Role of Microplastics as Anthropogenic Pollutants of Global Ecosystems

by

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ABSTRACT

Plastic pollution has become a global threat to ecosystems worldwide, with microplastics now representing contaminants reported to occur in ambient air, fresh water, seawater, soils, fauna and people. Over time, larger macro-plastics are subject to weathering and fragmentation, resulting in smaller particles, termed ‘microplastics’ (measuring < 5 mm in diameter), which have been found to pollute virtually every marine and terrestrial ecosystem on the planet. This thesis explored the transfer of plastic pollutants from consumer products into the built water environment and ultimately into global aquatic and terrestrial ecosystems.

A literature review demonstrated that municipal sewage sludge produced by wastewater treatment plants around the world contains detectable quantities of microplastics. Application of sewage sludge on land was shown to represent a mechanism for transfer of microplastics from wastewater into terrestrial environments, with some countries reporting as high as 113 ± 57 microplastic particles per gram of dry sludge.

To address the notable shortcoming of inconsistent reporting practices for microplastic pollution, this thesis introduced a novel, online calculator that converts the number of plastic particles into the unambiguous metric of mass, thereby making global studies on microplastic pollution directly comparable.

This thesis concludes with an investigation of a previously unexplored and more personal source of plastic pollution, namely the disposal of single-use contact lenses and an assessment of the magnitude of this emerging source of environmental pollution. Using an online survey aimed at quantifying trends with the disposal of lenses in the US,

it was discovered that 20 ± 0.8% of contact lens wearers flushed their used lenses down the drain, amounting to 44,000 ± 1,700 kg y^{-1} of lens dry mass discharged into US wastewater.

From the results it is concluded that conventional and medical microplastics represent a significant global source of pollution and a long-term threat to ecosystems around the world. Recommendations are provided on how to limit the entry of medical microplastics into the built water environment to limit damage to ecosystems worldwide.

DEDICATION

All of this work and anything meaningful I ever contribute is dedicated to my family. My mom and dad, Laura Mendoza and Bob Rolsky, have had my back at each stage of my life, through the ups and the downs. Their support has been unwavering. I look up to my parents each day of my life and consider how lucky I am to have them as friends, role models and family. Without your support and guidance, I would not be where I am today. I adore you both. To my sister, Mara Rolsky, thank you for always being there for me. I am so proud of who you have become and I call myself lucky to be your brother. To my brother Benji, thanks for paving the way to academia.

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MPs	Microplastics
WWTPs	Wastewater treatment plants
FTIR	Fourier-transform infrared spectroscopy
GC-MS	Gas chromatography–mass spectrometry
POI	Particle of interest
ATR	Attenuated total reflectance

INTRODUCTION

Plastic pollution: macro-scale consumer plastics turn into microplastic contaminants

Plastic pollution has been well documented as a threat to ecosystems worldwide[1]. With synthetic polymer mass production starting in the 1950s, the mass of plastic waste generated worldwide to date is estimated at over 6,000 million (M) metric tonnes (t)[1]. Considerable amounts of this production is recent, half of all the plastics ever made since 1950 have been produced in the past 13 years[1]. Much of the ubiquitous usage of synthetic plastic polymer materials is owed to their low cost, plasticity, and durability, which is desirable for in-use products but becomes an environmental liability upon improper disposal of plastic products[2]. None of the major plastic types currently on the market are biodegraded under prevailing conditions in the global environment; and since only about ~9% of all plastics ever made have actually been recycled or downcycled (i.e., polymers recaptured for lower value uses), plastic waste is accumulating at an alarming rate all over the world[1].

Macroplastics, defined as measuring greater than 5 millimeters in diameter, have the ability to cause asphyxiation or starvation when ingested by aquatic and terrestrial animals and are known to facilitate the long-range transport of potentially harmful, invasive species[3]. Microplastics (MPs), whose size range falls between 100 nanometers and 5 millimeters in diameter, are divided into two categories: primary and secondary MPs[4,5]. Particles smaller than 100 nanometers is considered a nanoplastic[4]. The former are created intentionally at a small size for use in cosmetics, whereas the latter, secondary MPs, are the product of degradation of larger plastic consumer products that are known to

disintegrate into fragments and fibers during normal wear and tear and, upon environmental release, as a result of UV radiation as well as wind and wave erosion[5]. MPs have been documented to reach and contaminate ecosystems all over the world, even entering the global food chain at differing trophic levels, from large charismatic species to small invertebrates[2]. They have been documented to biomagnify up the food chain into higher trophic species and are known to function as vectors of other contaminants, including persistent organic pollutants and microbial pathogens[5,6]. The occurrence and dispersal of environmental MPs stems from many anthropogenic sources, of recent interest being wastewater flowing out of communities around the world[7]. Multiple human health risks have been hypothesized to result from exposures to MPs through several pathways, including inhalation as airborne MPs, ingestion of water-borne MPs, and ingestion of seafood and other food items containing MP contaminants[8]. Human exposure to MPs is hypothesized to play a role in a range of unwanted health effects including endocrine disruption, tissue inflammation, and possibly cancer[9].

Methods of MP analysis

A range of analytical methodologies and tools are utilized for the isolation, detection, and identification of MPs within a variety of samples. Depending on the environmental source, sample matrix digestion followed by filtration normally is used to break down and remove organic materials prior to MPs isolation and detection. Density separation or elutriation, which separates particles based on physical characteristics due to their terminal velocity while falling, are two processes used for the purpose of sample cleanup[10,11]. Once particles of interest are isolated from the samples, polymer

identification is the next procedural step. A variety of analytical methods exist for polymer identification, with Fourier-transform infrared spectroscopy (FTIR) and micro-Raman spectroscopy being used most frequently. Others include Nile Red staining and gas chromatography mass spectrometry (GC-MS) with pyrolysis, among others, but all have different strengths and weaknesses (see Figure SI1)[12,13]. These analytical techniques allow for researchers to gather signals from unknown plastic particles that can then be compared to a database of polymeric standards to facilitate identification of the materials.

Current knowledge of MP contamination through wastewater

The presence of MPs in the aquatic environment has been documented for some time. A lesser studied aspect is the role of municipal wastewater as a source of MP pollution in the environment (see Figure 1). Available studies have demonstrated that MPs are present in WWTP influent and effluent as well as in raw sewage sludge and in treated sewage sludge, which commonly is referred to as 'biosolids'[14,15]. Currently, WWTPs are being given more attention as pathways for dispersion of MPs in the aquatic environment. As existing WWTP processing technology does not have capability to degrade or destroy MPs, items such as

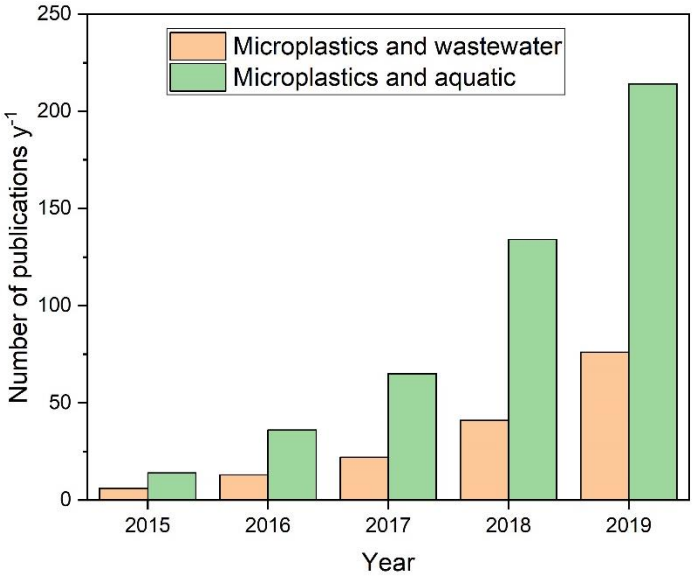

Figure P-1. The number of publications per year for "Microplastics and wastewater" and "Microplastics and aquatic" since 2015.

manufactured fibers, beads, and secondary MPs formed as consumer product fragments are entering WWTPs around the world without being subject to attenuation[15].

The persistence of MPs during wastewater treatment has important implications for the health and integrity of both aquatic and terrestrial ecosystems into which the pollutants become dispersed. MPs change the chemical and biological milieu as they can serve as a physical substrate for the development of microbial biofilms which are known to harbor microbial pathogens and can attract secondary chemical contaminants such as persistent organic pollutants[16]. Bacterial strains such as *E. coli* and *Vibrio spp.* have been detected on the surface of plastics retrieved from aquatic, natural environments[17]. The effects of the plastics and their attached biofilms on the rest of the ecosystem are not fully understood but it has been suggested that highly persistent contaminants can accumulate on plastic to levels one million times higher than those extant in the surrounding water[18]. Another concern revolves around plastic manufacturers' use of antimicrobial agents as a chemical coating on plastic products, which may foster the development and spread of genes and microorganisms featuring resistance to antimicrobials and pathogens of human health concern[19]. Studies have demonstrated that wastewater treatment plants (WWTPs) serve as sources of MPs in the marine environment as well, where rivers can carry the contaminants into coastal and oceanic ecosystems, thereby leading to a threat of contaminating seafood, which serves as a major source of protein for a fifth of the world population[20].

Current knowledge of MP movement within food webs

The extent to which MPs can biomagnify and become transported in marine food chains is not yet well-understood. Organisms at the bottom of the food chain are deemed to be most susceptible to the uptake of MPs in both freshwater or marine ecosystems[21]. That being said, a range of pathways exists for lower-tiered organisms to encounter MPs, mostly through ingestion (see Table 1).

Table P-1. Examples of species ingesting MPs

Species	Feeding strategy	Pathway
Algae[21]	NA	Nanoplastic adsorption
Microzooplankton[21]	Grazing	Small MP ingestion
Snail[22]	Grazing	Plastics adhered to seaweed and ingested
Shore crab[23]	Filter feeder	Uptake via gills and ingested
Blue Mussel[21]	Benthic suspension feeder	Ingestion of sinking MPs
Norway lobster[21]	Benthic scavenging	Passive ingestion while scavenging sea floor

A multitude of feeding strategies employed by aquatic biota allow for MPs to be ingested and move through aquatic food webs. Within aquatic ecosystems, various crab species were found to take up MPs via ingestion and egestion of food as well as through the processing of water in their gills while breathing[22].

Ingested MPs are hypothesized to exert a range of harmful effects on living organisms, with affected species ranging from small phytoplankton to larger whale and shark species, that may suffer from exposure of both the MPs themselves as well as the

toxic pollutants accumulated on the vast surface areas of the polymers[22]. Plastics not only serve as a vector of harmful chemistry but also can cause physical damage in exposed organisms. For example, ingested MPs have been observed to cause false satiation and reduced feeding in smaller organisms such as fish[24]. Other studies have uncovered damage done by MPs at the tissue and cellular level. Observed outcomes include inflammatory response in the tissues of aquatic a mussels as well as liver damage and early tumor formation in fish species fed both manufactured and secondary, environmental MPs[24,25].

The present dissertation is directed toward elucidating the role of WWTPs as a facilitator of environmental dispersion of MPs in global ecosystems, through reclamation of wastewater and land application of biosolids, a byproduct of wastewater treatment that frequently is disposed of on land as a soil filler, soil amendment, and fertilizer. Since there are a variety of reporting units and morphological classifications for MPs, a novel tool is suggested to create more continuity among MP studies. Another novel aspect of the proposed work is to better understand the role and importance of medical plastics, specifically plastic contact lenses, as environmental pollutants. Thus, major objectives of the present work are to:

a. *Determine the role of municipal wastewater and wastewater treatment in the environmental dispersion of MPs;*
b. *Improve the reporting of plastic pollution by proposing procedures for the standardization of the nomenclature of MPs and the units of reporting;*
c. *Determine the role of medically prescribed vision aids as a previously unrecognized source of MP pollution in aquatic environments.*

CHAPTER 1

MUNICIPAL SEWAGE SLUDGE AS A SOURCE OF MICROPLASTICS IN THE ENVIRONMENT

Abstract

Wastewater treatment plants are known to contribute to microplastic (MP) pollution in freshwater and terrestrial environments, but studies on MP abundance in sludge are scarce. This study aimed to (i) conduct a literature review to assess the number and extent of microplastics in sludge worldwide, (ii) determine extraction and analytical techniques used to isolate and identify these materials, and (iii) assess the fate and transport of these materials in the environment as a result of sludge disposal and reuse. Research in this area has increased as 12 countries have now reported and quantified MPs in sludge. This study highlights the need to assess the temporal and spatial differences in MP pollution in sludge, this relationship to land applied biosolids, and the risk to human and ecological health.

