

Report No. WI-2019-09 24 December 2019

## **CCOWS** Watershed Studies

Quantifying microplastic inputs from urban and agricultural watersheds in the Monterey Peninsula

## The Watershed Institute

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#### Acknowledgements

We would like to thank the following people for their assistance on this project:

Monterey Bay National Marine Sanctuary

• Pamela Krone

California State University Monterey Bay, School of Natural Sciences

- Riley Ransom (student)
- Joy Nguyen (Science Laboratory Support Technician)
- Jeanette Favaloro (Science Lab Instructional Support Technician)

Disclaimer: This report is the result of a pro bono study for the Monterey Bay National Marine Sanctuary by ENVS 660 Class Fall 2019 California State University Monterey Bay. It primarily represents graduate student work completed within the constraints of a fixed duration (five-week) college class setting.

This report may be cited as:

CSUMB Class ENVS 660: Caudillo A, Gennaro M, Klein J, Kortman S, Kwan-Davis R, Wandke J, Olson J. 2019. Quantifying microplastics in urban and agricultural watersheds in the Monterey Peninsula. Watershed Institute, California State University Monterey Bay, Publication No. WI-2019-09.

## **Executive Summary**

This report quantifies and compares microplastic inputs from drainages that flow into the Monterey Bay National Marine Sanctuary (MBNMS). Microplastics (MPs) are plastic fragments less than 5 millimeters (mm) that typically enter the marine environment via direct dumping, urban and rural run-off, and effluents from sewage plants. A recent study in the MBNMS found MPs throughout the water column and that particle-feeding species such as pelagic crabs are ingesting MPs. Particles move up the marine food web, eventually impacting populations of ecologically and commercially important predatory species in Monterey Bay. Urban and marine sources of microplastic pollution are well documented while agricultural sources of MPs have received relatively less attention and are not well-studied. The Monterey Bay region, known for its agricultural industry, particularly in the Salinas Valley, offers an opportunity to study and directly compare microplastic inputs from urban and agricultural watersheds.

As part of California State University at Monterey Bay's (CSUMB) Applied Environmental Science 660 class (ENVS 660), we examined microplastic (<2mm) quantity, form, polymer type, and load from three agricultural and urban watersheds in Monterey County. We sampled Quail, Gabilan, and Santa Rita creeks that flow through areas of agricultural use in the Salinas Valley. Urban sampling sites consisted of one storm drain in the City of Monterey (Twin 51's) and two in Pacific Grove (Sea Palm and Pico). We collected samples in the first week of December, several days after the first series of rain events in water year 2020. This study followed a similar methodology used in February and March 2019 by CSUMB School of Natural Sciences undergraduates Riley Ransom and Yulia Loshkiareva, under the mentorship of Pamela Krone (Monterey Bay National Marine Sanctuary), during which they sampled from several agricultural sites including Quail, Gabilan, and Santa Rita (Ransom et al. 2019).

Microplastics were detected from all sampling sites except for Gabilan Creek. We collected 131 microplastic particles of which 17 were >2mm and up to 10mm. Ninety-six particles were collected from urban sites and 35 from agricultural sites. Microplastics were mostly fibers (124), followed by fragments (4), films (1), pellets (1), and foams (1). From the urban samples, Pico had the most MPs all of which were fibers (43), Sea Palm had fibers, fragments, and foams (34), and Twin 51's had fibers (19) and one pellet.

From the agricultural samples, Santa Rita Creek only had fibers (25) and at Quail Creek, we detected fibers and films (10). Using spectroscopy analysis, we were only able to analyze 49 particles (37% of all particles). The remaining particles (82) were too small for analysis. Twenty-six particles did not match to any known library polymer while 23 particles matched a known library polymer. The polymers that were matched all originated from Sea Palm and they were matched to low-density polyethylene (2 particles, >75% match) and Poly(butyl acrylate) (21 particles, >80% match).

Microplastics were also more concentrated (parts/m<sup>3</sup>) in urban compared to agricultural samples. Microplastics from the Sea Palm sample were the most concentrated (34.8) and of the agricultural samples, Santa Rita was the most concentrated (18.9). A notably lower concentration of MPs (< 7 parts/m<sup>3</sup>) was observed by the previous study of agricultural sites. With respect to load (parts/min), agricultural samples were higher (33.3–38.4 parts/min) compared to urban samples (1–2.1 parts/min). However, when we examined unit-area loads, urban sites had higher loads (1.8–5.9 parts/min/km<sup>2</sup>) compared to agricultural samples (0.8–6.8 parts/min/km<sup>2</sup>). We suspect urban samples had a higher unit-area load and were more concentrated because the urban watersheds sampled were smaller and because it may take more time under wet conditions for MPs to mobilize in larger, agricultural watersheds.

Agricultural sites are likely to be a more significant source for MPs because of the greater proportion of agricultural land cover throughout Monterey County and consistent plastic use throughout agricultural fields in this region. We found weak evidence of a correlation between MP concentration per watershed area and land cover in agricultural watersheds (p = 0.053). This conclusion was drawn from three data points so the correlation should be interpreted as a preliminary result. However, these data suggest that agricultural watersheds may provide important and significant unquantified contributions of microplastics compared to urban watersheds around the Monterey Bay.

