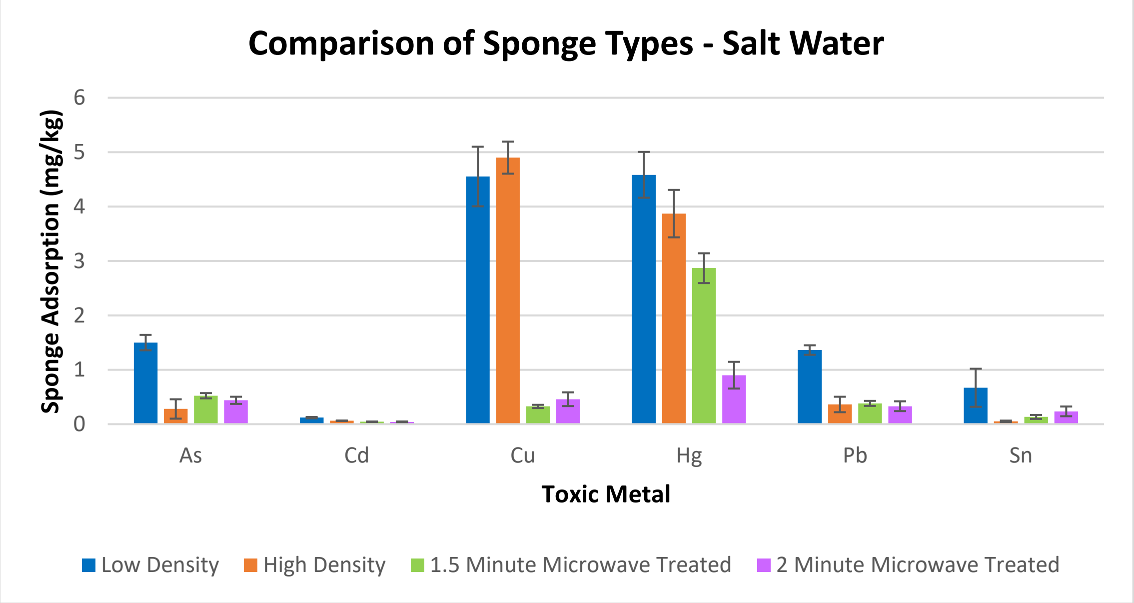

Figure 16: Comparison of non-treated and treated sponge types for selected toxic metals - salt water. The low density sponge adsorbed the selected metals most effectively.

Table 13: p-values for two-tailed Student's t-tests – toxic metals. LD was used as the base case to compare the other sponge types to.

p-values	As	Cd	Cu	Hg	Pb	Sn
Metals/PFAS Mix - Ultrapure Water						
LD vs. HD	0.019	0.058	0.18	0.017	0.0091	0.0016
LD vs. 1.5 min	0.0022	8.9 x 10^{-5}	0.00053	0.013	1.9 x 10^{-6}	0.00020
LD vs. 2 min	0.016	0.00052	0.00060	0.013	0.0051	0.046
Metals/PFAS Mix - Salt Water						
LD vs. HD	0.0019	0.0075	0.57	0.30	0.0012	0.27
LD vs. 1.5 min	7.2 x 10^{-5}	0.00057	0.0012	0.0018	6.1 x 10^{-6}	0.33
LD vs. 2 min	5.2 x 10^{-5}	0.0016	0.00079	2.1 x 10^{-7}	4.5 x 10^{-5}	0.61

3.4.1.1 *Optimal Form of Sponge for Toxic Metals Adsorption*

There was no one optimal form of the sponge for most effective adsorption of all of the toxic metals tested, with the most effective adsorbent varying depending on the specific metal and solution matrix being tested. Thus, different forms of the sponge should be considered for the remediation of different toxic metals. However, the sponge form that was shown to be the most effective adsorbent for many of the metals tested, and effectively adsorbed these metals across both solution matrices tested was the low density sponge.

Comparison of the adsorption capacity of the low density sponge in the ultrapure water matrix to the ADWG health guideline values (see Table 14) shows the material to be suitable for removing toxic metal contamination to allow for contaminated sites to meet the guideline values. The multiple or factor of difference shows the maximum exceedance of the ADWG health guideline value from which the sponge material would be able to decrease toxic metal contamination until the guidelines are met. While there are other considerations to be taken during application of a remediation material to a particular contaminated site, this value indicates whether the sponge may be suitable for highly contaminated sites with toxic metal concentrations that far exceed the guideline values or moderately contaminated sites wherein the exceedance is lower. For example, the average sponge adsorption of mercury is 2600 x the ADWG health guideline value, indicating that the sponge may be suitable for remediating fresh water environments that have been highly contaminated with mercury. On the other hand, the average sponge adsorption of barium is 0.14 x the guideline value, indicating it may only be suitable for remediating sites where barium contamination only slightly exceeds the guideline value. Chromium and nickel, while having health guideline limits in the ADWG, have not been included in this comparison due to not able differences between the two sample batches testing adsorption in ultrapure water containing both toxic metals and PFAS contamination. Appendix A shows the average adsorption values obtained for these metals.

Table 14: Comparison of selected toxic metal adsorption values to ADWG guideline values (ultrapure water test).

Toxic Metal	Sponge Adsorption in Ultrapure Water Matrix (mg/kg)	ADWG Health Guideline Value (mg/L)[47]	Multiple/Factor of Difference
Arsenic	1.1 ± 0.19	0.01	110
Barium	0.27 ± 0.059	2	0.14
Cadmium	0.086 ± 0.019	0.002	43
Copper	4.8 ± 1.3	2	2.4
Lanthanum	0.047 ± 0.010	0.002	24
Lead	0.74 ± 0.12	0.01	74
Manganese	0.94 ± 0.18	0.5	1.9
Mercury	2.6 ± 1.0	0.001	2600
Selenium	0.12 ± 0.062	0.01	12

Comparison to literature values for different adsorbents in section 1.2.2.1 however, shows that the sponge material is a less effective adsorbent for cadmium, copper, lead and nickel than the adsorbents tested in literature (zinc could not be compared due to sponge leaching). Although, these experiments used initial metals concentrations that were higher than the concentrations used in these experiments, meaning comparison between the experiments from literature and this work is somewhat difficult.

3.4.2 PFAS

The low density sponge samples were shown to have the highest average adsorption of all three PFAS compounds in both the ultrapure and salt water matrices, as can be seen in Figure 17 and

Figure 18. However, a significant difference between the PFAS concentrations adsorbed by the low density sponges compared to the other sponge types tested was only found between the low density sponges ad the 1.5-minute and 2-minute treated sponges in the salt water matrix (Table 15 shows the p-values used to determine this significant difference). As a result, all of the sponge types tested would be effective PFAS adsorbents in fresh water environments and both of the untreated sponges would also be effective in marine environments.