Introduction

Plastic pollution is a well-documented threat to ecosystems around the world, ever increasing as plastic production intensifies[26]. Microplastics (MPs) in particular have emerged as a source of concern due to their small size (< 5mm) and interactions with dangerous contaminants[27]. These small plastics are now being discovered in sewage sludge around the world. Despite their high removal ratio in some cases (84-99%), differences in water treatment strategies among wastewater treatment plants (WWTPs) and characteristics of the MPs still allow for a sizable amount of small plastics to pass

through the plants within solid materials or sludge[28]. Sludge once treated, termed biosolids, is sent to a landfill, incinerated or land applied, thus providing three pathways for MPs to enter the environment. Once in the environment, MPs present health threats to a variety of biota if ingested, sometimes negatively affecting such factors as species growth and reproduction[28]. Many countries use biosolids as an agricultural amendment and MPs have been found in soil which received biosolids from WWTPs, prompting more attention to the role of WWTPs as contributors to the release of environmental MPs as in some cases, MPs are able to leach from soils into the environment[29]. In addition to damage inflicted by MPs to the wastewater treatment process, such as inhibition of sludge hydrolysis and reduction of important microorganisms, their environmental implications present even more significant dangers. Chemical and physical threats have been associated with MPs due to their hydrophobicity and chemical composition[29,30]. The degradation of MPs can trigger the release of both manufactured additives in plastics (e.g., phthalates) as well as adsorbed contaminants (e.g., persistent organic pollutants) which can concentrate on the high MP surface area, up to a million times stronger than levels within the surrounding environment[30,31]. If ingested, the distribution and toxicity of chemical contaminants may increase and concentrate up the food chain, threatening humans and animals alike[30]. Environmental exposure can occur directly as primary MPs, where manufacturing creates these sizes for a particular use (e.g., microbeads for cosmetic purposes), or as secondary MPs that are the results of larger plastics fragmenting into the target size range over time[32].

Due to these factors, research chronicling the presence of MPs in sludge has increased. New information has emerged aiming to better understand the existence of

MPs in sludge, including morphological characteristics, their fate post-water treatment, and suggested impact on the environment. These plastics have been shown to leach from landfills, linger within agricultural soils, and contribute to atmospheric pollution once incinerated, suggesting that the presence and fate of MPs in sludge must be further studied[15,29,33]. Thus, we aim to assess the literature related to MPs in sewage sludge globally, including reported numbers, extraction and analytical methods, and fate and transport in the environment. Additionally, this review offers suggestions for future research to improve the study of sludge-borne MPs.

Quantification of MPs in Sludge

Fourteen papers collected and quantified MPs in biosolids, which include data from 12 different countries (see Table 1). Typically, MPs are reported within sludge by particle number per unit mass and reported particle numbers vary considerably between locations. For instance, the Netherlands had the lowest particle counts at 0.45 ± 0.2 MPs g^{-1} while Italy reported the highest at 113 ± 57 MPs g^{-1}. Countries that have been surveyed for MPs in sludge cover a wide range of populations, which likely contributes to the variability seen between samples.

Table 1-1. Counts of MPs reported per gram of sludge (dry weight) and associated WWTPs data.

Country	Population (Million)	Sludge produced (MMT/year)	Average MPs (#/g)	Number of WWTPs sampled
Italy	60	1	113 ± 57	1
Germany	80	2	40.1 ± 24	6
Finland	5	0.1	27.3	1
Sweden	10	0.2	17	1
Canada	37	0.7	9.65 ± 5.2	2
Ireland	4	0.004	8.5 ± 1.6	8
China	1.4*	35	8.03 ± 8	29
US	332	6	2.5 ± 1.5	2
Korea	77	4	2.2 ± 0.3	3
Scotland	5	0.1	1	1
Netherlands	17	0.6	0.45 ± 0.2	3

Particles were characterized by particle type using 16 different classifications of MP morphological descriptions, the most common label being fiber (100%), followed by fragment (71%), and sphere (35%) (see Figure 1a). A fraction of the shapes reported had rather ambiguous names, which were up for interpretation, such as “line” or “shaft”. These non-standardized shape delineations could hinder future comparisons.

In some cases, MPs in sludge were organized by size i.e. > 500 or < 500 µm[34] or average count, but total dimensional data were not reported. All published papers report microplastic particle counts, which does not provide information on total weight of the MP particles within that particular environment. As there can be a 20 times difference between the smallest and largest "microplastics", reporting only particle number does not allow for meaningful direct comparisons between locations from different studies. With varying abundances, the mass of MP (µg/g of biosolids) should be considered as a reporting unit, rather than particle number[35]. Without the ability to directly compare, researchers may be losing the ability to assess broad scale occurrences related to MPs, which may provide information pertinent to ecosystem health.

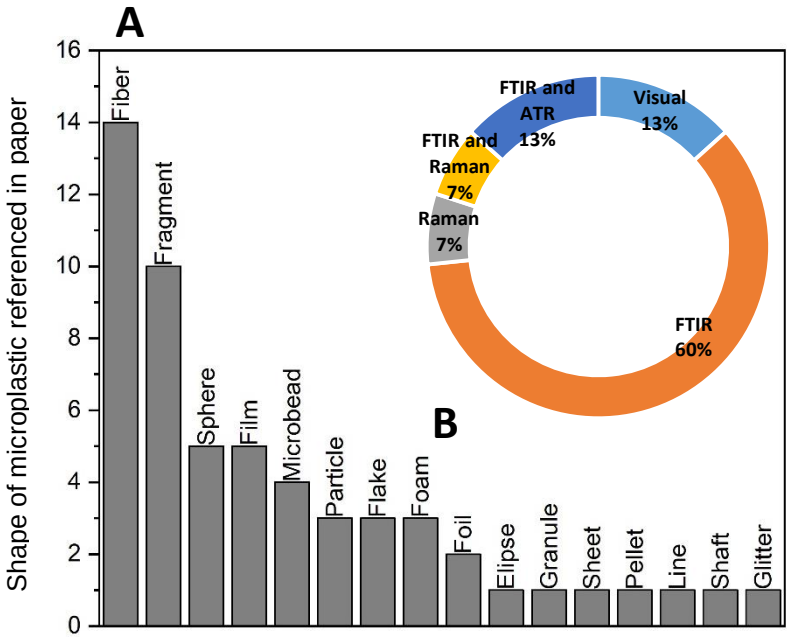

Figure 1-1. The (A) number of times a classification of MP is referenced in an article and (B) types of analytical tools used to identify the MPs. *Note FTIR = Fourier-transform infrared spectroscopy, ATR= Attenuated total reflection.

Extraction and Identification Methods of MPs

Extraction protocols for MPs in sludge are varied and often use a combination of methods[7,36–39], including the mixing of sludge with high-density solvent, such as sodium chloride or zinc chloride[15,40] for buoyancy separation, followed by capture via sieves or vacuum filtration[40]. The particular laboratory practices used for extraction and quantification were a function of research goals. For instance, Carr et al. chose a variety of sieve sizes from 400 to 200 µm to isolate a range of possible MP sizes[7], whereas Zubris and Richards, who were specifically seeking out plastic fibers, used a much smaller sieve (0.45 µm) when vacuum filtering their supernatant[41]. Elutriation columns were also used to separate MPs from more dense materials[15]. Non-standardization of extraction steps may translate into variable MP recovery between methods, which can contribute to differences in MP loading numbers for identical sites. For example, in regards to density separation, each solvent has a different density, which could alter the fraction of MPs reaching buoyancy. Aiming to add solvent enough to reach an optimal density to catch the most common polymers could mean missing out on other plastics whose density is higher than the optimal number. Contamination has been reported in virtually every study chronicling MPs in sludge. Thus, steps must be taken to evaluate this incidental occurrence. For example, researchers have found success integrating blank experiments to assess any airborne microfiber contamination[42].

After MP extraction, polymers were then searched for visually, using a microscopic source and often times, distilled water was added to help break up the organic material and avoid static electricity upon MP extraction[43]. Suspected plastic particles were confirmed most often via Fourier Transform Infrared Spectrometry (FTIR) (60%), followed by FTIR combined with attenuated total reflectance (ATR) (13%), then by

visual identification (13%) (see Figure 1b). Raman analysis was also used as a standalone technique (7%) and in conjunction with FTIR (7%). Both FTIR and Raman spectroscopy remain the most popular methods of MP identification[43]. It is often difficult to confirm a particle of interest (POI) to be plastic using a microscope alone. Gies et al. found that of all POIs initially isolated and extracted using light microscopy, only 32.4% were confirmed to be plastic polymers via FTIR[44]. There are tradeoffs to these analytical methods. With higher numbers of MP particles, it becomes more feasible to analyze a subset of the particles allowing for an underestimation of reported numbers. Also, identification techniques such as ATR-FTIR have reported issues identifying fibers due to the inability to differentiate plastic fibers from natural materials[43]. The attachment of organic materials, the presence of additives, or the use of oil may result in an incomplete match to an FTIR or Raman database, making the identity of the plastic material more difficult to pinpoint[44,45].

Most MPs entering a conventional WWTP are sequestered in sludge. Mahon et al. demonstrated that approximately 99% of MPs can persist in sludge, even after several treatment stages, such as lime stabilization or anaerobic digestion, aimed at degrading organic matter within a conventional WWTP[15]. Some research found that larger MPs are sequestered in sludge at in higher numbers than smaller particles, while other studies have demonstrated that smaller MPs have an increased chance of remaining in sludge because their size allows them to traverse the treatment processes[15,46]. A range of MP removal efficiencies within WWTPs exist within the literature but these numbers were contingent upon several factors including temporal variations and/or disparities between WWTP practices. Studies have shown removal techniques, such as membrane bioreactor

treating and rapid sand filters, have the greatest impact on MP removal, but not all WWTPs employ these removal technologies[47].

Seasonality can also play a role in MP variability within sludge. Lee et al. found that during a three-month period of high precipitation, the amount of MPs in sludge increased[48]. Sociality is also considered to have an effect on sludge MP concentration. In China, for example, an increase in infrastructure and industrial activities were positively correlated with higher concentrations of MPs found in sludge[49]. Li et al. found MP concentration in sludge to be also positively correlated with more infrastructure and increased industrial activity as well as smaller areas of afforested land[49]. There are variations in the amounts of MPs in sludge, some suggest differences in seasonality, urbanization, and treatment processes play a role, but better geographical data coverage are needed to better understand how these and likely other processes contribute to the accumulation of MPs in sludge.

A variety of analytical methods are utilized when seeking to isolate, extract, and identify MPs in sludge. Density separation is very commonly used to isolate the MPs and FTIR remains the most common method of identification. The presence of MPs in sludge is not surprising as they have been shown to survive multiple removal stages and degradative mechanisms therein. The amount of MPs discharged from WWTPs in sludge can be influenced by several factors, including seasonality and urbanization.

