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Transport and fate of microplastic particles in wastewater treatment plants

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ABSTRACT

Municipal wastewater treatment plants (WWTPs) are frequently suspected as *significant* point sources or conduits of microplastics to the environment. To directly investigate these suspicions, effluent discharges from seven tertiary plants and one secondary plant in Southern California were studied. The study also looked at influent loads, particle size/type, conveyance, and removal at these wastewater treatment facilities. Over 0.189 million liters of effluent at each of the seven tertiary plants were filtered using an assembled stack of sieves with mesh sizes between 400 and 45 μm. Additionally, the surface of 28.4 million liters of final effluent at three tertiary plants was skimmed using a 125 μm filtering assembly. The results suggest that tertiary effluent is not a significant source of microplastics and that these plastic pollutants are effectively removed during the skimming and settling treatment processes. However, at a downstream secondary plant, an average of one micro-particle in every 1.14 thousand liters of final effluent was counted. The majority of microplastics identified in this study had a profile (color, shape, and size) similar to the blue polyethylene particles present in toothpaste formulations. Existing treatment processes were determined to be very effective for removal of microplastic contaminants entering typical municipal WWTPs.

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1. Introduction

Microplastic particles, often smaller than 5 mm, are primarily made of polyethylene, polypropylene and other polymers. As the production and utility of plastic steadily increased over the decades, the occurrence of microplastics in the environment has likewise escalated and these new pollutants are now commonly found in rivers (McCormick et al., 2014, Yonkos et al., 2014), lakes (Eriksen et al., 2013, Free et al., 2014), and shorelines (Thompson et al., 2004, Browne et al., 2011). Microplastics have been shown to have negative impacts on aquatic organisms in our environment. von Moos et al. (2012) reported microplastics were taken up by cells of the blue mussel *Mytilus edulis*, where experimental exposures induced adverse effects on the tissue of the mussel. Cole et al. (2013) found microplastics were ingested by zooplankton, commonly drifting in salt and fresh water. Polybrominated diphenyl ethers (PBDEs), a group of flame retardants widely applied in electronics, were shown to be assimilated from microplastics by a marine amphipod, *Allorchestes Compressa* (Chua et al., 2014). Because of their hydrophobic nature (Cole et al., 2013), microplastics tend to absorb PBDEs, endocrine-disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs), along with other persistent organic pollutants in aqueous media. Concentrations of PBDEs, EDCs and PPCPs, which are detected at parts per trillion levels in many effluent samples (Nelson et al., 2011; Liu and Carr, 2013), could be adsorbed and enriched on the surfaces of microplastic particles (MPPs). These toxic pollutants may eventually enter into an ecosystem's food chain if the contaminated plastic residues are ingested by fish, aquatic invertebrates, and other wildlife (Ivar do Sul and Costa, 2014).

Microplastic particles (MPPs) are present in numerous personal care and cosmetic products such as lotions, soaps, facial and body scrubs and toothpaste. Many of these products are used daily in the United States and around the world. When used, the microplastics in cosmetics are rinsed directly down household drains; these MPPs and other plastic debris end up at municipal wastewater treatment plants (WWTPs). In some published reports (McCormick et al., 2014, Browne et al., 2011), WWTPs were mentioned as potential sources of microplastics in aquatic systems. However, other researchers were unable to confirm a direct link between

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microplastic pollution in rivers and WWTPs (Kein et al., 2015). The debate over whether discharged effluents contribute significantly to the accumulation of microplastics in our environment has widened. Moreover, at this time, it is unknown how these pollutants behave during transport through wastewater treatment facilities. Understanding the fate and transport pathways of microplastics in wastewater treatment processes is of great interest to plant design engineers and environmental scientists alike. New findings could help us to refine and improve existing treatment plant processes to manage or eliminate this new class of pollutants. Here, we report the first complete survey on the presence of microplastic particles in wastewater treatment systems as well as their transport and removal during typical wastewater treatment.

2. Material and methods

2.1. Microplastics

Five sizes of fluorescent polyethylene microbeads, red (10–45 μm), blue (53–63 μm), green (90–106 μm), violet (125–150 μm), and yellow (250–300 μm), were purchased from *Cospheric Innovations in Microtechnology* (Santa Barbara, CA 93160, USA). Additionally, microplastics in a dozen randomly chosen commercial products such as toothpaste, facial washes, body scrubs, and hand soaps were isolated (Fig. S1). In general, ~5 g of these products were placed into 8″-diameter sieves (mesh size: 45 μm), and washed thoroughly with deionized water (DI) to remove gels and other formulation additives. The micro-solids retained on the sieve were then placed on a 10-μm filter paper (S&S filter paper, USA), and washed exhaustively with DI water, and methanol, using a glass vacuum filtration apparatus. Isolated particles were air dried then examined under a microscope (Model 570, 0.7 to 4.2× American Optical Corporation, Buffalo, NY 14215, USA) to observe the colors, shapes and sizes.

2.2. Bench-scale studies

To evaluate buoyancy and settling properties of microbeads in mixed liquor (a mixture of raw wastewater and activated sludge) and effluent, 10 mg each of the fluorescent microbeads were mixed together then spiked into 1-L of mixed liquor or effluent. After manually shaking for 2 min, the solution was poured into a 1-L Imhoff cone. The distribution of microbeads was examined, after settling for 10 min.