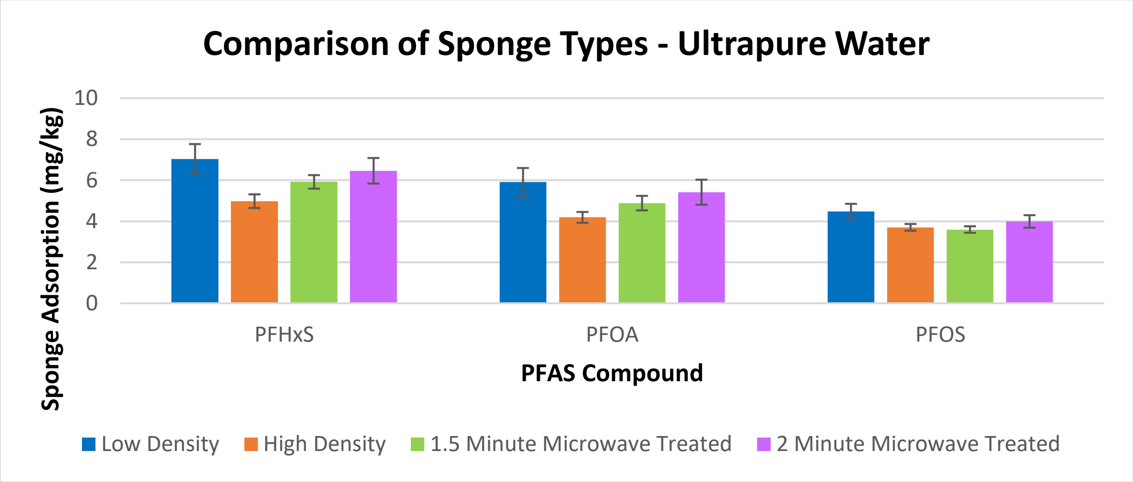

Figure 17: Comparison of non-treated and treated sponge types for tested PFAS - ultrapure water. All sponge types effectively adsorbed PFAS.

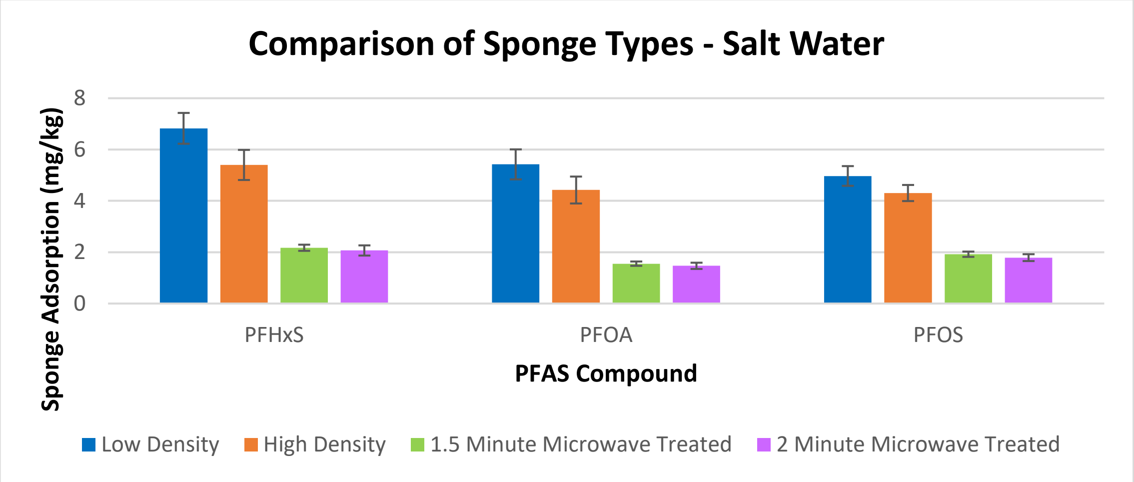

Figure 18: Comparison of non-treated and treated sponge types for tested PFAS - salt water. The untreated sponges adsorbed all three PFAS more effectively than the treated sponges.

Table 15: p-values for two-tailed Student's t-tests – PFAS. LD was used as the base case to compare the other sponge types to.

p-values	PFHxS	PFOA	PFOS
Metals/PFAS Mix - Ultrapure Water			
LD vs. HD	0.052	0.080	0.18
LD vs. 1.5 min	0.35	0.37	0.15
LD vs. 2 min	0.77	0.84	0.56
Metals/PFAS Mix - Salt Water			
LD vs. HD	0.15	0.27	0.29
LD vs. 1.5 min	0.00086	0.0017	0.00056
LD vs. 2 min	0.00042	0.0017	0.00051

3.4.2.1 *Optimal Form of Sponge for PFAS Adsorption*

Both untreated sponge types were found to be effective PFAS adsorbents in both ultrapure and salt water solutions matrices, however, since the low density sponges typically had higher adsorbed PFAS concentrations, this would be the optimal form of the sponge material for PFAS adsorption.

Comparison of the adsorption capacity of the low density sponge material in ultrapure water to the PFAS health guideline values show that the material is suitable for remediating PFAS contaminated sites (see Table 16). The large difference between the sponge adsorption concentrations and the guideline values indicate that the sponge material could even be suitable for remediating highly contaminated sites that are 10,000x the guideline values, as indicated by the multiples of difference.

Table 16: Comparison of sponge adsorption values to PFAS guideline values (ultrapure water test).

PFAS	Sponge Adsorption (mg/kg)	Australian Drinking Water Guideline Value (µg/L)[51]	Multiple of Difference
PFOA	5.9 ± 1.8	0.56	1.1×10^{4}
PFHxS	7.0 ± 1.9	0.07	1.0×10^{5}
PFOS	4.5 ± 1.0		6.4×10^{4}

Comparison to the literature values for different adsorbents in section 1.2.2.1 however, shows that the sponge material is a less effective adsorbent for PFOS and PFOA than the adsorbents tested in literature, with the exception of alumina[11] (PFHxS results are not in the literature values collated). Although, the experiments undertaken in these papers, as was the case for the toxic metals, did use initial PFAS concentrations that were much higher (ppm range) than the spiking concentration used in this work (ppb range), so increasing initial concentrations to the ppm range might also result in increased level of PFAS adsorption for the sponge material. This is plausible, especially considering a decrease in PFAS concentration was seen in the spiked solutions during LC-MS/MS analysis, allowing for the calculation of the expected adsorption values and indicating that the PFAS concentration tested in this work was not in an extreme excess.

3.5 Environmental Testing

3.5.1 Metals

The level of toxic metal adsorption by the environmentally applied sponge samples tested was generally low, with the exception of manganese, which is likely due to the environmental concentrations of these metals at Tuggerah Lake being low. Table 17 shows the seven metals that were found to have the highest uptake by the sponge, not including aluminium and zinc, due to their leaching, and iron, as it was shown to likely be contaminated by dust during the experimental process, resulting in much higher results than expected and compares them to the ADWG health guideline values. Based on the sponge adsorption concentrations, it is possible that the environmental concentrations of chromium, lead, manganese and mercury exceeded the ADWG health guideline values.