Pathways and mechanisms of exposure

Treated sewage sludge or biosolids, have a range of endpoints including but not limited to, beneficial reuse as agricultural amendments and soil composting, as well as

disposal mechanisms, including landfilling and incineration (see Table 2). All three of these disposal paths present opportunities for sludge-borne MPs to penetrate the environment. Specific MPs sent for disposal via incineration are destroyed, however harmful contaminants such as dioxins and polychlorinated biphenyls, can be emitted during their destruction[50]. It is thought that MP disposal by landfilling should sequester this material, however MPs have been found in landfill leachate, with the ability to migrate into groundwater and disrupt freshwater ecosystems[15,51]. Biosolids, when land applied, increase soil fertility, create more favorable soil properties, and contribute to the ability of the soil to recycle nutrients due to the addition of nutrients such as sulfur, magnesium, and sodium, present in the material[52,53]. MPs have been found within soil that was the recipient of sludge application and were also shown to undermine the positive aspects of biosolids by negatively affecting the water holding capacity, microbial activity, and the bulk density of soils[54]. Due to their ability to survive microbial assimilation, MPs delivered via biosolids can spend years accumulating on land in high numbers, between 125 and 850 tons MP/million inhabitants are added annually to European agricultural soils alone[55]. Atmospheric circulation is thought to aid in the remobilization of MPs away from fields, with shapes such as fibers, which have a lower removal efficiency than other MPs, penetrating porous soils more easily, suggesting a mechanism of environmental release post-land application[41,56,57]. Some studies have suggested it is unlikely that MPs in soil will undergo relevant disintegrating or degradation but much is still unknown regarding the movement or weathering of MPs within agricultural soils[54].

Table 1-2. Reported disposal strategies of biosolids by country expressed as a fraction in units of percent. Total land application includes both agriculture and soil/compost.

Country	Total Land Application	Agriculture	Incineration	Landfill	Soil/ Compost
Finland[58]	94	5	0	3	89
Norway[59]	82	82	0	0	0
Scotland[37]	64	24	35	1	40
Ireland[60]	63	63	0	35	0
Sweden[61]	63	36	2	22	27
Korea[42]	0	0	55	0	0
US[62]	55	55	15	28	0
China[63]	45	45	4	35	0
Canada[64]	43	43	47	4	0
Italy[65]	27	1	6	17	26
Germany[66]	48	38	18	34	10
Netherlands[67]	0	0	99	0	0

* "Other uses" account for small percentages accounting for the balance to 100%.

Chemicals linked to the presence and degradation of MPs have also been shown to pose a serious threat. For example, plasticizers, which are emollient additives to the plastics, have been linked to endocrine disruption in several animal species[68]. Many studies have demonstrated the dangerous interaction between MPs and surrounding contaminants. Toxic chemicals such as polychlorinated biphenyls have been shown to attach to the surface of MPs due to their mutual hydrophobicity[55]. Thus, WWTPs present an opportunity for this interaction to intensify due to the presence of contaminants such as heavy metals or persistent organic pollutants[69]. Studies have even shown MPs to act as reservoirs for antibiotic resistant genes, which may have dangerous

ecological implications post-release[70]. While in the treatment plant, MPs encounter physical and chemical degradative processes which can contribute to the adsorption of dangerous contaminants. For example, MPs have been found to exhibit a brittle surface, post-treatment, along with an abrasive and "hackly" surface, confirmed via scanning electron microscopy (SEM)[49]. These weathered MPs often have a negative charge; thus, have been shown to preferentially sequester heavy metals. Little is known about how degradative changes in the structure of microplastics affects the efficiency of these materials in transporting chemical and microbiological contaminants. Kelkar et al. found that during chlorination in the WWTP, the plastics' chemical structure can change, thereby increasing its toxicity[71].

Land applied biosolids are an important use for many countries, which is a function of the regulations or laws in that given location (see Table 2). Every country with reported MPs in sludge employ land application or landfilling of biosolids. Korea and Finland rely heavily upon composting whereas Canada, China, and the US use approximately half of their biosolids for agricultural purposes[72–74]. Finland also reported one of the highest concentrations of MPs in sludge. Combining this information with their total use of land applied biosolids presents a dangerous opportunity for large amounts of MPs to enter the environment and accumulate up the food chain[55]. Netherlands is an anomaly as around 99% of their biosolids are incinerated due to concerns over the presence of heavy metals but their reported number of MPs in sludge were the lowest of all countries surveyed[67,75]. China improperly disposes 80% of their total sludge, effectively increasing the total amount of "land applied" biosolids and MPs therein[76]. The relationship between MP sequestration in sludge and the subsequent

application of biosolids for agricultural purpose is very important to understanding the loading of these polymers in different environments and the subsequent ecological effects of these practices. The fate of the MPs, once land applied, is not well understood. Studies have shown that plastic particles were identifiable in the soil column over 15 years after the initial application and it has also been suggested that they can last up to 100 years due to reduced light and oxygen, conditions which in higher amounts, are normally associated with the degradation of MPs[41,50,77].

Future research directions

There are multiple knowledge gaps and areas of non-consensus that need to be addressed so that the magnitude of plastic pollution stemming from MPs can be determined. Temporal and spatial trends in MPs must be studied to get a more comprehensive idea of annual MP deposits into sludge and biosolids. An estimate of annual variation of MPs in wastewater and the subsequent ability for WWTPs to adequately handle such flows has yet to be studied, but is crucial to better understanding worldwide trends of MPs in sludge or biosolids[43]. Understanding the loading and transport of land-spread biosolids MPs will shed further light upon the transfer of terrestrial MPs to freshwater ecosystems[15]. Additionally, little is known about the ability of MPs to sequester and transport chemical and microbiological pollutants (including pathogens) across the landscape. Treatment plants contain a variety of harmful contaminants and pathogens, but the ability of MPs to adsorb them throughout all stages of the treatment process and thereafter are not well understood. Finally, there must be a standardization of reporting units for MP concentration. The particle size range of MPs

varies from 100 nm and 5 mm, units of mass are the most accurate representation of MP contamination within a given sample, which would in turn allow for more efficient comparisons between sampling locations [48]. Also, consensus on MP nomenclature would also help to identify shape, which will aid in elucidating fate and transport mechanisms.

Conclusions

Sewage sludge from around the world has been demonstrated to contain MPs. As the use of plastics continues to grow worldwide, MPs will only continue to be a problem to human and ecosystem health. Several analytical tools are used to confirm the identity of sludge-borne MPs and a range of morphological classifications have been used to report them. A standardization of research methodologies and reporting units could make it so trends between difference studies are possible. With this understanding, we can begin to crucially assess new technologies related to wastewater or biosolid treatment, and subsequent biosolid application.

TRANSITION 1

The first chapter assessed sewage sludge as a source for the unintended introduction of MPs into aquatic and terrestrial ecosystems. Once treated sludge has left the treatment facility in the United States, it is destined to be sent to a landfill, become land applied as biosolids, or may be incinerated. One major takeaway of Chapter 1 is the high degree of variability in reporting within papers chronicling MP contamination. Chapter 1 considered 14 research articles, which featured a combined total of 15 different types of MP classifications and a range of strategies and units for the reporting of MP contamination.

The second chapter of this dissertation is the first study to introduce an online calculator, specifically designed to standardize the dimensions of MP particles to units of mass, while also reducing the number of confusing, morphological MP classifications. My coauthors and I introduce some basic software coding, which incorporates the densities of conventional, polluted plastics along with the ability for researchers or citizen scientists to enter the type of MP particles from three options (fragment, bead and fiber). When entered into the online calculator for particle(s) of interest, the software tool calculates the total mass of plastic. An input of published data from a range of locations shows the variation that exists within one single size range of plastics, thus proving the need for better reporting units. Ultimately, this chapter is a call for the standardization of reporting units to be by weight, and it presents a simple template that may be expanded in the future to harmonize reporting and to enable a better comparison of results from different studies.

CHAPTER 2

ONLINE CALCULATOR FOR STANDARDIZING THE REPORTING OF ENVIRONMENTAL POLLUTION WITH MICROPLASTICS

Abstract

Current strategies for reporting environmental pollution with microplastics (MPs) are varied and ambiguous, rendering a comparison of results between studies and across different regions of the world difficult or impossible. This research introduces an online calculator as a new tool that enables a conversion of microplastic particle observations into the unambiguous unit of mass, an important step in facilitating a harmonization and better inventorying of MP pollution globally.

Introduction

Plastic pollution has become a threat to ecosystems and humans worldwide, with microplastics (MPs) measuring 5 millimeters or less in diameter now being recognized as a particularly worrisome risk[78]. This small-size plastic pollution can result from primary plastics intentionally produced, such as microbeads formulated into cosmetics, as well as secondary MPs resulting from the disintegration and degradation of larger macro- and meso-plastics over time[79]. Irrespective of their origin, these small plastic particles have the ability to penetrate most ecosystems around the world and have shown to carry harmful contaminants both within their inherent chemistry and adsorbed to their surface[80]. As research into MPs continues to expand, so do the techniques used to categorize and quantify this worrisome type of global pollution. Once MPs are isolated

from a substrate and identified, the characterization metrics vary, with typical reporting units for MPs being in the form of a shape, particle number, and singular or average dimension of particles[81,82]. This reporting format is problematic, as it is ambiguous as to the amount of plastic encountered, thereby making a comparison between studies difficult or even impossible. In response, the present chapter aimed to introduce an online calculator to help simplify and harmonize the reporting of MPs in the environment.

Methods

Microplastic Nomenclature. The spectrum of nomenclature typically used to describe MP particles in environmental samples was obtained from the literature search conducted in the previous chapter[83] . "Pellets" and "foams" are generally round in nature and analyzed as a bead, whereas "films", "granules" and "lines" were analyzed as fragments. "Filaments" were considered as fibers.

Software coding. An exemplary code was written in the software language R Studio 1.2.1335 using R 3.5.3 and R Shiny 1.3.2. as well. This code was obtained in part from a free, open-source online database that is fully accessible to any users. (see Appendix).

Results

The interface of the online calculator is shown in Figure 2-1. Data entry fields include shape, dimensions, and plastic material. If specific polymer data relating to plastic type are unavailable or uncertain, averaged value for density is automatically

applied. The online calculator collapses a spectrum of geometric shapes reported in the literature to just three morphological classifications: bead, fragment and fiber.

Users can choose the type of plastic, which subsequently selects the respective density and then automatically integrates this information into the calculations. Next, input is provided on the length, width, height, or diameter of the particles, as applicable. Once this information has been entered, the online tool reports out a result in the form of a mass (in units of grams, g).

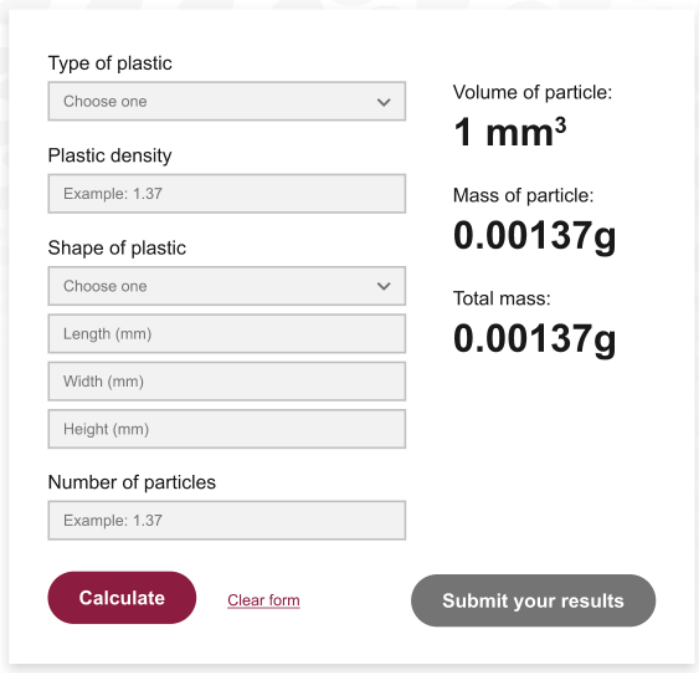

Figure 2-1. The interface of the online calculator. This features sections for users to submit customized dimensions, particle type and polymer type.

In order to highlight the discrepancies caused by ambiguous reporting of MP contamination, data collected from five peer-reviewed publications on MP contamination in the environment were selected, organized into a database and entered into the online

calculator. Data utilized of this illustrative use came from different areas of the world, including San Francisco US[81], Japan[84], the Atlantic Ocean[85], China[86], and the Great Lakes US[82]. The selected data had eight morphological classifications (fragment, pellet, fiber, film, line, filament, bead and foam) and several, singular dimension size ranges for the reported MPs (i.e., 0.355–0.999 mm, 1.000–4.749 mm, ≥ 4.75 mm). Using different permutations and combinations of provided dimensions, shape class, number of particles and densities, the tool was applied to calculate the different masses (g) of the plastic groups (see supplementary information for details). Size combinations covered each range within a size group predetermined by the authors of the studies, with upper, lower, and average values included as well. Results illustrate considerable uncertainty as to the mass of contaminants present in the form of MPs. From the 5 studies analyzed, fragments had the highest average variation with ~4 orders of magnitude difference from the smallest particles to the largest, followed by foams, films, and beads. Fibers and granules had the lowest average variation, around 2 orders of magnitude each, respectively.