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## 1 Introduction

Global plastic production has increased rapidly since the 1950s to meet increasing demands for manufactured goods and packaging. The ubiquitous use of plastics has led to significant marine plastic pollution, an environmental challenge spanning nearly all ecosystem types (Choy et al. 2018). Microplastic debris has become pervasive in the ocean, occurring on shorelines, coastal waters, and the seabed of the deep ocean, making microplastics an emerging issue within the past decade (Masura et al. 2015;UNEP 2016).

Globally, 0.8 to 2.5 million tons of microplastics end up in oceans every year (Ng et al. 2018). Microplastics (MPs) are small particles or plastic fragments measuring less than 5.0 millimeters in diameter (Masura et al. 2015; UNEP 2016). There are two ways MPs are formed and enter a body of water. Primary MPs consist of manufactured raw plastic material that enter the ocean via runoff from land (Masura et al. 2015). These are purposefully manufactured for industrial and domestic use, and include microbeads used in cosmetic and personal healthcare products (e.g. toothpaste, cleansing agents, skin exfoliators, medicines) (Thompson 2015; UNEP 2016). Textiles transported by sewage and storm water also account for a significant portion of primary MPs (Dris et al. 2015; Thompson 2015). Secondary MPs are large plastic items that are progressively broken down into MPs via mechanical, photo, or biological degradation (Masura et al. 2015; UNEP 2016).

In the marine environment, MPs are being transported to deeper waters through physical and biological processes and have entered marine food webs (Choy et al. 2018). Microplastics have been found in commercial fish, shellfish, bivalves, mollusks, and crustaceans (UNEP 2016; Lusher 2015). Marine organisms ingesting plastic debris may be exposed to contaminants absorbed to the plastic, and there is evidence that these contaminants are being moved up the food web to higher trophic levels (Masura et al. 2016). Even humans may be exposed to MPs through the consumption of marine food such as bivalves and crustaceans (Smith et al. 2018; UNEP 2016).

Rivers are thought to be a primary source of macro and microplastics to the marine environment. Globally, an estimated 80% of all solid beach litter originates from the

nearest rivers (Rech et al. 2014). Rivers are significant conduits for MPs, especially those draining areas with high population densities and industrial development (Hoellein et al. 2014; UNEP 2016). Microplastics can originate from direct dumping, urban and rural run-off, and effluents from sewage plants (Rech et al. 2014), and are sourced from plastic pellets, industrial abrasives, injection powders, vehicle tires, fabrics, clothing, and the degradation of macroplastics (UNEP 2016). Other studies have called for the measurements of MPs in agricultural runoff to help address the gap in data from this important source (Dris et al. 2015; Fahrenfeld et al. 2018; Moore et al. 2011; Steinmetz et al. 2016; Yonkos et al. 2014).

Plastic is used heavily in modern agriculture due to its ability to increase yields and expand growing seasons (Schrader 2000). As demand for food has increased, plastic use has also expanded to meet the need to distribute more food, to an estimated global use of 2 to 3 million tons per year (TMR 2013; Kyrkou and Briassoulis 2007). Plastic is used most commonly in agriculture as mulch, erosion control, crop protection, irrigation, windbreaks, and greenhouse covers (Espi et al. 2006). In many of these uses, plastics are used in the form of films made from Low density polyethylene (LDPE), and Linear low-density polyethylene (LLDPE) (Hurley 2008). The degradation of these materials introduces MPs into the soil (Steinmetz et al. 2016). The increased use of controlled-release fertilizers is a more recent source of MPs which are washed into aquatic systems during rainfall events (GESAMP 2016; Weithmann et al. 2018). The high level of plastic use in agricultural ecosystems, problems with clearing of waste plastics from fields, and inputs of existing MPs in biosolids used for fertilizer have resulted in agricultural ecosystems becoming some of the most microplastic-polluted terrestrial ecosystems (Kyrkou and Briassoulis 2007; Ng et al. 2018; Steinmetz et al. 2016).

The goal of this study was to examine MPs originating from agricultural and urban watersheds in Monterey County, on the central coast of California. Eleven percent of Monterey County is cultivated year-round primarily in the heavily irrigated Salinas Valley, which produces a significant amount of food for the United States and 26 foreign countries and is an industry valued at \$4 billion in 2018 (MCAC 2018). The Salinas Valley Watershed drains into the Monterey Bay and protected Monterey Bay National Marine Sanctuary, an iconic and ecologically important deep submarine canyon ecosystem. MPs are widespread in the Monterey Bay and are impacting several marine species that

support and fuel the populations of ecologically and commercially important predatory species (Choy et al. 2018). To assess the impact of MPs from terrestrial sources in coastal Monterey County we sought to answer the following:

- 1. What are the quantities of MPs flowing into Monterey Bay originating from agricultural and urban watersheds that drain into the Monterey Bay?
- 2. What are the amounts of different MPs according to form (e.g. fragment, foam, fiber) and polymer type?
- 3. What are the polymer types identified in the MPs collected in this study? We used attenuated total reflectance (ATR) with Fourier transform infrared (FT-IR) spectroscopy to characterize the chemical composition of microplastics.