To simulate the partitioning behaviors of microbeads in raw high-solids influent, ~1.7 g of toilet paper was blended in 300 mL of effluent using a heavy duty blender (Waring® Commercial, Torrington, CT 06790, USA) for 5 min 5–6 mg blue fluorescent microbeads (53–63 μm) was added to the paper slurry and shaken vigorously. The distribution of microbeads in the settled solution was then observed using a UV hand lamp.

To examine other possible removal modes of microbeads in tertiary plants, a 3′-diameter by 2′-tall bench-scale column was constructed to simulate gravity filters at tertiary plants which typically consist of ~24″ anthracite, ~12″ sand, ~54″ gravel. Our bench filter was assembled to approximate these ratios using the same media: 5″-anthracite, 2″-sand, 2″-small gravel, 3.5″-large gravel, and 5″-stone from column top to bottom (Fig. S4), respectively. The column was first conditioned with DI water, then flushed with 2 L of unfiltered secondary effluent. The flow was maintained at 4 mL/s. One liter of effluent was then spiked with 1 mg each of standard microbead particles (5 mg total), the effluent-bead slurry was then poured into the column. The microbead-spiked mix was filtered and the post-column filtrate collected. A second liter of effluent was used to rinse the spiked microbead vessel. The entire 1-L rinse was then poured into the bench filter to maintain head volume and column flow. 2.2 L of collected filtrate was then re-filtered through a 10-μm filter paper to isolate any microbeads that broke through the bench filter. The column was then back-flushed with DI water and air sparged for ~15 min 2 L of backwash water sample was collected.

To study the impact of biofilm on MPPs, two vials containing 20 mL of final effluent were dosed with 5 mL of mixed liquor. One of the vials was autoclaved at 121 °C for 34 min. After cooling, both the sterilized and non-sterilized vials were spiked with MPPs (~1.5 mg) extracted from toothpaste. The vials were capped and tumbled on a Dynabeads® rotary mixer at 20 revolutions per minute (RPM) for >48 h (Dynal Biotech. INC., Lake Success, NY 11042, USA).

2.3. Field sampling

The Sanitation Districts of Los Angeles County, one of the largest wastewater treatment utilities in the United States, operates twelve wastewater treatment facilities (Fig. 1). Four of these facilities have solids handling capabilities. Ten wastewater reclamation plants (WRPs) in this system provide tertiary treatment for approximately 681 million liters per day (MLD) of wastewater. Two sites discharge only secondary effluent. The smaller of the two secondary plants processes 0.3 MLD, while the larger, a combined wastewater/solids handling facility, currently treats 1.06 billion liters per day. Tertiary effluents were collected at seven WRPs (1–7). Secondary effluent was collected from the larger secondary plant (WWTP). All sampling events were conducted between June 2014 and January 2015.

2.4. Sampling methods

Two different sieving methods were used for filtering tertiary effluents at the location shown (Fig. 2). The first method employed a stack of 8″-diameter stainless steel sieve pans with mesh sizes ranging from 400 to 20 μm (Cole-Parmer, Vernon Hills, IL 60061, USA). Whenever possible, existing plumbing and flows from sampling boxes used for plant compliance samples were utilized. At other locations, plumbed final effluent streams were intercepted using PVC line splices. Calibrated effluent flows were filtered through a stack of sieves assembled from coarse to fine (Fig. S5). Flows were set 11.4–22.7 L per minute and were checked daily and adjusted if needed. After calibration, constant flows were maintained for the duration of filtration, in order to accurately determine the volumes of effluent filtered. Volumes were calculated using (*flow rate* × *time*). Sieve stacks were protected from direct sunlight and fugitive atmospheric debris by wrapping the filtration assemblies in aluminum/plastic shrouds.

The second method used a surface filtering assembly (Figs. S6 and 7) designed for skimming the water surface at the final outfall location. The filtering assembly was deployed at the effluent discharge outfall. Deployment times varied with flows and water quality. Surface skimming was closely monitored by checking flows and filtering performance. If clogging (i.e., any flow restrictions) was indicated, the assembly was immediately retrieved, taken to the lab to recover the residues then cleaned. Surface-skimmed volumes were estimated using [(*skimmer assembly length/weir outfall length*) × *discharged volumes*].

To investigate the transport of microplastics in each stage of tertiary treatment process (Fig. 2), WRP 1 was chosen because of logistical consideration and proximity to technical resources; and samples were taken from primary stage (influent pumps, skimming troughs located right after influent pumps), secondary stage (aeration tanks, return activated sludge (RAS)), and tertiary stage (secondary wastewater, gravity filters). Sampling at treatment stages of secondary WWTP (grit chamber located in the front of