Table 17: Toxic metals extracted from the Tuggerah Lake sponge samples compared to ADWG health guideline values.

Toxic Metal	Sponge Adsorption (mg/kg)	ADWG Health Guideline Values (mg/L)[52]
Barium	0.24 ± 0.26	2
Chromium	0.28 ± 0.073	0.05
Copper	0.99 ± 0.75	2
Lead	0.38 ± 0.26	0.01

Manganese	7.4 ± 3.4	0.5
Mercury	0.46 ± 0.38	0.001
Strontium	0.74 ± 0.42	N/A

3.5.2 PFAS

The PFAS were generally not detected above the LOQ in the environmentally applied sponge samples, indicating that there was likely minimal PFAS contamination in the local area where the sponge had been implemented. Further testing with environmental concentrations of PFAS would be needed to confirm whether the low PFAS concentrations seen in these results are also due to the sponge material.

3.6 Limitations

There were some key limitations throughout these experiments that are important to note, due to their impact on the results. First, variations in the porous structure of the individual sponge pieces used for sampling resulted in variations in the adsorption data obtained. Adsorption capacity was represented as per mass of sponge to limit the impact of this variation, however, normalising per mass does not account for differences in surface area between individual sponge samples that may be present. This was a limitation in the study design, however, when the sponge is used in the environment as a remediation material, it is not used individually. Instead a large amount of the shredded material is placed in a fabric outer casing, and applied as an adsorbent floating boom. This means that variations in adsorption capacity is a much smaller issue during environmental application.

Another key limitation is that this sponge material hasn’t been studied before, meaning that there was no characterisation data available for the material, including, most notably for these experiments, the binding characteristics of toxic metals and PFAS to the material. This has resulted in uncertainty around whether the extraction methods used as part of these experiments were able to completely extract all adsorbed toxic metals and PFAS from the sponge, and what variations to the extraction protocol may result in it becoming more or less effective for toxic metals and PFAS extraction.

Further, the adsorption capacity of the sponge material for aluminium and zinc was unable to be determined due to leaching of these metals from the sponge itself into the tested solutions resulting in any adsorption that may have occurred being undetectable and unquantifiable.

The final key limitation, which may also affect environmental application of the sponge material, is that disposal methods of toxic metal and PFAS-contaminated sponges after use have not yet been confirmed. Though reusability of the material was not tested in these experiments, it is unlikely that the sponges could be reused in perpetuity, especially considering the changes the acid extraction process made to the sponge samples, namely decreasing their ease of compression, which could affect reusability of the sponge and make it more likely that the sponges would need to be disposed of after some uses. Thus, a disposal protocol for the material would need to be developed before widespread application of the adsorbent for toxic metal and PFAS-contaminated environments.

Chapter 4: Conclusions and Future Directions

Chapter 4: Conclusions and Future Directions

4.1 Conclusions

In conclusion, this thesis determined the remediation potential of a semi-open cell polymeric foam for toxic metals and PFAS. The method included leaching tests and extractions of the material itself, spiked testing and analysis with four different solution matrices and treated and untreated version of the material and the extraction of material samples used at Tuggerah Lake.

The leaching tests and extractions of unspiked material determined that the aluminium and zinc already present in the sponge leaches into the water and is extracted at high amounts. This meant that any possible adsorption of aluminium and zinc by the sponge was unable to be detected or quantified in this work.

Initial spiking tests compared three different wash durations to determine whether toxic metals and PFAS were being taken up by the material, and whether this uptake was due to the contaminants adsorbing to the porous structure of the material or whether they were just loosely associated and would thus be washed off. The toxic metals and PFAS results showed that compounds were being adsorbed onto the porous structure of the material, with many metals and all PFAS showing much larger concentrations in the extracted solutions compared to the wash solutions. These results also meant that the 1-hour wash could be used for later experiments.

The four solution matrices tested were shown to impact adsorption levels of the toxic metals and PFAS compounds to different degrees for different compounds, which indicated how much the specific site conditions (fresh water or marine environments or the presence of an oil spill) would need to be considered before using the material for the remediation of toxic metals and PFAS in those environments. Metals such as arsenic and copper were effectively adsorbed by the sponge and showed little variation in adsorbed concentrations across the different solution matrices, whereas tin was another effectively adsorbed metal but was highly impacted by the solution matrix, adsorbing to the sponge 8.8x more effectively in the metals only ultrapure water solution than the other solutions. The lanthanides tested also showed similar adsorbed concentrations across the different solutions matrices but were also less effectively adsorbed by the material in general. All PFAS were shown to be effectively adsorbed by the sponge material across the four solution matrices, with the solution matrix that resulted in the highest adsorption of each compound (PFAS only ultrapure water for PFHxS and PFOA and PFAS only ultrapure water and oil as well as metals/PFAS mix salt water and oil for PFOS) only resulting in concentrations 1.6-2.0x higher than the other matrices.

The low density untreated version of the material was determined to be the optimal form for toxic metals and PFAS adsorption, as it adsorbed the most compounds in multiple solution matrices the most effectively of the sponge types tested. However, the treated sponges were shown to be more effective for some of the metals. The low density sponge was determined to be suitable for toxic metal and PFAS remediation when compared to the Australian drinking water health guidelines, but had typically lower adsorption values than adsorbents tested in other studies. Despite this, the determination of the optimal forms of the material and their level of effectiveness resulted in the achievement of the third objective of this thesis.

The environmental sponge samples tested indicated that during their application at Tuggerah Lake, environmental concentrations of chromium, lead, manganese and mercury could have exceeded the ADWGs. These tests also indicated that PFAS contamination was minimal at this particular location.

In summary, the testing of this semi-open cell polymeric foam and determination of the effects of different solution types and material modifications resulted in the identification of a material that shows potential for the remediation of toxic metals and PFAS.

4.2 Future Directions

Future directions should be aimed at full characterisation of the adsorbent material, including surface area experiments, adsorption and desorption kinetics and binding characteristics of toxic metals and PFAS. This could then allow for the optimisation of the acid and methanol extraction protocols developed in this paper to ensure full extraction of adsorbed toxic metals and PFAS by the sponge material.

Another avenue of future work would be to explore the reusability of the material for toxic metals an PFAS remediation. The material has been stated to be reusable for oil spill remediation, so determination of its reusability after toxic metal and PFAS adsorption would be key to further determining its capability as a remediation material for these contaminants.

Following these experiments, the sponge material could also be tested for applicability as a remediation material for additional PFAS compounds or other contaminant groups of interest.

The experiments undertaken in this paper showed the possibility of aluminium and zinc contamination of water sources due to their leaching from the sponge. Thus, the extent of this impact on the water source being remediated during environmental application of the adsorbent should be determined. Following this, application of the material to multiple stormwater and wastewater outlets would be another direction to explore, in order to compare the adsorption capacities in different solution matrices from these experiments to real-life fresh water and marine environments and obtain environmental data for sponge adsorption capacity in these environments.

