MICROPLASTICS IDENTIFICATION IN SOUTHERN CALIFORNIA COASTAL SEDIMENTS

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By

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ABSTRACT

Microplastics Identification in Southern California Coastal Sediments

By

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The exponential increase in plastic production, driven by consumer demand, has led to a significant rise in plastic waste, impacting ecosystems and public health. This issue is particularly evident in Southern California beaches, known for their recreational areas, attracting approximately 129 million annual visitors. Tourism and urban runoff contribute to the pollution of its beaches and harbors. A major concern is the transformation of this waste into microplastics (particles < 5 mm), which possess unique chemical and physical properties that exacerbate environmental pollution.

In this study, beach sediments were collected from Santa Monica, Venice, Playa Del Rey, Will Rogers, and Huntington beaches. Microplastics were isolated from the sediments using a modified protocol from the National Oceanic and Atmospheric Administration (NOAA). The modified NOAA protocol was validated using commercial polypropylene powder (0.001 – 0.005 mm) mixed with sand, achieving a recovery rate of 99.21 percent. The isolated microplastics were then examined using Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR). Out of the total 57 microplastics pieces collected from the beaches, 40 were identified as polypropylene with a fitting accuracy > 73.23 percent.

Lastly, preliminary tests were conducted to develop an electrochemical method for characterizing heavy metal contamination on microplastics. In this approach, a gold

chip was coated with a silica mesoporous film, which enhances sensitivity due to its porous structure and high surface-to-volume ratio. We detected copper as a model system using differential pulse voltammetry, though with limited sensitivity and detection limits. These issues need to be addressed in future studies.

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CHAPTER 1

Introduction

In recent decades, there has been a substantial increase in plastic production, reaching 368 million tons in 2019.[1] The majority of the plastic being produced comprises single-use applications, known for their affordability, versatility, and convenience.[2-3] However, this increased in production has resulted in a higher likelihood of plastic pollution in various environments. Coastal areas are vulnerable to plastic waste accumulation, affected by sources such as wastewater plants, tourism, wind, rivers, surface runoff, and littering.[4-7] Over time, these plastic wastes undergo photodegradation, biodegradation, hydrolysis, or thermal degradation depending on the conditions and interaction, leading to the formation of small plastic particles known as microplastics.[8]

Microplastics, with a length of less than 5 mm, are categorized as either primary or secondary.[9] Primary microplastics are intentionally manufactured for commercial applications, such as synthetic textiles or cosmetic products, while secondary microplastics result from the degradation of larger plastic through environmental factors.[10-13] In coastal environments, microplastics infiltrate multiple pathways, predominantly stemming from human activities, such as the release of microfibers during the laundering of synthetic textiles.[14] These microfibers enter the ocean or rivers through wastewater treatment plants and are further transported by wind and currents, leading to their accumulation in various parts of the sea and land, affecting ecosystems and organisms. Small pieces found in wet sand, such as meiofauna, are particularly affected, experiencing physiological damages, reproductive issues, and metabolism changes upon contact with microplastics, whether physically or through consumptions.[15-16]

Microplastics contain additives that are incorporated into plastic products during their manufacturing process to enhance specific characteristics, such as durability or impact resistance.[17] These additives can leach into various ecosystems, potentially causing harm to the public and different species.[18] Moreover, microplastics have a large specific surface area, enabling the absorption of heavy metal ions and organic pollutants.[19] The surface charge of microplastics can change over time due to environmental exposure and weathering processes. This can lead to some microplastics acquiring a negative charge, facilitating the binding of positive metal ions and allowing adsorption behavior to occur.[20] Electrostatic interaction and van der Waals forces contribute to the sorption capacity of the adsorption process.[21] Furthermore, microplastics exhibit different polarity, crystallinity, and sizes, leading to varying adsorption rates.[22] These binding serve as carriers, particularly in marine environments, causing a decrease in the pH of seawater and resulting in ocean acidification.[23] Ocean acidification has the potential to induce alterations in marine ecosystems.[24]

In California, studies have shown the presence of microplastics along the coastline, with single-use plastics, cigarette filters, and synthetic textiles being among the most commonly found types.[25] Pacific mole crabs, constituting 84% of California's beach habitat, are particularly affected by microplastics.[26] These crabs are consumed by larger species, creating a potential food chain issue that could extend into the human market.[27]

Although research on microplastics in coastal environments has been increasing, many beaches have not been thoroughly examined. Currently, limited research focuses on the characteristics of microplastics in Southern California beaches, including their abundance, composition, and heavy metal adsorption. This project aims to address this

gap by developing a framework for collecting beach sediments from various Southern California beaches. A modified NOAA protocol will be used to separate the potential microplastics from beach sediments. These microplastics will then be analyzed using ATR-FTIR and electrochemical detection through differential pulse voltammetry.

ATR-FTIR is an analytical technique that uses infrared radiation to study the vibrational properties of molecules, providing information about the chemical composition and molecular structure of the sample.[28] Currently, Inductively Coupled Plasma Mass Spectrometry (ICPMS) and Graphite Furnace Atomic Absorption Spectrometry (GFAAS) are known analytical instruments for heavy metal determination, though they require extensive instrumentation and operational expertise. Alternatively, electrochemical sensing is a cost-effective method, although with lower sensitivity.[29]

Silica mesoporous film has been reported to enhance the sensitivity of electrochemical detection due to its unique porous structure and high surface-to-volume ratio.[30] Therefore, we explored the possibility of using a bare gold chip with a silica mesoporous film for trace heavy metal analysis through differential pulse voltammetry. This technique, a form of linear sweep voltammetry, is used to study the redox properties of chemical substances and is commonly employed for the detection and quantification of trace amounts of analytes.[31-32]

Differential pulse voltammetry measurement involves applying a series of potential pulses while measuring the current responses.[33] Coating a bare gold chip with a silica mesoporous film can increase surface area, enhance adsorption, and improve sensitivity and selectivity for trace metal analysis.[34] Mesoporous silica offers rapid mass transfer and efficient enrichment for the electrochemical detection of metal ions due to its

high surface area and tunable pore size, further boosting the sensor's sensitivity and selectivity.[35-36] Gold is commonly used as an electrode material because of its high conductivity, which supports efficient electron transfer and enhances sensitivity in the detection process.[37]

Project Objectives

The primary goal of this project is to promote awareness of plastic waste, the presence of microplastics, and their potential harm to the environment and public health. This was done by separating and identifying microplastics from beach sediments collected from several Southern California beaches, including Santa Monica, Venice, Will Rogers, Huntington, and Playa Del Rey. This project also includes a pilot portion that explores the capability of electrochemical detection of heavy metal contamination within the identified microplastics.

