Wastewater treatment plants as a source of microplastics to the environment
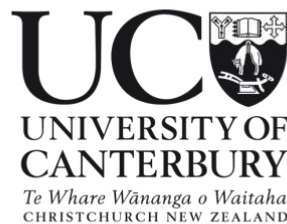
A thesis submitted in partial fulfilment for the degree

of

Master of Science in Environmental Science

By

Helena Charlotte Ruffell

University of Canterbury

2019

UNIVERSITY OF
CANTERBURY
Te Whare Wānanga o Waitaha
CHRISTCHURCH NEW ZEALAND

You cannot get through a single day without having an impact on the world around you.

What you do makes a difference, and you have to decide what kind of difference you want to make.

> - *Jane Goodall*

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Abstract

Microplastics are ubiquitous in the environment, due to the intensification in global commercial demand for plastics since the 1960s. The detection of microplastics in remote locations and in a range of aquatic organisms has raised questions about the sources of entry into the environment. Wastewater treatment plants (WWTPs) are thought to be a major source of microplastics to the environment, but their degree of contribution worldwide as a source is unknown. WWTPs are not designed to remove microplastics from sewage. This study is the first of its kind to characterise the contribution of microplastics to coastal ecosystems from different types of WWTPs in Canterbury.

A method was developed to extract and identify microplastics present in sewage influent and effluent. A field study of four WWTPs was undertaken in the Canterbury region. Representative influent and effluent samples were collected from each WWTP, comparing weekdays to weekends. Microplastics were extracted from the sewage by wet sieving, chemical digest, and vacuum filtration. Potential microplastics were visually identified, and their polymer type classified by Fourier transform infrared spectroscopy (FTIR). Microplastics were characterized from each of these WWTPs in terms of abundance, morphotype, size, and polymer type.

Microplastics were detected in the incoming influent and treated effluent and were more abundant in the influent (67%) than effluent (33%) which was consistent with the literature. Low removal efficiencies from each WWTP were detected in comparison to the literature. An additional temporal field study focusing on microplastic differences in the effluent from three WWTPs did not find a consistent trend.

It can be concluded that microplastics are present in WWTPs and are a significant source of microplastics through effluent discharged to coastal environments in Canterbury. Further work will be required to understand the environmental fate of the discharged microplastics to the Canterbury coastline and environmental impacts.

Abbreviations

ANOVA – Analysis of variance

Bt – Billion tonne

FTIR – Fourier transform infrared spectroscopy

HDPE – High density polyethylene

HPLC – High-performance liquid chromatography

LDPE – Low density polyethylene

Mt – Million tonne

NOAA – National Oceanic and Atmospheric Administration

PET – Polyethylene terephthalate

PP – Polypropylene

PPE – Personal protective equipment

PS – Polystyrene

PVC – Polyvinyl chloride

SS – Suspended solids

UV – Ultraviolet

WPO – Wet peroxide oxidation

WWTP – Wastewater treatment plant

1 Introduction

1.1 Plastic

The increasing presence of plastic litter in the environment has led to global concern over human reliance on this ubiquitous material. The production of plastic revolutionised the material world, introducing affordable products from readily-available raw materials.[1] Mass production of plastic products began after World War II, with approximately 1.5 million tonne (Mt) produced in 1950.[2] In 2015, it was estimated that 7,800 Mt of plastic had been produced since 1950.[3] At present, over 335 Mt of plastic are produced annually, with this number rising.[4] Made of repeating chains of subunits, plastics are a term for a variety of polymer types, each with unique properties that are desirable for different uses.[5] Plastics are heated and molded (along with additives including fillers, pigments, stabilisers, and flame-retardants) into an unlimited number of shapes for their desired function.[5]

Plastics can be classified into two broad groups: thermoset and thermoplastics.[1] Thermoset plastics are produced from polymers which form irreversible bonds, and therefore cannot be re-melted and re-formed after use. Common thermoset plastics are polyurethane foams and epoxy resins. Thermoplastics are those which can be re-melted and molded continually, and therefore can be recycled.[1, 5] Thermoplastics make up the majority of consumer goods[6] and are expected to be present in the majority of environmental samples (Table 1-1).[7] Common thermoplastics include polyethylene, polypropylene, polystyrene, and polyvinyl chloride.[6, 8]

1.1.1 Fate of waste plastic

Single use plastic is highly sought after for sterility and convenience, compared to more expensive alternative materials, such as glass and steel. Packaging has become the largest market of plastics.[9] The global shift from reusable to single use products has increased the mass of plastic in municipal solid waste to 10% in 2005, compared with less than 1% in 1960.[9] Around half of all plastic produced annually (roughly 150 Mt) is thrown away each year.[10] Of all the plastic produced to date, it is estimated that only 30% of plastic is still in use to this day.[11]

Some European countries (for example, Denmark and Sweden) incinerate the majority of their municipal solid waste, including plastics.[12] Incineration of mixed plastics reduces the cost for sorting and cleaning, as well as landfill space. Energy is also recovered during incineration, which may be used for electricity generation.[12] The incineration of plastic can release a range of toxic chemicals into the atmosphere including polycyclic aromatic hydrocarbons, phthalates, and dioxins.[13]

Approximately 4.8 – 12.7 Mt of plastic are expected to be released into the ocean each year, primarily from improper disposal.[9] An estimated 260 billion tonnes (Bt) of plastic pollution are already present in the ocean.[14] All plastic produced to this day (which has not been incinerated) has been estimated to still be present in particulate forms in the environment, especially when buried in terrestrial and aquatic sediments where degradation is limited.[15]

1.1.2   Recycling of plastic

Recycling one tonne of plastic can save up to 130 million kilo-Joules of energy, as opposed to manufacturing virgin plastic products.[10] This saving equates to 3.5 billion barrels of crude oil annually.[16] Recycling and reusing of thermoplastics are difficult and undesirable due to the complex makeup of chemicals and low-cost of producing virgin products. Impurities that act as barriers to plastic recycling include foreign materials (non-plastic components such as organic and biological material (for example food, dirt), and glass), non-targeted plastic (including polymer blends and multi-plastic products), chemical impurities, and additives.[17] Separation and cleaning of different polymers are costly and time-consuming. Re-melting and re-molding of plastics are also energy intensive, and often produces a poorer quality polymer.[10] Approximately 18% of waste plastics are recycled annually.[11]

Table 1-1. Typical applications of common plastic types, adapted from Shen and Worrell (2014).[6]

Recycling code	Polymer type	Applications
1	Polyethylene terephthalate (PET)	Bottles for soft drinks, water, detergents, pharmaceutical products; blister packs
2	High-density polyethylene (HDPE)	Thicker applications including barrels, jerry cans, crates; packaging for carpets and instruments
3	Polyvinyl chloride (PVC)	Blister packs, films for perishables
4	Low-density polyethylene (LDPE)	Foil and film
5	Polypropylene (PP)	Buckets, bottle caps, transparent packaging for flowers and confectionary; yoghurt cups
6	Polystyrene (PS)	Takeaway food containers, meat trays, ice boxes

1.1.3 Recycled plastic products

Polyethylene and polyethylene terephthalate are the two most commonly recycled plastic polymers.[12] Recycled plastic products are usually those which require little mechanical strength, like shopping bags, and food packaging.[12, 18] Products made of recycled plastic often contain an external and internal layer of virgin plastic, to ensure sterility for food grade applications.[12] The addition of recycled plastic to virgin polymer will decrease certain physical properties like colour, clarity, or impact strength.[12] Plastic may also be recycled for other purposes, including in concrete and roads, and the soft plastics recycling scheme producing 'plastic lumber' products including park benches and bollards.[11-12] These products signal the end of the recycling process, as multiple polymer types are mixed, and are not expected or able to be further recycled.[12]

1.2 Microplastics

Microplastics are defined as plastic particles smaller than 5 mm in size and are subdivided into 'primary' and 'secondary'.[19] Primary microplastics are purposefully produced plastic particles used in a variety of domestic, commercial, and industrial purposes as an abrasive, including uses in personal care products (termed 'microbeads'),[20] pre-production pellets (termed 'nurdles'), and air blasting.[21]

Secondary microplastics are formed by environmental degradation of plastic litter by photolytic, mechanical, and biological processes.[22] Complex combinations of environmental conditions, along with the individual polymer type and product shape, make fragmentation of plastic difficult to understand.[23] The fragmentation of plastic from weathering of paint, wear of vehicle tyres,[24] and the release of fibres from the general wear and washing of synthetic textiles and clothing can also generate microplastics.[25] Investigation into microfibres has been limited by numerous challenges associated with their identification and measurement, including the contamination of samples by ambient microplastics during processing.[26]

1.2.1   Microplastic mobility and presence in the environment

Microplastics are ubiquitous in the environment. There is a large, and continuously growing, body of literature of microplastics contamination in marine environments around the world. Few studies have been undertaken in freshwater environments, with the majority of those focusing on large lakes and rivers in populated areas,[27] and there are limited data available for terrestrial soils.[28] The mean concentrations of microplastic measured in surface waters are highly variable in the literature, and range from $0.020 - 0.463$ particles/m^2 in lakes,[29] and in rivers from $0.055 - 0.938$ particles/m^3.[30] In river sediments, microplastic concentrations from the Rhine in Germany ranged from $228 - 3763$ particles per kilogram (particles/kg), (dry weight).[31] Sediment from Lake Garda in Italy contained microplastic concentrations between $108 - 1108$ particles/m^2.[32]

Concentrations of microplastic in marine surface water follows a wide distribution. Microplastics are most abundant around coastal cities and enclosed areas such as harbours and estuaries.[27] Microplastic abundance in surface waters in British Colombia and the North Eastern Pacific Ocean ranged from 8 – 9180 particles/m^3 (across 34 sites), where the concentration of particles was found to be 4 – 27 times greater at sites closer to the shore, as opposed to those offshore.[33] Marine sediments act as a sink for microplastic particles, which in the aquatic environment, may be less buoyant over time as biological material adorbs and grows.[34] In contrast, little difference was found between concentrations of beach sediments (93 particles/kg, dry weight), and offshore sediments (97 particles/kg, dry weight) for a second study across the Belgium coast.[35]

Due to their buoyancy, microplastics are readily transported over large distances by ocean currents. Microplastic particles have been found to accumulate in all five of the ocean gyres.[36] Of particular concern are microplastics that have been discovered in remote areas, with few anthropogenic pressures. For example, concentrations of microplastic particles ranged from 0.0032 – 1.18 particles/m^3 of sea water from the Ross Sea, near Antarctica.[37] Arctic sea ice was found to contain concentrations of 38 – 234 particles/m^3.[38]

1.2.2   Adverse effects of microplastics on aquatic organisms

The ubiquity of microplastics poses a threat to a range of aquatic organisms, who can mistake these particles as food based on the colour and size, or feed indiscriminately on them.[39] Due to their constant fragmentation, microplastics are bioavailable to some of the smallest marine biota such as zooplankton, as well as the largest, such as marine megafauna (e.g. whales).[40] Filter-feeding organisms are known to indiscriminately ingest microplastics with the size range dependent on the organism.[41] Ingestion of microplastic particles through trophic transfer by predators has been observed, however, the extent to which this happens in the wild is not well understood.[42] Ingestion of plastic may cause physical injury to the gills, digestive tract, and internal organs they accumulate within.[39] Translocation of microplastic from the gut to the tissues, and haemolymph in the circulatory system of bivalves and crustaceans has been observed.[41-42] Egestion of microplastics in marine organisms is not well understood. Larger microplastics were removed from the gut of filter feeding organisms

faster than smaller particles.[43] Smaller particles are hypothesised to be retained in internal organs opposed to larger particles.[43]

The hydrophobic surfaces of microplastics can act as a vector for the uptake of, and exposure to, numerous classes of organic contaminants in aquatic environments.[44] These toxins, along with the additives present in the plastic, have the potential to desorb or leach from the plastic in biological systems.[44-45] Laboratory studies have demonstrated these contaminants may bioaccumulate in their tissues, and/or impart a toxic response, including reduced feeding rates and increased oxidative stress.[45-46] Little is understood about the direct responses of microplastic ingestion to human health, including the leaching of toxic additives of plastic in human metabolic systems.[47] Preliminary results from a study based in Austria have detected microplastics in human faeces.[48]

1.2.3   Sources of microplastics to the environment

Sources of microplastics and routes of entry to the environment are not well understood. An estimated 80% of plastic in the marine environment enters from land, with the remainder released from ocean-based activities.[24] Off-shore sources of microplastics in the aquatic environment include fragmentation of litter from commercial fishing and shipping boats, such as plastic nets, fishing lines and container stock.[49] For example, the cargo ship Rena grounded on the Astrolabe/Otaiiti Reef off the coast of Tauranga, New Zealand, on October 5th, 2011, spilling the contents of a number of containers, which included plastic nurdles, which as of 2017, continued to wash up onto the shoreline.[50]

Sources of microplastic from the terrestrial environment include littering and dumping of plastic waste, weathering of plastic-containing products (including vehicle lights and tyres) and wind-blown items.[27, 51] Urban stormwater and sewage networks may direct microplastics to aquatic waterways and oceans.[27, 52]Due to the large domestic and commercial use of microplastic containing products, wastewater treatment plants (WWTPs) have been hypothesised to be a significant source of microplastics to the environment, with limited studies published.[53] At present globally, there is a limited understanding of the behaviour and fate of microplastics during the wastewater treatment process,[53b] with no published

investigations from New Zealand. Although WWTPs were not designed to remove microplastics during treatment, current research has reported removal efficiencies of greater than 99% from the final effluent.[54] Whilst the size range of sieves filtering the wastewater samples were reported in these studies, the specific lower and upper sizes of microplastic particles detected were not. Despite relatively high removal rates, the levels of microplastics estimated to be released within discharged effluent remains a significant source to the environment, due to the large volumes of effluent released into the environment each year.[53b]

The degree to which microplastics can be removed depends upon the level of treatment the wastewater receives.[55] The majority of microplastic particles, primarily microfibres, are removed during primary treatment by entrapment and accumulation in sewage sludge.[56] Sludge can be modified and transformed into biosolids which are either sent to landfill, or co-composted or vermi-composted before application to land as a soil conditioner.[57] These biosolids may be a source of microplastics to the terrestrial environment, and subsequently aquatic environments through leaching of groundwater and run-off.[58]

1.3   Wastewater treatment plant processes

Urban and industrial wastewater and sewage are diverted to WWTPs, where they undergo treatment using a range of different physical, chemical, and biological processes, prior to discharge into the environment as effluent.[59] Wastewater influent is also comprised of inflow (from surface water and stormwater) and infiltration (from groundwater).[60] Resulting effluent may be discharged to aquatic ecosystems including rivers, wetlands, estuaries, and coastlines.[59-60] Effluent may also be irrigated onto land as a nutrient-rich water source.[60a, 61] Of the 330 WWTPs operating in New Zealand, 11% discharge effluent to land only, 13% use a combined land and water discharge systems, 75% discharge directly to surface water via an ocean or river outfall, and 1% of systems are unknown.[62]

Common physical and chemical processes occurring in WWTPs include primary screening to remove large material and litter, sedimentation of heavier materials, surface skimming to remove lighter material (like fats, grease, and organic matter), coagulation – flocculation to

adsorb organic contaminants, and filtration to remove fine particles.[60b] Standard WWTPs often undergo primary and secondary treatment, which involves removal of large solid materials, and secondary digestion of suspended and dissolved organic matter by microorganisms, followed by disinfection by sunlight to kill pathogens.[59] Tertiary treatment processes like microfiltration, chlorination, and ozonation are used to further target microbiological contaminants, often before discharge into sensitive ecosystems like estuaries and wetlands.[59, 60b] Sludge, a byproduct rich in organic matter, is removed throughout the treatment process. This can be further treated to remove pathogens, followed by intensive drying to be suitable for land application, or landfill deposition.[60]

The treatment processes used in WWTPs are not designed to remove microplastics.[58, 63] Screening filters range from coarse (13 – 25 mm), to fine (3 – 6 mm).[60a] The screens mechanically shift to scrape off built up organic and inorganic material into landfill skips, to reduce clogging of the screens.[60a] Microplastics smaller than the size of the screens are able to bypass the filters.[27]

1.3.1 Properties, behaviour and fate of microplastics in WWTPs and the environment

The density of individual polymer types can influence the fate of microplastics in the aquatic environment (Table 1-2).[64] In seawater, higher-density particles (greater than 1.02 g/mL) sink to the sea floor and accumulate in sediments.[65] Particles greater than the density of wastewater (such as polyamide/nylon, polyvinyl chloride, and polyethylene terephthalate) are almost completely retained in sewage sludge during primary and secondary treatments.[28] Higher-density particles are predicted to settle and be removed in sedimentation basins throughout the WWTP process.[54a] Lower-density microplastic particles are suggested to float on the surface or become trapped in surface flocs and can be removed during surface skimming.[54a] They may also remain suspended throughout the water column, with the potential to travel through the treatment process.[52]

Table 1-2. Density of common plastic polymers, adapted from Morét-Ferguson et al, (2010).[64]

Polymer	Density (g/mL)
Polypropylene (PP)	0.85 – 0.92
Low-density polyethylene (LDPE)	0.89 – 0.93
High-density polyethylene (HDPE)	0.94 – 0.97
Polystyrene (PS)	1.04 – 1.08
Polyamide/nylon (6) (PA6/N6)	1.15
Polyvinyl chloride (PVC)	1.16 – 1.41
Polyethylene terephthalate/polyester (PET)	1.38 – 1.41

The density of microplastic particles may be altered throughout the wastewater treatment process, primarily by the sorption of organic material and growth of biofilms (biofouling).[65] Biofilms can increase particle density, causing particles to sink and settle in bottom sediments.[24] Longer residence time in the treatment plant increase the potential for surface fouling by bacteria, and further influence sorption of other wastewater associated contaminants.[54a]

Photo-oxidative degradation by ultra-violet (UV) radiation facilitates the disintegration of common polymers in the environment, including LDPE, HDPE, and PP.[27] Low oxygen levels, biofouling, the presence of sediment, and high turbidity in the water column all reduce exposure to UV radiation.[27] Degradation by UV radiation is found to be effective on the surface of the water column and shorelines but is slower at greater depths in the water column, if microplastics are buried in sediment or soil, or obscured by poor clarity waters, such as those of WWTPs.[24, 66] Physical degradation may be aided by wave action, water turbulences, and abrasion of particles.[66] Certain microorganisms are capable of biodegrading plastics (mineralisation) into constituents including water, methane, and carbon dioxide, and this may occur in WWTPs.[67] Mineralisation of polymers in the marine environment was found to be a slow process, where sheets of LDPE, HDPE, and PP immersed at a depth of 3 m in seawater for 6 months lost 1.5 – 2.5%, 0.5 – 0.8%, and 0.5 – 0.6% of their mass respectively.[68]

1.3.2 Abundance of microplastic in influent, effluent, and sludge

A number of studies have assessed the fate of microplastics in WWTPs, by analysing their abundance in raw influent, treated effluent, and sludge (Table 1.3 and 1.4). Abundances in influent ranged from 1 – 7216 particles/L, and in effluent ranged from ~0.0007 – 81 particles/L (Table 1.3).[25, 52, 54-55, 58, 69] Abundance in sludge ranged from 0.113 – 170,900 particles/kg (dry weight) and 510 – 760 particles/kg (wet weight, Table 1.3).[54, 56, 58, 69b, 69e] Visual identification only was employed by one study, whilst the remainder utilised a combination of visual with Fourier transform infrared spectroscopy (FTIR) or Raman spectroscopy for confirmation. Visual inspection of particles may lead to bias, and over-estimation or under estimation. Difficulties arise when visually distinguishing between non-plastic and natural fibres present in wastewater, and when attempting to identify smaller particles, and a range of colours.[52]

High removal efficiencies from wastewater have been reported (from 72 – 99.9%), suggesting that a significant proportion of microplastic particles from the influent are removed during the treatment process.[52, 54-55, 58, 69a, 69b, 69d-f] This has led to debate as to whether wastewater treatment plants are a significant source of microplastics to the environment.[54a] Based on the results of their study, Carr *et al*. (2016) argued that the contribution of microplastics to the aquatic environment was minimal, with a predicted daily discharge of around 930,000 particles in treated effluent, and 1.09 billion particles retained in sludge (and therefore present in biosolids).[54a] A second study assessing a small WWTP serving 12,000 people in Sweden predicted around 1,500 microplastic particles were released into the environment with the effluent every hour, totaling to 36,000 particles per day.[54b] A third study in Scotland estimated that 65 million microplastic particles were released from the study WWTP each day.[69a] A study in Australia compared the difference in microplastic abundance between primary, secondary, and tertiary effluents from three WWTPs. Microplastic particle abundances decreased from 1.54, to 0.48, and 0.28 particles/L respectively, which suggests that microplastics are removed in multiple stages throughout treatment.[55]

Table 1-3. Average microplastic abundance in influent and effluent worldwide.

Country (# WWTPs)	Particle Size range (μm)	Treatment Type	Identification	[Influent] (particles/L)	[Effluent] (particles/L)	Removal Efficiency (%)	Source
Italy (1)	10 – 5,000	Tertiary	Visual and FTIR	2.5	0.4	84	Magni *et al.* 2019[69b]
Germany (1)	10 – 5,000	Secondary	Visual and Raman	NA	7.9 – 10	NA	Wolff *et al.* 2019[69c]
Denmark (10)	10 – 500	Tertiary	Visual and FTIR	7216	54	99.3	Simon *et al.* 2018[69d]
Finland (1)	250 – 5,000	Tertiary	Visual and FTIR/Raman	57.6	1	98.3	Lares *et al.* 2018[69e]
The Netherlands (7)	10 – 5,000	NA	Visual and FTIR	68 – 910	51 – 81	72	Leslie *et al.* 2017[58]
Australia (3)	>25	Primary, secondary, tertiary	Visual and FTIR	NA	1.54 (primary), 0.48 (secondary), 0.28 (tertiary)	NA	Ziajahromi *et al.* 2017[55]
USA (8)	20 – 400	Tertiary	Visual and FTIR	1	~0.0007	99.9	Carr *et al.* 2016[54a]
Scotland (1)	>65	Secondary	Visual and FTIR	15.7 +/- 5.23	0.25 +/- 0.04	98.41	Murphy *et al.* 2016[69a]
France (1)	100 – 5,000	Primary and biological	Visual	260 – 320	14 – 50	83.9 - 95	Dris *et al.* 2015[52]
Finland (1)	20 – 200	Tertiary	Visual and FTIR	430	8.6	98	Talvitie *et al.* 2015[69f]
Sweden (1)	>300	Mechanical, chemical, biological	Visual and FTIR	15	0.008	99.9	Magnusson and Norén, 2014[54b]
Australia (2)	NA	Tertiary	Visual and FTIR	NA	1	NA	Browne *et al.* 2011[25]

NA = not assessed.

Table 1-4. Abundance of microplastics in sewage sludge worldwide

Country (# WWTPs)	Particle Size range (µm)	Treatment Type	Identification	[Sludge] (particles/kg)	Source
Italy (1)	10 – 5,000	Tertiary	Visual and FTIR	0.113 (dry weight)	Magni *et al.* 2019[69b]
Finland (1)	250 – 5,000	Tertiary	Visual and FTIR/Raman	23,000 – 170,900 (dry weight)	Lares *et al.* 2018[69e]
The Netherlands (7)	10 – 5,000	NA	Visual and FTIR	510 – 760 (wet weight)	Leslie *et al.* 2017[58]
Ireland (7)	>250	Anaerobic digest, lime stabilisation, thermal drying	Visual and FTIR	4,196 – 15,385 (dry weight)	Mahon *et al.* 2017[56]
USA (8)	20 – 400	Tertiary	Visual and FTIR	1,000 (dry weight)	Carr *et al.* 2016[54a]
Sweden (1)	>300	Mechanical, chemical, biological	Visual and FTIR	720 (wet weight)	Magnusson and Norén, 2014[54b]

NA = not assessed.

Many of the removal studies (Table 1-3 and 1-4) did not account for the release of partially treated (or at times, untreated) effluent during high rainfall events. Based on the WWTP investigated by Murphy *et al.* (2016), an additional 620 million microplastic particles could be released per day (averaged out over the year) from untreated effluent from storm surges.[69a] Little is understood about the abundance of microplastics in storm surges into WWTPs, but while the volume of water increases, the proportion of microplastics entering the WWTP may not necessarily increase.[69a]

Variability in flow rates and microplastic concentration suggests that composite sampling throughout the day, and temporal sampling over the course of a year, (whilst accounting for extreme weather events) must be considered.[59, 69f] In a review of sampling methods of pharmaceuticals and personal care products (PPCPs) and illicit drugs, Ort *et al.* (2010) suggested sampling on consecutive days is recommended to account for hydraulic and solids retention time during treatment, which may range between a few hours, to several days.[70] Flow variations when sampling for both influent and effluent must be accounted for.[70] No microplastic studies reviewed accounted for the specific hydraulic retention time of each treatment plant from influent to effluent.