Finally, a disposal protocol for the sponge should be developed after its use as a toxic metal or PFAS remediation material, to ensure the adsorbent itself does not become another form of waste contaminating an environment.

References

1. Desbureaux, S.; Mortier, F.; Zaveri, E.; van Vliet, M. T. H.; Russ, J.; Rodella, A. S.; Damania, R., Mapping global hotspots and trends of water quality (1992–2010): a data driven approach. *Environmental Research Letters* **2022,** *17* (11), 114048.
2. Lin, L.; Yang, H.; Xu, X., Effects of Water Pollution on Human Health and Disease Heterogeneity: A Review. *Frontiers in Environmental Science* **2022,** *10*.
3. UNESCO World Water Assessment Programme, *The United Nations world water development report 2021: valuing water*. United Nations: 2021.
4. UNESCO World Water Assessment Programme, *The United Nations World Water Development Report 2024: water for prosperity and peace*. United Nations: 2024; p 153.
5. Briffa, J.; Sinagra, E.; Blundell, R., Heavy metal pollution in the environment and their toxicological effects on humans. *Heliyon* **2020,** *6* (9), e04691.
6. Tchounwou, P. B.; Yedjou, C. G.; Patlolla, A. K.; Sutton, D. J., Heavy metal toxicity and the environment. *Exp Suppl* **2012,** *101*, 133-64.
7. International Agency for Research on Cancer, IARC Monographs on the Identification of Carcinogenic Hazards to Humans - List of Classifications. World Health Organisation: 2024.
8. Jaishankar, M.; Tseten, T.; Anbalagan, N.; Mathew, B. B.; Beeregowda, K. N., Toxicity, mechanism and health effects of some heavy metals. *Interdiscip Toxicol* **2014,** *7* (2), 60-72.
9. Cima, F., Tin: environmental pollution and health effects. *Encyclopedia of environmental health* **2011,** *10*, 351-359.
10. United Stated Environmental Protection Agency, PFAS Structure Lists. 2022.
11. Abunada, Z.; Alazaiza, M. Y. D.; Bashir, M. J. K., An Overview of Per- and Polyfluoroalkyl Substances (PFAS) in the Environment: Source, Fate, Risk and Regulations. *Water* **2020,** *12* (12), 3590.
12. Gagliano, E.; Sgroi, M.; Falciglia, P. P.; Vagliasindi, F. G. A.; Roccaro, P., Removal of poly- and perfluoroalkyl substances (PFAS) from water by adsorption: Role of PFAS chain length, effect of organic matter and challenges in adsorbent regeneration. *Water Research* **2020,** *171*, 115381.
13. Pauletto, P. S.; Bandosz, T. J., Activated carbon versus metal-organic frameworks: A review of their PFAS adsorption performance. *Journal of Hazardous Materials* **2022,** *425*, 127810.
14. Vu, C. T.; Wu, T., Recent progress in adsorptive removal of per- and poly-fluoroalkyl substances (PFAS) from water/wastewater. *Critical Reviews in Environmental Science and Technology* **2022,** *52* (1), 90-129.
15. Glüge, J.; Scheringer, M.; Cousins, I. T.; DeWitt, J. C.; Goldenman, G.; Herzke, D.; Lohmann, R.; Ng, C. A.; Trier, X.; Wang, Z., An overview of the uses of per-and polyfluoroalkyl substances (PFAS). *Environmental Science: Processes & Impacts* **2020,** *22* (12), 2345-2373.
16. Fenton, S. E.; Ducatman, A.; Boobis, A.; DeWitt, J. C.; Lau, C.; Ng, C.; Smith, J. S.; Roberts, S. M., Per-and polyfluoroalkyl substance toxicity and human health review: Current state of knowledge and strategies for informing future research. *Environmental toxicology and chemistry* **2021,** *40* (3), 606-630.
17. Ackerman Grunfeld, D.; Gilbert, D.; Hou, J.; Jones, A. M.; Lee, M. J.; Kibbey, T. C. G.; O'Carroll, D. M., Underestimated burden of per- and polyfluoroalkyl substances in global surface waters and groundwaters. *Nature Geoscience* **2024,** *17* (4), 340-346.

18. Karbassiyazdi, E.; Kasula, M.; Modak, S.; Pala, J.; Kalantari, M.; Altaee, A.; Esfahani, M. R.; Razmjou, A., A juxtaposed review on adsorptive removal of PFAS by metal-organic frameworks (MOFs) with carbon-based materials, ion exchange resins, and polymer adsorbents. *Chemosphere* **2023,** *311*, 136933.

19. Zhang, Y.; Wang, B.; Ma, S.; Zhang, Q., Adsorption of per- and polyfluoroalkyl substances (PFAS) from water with porous organic polymers. *Chemosphere* **2024,** *346*, 140600.

20. Wee, S. Y.; Aris, A. Z., Environmental impacts, exposure pathways, and health effects of PFOA and PFOS. *Ecotoxicology and Environmental Safety* **2023,** *267*, 115663.

21. United Nations Environment Programme *The new POPs under the Stockholm Convention*; 2023.

22. Gallen, C.; Drage, D.; Eaglesham, G.; Grant, S.; Bowman, M.; Mueller, J. F., Australia-wide assessment of perfluoroalkyl substances (PFASs) in landfill leachates. *Journal of Hazardous Materials* **2017,** *331*, 132-141.

23. Lang, J. R. B. M. A., Jennifer A. Field, James W. Levis, and Morton A. Barlaz, National Estimate of Per- and Polyfluoroalkyl Substance (PFAS) Release to U.S. Municipal Landfill Leachate. *Environmental Science & Technology* **2017,** *51*, 2197-2205.

24. Kalita, E.; Baruah, J., 16 - Environmental remediation. In *Colloidal Metal Oxide Nanoparticles*, Thomas, S.; Tresa Sunny, A.; Velayudhan, P., Eds. Elsevier: 2020; pp 525-576.

25. Ouyang, D.; Zhuo, Y.; Hu, L.; Zeng, Q.; Hu, Y.; He, Z., Research on the Adsorption Behavior of Heavy Metal Ions by Porous Material Prepared with Silicate Tailings. *Minerals* **2019,** *9* (5), 291.

26. Li, J.; Wang, X.; Zhao, G.; Chen, C.; Chai, Z.; Alsaedi, A.; Hayat, T.; Wang, X., Metal–organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions. *Chemical Society Reviews* **2018,** *47* (7), 2322-2356.

27. Yeung, A. T. In *Remediation technologies for contaminated sites*, Advances in Environmental Geotechnics: Proceedings of the International Symposium on Geoenvironmental Engineering in Hangzhou, China, September 8–10, 2009, Springer: 2010; pp 328-369.

28. Pohl, A., Removal of Heavy Metal Ions from Water and Wastewaters by Sulfur-Containing Precipitation Agents. *Water, Air, & Soil Pollution* **2020,** *231* (10), 503.