To accomplish this goal, the individual objectives include the following:

1. Validate and optimize the methods for sediment collection, microplastic extraction, and characterization.
    1. Conduct preliminary sediment collection.
    2. Validate the modified NOAA protocol using sediment samples mixed with commercial microplastics.
    3. Optimize the ATR-FTIR protocol using commercial microplastics.
2. Collect sediments from the listed beaches above, extract and characterize microplastics following validated methods from Objective 1.
3. Validate and optimize the methods for characterizing heavy metal adsorption.
    1. Validate heavy metal analysis with gold chip using standard solutions.
    2. Optimize bare gold chip with silica mesoporous film for low-concentration heavy metal detection.

CHAPTER 2

Methods

Materials

Copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5\ H_2O$), iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7\ H_2O$), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2, 30%), sodium chloride (NaCl), hydrochloric acid (HCl), nitric acid (HNO_3), and ethanol (anhydrous, 99.5%) were purchased from Thermo Fisher Scientific (Waltham, MA, United States). Tetraethoxysilane (TEOS, 98%) and sodium nitrate ($NaNO_3$, 99%) were purchased from Alfa Aesar (Ward Hill, MA, United States). Cetyltrimethylammonium bromide (CTAB, 98%) was purchased from MP Biomedicals (Irvine, CA, United States). 3-Mercaptopropyl)trimethoxysilane (MPTMS) was purchased from Sigma-Aldrich (St. Louis, MO, United States). Fine polypropylene powder was purchased from NANOCHEMAZONE (Leduc, Alberta, Canada). The gold sensing chip (working electrode), silver/silver chloride (Ag/AgCl, reference electrode), platinum (Pt, counter electrode) was purchased from Biosensing Instruments (Tempe, AZ, United States). All solutions were prepared with double-deionized water from a Milli-Q Ultrapure water EQ 7000 Purification System (Burlington, MA, United States).

Microplastics in Southern California: Field Sampling Approaches

This study was conducted in Los Angeles and Orange counties, California. Five beaches were randomly sampled between 2022 and 2024 in autumn, winter, and summer (Figure 1 and Table 1).

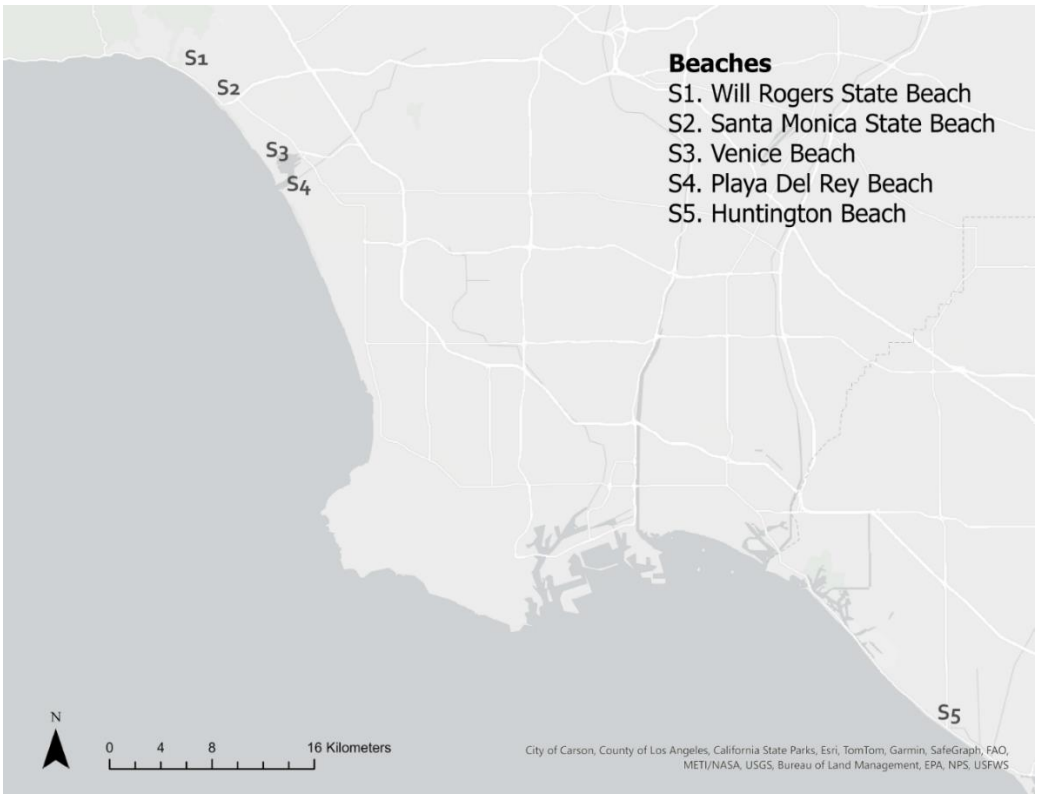


Figure 1. Map of Southern California beaches sample collection in Los Angeles and Orange counties.

Table 1. Southern California beaches expedition dates.

Beach	Season	Time(s)	Date
Santa Monica	Autumn & Winter	2	10/14/22 & 01/10/24
Venice	Winter	2	02/18/23 & 01/10/24
Will Rogers	Summer	1	06/06/23
Huntington	Summer	1	08/18/23
Playa Del Rey	Autumn	1	11/10/24

Santa Monica and Venice beaches were each sampled twice following the EPA's Microplastic Beach Protocol.[38] The first attempt involved collecting sediments from three distinct locations: in the seawater, at the middle of the beach, and within the vegetation

(Figure 2). This was done to determine the effectiveness of the sample preparation process and identify any noticeable differences in sample collection.