## 2 Methods

#### 2.1 Study Area

The study area includes three agricultural and three urban watersheds in Monterey County, on the central coast of California (Fig. 2.1A). Agricultural watersheds in the study area are located in the Salinas Valley, large areas of which are cultivated year-round as part of an annual four billion-dollar agriculture industry (MCAC 2018). Surface water in the Salinas Valley is influenced by precipitation and runoff from the Gabilan and Sierra de Salinas mountains and ultimately flows into the Monterey Bay and the Monterey Bay National Marine Sanctuary (MBNMS). The Salinas River is the largest river that flows into the MBNMS and is subject to large amounts of agricultural discharge (Anderson et al. 2003).

We sampled three streams that are tributaries to the Salinas River and flow through areas of agricultural land use: Quail Creek, Gabilan Creek and Santa Rita Creek (Fig. 2.1B). Land cover associated with agricultural use in the Quail Creek, Gabilan Creek and Santa Rita Creek watersheds is 15%, 8% and 62%, respectively, while developed land cover is 4%, 2% and 23%, respectively. Each of these streams is classified by the U.S. Geological Survey (USGS) National Hydrography Dataset as intermittent. Gabilan has the largest watershed area of the three streams and typically flows between the months of December

and May, based on monthly flow data from the former USGS gaging station (11152600). Mean monthly flow for Gabilan Creek between December and May from the period of record was most commonly below approximately 50 cubic feet per second (cfs). Quail and Santa Rita watersheds do not have USGS gaging stations, but the Central Coast Cooperative Monitoring Program reported flows at Quail Creek (station 309QUI) between 0 and 7.98 cfs in calendar year 2017 (Tetra Tech 2018). Monitoring data provided by MBNMS for Santa Rita Creek indicates periodic flow up to approximately 12 cfs in wet months, with flow only rarely occurring due to irrigation runoff in the dryer period of April through September (P Krone, personal communication, December 13, 2019).

Urban watersheds in the study are located in the coastal cities of Monterey and Pacific Grove, which do not have agricultural land cover but have a relatively high density of developed areas and impervious surfaces. Surface water runoff occurs primarily during storm events and enters the MBNMS through networks of storm drains. We sampled three storm drains at their outlets to the Monterey Bay: one storm drain located in Monterey and two in Pacific Grove (Fig. 2.1C). Developed land cover in the urban watersheds associated with the Pico, Twin 51's and Sea Palm sampling sites is 84%, 96% and 98%, respectively. Sampling at both agricultural and urban sites occurred on December 2nd and 5th, 2019, several days after the first series of rain events for water year 2020.

#### 2.2 Microplastic sampling

#### 2.2.1 Agricultural

We adapted the sampling methodology by Ransom et al. (2019) for collecting microplastics in agricultural and urban water bodies. At each sampling site, we collected a sample of debris from the water column and hydrologic data as described in McCormick et al. (2016). Hydrologic data was collected using flow tracker (Sontek<sup>©</sup> FlowTracker (6054–60211–B) and included ten measurements of average depth, velocity and discharge at 60% depth along a representative cross section of the sampling site.

We used a 0.5mm mesh size drift net to collect debris at a point in the tributary that was deep enough to submerge the net. The net was anchored to the stream bed with rebar



Figure 2.1 (A) Study area and locations of three urban and three agricultural sampling sites. (B) Agricultural watersheds; shaded zones with a solid boundary indicate watershed area above of sample sites. (C) Urban watersheds.

to which PVC (5cm height) was placed over to keep the net from touching the bottom and thus minimizing the amount of sediment collected. We deployed the net for 15 seconds to 25 minutes, depending on the flow at the urban sites to standardize the amount of volume captured at each site type. While sampling with the drift net, we had an open sample jar on the bank of the tributary to serve as a field blank to account for microplastic potentially present in the surrounding environment. We removed the net and rinsed the sides to flush any residual matter into a cup secured to the bottom of the net. We triple rinsed the contents of the cup into a glass jar with 4.75L of water until no contents remained in the cup. We secured the cup back onto the drift net and used two rinses (3L) of water to rinse the net again. We rinsed the contents of the cup three times into the open field blank sample jar, so that we could determine if MPs were not being completely rinsed from the net between sites.

We collected macroplastic samples from the banks of the tributaries to allow us to analyze potential sources for MPs. These samples were processed and analyzed following the same procedure as the MPs.

#### 2.2.2 Urban

Unlike agricultural sites, we could not submerge the net in the outflow pipe, thus we held the drift net under the outflow for 20 to 25 minutes, depending on the flow to standardize the volumes captured at each site type. At Pico, we used sandbags and a 3-inch diameter, 6-foot pipe to force most of the water through the drift net.

To measure discharge at urban sites, we collected three replicate measurements for the amount of time to fill a 1L graduated cylinder and calculated the average discharge. We followed the same process for rinsing and collecting field blanks as used at the agricultural sites. We also collected macroplastics from around the site upstream of the outflow.

#### 2.3 Processing microplastic samples

We followed the protocol previously established by Masura et al. (2015) for laboratory methods. Samples blanks were transferred onto stacked sieves (5mm and 0.3mm) to collect MPs and separate larger matter, such as leaves, from the sample. We rinsed the

sieves with distilled water to remove any salts and to allow any small particles trapped in the larger particles to fall onto the 0.3mm sieve. After rinsing, we transferred solid material from the 0.3mm sieve into a clean, dry beaker. When all the solids were transferred, we placed the beaker in an oven at 90°C for 24 hours or until the sample was completely dry. We followed this same process for the field blanks.