29. Mayakaduwage, S.; Ekanayake, A.; Kurwadkar, S.; Rajapaksha, A. U.; Vithanage, M., Phytoremediation prospects of per- and polyfluoroalkyl substances: A review. *Environmental Research* **2022,** *212*, 113311.

30. Farraji, H.; Zaman, N. Q.; Tajuddin, R.; Faraji, H., Advantages and disadvantages of phytoremediation: A concise review. *Int J Env Tech Sci* **2016,** *2*, 69-75.

31. Wang, J.; Wang, L.; Xu, C.; Zhi, R.; Miao, R.; Liang, T.; Yue, X.; Lv, Y.; Liu, T., Perfluorooctane sulfonate and perfluorobutane sulfonate removal from water by nanofiltration membrane: The roles of solute concentration, ionic strength, and macromolecular organic foulants. *Chemical Engineering Journal* **2018,** *332*, 787-797.

32. Xiang, H.; Min, X.; Tang, C.-J.; Sillanpää, M.; Zhao, F., Recent advances in membrane filtration for heavy metal removal from wastewater: A mini review. *Journal of Water Process Engineering* **2022,** *49*, 103023.

33. Bi, J.; Tao, Q.; Huang, X.; Wang, J.; Wang, T.; Hao, H., Simultaneous decontamination of multi-pollutants: A promising approach for water remediation. *Chemosphere* **2021,** *284*, 131270.

34. Yadav, A.; Bagotia, N.; Sharma, A. K.; Kumar, S., Simultaneous adsorptive removal of conventional and emerging contaminants in multi-component systems for wastewater remediation: A critical review. *Science of The Total Environment* **2021,** *799*, 149500.

35. Sophia A, C.; Lima, E. C., Removal of emerging contaminants from the environment by adsorption. *Ecotoxicology and Environmental Safety* **2018,** *150*, 1-17.

36. Zheng, M.; Xu, L.; Chen, C.; Labiadh, L.; Yuan, B.; Fu, M.-L., MOFs and GO-based composites as deliberated materials for the adsorption of various water contaminants. *Separation and Purification Technology* **2022,** *294*, 121187.

37. Jadoun, S.; Fuentes, J. P.; Urbano, B. F.; Yáñez, J., A review on adsorption of heavy metals from wastewater using conducting polymer-based materials. *Journal of Environmental Chemical Engineering* **2023,** *11* (1), 109226.

38. Fagbayigbo, B. O.; Opeolu, B. O.; Fatoki, O. S., Adsorption of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from water using leaf biomass (Vitis vinifera) in a fixed-bed column study. *Journal of Environmental Health Science and Engineering* **2020,** *18* (1), 221-233.

39. Stebel, E. K.; Pike, K. A.; Nguyen, H.; Hartmann, H. A.; Klonowski, M. J.; Lawrence, M. G.; Collins, R. M.; Hefner, C. E.; Edmiston, P. L., Absorption of short-chain to long-chain perfluoroalkyl substances using swellable organically modified silica. *Environmental Science: Water Research & Technology* **2019,** *5* (11), 1854-1866.

40. Srivastava, V. C.; Mall, I. D.; Mishra, I. M., Adsorption of toxic metal ions onto activated carbon: Study of sorption behaviour through characterization and kinetics. *Chemical Engineering and Processing: Process Intensification* **2008,** *47* (8), 1269-1280.

41. Chamarthy, S.; Seo, C. W.; Marshall, W. E., Adsorption of selected toxic metals by modified peanut shells. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology* **2001,** *76* (6), 593-597.

42. Du, Z.; Deng, S.; Bei, Y.; Huang, Q.; Wang, B.; Huang, J.; Yu, G., Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents—A review. *Journal of Hazardous Materials* **2014,** *274*, 443-454.

43. Karnib, M.; Kabbani, A.; Holail, H.; Olama, Z., Heavy Metals Removal Using Activated Carbon, Silica and Silica Activated Carbon Composite. *Energy Procedia* **2014,** *50*, 113-120.

44. Lockwood, T. E.; Talebi, M.; Minett, A.; Mills, S.; Doble, P. A.; Bishop, D. P., Micro solid-phase extraction for the analysis of per- and polyfluoroalkyl substances in environmental waters. *Journal of Chromatography A* **2019,** *1604*, 460495.

45. Vakilipour Takaloo, A., Corrosion Behavior of Heat Treated Nickel-Aluminum Bronze Alloy in Artificial Seawater. *Materials Sciences and Applications* **2011,** *02*, 1542-1555.

46. Australian Government - Australian Maritime Safety Authority *Identification of Oil on Water - Aerial Observation and Identification Guide*; 2014.

47. NHMRC, Australian Drinking Water Guidelines. 2011.

48. Australian and New Zealand Guidelines for Fresh & Marine Water Quality Toxicant default guideline values for water quality in aquatic ecosystems.

49. Australian Government - Department of Health and Aged Care *Environmental fate and effects of zinc ions - Evaluation statement (Draft)*; 2024.

50. Zenobio, J. E.; Salawu, O. A.; Han, Z.; Adeleye, A. S., Adsorption of per- and polyfluoroalkyl substances (PFAS) to containers. *Journal of Hazardous Materials Advances* **2022,** *7*, 100130.

51. HEPA *PFAS National Environmental Management Plan Version 2.0*; 2020.

52. Council, A. G.-N. H. a. M. R. C. N. R. M. M., Australian Drinking Water Guidelines. 3.8 ed.; Council, N. H. a. M. R. C. N. R. M. M., Ed. 2022.