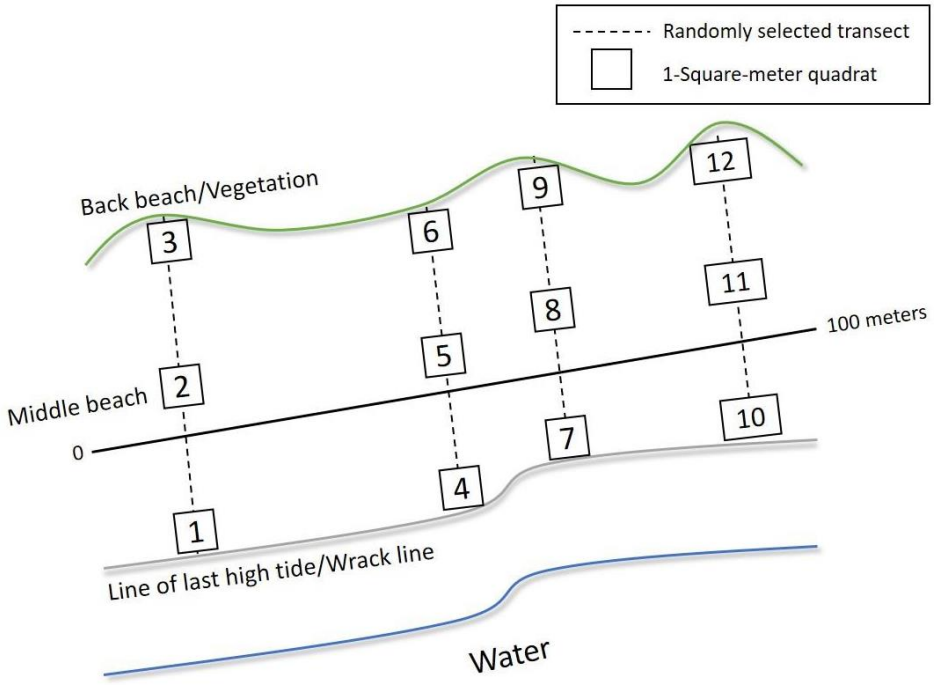


Figure 2. Schematic of sample collection. Adapted from US EPA, O. EPA's Microplastic Beach Protocol.

The second attempt, which included all the beaches, involved sampling at the high tide and the wrack line, where most debris accumulates due to ocean currents, wind–driven waste accumulation, and natural materials such as seaweed, driftwood, or shells that may contain plastic debris (Figure 3).[39-40] Along the beach trail, sand was collected approximately every 10 – 20 m using a shovel and passed through a 5 mm sieve into 1000 mL bottles (Figure 4). A total of nine bottles were used, and the collection process took place within a 1-square-meter quadrant, where each sampling reached a depth of approximately 2.5 – 5.0 cm.

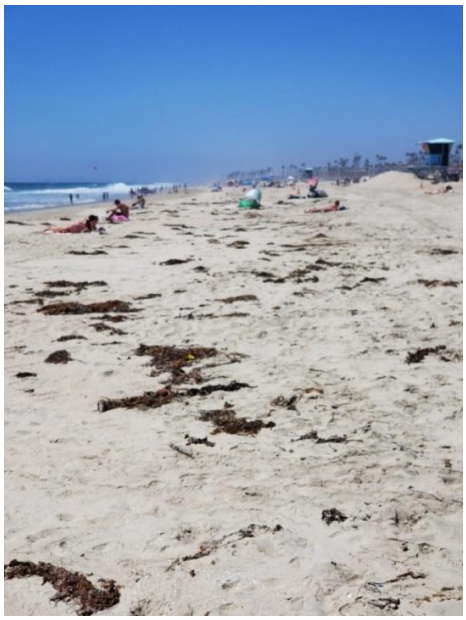


Figure 3. Strandline at Huntington Beach, California.



Figure 4. Sample collection at Will Rogers Beach, California.

Sample Preparation via Modified NOAA

Beach sediments listed in Table 1 were extracted following the NOAA protocol.[41] To facilitate the identification and classification of microplastics across various size

ranges, a Büchner funnel was used instead of the traditional method of stacked sieves (Figure 5). The traditional approach can increase the risk of airborne contamination and prolong the process of transferring potential microplastics to a beaker for drying and digestion. Although stacked sieves can separate samples by size, the Keyence VHX-7000 4k High Accuracy Digital Microscope was used to determine the size and capture high-resolution images of the samples.

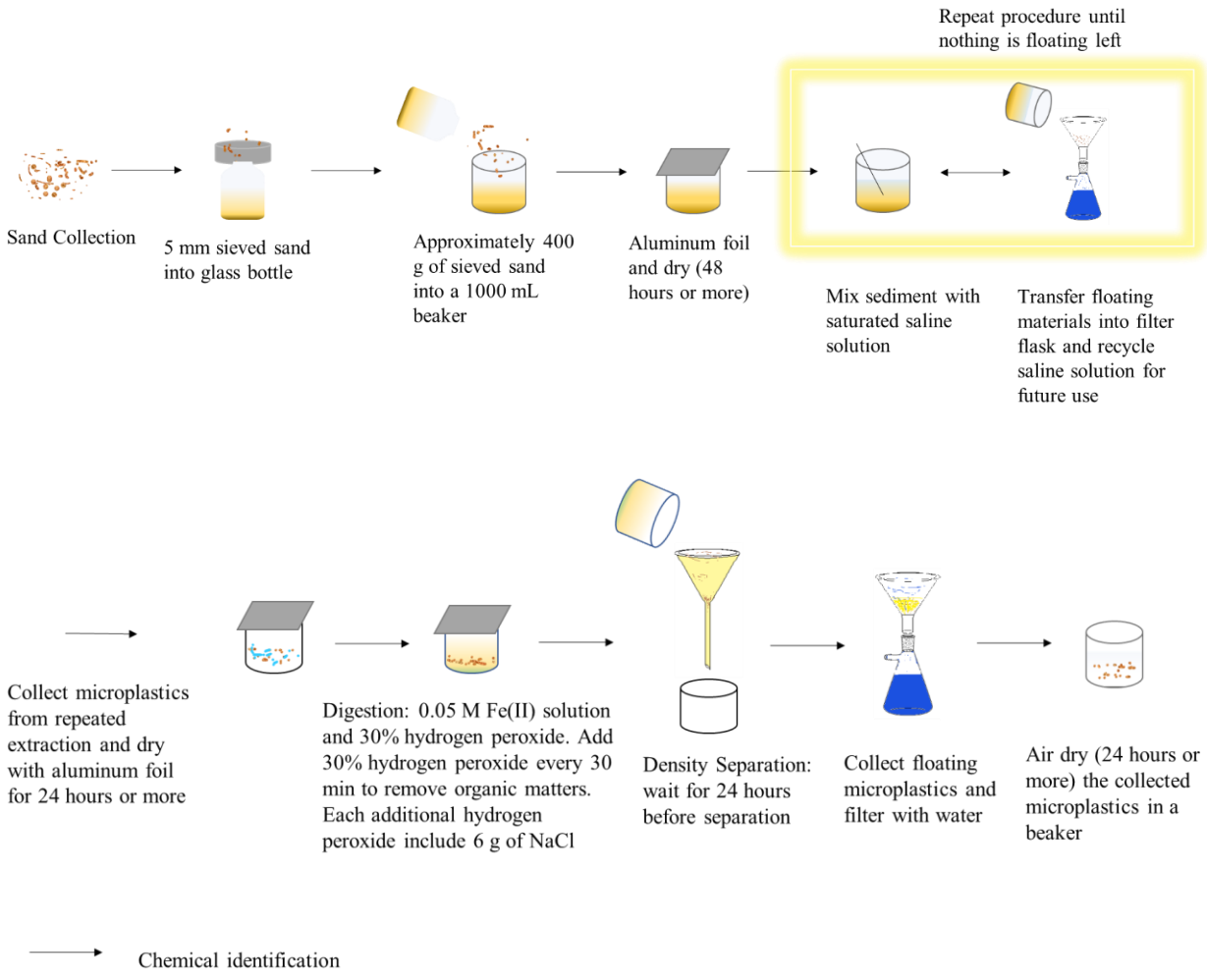


Figure 5. Schematic of the modified NOAA protocol.