With the dried sample, we dissolved organic matter in the sample using a chemical digestion of 20mL 0.05M Iron (II) Sulfate (FeSO<sub>4</sub>) and 20mL 30% Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>). The mixture sat for five minutes and then it was heated it to 75°C until the chemical reaction began. The chemical digestion took place for approximately one hour. If the reaction stopped, we added 20mL of H<sub>2</sub>O<sub>2</sub> to continue the reaction until there was no more bubbling, indicating digestion was complete. When the reaction was complete, transferred the sample to a 0.3mm sieve and rinsed it remove any residual chemicals until a pH of 7 was achieved. The sample was air dried overnight. The same digestion and rinsing procedure were carried out for a laboratory blank of 150mL of distilled water and small pieces (approximately 5mm) of the macroplastic samples.

We analyzed the inorganic debris under a dissecting microscope to identify what types of plastics were present. We used plastic types set by the MERI Guide to Microplastic Identification to classify each particle into one of two size categories (<2mm and >2mm) and a physical category hereafter referred to as "form". Common forms of MPs include fibers, foams, and fragments (MERI n.d.). Identifications were verified by two technicians before all MPs were placed in a glass vial.

#### 2.4 ATR FT-IR analysis

We determined the chemical composition of both the microplastic, macroplastic, and field blank samples using ATR FT-IR in transmission mode with 16 scans per sample and background scans after every hour of machine use (ThermoFisher Nicolet Summit FTIR with Everest ATR). ATR FT-IR compares the infrared (IR) spectrum of a sample to a library of known polymer spectrums and returns a match (% match). We adopted a match threshold of 60%, which is considered the lower limit of an 'intermediate' match by Kroon et al. (2018). In addition to using the spectrometer's built-in library, we built our own library of spectra based on the macroplastic samples we digested in order to potentially

identify the originating source of the microplastics we acquired. Along with a "matched" particle, we classified a particle as "unknown" if the sample did not match any spectrum. Microplastic samples that were too small for the ATR FT-IR were not analyzed and were considered "unassessed".

In order to confidently report matches above the 60% threshold we performed a twosided Student's t-test to assess the accuracy of the ATR FT-IR generated match for each MP to the corresponding polymer it was matched to. We were unable to export the spectra of known polymers from the ATR FT-IR libraries for analyses. Therefore, we substituted the spectrum of the best-matched macroplastic for known polymer spectra and compared it to the spectra of a microplastic sample. If there was no significant difference (p<0.05) we considered the match valid and reported the results (Appendix A).

# 2.5 Estimating microplastic density by land use type and hydrologic conditions

Determination of relative percentage of developed and agricultural land use by watershed was used to explore a potential relationship between land use and concentration of microplastics in surface water. We determined percentage of land use in each agricultural and urban watershed using ArcGIS and the 2016 National Land Cover Database (NLCD). We extracted land cover for each watershed and calculated the relative percentage of each land cover class. The relative percentage of "developed" land cover is the sum of NLCD classes Developed Open Space and Developed Low Intensity, Medium Intensity and High Intensity. The relative percentage of "agricultural" land cover was calculated as the sum of NLCD classes Hay/Pasture and Cultivated Crops.

To estimate the density of MPs that are present in the study sites we calculated attributes of plastic in the tributaries and outflows sampled including load (parts/minute), concentration (parts/m<sup>3</sup>), and volume (L) captured. Velocity was estimated from agriculture sites with a conservative approach based on actual velocity measurements by the Flow Tracker, and represented in the following equation:

$$V = V_{avg} + \frac{1}{2} (V_{max} - V_{avg})$$

where  $V_{avg}$  represents the average velocity of the stream as calculated from 10 equally spaced measurements along a cross section of the stream, and  $V_{max}$  is the maximum velocity. This estimate is considered conservative because the Flow Tracker determines velocity at 60% depth and the net was placed lower than that in the stream where velocity is not as high.

We also estimated load per watershed area, or unit-area load, for a better estimate of the amount of plastics in the watershed.

## 2.6 Statistical analysis

We performed a one-way analysis of variance (ANOVA) to test the significance of concentration, load, and load per watershed area to site type (agricultural or urban) (Appendix B). We assessed the relationship between percent human land cover (i.e., agricultural or developed) and MP concentration by fitting a linear model to test the significance of the correlation.

## 3 Results

## 3.1 Hydrologic conditions during field sampling

Urban sites had lower flow than agricultural sites (Table 3.1) and in order to capture similar volumes of discharge across all sites, we sampled urban sites for a longer time than agricultural sites. Across all sites the total volume of water we sampled MPs from was comparable and generally within the same order of magnitude, except for at Sea Palm and Gabilan where we only captured 977 L of water and 393 L of water, respectively. We visually estimated that 80% of the flow was captured at Pico which was accounted for in reported estimates of volume, concentration, and load. Gabilan was sampled on a day with heavy rainfall, which resulted in greater flows than all other sites, so we sampled for only 15 seconds to match the estimated urban discharge.