1.4 Presence of wastewater-derived microplastics in the environment

Hydrophobic contaminants can adsorb to the surface of microplastic particles, with polymer type affecting sorption potential.[71] Sorption of wastewater-associated contaminants (including organic and inorganic contaminants, and biologically harmful viruses and bacteria) may allow microplastic particles to act as a vector for transport of toxins into the aquatic and terrestrial environment.[53b] However, little is understood of the effects of different wastewater treatment levels on adsorbed contaminants.[53b]

1.4.1 *Wastewater-derived microplastic abundance in terrestrial soils*

Synthetic fibres have been proposed as an indicator of sewage sludge presence in the environment.[72] In the study investigating a range of soil fertilisers, synthetic fibres were identified in products that contained treated sewage sludge (added as a source of nitrogen).[72] Unfortunately, quantification of fibres was not assessed. Investigation into experimental soil

columns containing sewage sludge products by Zubris and Richards (2005) identified the presence of microplastic fibres, with retained fibre characteristics, five years after application.[73] The concentration of fibres ranged from 0.58 – 1.21 particles/g of soil.[73] The same study observed the presence of fibres from field application sites up to fifteen years after sewage sludge was applied. The concentration of fibres was not reported, and limited land application history was recorded over the course of the study.[73] Land application of biosolids may not be suitable to the terrestrial environment due to the high retention of microplastics and their subsequent long residence time in soil. An estimated 127 – 864 tonnes of microplastic particles (per one million inhabitants) are deposited annually on European agricultural soils from sewage sludge or processed biosolid application.[28]

1.4.2   Wastewater-derived microplastic abundance in the marine environment

WWTP effluent outfalls are proposed to be a point source for microplastics entering the aquatic environment.[69f] Abundances of microplastics in the receiving marine sediment and surface water near effluent discharges in Finland ranged from 1.7 – 4.7 fibres/kg and 7.2 – 10 synthetic fragments/kg in sediment (wet weight), and 0.01 – 0.65 fibres/L and 0.5 – 9.4 synthetic fragments/L of surface water.[69f] No significant difference was found between these sites near the WWTP outfall, compared to reference sites. This was suggested to be from the rapid mixing and transport of microplastic particles from the discharged effluent in the open ocean, preventing settling in sediment near to the outfall.[69f]

A second study in Sweden investigated the abundance of microplastic in marine surface water at distances from the effluent outfall. Abundance declined with distance away from the outfall, with 1.82 fibres/m^3 and 0.08 fragments/m^3 present 20 m away from the outfall, and 1.29 fibres/m^3 and 1.14 fibres/m^3, 50 m and 200 m away respectively, with no fragments identified.[54b] The abundance of microplastic at the reference site (3500 m from the effluent outfall), was 0.45 fibres per m^3, with no fragments identified.[54b] It is difficult to find a suitable reference site due to the ubiquity and mobility of microplastics.[54b]

A third study collected sediment samples at sites near to and away from, a WWTP effluent outfall near Rothera Research Station, Antarctica. Microplastic concentrations near to the

outfall ranged from 0 – 467 particles/L, compared to 0 – 66.67 particles/L in sites away from the outfall.[74] The majority of particles found were fibres, indicating the potential origin from washing machine effluent.[74]

1.4.3 Wastewater-derived microplastic abundance in rivers

Rivers receiving WWTP effluent are hypothesised to harbour a greater proportion of microplastics compared to the marine environment.[75] Microplastics in rivers may be retained in the sediment, or be transported to downstream tributaries, lakes, estuaries, and coastal waters.[75] Microplastic abundance from a study in Canada was generally higher downstream, 1.99 and 17.93 particles/m^3, compared with sites upstream of a WWTP outfall in a study from the United States of America (USA), 0.71 and 1.94 particles/m^3, respectively.[75-76] In contrast a study from the United Kingdom (UK) detected higher concentrations upstream at 4 out of 28 sites, however, polymer identification of microplastics by FTIR was not reported.[77] No difference was found between microplastic concentration upstream and downstream of an effluent plume in a second study in France (0.28 and 0.29 particles/m^3).[52] The highest concentration, 0.47 particles/m^3, was found at a site further downstream, which received effluent of a smaller WWTP.[52] However, the contribution of low flow, and a high percentage of natural debris may have led to an underestimation of particles in the latter study. Sediment samples downstream of three municipal and industrial effluent along the St. Lawrence River (USA) ranged from 46 – 136,926 particles/m^2.[78] Concentrations upstream of these sites ranged from 7 – 243 particles/m^2.[78] These studies concluded that there are other sources of microplastics to a river catchment which need to be identified, along with topographical factors that may influence settlement in sediment.

The reviewed literature all suggest that microplastics originating from treated effluent are present in the receiving environment.[76-78] However, little is understood about the contribution of other sources to the environment, in relation to wastewater. A comprehensive investigation into the relationship of microplastic presence and average abundance in WWTP influent, effluent, sludge/biosolids, as well as measurement in the receiving environment is required to determine the contribution from a single population to the study region.

1.5   Thesis objectives and layout

The environmental chemistry research group at the University of Canterbury has identified the presence of microplastics on Canterbury shorelines,[79] as well as in tissues from wild green-lipped mussel (*Perna canaliculus*) around Canterbury and New Zealand.[46c] However, the sources of microplastics to the environment have not been assessed in the Canterbury region, as well as across New Zealand. This study will be the first of its kind to assess the contribution of microplastics to the environment made by WWTPs in New Zealand.

The main objectives of this study were to:

- Establish a method for the extraction and handling of fragments, fibres, films, and beads isolated from wastewater influent, effluent, and biosolids;
- Determine the relative abundance, particle sizes, morphotypes, and polymer types present in wastewater influent and effluent from WWTPs; and
- Determine the seasonal variability of the abundance and types of microplastics in WWTP effluents.

Sampling methods, extraction method development, and the finalised extraction protocol are presented in Chapter 2. Results from the characterisation and temporal variation of microplastics present in WWTPs are covered in Chapter 3. Finally, a discussion of the implications and limitations of the study is detailed in Chapter 4. An example of detected microplastics, FTIR spectra, reference libraries, and rainfall data are present in the Appendices.

2   Materials and methods

2.1 Chemicals and materials

Analytical grade solvents (acetone, ethanol), and high-performance liquid chromatography (HPLC) grade acetone, ethanol, and methanol were purchased from Thermofisher. Iron (II) sulfate heptahydrate, sulfuric acid, Virkon, and Decon 90 were purchased from Thermofisher. Hydrogen peroxide was purchased from Jasol New Zealand. Ultra-pure water (< 18 MΩ) was sourced from a RephiLe Bioscience Ltd filtration system, fitted with a 0.2 µm PES high flux capsule filter. Deionised water was sourced from an in-house filtration system. Whatman grade GF/C glass microfibre filter (1.2 µm pore, 47 mm diameter) were purchased from Sigma-Aldrich. Stainless steel sieves (200 mm diameter) were purchased from Tyler.

2.2 Cleaning

Field analysis equipment (polypropylene autosampler bottles and lids), stainless steel 18 L bucket, plastic funnel, plastic measuring jug, plastic stir stick) were rinsed once with deionised water, three times with methanol, and three times with HPLC grade acetone.[80] After cleaning, autosampler bottles were covered with Parafilm, and lids covered with aluminium foil. After wastewater sampling, all equipment, including vinyl tubing, were soaked overnight in Virkon. Amber glass bottles used for field analysis were rinsed three times with ultra-pure water, and once with analytical grade acetone. All laboratory glassware, sieves, stainless steel bucket, and plastic funnel were washed three times with ultra-pure water, and once with analytical grade acetone prior to use.[80] After use, all equipment was soaked in Decon 90.

2.3 Quality control and quality assurance

2.3.1   Contamination mitigation

Contamination of samples throughout all stages of sampling, sample processing, and analysis were minimised to ensure accurate and valid results. Glass and metal equipment were used wherever possible in order to limit plastic contamination. In instances where plastic was used,

it was visually inspected for loose fragments and flaking. Cotton laboratory coats were worn at all times of sample processing, extraction, and analysis. Clothing worn underneath were made of natural fibres as much as possible. During sampling, appropriate personal protective equipment (PPE) was worn, and was selected to shed minimal fibres.

All laboratory work was undertaken in an aluminium foil-lined fumehood, with the foil brushed down with a natural bristle paintbrush and wiped with 70% ethanol (analytical grade) before work commenced in accordance with forensics contamination mitigation techniques.[81] After cleaning, all equipment openings were covered in aluminium foil (sieves, beakers, vacuum filter funnel; Figure 2-1). All stages of laboratory work (sieving, digest, and vacuum filtering) were covered in aluminium foil.

Figure 2-1. Aluminium foil-lined fumehood, with extraction equipment openings (sieves and beakers) covered with aluminium foil to reduce airborne microplastic contamination.

2.3.2   Control samples

Control samples were taken during sampling and extraction in order to quantify contamination sources. A 4 L sample of deionised water was split across four autosampler bottles. This was to account for airborne contamination, and any contribution from the polypropylene autosampler bottles. A method blank was run using 4 L of deionised water. As

each sample took a week to process from start to finish (including controls and 10 L of sample split over three 4 L bottles, each was sieved, digested, and vacuum filtered), forensic techniques of tape lifting for airborne contamination was adapted.[81] A microscope slide with exposed double-sided tape (Figure 2-2), was placed at the back of the fumehood, for the duration of sample processing. This was replaced for each sample.
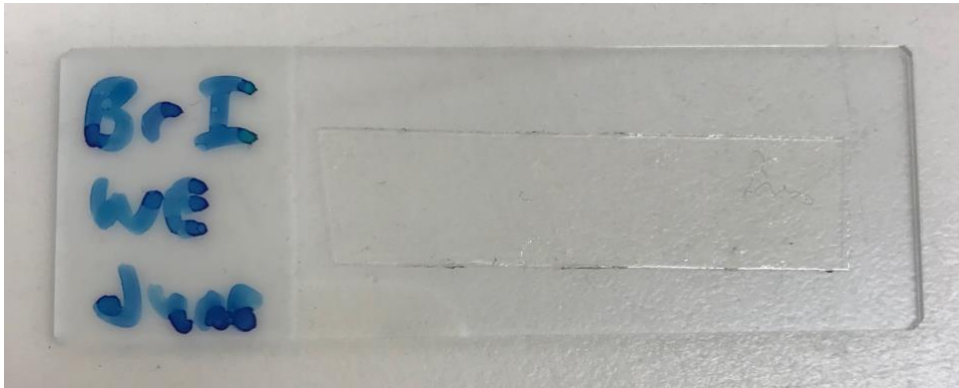
Figure 2-2. Microscope slide of exposed double-sided tape for forensics tape lifting technique.

2.4 Method development for the extraction and handling of fibres

As fibres are of key interest due to the high numbers reported in the literature,[25] special attention was paid to the contamination mitigation, extraction, handling, and analysis of fibres. Contamination mitigation protocols (Sections 2.3.1 and 2.3.2) were followed and fibre extraction techniques were developed (Section 2.5). Thermal degradation of fibres was assessed visually under dissection microscope, and spectrally, using FTIR. The procedure for the handling and analysis of fibres was developed by analysing seven merino/synthetic blend yarn (Table 2-1; Figure 2-3), and ten swatches of synthetic blend and natural fibre fabrics (Table 2-2; Figure 2-4).

Table 2-1. Merino/synthetic blend yarns analysed for fibre method development.

Spool Number	Blend
1	Merino 50%/Tencel 50% (waxed)
2	Merino 56%/Polyester 44%
3	Merino 52%/Tencel 35%/Nylon 13 %
4	Merino 87%/Nylon 13%
5	Merino 100%
6	Merino 50%/Tencel 50%
7	Merino 50%/Tencel 50%

Figure 2-3. Merino/synthetic blend yarn spools. Top image, left to right: spool 7, spool 4, spool 5, spool 1. Bottom image, left to right: spool 2, spool 3, spool 6.
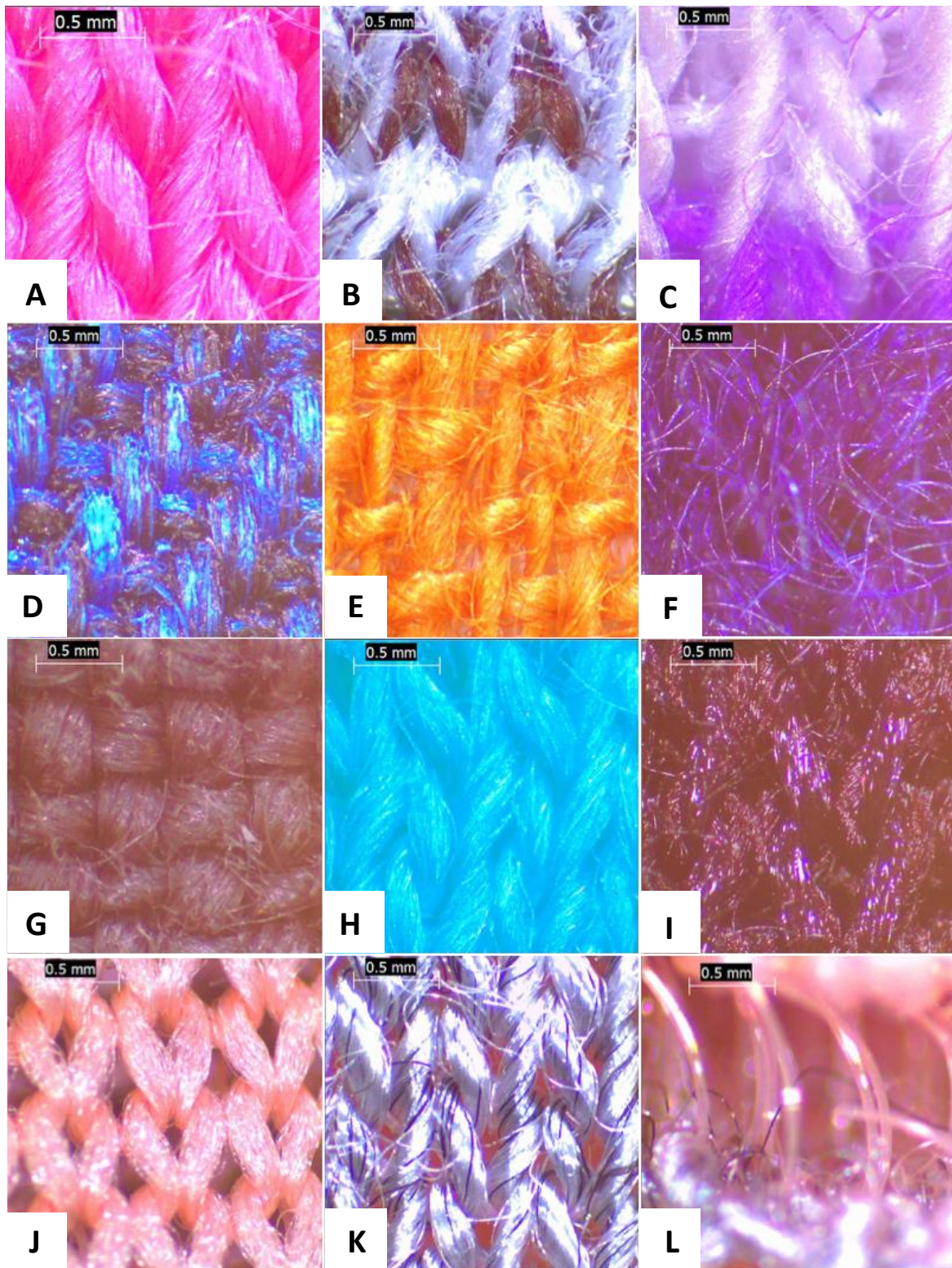
Figure 2-4. Synthetic blend and natural fibre fabric swatches. (A): Swatch 1, (B): Swatch 2, (C): Swatch 3, (D): Swatch 4, (E): Swatch 5, (F): Swatch 6, (G): Swatch 7, (H): Swatch 8, (I): Swatch 9, (J): Swatch 10 (underside), (K): Swatch 10 (upper side), (L): Swatch 10 (middle section).

Table 2-2. Synthetic blend/natural fibre fabric swatches analysed for fibre method development.

Swatch Number	Blend
1	Merino 100%
2	Polyester 100%
3	Polypropylene 100%
4	Nylon 100%
5	Cotton 100%
6	Cashmere 100%
7	Hemp 100%
8	Wool 60%/Acrylic 40%
9	Tencel 80%/Polyester 20%
10	Rayon 50%/Polyester 45%/Spandex 5%

Separation of individual fibres from a strand was undertaken using tweezers, under a dissection microscope (Leica EWZ4). The physical differences between the synthetic and natural fibre could be observed visually under the microscope, as natural fibres contain hatching throughout the fibre, whereas synthetic fibres are generally uniformly opaque (Figure 2-5). Each fibre was prepared for FTIR analysis by suspending across two pieces of double-sided tape. Each fibre was analysed in transmission mode, with spectral range of 4000 – 600 cm^{-1}, with 4 scans per sample. Spectra were saved and added to a fibre reference library.
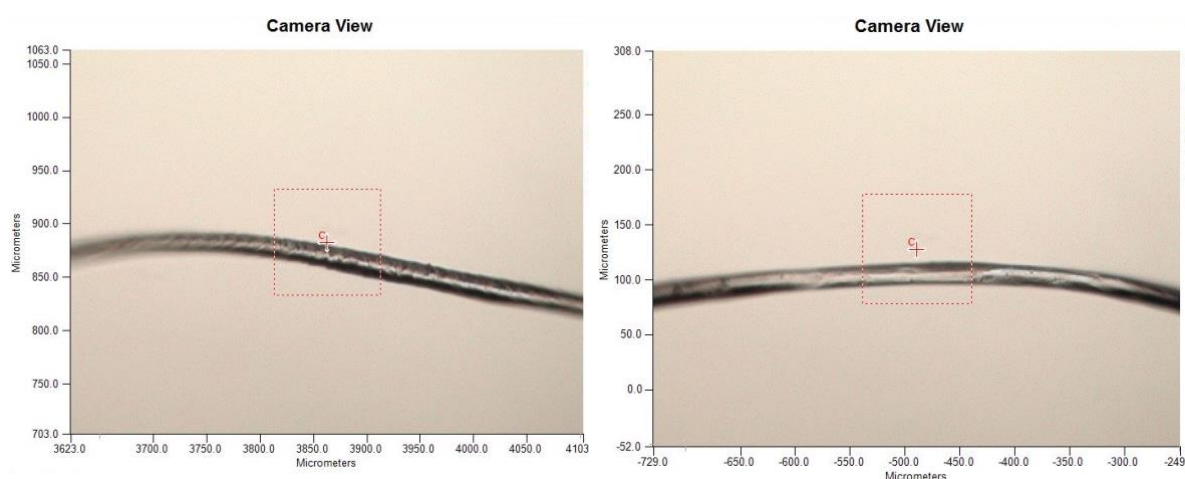
Figure 2-5. Close-up of merino fibre (left) and tencel fibre (right) under the FTIR camera.

2.5 Analytical method validation

2.5.1 Sample collection and wet sieving

Microplastic particle morphotype assessed in this study were fragments, fibres, films, or beads. Fragments were described as particles with a depth, compared to films which were particles that were very thin. A total volume of 4 L of both influent and effluent were collected from Governors Bay WWTP. The extraction method used was based on the National Oceanic and Atmospheric Administration (NOAA) method for extraction of microplastics from water samples.[82]

Influent and effluent samples were split into 1 L subsamples, which included one unspiked, and three spiked (with 10 pieces each of polyester glitter, polyethylene microbeads, and acrylic fibres) samples. These were poured over a stack of stainless-steel sieves (Figure 2-6) of pore size 32 μm, 63 μm, 125 μm, and 4 mm over an 8 L stainless steel bucket. The contents of the sieves were washed off into separate 600 mL glass beakers with ultra-pure water, with the aid of a plastic funnel. The 1 L filtrate (< 32 μm) was also collected, in a large 3 L glass beaker. A spiked and an unspiked blank of ultra-pure water was run in addition to the wastewater samples.

The NOAA method evaporated all liquid in the sample in an oven at 90°C to determine the dry weight of the remaining plastic.[82] Due to the high volume of water required to ensure each sieve was thoroughly washed off (an average of 400 mL), the water did not evaporate. On visual inspection of the solution, it was noted that some of the microbeads had slightly melted. The evaporation step was omitted for further trials.
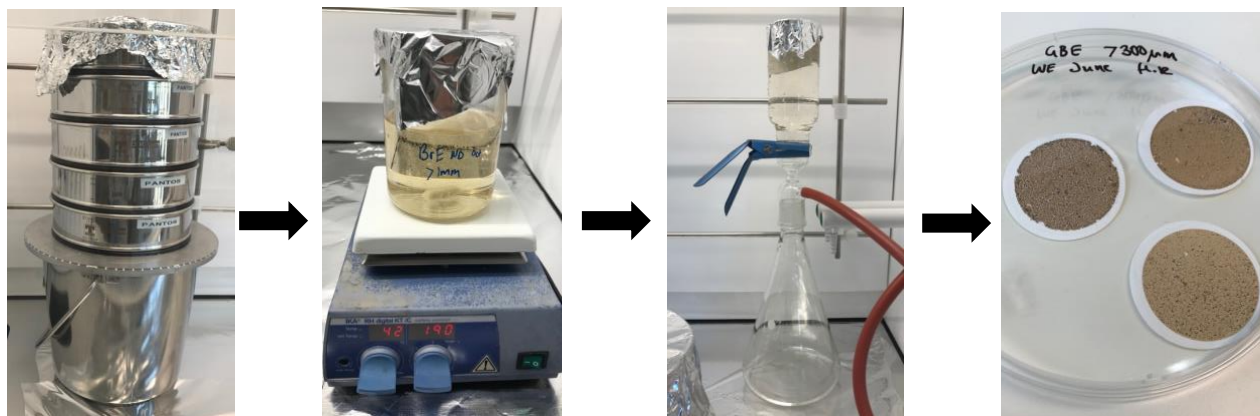
Figure 2-6. Flow-chart of extraction method. Left to right: Stack of stainless-steel sieves mounted on a 8 L stainless steel bucket; resuspended material collected on the sieve undergoing WPO digest; vacuum filtration of digested sample; filtered samples on glass fibre filters.

2.5.2   Wet peroxidation oxidation

Samples underwent a wet peroxide oxidation (WPO) digest using 0.05 M aqueous iron (II) solution to 30% hydrogen peroxide to remove organic material present. The iron (II) solution was prepared by adding 15 g of iron (II) sulfate heptahydrate, to 1 L of deionised water, with 6 mL of concentrated sulfuric acid. Following the NOAA standard method, 20 mL of iron (II) solution and 20 mL of 30% hydrogen peroxide were added to each sample which was washed off the sieves into the 600 mL beakers.[82] Two litres of the filtrate were digested at a time, and 150 mL each of iron (II) solution and 30% hydrogen peroxide were added. After waiting for five minutes, the sample was placed on a hotplate with a magnetic stirrer and left to stir at room temperature (21°C) for half an hour (Figure 2-6). Instead of heating to 75°C (as per the NOAA method), each sample was heated at 45°C after 30 minutes, to avoid thermal degradation of plastic. Subsequently, the samples were left for an average of three hours at that temperature, or until the majority of organic matter capable of being broken down had digested.

2.5.3   Vacuum filtering

After digest, the beaker contents were vacuum filtered onto a glass fibre filter (Whatman, 47 mm diameter, 1.2 μm pore size, Figure 2-6). The beaker was rinsed three times with ultra-pure water, along with the vacuum filter funnel. The filter papers were dried under vacuum

for a minimum of one hour, or until dry. The filter papers were removed from the vacuum filtering apparatus and stored in covered plastic petri dishes for analysis (Figure 2-6). When removing the dried filter papers from the vacuum apparatus during the method development, it was observed that the spiked fibres, glitter, and microbeads were prone to being blown away by the airflow inside the fume hood. An assessment of the difference between the removal of the filter paper from the apparatus inside versus outside the fume hood was made. It was observed that no particles were prone to being blown off when the filter paper was removed outside the fume hood.

2.5.4   Analysis of filter papers

Filter papers were analysed under dissection microscope (Leica EZ4W), with a magnification range of 8 – 32x. Each filter paper was analysed three times. A few particles of each type (fibre, glitter, microbead) were selected for FTIR analysis (Perkin Elmer Spectrum 2 FTIR, with Spotlight 200i microscope, Spectrum software version 10.5.2.636) to assess spectral deformation resulting from processing. This was compared against particles of the same type, which had not been through the method. No spectral deformation was observed.

2.5.5   Recoveries of analytical method validation

The spiked control returned an 87% recovery of spiked particles, with an additional 6 fibres present due to airborne contamination. It was observed during analysis of this sample that fibres were blowing off the filter paper when removed from the apparatus inside the fumehood. A subsequent spiked blank with the filter paper removed from inside the fumehood, returned a 100% recovery of spiked particles. An additional 10 fibres were present as contamination. Unspiked blank samples comparing removal inside versus outside of the fumehood returned contamination by 21 particles (6 fragments, 15 fibres), and 13 particles (8 fibres, 5 fragments), respectively. These results highlighted the importance for strict contamination mitigation. It was decided that the filter paper would be removed from the apparatus outside of the fumehood in order to minimise the risk of microplastic loss.

2.6 Assessment of microplastics in influent and effluent

2.6.1 Sample collection and site selection

Five WWTPs were initially selected in the Canterbury region – Christchurch, Kaiapoi, Lyttelton, Governors Bay, and Ashburton (Figure 2-7 and 2-8). Due to technical difficulties and time constraints, it was decided that the Ashburton WWTP would no longer be sampled. These WWTPs were chosen to analyse spatial and population differences in Canterbury, as well as different degrees of treatment and environmental discharge types (Table 2-3). To characterise the microplastics, each WWTP was sampled for influent and effluent, with sampling timed to account for the hydraulic retention time of the plant (Table 2-3).