Each sediment sample, weighing approximately 400 g, was dried at 90°C for 48 hrs or until fully dry to eliminate any residual moisture. The dried sediments were then mixed with a saturated NaCl solution at a density of 1.2 g/mL, which increased the density of the solution and facilitated the flotation of debris and potential microplastics (Figure 6). The mixture was then transferred to a Büchner funnel for sample collection, and the saturated solution was reused several times until no more floating materials were present (Figure 7). The samples collected from the funnel were then dried for 24 hrs or until completely dry.

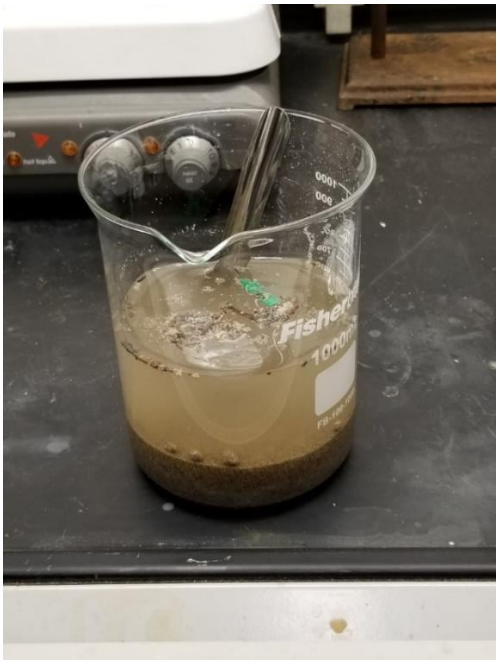


Figure 6. Density separation of potential microplastics using saturated NaCl solution.



Figure 7. Top view of potential microplastics (left) and bottom view of reusable saturated NaCl solution (right).

The dried samples were mixed with 20 mL of 0.05 M Fe(II) solution containing $FeSO_4 \bullet 7\ H_2O$, 3 mL of concentrated H_2SO_4, and 20 mL of 30% H_2O_2 to maximize the removal of organic matter. The reaction between H_2O_2 and Fe(II) generates hydroxyl radicals, which are powerful oxidizing agents effective in breaking down carbon-based materials.[42] After a 5 mins of exposure to the solution, the sample was heated at 75°C on a hot plate for 30 mins. In cases where substantial organic matter was presented, an additional 20 mL of 30% H_2O_2 mixed with 6 g of NaCl was added (Figure 8).



Figure 8. Wet Peroxide Oxidation: Before oxidation (left), generation of hydroxyl radicals (middle), and after oxidation with NaCl pellets (right).

After the digestion process, the solution was transferred to a glass funnel with a diameter of 122 mm and allowed to settle for 24 hrs (Figure 9). The floating samples were collected and moved to a Büchner funnel, where they were rinsed with deionized water. The microplastics were then air-dried and wrapped in aluminum foil for 24 hrs. Finally, the samples were stored in an aluminum foil petri dish for further analysis (Figure 10).



Figure 9. Density separation after digestion.



Figure 10. Stored microplastic samples from Huntington Beach, California.

Digestion – Wet Peroxide Oxidation

After the initial density separation, the collected samples are processed for digestion, during which organic pollutants are removed using wet peroxide oxidation, specifically with Fenton's reagent. This process utilizes an Fe(II) solution as a catalyst and H_2O_2 to form hydroxyl radicals, which undergo oxidation processes.[43] These reactions involve the transfer of electrons from the organic compounds to the hydroxyl radicals.[44] When the hydroxyl radicals accept electrons from organic molecules, the organic compounds undergo oxidation, changing their chemical structure. During this process, the Fe(II) is oxidized to Fe(III), as seen in reaction 1.[45] Adding additional H_2O_2 will reduced Fe(III) back to Fe(II), as observed in reaction 2, allowing the Fenton's reagent to be used continuously.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\bullet + H^+ \quad (2)$$

Although microplastics are composed of hydrocarbons, they are designed to be durable, with overall stable polymer chains that allow them to tolerate reactions at 75°C.[46] According to the NOAA protocol, further increases of temperature can accelerate the reaction, causing violent boiling and potential damage to the microplastics, leading to an overall loss of materials.[47] However, hydroxyl radicals remain highly reactive and can still effectively oxidize and degrade microplastics and organic pollutants. They tend to react with other molecules due to their non-selective reactivity, and will interact with almost any organic compounds, regardless of temperature.[44] While higher temperature may accelerate the reaction, lower temperature with slower reaction rates can still be relatively effective.

Validation of the Modified NOAA Protocol

One commercial polypropylene sample weighing approximately 0.1 g underwent an initial density separation using the modified NOAA protocol to evaluate the efficiency of the extraction rate using processed sand. Four commercial polypropylene samples, each weighing approximately 0.25 g, underwent the procedure outline in the digestion method, utilizing sand from Will Rogers Beach to observe whether the plastic was affected by the wet peroxide oxidation. The digestion time for each sample varied, including intervals of 30 min and 1 – 3 hrs.

Chemical Identification via ATR-FTIR

A Thermo Nicolet 6700 FT-IR spectrometer with a Smart Orbit ATR accessory, operated using OMNIC software, was used for microplastics identification. The experiment consisted of 128 scans at a resolution of 1 cm^{-1}. Correction for H_2O and carbon dioxide (CO_2) were applied to minimize background noise and moisture. The spectrum was expressed as log(1/R), which represents the transmittance as reflectance, measuring the amount of light reflected off the sample rather than transmitted through it.

Copper Standard Preparation

0.20 g of $CuSO_4 \bullet 5\ H_2O$ was dissolved in double-deionized water in a 500 mL volumetric flask. The solution was then diluted to concentrations of 1 mM, 0.01 mM, and 0.001 mM.