Table 3.1. Hydrologic data used to calculate microplastic concentration, load, and unit-area load for each site. Items referred to as "captured" reflect water that has flowed through the sampling net, while those referred to as "total" reflect the entire channel. At Pico only 80% of flow was captured, and results reflect that.

		Watershed Area	Sample Duration	Net Velocity	Captured Area	Total Area	Captured Flow	Total Flow	Captured Volume	Total Volume
	Site	(km²)	(min)	(m/s)	(m²)	(m²)	(L/s)	(L/s)	(L)	(L)
tural	Gabilan	103.11	0.26	0.31	0.08	0.93	25.0	193.6	393	3040
gricul	Quail	40.5	2	0.21	0.10	0.67	20.8	86.1	2490	10332
۷	Santa Rita	5.64	7	0.03	0.10	1.08	3.2	21.6	1323	9072
Urban	Pico	0.75	25	NA	NA	NA	2.3	2.8	3400	4250
	Sea Palm	0.23	25	NA	NA	NA	0.7	0.7	977	977
	Twin 51's	0.54	20	NA	NA	NA	7.6	7.6	9120	9120

#### 3.2 Microplastic abundance and form by land use type

We detected a total of 131 MPs (Table 3.2); 96 MPs came from urban sites and 35 from agricultural sites. We observed 17 particles (13% of total) between >2mm and 10 mm. These larger particles were included in the analysis of MPs because we assumed these particles to have the same biological effect as MPs <2 mm. Most of the MPs were fibers and only a small number were any other form (Fig. 3.1).

Table 3.2. Number of microplastics detected in microscopy based on site.

	Site	Sample	Blank	Total
ural	Gabilan	0	3	3
icult	Quail	10	1	11
Agr	Santa Rita	25	5	30
_	Pico	43	20	63
Jrbar	Sea Palm	34	9	43
	Twin 51's	19	5	24



Figure 3.1. Microplastic (MP) forms observed from samples collected at each site. Out of 131 particles, 95% were classified as fibers with only a few classified as fragment, film, pellet or foam.

We found MPs in blanks from each site, ranging from 1 to 20 particles (Table 3.2). Similar to the samples collected from runoff or outflow, most of the blank MPs were classified as fibers, although some fragments were observed.

Concentrations (parts/m<sup>3</sup>) of MPs in urban sites were slightly, but not significantly greater than those of agricultural sites (range of 2.1 to 34.8 and range of 0 to 18.9, respectively, p = 0.892) (Fig. 3.2A). Load estimates were greater for agricultural sites, but not significantly so (p = 0.135) (Fig. 3.2B). The watershed areas calculated for urban sites were smaller than those of agricultural sites (Table 3.1). When load was standardized by watershed area, unit-area load (parts/min/km<sup>2</sup>) did not differ greatly between agricultural and urban sites (range of 0 to 6.8 for agriculture and 1.8 to 5.9 for urban) (Fig. 3.2C) (Appendix B).



Figure 3.2. Comparison of microplastic concentration, load, and unit-area load across all sites. (A) Concentration was higher in urban sites, on average, because less water was sampled than in agricultural sites. (B) Loads were higher in agricultural sites due to higher discharge. (C) Unit-area loads were higher in urban sites than in agricultural sites and are more similar across sites and on average within the same order of magnitude.

## 3.3 Polymer types identified with ATR FT-IR analysis

We were only able to analyze 49 particles using ATR-FTIR, 26 from urban and 23 from agricultural sites; 82 of the MPs (63%) were too small for technicians to see and retrieve from sample storage vials for analysis (Fig. 3.3). Of the particles analyzed, 24 did not match to any known library spectrum, a majority of which were from agriculture sites (Fig. 3.4, Appendix C).

The ATR FT-IR percent match results to known polymers indicate only one particle (Sea Palm Fragment 3) was statistically different (p < 0.01) from the FT-IR-generated match (Appendix A). This may be because we had to use the best-matched macroplastic sample spectra to perform the t-tests instead of the actual spectra of known polymers from the ATR FT-IR libraries.

Spectra of the urban MPs correlated mostly with poly(butyl acrylate) (PBA) and lowdensity polyethylene (LDPE), whereas agricultural plastics did not correlate with any known polymer in the available spectra libraries (Fig. 3.4). All 23 of the identified MP spectra matched had at least a 60% match to known library polymer spectra, with 9 matches greater than 80%.



Figure 3.3. Percent of polymer types determined by ATR FT-IR based on the 49 of the 131 assessed particles via ATR FT-IR.



Figure 3.4. Number of polymer types found at agricultural and urban sites. None of the agricultural microplastics were identified to any known spectrum of polymers. One agricultural microplastic matched the spectrum of a separate microplastic sample, which did not match any known library spectrum.



Figure 3.5. Correlations between percent land cover and concentration of plastics at agricultural sites and urban sites.

## 3.4 Correlation of plastic and land cover type

Percent agricultural land cover was weakly correlated to the concentration of plastics for agricultural sites (p = 0.053, Fig. 3.5). Percent land cover type and concentration for urban sites was not as correlated (Fig. 3.5). All correlation plots can be found in Appendix D.