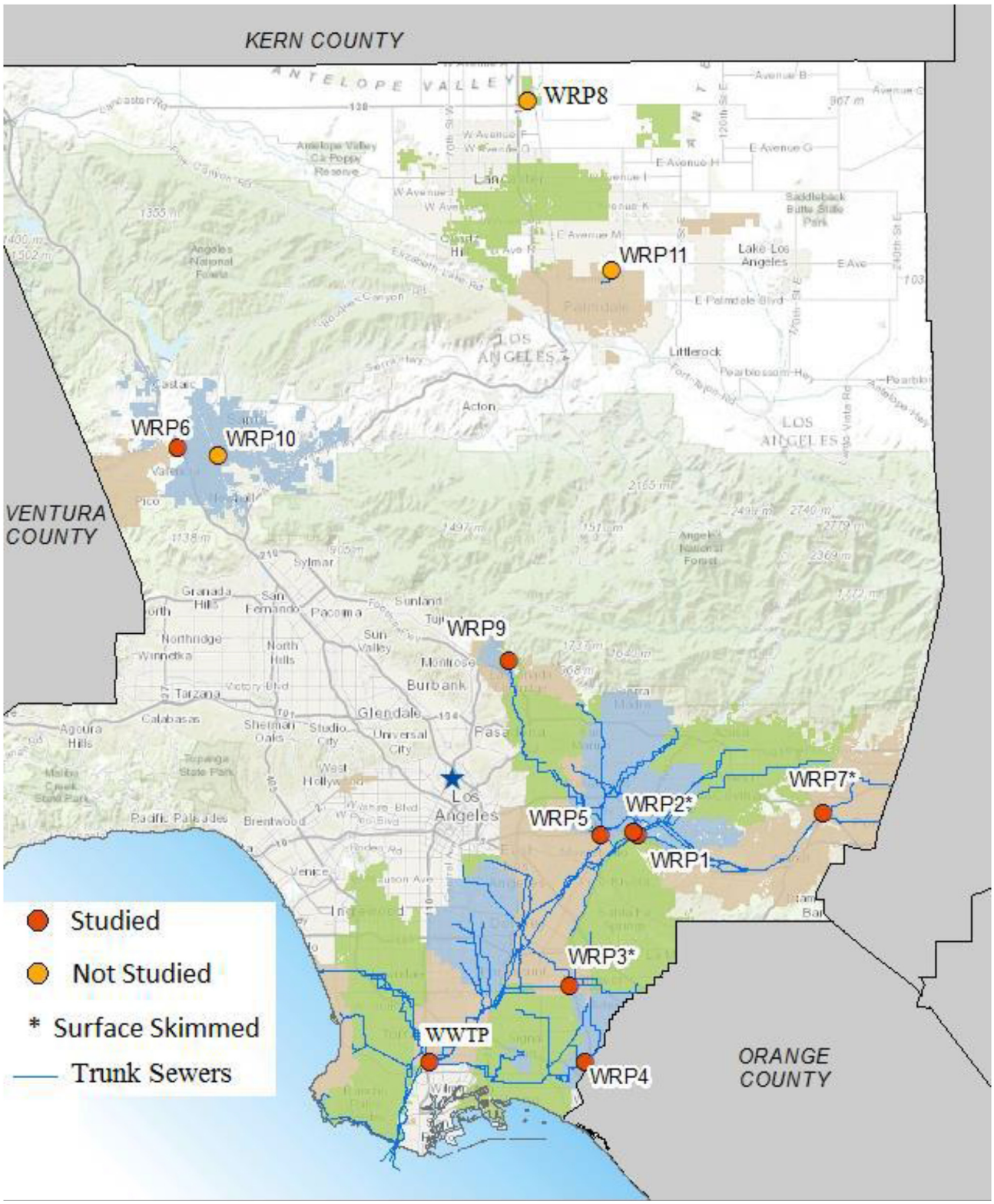

Fig. 1. Map showing treatment plant locations.

skimming troughs, skimming troughs, centrate system for biosolids treatment, biosolids) was also conducted.

2.5. Sample processing

Residues retained in 8″-diameter sieves or trapped in the surface filtering assembly during tertiary effluent sampling were removed from the mesh with DI water using a fine spray. The

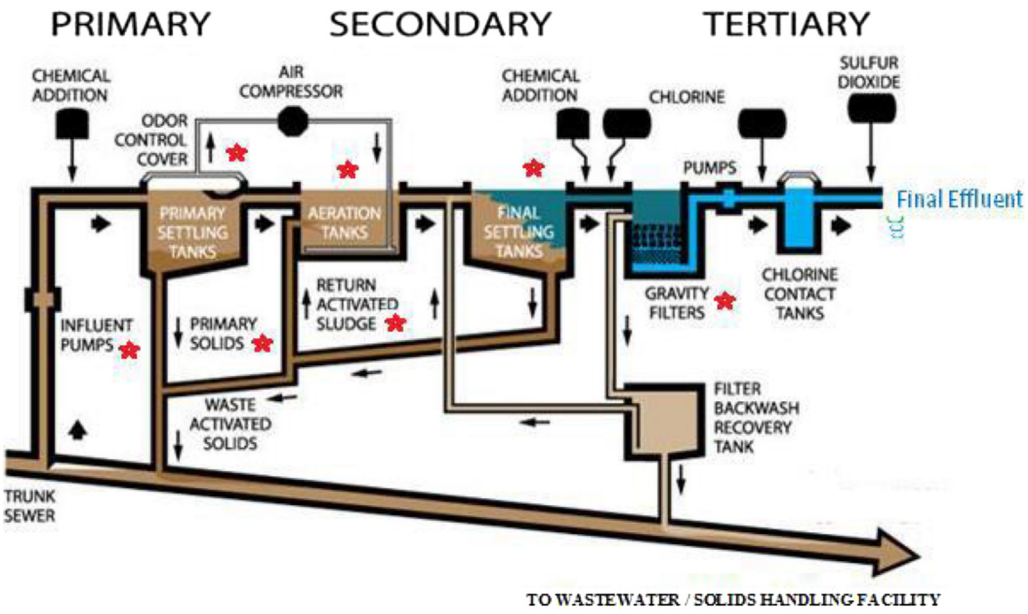

Fig. 2. Typical processes of a tertiary WRP. Primary, Secondary, Tertiary processes are indicated. (★ sampling locations, ➧ flow of wastewater, ↓ flow of sludge and solids, ⩊ sieving/surface-skimming location at the end of the tertiary treatment).

residues were then transferred into a 15 mL graduated plastic centrifuge tube. After centrifuging the tube at 4000 RPM for 20 min, the volume of the residues was determined. All filtered residues from tertiary effluents were analyzed under microscope.