Deposition Solution

The coated gold chip was cleaned with EtOH and then rinsed with H_2O three times. Then hydrogen flame annealing, pretreated with MPTMS, and rinsed with EtOH. The deposition solution was prepared by mixing 20 mL of EtOH, 20 mL of H_2O, and 893 μL of TEOS in a 20 mL Falcon tube. The mixture was then transferred into a 150 mL beaker containing 0.34 g of $NaNO_3$, and 0.466 g of CTAB. The pH was adjusted to 3 using 0.1 M HCl. The beaker was wrapped in parafilm and stirred for 2.5 hours at 240 rpm.

Electrochemical Detection via Differential Pulse Voltammetry

A potentiostat workstation operated with CH760E software was used for copper electrochemical detection. Both bare gold and coated silica mesoporous surfaces were tested after pretreatment using amperometry. This involved applying a fixed potential voltage of – 1.2 V for 10 s to the MPTMS coated chip. Following the deposition, the chip was rinsed with 19.5 mM HCl, 50 mM $NaNO_3$, and 40 mM CTAB in 10 mL of H_2O and 10 mL of EtOH and rinsed again in H_2O. The chip was then dried overnight in an oven at 130°C.

After overnight drying, the surfactant CTAB forms micelles that serve as templates for creating mesoporous structures. This enhances the surface area and electrochemical performance of the electrode, enabling better interaction with the copper solution. The CTAB template was removed by mixing the coated chip in a 0.1 M HCl solution for 15 min.

Anodic stripping voltammetry was performed at a potential of – 0.8 V for 300 s. The pulse settings included a pulse width of 0.05 s, a pulse period of 0.20 s, an initial

voltage of 0.1 V, and a final voltage of 0.4 V. The settings also included an increment voltage of 0.005 V and a scan rate of 25 mV/s. After the copper layer was deposited during pretreatment, the copper was stripped by the applied voltage, allowing for the detection of the copper oxidation peak.

CHAPTER 3

Results and Discussion

Validation of the Modified NOAA Protocol

The adaptation of the sampling protocol using saturated NaCl solutions achieved an efficiency of 99.21 percent in extracting microplastics from processed sand sourced from Pure Original Ingredients. Fine polypropylene powder, ranging from 0.001 – 0.005 mm, was used. However, when extracting microplastics from the addressed beaches, most of the samples obtained ranged from 1 – 2 mm, suggesting that smaller particles may not have been adequately accounted for during the extraction process. The efficiency rate of 99.21 percent falls within the acceptable range, as the extraction yield for certain types of microplastics, such as low-density polyethylene, high density polyethylene, and polyamide, following the NOAA protocol also exceeds 90 percent.[47]

Commercial standard polypropylene was exposed to Fenton's reagent for approximately 30 mins and for 1 – 3 hours, following the NOAA protocol. Polypropylene was identified using the ATR-FTIR, as shown in Figure 11. However, the peak intensities varied due to the baseline. All four samples were not consistent with each other, and the resulting peaks may have been affected by inconsistencies in the sample loading phase of the instrument or by moisture, as there was significant noise. Although the temperature of 74 – 75°C was maintained throughout the experiments, adding additional H_2O_2 two to three times did not result in significant changes during the degradation of organic pollutants. This is probably due to diluting the solution, and samples containing large

amounts of debris were not fully removed. Some samples included microplastics and wood, as shown in Figure 9.

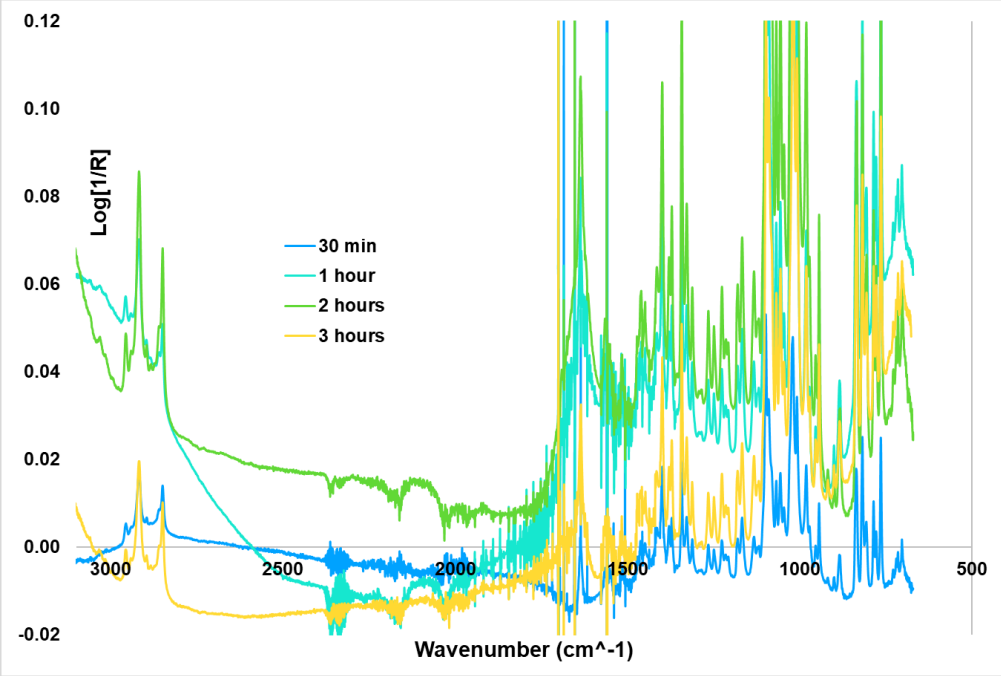


Figure 11. Commercial polypropylene digested ranging from 30 min to 1 – 3 hours.

Commercial Plastics

Common commercial plastics often have densities less than 1.4 g/mL (Table 2). Degraded plastics or microplastics can lead to a decrease in density. Although most plastics can be collected through NaCl density separation, there are some exceptions such as polyethylene terephthalate (PET) or polyvinyl chloride (PVC), which can have higher densities. PVC can sometimes be collected when the material is degraded, while PET cannot be isolated using saturated NaCl due to its density of 1.2 g/mL. In addition. most plastics are not composed of a single polymer or additive. Instead, a combination of polymers and additives is often used to achieve specific properties and characteristics.