Discussion

Due to the notable spread in that exists as demonstrated in Figure 1, reporting MPs as the number of particles per unit of substrate is not as accurate as standardizing the dimensions to units of weight. Fibers were consistent with the lowest degree of variability, which is to be expected since many fibers are shed instead of fragmented. Fragments, foams, and pellets on the other hand, have more mass variability, potentially due to different degradation rates. Flatter MPs with a single, exposed face receive more

photodegradation than other particles that are cubic or more round in shape, for example, which tend to roll while in aqueous environments, thus equally distributing the light[87].

There is a small variety of densities for popular types of polluted plastics, typically ranging from 0.8 to 1.2 g ml^{-1}, although these numbers are known to change as a result of weathering[87]. The calculator allows the user to choose a plastic type, which automatically accesses a predetermined density value for the selected plastic type. If users of the calculator were not able to identify the polymer type, an average of all the densities is integrated into the model. An additional tool incorporated into the calculator, is the choice of MP shape. With a range of morphological MP classifications in the literature[83], some of the nomenclature can become very confusing. One potential downside of this classification by mass is losing track of the danger posed by smaller plastics to cause more harm than larger plastics by invading the tissues of organisms, for example[23]. In order to compensate for this, a component will be added to the calculator that automatically computes the risk posed by the particles, based on the dimensions and type of polymer entered into the database.

This article calls for the standardization of MP reporting units to be relative to particle mass rather than particles within a range of sizes. Standardization of data organization would also benefit the field greatly as many studies report MP abundance differently from one another making comparisons difficult. The calculator serves as a template, which can be developed further to aid in developing the most accurate MP results possible. Citizen scientists who are interested in quantifying MP mass after conducting beach clean-ups, for example, could utilize future versions of the calculator.

The calculator also helps define and limit MP morphological classifications to create more continuity amongst MP research and will integrate a component to include the risk factor for the particles entered.

TRANSITION 2

Whereas the second chapter of this thesis was concerned with the categorization and reporting of established, literature documented MP pollution, the third chapter explored a potentially important additional source of plastic pollution, medical polymers used in the manufacture of disposable vision aids marketed as soft contact lenses. A quick assessment of the literature showed that contact lenses had never been considered as a form of environmental pollution, making this concept novel. Assuming that most users are applying contact lenses and taking them off again within a bathroom, intentional flushing of lenses down the drain constitutes a potentially problematic disposal route. The third chapter of this thesis aimed to evaluate this potentially pre-existing but unrecognized source of plastic pollution. The approach taken was to first survey the community of contact lens wearers in order to ascertain flushing as a periodically practiced disposal strategies and, thereafter, investigate the source strength and fate of MPs from medical polymers used in contact lenses by performing inventory calculations in conjunction with laboratory and field experiments. This work then also provided a first opportunity to compute MP pollution not by particle count but by the more robust unit of weight that was introduced in the previous chapter.

CHAPTER 3

NATIONWIDE MASS INVENTORY AND DEGRADATION ASSESSMENT OF PLASTIC CONTACT LENSES IN US WASTEWATER

Abstract

Plastics pose ecological and human health risks, with disposable contact lenses constituting a potential high-volume pollution source. Using sales data and an online survey of lens users (n = 416) alongside laboratory and field experiments at a conventional sewage treatment plant, we determined the environmental fate and mass inventories of contact lenses in the United States. Survey results revealed that 20 ± 0.8% of lens users flush their used lenses down the drain, a loading equivalent to 44,000 ± 1,700 kg y^{-1} of lens dry mass discharged into US wastewater. Biological treatment of wastewater did not result in a measurable loss of plastic mass (p = 0.001) and caused only very limited changes in polymer structure, as determined by Raman spectroscopy. During sewage treatment, lenses were found to accumulate as fragments in sewage sludge, resulting in an estimated accumulation of 24,000 ± 940 kg y^{-1} of microplastics destined for application on US agricultural soils contained in sewage sludge. A still larger mass of plastic waste, approximately 14.7 ± 0.58 million kg y^{-1} from blister packaging of the lenses, was estimated to go to US landfills and incinerators. Recycling of contact lens packaging amounted to only 0.04% of the total waste volume associated with contact lens use. This is the first study to identify contact lenses, and more specifically silicon hydrogels, as a previously overlooked source of plastic and microplastic pollution.

Introduction

Whereas low-value consumer plastics including single-use grocery bags and throw-away utensils have been studied extensively as sources of global plastic pollution, higher value medical plastic products, such as disposable contact lenses (CLs), have received relatively little attention to date for their role as potential contaminants of aquatic and terrestrial environments[88,89]. Yet, vision aids placed directly on the retina are a prominent single-use medical plastic article and they have become the default choice in contact lens products, whose use or application carries known risks of potentially dangerous or even life-threatening infections in patients.

The global CL industry is worth an estimated US$6 billion (B) y^{-1}, with the United States (US) alone accounting for about 41.7% of the world market or US$2.5B annually[90,91]. According to 2017 data, an estimated 198 million (M) Americans require vision correction, with about 45 M opting for CLs[91,92]. The market share of plastic CLs has steadily increased in the US. From 2001 to 2012, the number of CL users expanded from 27.4M to 36.6M adults[90]. Approximately 90% of these users choose soft lenses, with high-frequency CL replacement schedules ranging from daily to (bi)weekly to monthly[92,93]. Optometrists have reported that approximately 80% of patients have interest in wearing daily disposable lenses, reflected in the increasing usage trend of daily disposable lenses, which constitute approximately 40% of the CL market in the US[91].

Environmentally sound disposal options for CLs are mostly lacking, with only one major medical company in the U.S. instituting a recycling program with a partnering plastic recycler[94]. Also, most products contain no recommendations on how to properly dispose of both the lenses and their packaging materials. Absent of disposal instructions,

one plausible disposal pathway of potential concern to the environment is the flushing of used CLs down the drain. Flushed lenses would then reach municipal wastewater treatment systems, where the fate and degradation potential of the unusual hydrogel chemistries at present remain uncertain. Wastewater-borne CLs also may become sequestered in sewage sludge, a byproduct of conventional sewage treatment, which is being disposed of via landfilling, application on land, or incineration[80].

Upwards of 80% of marine plastic pollution is known to result from inappropriate disposal of plastic products, and wastewater treatment plants are considered an important source for the dispersion of microplastic pollutants[43,80]. Sewage sludge disposal into coastal waters has long been banned in the US but it is still being practiced in many developing nations. Here we present the first peer-reviewed report aimed at elucidating the disposal behaviors of contact lens users and the fate of contact lenses during conventional activated sludge wastewater treatment, as performed on most of the sewage generated across the United States.

Materials and Methods

Contact lens sourcing.

Contact lenses from a vast spectrum of vendors and brands were donated by a group of anonymous optometrists from their respective inventories of product samples, provided by the manufacturers. The average weight of a contact lens (hydrogel), packing material (polypropylene blister pack tub), and the aluminum lid of the blister pack were determined using an Ohaus Adventurer weighing scale (AR1530, China).

Online survey.

An anonymous, online survey (Arizona State University Institutional Review Board (IRB) STUDY00008394) was administered, yielding 416 responses total. The age range of CL users was gathered from the survey for comparison with reported, yearly trends in CL usage to assess the representativeness of the user sample. Survey questions investigated the most frequently used types of lenses, age range of users, and which disposal strategy was employed.

Raman spectroscopy.

Contact lenses from the WWTP experiment and accompanying controls were analyzed using a Raman Spectrometer. Micro-Raman imaging was conducted using a Renishaw InVia confocal microscope and Raman spectrometer (Renishaw InVia, London, UK) at magnifications 5x, 20x, 50x and 100x and a numerical aperture of 0.75. Samples were analyzed using a 15-mW laser of a 488-nm wavelength at 5-10% laser intensity using exposure times of 10 seconds. A silicon wafer was employed to be the calibration standard in all data collection. Successful focus was achieved in increments using the 5x, 20x, and 50x lenses. Acquired spectra were exported to Origin Pro analysis software for data processing. In cases where the particle had experienced significant degradation, the laser intensity was adjusted to gather clearer spectra. Final spectra were visually compared to a database of known contact lens spectra to assess degradation.

A spectral databased was constructed from an assortment of contact lenses provided by the optometrists. Raman spectra of interrogated contact lenses fell into five groups, based on spectral similarities. Two polymer types within the daily-disposable-

wear category, etafilcon and omafilcon, had been highlighted in research[95] before and were found to deserve particular attention, as corroborated by their notable sales data obtained from an anonymous optometry clinic.

***In situ* experiment at a wastewater treatment plant (WWTP).**

The anoxic and oxic chambers of the biological treatment unit of a full-scale WWTP in the southwestern US were selected for *in situ* experimentation, to expose CLs to the microbiome characteristic of conventional sewage treatment. Two types of contact lenses (omafilcon and etafilcon) were exposed to the anoxic and oxic chambers for 14 h, 96 h, and 192 h. Replicate CLs were suspended using nylon mesh bags and ropes, with 500-gram tungsten weights. Exposure times were based on actual solid retention times at this, and two other Southwestern WWTPs. Each type of CL was deployed in triplicate. Once planted CLs were retrieved from the WWTP treatment unit, the lenses were rinsed with deionized water and dried for one hour under nitrogen gas, weighed on a scale, and subjected to spectral analysis. To confirm the fact that polymer degradation was due to interaction of CLs with microorganisms (rather than chemical or physical interactions), experimental controls were implemented in which CLs were exposed to wastewater from which microorganisms were removed[96] by centrifugation followed by filtration of the supernatant through a 0.2 µm-pore-size filter disk. The liquid was centrifuged in an Eppendorf centrifuge 5810 R (Hamburg, Germany) for 10 minutes at 4000 *g* and 25°C. The supernatant was collected and used as a control for the experiment. Omafilcon and etafilcon were exposed to the filtrate for 14 h, 96 h, and 192 h in triplicate. CLs were subjected to these liquids in triplicate, with no significant changes being noted upon incubation for 14, 96 and 192 hours.

Determination of lens density.

Sodium chloride or sodium thiosulfate solutions were prepared at different concentrations to determine the densities and sedimentation behavior of hydrated CL polymers (Table S1). The propensity for hydrated and dried CLs to become fragmented was determined in triplicate in laboratory experiments.

Determination of susceptibility of lenses to fragmentation.

The susceptibility of CLs to fragmentation was determined by exposing fully hydrated vision aids to shear stress via (a) vortexing with and without solids and (b) repeated contact with glass slides. The stability of dried lenses was determined by placing them into a glass vial, and then shaken with force for 10 seconds.

Hydrogels and anaerobic sludge digestion.

Contact lenses were added to four liters of waste activated sludge (WAS) collected from a Southwestern WWTP and incubated under exclusion of oxygen under conditions mimicking large-scale, anaerobic sludge treatment[97].

Hydrogel stability during lime stabilization of sludge.

Hydrated lime is commonly used in WWTPs as an agent to facilitate removal of heavy metals and to inactive microorganisms[98]. Replicate lenses made from omafilcon or etafilcon were exposed to a solution of 12% hydrated lime (BFG Supply) for three weeks and changes in weight and Raman spectra of the lenses were determined as described above.

Detection of user-discarded lenses in sewage sludge.

Based on the density determination and biodegradation experiments, CLs discarded by consumers were presumed to become sequestered in raw sewage sludge. To

verify the fate of discarded CLs during sewage treatment, a total mass of 4.5 kg of digested sludge, representatively sampled from the full-scale plant, was retrieved and visually inspected for hydrogel lenses and fragments thereof. Plastic fragments found in the biosolids were then analyzed by Raman spectroscopy and obtained spectra compared to reference spectra of contact lens polymers in the database.