High solid residues (40–100 mL) from secondary effluent were first combined in a beaker then DI water was added. The mixture was stirred vigorously using a magnetic stir plate to form a homogeneous slurry (500 mL). Representative 5 mL aliquots were then pipetted directly from the stirred slurry. Each 5-mL aliquot was placed into a gridded petri dish for screening and counting. Over 20% of the overall sample volume was examined. This procedure was repeated for processing residues collected from high-solids unfiltered secondary at WRP 1.

Grab samples from skimmings, scum in aeration tanks, sewage sludge, gravity filter backwash, and biosolids were digested with a diluted solution of bleach (Clorox, 8.25% sodium hypochlorite). In general, to ~5 g of a grab sample, 2–3 mL of 3% sodium hypochlorite was added to disinfect the sample and bleach the matrix. After hypochlorite addition, the disinfected samples were examined immediately under microscope in a fume hood.

2.6. Characterization of samples

Residues and other processed samples were visually examined using the microscope (see above) in conjunction with tactile and physical properties. Unlike plastics, starches and fats are friable and disintegrate easily under the mild pressure of a micro spatula. Spherical or irregularly shaped fragments, fibers and other ambiguous microplastics were isolated from the samples. Further examination of the suspected particles was carried out using one of the following microscopes; 1) Nikon Eclipse 80i, 100× 40× 20× 10× objective lens (Nikon Instruments Inc., Melville, NY 11747, USA); 2) Olympus BX50, 100× 10x 4× objective lens (Olympus America INC., Melville, NY 11747, USA). Some isolated MPPs and other ambiguous fragments were then analyzed by FTIR (Model FTIR-4600, JASCO Incorporated, 28600 Mary's Court, Easton, MD 21601, USA). To facilitate particle counting, gridded Petri dishes with sequentially numbered grids were used. This template eliminated duplicate or missed counts and assisted in locating and identifying ambiguous particles under the microscope if second party confirmation was required. Toothpaste particle counts were aided by suspending the MPPs in *t*-butanol, which provided a uniform dispersion of polyethylene fragments in the solution.

3. Results and discussion

3.1. Bench-scale studies

Dispersion (buoyancy and settling) tests of microbeads in mixed liquor showed that a majority of the particles floated on the surface (Fig. 3(a)). The buoyancies of these fluorescent beads were consistent with the densities (1.0–1.143 g/mL) specified by the manufacturer. However, in simulated partitioning tests, the majority of the fluorescent microbeads were trapped with the solid toilet paper floc, while about 40% remained floating on the surface of the solution. When the floating microbeads were removed and a second vigorous shaking applied to the sample, a fraction of the trapped beads resurfaced.

Our bench studies also showed that microbeads (10–300 μm) could be effectively retained by the media used in typical tertiary gravity bed filters. No breakthrough was observed after filtering 2 L of spiked secondary effluent. Greater than 95% of the spiked microbead particles representative of the full spiked range were recovered in the filtered backwash mix.

The MPPs that were observed most frequently during the course of these plant studies were irregularly shaped, blue polyethylene particles, the type found in some widely used whitening toothpaste formulations. Approximately 100 mg of white and blue particles were isolated from 5.4 g of the toothpaste using the methods described earlier. This amount represents about 1.8% of the total weight of the toothpaste. The blue and white particles had different densities and could be separated easily in water. The blue polyethylene fragments (Fig. 3(b)) floated to the surface of water; the white higher density component settled to the bottom. The white particles were very stable to heat, but broke apart easily with minimal spatula pressure, properties were consistent with mica, as listed on the product package. The blue particles recovered from the toothpaste exhibited properties of polyethylene plastics