These may include plasticizers, stabilizers, or flame retardants, which can cause significant or minimal fluctuation in density.[48-49]

Table 2. Density of common plastics adapted from the University of Rhode Island.[50]

Plastic	Name	Density – Range (g/mL)
Polyethylene terephthalate	PET	1.38 – 1.39
High density polyethylene	HDPE	0.95 – 0.97
Low density polyethylene	LDPE	0.92 – 0.94
Polypropylene	PP	0.90-0.91
Polystyrene	PS	1.05 – 1.07
Polyvinyl chloride	Vinyl	1.16 – 1.35

Sample Collection

A total of 117 samples were collected, yielding 57 microplastics pieces from four beaches along the coast of Southern California (Table 3). Will Rogers State Beach was excluded from the analysis as it was collected solely for testing purposes. Huntington Beach harbors a significant number of plastics due to its popularity as a surf beach. In contrast, other beaches in Los Angeles County, such as Santa Monica and Venice, have about half the amount of microplastics despite their status as popular tourist destinations. Although Playa Del Rey is not a major tourist spot, its proximity to Los Angeles International Airport attracts many visitors each year. Frequent volunteer cleanup efforts at these beaches may impact the amount of microplastics collected.

Table 3. Microplastics collection

Beach	Total Sample	Amount of Sample Containing Plastics	Microplastics
Will Rogers	31	13	N/A
Huntington	30	21	26
Playa Del Rey	32	13	13
Venice (V2)	25	12	12
Santa Monica (SM2)	30	6	6

Most samples were collected from depths of 1 – 3 inches or from the surface layer, moving several meters before repeating the process. Surface samples mainly consist of plastic debris resulting from wind, ocean currents, or recent beach activities. While the majority of microplastics found in the environment are typically in the form of microfibers or synthetic textile materials, the collected samples were primarily fragments.[51] External factors such as season, weather, and time may affect the results. For example, summer often sees an increase in tourism and beach visits compared to winter. The location of the sample collection can also play a role; for instance, microfibers are more likely to be found near piers or fishing locations. Additionally, a significant portion of the samples were collected during the off-season when tourism is limited, and in less populated areas, which is also a variable to consider.

Santa Monica Beach and Venice Beach were each visited and sampled twice, with the initial attempts focusing on different characteristics such as collecting samples from seawater, along the strandline, and from dried sand. A noticeable difference was observed between the regions, with minimal debris present on the surface of the sand, except along the strandline. This disparity is attributed to ocean currents carrying debris ashore.

However, after rainy events, samples collected from dried sand region may potentially contain higher amount of debris runoff from nearby cities.

Mass of Beach Sediments

Each sample weighed approximately 400 g (Table 4). The amount of sand weighed in the beaker according to NOAA guideline does not impact the quantity of microplastics collected. However, when using a 1000 mL beaker, if the sand weighed 600 g or more and is mixed with the saturated NaCl solution, some debris with a density of less than 1.2 g/mL will not be collected due to limited space in the beaker. Therefore, ideally, each sample should weigh around 400 g.

Table 4. Sample weighed average per beach.

Beach	Total Sample	Sand (g)	Dried Sand (g)
Will Rogers	31	N/A	N/A
Huntington	30	441.35	399.83
Playa Del Rey	32	402.01	389.23
Venice (V2)	25	434.00	418.43
Santa Monica (SM2)	30	464.8	451.35

FTIR Analysis

After isolating debris, microplastics were collected and analyzed using ATR-FTIR and optical microscopy (Figure 12-16 and Table 5-8). The majority of polymers identified were polypropylene, polystyrene, and polyethylene, typically found in fragmented form. These polymers are also commonly found in commercial products such as plastic containers, bottle caps, and Styrofoam.

The match rate of the identified polymers was approximately 60 percent or higher, with some exceptions falling below 60 percent. However, some identified polymer matches from the library may be affected by factors such as the sample loading position or the characteristics of the samples, such as thinness or thickness, which can result in a high amount of background noise or interference.

Lower peak intensity due to factors such as degradation and structural composition, such as flatness, contributed to low match rate despite the plastic characteristics of the samples. Grinding the sample could improve the match rate and overall spectrum, but results in the loss of the sample afterward.



Figure 12. Microplastic sample from Playa Del Rey Beach. Rocky characteristics showed a 69.19 percent match rate of identified polypropylene.

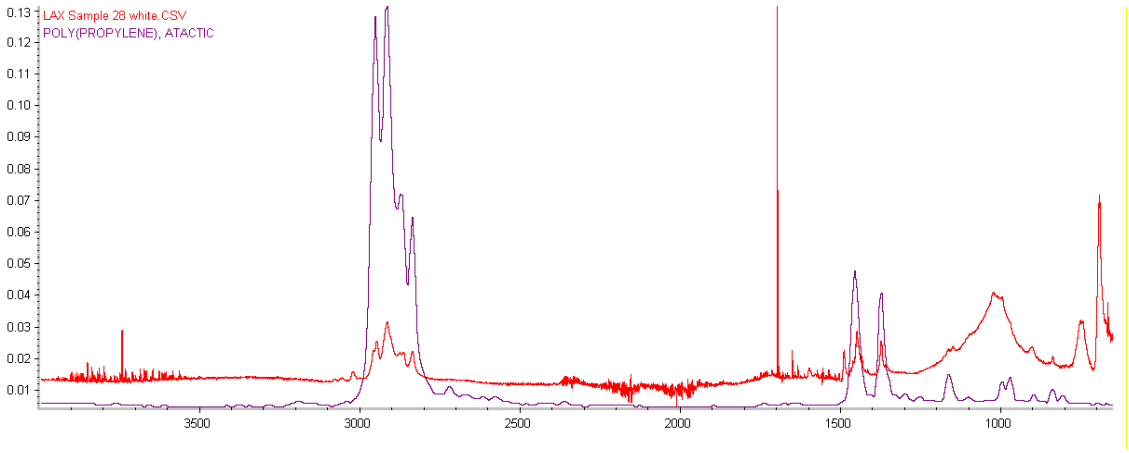


Figure 13. Playa Dey Rey FTIR Sample 28.

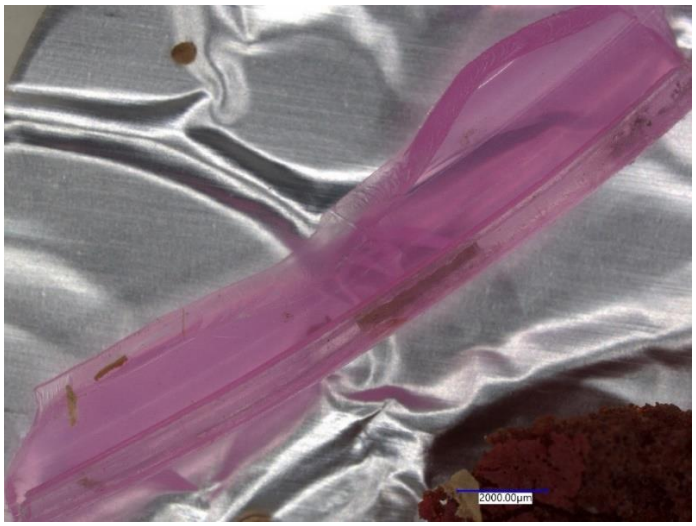


Figure 14. Microplastics sample from Venice Beach.