Mass balance.

Data on quantities of CLs used in the US (2000 – 2017) was gathered from the Center for Disease Control (CDC) and from publicly released reports of CL manufacturing companies[91]. A mass balance was performed, incorporating information on the percentage of CL flushers determined in the online user survey and on the total number of US contact lens users (45 million), to calculate the number of CLs expected to be discarded down the drain in the US annually. Assuming that, on average, 1.9 lenses are worn by users at any one time (i.e., single-lens use is uncommon). Using conservation of mass assumptions, the average dry weight of a single contact lens ($M_{CL,each}$) was as determined by weighing individual dried lenses (M_{CL1}; n= 5), as shown in equation 1:

$$M_{CL,each} = \frac{M_{CL1}+M_{CL2}+M_{CL3}+M_{CL4}+M_{CL5}}{5} \quad \text{(Equation 1)}$$

The weight of packaging material of individually wrapped lenses ($M_{PK,each}$) was comprised of the average weight of plastic tub ($M_{Pl,each,}$) and aluminum lid ($M_{Al,each}$) as shown in equation 2:

$$M_{PK,each} = M_{Pl,each}+M_{Al,each} \quad \text{(Equation 2)}$$

Using this information, the total weight of plastic tubs ($M_{Pl,T}$) and aluminum lids ($M_{AL,T}$) consumed per year in a specific geographic region was calculated according to equations 3 and 4:

$$M_{Pl,T} = M_{Pl,each} * CL_T \quad \text{(Equation 3)}$$

$$M_{Al,T} = M_{Al,each} * CL_T \quad \text{(Equation 4)}$$

The total amount of contact lenses used in the US including daily, weekly/biweekly and monthly (CL_T) lenses was calculated using equation 5,

$$CL_T = (X_D f_D D + X_W f_W W + X_M f_M M) * 1.9 \quad \text{(Equation 5)}$$

where, X_D, X_w and X_M are the number of people using lens products designed for use daily, weekly or monthly, respectively, and where f_W, f_D and f_M represent the fractions of contact lens users wearing specific lens products designed for daily, weekly or monthly use, and D, W, and M representing the average number of days, weeks and months per year.

The total annual mass of lenses ($M_{CL,T}$) used by geographic region was calculated with equation 6,

$$M_{CL,T} = (X_W f_W W + X_D f_D D + X_M f_M M) * 1.9 * M_{CL,each} \quad \text{(Equation 6)}$$

assuming again an average simultaneous use of 1.9 lenses per person. The total mass of lenses accumulating annually in sewage sludge ($M_{CL,SS}$), was calculated using equation 7:

$$M_{CL,SS} = M_{CL,T} * X_{Flush} \quad \text{(Equation 7)}$$

where X_{Flush} is the fraction of people flushing their lens products down the drain or sink, as determined by the online survey, assuming conservation of mass and settling in water of lenses that were experimentally determined to feature densities of greater than unity when hydrated. The annual mass loads of contact lenses contained in sewage sludge (SS)

destined for (i) land application ($M_{CL,LA}$), (ii) incineration ($M_{CL,IC}$) and (iii) disposal in landfills ($M_{CL,LF}$) were calculated as shown in equations 8, 9 and 10:

$$M_{CL,LA} = M_{CL,SS} * LA \quad \text{(Equation 8)}$$

$$M_{CL,IC} = M_{CL,SS} * IC \quad \text{(Equation 9)}$$

$$M_{CL,LF} = M_{CL,SS} * LF \quad \text{(Equation 10)}$$

where *LA*, *IC* and *LF* represent the fractions of sewage sludge that is land applied, incinerated or land filled in the U.S., respectively.

The total annual mass of contact lens packaging materials reaching recycling facilities was estimated for the polypropylene plastic tubs ($M_{Pl,Recycled}$) and aluminum lids ($M_{Al,Recycled}$) using equations 11 and 12,

$$M_{Pl,Recycled} = M_{Pl} * X_{Pl,Rec} \quad \text{(Equation 11)}$$

$$M_{Al,Recycled} = M_{Al} * X_{Al,Rec} \quad \text{(Equation 12)}$$

where $X_{PL,Rec}$ and $X_{Al,Rec}$ are the fractions of plastic tubs and aluminum lids recycled in the U.S.

The number of CLs sequestered annually in US sludge ($N_{Cl,SS}$) was calculated using equation 13:

$$N_{Cl,SS} = N_{Sold} * X_{Flush} \quad \text{(Equation 13)}$$

where N_{Sold} is the number of CL sold. The relative abundance of CLs expected to be present as macro- and microplastics per kg of biosolids ($A_{Cl,SS}$) in units of lenses per kg of sewage sludge was estimated using equation 14:

$$A_{Cl,SS} = \frac{N_{CL,SS}}{M_{SS}} \quad \text{(Equation 14)}$$

where M_{SS} is the dry mass of sewage sludge produced annually in the US[83].

The standard error of the sample population (P = 0.2) was calculated with equation 2, using the number of samples from the population (n), with a 95% confidence interval (Z = 1.96):

$$SE_P = Z\sqrt{\frac{P(1-P)}{n}} \quad \text{(Equation 15)}$$

Results

We used an online consumer survey, laboratory and field experiments as well as mass balance computations and Raman spectrometry to investigate the fate of disposable contact lenses in the United States.

Results of online consumer survey indicate unplanned disposal habits.

An anonymous, five question online survey was conducted to assess the demographics and disposal strategies of CL users, with the demographic information helping to inform on the representativeness of the user sample reached by the survey tool. Among 416 individuals taking the survey, a vast majority (n=275) also elected to answer questions relating to contact lens disposal. Literature reported CL user demographics identify the highest number of lens users among ages 18 - 29 (32%), followed by 30 - 39 (25%), 40 - 49 (20%), 50 - 59 (15%), and 60+ (9%) (15). Our survey question results closely followed these trends with ages 18 - 29 having the highest rate of use (44 ± 6%) followed by age groups 30 - 39 (30 ± 6%), 40 - 49 (18 ± 4%), 50 - 59 (6 ± 2%), and 60+ (2 ± 2%). This data established that the sample population reached by the online survey was representative of the larger population of U.S. contact lens users nationwide.

The main purpose of the survey was to reveal lens wearers' disposal behavior. According to survey results, the most popular disposal strategy for used CLs in the US is their placement in household trash (80 ± 3%) but 20 ± 0.8% of CL users admitted to flushing lenses down the drain. With the fate of CLs during wastewater treatment being unknown, we conducted field and laboratory experiments to assess their persistence and settling behavior.

Fate of contact lenses during wastewater treatment.

To investigate the persistence of CL polymers during sewage treatment, CLs were exposed to both oxic and anoxic unit operations of a denitrifying, large, activated sludge wastewater treatment plant in the US. Raman spectrometric analysis of CLs before and after incubation for 14 h indicated no or only very limited spectral changes (Figure 1) over this time duration that matched or exceeded the hydraulic residence time of most treatment facilities across the nation. Even after exaggerated exposure for up to 8 days, no or only very modest changes were observed in the Raman spectra of hydrogel polymers subjected to biological attack (Fig. 1; 96 h and 192 h data series).

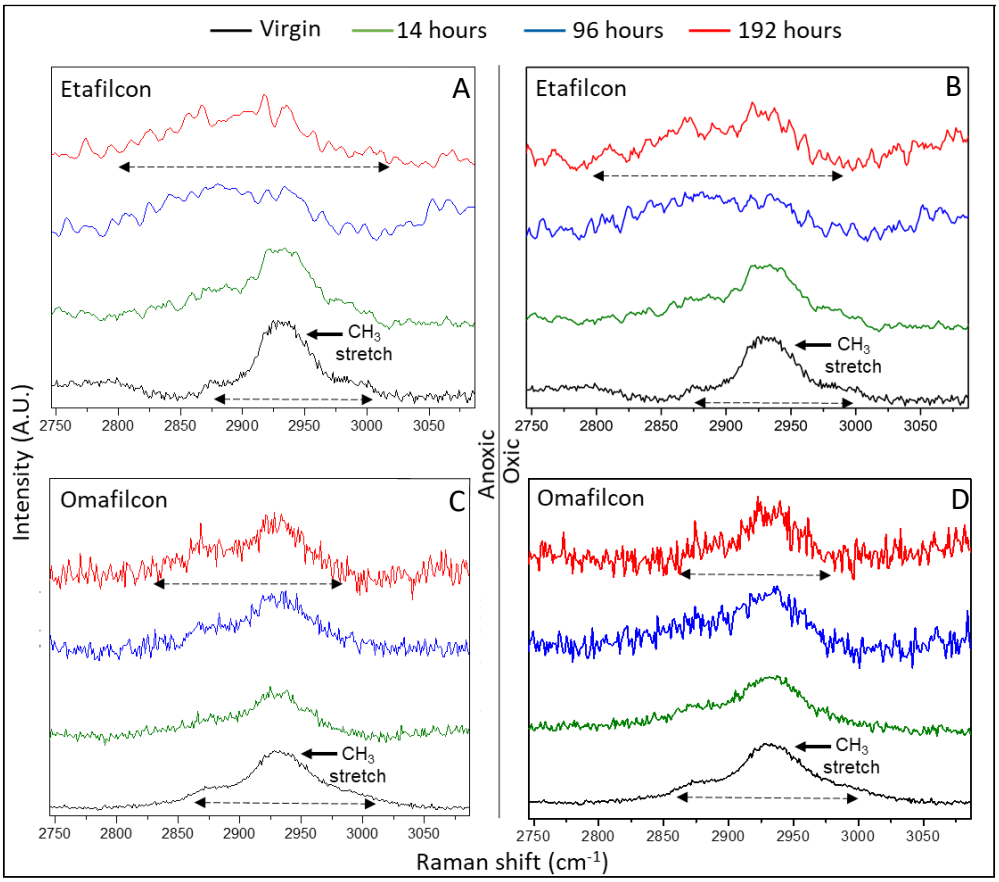

Figure 3-1. Persistence of different contact lens polymers during long-term exposure to oxic and unoxic conditions prevailing in a typical denitrifying activated sludge U.S. wastewater treatment plant. Stacked Raman spectra of etafilcon and omafilcon contact lenses exposed for 0 d (virgin plastics) (*n*=3), 14 h (*n*=3), and 192 h (*n*=3) in the oxic and anoxic chambers of the biological treatment plant showed no or only minimal structural changes, indicating general persistence of hydrogel polymers during the biological treatment stages of denitrification and aerobic digestion. Dotted arrows indicate peak broadening over time. Similar to the results shown, lack of biodegradation also was obtained for 11 additional hydrogel chemistries routinely used in CLs (see Table S3).

A peak of the hydrogel polymer etafilcon A at 2875 – 3000 cm^{-1} showed minimal spectral changes over time in the oxic and anoxic treatment steps upon incubation for up to 96 h. Long-term exposure for up to 192 h preserved general spectral features in both polymers shown, with peak broadening being observed for etafilcon but not for omafilcon (Fig 1; Panels A and C).

Daily use CLs have been increasing steadily since 2010 (see Figure 2A). To verify the presence of these CLs at a WWTP, ~4.5 kg of biosolids were analyzed directly via visual inspection (Figure 2B). Suspected CL fragments were located and their authenticity verified as narafilcon CL fragments using Raman analysis (see Figure 2C). The presence of CL fragments in sewage sludge confirmed flushing as a routinely practiced disposal behavior of CL users, as identified in the online survey, and also signaled that the macroscopic lenses are subject to fragmentation into smaller microplastics during sludge processing. Fragmentation of both wet and dry contact lenses also was observed in the laboratory upon application of physical stress. Both wet and dry lenses broke apart when exposed to physical stress and friction, giving rise to large and small CL fragments, the latter constituting microplastics measuring less than 5 mm in length.

Fate of contact lenses during sewage sludge treatment.