Appendices

Appendix A: Sponge Adsorption Values for Toxic Metals

METALS ONLY ULTRAPURE WATER																									
	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Rb	Sr	Cd	Sn	Ba	La	Pr	Nd	Sm	Eu	Gd	Dy	Hg	Pb
avg LD	976.573	0.113	0.542	2.277	12.602	0.063	0.338	4.208	3217.800	0.192	1.725	0.244	0.012	14.893	0.550	2.604	0.518	0.125	0.095	0.126	0.104	0.092	0.098	0.093	1.401	1.612
avg HD	671.744	0.067	0.357	1.473	8.362	0.109	0.182	4.048	2311.235	0.507	0.965	0.322	0.010	8.675	0.346	1.461	0.219	0.105	0.084	0.110	0.091	0.081	0.085	0.083	1.061	0.941
std dev LD	284.309	0.027	0.234	0.724	4.964	0.040	0.218	0.986	651.301	0.068	0.322	0.080	0.005	3.377	0.229	0.608	0.119	0.020	0.016	0.022	0.019	0.016	0.017	0.016	0.469	0.458
std dev HD	353.007	0.039	0.149	0.528	2.484	0.057	0.104	0.783	1028.274	0.654	0.675	0.082	0.003	4.757	0.090	0.780	0.197	0.043	0.038	0.047	0.041	0.038	0.038	0.040	0.486	0.404
MIX ULTRAPURE WATER																									
	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Rb	Sr	Cd	Sn	Ba	La	Pr	Nd	Sm	Eu	Gd	Dy	Hg	Pb
avg LD	711.256	0.069	1.772	1.741	19.166	0.042	1.137	4.304	2804.934	0.078	1.369	0.238	0.010	11.504	0.287	0.311	0.352	0.072	0.050	0.079	0.061	0.046	0.052	0.046	1.470	0.942
avg HD	535.938	0.053	3.691	1.355	28.666	0.098	2.016	5.737	1903.188	0.059	0.617	0.249	0.011	6.069	0.316	0.000	0.120	0.057	0.040	0.062	0.048	0.037	0.043	0.038	0.882	0.556
std dev LD	135.896	0.010	2.126	0.304	10.760	0.019	1.066	1.052	561.625	0.031	0.352	0.056	0.002	2.297	0.118	0.738	0.067	0.012	0.010	0.016	0.014	0.010	0.012	0.010	0.442	0.191
std dev HD	102.195	0.025	5.749	0.502	30.878	0.078	2.735	4.507	1141.733	0.037	0.458	0.055	0.003	3.947	0.361	0.000	0.151	0.018	0.012	0.018	0.012	0.011	0.012	0.010	0.320	0.180
METALS ONLY SALTWATER																									
	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Rb	Sr	Cd	Sn	Ba	La	Pr	Nd	Sm	Eu	Gd	Dy	Hg	Pb
avg LD	2688.971	0.060	0.746	2.323	31.042	0.064	0.713	5.263	4461.538	0.185	1.464	0.217	0.014	15.776	0.207	0.000	0.631	0.139	0.110	0.150	0.130	0.100	0.108	0.094	1.359	0.972
avg HD	1301.484	0.021	0.573	1.212	13.388	0.082	0.777	6.221	2340.233	0.112	0.514	0.233	0.013	7.371	0.146	0.000	0.303	0.102	0.086	0.115	0.103	0.082	0.090	0.079	0.878	0.538
std dev LD	526.852	0.016	0.065	0.382	40.594	0.032	0.101	1.729	612.432	0.069	0.272	0.072	0.004	3.203	0.066	0.000	0.136	0.027	0.024	0.028	0.027	0.021	0.021	0.019	0.565	0.187

std dev HD	693.303	0.024	0.192	0.645	6.417	0.025	0.742	2.454	1388.814	0.084	0.551	0.077	0.007	5.109	0.025	0.000	0.254	0.041	0.032	0.048	0.041	0.029	0.033	0.029	0.410	0.316
METALS ONLY WATER + OIL																										
	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Rb	Sr	Cd	Sn	Ba	La	Pr	Nd	Sm	Eu	Gd	Dy	Hg	Pb
avg LD	2048.766	0.097	0.857	2.624	20.491	0.039	0.184	4.197	4134.395	0.200	1.672	0.365	0.019	14.437	0.261	1.963	0.502	0.167	0.140	0.195	0.174	0.129	0.173	0.134	2.441	0.918
avg HD	1235.149	0.067	0.597	1.296	15.606	0.112	0.858	5.045	2491.679	0.112	0.639	0.431	0.016	7.810	0.272	0.501	0.246	0.105	0.086	0.122	0.108	0.082	0.106	0.084	1.395	0.530
std dev LD	1698.230	0.021	0.294	1.410	5.060	0.034	0.154	1.916	1115.680	0.186	0.223	0.134	0.009	4.055	0.097	1.245	0.230	0.142	0.139	0.178	0.172	0.133	0.172	0.135	0.681	0.269
std dev HD	1582.904	0.032	0.263	0.893	6.520	0.079	2.123	1.834	1864.442	0.145	0.731	0.111	0.013	7.714	0.126	0.461	0.352	0.128	0.115	0.155	0.145	0.110	0.141	0.111	0.568	0.478
METALS ONLY SALTWATER + OIL																										
	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Rb	Sr	Cd	Sn	Ba	La	Pr	Nd	Sm	Eu	Gd	Dy	Hg	Pb
avg LD	2891.011	0.100	0.620	2.274	17.692	0.050	0.236	4.212	4568.977	0.207	1.705	0.289	0.017	17.197	0.302	1.212	0.718	0.174	0.140	0.200	0.178	0.132	0.172	0.134	2.348	1.079
avg HD	906.902	0.060	0.412	1.038	9.186	0.077	0.019	4.126	2038.766	0.081	0.458	0.347	0.011	6.369	0.171	0.372	0.244	0.081	0.065	0.093	0.084	0.063	0.084	0.064	1.543	0.401
std dev LD	1563.184	0.019	0.120	0.736	2.672	0.037	0.170	1.209	1651.640	0.120	0.412	0.135	0.007	5.698	0.085	1.205	0.331	0.088	0.079	0.108	0.098	0.076	0.097	0.073	0.427	0.238
std dev HD	773.201	0.024	0.113	0.438	3.614	0.037	0.032	1.138	947.636	0.046	0.496	0.117	0.004	3.872	0.038	0.615	0.238	0.040	0.035	0.051	0.047	0.035	0.045	0.035	0.609	0.204
MIX SALTWATER																										
	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Rb	Sr	Cd	Sn	Ba	La	Pr	Nd	Sm	Eu	Gd	Dy	Hg	Pb
avg LD	3187.661	0.077	0.000	2.332	18.512	0.066	0.000	4.725	2994.730	0.091	1.262	0.182	0.003	16.410	0.104	0.131	0.921	0.116	0.070	0.083	0.055	0.059	0.053	0.057	0.976	1.149
avg HD	2112.748	0.046	0.046	1.365	9.878	0.042	0.000	4.700	1697.305	0.068	0.356	0.347	0.001	8.002	0.066	0.058	0.439	0.081	0.050	0.060	0.042	0.043	0.040	0.041	0.695	0.396
std dev LD	1447.744	0.024	0.000	0.898	7.733	0.019	0.000	1.176	1223.428	0.059	0.701	0.218	0.003	7.701	0.035	0.051	0.437	0.037	0.021	0.029	0.017	0.018	0.015	0.016	1.006	0.591
std dev HD	823.588	0.010	0.138	0.369	5.292	0.005	0.000	1.093	554.308	0.038	0.422	0.203	0.001	3.156	0.016	0.025	0.162	0.021	0.013	0.014	0.012	0.011	0.011	0.010	0.559	0.371
MIX WATER + OIL																										
	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Rb	Sr	Cd	Sn	Ba	La	Pr	Nd	Sm	Eu	Gd	Dy	Hg	Pb
avg LD	1094.896	0.067	0.000	1.693	21.189	0.052	0.000	4.302	2006.627	0.054	1.292	0.230	0.001	12.265	0.114	0.817	0.420	0.080	0.049	0.060	0.038	0.041	0.039	0.041	1.645	0.915
avg HD	699.583	0.052	0.010	1.086	11.218	0.046	0.000	4.670	1391.428	0.042	0.611	0.348	0.000	6.401	0.073	0.414	0.167	0.057	0.035	0.041	0.028	0.031	0.029	0.031	0.792	0.478
std dev LD	179.313	0.012	0.000	0.437	13.726	0.014	0.000	1.044	579.101	0.021	0.279	0.079	0.001	3.323	0.033	0.118	0.120	0.024	0.016	0.019	0.013	0.015	0.015	0.014	0.989	0.230
std dev HD	464.043	0.016	0.023	0.572	6.000	0.017	0.000	1.379	817.011	0.053	0.597	0.151	0.000	4.758	0.025	0.244	0.189	0.031	0.020	0.022	0.016	0.017	0.017	0.018	0.937	0.403
MIX SALTWATER + OIL																										