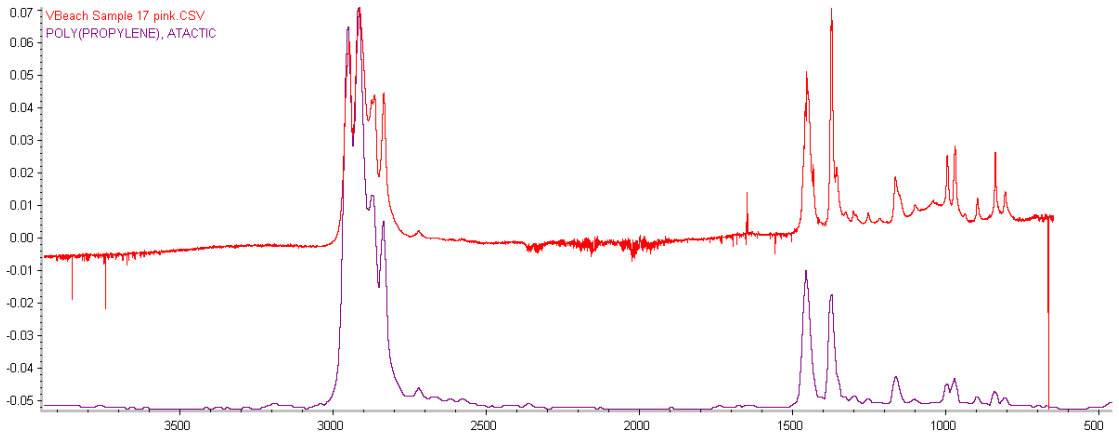


Figure 15. Venice FTIR Sample 17. During the sample loading process, the sample was flattened to achieve appropriate thickness, resulting in a match rate of 90.90 percent for polypropylene. Polypropylene is characterized by C-H stretching (2800-3000 cm^{-1}), CH_3 group (1375-1385 cm^{-1}), CH_2 (1455-1470 cm^{-1}), and C-C stretching (1150-1185 cm^{-1}).

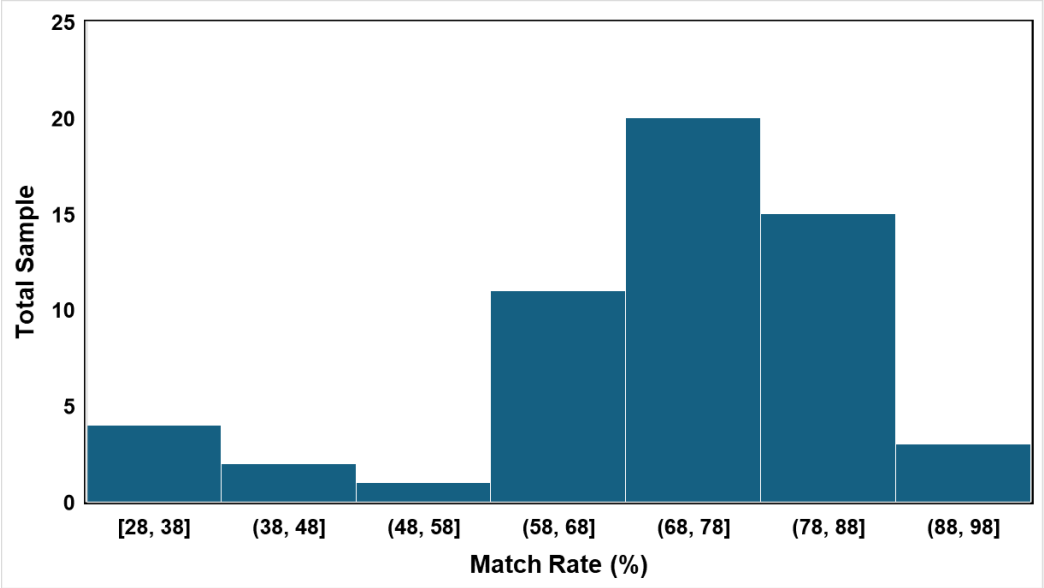


Figure 16. FTIR distribution of match rates for all beaches.

Table 5. Huntington Beach FTIR.

Sample	Characteristics	Identified Polymer	Match Rate
1	Red	Polypropylene	80.78
2	Green	Polypropylene	84.38
2	Red	Polypropylene	70.89
3	Green	Polypropylene	86.06
3	Orange	Polypropylene	85.14
4	Green	Polypropylene	70.77
5	Blue Green	Polypropylene	71.55
5	Green	Polypropylene	78.33
5	Green	Polypropylene	80.94
8	Orange	Polypropylene	81.19
9	Red	Polydimethylsiloxane	60.50
9	Yellow Brown	Polypropylene	66.32
10	Red	Polyester Resin	42.26
11	Green	Polyethylene	72.55
11	Green	Polypropylene	60.35
13	Green	Polypropylene	64.04
13	Yellow	Polymethyl Methacrylate	63.67
14	Blue	Polypropylene	82.75
16	Brown	Polypropylene	67.38
17	Green	Polypropylene	72.88
17	Red	Polypropylene	76.55
18	Blue	Polypropylene	68.09
23	Red	Polypropylene	88.03
24	Green	Polypropylene	69.95
29	Brown	Polypropylene	81.06
29	Brown	Polypropylene	83.04

Table 6. Playa Del Rey FTIR.

Sample	Characteristics	Identified Polymer	Match Rate
8	Green	Polypropylene	73.37
9	Red Orange	Polypropylene	69.98
13	Yellow	Polypropylene	75.23
16	Green Blue	Polyethylene	64.91
22	Blue	Polypropylene	63.23
22	Blue	Polypropylene	82.66
23	Pink	Polymethylphenylsiloxane	28.55
24	Red	Polypropylene	86.07
28	White	Polypropylene	69.19
29	Green	Polypropylene	52.13
29	Green	Polystyrene	70.21
29	Green Yellow	Polyethylene	68.16
30	Red	Polystyrene	30.66

Table 7. Santa Monica FTIR

Sample	Characteristics	Identified Polymer	Match Rate
8	Red	Polypropylene	45.26
9	Green	Polypropylene	81.36
10	Green	Polypropylene	34.62
16	White	Polypropylene	76.92
22	Red	Polypropylene	58.66
27	Red	Polypropylene	68.79

Table 8. Venice Beach FTIR

Sample	Characteristics	Identified Polymer	Match Rate
4	Green	Polypropylene	N/A
5	White	Polystyrene	66.57
9	Red	Polystyrene	76.66
10	White	Polystyrene	66.71
12	Blue	Polypropylene	77.87
15	White	Polystyrene	70.91
17	Pink	Polypropylene	90.90
17	Red	Polyether Urethane	71.85
17	White	Polyamide 6	27.87
18	Green	Polypropylene	79.38
20	Green	Polyethylene	89.30
20	Red	Polyethylene	79.13

Limitation

Despite yielding microplastics from the NOAA procedure, some limitations arise in the density separation and digestion methodologies. Typically, a minimum of three repeated filtrations during density separation is recommended to maximize the yield of microplastics. However, uneven filter paper and repeated filtration may result in the loss of microplastics during the process, especially with finer particle samples, as most collected samples range from 1 – 2 mm and are visible to the naked eye.