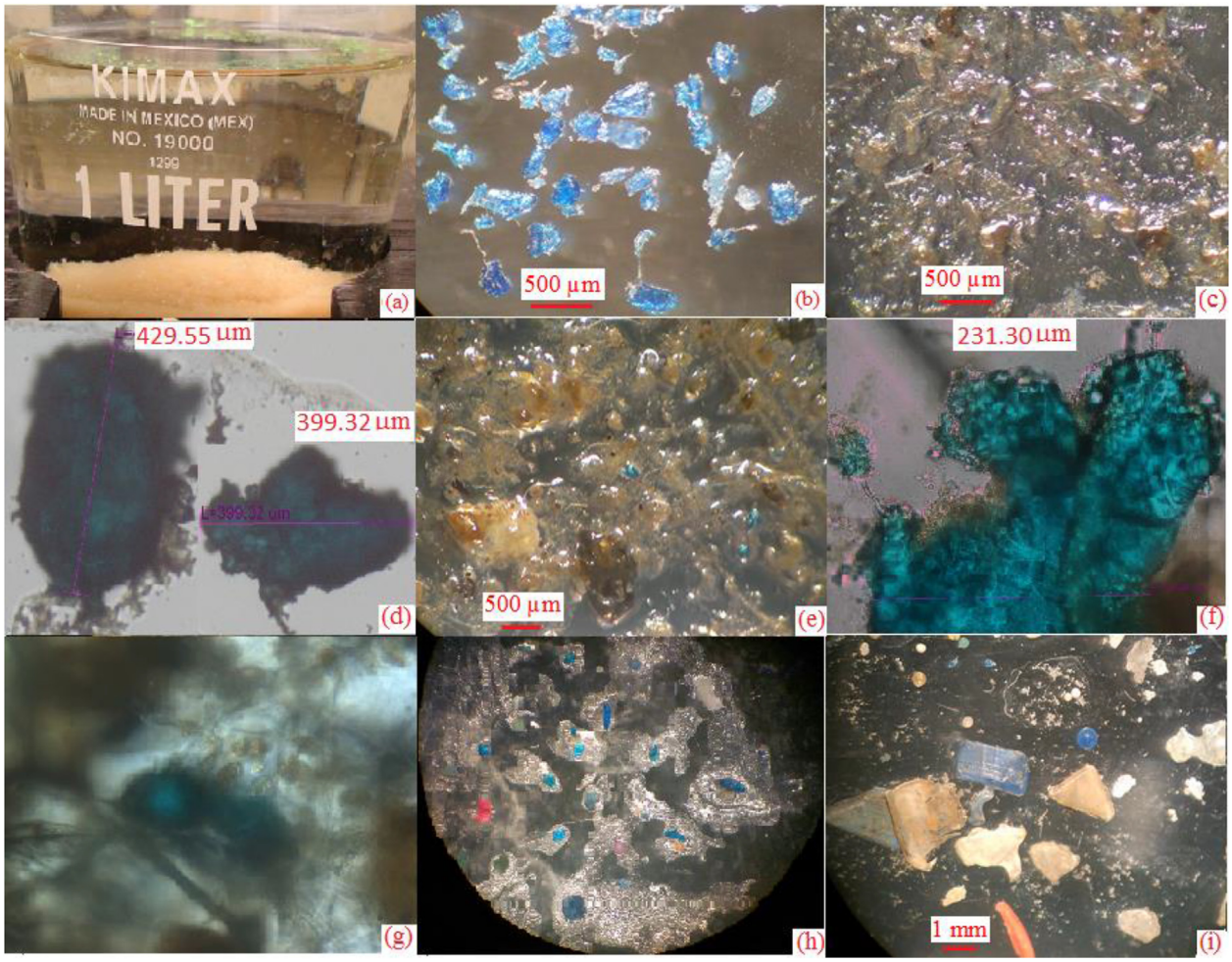

Fig. 3. (a) Distribution of microbeads in mixed liquor. (b) MPPs in a toothpaste. (c) Bio-residues in 180 µm sieve without MPPs. (d) Blue MPPs in a sample from skimming troughs at a WRP. (e) Blue MPPs and bio-residues in 180 µm sieve at WWTP. (f) Blue MPPs found in final effluent at WWTP. (g) Blue microplastics covered with brownish biofilms. (h) MPPs in a primary skimming sample at WWTP. (i) MPPs in the centrate at WWTP.

(Fig. S8(b,c)). These MPPs were between 90 and 300 µm in width and 100–600 µm in length, the majority being larger than 100 µm (Fig. 4). In a typical toothpaste application (~1.6 g), ~4000 blue polyethylene fragments were counted.

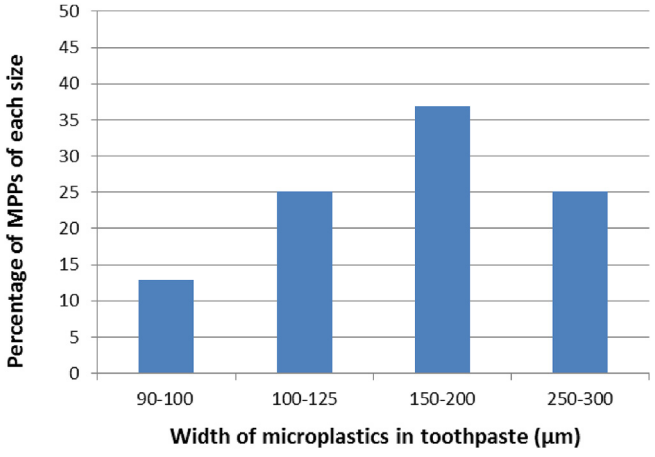

Fig. 4. Average size distribution of microplastics in toothpaste (particle length: 100–600 µm) determined using a point to point micrometer.

The impact of biofilm on MPPs was also examined using isolated blue MPPs. In this experiment, a majority of the MPPs floated to the surface in each vial spiked with mixed liquor. After >48 h of mixing, the blue particles in the autoclaved vial were still distributed primarily on the surface. The particles in the non-sterile vial appeared to be more randomly distributed throughout the aqueous phase, due to density or other physical changes caused by the biofilm coating.

3.2. Tertiary WRPs

Often, relatively small volumes of grab or composite samples are employed in plant studies. For this evaluation, however, we attempted to use larger volumes that were statistically more representative of total plant flows. Processing large effluent volumes, in this case, was manageable because filtrations were performed *on site* using convenient large volume sampling methods (Hidalgo-Ruz et al., 2012). In most sampling events, a three-sieve stack with mesh sizes of 400, 180 and 45 µm was used. In two events where the water quality was suitable and short-term clogging unlikely (WRP 1), a fourth finer mesh sieve (20 µm) was added to catch even smaller residues in the effluent. However, the 20 µm sieve was prone to clogging at most of the WRPs.