Kaiapoi WWTP

Incoming influent is screened to remove large particulates, before mechanical aeration to further reduce organic material. Wastewater then enters an infiltration wetland.[83] Primary effluent from Rangiora WWTP enters the wetland and mixes with Kaiapoi wastewater.[84] UV disinfection is employed in instances of high bacterial growth. Treated effluent is discharged via ocean outfall 1.5 km offshore, north of Kaiapoi town district.[83]

Christchurch WWTP

Influent is screened to remove large rags and grit, prior to primary sedimentation. The liquid fraction is pumped to trickling filter, where bacteria consume available nutrients. Water passing through aeration tanks and clarifiers are separated from solids. Solids from primary sedimentation, aeration tanks, and clarifiers are pumped to digesters for sludge dewatering and thermal drying into biosolids. The liquid fraction is pumped to a series of six oxidation ponds, before discharge via ocean outfall 3 km offshore, near New Brighton.[85]

Governors Bay and Lyttelton WWTPs

Both treatment plants undergo primary screening to remove large materials, and extended aeration to reduce organic load. Wastewater is treated by UV disinfection prior to discharge. Sludge is dewatered and transported to Christchurch WWTP for thermal drying. The liquid fraction from both WWTPs at the time of sampling are discharged into Lyttelton Harbour.[86]
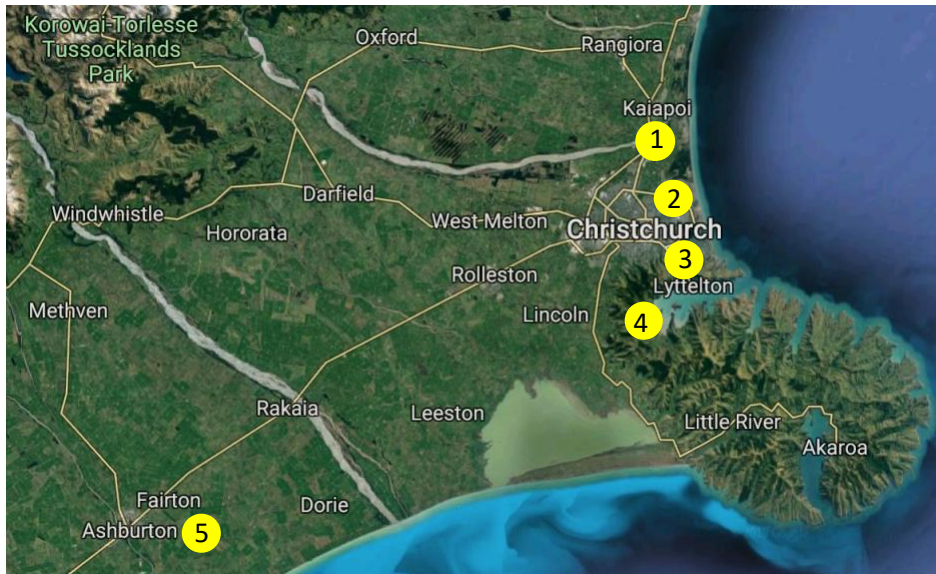
Figure 2-7. Satellite map of the Canterbury region, with sampled WWTP approximate positions of Kaiapoi WWTP (1), Christchurch WWTP (2), Lyttelton WWTP (3), Governors Bay WWTP (4), and Ashburton WWTP (5) (Map courtesy of Google Maps).
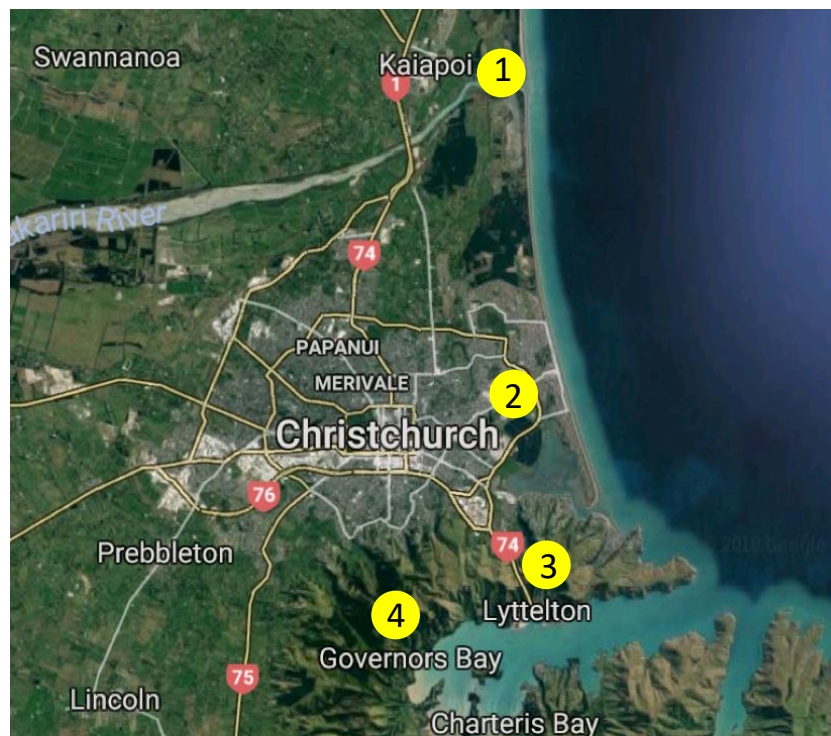
Figure 2-8. Satellite map of the wider Christchurch area, indicating the approximate position of Kaiapoi WWTP (1), Christchurch WWTP (2), Lyttelton WWTP (3), and Governors Bay WWTP (4) (Map courtesy of Google Maps).

Table 2-3. WWTP data including population served, connections, retention time, flow rate, sludge production, and effluent discharge.

Treatment Plant	Treatment Type	Population (2018 Provisional Census Data)[87]	Number of Connections	Retention time from influent to effluent (hours)	Flow rate per day (m^3)	Flow rate per year (m^3)	Sludge production (Yes/No)	Effluent Discharge
Kaiapoi[83-84]	Tertiary	30,250[a]	11,535[b]	48	10,691[c]	3,902,215	No	Ocean outfall, North Canterbury
Christchurch[88]	Tertiary	377,200	NA	5	186,952	68,237,480	Yes	Ocean outfall, New Brighton
Lyttelton[88]	Tertiary	3,040	1,426	24	828	302,220	Yes	Ocean outfall, Lyttelton Harbour
Governors Bay[88]	Tertiary	870	294	24	176.3	64,350	Yes	Ocean outfall, Lyttelton Harbour

NA = not assessed

[a]Population served at Kaiapoi WWTP includes Rangiora (18,400) and Kaiapoi (11,850)

[b]Connections at Kaiapoi WWTP includes Rangiora (6,924) and Kaiapoi (4,611)

[c]Flow rate per day at Kaiapoi WWTP includes effluent from Rangiora (6,558) and influent from Kaiapoi (4,133)

The characterisation sampling took place during June 2018, and two rounds of sampling were undertaken for each WWTP, one occurring during the week, and the other over the weekend, to account for any lifestyle variability that may occur between the working week and weekend (Table 2-4). Samples of influent and effluent were collected on a weekday and a weekend. A total of 16 wastewater samples (at 10 L for 14 samples, and 9 L for 2 samples) were collected, at a total of 158 L. From the months of July to December, temporal variation of the WWTPs was investigated. Sampling was reduced to three WWTPs (Christchurch, Kaiapoi and Lyttelton), of effluent only, bi-monthly (August, October, December) due to time constraints with the length of time it took to process a sample (Table 2-5). A total of 9 wastewater samples (at 10 L each) were collected, at a total of 90 L. Across both investigations, 16 wastewater samples were collected, at a total volume of 248 L. Each sample followed the same sampling, extraction, and analysis procedure (Figure 2-9).

Table 2-4. Wastewater samples collected for characterisation of WWTPs, (10 L sample).

WWTP	Weekday	Weekend
Christchurch	Influent and Effluent	Influent and Effluent
Kaiapoi	Influent and Effluent	Influent and Effluent
Lyttelton	Influent and Effluent*	Influent and Effluent*
Kaiapoi	Influent and Effluent	Influent and Effluent

*9 L were collected

Table 2-5. Wastewater samples collected for temporal investigation of WWTPs, (10 L sample).

WWTP	August	October	December
Christchurch	Effluent	Effluent	Effluent
Kaiapoi	Effluent	Effluent	Effluent
Lyttelton	Effluent	Effluent	Effluent
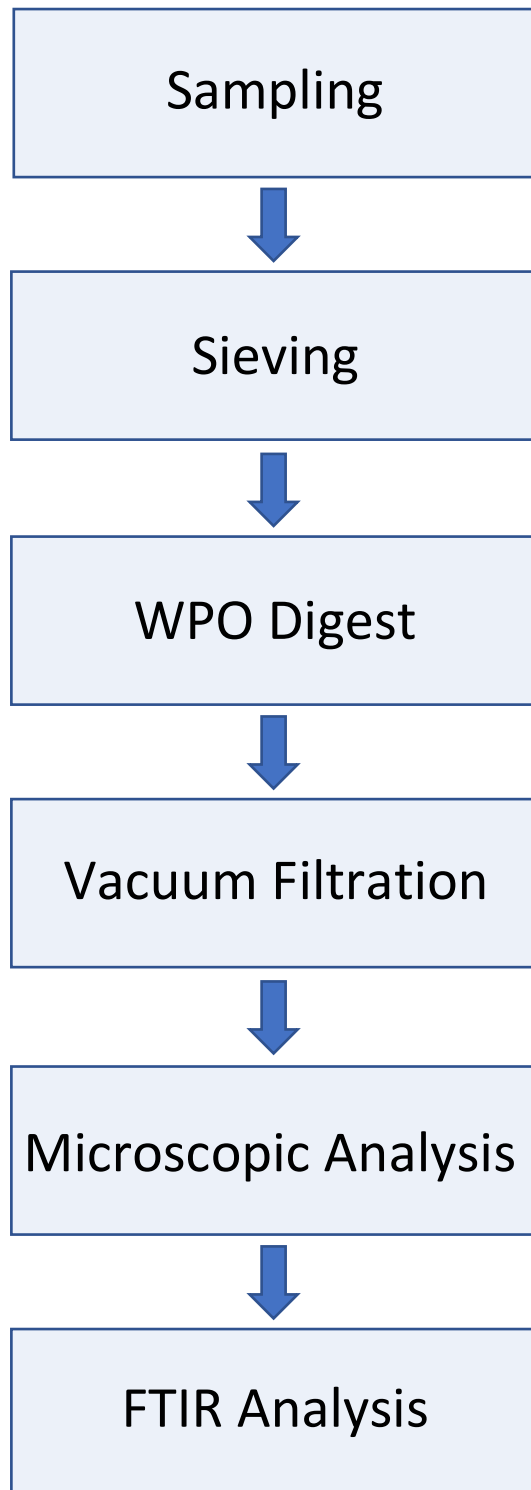
Figure 2-9. Flow chart of sampling, extraction, and analysis procedure.

2.6.2 Health and safety considerations

Required vaccinations (hepatitis A, hepatitis B, tetanus) were obtained prior to the first sampling trip. University Health and Safety protocol was followed for all field work and laboratory work. Site inductions were undertaken during the first onsite visit, with a permit to work received. Appropriate PPE (sturdy covered shoes, clothing covering arms and legs, high-visibility vest, hard hat, nitrile gloves) were worn during each sampling trip. Field equipment was sprayed with 70% ethanol after contact with wastewater. After decanting the homogenised wastewater in the laboratory, sample bottles and work benches were wiped down with 70% ethanol, and samples stored immediately at 4°C.

2.6.3 Field sampling protocol

Influent and effluent samples were collected using two ISCO 3700 autosamplers (Figure 2-10), and one ISCO 2700 autosampler. Each sampler was calibrated prior to use at each WWTP, by sampling 250 mL of wastewater on site, and measuring the amount collected with a measuring jug. Vinyl tubing (internal diameter 9.5 mm) was primed in the laboratory with deionised water, and with 3x 250 mL of wastewater (total 750 mL) onsite prior to sample collection. The wastewater collected for priming was discarded, with the autosampler bottle replaced with a clean bottle for sample collection.

Figure 2-10. ISCO 3700 Autosampler with vinyl tubing onsite at Christchurch WWTP, positioned at the effluent sump.

A 24-hour composite sample was collected for both influent and effluent at each WWTP, to account for hourly flow variability. A volume of 10 L was collected each of influent and effluent, over 17 autosampler bottles (Figure 2-11). A 250 mL sample was taken time proportional, in 30-minute intervals, with three samples per bottle. Deionised water blanks (4 L) were spread across four autosampler bottles as a field blank. Once the autosampler had finished, the bottles were capped immediately, and stored on ice, for transport back to the laboratory. The samples were then homogenised and stirred in an 18 L stainless steel bucket. Ten litres were taken for this project and were decanted across three 4 L amber glass bottles followed by storage at 4°C until analysis. Due to time constraints, the ICSO 2700 sampler was used for two samples, which can only collect a maximum of 10 L. Therefore, a total of 9 L of effluent was collect for each Lyttelton effluent weekday and weekend sample in June.

Figure 2-11. Polypropylene ISCO 3700 autosampler bottles in base of autosampler.

2.6.4   Finalised extraction method

A single 4 L bottle was processed at a time, for both wastewater samples (3x bottles) and blanks (2x blanks). The sample was poured over a stack of stainless-steel sieves, with pore sizes of 20 μm, 300 μm, and 1 mm. After the second wastewater sample bottle was sieved, it was observed that the 20 μm sieve would readily become clogged. A 50 μm sieve was added to the stack when the next bottle was being processed to alleviate clogging of the 20 μm sieve. For a number of samples, the 50 μm sieve clogged readily, and sample filtration was extremely slow, even after being left for a number of hours. To ensure each sample bottle was sieved over the course of a single day, 20 mL aliquots of 30% hydrogen peroxide were added directly to the 50 μm sieve, to digest the clogged material and keep the wastewater flowing. A 2 mm sieve was added to the top of stack, to catch the large amount of organic matter (seeds, leaves, and sticks) present in some of the influent samples (Figure 2-12). The contents of this sieve were discarded after visual inspection for microplastic. Any particles resembling plastic were added using tweezers to the 1 mm size fraction sieve. The sieves used for the remainder of samples were 20 μm, 50 μm, 300 μm, 1 mm, and 2 mm. It took a whole day to sieve each sample bottle, including glassware and equipment cleaning time.

Figure 2-12. Large organic matter (seeds and sticks) present on the 2 mm sieve.

The contents on each sieve and the filtrate followed the same extraction procedure as Section 2.5.2 and 2.5.3 of the method development. Due to the higher organic matter of these samples (due to processing a larger volume), additional 20 mL hydrogen peroxide aliquots were added during the WPO digest stage and were left for a longer period of time (>3 hours). Two size fractions could be digested simultaneously with the use of two hotplates, with digesting taking a day to complete each of the four sieve size fractions of a single sample bottle. The filtrate samples were digested 2 L at a time and were left overnight to digest on the hotplate. These samples were vacuum filtered onto glass filters, and once dry, stored at room temperature in plastic petri dishes for analysis. All sieve contents and filtrate of a single sample bottle were able to be vacuum filtered over the course of a day. Each full sample (of 2x bottles of blanks and 3x bottles of wastewater) took a full seven days to extract.

2.7 Microscopic and FTIR analysis of filter papers

All tape lifting, autosampler and method blank, and sample filter papers were visually analysed using the dissection microscope, with each suspected microplastic particle photographed. Microplastic particles and fibres present on the blanks of each sample that were also present on the wastewater samples were not included for FTIR analysis. All glass filters of each sample were able to be visually analysed in one day. Suspected microplastics on the sample filter papers were individually picked out with tweezers and mounted on a calcium fluoride (CaF_2) disk (with a drop of 96% HPLC grade ethanol to aid in transfer) for FTIR analysis (Figure 2-13). The CaF_2 disk interfered with the spectra from regions <1000 cm^{-1}, and so the spectral range chosen was from 4000 – 1000 cm^{-1}, with 4 scans. Thicker particles that produced unsatisfactory spectra were transferred onto a diamond compression cell (Almax Easylab) and were analysed in transmission mode after they had been compressed. Spectra were analysed against a series of pre-loaded polymer reference libraries (Appendix 3), along with independent peak analysis against known spectra from the literature. Each full sample (of microplastics found on all three glass filters of the 300 μm and 1 mm sieve size fractions across the three bottles) took two days to analyse.

Figure 2-13. CaF₂ disk mounted onto a slide for FTIR analysis.

3 Results and discussion

3.1 Blank and sample extractions

Sample blanks were analysed visually under a dissection microscope and each suspected microplastic particle located on the blanks was photographed. An average of 11 particles per blank was found. Fibres were the most abundant particle type, with the most common fibre colours being blue and colourless. Suspected microplastic particles present in wastewater samples were checked against those found in the blanks. Those particles similar to the blanks were not analysed further and discounted. Contents of the 300 µm and 1 mm sieve were analysed only, due to difficulty in analysing the glass filters of the lower size fractions with high levels of organic material present. As a result, this study is not a definitive representation of all of the microplastics present in a 10 L wastewater sample.

3.2 Microplastics identified in characterisation and temporal samples

A total of 412 particles were identified by FTIR as microplastic across 248 L of wastewater (example spectra in Appendix 1, example microplastics in Appendix 2). Microplastics were present in a concentration of 2.4 particles/L in influent and 1.3 particles/L in effluent. A volume of 9 L was collected for both Lyttelton weekday and weekend effluents; hence the abundance has been adjusted to 10 L, resulting in an abundance of 412.1 particles across 250 L of wastewater. Microplastic particles were categorised by morphology, and identified as either a fragment, fibre, film, or bead (Figure 3-1). Across all samples, Fragments were the most abundant morphotype at 53% across all samples, with fibres, films, and beads comprising 40%, 6% and 1% respectively. The size of microplastics ranged from 30 µm to 8 mm in diameter. Whilst the definition of a microplastic particle is less than 5 mm in length, fibres greater than 5 mm only were included as they were coiled up into a size smaller than 5 mm. Interestingly, the weekend influent from Christchurch (in June) contained an aggregation of 28 synthetic fibres entangled with cellulose fibres (Figure 3-2).
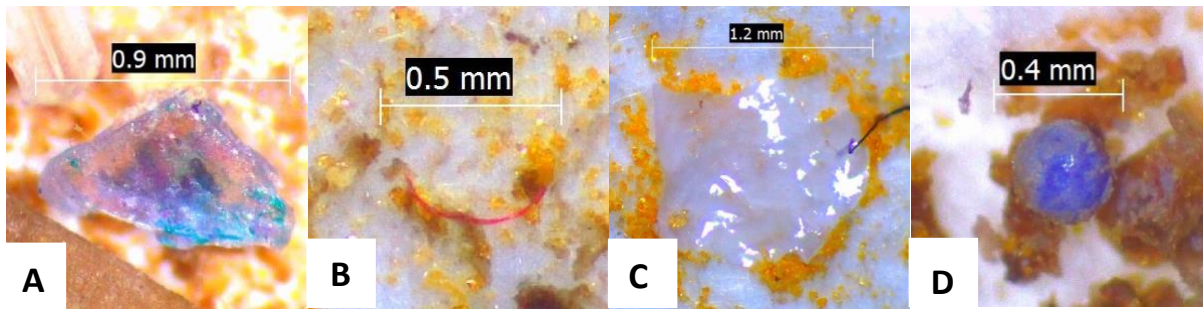
Figure 3-1. Left to right: (A) fragment from Lyttelton weekday influent, June; (B) fibre from Christchurch WWTP effluent, December; (C) film from Lyttelton effluent, December; (D) bead from Governors Bay weekend effluent, June.
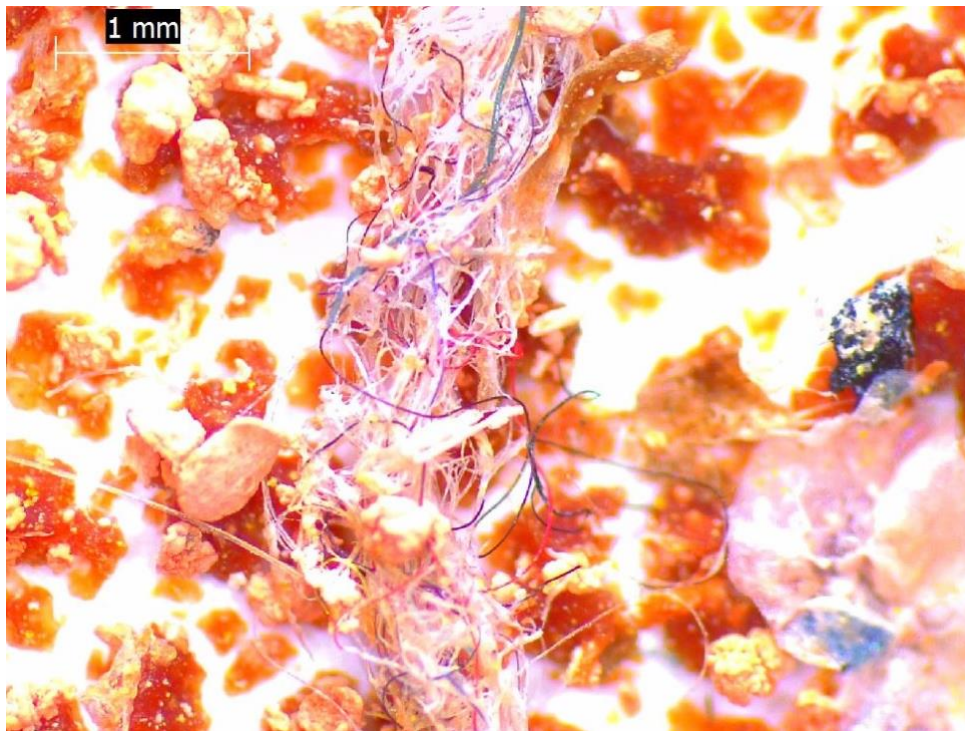
Figure 3-2. Entanglement of synthetic and cellulose fibres in Christchurch influent collected at the weekend (June).

3.3   Characterisation of microplastics in WWTP influent and effluent

3.3.1   Abundance of microplastics

An adjusted total of 290.1 plastic particles were identified by FTIR in the characterisation samples (Figure 3-3), with 67% present in influent (n = 195), and 33% present in effluent (n = 95.1). Total removal efficiency from influent to effluent was 51%, indicating that microplastics are removed throughout wastewater treatment. Total morphotype proportions were similar between influent and effluent with the influent consisting of 49% fragments (n = 96), 46% fibres (n = 90), 4% films (n = 8), and 1% beads (n = 1). The effluent consisted of 53% fragments (n = 49.99), 39% fibres (n = 37), 7% films (n = 7.11), and 1% beads (n = 1) (Figure 3-4).

3.3.2   Microplastics concentration in influent and effluent

The removal potential of each WWTP (Table 3-1) was calculated from the differences between paired influent and effluent samples from weekdays or weekends within a WWTP location. Particle abundance decreased from influent to effluent for each corresponding weekday or weekend sample at Christchurch, Kaiapoi, and Lyttelton WWTPs (Figure 3-5). At Governors Bay, particle abundance (n) increased for weekday influent (n = 17) to effluent (n = 19). No difference in particle abundance was observed for weekend influent (n = 20) and effluent (n = 20) at Governors Bay. The concentration of microplastics entering the WWTP (per 10 L composite sample) in the influent was lower on weekdays than weekends for Christchurch (weekday n = 26, weekend n = 48) and Governors Bay WWTPs (weekday n = 17, weekend n = 20). The concentration in influent was higher on a weekday for Kaiapoi (weekday n = 16, weekend n = 9) and Lyttelton WWTPs (weekday n = 32, weekend n = 28). Christchurch and Lyttelton WWTPs showed similar removal efficiencies between weekday and weekend influent and effluent samples (Table 3.). Wider variation in removal was observed at Kaiapoi and Governors Bay between weekday and weekend.

Table 3-1. Percent reduction of microplastics from influent to effluent in characterisation samples.

WWTP	Weekday Reduction (%)	Weekend Reduction (%)	Average Reduction (%)
Christchurch	73	71	72
Kaiapoi	38	56	47
Lyttelton	66	71	69
Governors Bay	-12	0	-6

3.3.3   Weekday and weekend morphotype

Microplastic morphotype varied between influent to effluent for each WWTP (Figure 3-6). Fragments and fibres were the most common particle types, with films and beads present in small quantities. Weekday influent from all WWTPs displayed a higher abundance of fragments than fibres. For weekend influent samples, fibres were the most abundant morphotype observed at Christchurch, Kaiapoi, and Lyttelton WWTPs. Fragments were the most abundant morphotype in Governors Bay weekend influent. Christchurch, Kaiapoi, and Lyttelton particle morphotype followed a similar fragment and fibre proportion for each corresponding weekday and weekend influent sample, which may indicate non-selective removal of a certain morphotype within a WWTP. Fragments were the most abundant in weekday samples, and fibres most abundant on weekend samples of those three WWTPs, which may indicate lifestyle differences regarding morphotype.

Christchurch WWTP displayed similar morphotype distributions in weekday influent (77% fragments, 23% fibres) and effluent (71% fragments, 29% fibres). In the weekend effluent, an opposing trend of fragments dominating both influent (fragments 17%, fibres 83%) and effluent (fragments 36%, fibres 64%) was observed. Christchurch influent morphotype varied between weekday with fragments dominating compared to weekend influent with a higher proportion of fibres present.