In controlled laboratory experiments mimicking full-scale sludge treatment, CLs were exposed to conditions prevailing during anaerobic digestion (see Figure 2E) and separately to treatment with hydrated lime (see Figure 2G), two common processes used for sewage sludge stabilization[98,99]. The CLs persisted throughout the three-week

exposure duration in both conditions, with only lime treatment resulting in limited physical changes, as evidenced in the corresponding Raman spectra obtained (see Figure 2).

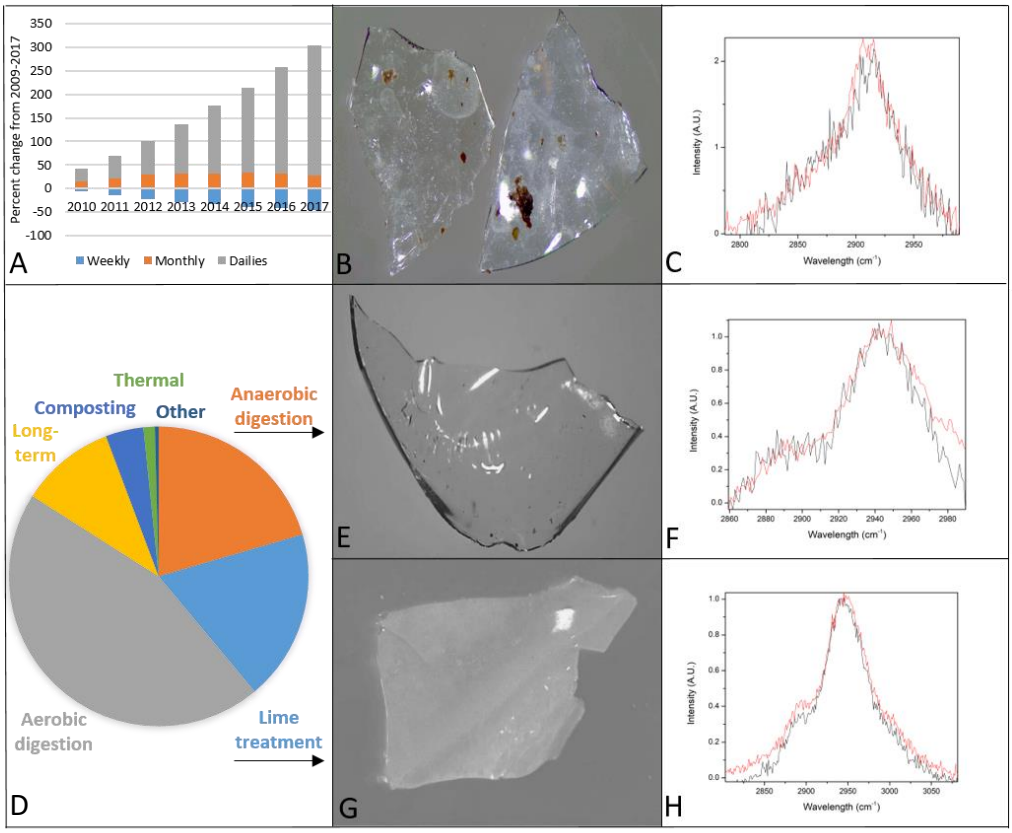

Figure 3-2. Time trend of consumer purchasing preferences and fate of disposable CLs during conventional processes for sewage sludge stabilization and treatment. Daily disposable CLs have increased in popularity (panel A) and were searched for in, and then isolated from, WWTP biosolids (B) and later identified as narafilcon using a Raman spectrometer (C). Black lines represent the database spectra of virgin CL hydrogel, whereas the red lines correspond to experimentally exposed CLs. Anaerobic digestion is used in nearly half of all US WWTPs (D); therefore, a laboratory-scale, anaerobic digester was used to incubate CLs for three weeks, with results showing

insignificant degradation using both visual inspection (E) and μ-Raman spectroscopy (F). About 18% of all US WWTPs utilize lime treatment for sludge stabilization; therefore, CLs were exposed to hydrated lime for three weeks, with limited degradation occurring as determined by visual inspection (G) and μ-Raman spectroscopy (H).

Assessment of the mass and waste volume of contact lenses.

With a reported 45M Americans using CLs each year (CDC, 2018), 13.9 ± 0.55 billion individual lenses are projected to be used and discarded annually. A five-question, online survey aimed at better understanding CL disposal strategies indicated that 20 ± 0.8% of CL users flush their used lenses down the drain, a disposal mode translating to 44,000 ± 1,700 kg of lens polymer dry mass of hydrogel polymers discharged into domestic U.S. sewage[100] (see Figure 3). Whereas macro- and microplastics previously have been reported in sewage sludge[15], information on CLs in biosolids thus far has been lacking. In laboratory experiments, we found that hydrated CLs are denser than water (Table 1, supp. info), with densities ranging from 1.3-1.4 g cm^{-3}. This suggests as a likely fate of wastewater-borne CLs their sequestration in sewage sludge during treatment. We estimate the mass of CLs sequestered US nationwide in municipal sewage sludge annually to be on the order of 42,300 - 45,700 kg assuming an almost complete capture efficiency, with 24,000 ± 940 kg thereof being applied on land contained in sewage sludge deemed fit for disposal on U.S. land (contained in biosolids), while an estimated 12,000 ± 475 kg is landfilled, and an additional 6,000 ± 230 kg is incinerated. Contact lens packaging made of plastic typically becomes part of the municipal solid waste stream, contributing an even larger plastic US inventory of 14.7 ± 0.58M kg annually diverted to landfills and incinerators, with recycling representing a minor disposal route,

presently accounting for a mere 0.04% of the total volume[94]. This does not include the 2.8 ± 0.11M kg in waste stemming from the aluminum lid. The over 16,000 WWTPs operated in the US produce an estimated 5.1-6.5 million metric dry tonnes per year of sewage sludge[15]. Based on our survey data and the number of CLs recycled annually, we estimate that one metric tonne of dry, treated US sewage sludge contains an average of 420 ± 8 lenses in the form of lens fragments and CL-derived microplastics.

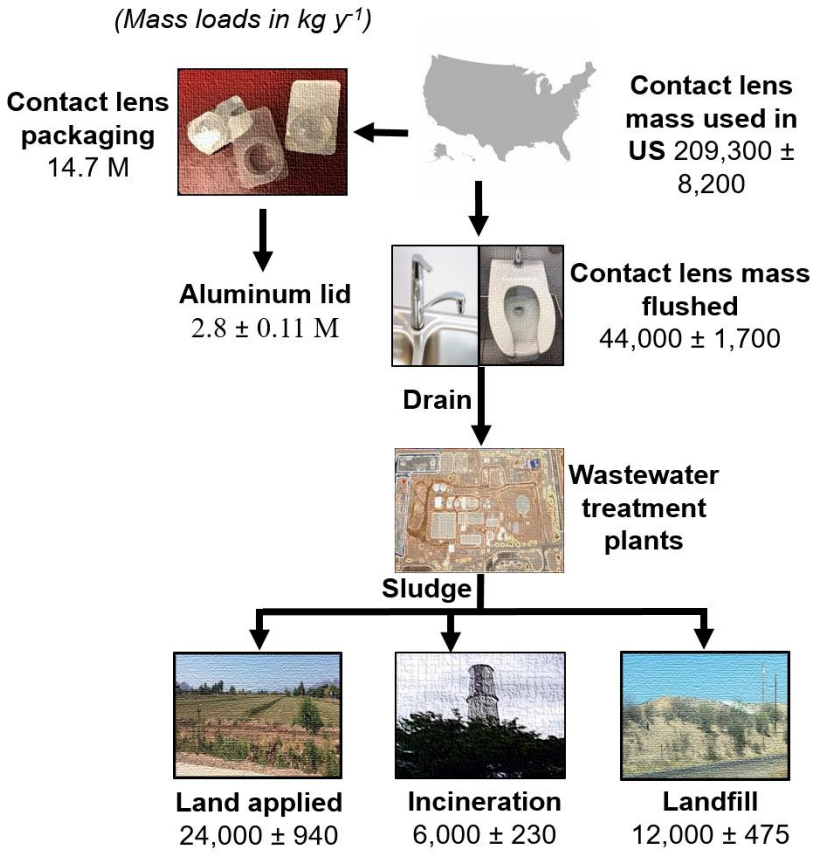

Figure 3-3. Inventory of plastics from contact lenses and packaging material in the U.S. Also included, the environmental fate of these polymers as determined by a national mass balance assessment, in units of kg y^{-1}. Data gathered from our survey and publicly available resources were used to compute the amount of plastic waste originating from

CL use in the United States. We then estimated the amount of plastic CL that, upon down-the-drain disposal, will persist during conventional wastewater treatment to accumulate in sewage sludge which is land applied, incinerated, or disposed of in landfills.

Discussion

CLs are made of silicone hydrogels, which are synthetic plastics manufactured from a spectrum of polymers that can feature hydrophobic binding sites for sparingly water-soluble compounds[101–103]. We demonstrate here that this type of plastic polymer represents a previously unrecognized environmental pollutant. Results from the mass balance highlight the considerable quantity of CLs that are flushed down the drain yearly in the US. Biological wastewater treatment was demonstrated to be ineffective for transforming hydrogel polymers of the kind used for the vision aids. Neither oxic nor anoxic sewage treatment resulted in any significant changes in the hydrogel chemistry.

Laboratory experiments demonstrated that hydrated (wet) hydrogels are subject to gravity sedimentation, suggesting sedimentation as a common fate during wastewater treatment, resulting in the sequestration of hydrogel polymers in primary and secondary sewage sludge, both of which typically are then combined at the plant and subjected to disposal with or without further treatment. The two most widely practiced sludge stabilization treatments in the US, anaerobic digestion and lime stabilization, did not result in any significant structural changes of the polymers, as determined in laboratory and field observations (Figs. 1 and 2); whereas CLs sequestered in sewage sludge underwent little to no chemical degradation, the vision aids were determined to become

subject to physical breakdown by fragmentation, a process giving rise to plastic fragments including microplastics measuring less than 5 mm in length.

Whereas not investigated in this work, it is possible and plausible that fragmentation of CLs also may occur from hydraulic shear forces during passage of hydrogel lenses through the aqueous wastewater treatment unit opera. Adsorption of gas bubbles then may provide small lens fragments with neutral or positive buoyancy, which would enable them to exit treatment plants in reclaimed water. Such lens fragments contained in treatment plant effluent would be exceedingly difficult to detect, requiring filtration of large volumes of wastewater with subsequent analysis of filtrate, a difficult task not attempted in this study. Indeed, to date, no studies concentrating on microplastics in surface and ocean water have reported microplastics made from hydrogels. This lack of prior detection may indicate absence of the materials in these environments or, more likely, may be the result of a reporting bias toward polymers that are integrated into spectral reference databases and that are more frequently monitored for as part of microplastic pollution studies.

Whereas biosolids previously have been shown to contain plastic pollutants[104], the present study established hydrogels as a new type of synthetic polymer pollutant in the form of both macro- and microplastics. Since 50% of US sewage sludge is applied on land as biosolids[105], most of the flushed polymer mass of CLs is expect to become a source of pollution of US terrestrial environments, including agricultural soils. This terrestrial pollution source is only expected to increase in the future, as use of daily, disposable CLs continues to displace glasses and reusable CLs as the vision aids preferred today. Clinical studies have shown participants to favor soft CLs over

monovision sources in regards to distance, focus, and night driving[106]. Daily disposal CLs have also become much more popular due to manufacturer-recommended replacement schedules and patient compliance[91,107]. The anticipated increasing trend of daily lens use would then result in increased amounts of hydrogel polymer inputs into the environment.

Prior work had suggested that the presence of microplastics in agricultural soils may serve to indicate historic disposal of sewage sludge on land[104]. However, conventional polymers such polyethylene have many uses and may find their way into soil environments by a number of pathways other than sewage sludge application[77]. Findings from the present work suggest that hydrogels from CLs – due to their persistence, unique use profile and distinct Raman spectra – may serve in the future as an even more definitive indicator of sludge application on land.