#### 3.5 Comparison to previous work

In February and March 2019, Ransom et al. (2019) surveyed MPs at the same agricultural sites sampled in this study. We compared concentrations of MPs and the volume of water captured between the late winter 2019 sampling (R. Riley, unpublished data, December 13, 2019) and this Fall 2019 study to assess potential patterns or differences in MP abundance across the two seasons.

Ransom et al. collected a total of 568 MPs in agricultural sites consisting of various proportions of the five forms of MPs (Table 3.3, Appendix E). The volume of water sampled at agricultural sites by Ransom et al. was one to two orders of magnitude greater than this study in December 2019 (Figure 3.6). The larger amount of volume captured by Ransom et al. resulted in a lower average MP concentration (3.9 parts/m<sup>3</sup>) than ENVS 660 (7.9 parts/m<sup>3</sup>) at the same agricultural sites.

Table 3.3. Comparisons of microplastic (MP) counts from Ransom et al. and ENVS 660. Ransom et al. collected ten times more MPs at each site than ENVS 660 collected. MP counts by Ransom et. al. were averaged between two technician's microscopy counts conducted during two independent sessions.

	Site	Date (2019)	Sample Duration (min)	Captured Volume (L)	Total MP	Film	Fiber	Fragment	Pellet	Foam
t. al	Gabilan	23-Feb	20	69080	172	80	86	3	4	0
som e	Quail	9-Mar	25	69828	141	46	80	15	1	0
Ran	Santa Rita	10-Feb	20	35482	256	133	40	64	19	0
20	Gabilan	2-Dec	0.3	393	0	0	0	0	0	0
IVS 6(	Quail	5-Dec	2	2490	10	1	9	0	0	0
EN	Santa Rita	5–Dec	7	1323	25	0	25	0	0	0



Figure 3.6. Comparison of volume of water captured and total microplastic concentration based on respective Ransom et al. (2019) and ENVS 660 studies of three agricultural sites. Ransom et al. (2019) sampled a much greater volume of water across all sites compared to ENVS 660, thus the total concentration of MPs was lower in their study.

## 4 Discussion

#### 4.1 Microplastic abundance in agricultural vs urban samples

Considering that the average urban unit-area load (3.5 parts/min/km<sup>2</sup>) was greater than that from agricultural sites (2.5 parts/min/km<sup>2</sup>), our findings suggest that urban areas may provide slightly more MPs per square kilometer. In agriculture-dominated regions such as Monterey County (11% agricultural, 5% urban) (NLCD 2016), the total contribution of MPs from agricultural watersheds could be similar or greater than urban watersheds. It is important to consider the influence of agriculture in the Monterey region on MP pollution given the substantial area it occupies and connectivity via rivers and streams to the MBNMS.

We attribute the differences in unit-area loads between urban and agricultural watersheds to two potential mechanisms that are distinct to the respective land use types. First, MPs may be more evenly dispersed throughout agricultural watersheds compared to urban watersheds and may require disturbances and larger flows before

being mobilized. This can make detection of MPs from agricultural areas particularly difficult because they are not necessarily concentrated in runoff like MPs from urban environments or flushed out as guickly following the first significant storm events of the water year. For example, MPs may not mobilize as quickly as chemicals during the first seasonal precipitation-induced runoff event, and in agricultural-dominated watersheds are more likely to get bound in sediment substrates and vegetated banks of waterways. In contrast, urban runoff is concentrated in concrete-lined gutters, ditches and outfalls that facilitate particle transport in water and to outfalls, which for the Monterey Bay region, ends at the ocean. In urban watersheds MPs may mobilize instantly over pavement and flow into storm drains even under a small rain event. Second, presence of MPs in agricultural watersheds may be influenced by seasonal farming practices including cultivation, fertilization, and installation or removal of plastic products while plastic inputs to urban areas are likely more constant. Sampling for this study occurred in early winter, a period of relative inactivity in agricultural fields, which could have resulted in fewer plastics being transported through waterways and a lower MP concentration, whereas urban sampling at the beginning of the rainy season may have captured MP that was more easily mobilized by recent storm activity. Regardless of these differences, our findings confirm that both land use types produce MPs in runoff and are equally worthy of careful study.

#### 4.2 Correlation analyses

Correlation tests performed for agricultural sites suggested a very strong relationship between percent land cover in cultivation and concentration of MPs as well as land cover in cultivation and unit-area load. The apparently strong correlation is heavily influenced by the Santa Rita sample, which is in a relatively small subwatershed with a predominance of agricultural land cover. These qualities contrast sharply with the larger and more complex watersheds of Gabilan and Quail Creeks which have a lower percentage of agricultural land cover and a majority of the watershed in mountainous terrain (Fig. 2.1). Nevertheless, a strong correlation supports the hypothesis that more agricultural land use equates to more use of plastic and respectively higher amounts of MP in waterways. Weak correlation at urban sites between developed land cover and MP concentration could be suggestive of an uneven distribution of plastic sources in urban areas. More MP could potentially come from areas with a high density of pedestrian traffic, eating establishments, or residential lots. Storm drains servicing developed areas with larger lots or more open space could potentially produce less MP, such as the Twin 51's storm drain, which collects runoff primarily from the Presidio of Monterey and not the more densely urbanized areas of Monterey. Future studies could explore the potential relationship between land cover and MP concentration in a more meaningful way by evaluating a larger sample size and comparing watersheds of comparable size and differing amounts of land cover. Correlation tests could also consider the physical characteristics of watersheds (e.g. slopes, drainage density) that could contribute to the transport and concentration of MPs in both urban and agricultural settings.