For the Kaiapoi WWTP, proportions of fragments and films from weekday influent (69% fragments, 25% fibres, 6% films) to effluent (50% fragments, 50% fibres) decreased, with a complete removal of films. Additionally, the proportion of fibres decreased from 67% to 25%, for weekend influent and effluent respectively. A higher proportion of fragments (69%) was observed on a weekday in the influent, with the opposite trend observed on a weekend with a higher proportion of fibres (67%).

A decrease in fragments and fibres was observed from weekday influent to effluent at Lyttelton WWTP, with a higher proportion of fragments removed (66% in influent to 45% in effluent). A high number of fibres, and all films and beads were removed from the corresponding weekend influent (n = 13) to effluent sample (n = 4.44). More fragments were observed in the weekday influent (66%), with fibres the most abundant in the weekend influent (46%).

Morphotype proportion differed between samples from Governors Bay. Fragments were present in equal proportions in weekday influent and effluent (47%). Fibres decreased in proportion from 41% to 26%, compared to films which increased from 12% to 26% in influent to effluent respectively. Fragments were the dominant morphotype in both weekend influent and effluent, with proportion decreasing from 80% in influent to 65% in effluent.

3.3.4   Microplastic particle size distribution between influent and effluent

The size of microplastic particles detected in the characterisation samples across all WWTPs ranged from 30 µm to >5 mm. Size distribution in influent followed a similar distribution of that to the total effluent (Figure 3-7). Christchurch influent particle size distribution has a mean of 907 µm. Data displayed is limited to particles <5 mm only due to difficulty in displaying these data points on the chart without recorded sizes. Kaiapoi had a wide particle size distribution in influent samples, with a much narrower range in effluent, which may signal either a significant removal of large particles or fragmentation of large particles. Lyttelton and Governors Bay had similar size distributions for influent and effluent samples, with the majority of particles under 2 mm, and means ranging from 657 – 991 µm (Figure 3-8).
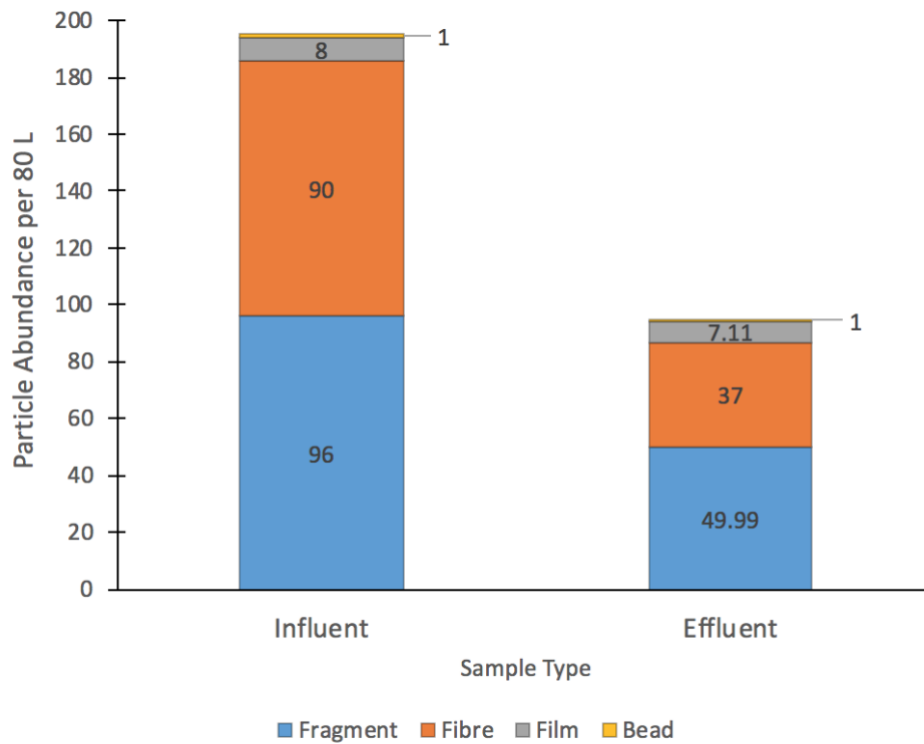
Figure 3-3. Total microplastic morphotype abundance in June influent and effluent, from Christchurch, Kaiapoi, Lyttelton, and Governors Bay WWTPs.
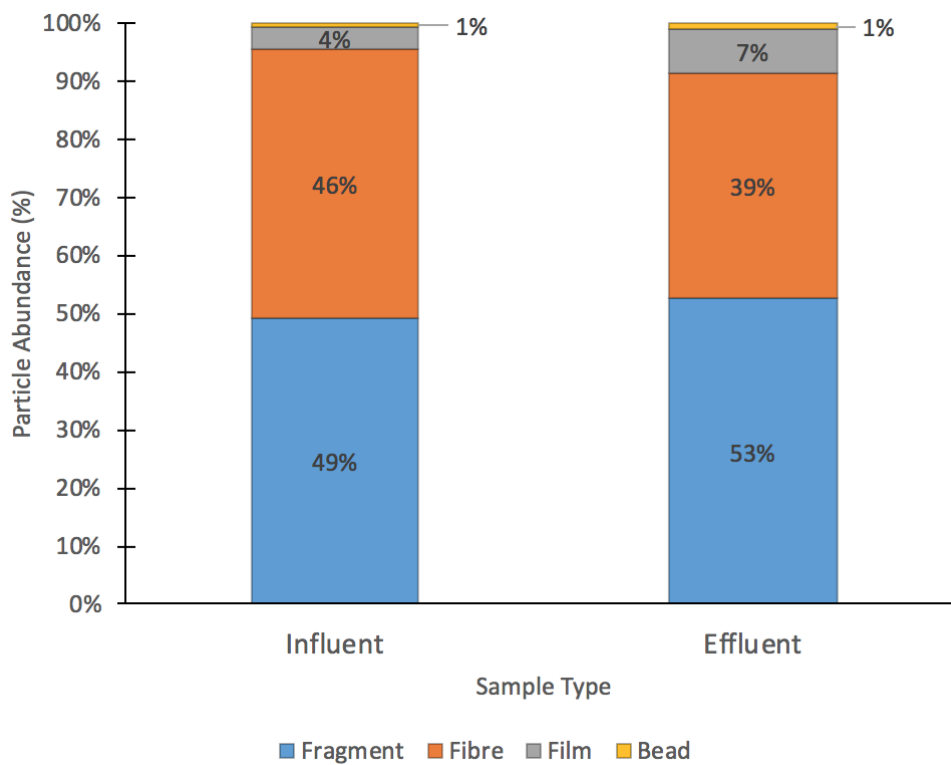
Figure 3-4. Total microplastic morphotype proportion in June influent and effluent from Christchurch, Kaiapoi, Lyttelton, and Governors Bay WWTPs.
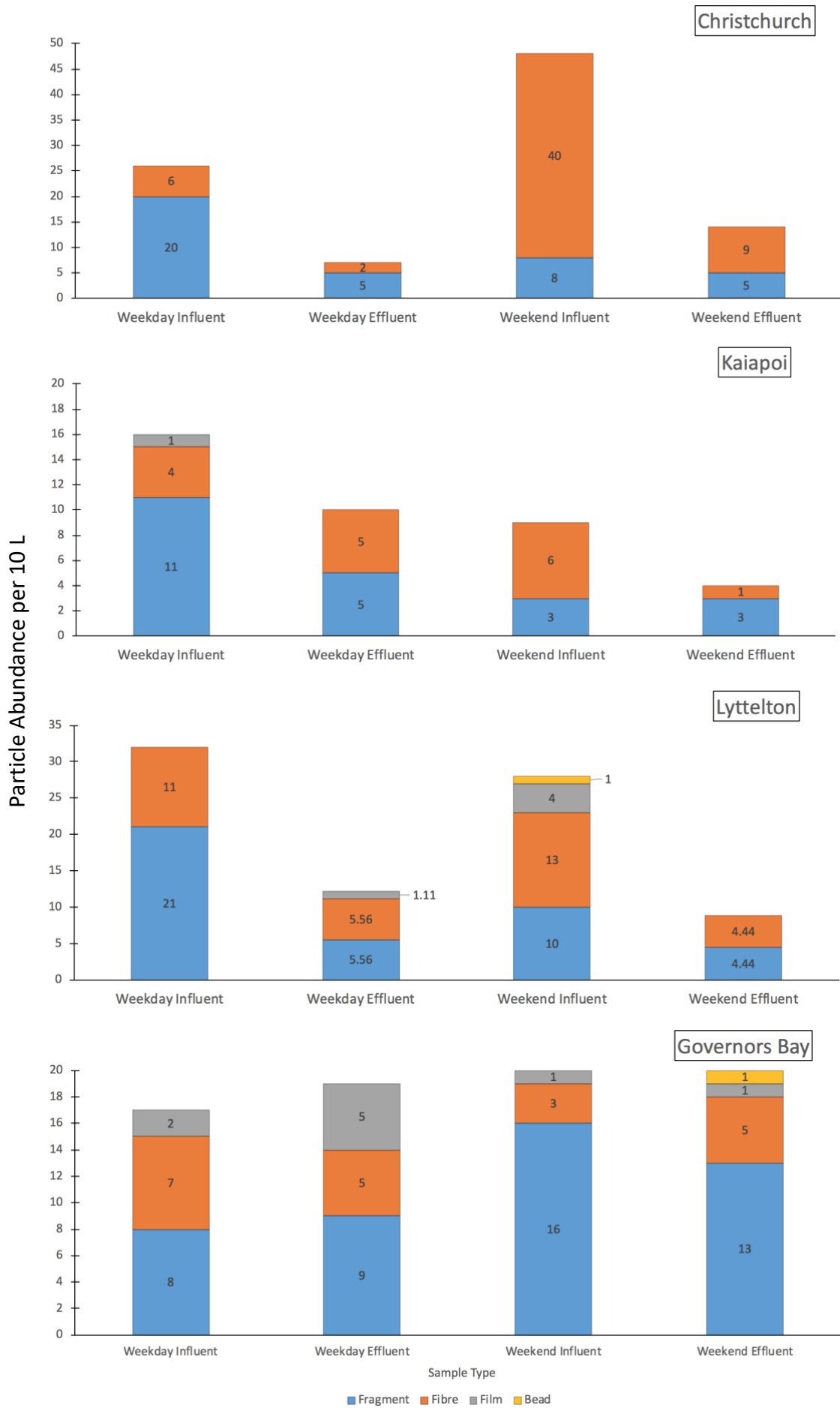
Figure 3-5. Microplastic morphotype abundance in June weekday and weekend influent and effluent, from Christchurch, Kaiapoi, Lyttelton, and Governors Bay WWTP. Note Y-axis scale is different.
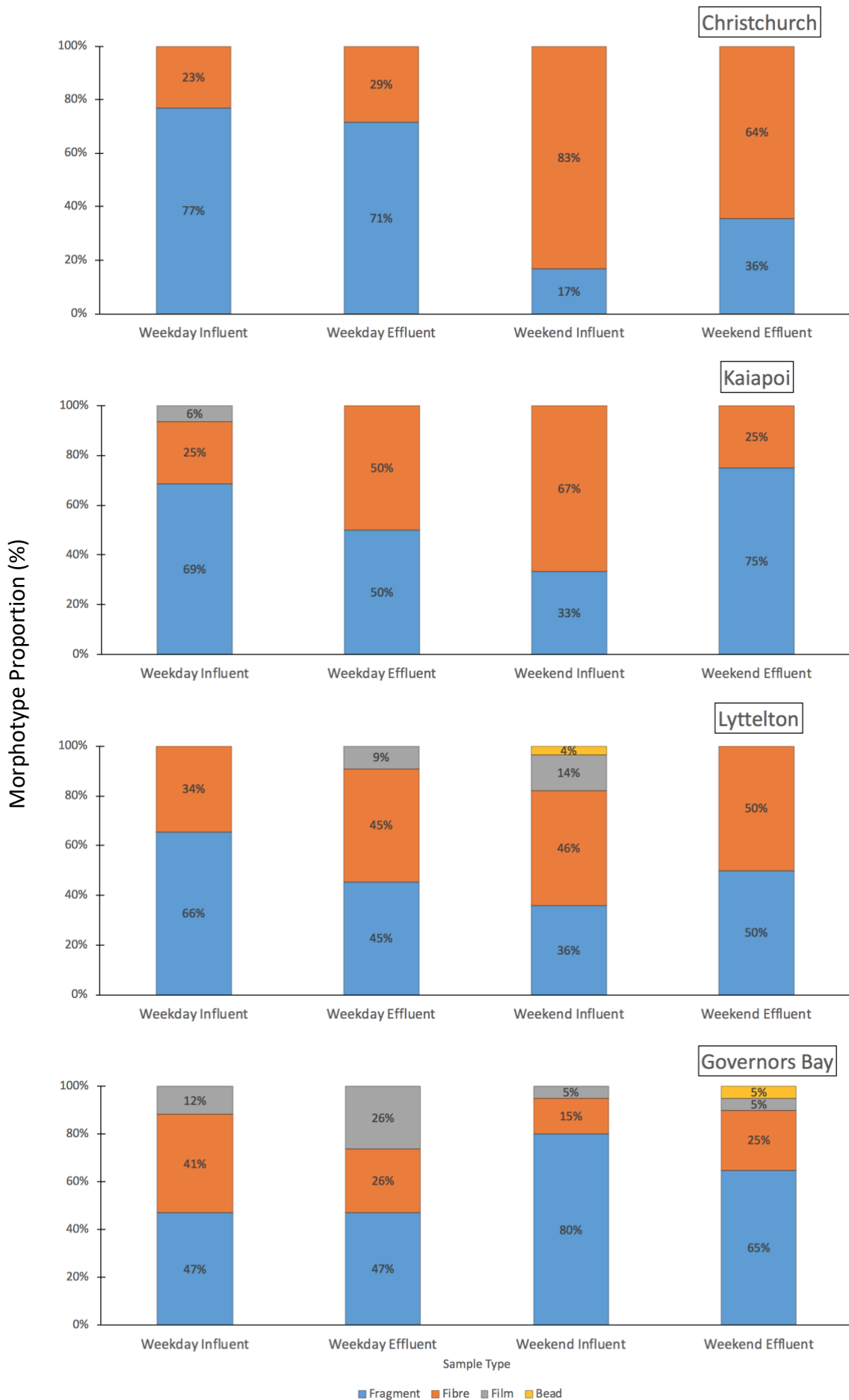
Figure 3-6. Microplastic morphotype proportions in June weekday and weekend influent and effluent, from Christchurch, Kaiapoi, Lyttelton, and Governors Bay WWTP.
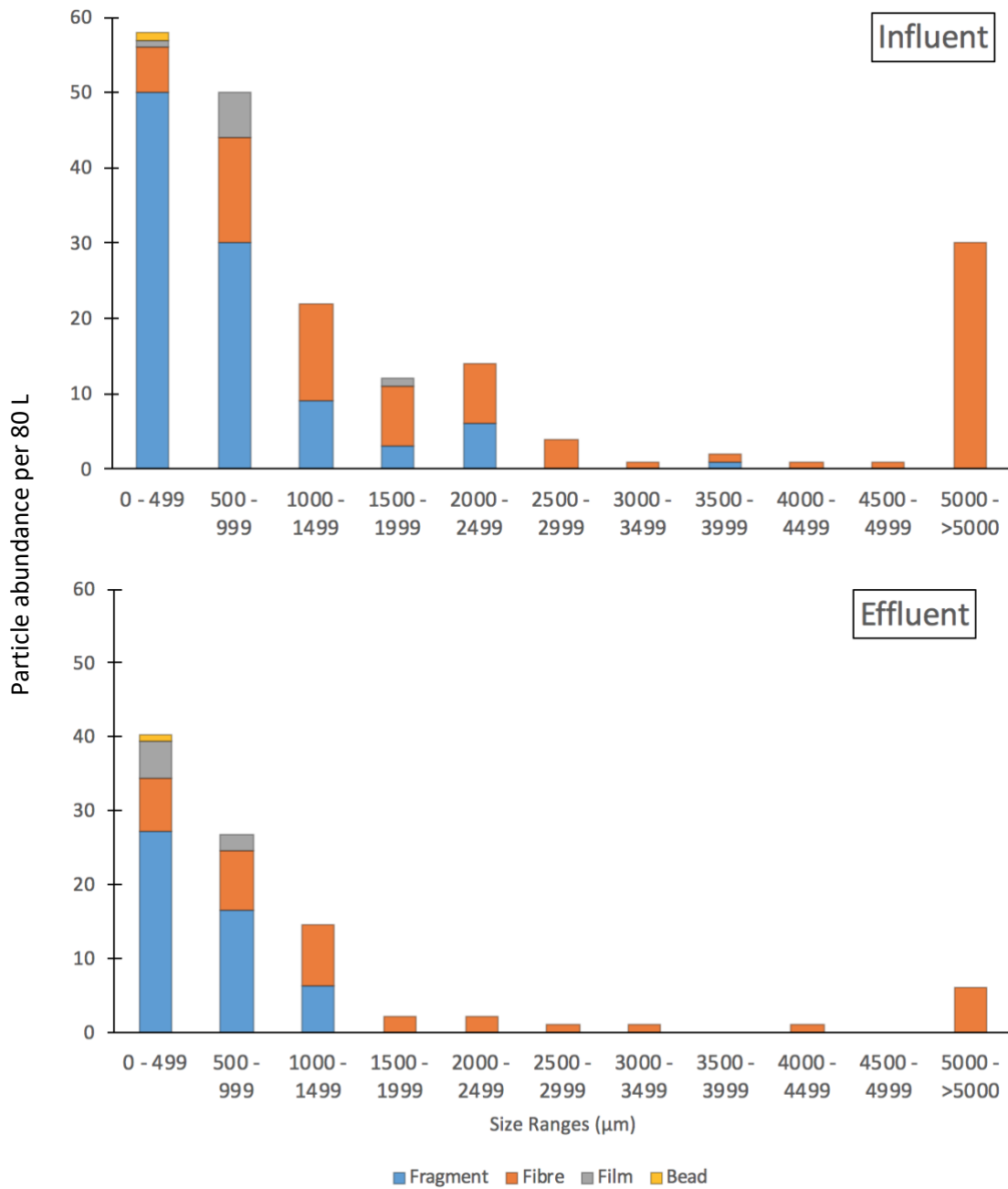
Figure 3-7. Microplastic particle size distribution in influent and effluent, from Christchurch, Kaiapoi, Lyttelton, and Governors Bay WWTPs.
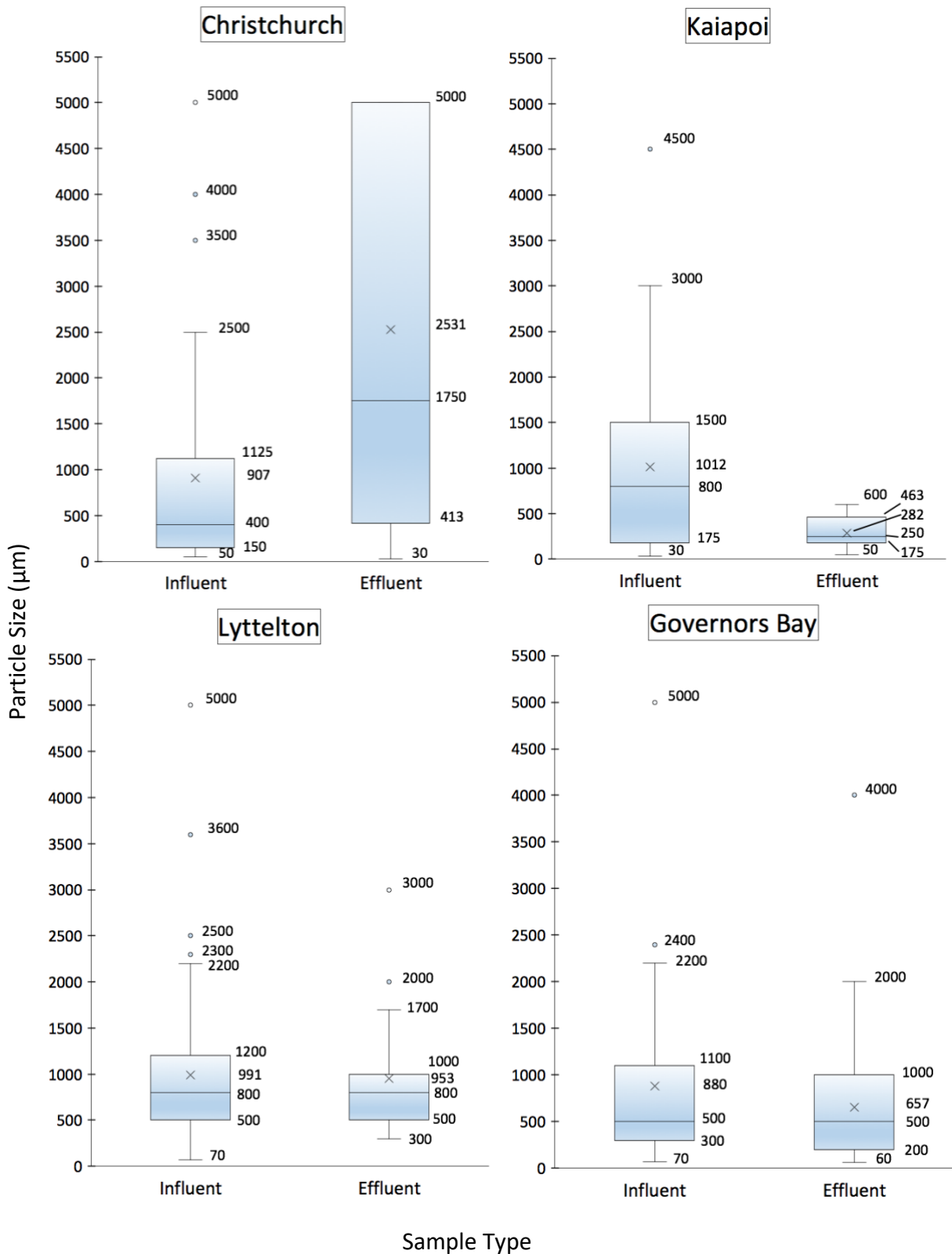
Figure 3-8. Particle size distribution in influent and effluent from Christchurch, Kaiapoi, Lyttelton, and Governors Bay WWTPs. Results presented in box and whisker plots displaying mean (cross), median, lower and upper quartile, minimum and maximum, with outliers represented as circles. Note that fibres >5 mm were not displayed.

3.3.5 Polymer type characterisation of influent and effluent

Similar polymer type proportions were identified between influent and effluent (Figure 3-9). Polyester was the most abundant polymer type in both wastewater types across all WWTPs, with 46% in influent and 47% in effluent followed by acrylic (10% influent, 16% effluent), polyethylene (15% influent, 8% effluent) and polypropylene (10% influent, 7% effluent).
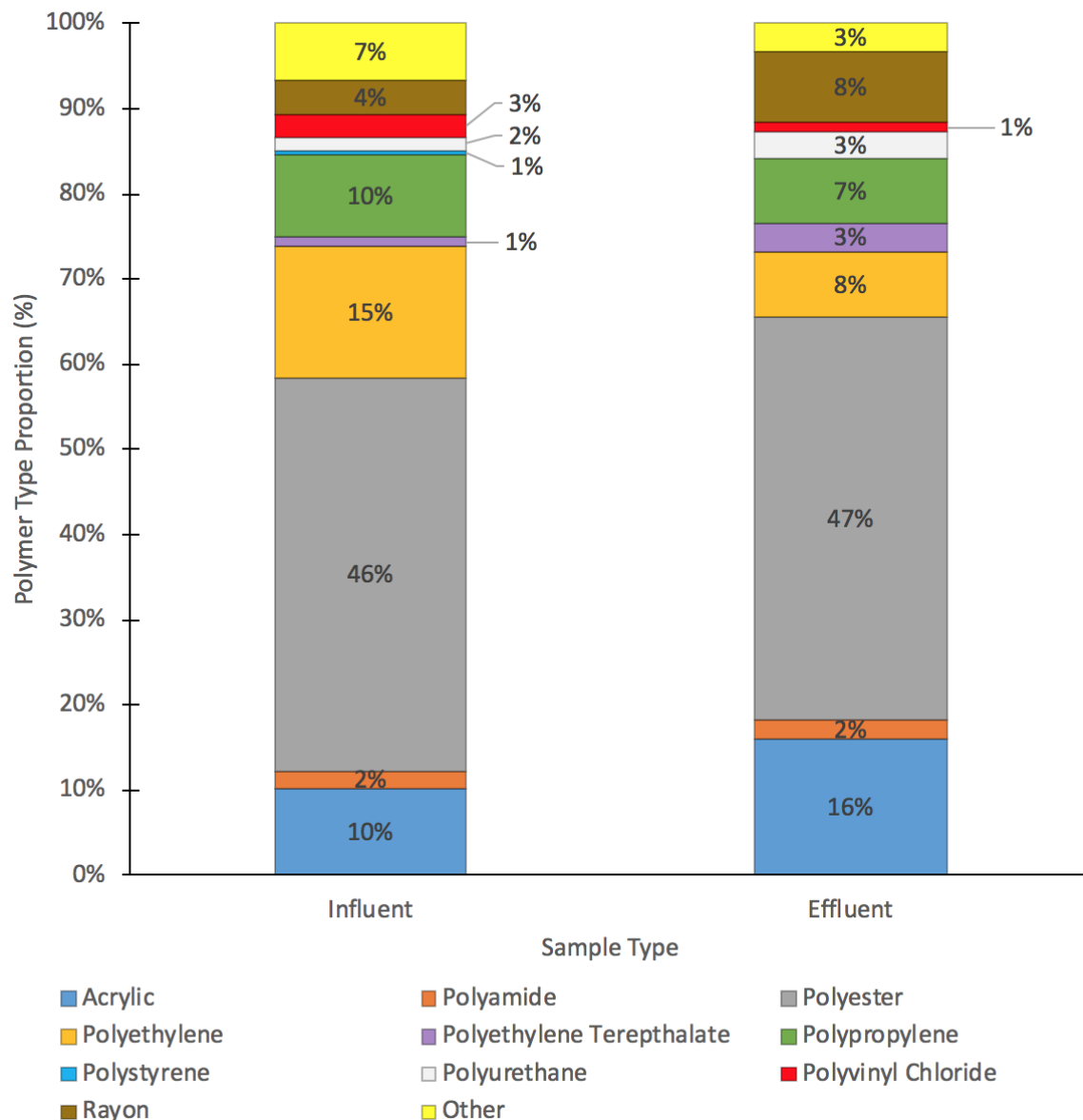
Figure 3-9. Total microplastic polymer type proportions in influent and effluent collected in June, from Christchurch, Kaiapoi, Lyttelton and Governors Bay WWTPs. Influent 'Other' = PVC/acrylic styrene co-polymer, phenolic resin, epoxide resin, polyvinyl acetate, silicone. Effluent 'Other' = silicone and phenolic resin.