	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Rb	Sr	Cd	Sn	Ba	La	Pr	Nd	Sm	Eu	Gd	Dy	Hg	Pb
avg LD	4228.337	0.085	0.398	2.742	20.756	0.084	0.256	4.903	3508.364	0.110	1.698	0.159	0.005	20.200	0.130	0.493	3.768	0.140	0.090	0.103	0.072	0.075	0.070	0.071	3.197	1.466
avg HD	2208.127	0.054	0.044	1.393	8.616	0.056	0.000	5.711	1782.356	0.083	0.478	0.340	0.002	8.990	0.066	0.071	2.126	0.085	0.054	0.061	0.042	0.045	0.040	0.041	1.991	0.492
std dev LD	638.745	0.015	1.131	0.274	7.943	0.027	0.769	2.678	487.229	0.040	0.276	0.102	0.004	1.917	0.022	0.764	1.953	0.018	0.014	0.014	0.010	0.013	0.012	0.013	0.983	0.186
std dev HD	1749.522	0.028	0.133	0.945	6.242	0.024	0.000	2.955	1376.901	0.079	0.783	0.230	0.004	7.006	0.041	0.061	1.146	0.055	0.034	0.039	0.026	0.030	0.028	0.028	0.856	0.634
STATS MIX ULTRAPURE WATER: NON-TREATED																										
	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Rb	Sr	Cd	Sn	Ba	La	Pr	Nd	Sm	Eu	Gd	Dy	Hg	Pb
avg LD	728.117	0.034	0.000	0.944	9.470	0.029	0.002	4.801	1260.802	0.068	1.058	0.121	0.007	7.396	0.086	0.783	0.274	0.047	0.030	0.037	0.025	0.025	0.025	0.025	2.581	0.742
avg HD	402.904	0.030	0.000	0.604	5.938	0.031	0.000	4.020	895.242	0.037	0.414	0.268	0.008	3.478	0.068	0.322	0.078	0.034	0.024	0.030	0.018	0.019	0.018	0.020	1.167	0.341
std dev LD	132.068	0.010	0.000	0.179	3.623	0.006	0.004	1.335	208.044	0.020	0.190	0.062	0.002	1.518	0.019	0.132	0.059	0.010	0.005	0.004	0.006	0.005	0.004	0.004	0.966	0.122
std dev HD	268.878	0.010	0.000	0.278	3.990	0.005	0.000	1.027	510.410	0.019	0.408	0.144	0.004	2.739	0.012	0.196	0.102	0.018	0.014	0.017	0.011	0.012	0.010	0.014	0.567	0.262
STATS MIX SALTWATER: NON-TREATED																										
	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Rb	Sr	Cd	Sn	Ba	La	Pr	Nd	Sm	Eu	Gd	Dy	Hg	Pb
avg LD	3525.118	0.055	0.013	2.124	13.307	0.057	0.000	4.552	2905.842	0.101	1.500	0.099	0.012	16.632	0.120	0.669	1.724	0.119	0.074	0.086	0.058	0.060	0.057	0.057	4.584	1.363
avg HD	1761.986	0.033	0.000	1.161	8.609	0.051	0.000	4.899	1404.723	0.031	0.280	0.360	0.003	7.080	0.063	0.051	0.968	0.067	0.041	0.049	0.033	0.034	0.029	0.032	3.871	0.362
std dev LD	642.023	0.006	0.035	0.384	1.661	0.011	0.000	1.449	530.411	0.058	0.373	0.061	0.004	2.587	0.032	0.926	0.431	0.020	0.013	0.014	0.009	0.011	0.010	0.008	1.115	0.232
std dev HD	1245.742	0.012	0.000	0.463	4.008	0.017	0.000	0.780	657.141	0.021	0.471	0.114	0.004	4.147	0.012	0.037	0.436	0.027	0.016	0.016	0.012	0.013	0.009	0.010	1.153	0.376
STATS MIX ULTRAPURE WATER: TREATED																										
	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Rb	Sr	Cd	Sn	Ba	La	Pr	Nd	Sm	Eu	Gd	Dy	Hg	Pb
avg 1.5 min	138.504	0.029	0.000	3.419	7.611	0.022	0.000	0.338	1142.966	0.041	0.400	0.047	0.002	5.000	0.022	0.290	0.081	0.078	0.038	0.058	0.031	0.028	0.030	0.032	1.007	0.145
avg 2 min	339.716	0.045	0.053	7.082	14.644	0.025	0.000	0.428	1944.144	0.106	0.635	0.062	0.016	11.206	0.033	0.500	0.154	0.146	0.058	0.107	0.047	0.040	0.046	0.048	1.759	0.352
std dev 1.5 min	59.410	0.007	0.000	1.190	2.252	0.018	0.000	0.209	740.372	0.026	0.279	0.046	0.003	1.301	0.007	0.152	0.028	0.034	0.020	0.028	0.017	0.017	0.017	0.019	0.551	0.088
std dev 2 min	201.461	0.011	0.091	2.290	3.386	0.007	0.000	0.273	688.972	0.077	0.249	0.066	0.011	3.501	0.006	0.271	0.049	0.053	0.037	0.041	0.034	0.035	0.030	0.031	0.602	0.211
STATS MIX SALTWATER: TREATED																										

	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Rb	Sr	Cd	Sn	Ba	La	Pr	Nd	Sm	Eu	Gd	Dy	Hg	Pb
avg 1.5 min	1509.017	0.057	0.000	7.214	14.623	0.024	0.000	0.326	1681.600	0.134	0.523	0.066	0.023	13.038	0.045	0.133	1.277	0.195	0.099	0.142	0.083	0.080	0.079	0.084	2.867	0.381
avg 2 min	1321.227	0.052	0.190	4.521	11.053	0.019	0.000	0.459	1488.648	0.108	0.438	0.055	0.015	8.953	0.040	0.235	1.624	0.127	0.066	0.095	0.056	0.053	0.052	0.056	0.900	0.330
std dev 1.5 min	388.721	0.005	0.000	1.467	1.960	0.004	0.000	0.079	228.382	0.041	0.127	0.041	0.010	1.994	0.014	0.097	0.426	0.038	0.026	0.029	0.024	0.023	0.020	0.022	0.725	0.123
std dev 2 min	787.112	0.016	0.502	1.006	3.027	0.009	0.000	0.335	507.228	0.039	0.175	0.049	0.009	2.384	0.026	0.237	1.035	0.033	0.016	0.020	0.012	0.013	0.013	0.013	0.649	0.238