Plastics have been known to adsorb contaminants at high concentrations due to mutual hydrophobicity[80,108], thus CLs may concentrate contaminants during transport throughout the wastewater and sludge treatment process[108]. Plastics, when incinerated, can release adsorbed contaminants as well as CO_2 from the oxidation of polymers[109]. Between 18% and 33% of biosolids produced nationwide in the US are reportedly incinerated. Future trends of incineration are difficult to forecast, as regulations for sludge disposal continue to be subject to scientific review and regulatory change. On the one hand, the mass incinerated may be expected to increase because of higher interest in power generation from biosolids and tighter restrictions among states and municipalities for disposing biosolids on land[110]. On the other hand, incineration is much more cost-intensive process than is the land application of sludge, and the wastewater industry is

continuing its commendable efforts to reclaim to the highest degree possible the beneficial nutrients and carbon contained in sewage sludge.

Whereas this study produced new knowledge on the persistence, fate, and environmental dispersal of hydrogels, it featured some notable limitations. Within the survey, a question regarding user age range was answered only by 66% of respondents, thereby reducing statistical power. Also, an estimated 20% of households in the US use on-site septic systems for wastewater treatment[111]. Whereas septic tanks get pumped periodically and the pumped sludge is then subjected to conventional sewage treatment in municipal plants, the behavior of CL hydrogel polymers during long-term, multi-year storage in septic tanks presently remains unknown.

The data collected in this work suggest that the material stream associated with medical plastics from CLs at present is poorly managed. With one company's notable exception, consumer packaging and user instructions contain no information on how to properly dispose of both the packaging and the used lenses. None of the manufacturers point out to consumers on the packaging of their products that plastic lenses need to be disposed of properly in order to avoid long-term environmental pollution, and the single, currently existing CL recycling program in the U.S. captures only an estimated 0.04% of the overall material flow, despite the fact that it accepts any and all lenses, irrespective of the manufacturer. Responsible continued use of hydrogels in optometry will require significant improvements in product labeling, recycling program expansion, and informational campaigns to educate users about potential risks posed by the disposable vision aids to ecosystem integrity.

TRANSITION 3

In Chapter 3, an unusual and novel source of plastic pollution was identified. The data demonstrates that contact lens users who flush their used lenses down the drain are contributing to plastic pollution in the environment, since conventional WWTPs are not only unable to degrade the lenses, but can fragment them into microplastics.

The goal of my work was to expose lesser-known sources of microplastic pollution while suggesting better matrices by which contamination could be reported and/or analyzed. To conclude, Chapter 4 contains a summary and brief evaluation of plastic usage while making recommendations for the road ahead.

CHAPTER 4

THE ROAD AHEAD FOR GLOBAL PLASTIC USAGE

The production of plastic does not seem to be slowing down[1]. Macroplastics having entered the environment will continue to break down to form microplastics even if the production of first-generation, conventional, non-biodegradable plastics were to slow down or cease. Because of this, MPs will continue to represent a major and growing threat to global ecosystems and human health. Hazards result from their non-biodegradable properties and their propensity to attract, adsorb, and accumulate chemical contaminants, bacteria, and pathogens on their surfaces, and from their ability to biomagnify up the food chain[112–114]. MPs also contain plasticizers, such as flame retardants, which present a threat to ecosystem and human health[115]. Once ingested, these small particles have shown to illicit negative health effects on lower-tier organisms, suggesting they could have a similar impact on other organisms they interact with[115]. These traits and the potential ubiquity of MPs represent a major cause for concern.

This research helped to uncover how rampant MP pollution is throughout a variety of ecosystems. The work showed them to be present in wastewater, which will lead to their existence in landfills, and land applied soils. WWTPs are now considered major sources of MPs to both aquatic and terrestrial environments. One noticeable trend in the MP literature became the disagreement amongst studies on both the morphological nomenclature to describe MPs as well as the most accurate reporting unit for MP contamination. Within the literature, MP particles that are grouped together by size, for example, can have orders of magnitude differences in weight, showing this classification system to be less accurate and less comparable. A novel tool was proposed to help

consolidate this information more efficiently. The online calculator introduced in this work will be accessible to scientists and the public alike, thereby facilitating broader use and enabling citizen science to take stock of and combat plastic pollution. Lastly, this work identified improperly disposed daily contact lenses as newly recognized environmental pollutants. These medical vision aides made from plastics are being flushed down the drain and their paths through WWTPs, into solid waste or the environment, were documented, adverse environmental outcomes that are linked to the ability of plastics to withstand degradative processes of conventional wastewater treatment. This new form of plastic pollution is easier to deter as a since it can be disposed of via solid waste or can now even be recycled, due in part to a new program that this research helped emphasize. It has been suggested that microplastic pollution in soils can be utilized as a biomarker of sludge application but with new research highlighting the propensity for MPs to move around ecosystem via weather events, that becomes a harder task. Using MPs from contact lenses could give a more accurate representation of sludge deposit, as they are highly unlikely to originate from anywhere excluding biosolids.

Future Research Needs.

This research helped to uncover several important topics as they pertain to MP pollution but many areas still require more exploration. First, MPs have been reported in sewage sludge globally, but much research is lacking, such as temporal variations in MP concentrations. This is significant because weather events such as higher amounts of rainfall can greatly influence the MP concentration found in sewage sludge. The

applicability of our online particle-to-mass calculator has yet to be studied or built upon. As this could be an important tool in both the standardization of MP taxonomy as well as the accuracy of reported data, this website's evolution is one we will follow closely. We discovered MPs in some very important organisms and ecosystems but they were localized to one region of the world. The presence of MPs and propensity therein to move up the food chain, as well as their effects on their surroundings, need much more attention. Our work with contact lenses uncovered a system by which human behavior can change for the better. Scientific research coupled with media attention has the ability to completely alter the habits of humans and this is a concept that requires further attention from a social science standpoint. There are sizable gaps in the knowledge as it pertains to the effects of plastic pollution, as well as microplastics, on the living and built environments, but broadly speaking, enough evidence supports the notion that first generation, non-biodegradable plastics should be replaced with more sustainable materials. Unless their long-lasting lifespan, ineffective recycling characteristics and threats to the environment are addressed, plastics will continue to dominate the waste stream and environment as a dangerous form of pollution. Enough is understood about this epidemic to be able to reduce unnecessary plastic usage. For example, of the 300 million Mt. of plastic produced yearly, 50% are only used once before they are discarded[116]. Avoidable plastics such as these should be addressed via legislative and/or non-legislative strategies for their ultimate decrease in production and usage.

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APPENDIX A

SUPPORTING INFORMATION

INTRODUCTION AND CHAPTER 1

Table SI1. The comparison between MP identification techniques

Parameters	**Raman Spectroscopy**	**FTIR Spectroscopy**	**Nile Red fluorescence**	**Pyrolysis–gas chromatography–mass spectrometry (pyr-GC/MS)**
Type of measurement	Visible, Infrared, and UV light	Infrared light only	Fluorescent dye and spectroscopy	Heat decomposes material, separates small molecules via GC, detected via MS
Sample preparation requirements	Minimal, repeatable	Involves more time and effort, somewhat repeatable	Staining and fluoresce spectroscopy, repeatable	Minimal preparation via transfer of particles to pyrolysis cup, non-repeatable
Microplastic identification	Can be used to identify any particle of varying color or shape i.e. fibers	Difficult to analyze red plastics and can melt fibers	Many plastics types have been identified excluding PVC, PA and polyester	Independent of shape and size
Mechanism	Based on scattering rather than absorption	Works on the amount of radiation absorbed	Based on isolating the stained wavelength to recover polymers	MS measures volatile molecules post-release
Why it is better	Non-destructive and non-invasive, with clear spectrum through inelastic scattering	More inexpensive, less fluorescence, and more databases available.	Much less expensive with a high recovery rate	More detailed information relating to the chemical nature or organic additives can be extracted

Table S1. Reported number of MPs per gram from literature search. Keyword search included: Microplastics and sludge, Microplastics and biosolids, Plastic and sludge, Plastic and biosolids. Search engines used: Google Scholar, Pubmed, and ISI Web of Knowledge.

Country	**#MP/g**	**AVG**	***STerror***	**Ref**
US	1			14
	4	2.5	*1.5*	21
Germany	1.3			24
	1.8			24
	1			24
	125			24
	1.4			24
	110	40.0833333	*24.55799146*	24
Netherlands	0.068			20
	0.51			20
	0.76	0.446	*0.202309993*	20
Ireland	10			19
	3			19
	6			19
	5			19
	15			19
	14			19
	11			19

	4	8.5	*1.636634177*	19
China	240.3			26
	0.02			29
	0.0132			29
	0.0138			29
	0.0159			29
	0.0253			29
	0.0077			29
	0.0169			29
	0.0296			29
	0.0149			29
	0.0248			29
	0.0201			29
	0.0292			29
	0.0143			29
	0.0321			29
	0.0231			29
	0.0385			29
	0.0457			29
	0.0242			29
	0.018			29
	0.0126			29
	0.0375			29
	0.046			29
	0.0102			29
	0.0377			29
	0.0111			29
	0.0244			29
	0.0192			29
	0.0222			29
	0.0227	8.03236333	*8.009229066*	29
Sweden	17	17		15
Finland	27.3	27.3		23
Italy	113			41
Korea	1.6			28
	2.3			
	2.6	2.16666667	*0.296273147*	
Canada	14.9			25
	4.4	9.65	*5.25*	
Scotland	1			16

APPENDIX B

SUPPORTING INFORMATION

CHAPTER 2

Study 1:

model shape	**shape**	**0.355–0.999 mm**	**1.000–4.749 mm**	**≥ 4.75 mm**
rectangle	fragment	68,000	35,000	2100
sphere	Pellet	3100	970	0
cylinder	Fiber	80,000	Name	1200
rectangle	Film	8200	22,000	MP Types
sphere	Foam	2300	12,000	460
	Total Count/km2	160,000	140,000	7200
Size range	**fragment**			
0.355–0.999 mm	3	8.57	24.14	68
1.000–4.749 mm	68	789.7	166.3	3750
≥ 4.75 mm	262.5			

Bead				**fiber**			
0.07	1.6	0.47		0.005	0.0093	0.01	

0.5	54.4	13.7		0.01	0.03	0.056	
				0.001			

film				**foam**			
0.01767	0.13994	0.06108		0.02154	0.14223	0.48002	
0.3762	8.48801	3.3858		2.512	67.824	269.216	
1.49625				12.0367			

Study 2:

Dimensions (g)			**Type and number of particles**			
D1	D2	D3	**Foam**	**Filament**	**Bead**	**Fragment**
0.1	0.2	0.15	NA	NA	13	12
0.2	0.3	0.25	NA	NA	27	24
0.3	0.4	0.35	NA	NA	17	15
0.4	0.5	0.45	27	NA	25	22
0.5	0.6	0.55	NA	NA	16	15
0.6	0.7	0.65	NA	NA	NA	3
0.7	0.8	0.75	NA	NA	NA	6
0.8	0.9	0.85	NA	NA	NA	9

0.9	1	0.95	NA	4	NA	2
1	1.1	1.05	NA	NA	NA	4
1.1	1.2	1.15	NA	NA	NA	1
1.2	1.3	1.25	NA	NA	NA	1
1.3	1.4	1.35	2	NA	NA	1
1.4	1.5	1.45	NA	NA	NA	3
1.5	1.6	1.55	2	NA	NA	1
1.6	1.7	1.65	NA	NA	NA	3
1.7	1.8	1.75	NA	3	NA	2
1.8	1.9	1.85	NA	NA	NA	NA
1.9	2	1.95	NA	NA	NA	NA
2	2.1	2.05	NA	7	NA	6
3	3.1	3.05	NA	NA	NA	1
4	4.1	4.05	NA	NA	NA	NA
5	5.1	5.05	NA	NA	NA	NA
6	6.1	6.05	NA	3	NA	NA

Foam	**Filament**

NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
0.0076	0.01484	0.01082	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	2.5434E-06	2.826E-06	2.6847E-06
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
0.01932	0.02413	0.02163	NA	NA	NA
NA	NA	NA	NA	NA	NA
0.02967	0.03601	0.03274	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	3.60315E-06	3.8151E-06	3.7091E-06
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	0.000009891	1.0386E-05	1.0138E-05
NA	NA	NA	NA	NA	NA

NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	0.000012717	1.2929E-05	1.2823E-05

Foam			**Filament**		
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
0.0076	0.01484	0.01082	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	2.5434E-06	2.826E-06	2.6847E-06
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
0.01932	0.02413	0.02163	NA	NA	NA

NA	NA	NA	NA	NA	NA
0.02967	0.03601	0.03274	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	3.60315E-06	3.8151E-06	3.7091E-06
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	0.000009891	1.0386E-05	1.0138E-05
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	0.000012717	1.2929E-05	1.2823E-05

Bead			**Fragment**		
6.2046E-05	0.0005	0.00021	1.368E-05	0.00011	4.617E-05
0.00103092	0.00348	0.00201	0.0002189	0.00074	0.0004275
0.00219072	0.00519	0.00348	0.0004617	0.00109	0.0007332

0.00763648	0.01492	0.01087	0.0016051	0.00314	0.0022854
0.0095456	0.01649	0.01271	0.0021375	0.00369	0.002845
NA	NA	NA	0.0007387	0.00117	0.0009392
NA	NA	NA	0.0023461	0.0035	0.0028856
NA	NA	NA	0.0052531	0.00748	0.0063009
NA	NA	NA	0.0016621	0.00228	0.0019548
NA	NA	NA	0.00456	0.00607	0.0052788
NA	NA	NA	0.0015173	0.00197	0.0017338
NA	NA	NA	0.0019699	0.0025	0.0022266
NA	NA	NA	0.0025046	0.00313	0.0028048
NA	NA	NA	0.0093845	0.01154	0.0104263
NA	NA	NA	0.0038475	0.00467	0.0042452
NA	NA	NA	0.0140083	0.0168	0.0153631
NA	NA	NA	0.0112016	0.0133	0.0122194
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	0.05472	0.06335	0.0589275
NA	NA	NA	0.03078	0.03396	0.0323448

NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA

Study 3:

Dimensions (mm)			**Size mm**	**# of MPs**	**Masses (g)**		
1.25			<1.25	320	0.0003222		
1.25	2.5	1.875	>1.25-2.5	900	0.0009061	0.00181	0.00136
2.5	3.75	3.125	>2.5-3.75	575	0.0011578	0.00174	0.00145
3.75	5	4.375	>3.75-5	250	0.0007551	0.00101	0.00088

Study 4:

Dimensions (mm)			**# particles**	**fibers**			**granules (beads)**		
0.5	1	0.75	504	0.0002	0.00036	0.00027	0.30069	2.40549	1.0148166
1	2	1.5	300	0.0002	0.00042	0.00032	1.43184	11.4547	4.83246

2	3	2.5	100	0.0001	0.00021	0.00018	3.81824	12.8866	7.4575
3	4	3.5	45	1E-04	0.00013	0.00011	5.79895	13.7457	9.208521
4	5	4.5	25	7E-05	8.8E-05	7.9E-05	7.63648	14.915	10.873035
		5	35			0.00012			20.881

Study 5:

Size Range	**Fragment**	**Film**	**Foam**	**Pellet**	**Line**
0.355–0.999 mm	247,106.50	3943.5	54,340.90	430,029.80	1328.9
1.000–4.749 mm	123,906.20	1332.2	18,208.40	5614.1	2571.9
>4.75 mm	11,219.80	4006.1	1810.5	420.9	449

Dimensions (mm)			**Foam**			**Pellet**		
0.355	0.999	0.677	10.68734	238.1667	74.12258	84.5749	1884.75	586.573
1.00	4.75	2.8745	80.04413	8573.062	1901.15	24.6796	2643.29	586.172
4.75	5	4.875	852.9765	994.8698	922.1044	198.298	231.285	214.368

Dimensions (mm)			**Line**		
0.355	0.999	0.677	0.000333	0.000938	0.000636
1.00	4.75	2.8745	0.001817	0.008629	0.005223
4.75	5	4.875	0.001507	0.001586	0.001546

Line		
0.00033	0.00094	0.00064
0.00182	0.00863	0.00522
0.00151	0.00159	0.00155

The online calculator offers a standardized way of defining a) plastic particle shapes (e.g. fiber, bead, etc) and particle modeled dimensions. The online calculator was developed in R Studio 1.2.1335 using R 3.5.3 and R Shiny 1.3.2. The R packages rgl and shinyRGL were used for 3D visualization of the modeled particle dimensions. The application is currently hosted on https://shinyapps.io, and estimates the total volume and mass of plastic on a per-particle and per \-sample (with *n* number of particles) basis.

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APPENDIX C

SUPPORTING INFORMATION

CHAPTER 3

SI Table 1. Varying densities at which contact lens types became buoyant.

Polymer	1 g/ml*	1.1 g/ml*	1.2 g/ml*	1.3 g/ml*	1.4 g/ml**
Omafilcon	✗	✗	✗	✗	✓
Nesofilcon	✗	✗	✗	✗	✓
Nelfilcon	✗	✗	✓		
Narafilcon	✗	✗	✓		
Etafilcon	✗	✗	✗	✗	✓

***= Sodium Chloride; ** = Sodium Thiosulfate**

SI Table 2. Additives associated with different CL types.

Company	Additive	In the material	In the buffer solution	Purpose
Vistakon (Acuvue advance and Acuvue Oasys)	1. Polyvinyl alcohol (PVA)* 2. Polyvinylpyrrolidone (PVP) ** 3.Methylcellulose (0.0005% concentration)	No	Yes	Adsorptive, film forming and lubricating properties, retain moisture, wetting agent
Bausch & Lomb (Soflens 38 lens)	PVA poloxamine	No	Yes	Lubrication and shape retention Retaining moisture
CIBA vision (air optix aqua and Air optix night and day aqua)	1 % Copolymer 845 - O	Yes	No	Moisture retention
CIBA vision (Aqua releases lens)	PVA	Yes	Yes	Lubrication

CIBA vision (Fresh look one day package)	0.02% poloxamer	No	Yes	Not mentioned
CIBA vision (AquaComfort Plus)	hydroxypropyl methylcellulose (HPMC) PEG	No	Yes	Wetting agent
CIBA vision (AquaComfort Plus)	PEG* PVA	Yes	No	Conditioning contact angle
Vistakon (Acuvue 1 day moist)	PVP	Yes	No	Not mentioned
CooperVision	No polymeric material used in the lenses			

Source: Contact lens spectrum

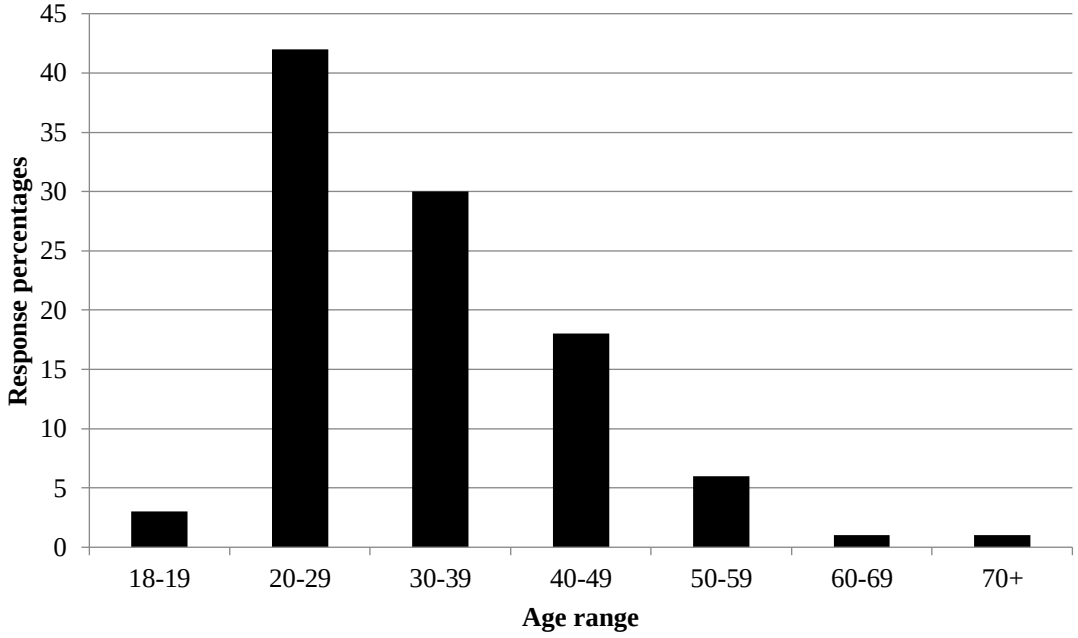
SI Table 3. Inventory of contact lenses obtained from a local, anonymous optometrist.

Serial number	Brand	Polymer type	Duration
1	*Acuve Vita*	Senofilcon C	Monthly
2	*Alcon Dailies Aqua Comfort Plus*	31% Nelfilcon A	Daily
3	*B & L Biotrue*	Nesofilcon A	Daily
4	*Acuve Oasys*	Senofilcon A	Daily
5	*Vision Source Fresh Day*	44% Somofilcon A	Daily
6	*Acuve Trueye*	Narafilcon B	Daily
7	*Ciba Vision*	31% Nelfilcon A	Daily
8	*Acuve Trueye*	Narafilcon A	Daily
9	*Cooper Vison Proclear (trial)*	38% Omafilcon B	Daily
10	*Cooper Vision Proclear*	40% Omafilcon A	Daily
11	*B & L Soflens Multifocal*	Polymacon	Bi-weekly
12	*Cooper Vision*	45% Fanfilcon A	Daily
13	*Acuve Moist*	Etafilcon A	Daily

Fragmentation test

Wet lenses began to fragment upon repeated transfer and manipulation with tweezers during optical inspection and coming into contact with microscopy glass slide surfaces. Dried lenses were found to be much more fragile, disintegrating quickly into multiple microplastics (5+/- 1) upon shaking for thirty seconds in a glass vial.

Supplementary Figures



SI Figure 1. Responses indicating the age range of CL users partaking in the online survey.

APPENDIX D

PROJECTS ASSISTED WITH

1. Choy, C. Anela, et al. "**The vertical distribution and biological transport of marine microplastics across the epipelagic and mesopelagic water column**." Scientific reports 9.1 (2019): 1-9.

Choy et al., 2019.pdf

Throughout the marine water column, MPs were demonstrated to exist at depths ranging from 5m down to lowest sampled depth, at 1000m below the surface of the ocean[108]. Following this, it was confirmed that MPs were present in the stomach of the most abundant species of micronekton in the world, a group comprised of cephalopods, crustaceans, and small fish[109]. These organisms play a vital role within their ecosystem and are considered one of the most important grazing animals in the ocean due to their ability to consume energy created during primary production[109,110].

I contributed as principal analyst on the study. Water was filtered at varying depths, the filters were sent to me and I first extracted all particles of interest before later gathering spectra via a Raman Spectrometer, which were run through a code that identified the polymers. The stomachs of crabs and larvaceans were also filtered and sent to me. The process was repeated with all particles of interest from the stomachs being run through the spectrometer.

2. **Movement of Marine-Based Microplastics from Seabird Guano to Terrestrial Ecosystems**
   Alyssa Anderson
   Committee: Cayle Lisenbee, Charles Rolsky, Rolf Halden

Here, I served as the lead principal analyst alongside an honors undergraduate working with me on the project. We were sent dried, Red Footed Booby fecal samples from the

Palmyra Atoll. In the lab, we developed a method to digest the feces, filter it, search for particles of interest and then analyze them via Raman Spectroscopy.

APPENDIX E

AWARDS AND HONORS

Chosen as a College of Liberal Arts and Sciences Student Leader (2019)

Emmy award winner, National Academy of Television Arts & Sciences – Rocky Mountain Southwest Chapter (2018)

Research chosen by 2018 American Chemical Society conference for worldwide promotion

Nominated for ASU's Outstanding Faculty Mentor Award (2018)

Nominated for ASU Faculty Women's Association Distinguished Graduate Student Award (2017)

Awarded Continuing Excellence Award through GPSA (2015)

Awarded Teaching Excellence Award through GPSA (2014)