3.3.6 Polymer type difference within WWTPs

Variation in polymer type abundance was observed between samples from individual WWTPs (Figure 3-10). Polyester was highly abundant in all samples. Christchurch WWTP samples had a wide variation of polymer types within weekday and weekend influent and effluent samples, which may arise from the large number of connections that the WWTP services. Kaiapoi, Lyttelton, and Governors Bay WWTPs had different polymer type distributions between them. However, similar polymer types and proportions were present within each of those three WWTPs.

Paired influent and effluent samples within a WWTP did not show significant polymer type reduction. Lower-density polymer types, (such as polypropylene and polyethylene), and higher-density polymers (polyester) were present in similar proportions in influent and the corresponding effluent. Common polymer types were equally distributed between their corresponding influent and effluent sample but differed in proportion. Additionally, effluent samples contained the greatest range in polymer types, further suggesting non-selectivity in removal.

3.3.7 Colour of influent and effluent particles in June samples

A wide range of particle colours were found within influent and effluent samples from each WWTP (Figure 3-11). The most abundant colours across all influent samples were blue (22%), and green (21%), followed by colourless (13%) and red (11%). In effluent, the most abundant colours were blue and red (both 22%), followed by grey (10%), white and green (both 9%), and colourless (8%).
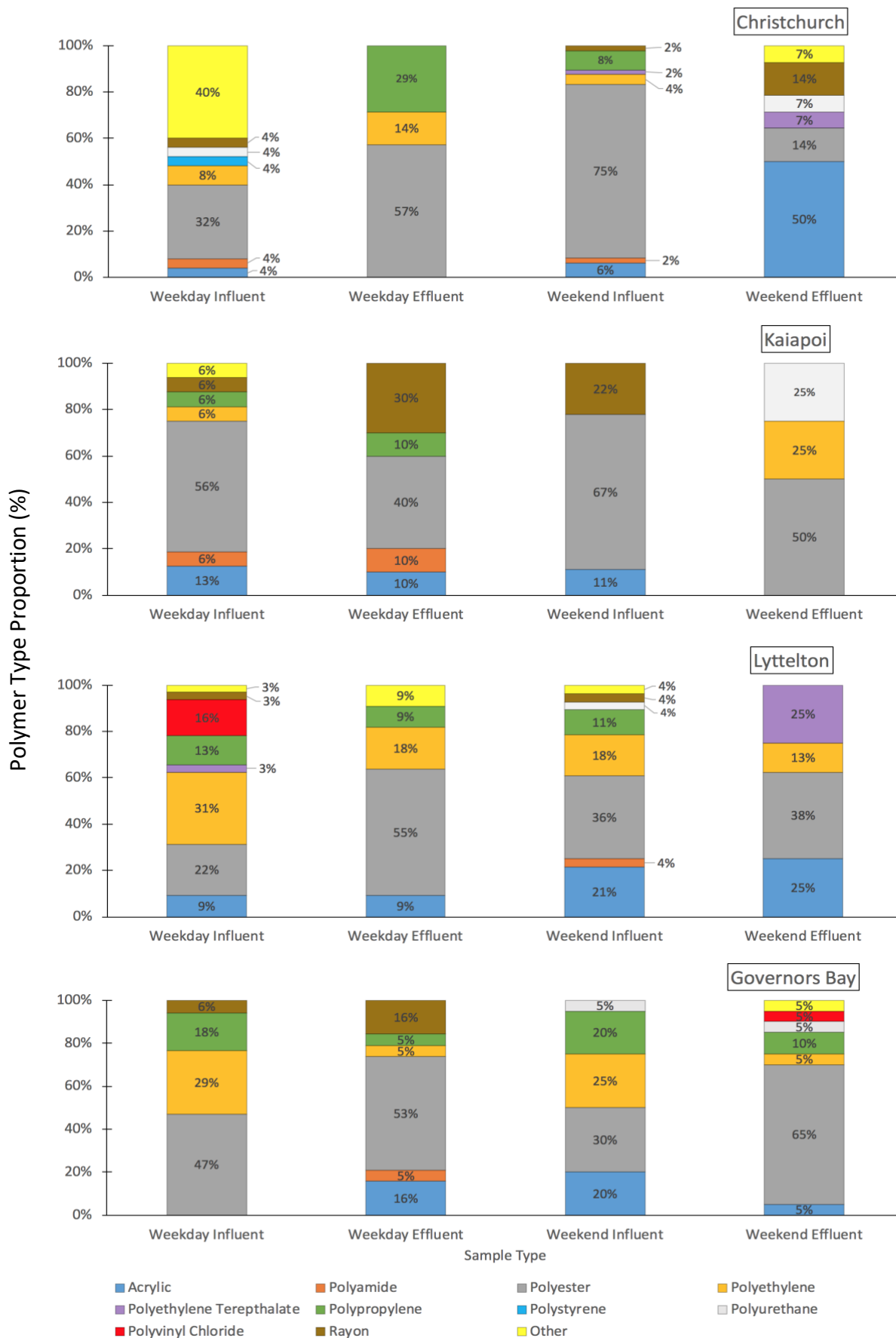
Figure 3-10. Microplastic polymer type proportion in June weekday and weekend influent and effluent, from Christchurch, Kaiapoi, Lyttelton, and Governors Bay WWTPs. 'Other': Christchurch: weekday influent = PVC/acrylic styrene co-polymer, phenolic resin; weekend effluent = phenolic resin. Kaiapoi: weekday influent = epoxide resin. Lyttelton: weekday influent = polyvinyl acetate; weekday effluent = silicone; weekend influent: silicone. Governors Bay: weekend effluent = phenolic resin.

48
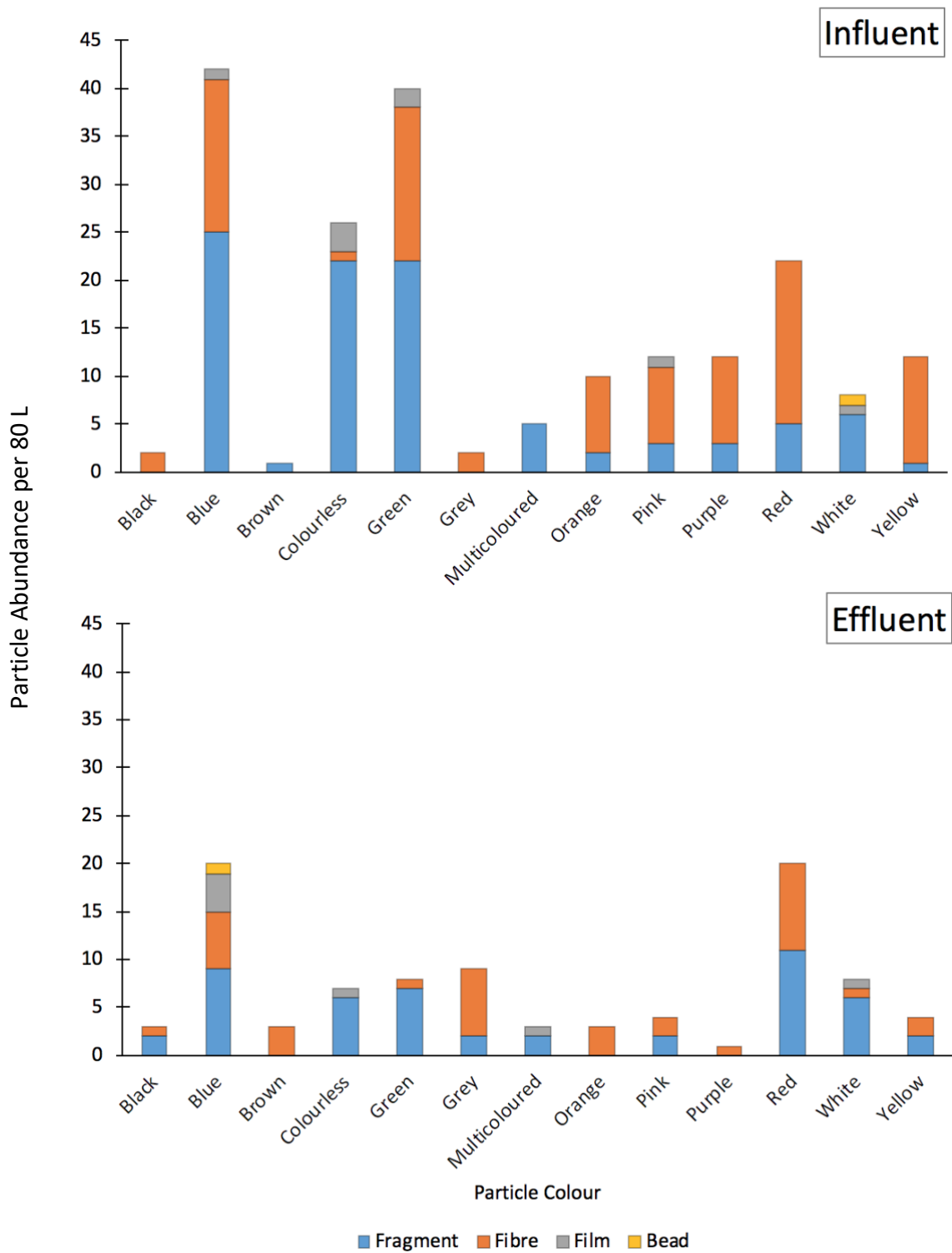
Figure 3-11. Microplastic particle colour abundance present in June weekday and weekend effluent, from Christchurch, Kaiapoi, Lyttelton, and Governors Bay.

3.4 Temporal variability of microplastics in effluent

A total of 122 confirmed microplastic particles were isolated and identified from the 90 L of effluent sampled from Christchurch, Kaiapoi and Lyttelton WWTPs during August, October, and December. Fragments composed 59%, fibres 33%, and films 8% of the microplastics. No beads were detected. Effluent collected in August, October, and December was compared with the effluent sample of the corresponding WWTP taken on a June weekday from Christchurch, Kaiapoi and Lyttelton WWTPs (Figure 3-12). Total abundance of microplastics in effluent shows a similar amount of microplastics leaving the WWTP in the months of June and August (n = 29.22 and n = 29, respectively), and October and December (n = 48 and n = 45, respectively). A higher total abundance was observed in October and December. Similar particle morphotype proportions were found for fragments, fibres, and films between June and August, and October and December samples. Fragments were the dominant morphotype in October and December effluent. A higher proportion of fibres was found in June and August effluent compared to October and December effluent (Figure 3-12).

3.4.1 Temporal particle abundance

Particle abundance at the Christchurch WWTP ranged from 7 to 19 particles per 10 L (Figure 3-13). An increase in particle abundance was observed from June to October, where it peaked, followed by a decrease in abundance in December. Fragments were the dominant particle type from June – October, with percentages of 71%, 80%, and 68%, respectfully. Particle type proportion in December differed with the majority being fragments (54%) and the remainder being fibres.

For the Kaiapoi effluent, particle abundance ranged from 2 to 11 particles per 10 L (Figure 3-14). Little difference in abundance was identified between June, October, and December with no obvious temporal trend. The proportions of morphotypes varied, with an equal abundance of fragments and fibres detected in June; fibres only were detected in August; and fragments were predominant in October and December.

Microplastic abundance in Lyttelton effluent increased from 12.22 to 21 particles per 10 L from June to December (Figure 3-15). No distinct trend in particle type proportions for fragments, fibres and films across the bi-monthly samples was observed. The abundance of morphotypes varied. There was no difference between fragment and fibre abundance in June. Fibres were the most abundant in August, and fragments the most abundant in October and December.
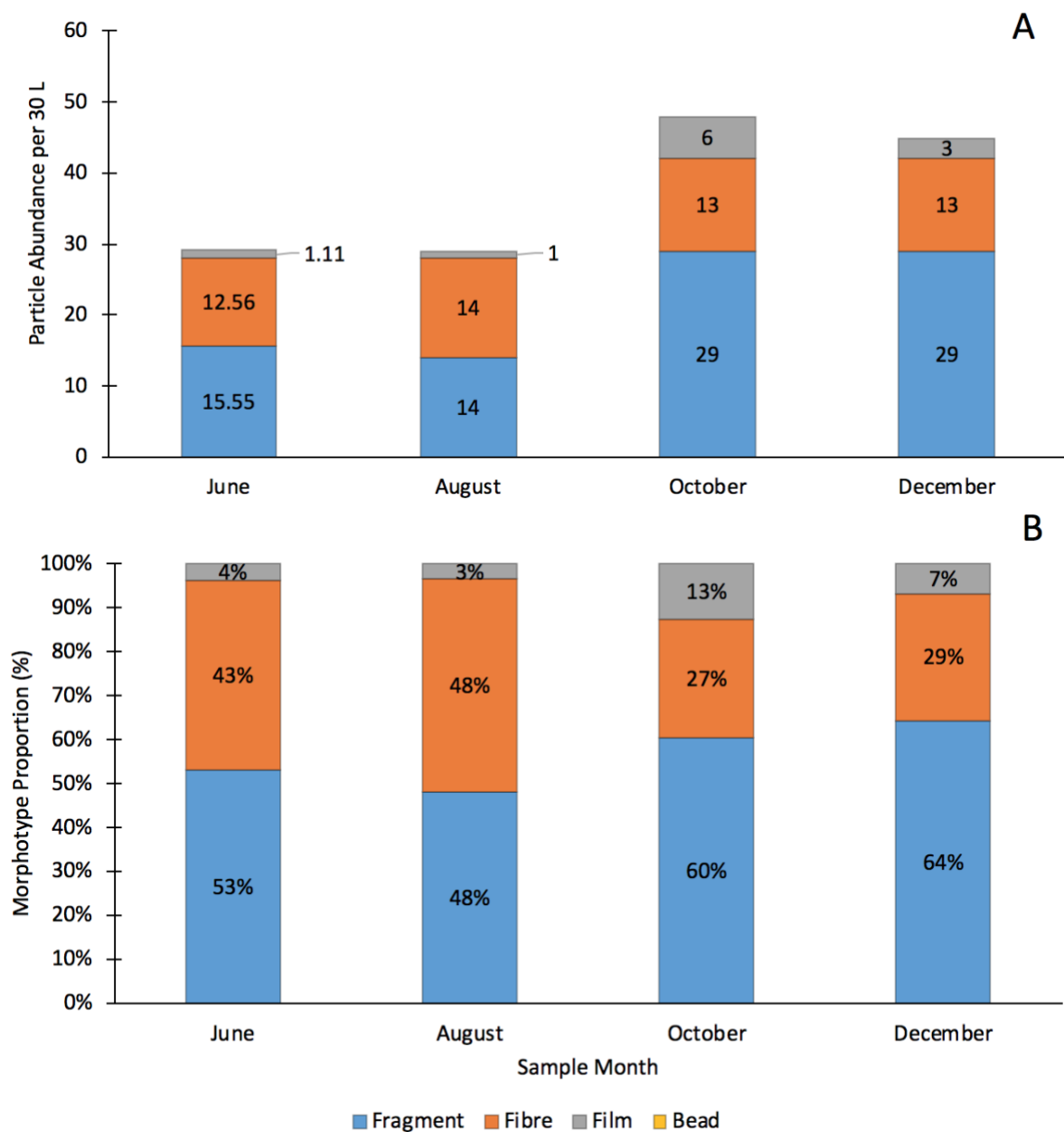
Figure 3-12. Total microplastic abundance in weekday effluent from Christchurch, Kaiapoi, and Lyttelton WWTPs in June, August, October, and December. (A) Total and morphotype abundance, (B) Morphotype proportions per sample
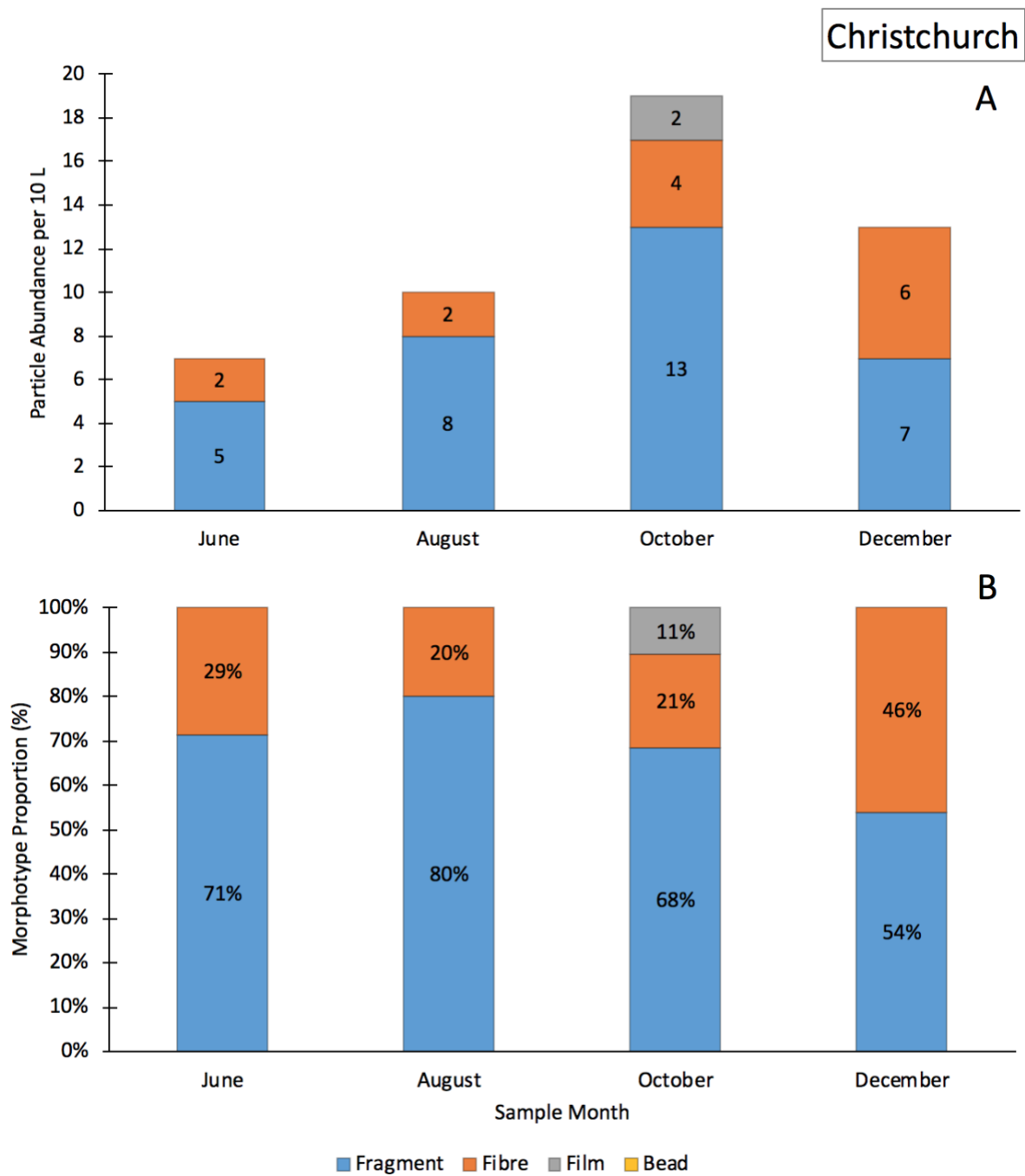
Figure 3-13. Microplastic and morphotype abundance in Christchurch WWTP effluent in June, August, October, and December. (A): Total and morphotype abundance. (B): Morphotype proportion per sample.
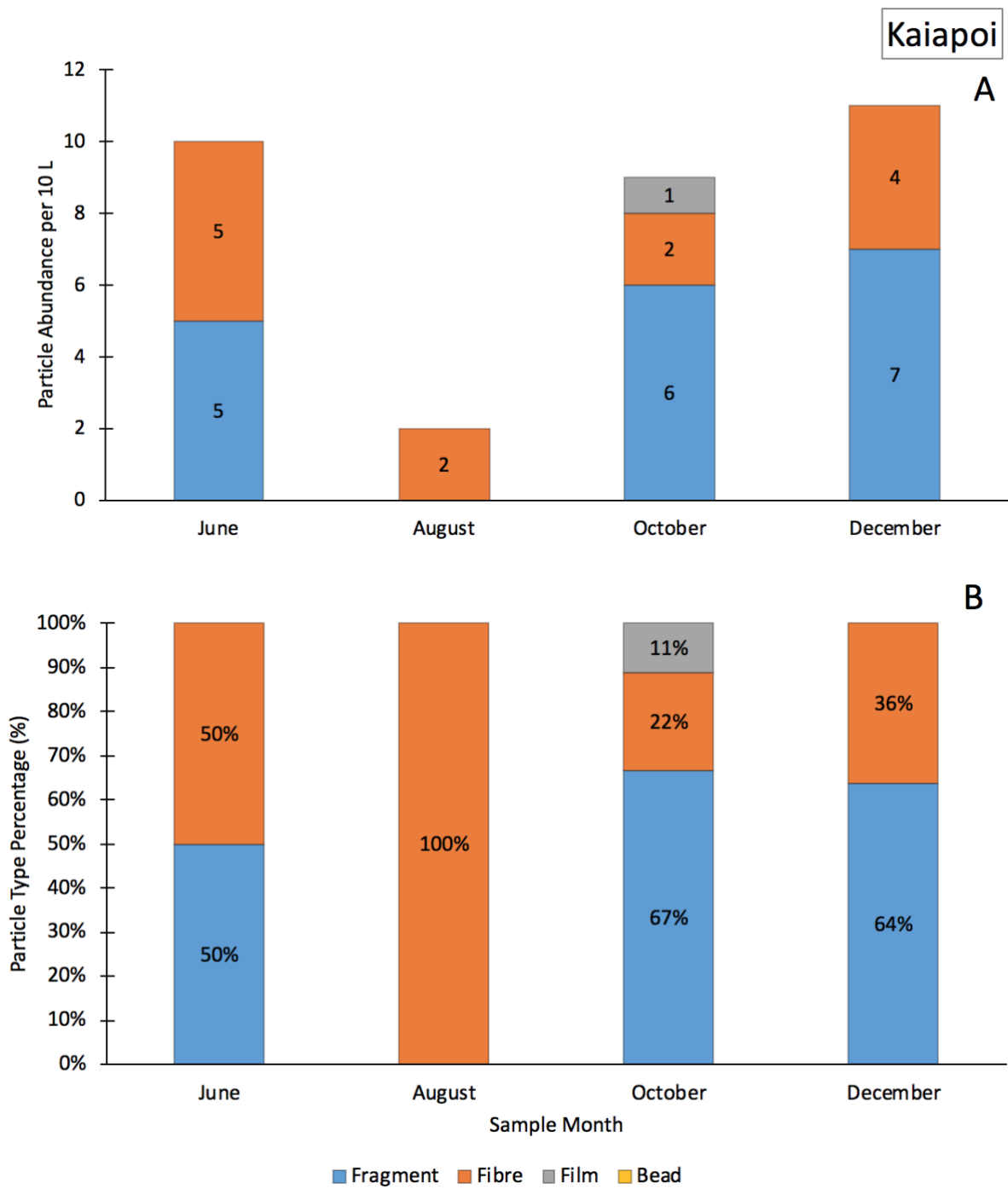
Figure 3-14. Microplastic and morphotype abundance in Kaiapoi WWTP effluent in June, August, October, and December. (A): Total and morphotype abundance. (B): Morphotype proportions per sample.
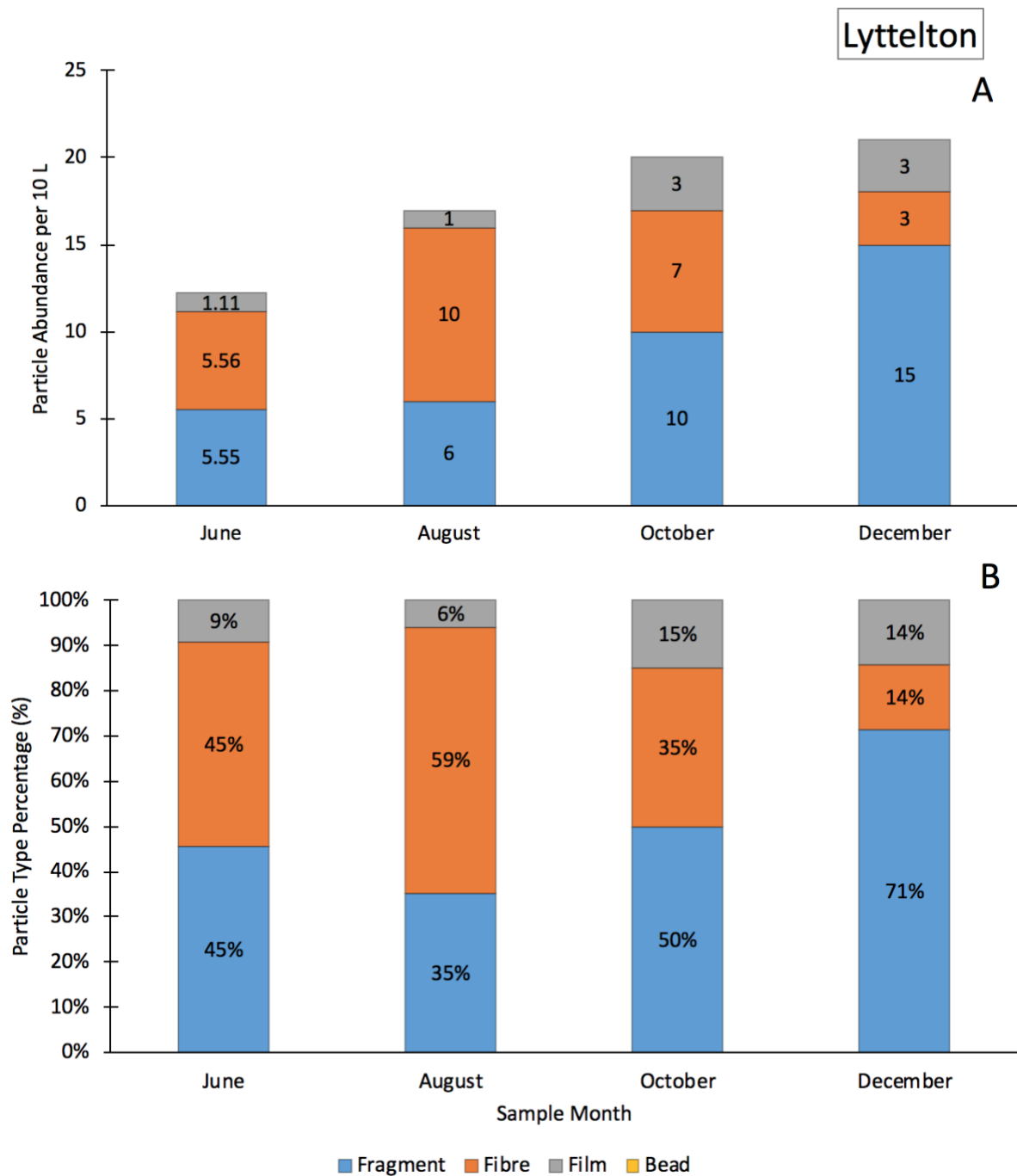
Figure 3-15. Microplastic and morphotype abundance in Lyttelton WWTP effluent in June, August, October, and December. (A): Total and morphotype abundance. (B): Morphotype proportion per sample.