In Table 1, sampling dates, total volumes of effluent sieved and

amounts of residues collected for seven tertiary WRPs are summarized. After filtering over 1.89×10^5 L of effluent at each of these tertiary plants, we found no particle or fibrous microplastics in any of the below-water-surface discharges. The majority of the sieve collected residues were composed of microbially-derived detritus. These were identified using a microscope, and were abundant in the sieves at all plant facilities. The amount of residues collected in the 400 μm sieve was lowest, except for WRP 3. The volume of microbial residues collected in the 45 μm sieve, as expected, was the highest. The volume of residues collected varied between plants. Filtered biological remains (Fig. 3(c)) mirrored the spectrum of microorganisms present in the biologically active stages (aeration and anoxic zones of the plants). The images of some microorganisms (Fig. S3(a,b)) and the FT-IR spectrum (Fig. S8(d)) of a bio-residue sample are shown in Appendix A. Rotifers were the most abundant type of microorganism in the bio-residues, in most cases, up to 60% of the total residue by volume. Residues retained in the smallest mesh sieve (20 μm) contained essentially the same microorganism distribution and profiles as those seen on the 45 μm sieve.

Because the effluent pumps at all plants had intakes below the discharge surface, complementary surface filtration was conducted at three sites to intercept any floating microplastics or surface debris that could have been missed in the initial filtration design. Table 2 shows sampling days, time, volumes of effluent skimmed, and the number of MPPs identified at each plant. For WRP 2, >90% of the residues collected in the surface filtering assembly were grass, weeds and other vegetation. The large quantity of floating vegetative residues at WRP 2 was likely contributed by ground keeping activities near the effluent outfall. At WRP 7, effluent was sieve-filtered and surface-skimmed simultaneously. The mesh size of the bottom sieve was also chosen to match that of the surface skimmer (125 μm). Only five microplastic particles were found in the skimmer, none were found in the sieved effluent of WRP 7. A total of 31 MPPs including 3 thread-like fragments were found in 28.4 million liters of surface-filtered effluent at the three plants studied (Fig. S2(a)). Fibrous plastics (Fig. S3(c)) that could be distinguished microscopically from the filtered bio-residues (Fig. S3(b)) were not observed in any of the final discharges studied.

A variety of locations within WRP 1 (Fig. 2) were sampled in an effort to map MPPs' presence, conveyance and, most importantly, removal in the system. At the gravity filters, 45.2 L of the backwash were collected during the filter cleaning cycle. Although our model bench filter showed that a simulated gravity bed filtration would effectively retain microbeads in the 10–300 μm size range, no MPPs were detected in any of these backwashed samples which contained very high concentrations of anthracite fragments, filter media fines and biological solids. These results revealed that tertiary effluents were essentially free of MPPs. The detection of only three dozen MPPs during surface sieving could have been caused by occasional MPPs' breakthroughs, or resulted from fugitive airborne contamination in the open channels leading to the outfalls at tertiary plants (Figs. S6 and 7) (Rillig, 2012; Rocha-Santos and Duarte, 2015).

Sieve filtration was also applied to unfiltered secondary wastewater at the same plant. 5.68×10^3 L of secondary wastewater was filtered using stacked sieves. To extend sampling times, only two sieves of larger mesh sizes (400 and 180 μm) were used to delay clogging caused by the high levels of solids in unfiltered secondary. A total volume of 600 mL of solid residue was collected on the two sieves. Only one MPP was observed in those residues, no identifiable fibers were found (Table 3). Return activated sludges from the final settling tanks were also sampled. On average, one particle in 20 mL of RAS was observed in these samples; no synthetic fibers were identified after sample processing. This suggests that the majority of microplastic fragments and other fibrous residues were being removed during the early skimming and settling stages of primary treatment.

Grab samples were collected at several locations in the primary raw sewage treatment train. Skimming troughs were sampled during both the day and night shifts (8 h per shift) to evaluate whether plant influent plastic particle loads were variable. Equivalent counts of MPPs (~5 MPPs per gram of surface-skimmed sludge) were found during both shifts (Fig. 3(d)). Surface scum in the aeration tanks was also investigated. Many sampling and counting difficulties were encountered at these sites, which stemmed from the non-uniform distribution of solids in the tanks, and the complicated and unpleasant nature of the matrix. Particle counts at these locations were, therefore, only rough estimates.

Sample digestion using strong mineral acids was initially employed to reduce organic solids in the matrix. Acidic mixtures of varying ratios and concentrations were utilized. These reductions were performed using either a heating block or microwave digestion at 110–120 °C. Although this approach eliminated the majority of the matrix issues, performing digestions at elevated temperatures was problematic, because polyethylene and polypropylene plastics have melting points slightly above this range. Some MPPs in samples were even observed to melt at 90 °C, then form consolidated brittle lumps after the digested residues cooled to room temperature. By substituting hypochlorite for acid digestions, we were able to disinfect septic samples and reduce matrix issues simultaneously. The milder hypochlorite conditions eliminated melting concerns and removed other unwanted physical transformations, which facilitated visual identification and particulate

Table 1
Results of stacked sieve filtration at tertiary WRPs.