#### 4.3 ATR FT-IR analysis

The quantity of MPs identified from urban sites suggests that urban watersheds may have greater use of common plastics, such as water bottles or food wrappers. The high percent of MP matches to PBA could suggest that clothing is a source of MPs in urban watersheds, along with other sources of PBA, such as adhesives. LDPE is a common plastic that is used in many products, resulting in its expected presence in urban samples.

Despite the limitations, ATR FT–IR did demonstrate the ability to produce acceptable matches to known polymers for the small sample size we had; MPs were matched well over the 60% threshold for at least an 'intermediate' match reported by other studies (Kroon et al. 2018, Weithmann et al. 2018). Macroplastics matched known polymers more often and to a greater degree than microplastics did. Many macroplastic samples were matched over 90% while microplastic matches did not exceed 88%, both of which are considered a 'high' match by Kroon et al. (2018).

#### 4.4 Study Limitations

The main limitations of this study come from the small sample size of only three data points per watershed type, the imperfect standardization of sample volume, limited ability of ATR FT-IR to identify very small particles, and an inability to determine the origin of MPs found in field blanks.

Our study was specifically limited by the condensed period of time over which we surveyed MPs and a small sample size (3 per location type). The lack of a larger sample size and representation of temporal variation limit our ability to confidently infer broader spatial and temporal trends. In addition, the average agricultural unit-area load was influenced by a zero value at the Gabilan site. Absence of MPs in the Gabilan sample may be due to the short sample duration (15 seconds) and/or less MPs in Gabilan Creek during high-flow conditions. It is possible that if sample collection had occurred during lower flow conditions, a longer sample duration could have captured MPs in Gabilan Creek, resulting in a higher average MP concentration at agricultural sites.

The polymer types found through ATR FT-IR in agricultural sites were not well characterized compared to those of urban sites. The lack of matches to polymer types from agricultural sites could be attributed to unique or proprietary plastic types or blends used in agriculture for which spectra do not exist in available libraries. Hendrickson et al. (2018) stated that accurate polymer identification of MPs is confounded by copolymers and additives, which likely affect our samples.

The large number of MPs that did not match to any known polymer could also be caused by factors relating to characteristics of the particles and/or functionality of the ATR FT– IR instrument. Chemical residue on the particles, photooxidation, or degradation can all interfere with accurate identification of MPs (Hendrickson 2018). The IR waves from the ATR FT–IR only penetrate the first few microns of the sample, thus if the sample is covered in a film or residue, for example from the chemical digestion, the spectra could be obscured or altered. To obtain a reading from the ATR FT–IR, the sample must be on the center of the crystal to be detected, which is especially difficult with very light or small particles such as fibers (Horton et al. 2017). Harrison et al. (2012) found transmission mode, which we measured with, can cause refraction or scattering on particles with irregular surfaces, such as fibers. It is also worth considering that some unknown particles were not actually plastic; other researchers have reported up to 70% of the visually identified particles are not confirmed as plastics by FT–IR spectroscopy (RC Thompson, pers comm, as cited in Hidalgo–Ruiz 2012).

MPs found in field blanks in this study raise considerations for their source that could require different corrections of MPs detected in non-blank samples. We used one net for

agriculture sites, another for urban, and the same net used across sites was rinsed a second time to collect a field blank. MPs in field blanks could therefore represent particles that were not fully rinsed off the net from the previously gathered sample, leading to an underestimate in earlier samples and overestimate in later samples. Also, during sampling and spraying of the net, plastic fibers from technician's clothing could have contaminated both the stream sample and field blank, which would lead to higher MP counts. To investigate the source MPs in field blanks, future studies could perform multiple rinses using the same net to determine how MP count changes over consecutive rinsing efforts. A decreasing MP count in consecutive field blanks could indicate the main source of MPs in blanks is due to incomplete rinsing of the net, while a relatively constant MP count in consecutive field blanks could indicate that the source of MPs in blanks is due to contamination from technician's clothing. Another concern for contamination is carryover between sites by incomplete rinsing of the net from previous samples. This potential problem could be solved by performing several blanks after every sample or by using a new net per site. There may also be a notable role in the atmospheric deposition of MP fibers; Dris et al. (2016) observed atmospheric fallout of MP fibers as an important source of microplastics, particularly in urban areas where higher fluxes of MP fibers were detected.

#### 4.5 Comparison to previous work

The variety of MP forms collected by Ransom et al. differed compared to samples collected by ENVS 660; in this study we found little diversity in forms, and fibers dominated the MP particles we collected. This may be owing to the seasonal difference between when surveys occurred across respective studies.