3.4.2   Temporal variability of polymer type

Microplastic polymer type proportion for the Christchurch effluent varied between sample months, with fewer polymer types seen in June (Figure 3-16). The predominant polymer types differed each month, with polyester in June, polypropylene in August, silicone (Other) in October, and rayon in December. There was no similarity between polymer type proportions over the months. In the Kaiapoi WWTP, polymer types present in June, October, and December effluent varied (Figure 3-17), with no polymer type dominating in December. In the June effluent, polyester was the most abundant polymer type, and in October, silicone was the most predominant. Polyester was the only polymer type present in August (n = 2). In the Lyttelton effluent (Figure 3-18) similar polymer types were present with all months containing acrylic, polyester, polyethylene, polypropylene, and rayon. Polyester and polyethylene were present in opposing proportion in June (polyester 55%, polyethylene 18%), to December (polyester 14%, polyethylene 57%). No difference in proportion was seen for polyester and polyethylene in August (polyester 29%, polyethylene 35%) and October (polyester 25%, polyethylene 30%).
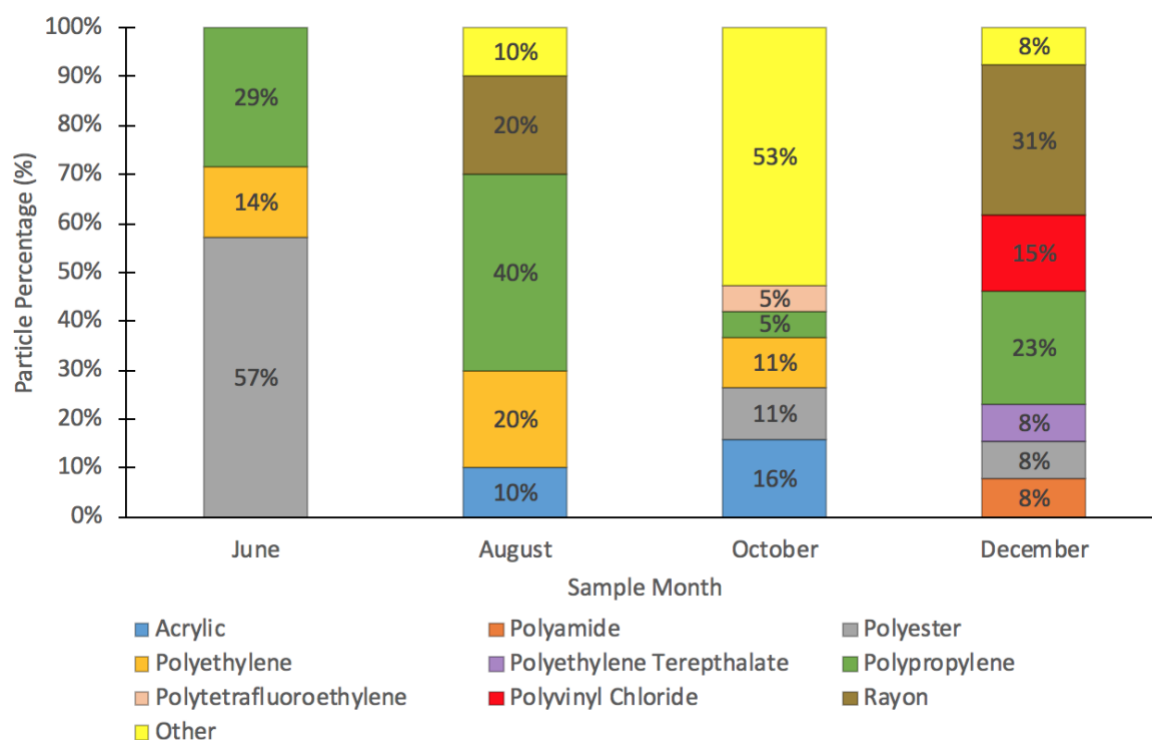
Figure 3-16. Microplastic polymer type in Christchurch effluent, during June, August, October, and December. 'Other': August = polybutene, October = silicone, December = polybutene.
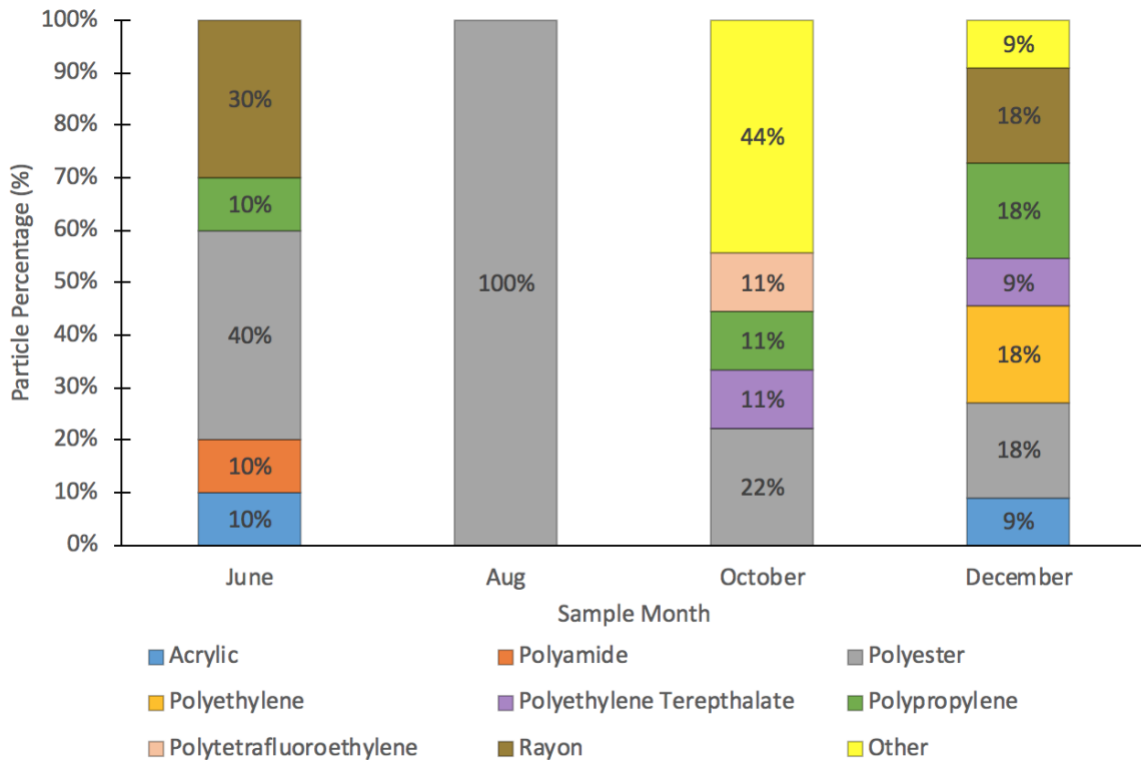
Figure 3-17. Microplastic polymer type in Kaiapoi effluent, during June, August, October, and December. 'Other': October = silicone, December = polyacetal-copolymer.
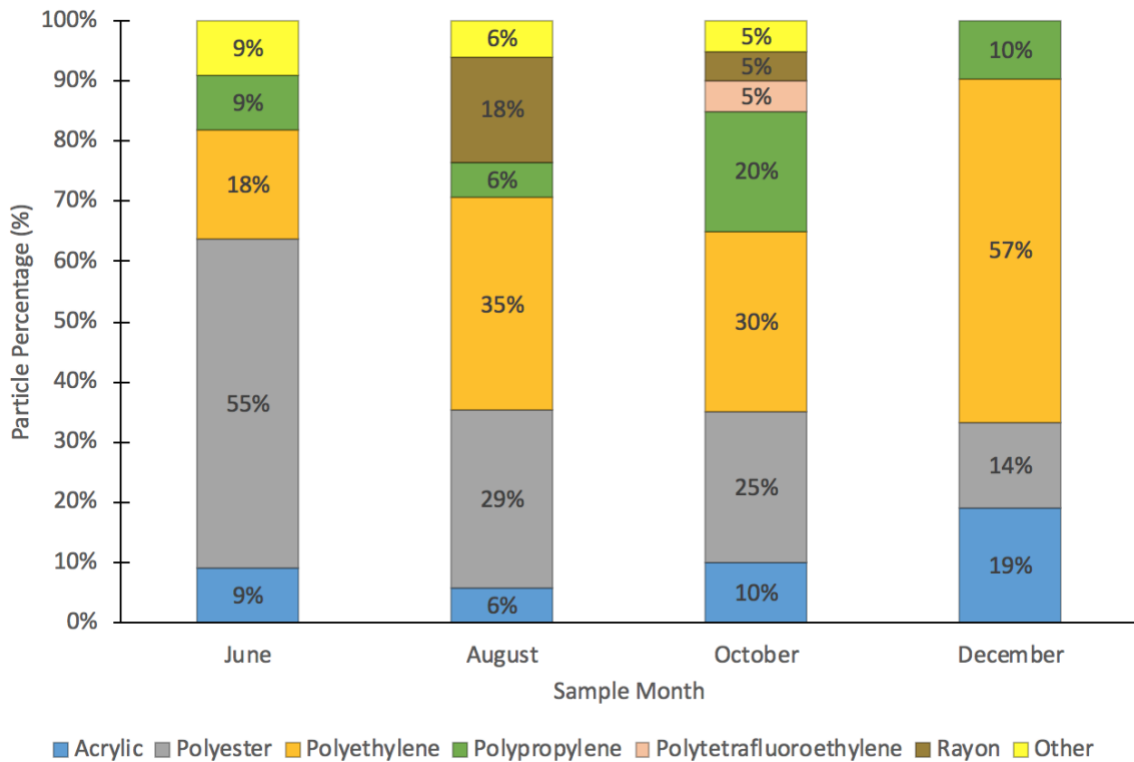
Figure 3-18. Microplastic polymer type in Lyttelton effluent, during June, August, October, and December. 'Other': June = silicone, August = polybutene, October = polybutene.

3.4.3   Temporal variation in microplastic particle colour

Across all the microplastic particles, colourless particles were the most abundant (51%), followed by red (11%), pink (9%) and purple (7%). Black, blue, green, grey, and white made up the remaining 22% of microplastics (Figure 3-19).
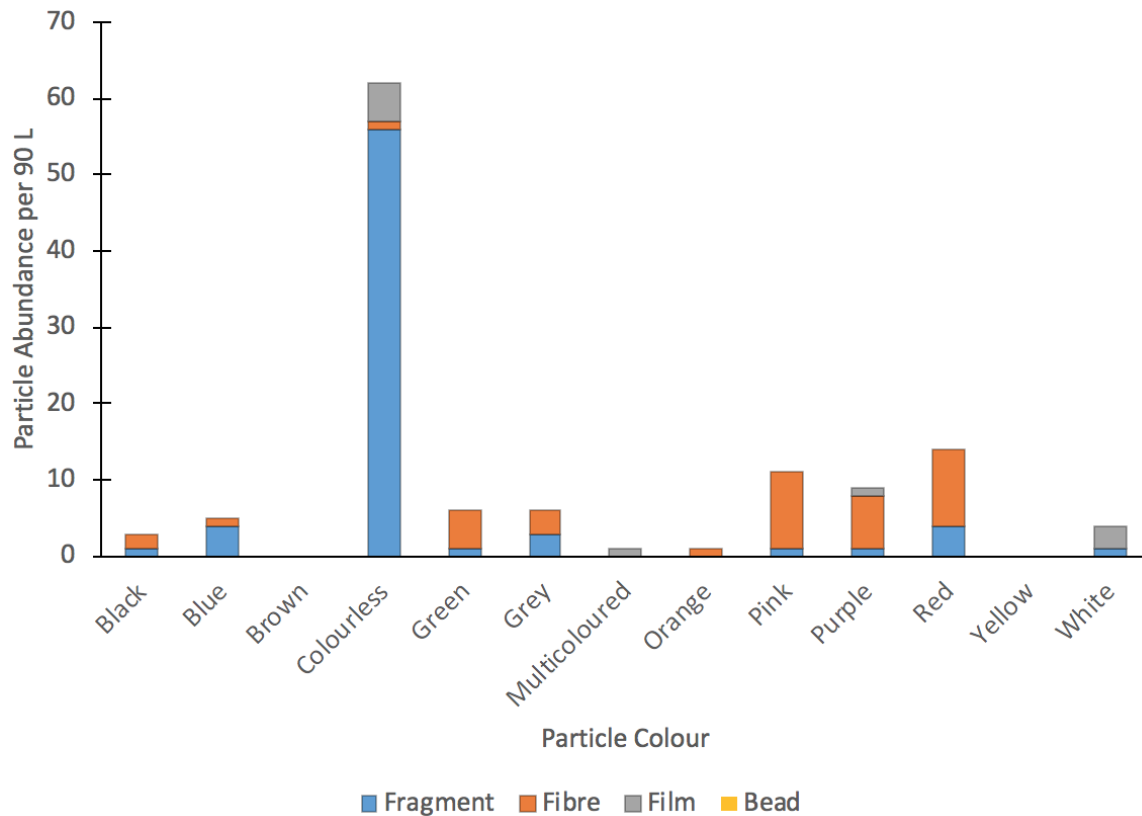
Figure 3-19. Microplastic colour distribution in effluent from Christchurch, Kaiapoi, and Lyttelton, from August, October, and December.

3.4.4   Estimated discharge of microplastics to the receiving environment

Using daily flow data for each WWTP (Table 2-3) and the average abundance of microplastics (June weekday and weekend effluent, and August, October, and December effluent for Christchurch, Kaiapoi, and Lyttelton WWTPs; the mean of the June weekday and weekend effluent was used for Governors Bay) the predicted daily and yearly discharges of microplastics to the environment were calculated (Table 3-2). Removal efficiency varied with WWTP, with Christchurch WWTP the most efficient, and no removal seen at Governors Bay.

Table 3-2. Predicted daily and yearly discharge of microplastics to the aquatic environment from Christchurch, Kaiapoi, Lyttelton, and Governors Bay WWTPs.

WWTP	Particles per litre of effluent (particles/L)	Daily discharge of microplastics (particles/day)	Yearly discharge of microplastics (particles/year)	Average reduction efficiency (%)
Christchurch	1.3	2.4×10^8	8.9×10^{10}	72
Kaiapoi	0.7	7.8×10^6	2.8×10^9	47
Lyttelton	1.7	1.4×10^6	5.2×10^8	69
Governors Bay	2.0	3.4×10^5	1.3×10^8	-6

3.5   Discussion

3.5.1   *Concentration of microplastics in influent and effluent*

In this study microplastics were more abundant in influent (2.4 particles/L) than effluent (1.3 particles/L). These measured concentrations were within the lower range of those reported in the literature (1 – 2.5 particles/L for influent, and ~0.0007 – 1.54 particles/L for effluent).[25, 54-55, 69b, 69e] At present, no standard sampling design, method extraction, and analysis protocol exists for the investigation of microplastics in WWTPs. The study designs in the literature varied with number of WWTPs, replicates, wastewater volume, sample type (ie grab, on-site filter, composite sample), sieve size fractions, extraction method, and analysis (ie visual vs spectroscopic validation, full sample set vs subsample). This study was unique to the literature as the 24-hour composite samples of influent and effluent in the characterisation study were collected to match with the average hydraulic retention times of each WWTP. The temporal study was also unique in that the sampling of effluent was assessed over the winter – summer season for three WWTPs. In this study, the concentrations reported may be an underestimation due to the smallest sieve size fraction analysed being 300 μm, however, the smallest particles detected were 30 μm in diameter. The concentrations reported in the literature may also be an underestimation of the true abundance of microplastic particles, as the sieve size fractions assessed in the literature varied, with a few studies reporting particle sizes smaller than that of the smallest sieve pore size.[69a, 69b, 69e]

3.5.2 Weekday and weekend abundance of microplastics

This study investigated whether a difference existed in the microplastics present in weekday and weekend samples of wastewater influent for WWTPs. The microplastic abundance in influent was higher in Kaiapoi and Lyttelton WWTPs on a weekday compared to weekend, with the opposite seen in Christchurch and Governors Bay, with a higher abundance on the weekend compared to weekday (Figure 3-5). No significant trend was observed between WWTPs to indicate whether particle abundance was higher on a weekday or weekend. Understanding of weekday and weekend abundance of microplastics in WWTPs is more complex than lifestyle variation between the traditional working week and weekday. Christchurch and Kaiapoi WWTP receive septic tank waste on different days of the week which may influence weekday and weekend contribution.[88] These two WWTPs are further influenced by pumping of sewage long distances to the respective WWTPs, which may take from a number of hours to a full day.[88] Lyttelton and Governors Bay WWTPs are not significantly affected by pumping times of sewage as they serve a relatively small area, and microplastic abundance may be more representative of the incoming sewage on the given day.[88]

A previous study in Finland has showed microplastic concentration to vary across three days of the week in influent (900, 390, and 630 particles/L on Tuesday, Thursday, and Sunday respectively) and effluent (as 2.8, 1.4 and 1.4 particles/L on Tuesday, Thursday, and Sunday respectively.[69f] Sampling of influent and effluent were repeated a week apart in a second study from the Netherlands, with varying concentrations detected in influent (86 and 60 particles/L for the first and second week respectively), and effluent (18 and 36 particles/L for the first and second week respectively), demonstrating the variation between sampling events.[58]

3.5.3 Temporal abundance of microplastics in effluent

A trend of increasing microplastic abundance was seen in the Christchurch (Figure 3-13) and Lyttelton (Figure 3-15) effluent across the months of June to October. Abundance in effluent increased in Lyttelton in December, however, abundance decreased in December in

Christchurch. Kaiapoi abundance increased from August to December, but abundance was comparatively high in June with October and December (Figure 3-14). These results do not show a consistent trend within WWTPs. More frequent sampling over the course of a few months is required to capture temporal variability.

As there is a lack of data investigating seasonal concentration of microplastics in WWTPs, only limited comparisons between temporal trends in this study and the literature can be made. One study in Finland sampled influent and effluent on a Monday every two weeks, across three months (autumn – winter).[69e] Microplastic concentrations across both mediums followed similar patterns, however, there was significantly greater variability in particle abundance in the influent samples across the weeks sampled. Their conclusions suggested that single sampling events do not give an accurate representation of microplastic abundance in WWTPs.[69e]

Rainfall, stormwater, and groundwater intrusions may affect the concentration of microplastics in WWTPs. In this study, only a few sampling occasions occurred in instances of high rainfall (>5 mm, Appendix 4). In June characterisation samples (Figure 3-5), high rainfall was seen during weekday influent sampling of Christchurch WWTP (20 mm and 4 mm), with low rainfall during weekend influent sampling (0.2 mm and 0 mm). Abundance was lower on the instance of high rainfall (n = 26) than little rainfall (n = 48). In contrast, abundance in Kaiapoi weekday influent was higher (n = 16) in instances of high rainfall (2.2 mm and 20 mm) compared to weekend influent (n = 9) in instances of low rainfall (0 mm and 0.2 mm).

In the temporal samples, particle abundance in the Christchurch December effluent (11.2 mm) was lower than the corresponding October effluent and higher than June and August effluent (Figure 3-13). Rainfall on the sampling days in August and October were low (0.2 mm and 2.8 mm in August and 0.6 mm and 0.2 mm in October). In contrast, rainfall was high on the sampling days in June (20 mm and 4 mm). Rainfall has been found to influence microplastic concentration in WWTPs in one German study. Sampling of effluent occurred over two months, with a total of three grab samples taken in dry weather conditions, and four grab samples taken in wet weather conditions. A total of 3 microplastics/L were detected in dry weather conditions, with 2.3 fragments/L and 0.73 fibres/L.[69c] A higher abundance of

microplastics were found in wet weather conditions, with a total of 6 microplastics/L, consisting of 4.5 fragments/L and 1.5 fibres/L.[69c] The study concluded a higher abundance of microplastics during rainfall events was due to the higher flow velocity during the WWTP, reducing the settling potential for microplastics.[69c] In heavy rainfall and storm events, a higher proportion of untreated wastewater may be released (Section 1.3.3). In Canterbury, contribution from stormwater and groundwater intrusion into WWTPs is significant, due to breakages in pipes resulting from the 2010 and 2011 earthquakes.[88] No weekday/weekend or seasonal trend in rainfall was observed in this study, indicating more complex factors may be involved, including infiltration from groundwater and stormwater may influence microplastic concentration in the region.

3.5.4   Observations on microplastic morphotype

Particle morphotype did not influence removal from influent to effluent of a WWTP (Figure 3-6). Fragments and fibres were both present in high abundance. Films and beads were present in very small abundances, so inferences on their removal cannot be made. These results differ from previous studies where a decrease in proportion of fibres from influent to effluent was observed, indicating selective removal of fibres.[54b, 69f]

The difference in morphotype proportions between weekday and weekend samples may also indicate differences in lifestyle between the traditional working week and rest weekend. Proportion of fragments were significantly higher in weekday influent samples from Christchurch, Kaiapoi and Lyttelton WWTPs, compared to their corresponding weekend influent samples which displayed a significantly higher proportion of fibres (Figure 3-6). The higher proportion of fibres on a weekend may indicate increased instances of clothing and textiles laundered at the end of the working week. Governors Bay WWTP displays a near equal proportion of fragments and fibres in weekday influent, with proportion of fragments increasing as the major morphotype present in weekend influent. This observation may be due to how geographically discrete Governors Bay is to Christchurch City, and more residents may choose to work from home, (or are retired), which may not alter the microplastic difference between weekdays and weekends. A few small businesses operate in Governors

Bay (compared to Christchurch, Kaiapoi, and Lyttelton)[89] which may not significantly influence any weekday or weekend microplastic concentrations. Morphotype variation was not assessed seasonally in the sampled literature.

No significant trend in morphotype was seen across June weekday and weekend effluent samples (Figure 3-5, 3-6). It was hypothesised by Browne *et al.* (2011) that more synthetic fibres would enter the marine environment via WWTPs in winter, due to the greater amount of clothing worn and the type of textiles used in winter, and a 700% increase in washing machine usage.[25, 90] In this study, the proportion of fibres was higher in June (weekday) and August effluent for Kaiapoi (Figure 3-14) and Lyttelton (Figure 3-15) WWTPs then subsequent warmer months, indicating that more synthetic textiles may be worn and laundered in colder months. However, no temporal trend in fibre abundance was identified for the Christchurch WWTP (Figure 3-13).