Airborne particles may also contribute to cross-contamination, as experiments were not operated under a laminar flow hood. Moreover, even if small particles were obtained, it would be difficult to characterize them using the ATR-FTR for particles less than 0.01 mm due to insufficient scattering.[52]

The digestion process could be improved. Despite conducting the experiments at 75°C, which was considered optimal for the degradation of organic pollutants without affecting the microplastics, adding additional H_2O_2 after three or more times did not

affect the sample. This may dilute the solution, resulting in a weaker reaction and less efficient breakdown of any residual organic matter.

Electrochemical Detection of Silica Mesoporous coated Gold Chip via Differential Pulse Voltammetry

The electrochemical detection of copper ions was performed using differential pulse voltammetry at a concentration of 1 mM with a bare gold chip (Figure 17). The potential range used was 0.1 – 0.5 V, a typical range for detecting copper ions. An oxidation peak was observed, indicating the detection of the copper analyte with minimal interference. However, when a coated silica mesoporous film was introduced to the system with copper ions concentration of 1 mM, 0.01 mM, and 0.001 mM, the current shifted and increased, suggesting a decrease in copper detection efficiency compared to the bare gold chip (Figure 18). The coated chip may have degraded from overuse, leading to reduced performance.

In Figure 18, copper was still detectable at concentration of 10 μM, though the observed oxidation peak was broader and exhibited irregular baseline. Further, dilution to 1 μM resulted in a lack of detection. While copper ions were detected at 1 mM, 0.01 mM, and 0.001 mM concentrations, lower levels may be needed for effective copper detection in microplastics. For instance, mesoporous silica film with indium tin oxide can detect mercury concentration in soil as low as 0.2 μM.[35] Additionally, analytical instruments such as ICP-MS can detect copper concentration as low as 0.15 μg/L.[53]

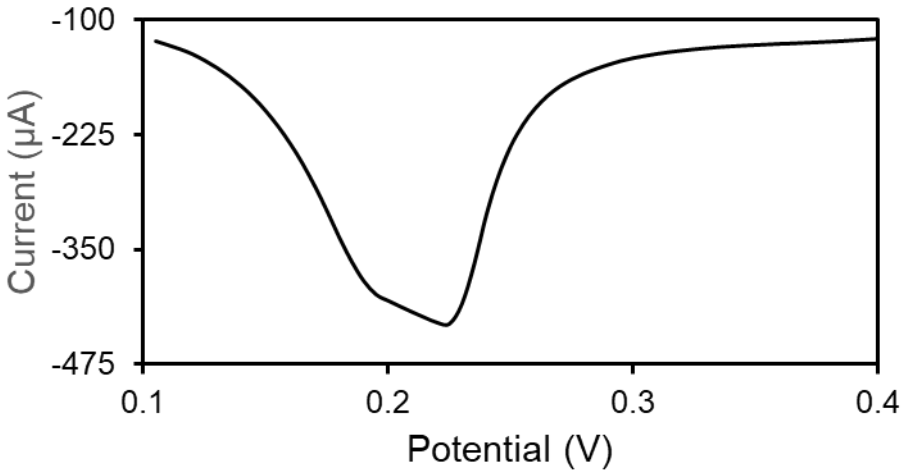


Figure 17. Differential Pulse Voltammetry: 1 mM Copper on a Bare Gold Chip.

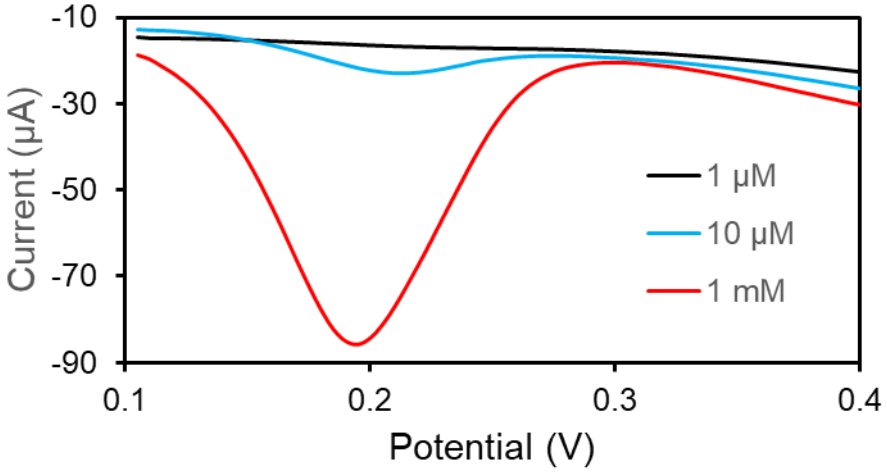


Figure 18. Differential Pulse Voltammetry: 1 mM, 10 µM, and 1 µM Copper on a Coated Silica Mesoporous Film Gold Chip.

CHAPTER 4

Conclusion

Microplastics were discovered along the coast of Southern California beaches. Following EPA fieldwork protocol and a modified NOAA procedure, microplastics were extracted from collected beach sediments. The primary materials found were polypropylene, polystyrene, and polyethylene, which are commonly used in everyday products.

These findings were unexpected, as many sources reported that microfibers are the most common type of microplastics. This suggests a potential discrepancy in the sample collection process since the majority of the samples were about 1 – 2 mm in size. Nevertheless, the different types of plastic identified highlight the urgent need for targeted waste reduction measures. Understanding the nature of these microplastics is critical for devising effective coastal waste management strategies on Southern California beaches.

A preliminary test was conducted on copper using differential pulse voltammetry on bare and coated silica mesoporous film gold chips. Both methods confirmed the detection in copper, but the detection was limited to high concentrations. Analytical instruments can detect heavy metals, including copper at low concentrations. Future studies could focus on improving the sensitivity of the chip or utilizing screened printed electrodes (SPEs), a type of sensor commonly used in electrochemical applications due to their versatility and cost-effectiveness.

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