Appendix B: Sponge Adsorption Values for PFAS – Calculated Adsorption

PFAS ONLY ULTRAPURE WATER			
	PFHxS	PFOA	PFOS
avg LD	7.002	6.466	3.367
avg HD	6.916	6.401	3.353
std dev LD	1.003	1.279	0.661
std dev HD	1.071	0.952	0.601
MIX ULTRAPURE WATER			
	PFHxS	PFOA	PFOS
avg LD	5.051	3.357	2.580
avg HD	4.270	3.199	2.183
std dev LD	1.089	1.244	0.627
std dev HD	0.852	0.845	0.345
PFAS ONLY SALTWATER			
	PFHxS	PFOA	PFOS
avg LD	3.618	3.490	4.313
avg HD	2.673	2.496	3.588
std dev LD	2.788	3.569	1.826
std dev HD	1.520	2.158	0.925
PFAS ONLY WATER + OIL			
	PFHxS	PFOA	PFOS
avg LD	4.608	4.587	5.513
avg HD	3.758	4.067	5.051
std dev LD	3.102	4.199	2.559
std dev HD	3.106	3.861	2.183
PFAS ONLY SALTWATER + OIL			
	PFHxS	PFOA	PFOS
avg LD	3.122	3.114	3.557
avg HD	2.315	2.412	3.474
std dev LD	2.047	2.679	1.321
std dev HD	2.629	3.057	1.545
MIX SALTWATER			
	PFHxS	PFOA	PFOS
avg LD	4.052	2.699	3.306
avg HD	3.733	2.618	3.206
std dev LD	2.388	1.828	1.302
std dev HD	2.022	1.863	1.603

MIX WATER + OIL			
	PFHxS	PFOA	PFOS
avg LD	4.522	3.569	3.294
avg HD	4.327	3.249	3.317
std dev LD	2.597	2.115	1.744
std dev HD	1.425	1.251	0.947
MIX SALTWATER + OIL			
	PFHxS	PFOA	PFOS
avg LD	5.590	4.425	5.270
avg HD	4.852	3.957	5.054
std dev LD	3.040	2.967	2.151
std dev HD	3.088	2.746	2.235
STATS MIX ULTRAPURE WATER: NON-TREATED			
	PFHxS	PFOA	PFOS
avg LD	7.036	5.908	4.475
avg HD	4.979	4.190	3.703
std dev LD	1.922	1.822	0.990
std dev HD	0.882	0.698	0.434
STATS MIX SALTWATER: NON-TREATED			
	PFHxS	PFOA	PFOS
avg LD	6.827	5.423	4.971
avg HD	5.400	4.424	4.307
std dev LD	1.589	1.547	1.016
std dev HD	1.552	1.387	0.830
STATS MIX ULTRAPURE WATER: TREATED			
	PFHxS	PFOA	PFOS
avg 1.5 min	5.920	4.885	3.597
avg 2 min	6.462	5.417	3.990
std dev 1.5 min	0.875	0.932	0.419
std dev 2 min	1.645	1.617	0.807
STATS MIX SALTWATER: TREATED			
	PFHxS	PFOA	PFOS
avg 1.5 min	2.174	1.554	1.921
avg 2 min	2.069	1.470	1.789
std dev 1.5 min	0.317	0.223	0.275
std dev 2 min	0.525	0.322	0.354

Appendix C: Sponge Adsorption Values for PFAS – Actual Adsorption

PFAS ONLY ULTRAPURE WATER			
	PFHxS	PFOA	PFOS
avg LD	3.601	0.618	11.414
avg HD	3.050	0.494	10.727
std dev LD	0.846	0.224	2.578
std dev HD	0.800	0.232	2.554
MIX ULTRAPURE WATER			
	PFHxS	PFOA	PFOS
avg LD	6.221	3.530	6.731
avg HD	6.433	3.517	8.275
std dev LD	2.881	1.732	3.666
std dev HD	1.876	1.545	2.076
PFAS ONLY SALTWATER			
	PFHxS	PFOA	PFOS
avg LD	0.399	0.080	0.962
avg HD	0.280	0.044	0.924
std dev LD	0.382	0.079	0.863
std dev HD	0.406	0.060	1.337
PFAS ONLY WATER + OIL			
	PFHxS	PFOA	PFOS
avg LD	0.734	0.238	1.138
avg HD	0.680	0.125	1.410
std dev LD	0.833	0.322	1.115
std dev HD	0.551	0.108	1.127
PFAS ONLY SALTWATER + OIL			
	PFHxS	PFOA	PFOS
avg LD	0.314	0.059	0.823
avg HD	0.316	0.045	0.960
std dev LD	0.369	0.081	0.804
std dev HD	0.234	0.037	0.630
MIX SALTWATER			
	PFHxS	PFOA	PFOS
avg LD	0.394	0.152	0.526
avg HD	0.251	0.151	0.474
std dev LD	0.448	0.089	0.503
std dev HD	0.193	0.084	0.345

MIX WATER + OIL			
	PFHxS	PFOA	PFOS
avg LD	0.889	0.688	1.234
avg HD	0.422	0.303	0.812
std dev LD	0.667	0.465	0.769
std dev HD	0.345	0.218	0.655
MIX SALTWATER + OIL			
	PFHxS	PFOA	PFOS
avg LD	0.321	0.215	0.592
avg HD	0.416	0.327	0.666
std dev LD	0.338	0.181	0.697
std dev HD	0.398	0.345	0.581
STATS MIX ULTRAPURE WATER: NON-TREATED			
	PFHxS	PFOA	PFOS
avg LD	0.782	0.626	0.893
avg HD	0.402	0.301	0.570
std dev LD	0.597	0.484	0.694
std dev HD	0.366	0.264	0.470
STATS MIX SALTWATER: NON-TREATED			
	PFHxS	PFOA	PFOS
avg LD	0.862	0.615	0.896
avg HD	0.847	0.662	1.340
std dev LD	0.210	0.162	0.154
std dev HD	0.555	0.431	0.803
STATS MIX ULTRAPURE WATER: TREATED			
	PFHxS	PFOA	PFOS
avg LD	1.195	0.802	1.651
avg HD	1.305	0.904	1.674
std dev LD	0.805	0.523	1.287
std dev HD	1.186	0.845	1.481
STATS MIX SALTWATER: TREATED			
	PFHxS	PFOA	PFOS
avg LD	0.869	0.559	1.291
avg HD	0.521	0.350	0.721
std dev LD	0.879	0.542	1.341
std dev HD	0.859	0.544	1.252