No particular morphotype was consistently dominant in the temporal effluent samples. In contrast, a high proportion of fibres (as opposed to fragments) were found in the effluents of a number of previous studies from Australia, France, Italy, and The Netherlands.[25, 52, 55, 58, 69b] Of particular interest is the high proportion of fibres present in the effluent even after advanced treatment processes in the Australian study.[55] In contrast, higher proportions of fragments than fibres were detected in the effluent of a number of other studies from Denmark, Finland, Sweden, and the USA.[54, 69d, 69f]

An aggregate of synthetic fibres mixed with cellulose fibres was detected in an influent sample from Christchurch WWTP (weekend sample). No fibre aggregates were detected in effluent samples. Synthetic fibres have been previously hypothesised to aggregate with cellulose fibres from toilet paper and plant material and be removed in bulk along with other settled flocs during treatment process.[54a, 91] The aggregation of fibres removed in sludge from the treatment process could skew the spread of fibres in produced biosolids. It is important that further investigation into the distribution of fibres in sludge and biosolids is undertaken.

3.5.5　Observations on microplastic polymer type

Microplastic polymer type has been linked to, but is not dependent on, its fate in the WWTP process. The specific density of each polymer type plays an important role in determining the settlement behaviour of microplastic within a body of water (Section 1.3.2), with low-density and high-density polymer types predicted to be selectively removed during the WWTP process. In this study, low-density (eg polyethylene and polypropylene) and high-density polymers (eg polyester) were present in significant amounts in effluent samples from both the characterisation (Figure 3-10) and temporal sampling studies (Figure 3-16, 3-17, 3-18).

Little difference was found between the polymer types present in weekday and weekend influent and effluent samples of an individual WWTP (Figure 3-10), indicating the variability of contribution from household, commercial, and industrial wastewater inputs. The absence of polymer types in corresponding effluent (that were present in influent) may again indicate the density-based reduction of a certain polymer type. Polymer types present in small proportions cannot be confirmed as being selectively-reduced based on their polymer type, as they are present in such low abundances. A small proportion of polymer types present in the effluent in this study were not present in the corresponding influent. Polymer types only present in effluent highlights the variation present within wastewater, and the diverse functions of a specific polymer type. One study in Italy detected certain polymer types present in the effluent only, suggesting the WWTP equipment itself may act as a source of microplastics to the environment.[69b] More large-scale investigations of polymer type proportion in influent and effluent are required (including polymer type analysis of WWTP equipment), due to the ubiquity of plastic and variability of wastewater.

Polymer type may not influence the removal of a microplastic particle. In this study, the most abundant polymer types in influent were polyester, polyethylene, acrylic, and polypropylene, consistent with the literature.[69a, 69b, 69d] In effluent, polyester, polyethylene, acrylic, polypropylene, and rayon were the most abundant polymers, which were consistent, with the exception of polyamide being more abundant in the literature than rayon.[25, 55, 69b, 69d] These studies, however, did not discuss the influence of density in the distribution of polymer type between influent and effluent.

The variation in polymer type in this study and in the literature may indicate that there are more complex factors determining the fate in WWTPs than specific density of the polymer types. Buoyancy may also be influenced by manufacturing process and polymer use, for example, some plastic products (such as polystyrene packaging) may be produced with pockets of air to increase the buoyancy of a specific polymer type.[92] Fouling in the aquatic environment may occur as quickly as a few minutes, to an hour,[93] and can alter the density of particles, causing polymer types of a lower density to sink.[54a] In contrast, fouling may modify the surface properties of the hydrophobic microplastic, where it may have a greater affinity for aggregation with other bacterial assemblages on the surface.[54a] In WWTPs, particles may become trapped in unstable flocs, which may prevent removal through surface skimming or sedimentation.[54a] There is a need for sinking and hydrological flocculation studies with representative biofilms of WWTPs to understand the fate of polymer types in WWTPs.

3.5.6   Size distribution of microplastics between influent and effluent

A high proportion of microplastic particles in the influent and effluent characterisation samples (Figure 3-7, 3-8) were skewed towards the lower end of the size distribution (<1 mm), potentially due to fragmentation occurring prior to and throughout the WWTP process. Overall there was no difference in particle size distribution between influent and effluent from Christchurch, Lyttelton or Governors Bay WWTPs, indicating non-selectivity for the removal of microplastic particle based on size. Similar particle sizes observed between influent and effluent may also indicate that microplastics may not be fragmented during treatment. The difference observed in Kaiapoi may be due to the fact that larger microplastics may be heavier and are more likely to drop out of the water column in wetlands.

Microplastics close to the specified pore diameter of a particular sieve were present in samples (Figure 3-7), with particles 1500 – 4000 μm largely missing from the dataset. This may be due to the inclusion of the 2 mm sieve to catch larger organic materials (seeds and grit). The contents of the sieve were visually inspected for microplastics, and if any were detected, were picked out and placed onto the 1 mm sieve.

In contrast to the size distribution in this investigation, one study from France found the majority of microplastics in influent to fall in sizes between 1000 – 5000 µm.[52] The distribution in effluent of the French study was comparable to the distribution in this study, with the majority of particles between 100 – 500 µm (Table 4.1).[52] A second study from Italy found the majority of microplastics to fall in size fractions 100 – 500 µm and 1000 – 5000 µm in influent, compared with the majority in 100 – 500 µm in effluent (Table 3-3).[69b]

Table 3-3. Size distribution of microplastic particles in influent and effluent from Dris et al. (2015)[52] and Magni et al. (2019)[69b]

Sample Type	10 – 100 µm	100 – 500 µm	500 – 1000 µm	1000 – 5000 µm
Dris *et al*. (2015)				
Influent	NA	29%	26%	45%
Effluent	NA	66%	43%	7%
Magni *et al*. (2019)				
Influent	12%	36%	17%	35%
Effluent	27%	52%	7%	14%

NA = Not assessed.

Wet sieving of wastewater samples was necessary to enable both resolution and separation of microplastic particles from the digested solid matrix. This could only be achieved by separating microplastics by particle size on five different-sized sieves. As shown in this study, microplastics smaller or even larger than the specified pore size on a particular sieve were present. A large proportion of microplastics were smaller than 300 µm, which were present on both the 300 µm and 1 mm size fraction filters. Smaller microplastic particles may adhere to larger organic material or even to the sieve itself, compared to larger particles which may pass through a sieve in a different orientation. It is recommended that each microplastic particle is measured for this reason, if possible. The size distribution or individual measurement of microplastic particles are not frequently recorded in the literature.

3.5.7 Colour of microplastic particles in influent and effluent

In the characterisation samples, the most abundant colour of particles in influent were blue and green, and blue and red in effluent (Figure 3-11). The temporal samples, in contrast, showed colourless particles to be the most dominant, followed by red, pink, and purple in smaller percentages (3-19). These proportions from the characterisation study were consistent with a previous study from Scotland, where colour was documented in influent and effluent with the majority of particles red (26.7%), blue (25.4%) and green (19.1%).[69a] A number of coloured microplastics particles displayed signs of weathering, exposing the transparent particle underneath (Figure 3-20). The large proportion of colourless particles in the temporal effluent may be from the weathering of colour during the WWTP process. Discolouration and yellowing of microplastic particles may also occur over long periods of time in the environment and can be used as an indicator of particle age.[94]
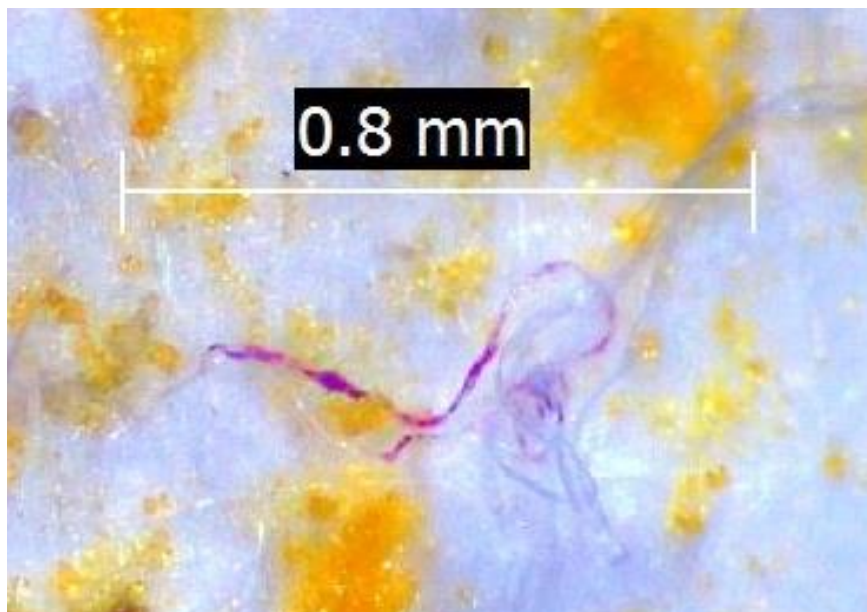
Figure 3-20. Loss of colour from purple to transparent observed in fibre from Christchurch effluent (October).

3.5.8 Reduction of microplastics throughout WWTPs

The abundance of microplastics decreased from influent to effluent, with average removal efficiencies ranging from no removal to 72% (Table 3-1). Reduction rates from Christchurch

and Lyttelton WWTP (72% and 69% respectively) are comparable with those reported in the literature (72%).[58] The largest difference in reduction was observed at Kaiapoi WWTP between weekdays and weekends (38% and 56% respectively), highlighting the variability of particle abundance each day. No reduction was observed at Governors Bay WWTP, however, an average increase of microplastic from influent to effluent was observed (+6%). Increase of particle abundance from influent to effluent is not expected, however, it is not impossible, due to the potential for fragmentation of larger particles during the treatment process, multiplying the abundance, which may mask any removal. A greater volume of wastewater, investigation into the sludge, and more frequent sampling of WWTPs would be required, to further assess the microplastic fate at this WWTP. Increase of microplastic abundance through the WWTP process may also arise from airborne contamination, and particles fragmenting from WWTP equipment.[69b] The decrease of microplastics during the treatment process highlights the potential removal of microplastics in sedimentation and surface skimming of sludge.[69a]

3.5.9   Daily and annual discharge from each WWTP

The predicted daily discharge of microplastics to the environment from WWTPs in this study (Table 3-2) ranged from 3.4×10^5 to 2.4×10^8 particles, which is consistent with the high values estimated from the literature ($3.6 \times 10^4 – 6.5 \times 10^7$).[54, 69a] The concentrations of microplastics entering the receiving environment daily are of concern for the continuous release of wastewater. Annual concentrations of microplastics entering the receiving coastlines in Canterbury in this study were estimated to range from 1.3×10^8 to 8.9×10^{10} microplastic particles (Table 3-2).

3.5.10   Variation in WWTP treatment types

Investigation into the different treatment types at four WWTPs and their influence on the reduction of microplastics from influent to effluent is complex. All WWTPs assessed in this study employed tertiary treatment of effluent, but there were significant differences between the treatment stages. The aeration step was present in all WWTPs. Christchurch WWTP

contained the most treatment steps and the shortest retention time and returned the highest removal efficiency (72%). The Kaiapoi WWTP features fewer treatment stages, however, had the longest residence time, and demonstrated a lower microplastics removal efficiency of 47%. Lyttelton and Governors Bay WWTPs have similar treatment stages and retention times but were observed to have significantly different removal efficiencies of 69% and -6%, respectively. The variation between tertiary treatments shown in this study suggests that there are more complex factors influencing the removal of microplastics during wastewater treatment. The removal efficiencies from the Kaiapoi and Governors Bay WWTPs were not comparable with the tertiary WWTPs in the literature. This difference may be due to these WWTPs being less-sophisticated examples of tertiary treatment plants, as well as serving relatively small populations compared with those in the literature.

In this study, particle abundance in effluent is more strongly-influenced by the population size associated with a WWTP, than the calculated removal efficiencies of the WWTP. The Christchurch WWTP had the highest removal efficiency but had a higher number of particles in the effluent (1.3 particles/L) than the Kaiapoi WWTP, which had the lowest removal efficiency, and the lowest abundance of microplastics in the effluent (0.7 particles/L). Lyttelton and Governors Bay had similar concentrations of microplastics in effluent (1.7 particles/L and 2.0 particles/L, respectively), but had very different removal efficiencies. No trends in morphotype, size, or polymer type in effluent between WWTPs based on their treatment stages or hydraulic retention times were identified to indicate a difference between treatment type in this study. However, an Australian study showed the trend of decreasing concentrations of microplastics detected in effluent from primary, secondary, and tertiary WWTPs respectively.[55] No comparisons between the removal potential based on abundance, morphotype, and polymer type between the WWTPs in this Australian study could be made, as influent was not sampled. Because of the variation between WWTPs shown in this study, comparisons between different treatment types from WWTPS in the literature cannot be readily made due to the variation in study designs.

3.6   Limitations

3.6.1   Sampling

Due to time constraints, sampling was limited to one occasion for each characterisation sample collected in June, and sampling frequency was decreased for the temporal samples to one effluent sample at three WWTPs, bi-monthly from August to December. Repeated weekday and weekend influent and effluent sampling within a month, and over a series of months would allow for a more accurate characterisation of an individual WWTP to account for daily variability. Whilst 10 L of wastewater was labour-intensive to process, some studies have used onsite sieving of wastewater. However, the amount taken in these studies was variable due to the instance of clogging and were not representative of a 24-hour sample.[55, 69a, 69f] Rainfall measurements were recorded (Appendix 4) from the Meteorological service of New Zealand (MetService) website.[95] Measurements on the website were taken for the two-day period that the sampling fell across. In future studies, flow data on days of high rainfall events would be useful to understand the correlation between concentration and flow.

Effluent from Christchurch WWTP was sampled prior to discharge into the oxidation ponds, so values may not be indicative of what is entering the Canterbury coastline through the outfall. Effluent from Kaiapoi, Lyttelton, and Governors Bay were sampled before discharge through their respective ocean outfalls. As the Kaiapoi effluent was sampled after treatment through the wetland, there was the potential for microplastics to travel long distance through shallow, slow-flowing water bodies.

3.6.2   Sample handling after preparation

The majority of wastewater samples contained high levels of organic and particulate material which were retained on the sieves. Seeds, insect exoskeletons, grit, and silt were not able to be entirely digested, and were present in large quantities on some glass filters. The undigested material was displaced using metal tweezers to uncover any buried microplastics. A small proportion of the total microplastics present on the filters may not have been identified as some particles may have been obscured by particulate material. Due to the

higher level of particulates present on glass fibre filters from sieves 50 μm and lower (Figure 3-21), sieve size fractions of 300 μm and 1 mm were analysed only. Size distribution on the 300 μm and 1 mm sieve were not exclusive to the sieve size, and so the results display the pooled sieve size fractions together.

Despite checking each glass filter three times for microplastics during microscopic analysis, values may be an underestimation, due to particles buried, unable to be detected at the highest microscope magnification (32x) and blending in to the background based on their colour. Smaller particles were difficult to pick up with tweezers, and others were brittle and would fragment when touched, as described in the literature.[24]

Figure 3-21. High levels of organic and particulate material present on filters from 50 μm sieves, from Governors Bay Weekday Influent.

3.6.3   FTIR limitations

Despite a lower detection limit of 7 μm of the FTIR used, the spectrum produced in transmission mode for particles <50 μm were weak or had high interference. Reflectance and transmission mode did not return adequate spectra for thicker particles. The diamond compression cell was employed for small particles and thick particles and the majority were

able to return a spectrum in transmission mode. However, surface fouling hindered the return of suitable spectra for many microplastic particles, which was also seen in the literature.[69f] Acceptable spectra from fouled microplastics were achieved by gently washing the particle in the drop of ethanol on the CaF_2 disk (used as a transfer aid), with greater agitation required to remove fouling on some particles. Overall the lowest achievable detection limit for this study was 30 μm.

3.6.4   Results limitations

The removal efficiencies were calculated based on the results from the average of June weekday and weekend paired influent and effluent samples. Whilst the average hydraulic retention times of WWTPs were accounted for and 24-hour composite samples were collected, the retention times may differ based on the instantaneous flow across the period of a day. The flow data used was an average across a whole year.

This study is a small preliminary investigation of the difference in abundance of microplastics in influent and effluent from a variety of WWTPs, and whether WWTPs are a significant source of microplastics to the aquatic environment. The values calculated for the daily and yearly average of microplastics released to the environment are only an estimation based on the results of this study. More sampling is required to accurately assess the average daily and yearly discharge of microplastics.

3.6.5   Statistical analysis

Due to the nature of the sampling design, statistical inferences between samples could not be made. To test the statistical differences between two proportions (for example of a single WWTP, to test the proportion of microplastics by weekend/weekday or influent/effluent), a z-test would require a sample number greater than 20 – 30. Assumptions of normality, equal variance, and independence would also be required. Differences between influent and effluent would not be able to be made, as the concentration in effluent is not independent from influent. Due to the nature of the variables included in this study (particle counts,

morphotype counts, polymer type proportion, size distribution, colour distribution) it cannot be assumed that the data is normally distributed. Due to the ubiquity of microplastics in WWTPs, equal variation between a sample is not observed. To test the difference between multiple WWTPs, an analysis of variance (ANOVA) statistical test could have been made, if the same sample size requirements and assumptions as the z-test were met.

4 Conclusions, implications, and further work

4.1 Chapter layout

A summary and conclusion of the findings from this study is presented in Section 4.2. Section 4.3 discusses the implications of WWTPs as a source of microplastics to the environment. This discussion includes the fate of microplastics in different stages of the WWTP, which may be removed through the skimming and sedimentation of sludge or settling in sediments of constructed wetlands/oxidation ponds. The fate of microplastics in the aquatic environment along with the potential cultural and ecological impacts of microplastics released from WWTPs are discussed, and recommendations for the mitigation of microplastics entering WWTPs and further work are presented in Sections 4.4 and 4.5.

4.2 Conclusions

This study aimed to characterise microplastics from four WWTPs in terms of the abundance, morphotype, size, and polymer type of microplastics in influent and associated effluent across weekdays and weekends. Temporal variability of microplastics in effluent from three WWTPs was investigated, to assess the abundance and type of microplastics bi-monthly from winter (June) to summer (December). Microplastics were detected in influent and effluent (an average of 2.4 and 1.3 particles/L respectively) at concentrations which were comparable with the literature.

Microplastics were detected in both the influent and effluent samples of all four WWTPs examined. Removal of microplastics from influent to effluent was observed in three of the WWTPs and are thought to be present in sludge products or drop out of the water column into a wetland or oxidation pond sediments. Low removal efficiencies compared to the literature were in this study, however concentration in effluent was comparable. No temporal trend in the abundance of microplastics (weekday vs weekend, and seasonally) was observed potentially due to the relatively small sample volume. Fragments and fibres of a wide variety of polymer types were detected in high proportions in effluent. No significant difference in particle morphotype, polymer type, or particle size was observed between influent and effluent samples, suggesting more complex factors in microplastic removal within WWTPs.

4.3 Implications

4.3.1 Fate in sludge/solids

Microplastics absent from the final effluent may have been removed with the skimming and sedimentation of sewage sludge which is removed throughout the WWTP process. Reduction of microplastic from influent to effluent was seen in this study and in the literature, suggesting a high proportion of microplastics to be retained in the sewage sludge. Abundance of microplastic in sewage sludge from the WWTPs in this study is unknown. Sludge from Christchurch, Lyttelton, and Governors Bay WWTP are thermally dried at 37 − 55°C at the Christchurch WWTP into biosolids. Approximately 3,500 tonnes (dry weight) of biosolids are produced annually at Christchurch WWTP.[85] All biosolids produced are used to rehabilitate the land of the Stockton Mine, on the West Coast of the South Island.[85] Investigation into the biosolid application site is needed to understand the fate of microplastics in the terrestrial environment. Sludge is not physically removed at Kaiapoi, however, remains in the treatment plant process, where it drops out of solution during wetland treatment.[83]

Whilst mechanical, photo-oxidative, chemical, and biological fragmentation of microplastics during wastewater treatment has been hypothesised, little is understood about the fate of microplastics during dewatering and thermal drying of sewage sludge in the production of biosolids. Microplastics present in sewage sludge are destroyed when sludge is incinerated.[58] An average of 5 microplastics per 5 g (dry weight) sample was found, indicating that microplastics are present in dried biosolids.[54a] These results may not be representative of a true sample, as no polymer type proportion comparison was made before and after thermal drying, and some polymer types could be lost.

High abundances of microplastics in sludge have been reported in the literature (Table 1.3). The sample size collected was small in these studies, ranging from 11 − 30 g (wet weight), 3 − 20 g (dry weight), and 50 mL. In these studies, a single grab sample of sludge and biosolids were collected, which may not give an appropriate representation of a temporal sample. Values may be an over-estimation, as the sample may be biased to the result of peak fluxes and peak microplastic concentrations. In one study, the suspended solids (SS) in influent was

compared to the SS in sludge (i.e. a concentration of 500 mg SS in each sample) to determine a representative sample based on the incoming concentration of microplastics.[54b] Based on their findings, three other studies estimated the daily removal of microplastic in sludge to range from 460 – 3400 million particles.[54a, 69b, 69e]

4.3.2   Fate in oxidation ponds/constructed wetlands

Effluent from Christchurch and Kaiapoi WWTPs pass through an oxidation pond (Christchurch), or constructed wetland (Kaiapoi) to further prolong treatment before discharge into the coast. Sediments of oxidation ponds and wetlands are hypothesised to trap microplastic particles present in outgoing effluent.[21, 51] In this study, the concentration difference prior to and after wetland or oxidation pond treatment was not investigated. Effluent from Kaiapoi WWTP was sampled after treatment through the wetland, demonstrating the capability of microplastics to pass through wetland treatment. Investigation into the concentration of microplastics prior to discharge into the wetland is required to assess the proportion of microplastics settling in the wetland. Effluent from Christchurch WWTP was sampled prior to oxidation pond treatment. Whilst concentrations of microplastics present in effluent from Christchurch WWTP is not an accurate indication of microplastic release through the New Brighton ocean outfall, further sampling of effluent water prior to outfall entry may give a more accurate representation of microplastics entering the ocean. Long residence times in open tanks, constructed wetlands and oxidation ponds may increase the incidence of airborne microplastics, increasing the abundance of total microplastic in effluent.[63]

Unfortunately, knowledge of transport, settling, and fate of microplastics in oxidation ponds and constructed wetlands is absent.[96] Shallow, low flow bodies of water like lakes and estuaries may be comparable to wetlands and oxidation ponds (despite water fluxes from tributaries in lakes and estuaries, as well as tidal patterns observed in estuaries). Settling patterns are not well understood, but a multitude of factors could contribute to the fate of microplastics in a wetland or oxidation pond. These include microplastic characteristics of

density, (including altered density due to fouling), shape and size, coupled with hydrological factors of residence time, flow, wind-driven surface currents, depth, and turbidity.[97]

An Italian study investigating microplastic concentrations in sediment of two lagoons receiving wastewater effluent may infer how microplastics may act in a constructed wetland or oxidation pond. Mean microplastic concentrations in each lagoon were 1,501 and 1,394 particles/kg (dry weight), respectively.[98] These values are comparable with those found in freshwater sediments (Section 1.2.1). The results found microplastic accumulation was higher in sites with low hydrodynamism, in the centre of the lagoon. Concentrations were lowest on the border of the lagoon, where water currents exceed 1 m/s. The highest concentrations were found in confined areas of the border, close to input sources.[98] These results suggest that hydraulic flow may influence microplastic settling in shallow water bodies.

Under certain circumstances microplastics trapped in sediments of wetlands and oxidation ponds may be released. For example, instances of high flow during rainfall and storm events may re-suspend microplastics settled in sediments of wetlands and oxidation ponds. Hydrology was found to affect the concentration of microplastics in tributaries of the Great Lakes of the USA. Concentration was higher in instances of high run-off, compared to low-flow conditions.[99] Mean microplastic concentration in riverbed samples from sites in Manchester, UK, decreased after a high flood event, from 6,350 to 2,812 particles/kg (wet weight).[100] Investigation into concentration of microplastics in sediments of these wetlands and oxidation ponds at Christchurch and Kaiapoi WWTPs before and after high rainfall events is required to understand the retention capabilities of the sediments in these shallow water bodies.