Differences in sampling conditions between Ransom et al. and ENVS 660 could help explain the concentrations of MPs were observed in the earlier study compared to this one. The previous study took place in late winter after many rain events, whereas this study took place in the fall when the first rains had just occurred the week prior to and during sampling. Large winter flows with a high amount of sediment mobilized in the water, as was observed in the previous study (P Krone, personal communication, November 7, 2019), could result in the net becoming clogged and preventing flow through the net. We addressed this potential issue by placing PVC pieces over the rebar that held the net in place, which raised the bottom of the net 5 cm off the stream bottom where we expected a comparatively higher load of sediment in the water column. Early season flows could also potentially flush out MPs that have accumulated in the watershed during the dry season and lead to lower concentrations during subsequent flows. Fibers may be the most mobile form of MPs, and as such, mobilize before other forms during any rain event. Similarly, greater volumes of water do not translate to higher concentrations of MPs, as there may be a set amount of MP available to be transported, and more rainfall will only dilute this amount.

Comparison of MP load (particles/min) between the two studies is not possible because in the previous study, channel-wide flow was not measured at each site. To advance the effort to quantify and compare MP abundance (load) across studies, methodology should include the measurement of flow which is an important metric for quantifying the amount of MP being delivered to the ocean from a watershed.

# 5 Conclusion

We examined microplastic quantity, form, and polymer type from agricultural and urban watersheds in Monterey County that drain into the Monterey Bay National Marine Sanctuary in California's central coast. Key findings discussed in the previous sections are summarized here.

- Quantity -
  - More particles were collected from urban (96) than agricultural (35) samples (n=131). Of three urban sites sampled, the Sea Palm sample yielded the most particles (34), then Pico (43), and lastly, Twin 51's (19). Of the agricultural sites, Santa Rita yielded the most particles (25), then Quail (10). No particles were detected at Gabilan.
  - We found microplastics were slightly more concentrated in runoff from urban watersheds than from agricultural. The greatest estimated concentration was for the urban Sea Palm watershed (34.8 parts/m<sup>3</sup>) compared to the greatest concentration for agricultural watersheds, Santa Rita (18.9 parts/m<sup>3</sup>). Unit-area loads were also higher in urban sites (1.76-5.91 parts/min/km<sup>2</sup>) than in agricultural sites (0-6.8 parts/min/km<sup>2</sup>).

- Form Fibers were the dominant form of microplastics collected and were detected at all sites. The most fibers were detected from the Pico sample (43), then Sea Palm (29), and lastly, Twin 51's (18). We also detected fragments (4) and foam (1) from Sea Palm, and a pellet from Twin 51's. Of the agricultural sites, Santa Rita only had fibers (25). Nine fibers were detected from Quail, including one film particle.
- **Polymer types** We were only able to analyze 49 particles using ATR-FTIR and of those, only 23 were matched to a known spectrum of plastics. All of the matched particles were collected from urban sites and these matched to the spectrum of low-density polyethylene and poly(butyl acrylate).

We suspect agricultural watersheds discharge a substantial amount of MP's to the MBNMS, especially given land use patterns in Monterey County. Agriculture accounts for a high percentage of land cover in Monterey County where there tends to be consistent and wide-spread plastic use throughout agricultural fields. We found a strong correlation between microplastic concentration and land cover in agricultural watersheds; however, this result was drawn from only three data points. This correlation result could be more robust with additional agricultural sample sites.

To accurately assess the variable MP load of agricultural streams, future work should aim to sample at different times of year in relation to first rain events, large storm events, and agricultural activity. Continued work in this field would benefit from including flow measurements, which are an important metric for quantifying the amount of MP being delivered to the ocean from a watershed, and would advance the effort to quantify and compare MP abundance (load) across studies.

# 6 Appendices

Appendix A. Results of Student's two-sided t-test for assessing the accuracy of ATR FT-IR percent match results to known polymers. Results indicate only one particle (Sea Palm Fragment 3) was statistically different (p < 0.01) from the FT-IR-generated match. This may be because we had to use the best-matched microplastic sample spectra to perform the t-tests instead of the actual spectra of known polymers from the ATR FT-IR libraries.

Microplastic sample	P-value	Matched polymer
Sea Palm Fibers	0	Poly(butyl acrylate)
Sea Palm Fragment	$2.57 \times 10^{-50}$	Poly(butyl acrylate)
Sea Palm Fragment 2	0	Low-density polyethylene
Sea Palm Fragment 3	0.65	Low-density polyethylene

Appendix B. Results of a one-way ANOVA to explore the average of different microplastic (MP) densities as a function of site type, agricultural or urban.

Dependent variable	Group	Degrees of freedom	Sum of Squares	Mean of Squares	F value	P value
Total MP	Agricultural/ Urban	1	620.20	620.20	4.06	0.11
Concentration	Agricultural/ Urban	1	5.40	5.42	0.02	0.89
Load	Agricultural/ Urban	1	761.60	761.60	3.50	0.14
Unit-area load	Agricultural/ Urban	1	4.97	4.97	1.10	0.35

Appendix C. Microplastic (MPs) particles collected at agricultural and urban sites. The number of particles processed by ATR FT-IR was less than the number of particles detected during microscopy because many of the particles were too small to be taken out of vials for placement onto the spectrometer (unassessed particles). Of the particles processed, most were identified and only a few not matched (unknown) to a spectrum.



Appendix D. Results of correlation tests between unit-area microplastic loads or concentrations and percent land cover in agricultural, urban, or both.



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Appendix E. Abundance of microplastic forms observed by Ransom et al. 2019 and ENVS 660. Ransom et al. observed a higher abundance and wider variety of forms than ENVS 660.



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