Site	Sampling date(s)	∑Volumes filtered (L)[a]	Residues in 45 μm sieve (mL)[b]	Residues in 180 μm sieve (mL)	Residues in 400 μm sieve (mL)
WRP 1	6/17-28 7/28-8/1	1.93×10^5	12.9	1.9	1.0
WRP 2	6/27-7/2 8/4-8	1.89×10^5	7.1	0.2	ND
WPR 3	7/22-26 7/30-8/1	1.96×10^5	2.1	ND[c]	0.2
WRP 4	8/4-11	2.32×10^5	5.0	0.2	ND
WRP 5	7/8-10 8/14-19	1.96×10^5	18.6	7.5	0.5
WRP 6	9/15-22	2.29×10^5	2.0	1.6	1.0
WRP 7	12/30-1/6	1.96×10^5	1.0	ND	ND

[a] A total of volumes.
[b] A 125 μm sieve was used for WRP 7.
[c] None was found.

Table 2
Result summary of surface-skimmed tertiary effluent.

Site	Duration days[a]	Deployment time (hours)	Fraction discharge skimmed	Volume skimmed ($\times 10^6$ L)	Residues in 125 μm sieve (mL)	MPP counts
WRP 2	8	13.24	20%	9.46	52	23
WRP 3	2	28.00	10%	9.42	1.0	3
WRP 7	3	6.46	100%	9.57	1.2	5

[a] Skimming performed from 12/9/2014 to 1/6/2015.

Table 3
MPPs distribution at WRP 1.

Location	MPP counts
Primary tank skimming's	Highest count (~5/g)[a]
Scum in aeration tanks	Low to medium counts[a]
Return activated sludge	One/20 mL[b]
Secondary effluent	One/5.68 $\times 10^4$ L
Gravity filter backwash	None found/45.4 L[b]
Final effluent	None found/1.93 $\times 10^5$ L

[a] Could not be correlated to influent volume.
[b] Average of 4 replicates.

source tracking.

The high counts of microplastics discovered at the skimming troughs confirmed the presence of microplastics in the WRPs influent. To estimate the number of MPPs in raw influent, we attempted to sieve the influent flows using an assembled sieve cascade (mesh size: 9.5 mm–180 μm). Unfortunately, these filtration attempts failed because the sieves were rapidly clogged by paper and other solid residues in the raw influent. Attempts to isolate particles by utilizing acidic digestion also failed because of excessive solid loads. We then tried to isolate any MPPs by exploiting their inherent buoyancies. This was performed by sparging 5 L of influent for 4 h in a large beaker (Claessens et al., 2013). At the conclusion of aeration, the surface of the sample was closely inspected using a magnifying glass. No MPPs were observed. At tertiary plants, a large portion of microplastics entering the plants tended to mix with sludge and settle. These settled primary solids (Fig. 2) are then conveyed to the wastewater/solids handling facility for processing.

3.3. Wastewater/solids handling facility (a secondary plant)

Settled solids and surface skimmings' containing the majority of microplastics removed from tertiary upstream facilities (WRP 1–5, 7, 9; see Trunk sewers in Fig. 1) are sent downstream to a wastewater/solids handling facility. This WWTP has the capacity to process an estimated 1.51 $\times 10^9$ L per day and is by far the largest and most complex of the wastewater handling facilities; as such, it presented unique challenges for this study. 4.23 $\times 10^5$ L of discharged final effluent at this facility was filtered using three stacked sieves (400 μm, 180 μm, and 100–150 μm). A total of 41 mL of solid residues was collected in the sieves. Under the microscope randomly shaped blue MPPs were observed to be mixed with other solid residues (Fig. 3(e)). After the solids were diluted to 500 mL with DI water in a large beaker; some irregularly shaped blue MPPs were immediately visible, even without magnification, on the surface. In the diluted solution, the majority of these MPPs seemed to settle or associate with the microbial detritus. Prolonged stirring of the solution appeared to dissociate or dislodge some of the plastic residues from the solids, and change their distribution in solution. Some of the white/transparent spherical particles found in the filtered residues were determined to be soft and hydrated using a micro spatula and were non-plastic. These micro-solids were found in some formulations extracted from cosmetic products. Other white or transparent fragments were confirmed to be plastic (Fig. S2(b)); in the microscopically examined fractions none of the residues appeared to be fibrous. A total of 373 particles of various color, shapes and sizes were identified in 4.23 $\times 10^5$ L of effluent at this facility, more than 90% of these MPPs were irregularly shaped blue polyethylene fragments. Under the microscope, the blue microplastics (Fig. 3(f) and S8(e)) appeared to be identical to particles isolated from toothpaste. It was also discovered that the microplastic residues were, without exception, covered with a brown layer of biofilm. On many particles, biofilm coatings were observed to completely encapsulate the microplastics (Fig. 3(g)). Because 373 particles were detected in 4.23 $\times 10^5$ L of secondary effluent, we estimated that, on average, one micro-particle was being discharged with every 1.14 $\times 10^3$ L of effluent at this solids handling WWTP. This equated to an overall total daily discharge count of ~0.93 $\times 10^6$ MPPs.

At the same facility, grab samples from the primary and secondary skimming chambers were examined. Two dozen MPPs were found in ~5 g of sample from a primary skimmer. Most MPPs were blue polyethylene fragments (Fig. 3(h)). Surprisingly, almost no MPPs were found in the secondary skimming samples. This supports a conclusion that the early stage skimming of floating solids in the primary is a very efficient removal mode for MPPs. Other areas where high microplastic counts were evident were in the centrate concentrate zones (Fig. 3(i), S2(c)). A summary of transport and removal of microplastics at this treatment facility along with estimated influent MPP loads are shown in Table 4.