4.3.3   Microplastics discharge from WWTPs in Canterbury

Effluent from all of the WWTPs assessed in this study is currently discharged out to sea, with an estimated 9.2×10^{10} microplastic particles released to the Canterbury coastline annually.[83, 85-86] The concentrations of microplastics in effluent for Kaiapoi, Lyttelton, and Governors Bay are indicative of what is being released directly into the environment with the final effluent. Concentrations from Christchurch WWTP effluent are indicative of the amount released into

the oxidation ponds. Microplastics may pass through the oxidation ponds and enter the ocean through the outfall. Lyttelton and Governors Bay WWTPs (along with Diamond Harbour WWTP) will be decommissioned in the near future, with sewage diverted to Christchurch WWTP for treatment.[86] The results from Lyttelton and Governors Bay WWTPs are a good representation of small WWTPs serving small coastal communities in New Zealand. The contribution of microplastic to the environment from WWTPs has been estimated to increase with rising urbanisation of cities, leading to larger volumes of wastewater to process each day.[25] With diversion of sewage from Lyttelton, Governors Bay, and Diamond Harbour, the volume of wastewater treated at Christchurch WWTP will significantly increase, in addition to that resulting from predicted population growth (less than 1% growth per year).[101]

4.3.4   Cultural relevance

The majority of treated effluent in New Zealand (75%) is discharged directly into rivers or the ocean.[62] In Māori culture, bodies of water are sacred, and have a life-giving force (*mauri*), which should not be degraded by mixing with poor-quality water. Disposal of effluent into waterways and the ocean degrades the *mauri* of the water body, impeding the cultural practice of *mahinga kai* (food gathering) in these areas. The *mauri* is said to be restored to water from effluent once it has been passed through land for further treatment.[102] However, effluent should only be treated on non-productive land to separate human waste from cultivated food.[103] Land treatment of effluent may be preferred as a means of recycling water and nutrients, as opposed to depleting freshwater resources for irrigation, and using commercial fertiliser to increase soil nutrients.[61] From the findings of the assessed literature and this study, the re-use of treated effluent for land irrigation may also be a significant source of microplastics to the terrestrial environment.[104]

4.3.5   Fate of WWTP discharged microplastics in the environment

The fate of microplastics released into the coastal environment via WWTPs in Canterbury was not investigated in this study. Due to the complexity of microplastic fate based on polymer type and coastal morphology, estimations cannot be made from the literature. In their

assessment of sediment samples near a wastewater outfall in Antarctica, Reed *et al.* (2018)[74] speculated that the low concentrations of microplastics in a selection of sites were due to the presence of ocean currents, potentially transporting the microplastics away from the area. In contrast, in another study off the Belgian coast, concentrations of microplastics were significantly higher in harbour sediment (167 particles/kg, dry weight) than beach (93 particles/kg, dry weight) and off-shore sediments (97 particles/kg, dry weight).[35] The higher concentration found in the harbour could be due to the topographical and hydrological component differences to the beach and open ocean. A low flushing rate coupled with a narrow inlet entrance may cause tidal eddies to form.[105] Microplastic particles trapped in the tidal fluxes may settle in the bottom sediments, instead of being flushed out of the harbour.[35]

Microplastic fate in coastal environments involve (but may not be limited to) factors such as beaching, surface and subsurface mixing, biofouling, sedimentation and resuspension, horizontal transport, and ingestion by aquatic organisms.[24, 106] Mechanisms controlling the transport and sedimentation of microplastics in coastal environments are uncertain, but the primary factors involved include winds, tides, ocean currents, thermohaline gradients, and substrate type.[106] Microplastics have been discovered in coastal sediments around the Canterbury region at a concentration ranging from 0 – 45.4 particles/kg (dry weight). Concentrations were higher at exposed beaches, compared to harbour and estuarine sites.[79]

4.3.6   Risk to organisms in coastal environments

Microplastics are bioavailable to a wide range of marine organisms in the aquatic environment due to the variation in particle size, regardless of trophic level.[39] Smaller organisms may show selectivity for particles up to a certain size limit.[107] A variety of other factors may influence ingestion of microplastics. Bioavailability of particular polymer types may differ based on the zone within the water column the organism is present in. Polymers less dense than seawater may float on the surface of the water column and will be more bioavailable to surface feeding organisms.[39] More dense polymer types (including those which has had their density altered due to fouling) which may be present lower in the water column or in sediments, are more available to bottom-dwelling organisms. Defouling of

microplastics by foraging benthic organisms may also reduce the density of a particle, where it may be resuspended into the water column.[24] Fragmentation of microplastic in the environment increases total particle abundance, and as a result increases the availability to more organisms.[39, 41] In this study, a range of polymer types were detected in the effluent, which may be bioavailable to marine organisms throughout the water column.

Visual predators may mistake microplastic of the same colour as their prey, like white, tan, and yellow.[108] In one study from the USA, ocean water samples and fish guts were analysed for microplastic particles. Water samples returned equally high proportions of white and colourless microplastic spheres. The contents of the fish guts, however, only contained white microplastic spherules, which may indicate selective uptake based on colour.[109] A similar study in samples from the North Pacific Central Gyre found microplastic colours of white, colourless, and blue to be equally highly proportional in sea water and fish gut samples.[110] A third study with samples off the coast of Easter Island, in the South Pacific Subtropical Gyre, found selectivity in fish for blue microplastic particles, over white and orange which were also found in high quantities in the water column.[111] A fourth study from the Southeast Pacific Ocean analysing the gut of planktivorous fish found a wide variety of microplastic colours present, indicating non-specificity for prey based on colour.[112] The most abundant colours of microplastic in this study were blue, red, and colourless. More in-depth animal behaviour studies may be required to understand the selective ingestion of microplastic particles by a range of marine organisms.

Ingestion of microplastic differs between organisms. Microplastics caught in algal aggregates may be more available for ingestion by zooplankton and other herbivores/omnivores.[113] Benthic dwelling organisms may ingest microplastics while foraging on detritus.[113] Marine megafauna may ingest microplastics through trophic transfer, or the filtering of water.[40b] Other carnivorous predators may select for actively moving prey, so are not expected to directly ingest microplastics, but instead may indirectly ingest microplastics from their prey.[113] Trophic transfer of microplastic has been observed from the analysis of seal scats (kept in captivity) consisting of similar polymer types to those found in the fish (caught in the wild) that they are fed.[42b]

Filter feeding organisms like bivalves have been shown to passively ingest microplastic particles.[41] Two commercially grown species *Mytilus edulis* (mussel) and *Crassostrea gigas* (oyster) were found to contain on average 0.36 and 0.47 microplastic particles/g respectively.[43] In the same study, after a three-day depuration of the same species, microplastic concentration decreased to 0.24 and 0.35 particles/g for *Mytilus edulis* and *Crassostrea gigas* respectively.[43] A lab-based study found microplastics to translocate from the gut of *Mytilus edulis* to the circulatory system and haemolymph, where particles were observed to remain after 48 days.[41] Microplastics have shown to be present inside the gut of the culturally and economically important green-lipped mussel (*Perna canaliculus*), collected from coastal sites around New Zealand.[46c]

Microplastics originating from WWTPs may transport a number of sorbed hydrophobic chemical and biological contaminants to the marine environment, potentially exposing contaminants to a range of organisms.[44] Microplastics enhanced the uptake of triclosan, an antimicrobial, into the tissues of green-lipped mussels.[46c] Culturally important *kaimoana* (seafood) and commercially important species may be at risk in New Zealand from microplastics (and associated sorbed contaminants) in the coastal environment, including those released from WWTPs. As the health effects to humans are still unknown, the potential impacts from the presence of microplastics in seafood could put the industry at risk.

4.4   Prevention of plastic entering WWTPs

Presently, there has been little discussion on the next steps towards reducing the contribution of wastewater-derived microplastics to the environment. Employing greater levels of treatment and filtration at WWTPs has been proposed, however, these are costly to implement.[114] Greater attention is being diverted towards the prospect of biological degradation of plastic in WWTPs. Few species (including strains of *Pseudomonas*) have been identified to display plastic mineralisation capabilities, however, limited research is available.[67] Microbeads are regarded worldwide to enter the environment primarily through WWTPs, predominantly due to their usage in personal care products.[20-21, 115] In June 2018, New Zealand joined a host of other nations (including the UK, USA, and Australia) who banned the production and sale of microbead containing personal care and cleaning products.[116]

Whilst the microbead ban is a step in the right direction for reducing the number of microbeads entering WWTPs, microbeads make up a small proportion of the total microplastic particles in wastewater.[63] This is consistent with the findings of this study, with a total of two microbeads identified out of 412.1 particles across 250 L of wastewater. One of those was present in the effluent, indicating the potential for microbeads to pass through WWTPs. Microbeads are a morphotype which gains significant attention as the most concerning type of microplastic. Due to the dominance of synthetic fibres in the effluent of their studies, Ziajahromi *et al.* (2017)[55] and Lares *et al.* (2018)[69e] suggested that synthetic fibres are of greater concern and deserve more attention to the mitigation of their release.

An assessment into the factors influencing fibre release from textiles during washing confirmed that 1) fleece textiles shed more fibres than knits, 2) more loosely knit textiles shed more fibres, 3) worn textiles shed more fibres than new, and 4) washing textiles with detergent results in an increase of fibres shed than without detergent.[117] This particular study suggested that improved yarn and textile production techniques are required to be implemented to minimise the shedding of fibres from synthetic textiles.[117] Improved technology is also required in the design of washing machines, including production of removable filters to prevent fibre release from existing machines.[25, 118] In-wash products such as the Cora Ball and Guppyfriend Bag have been designed to trap loose fibres and prevent the release of fibres into the washing machine effluent.[119] Greater investigation into the effectiveness and consumer usability of these types of products is required.

In this study, fragments were slightly more abundant (52.9%) than fibres (40.5%). The origin of fragments is difficult to ascertain, and targeting specific plastic products is also difficult to implement.[118] Greater investigation in to the relative contribution of microplastic into residential, commercial, and industrial sewage is required to target the area of greatest contribution. Further investigation into the types of plastic products used may influence policy on the regulation, use, and disposal of plastic products in these settings.

4.5 Further work

This study was a small-scale investigation into whether WWTPs are a source of microplastics to the environment in Canterbury, New Zealand. All treated effluent samples from each WWTP contained microplastics, strongly suggesting that effluent is a source of microplastics to the environment. To understand this source better, recommendations for further work include an in-depth characterisation of microplastics present in each WWTP, including further temporal assessment over a variety of months. In future, more comprehensive studies, higher-volume wastewater samples, and more frequent sampling events over different seasonal periods would provide more representative sampling of influent and effluent at each WWTP. The inclusion of sampling at different treatment stages inside WWTPs (in particular wet sludge, dried biosolids, sediment of constructed wetlands/oxidation ponds, and land applied with biosolids) may also help elucidate the complex fates of microplastics from WWTPs. The findings from these investigations may also inform the design and re-engineering of certain treatment stages for greater removal of microplastics.

Worldwide, a standardised protocol for WWTP sampling and microplastic characterisation is needed to accurately assess the variation in microplastic abundance associated with different population sizes, treatment types, and seasonal and weather effects. Further investigation into the transport and fate of microplastics in the receiving environments from WWTPs is also needed to fully describe the issue of microplastic persistence and the role of WWTPs in microplastic pollution. Legacy effects of microplastics have been detected in soil, as microplastics in sewage sludge applied on land were detected 15 years after application.[73] The mobility of microplastics in these different mediums needs to be assessed to understand the long-term impacts of persistent discharge/application of microplastics to the environment.

Greater understanding of the chemical contaminants associated with plastics – those integrated as additives, and those that preferentially adsorb to the surface – and their leaching potential in different environments and organisms is also required to understand the direct and indirect toxicity of microplastics. This includes the potential 'rafting' of pathogens through WWTPs into the environment.

Greater understanding of the relative contributions from both commercial and personal activities to influent microplastic load is needed in order to write more effective, targeted regulatory policy to mitigate sources of plastic waste to WWTPs, and the receiving environment.

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Appendices

Appendix 1: Example spectra of microplastics isolated in the Characterisation and Temporal Studies
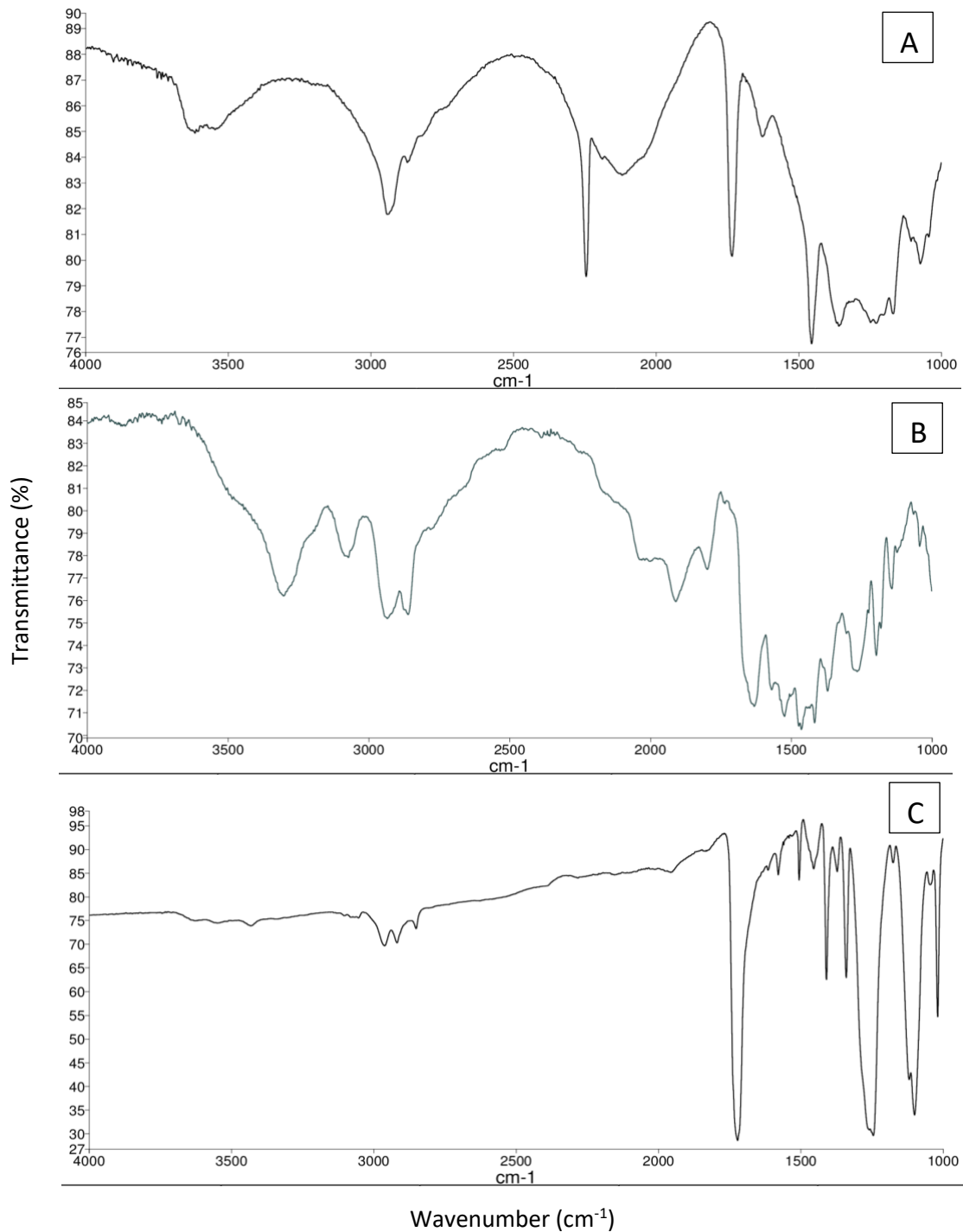
Figure A1: Example FTIR Spectra: (A): acrylic, (B): polyamide, (C): polyester.
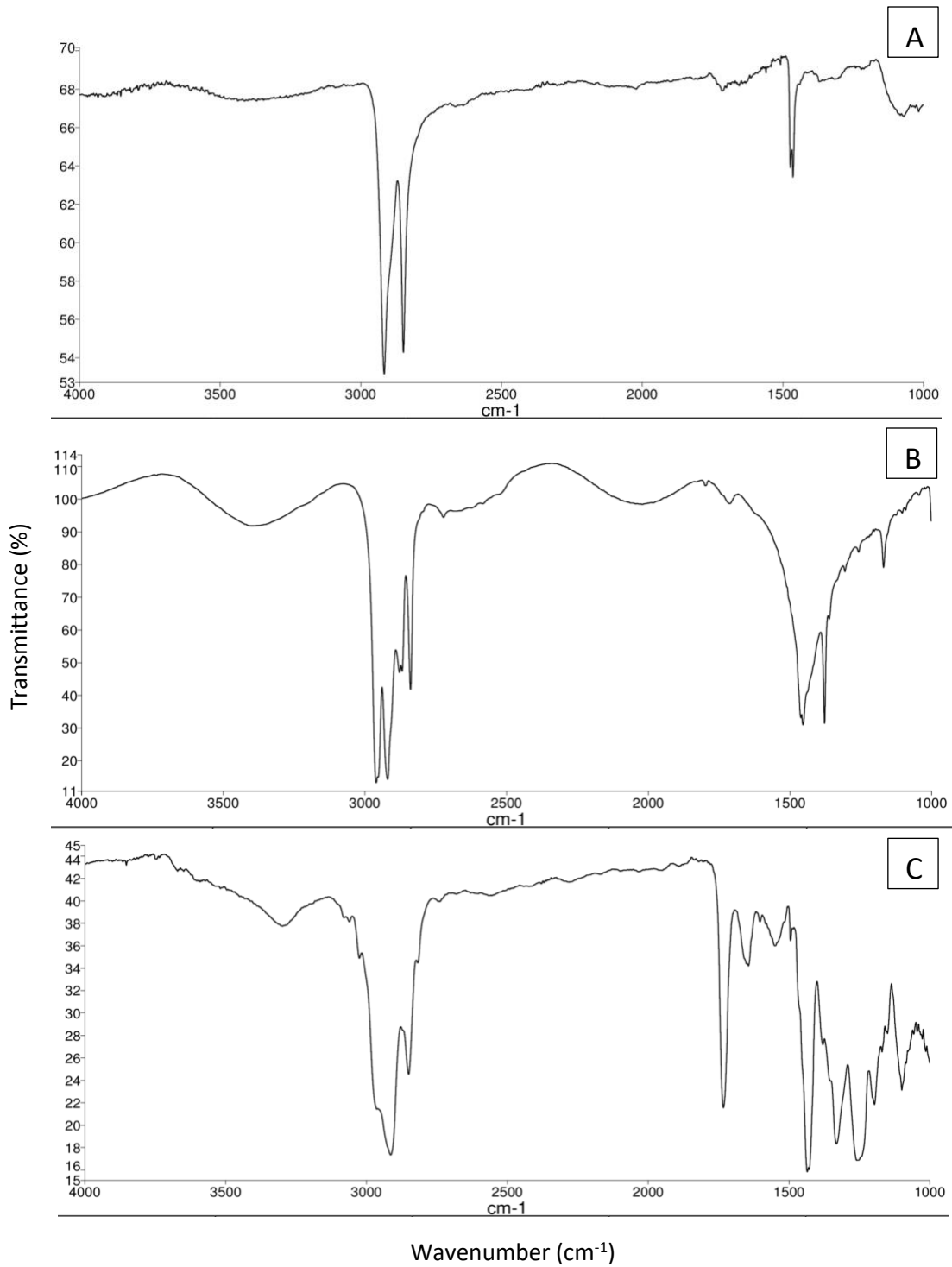
Figure A2: Example FTIR spectra: (A): polyethylene, (B): polypropylene, (C): polyvinyl chloride

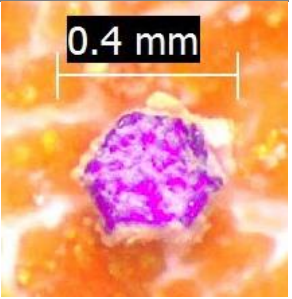**Appendix 2: Sample of microplastic particles detected in influent and effluent**
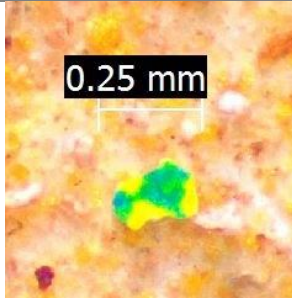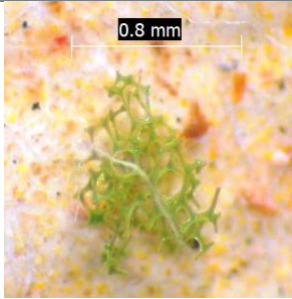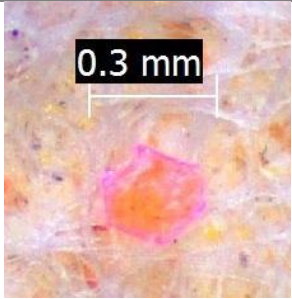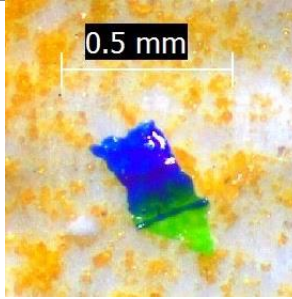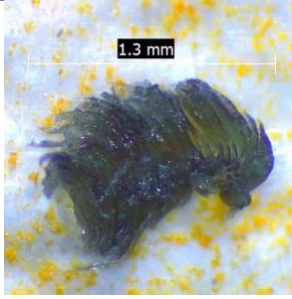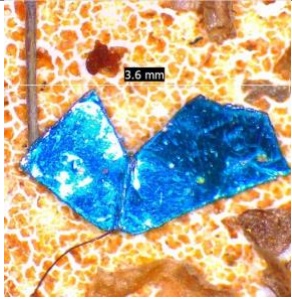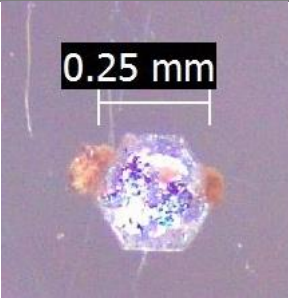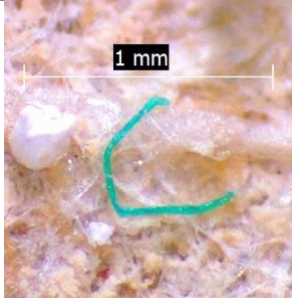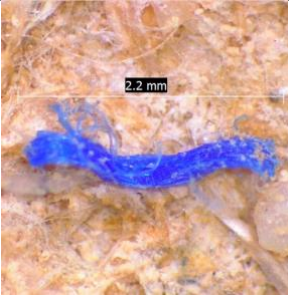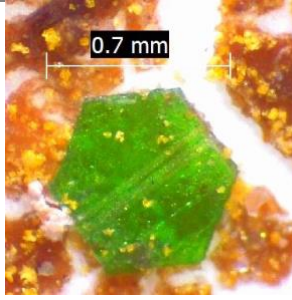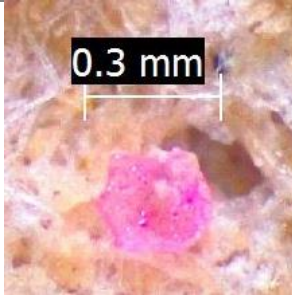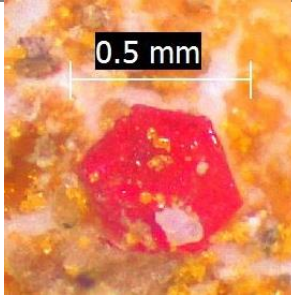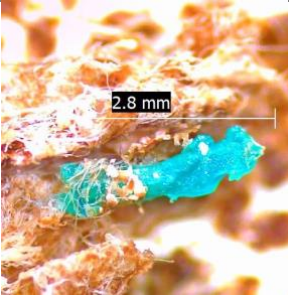
Christchurch Weekday influent **Polyethylene**	Christchurch Weekday influent **Phenolic resin**	Christchurch Weekday influent **Polyester**	Christchurch Weekend influent **Polyester**
Kaiapoi Weekday effluent **Polyester**	Kaiapoi December effluent **Polypropylene**	Lyttelton Weekday influent **Polyvinyl chloride**	Lyttelton Weekday influent **Polyester**
Lyttelton Weekend influent **Polyester**	Governors Bay Weekend influent **Polyester**	Governors Bay Weekend influent **Polypropylene**	Governors Bay Weekend influent **Polypropylene**
Governors Bay Weekend effluent **Polyester**	Governors Bay Weekend influent **Polyester**	Governors Bay Weekend effluent **Polyester**	Governors Bay Weekday influent **Polyethylene**

Figure A3: Example microplastic particles from Christchurch, Kaiapoi, Lyttelton and Governors Bay WWTPs.

Appendix 3: Pre-loaded polymer reference libraries

Note: version number information was unavailable. FIBERS3, fiberfbi, fibers2, POLYADD1, Hummel Polymer Sample Library, Polystyrene Quality Control Sample, Coatings Technology, Synthetic Fibers by Microscope, Georgia State Forensic Automobile Paints, Hummel Polymer and Additive, Sprouse Polymers by Transmission, Sprouse Polymers by ATR, Sprouse Polymer Additives, Industrial Coatings, Polymer Additives and Plasticizers, Commercial Materials Polypropylene Additives, Commercial Materials Epoxy Compounds.

Appendix 4: Weather data for characterisation and temporal studies

Table A1: Rainfall data in Canterbury during influent sampling trips, courtesy of Metservice.[95]

	Christchurch	Kaiapoi	Lyttelton	Governors Bay
Weekday day 1	20 mm	2.2 mm	0 mm	0 mm
Weekday day 2	4 mm	20 mm	0 mm	0 mm
Weekend day 1	0.2 mm	0 mm	0.4 mm	0.4 mm
Weekend day 2	0 mm	0.2 mm	3.4 mm	3.4 mm

Table A2: Rainfall data in Canterbury during effluent sampling trips, courtesy of Metservice.[95]

	Christchurch	Kaiapoi	Lyttelton	Governors Bay
June				
Weekday day 1	20 mm	0 mm	0 mm	0 mm
Weekday day 2	4 mm	0 mm	0 mm	0 mm
Weekend day 1	0.2 mm	0.8 mm	2.4 mm	2.4 mm
Weekend day 2	0 mm	3.2 mm	0.2 mm	0.2 mm
August				
Weekday day 1	0.2 mm	0 mm	0 mm	NA
Weekday day 2	2.8 mm	0.2 mm	0 mm	NA
October				
Weekday day 1	0.6 mm	0 mm	0 mm	NA
Weekday day 2	0.2 mm	0.2 mm	1 mm	NA
December				
Weekday day 1	11.2 mm	0 mm	3.2 mm	NA
Weekday day 2	1.6 mm	3.2 mm	0.2 mm	NA

NA: Not assessed