In biosolids, an average of 5 particles in 5 g of the sample was found; here also, most of the particles identified were similar to the MPPs found in the plants. Methods (Hidalgo-Ruz et al., 2012) for isolating microplastics in sediments were applied in an attempt to separate fibers in settled sludge/solids or biosolids. Unfortunately, isolation of plastic fibers was challenging in composted matrix. Based on a daily production of 1.09 $\times 10^6$ kg per day of biosolids, we estimated that ~1.09 $\times 10^9$ MPPs were being removed from that facility daily with the biosolids, along with ~7.78 $\times 10^6$ particles in grit from the grit chambers and ~0.93 $\times 10^6$ particles in the final effluent discharged. Comparing the projected total daily influent counts (1.10 $\times 10^9$ microplastic) to the estimated daily discharged counts, we calculate the plant removal efficiencies to be in the range of 99.9%. Based on combined daily flows, we also estimated an average count of one MPP per liter of influent. This one-particle-per-liter count in raw influent was confirmed in a parallel study performed at WRP 6, another plant with on-site solids handling.

This finding is consistent with low percentages of plastic fibers found in sediments of a lagoon and rivers receiving the effluent input from WWTPs (Vianello et al., 2013, Kein et al., 2015). When present, plastic fibers in raw influents are intimately mixed with the mass of cellulosic fibers (Remy et al., 2015) from toilet paper and food solids, and are then removed with the settled flocs. Treatment plants are expressly designed to handle these flocs at the primary and secondary treatment stages.

In raw high-solids influent, lower density MPPs should float, or settle when trapped in solid flocs, in either case these particles should still be amenable to easy removal via skimming or settling in the plants. Other factors, however, may affect MPPs removal

Table 4
Survey results at WWTP including daily estimates of influent loads.

Location	Sample	MPP counts	Estimated total daily MPP counts
Grit	2.1 g	1[a]	~7.78×10^6
1° Skimming	5 g	20[a]	
2° Skimming	5 g	None found[a]	
CTS[b] influent	100 mL	51	
Thickened centrate	100 mL	267	
Biosolids	5 g	5[a]	~1.09×10^9
Final effluent	4.23×10^5 L	373	~0.93×10^6
∑Grit + biosolids + final effluent			1.10×10^9 per day
Grit + biosolids			1.10×10^9 per day (~99.9% removal by the plant)
Influent			One particle per liter

[a] Average number of 2 or 3 replicates.
[b] Centrate thickening system.

efficiencies. Microparticles could become trapped in unstable flocs which may not settle in an efficient manner. This would lead to a dynamic redistribution of particles in the aqueous phase and allow some to escape removal during the skimming and settling stages. The ubiquitous presence of biofilms witnessed on discharged solids in the secondary effluent may have affected the physical properties of these plastic particles. This was observed in the biofilm bench study. These bio-coatings may act as wetting agents and may modify the surface properties of hydrophobic polyethylene fragments, or the biofilm could alter the particles' relative densities compared to that of "clean" or uncoated plastics. Any such changes could measurably impact removal efficiencies of MPPs at municipal treatment plants. Neutrally buoyant particles are more likely to escape both skimming and settling processes, two of the more critical solids removal modes. It thus appears likely that biological surface deposits may be responsible for at least a portion of microplastics observed in secondary discharges studied. We can associate longer contact times (CT) in the treatment train with an increased potential for surface fouling. Increased CT of solids in the system may contribute to the higher MPP counts seen in the effluent at the WWTP where CT for at least a portion of the MPP counts greatly exceeded those at tertiary upstream sites. The impact of CT and a plant's nutrient levels on surface fouling may be an area worthy of further research.

Existing treatment process designs appear to be surprisingly effective at removing this new class of pollutants. Analysis of samples taken from multiple locations within treatment plants showed that the majority of these contaminants were removed at the primary treatment stages via skimming and settling processes. Tertiary WRP processes appear to be effective at removing microplastic contaminants in their influents, even the secondary downstream wastewater/solids handling facility showed removal efficiency above 99.9%. Our findings also reveal that some consumer products may be contributing disproportionately more than others to WWTP microplastic loads. The MPPs observed in the study were largely derived from consumer personal care and cosmetic products (Fig. S8(f)), which had distinctly different appearance and profiles to the plastic types commonly observed in the environment. The most common fragments appear to be derived from some toothpaste formulations. These elevated counts may simply be related to the product's popularity, use frequency, and application amounts.

4. Conclusions

Surprisingly, the importance of effluent filters in the removal of MPPs appears to be minimal. Microplastic particles were found to be removed mainly in the primary treatment zones via solids skimming and sludge settling processes. The results of this study further suggest that effluent discharges from both secondary and tertiary wastewater treatment facilities may be contributing only minimally to the microplastic loads in oceans and surface water environments. Plastics entering wastewater treatment facilities, for the most part, differ from those that are commonly disposed of in storm drains, beaches, oceans, and freshwater locations such as lakes and rivers. The primary sources of microplastics in these environments were reported to be derived mainly from discarded consumer packaging (containers, bags, bottles) and industrial garbage. In the open environment such plastics undergo photodegradation induced by UV irradiation as well as mechanical erosion which lead to embrittlement and fracturing. Such processes, which are responsible for the progressive breakdown of disposed plastics, are mostly absent during wastewater treatment.

Recently the cosmetic and beauty products industries have increased their awareness of the environmental harm caused by these pollutants. The cosmetic product formulators have already begun to gradually phase-out and replace these additives with more environmentally benign alternatives. Moreover, some states (e.g., California, New York, New Jersey, and Illinois) have proposed a ban on the use and sale of cosmetics containing microplastics.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2016.01.002.

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